Methods for Collection and Analysis of Water Samples

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By F. H. RAINWATER *and* L. L. THATCHER

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PREFACE

The Geological Survey has the responsibility for measuring and evaluating water moving through that portion of the hydrologic cycle between the time the water from the atmosphere reaches the earth's surface and the time it is returned to the atmosphere or enters the ocean. During this part of the cycle, water may appear in many environments and under different conditions, and a full understanding of the problems of hydrology requires the application of various specialized scientific techniques. The Quality of Water Branch of the Water Resources Division determines and appraises the chemical and physical characteristics of the Nation's water resources.

These activities include (1) systematic collection, compilation, and evaluation of basic data relating to the chemical and physical quality of surface and ground waters as required for the development and utilization of industrial, municipal, and agricultural water supplies; (2) research and development studies to improve investigational techniques; (3) fundamental studies of the occurrence and significance of dissolved and suspended substances; and (4) preparation of results of water-quality research and investigations for publication. This manual covers only the data-collection segment of the work between and including the selection of the sampling site and the completion of the laboratory determination of water characteristics attributable to the presence of dissolved material. Other phases of chemical-quality investigations are discussed by J. D. Hem, 1959, in "Study and Interpretation of the Chemical Characteristics of Natural Water," U.S. Geological Survey Water-Supply Paper 1473.

This manual was prepared by the U.S. Geological Survey, Water Resources Division, under the immediate supervision of W. F. White, chief, Chemical Quality Section of the Quality of Water Branch. Many associates contributed helpful suggestions and reviewed the analytical procedures.

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By F. H. Rainwater and L. L. Thatcher

ABSTRACT

This manual contains methods used by the U.S. Geological Survey to collect, preserve, and analyze water samples. Throughout, the emphasis is on obtaining analytical results that accurately describe the chemical composition of the water in situ. Among the topics discussed are selection of sampling sites, frequency of sampling, field equipment, preservatives and fixatives, analytical techniques of water analysis, and instruments. Seventy-seven laboratory and field procedures are given for determining fifty-three water properties.

INTRODUCTION

In January 1887, a committee on methods for stating water analyses reported to the Chemical Society of Washington: "Indeed, the researches of Clark, Frankland, Armstrong, Miller, Wanklyn, and others, within recent years, have brought the subject of water-analysis into such a satisfactory form that little seems to be desired in addition, except some uniformity as to the statement of results." Nevertheless, the science of water-quality investigation has progressed during the intervening years. Spectrophotometry, flame photometry, the Schwarzenbach reactions, and other advances have revolutionized water analysis in recent decades. Further advances are on the horizon. Better methods for collecting, fixing, and preserving samples can be expected.

The purpose of this manual is to set forth methods of collection and analysis of water samples used by the Geological Survey in making water-quality investigations. An earlier manual, containing only analytical methods, was released in 1950 in preliminary form and was intended for use only in laboratories of the Survey. This manual has been expanded appreciably both in respect to scope and number of analytical methods. Although excellent and authoritative manuals on water analysis are available, most of them emphasize primarily either domestic, industrial, or agricultural water utilization. No single reference or combination meets all requirements as a guide to the broader phases of water-quality studies conducted by the Survey.

It is not practical to set forth procedures which can be followed with all the varied types of water and conditions throughout the United States. However, the procedures generally will be applicable to the study of most natural waters. In addition to the detailed instructions compiled here, based largely on experience of Survey chemists in the field of water chemistry, additional information can be found in the references given. This manual can serve both as a general reference for chemists and others engaged in water-resources investigations and as a field and laboratory guide for newly appointed personnel.

The development of new and improved methods is a continuing process. The selection and publication of the best methods in a manual of this kind are done with the knowledge that some of them may be superseded by better methods by the time the manual is printed. Nevertheless, it has been found essential to the work of the Geological Survey to provide a comprehensive manual of methods of analysis and pertinent related information for the guidance of technical personnel. It is expected that the manual will have to be revised in the next several years.

Several manuals describing the analysis of water samples have been prepared by technical associations, and a need has been recognized for the development of uniform methods by which these analyses can be done on a practical basis. For example, essentially the same method for the determination of chloride may be included in manuals of three different associations. Details of this method, however, such as strength of solutions and volumes taken for titration, may vary. It is believed that uniformity can be achieved without affecting the accuracy or application of the method. To this end the Joint Committee on Uniform Methods of Water Examination, composed of agencies in the United States that publish methods for water analysis, has been established to explore ways and means of effecting uniform procedures. The Geological Survey is identified with this effort.

Trade names used in the manual in connection with equipment, supplies, and reagents do not constitute an endorsement of the instrument or product. Knowledge of the operating principles of the various instruments is essential to performance of the duties of the analytical chemist. Trade names are used when necessary to describe the exact conditions under which statements pertinent to performance of the various operations in water sampling and analysis apply.

SECTION A. COLLECTION OF WATER SAMPLES

Water samples are collected and analyzed to ascertain characteristics of a body or mass of water. The sample is usually only an infinitesimal part of the total volume and is therefore representative of the total mass only to the degree that uniformity of chemical composition exists within the total mass. In their natural state, surface and ground water are subjected to forces that promote mixing and homogeneity. The fact that such tendencies exist, however, is not sufficient cause for assuming that a body of water is so well mixed that no attention to sampling technique is required. Often, because of local conditions, the body of water may not have uniform composition.

The composition of water is subject also to change with the passage of time. The chemical quality of surface or ground water is the resultant of the geologic, hydrologic, biologic, and cultural environment of the water and varies from time to time as well as from place to place. Generally, changes in the quality of surface water are more pronounced and rapid than in ground water. However, marked changes in ground-water quality can, and often do, accompany such shifts in hydrologic equilibrium as variations in recharge or discharge rate, salt-water encroachment, or induced infiltration of surface water.

A:1 SAMPLING-SITE SELECTION

The type of investigation, purpose of the study, and anticipated variation in chemical quality determine to a large degree the location of the surface- or ground-water sampling site and the frequency of sample collection.

A:1a SELECTION OF SURFACE-WATER SAMPLING SITE

Stations for sampling dissolved material in surface water are usually operated by the Geological Survey to determine the discharge of dissolved constituents past a point, to describe the changes in water quality with respect to time, to collect data that will aid in predicting water quality in the future or in estimating the nature and magnitude of past events, to study the effect of geologic, hydrologic and cultural changes on water quality, or a combination of these purposes.

Adequate sampling of a flowing stream must take into account initially the need for defining the water quality in the stream cross

section at the sampling site at the time of sampling, and secondly the need for a sufficient number of samples distributed in time to define the changes in quality of the water passing the sampling station. One sample can adequately define the water quality at a given time if the chemical quality is homogeneous throughout the cross section. Theoretically, if the water in the cross section is not uniform, a sample representing the average composition might be obtained by compositing depth-integrated samples of equal volume taken at several points simultaneously at centroids of equal flow, but, generally, on small and medium-size streams, and on some large streams, a sampling site can be found where the composition of the water is uniform. The problem of obtaining adequate samples is thus simplified, and the cross section can be represented by one sample taken at or near the center of flow. However, more than one sample may be required in the cross section of large streams.

Heterogeneous quality throughout the cross section can result from incomplete upstream mixing of ground-water inflow; tributary inflow; industrial, domestic, and agrarian effluents; or from tides and other backwater. Unmixed tributary inflow may be discernible for many miles down broad shallow streams; tidal stratification may be more perceptible in deep channels. The extent to which mixing occurs laterally and vertically in the cross section is governed principally by turbulence, which characterizes the movement of water in the stream. Differences in water velocity, both horizontally and vertically, aided by the configuration of the channel, also promote mixing. The effects of temperature and wind are of minor importance except in sluggish streams (especially tidal streams), lakes, and reservoirs.

Although differences in mineral content may be detected in the field by specific-conductance measurements or simple chemical tests, frequent laboratory analysis of samples for ascertaining uniformity is advisable.

The study of the chemical quality of tidal rivers is often beset with complexities not present in investigations of nontidal streams. Keighton (1954) points out some of the natural forces and physical factors affecting the planning of water-quality investigations in tidal rivers and suggests sampling procedures that will determine adequately the variable quality of the water.

Easy access to the station, reliability of sample collectors, and availability of streamflow records are other items to be considered in selecting surface-water sampling sites. Locating a chemical-quality station at a stream-gaging station has decided advantages because adequate water-discharge data are essential for computing

the dissolved load carried by the stream. However, the criteria for a good stream-gaging station and a water-quality station are not identical, and sometimes the most suitable location for one may be undesirable for the other. Rather than consider the presence of a stream-gaging station as a prerequisite for a chemical-quality station, the chemist may explore the possibility of obtaining water-discharge data at the chemical-quality station by direct or indirect means.

Each sampling station should be selected, so far as possible, to fit into a comprehensive network of sampling stations to cover a State or drainage basin. Even though an individual station is established to meet a specific need for information, the possibility of placing and operating it to supply data for other studies of chemical quality should not be overlooked. If two or more sites will give about equally usable information for the immediate needs, preference should be given to the one that most nearly fits the following criteria:

1. Best fits an overall plan for evaluating chemical quality on a broad basis.
2. Gives information that can be correlated with periodic information at other sites or that will supplement such periodic information.
3. Gives the total of dissolved material discharge from an area.
4. Is at a transition from the surface outcrop of one geologic formation to another.
5. Is at a place where future storage or diversion may be developed.

The selection of sites for sampling lakes and reservoirs depends on the degree of accuracy required in determining the composition and on the degree of mixing. Water circulation and movement caused by wind, temperature changes, and currents between points of inflow and outflow cause mixing. Other factors such as irregularity in shape of the body of water, difference in composition of inflow and stored water, evaporation, solution or evolution of gases at the air-water interface, and activity of aquatic plant and animal life all tend to bring about heterogeneous quality. A thorough study of water composition can be made by sampling along a three dimensional grid pattern; samples can be collected at different depths at each grid intersection. A more economical and conservative approach might be to sample at different depths along selected cross sections in the body of water. The adequacy of such a sampling program depends on the judicious selection of the cross section and sampling points. When only one sample is collected to define the average character of the lake or reservoir it should be collected near the center of the water mass. Conversely, in order to evaluate quality of reservoir water for the user downstream, the sampling site or station should be located at or near the point of discharge.

A:1b SELECTION OF GROUND-WATER SAMPLING SITE

Ground water is analogous to a surface-water reservoir in that most usable ground water is in motion, although the rate of movement may be very slow and the areal extent very wide. A well can be considered as a sampling point in a large body of slowly moving water, which differs in chemical composition vertically as well as areally. Most of the forces which cause mixing in bodies of surface water are absent or much weaker in ground-water reservoirs. Turbulence is virtually nonexistent. The major forces that tend to mix ground water are probably the differences in velocities as the water moves through material of heterogeneous permeability, pressure differentials and, to a lesser extent, ionic diffusion. The degree of movement induced by pumpage and natural discharge affects the quality. The diversified nature and solubility of the rocks with which the water comes in contact and variations in rate and chemical composition of recharge from precipitation and from the surrounding area tend to make the water heterogeneous.

Sampling programs are planned to determine the mineral content of ground water through the aquifer, although a completely comprehensive answer is not always practical. Efficient collection of water-quality data and intelligent selection of the ground-water sampling site generally require more judicious consideration than the selection of a surface-water sampling site because the elements influencing water quality are not as easily observed.

Because of the diversified purposes of ground-water investigations, it is impractical to attempt specific direction for the selection of sampling sites. Nevertheless, some general suggestions can be given. If changes in ground-water quality are not considered in the investigation, there are perhaps two equally satisfactory approaches to the problem of adequate and economical coverage of ground-water quality of an area; both employ comprehensive and partial analyses. One approach utilizes the determination of key constituents (one or several) in a large number of samples collected over the entire area. By this means an areal water-quality pattern is developed that is then of value in selecting the sites for collection of samples for comprehensive analysis. In some investigations the identity of the key constituents may be unknown at the beginning of the investigation. Then, the reverse approach may be required, and comprehensive analyses may be made early in the study, and these data augmented by partial and additional comprehensive analyses of samples collected at other sites to complete the water-quality picture. Either method requires the greatest of care in the selection of sampling points from available sites.

In selecting a sampling site to detect water-quality changes or stability, control of the variables that affect the change or stability should be considered. The hydrologic regimen during the investigation should not be modified. For example, if irrigation is begun in the vicinity of the well selected as a sampling site to study variations in quality resulting from natural-recharge patterns, the data collected may be essentially valueless.

Although some ground-water studies may be concerned only with surveying the chemical characteristics of the water, the data are often used in conjunction with other geologic and hydrologic information. Consequently, the value of the water analysis is usually directly proportional to the facts known about the source of the sample. One general observation is pertinent: The most useful samples are collected from wells for which good well schedules and other data are available.

A:2 SAMPLING FREQUENCY

Samples of surface and ground water should be collected at intervals such that no important change in quality could pass unnoticed between sampling times. This requisite immediately gives rise to two additional questions: What magnitude of change is important, and what are the physical and economic factors that must be considered in obtaining the record? By necessity the sampling schedule adopted is usually a compromise between the accuracy and detail desired in the water-quality record and the funds and personnel available for the work.

Streams are constantly subjected to forces and changing environment which bring about variations in the chemical character of the waters. These variations may be relatively small in areas subjected to intensive weathering for long periods of time, such as the Piedmont province of the Atlantic coastal region. Younger, incompletely leached rocks and scattered, infrequent and often intense rainfall in the arid and semiarid Western States constitute an environment conducive to erratic and often extreme changes in water quality. Since the beginning of water-resources investigations in this country, the chemical-quality hydrologist has been confronted with the problem of the frequency of sampling required to detect adequately the changes in the chemical composition of a stream. On the basis of water-quality studies of a large number of streams and the practical economics of sampling-station operation, the U.S. Geological Survey has arbitrarily concluded that the collection of samples once daily is the minimum frequency necessary to define adequately the water quality for the majority of water uses, and daily sampling is

considered as standard for the usual comprehensive chemical-quality investigation. However, less frequent sampling schedules are often used, and the value of analysis of weekly or monthly samples in reconnaissance or unit basin studies should not be minimized.

The chemical quality of ground water at the sampling point may vary in response to changes in rate of water movement, to pumpage, or to differences in rate and chemical composition of recharge from precipitation and from the surrounding area. Although concentrations of dissolved constituents in ground water from any one well may vary widely, sometimes severalfold, in general the changes are much slower than those commonly associated with surface water. Until disproved, it is safer to assume that the quality of water from a well fluctuates rather than that it is uniform for long periods of time. Changes in ground-water quality usually can be described satisfactorily by monthly, seasonal, or annual sampling schedules.

A:3 SAMPLING EQUIPMENT

The water chemist has a wide variety of sampling equipment from which to choose. Only those items that have been used satisfactorily by the Geological Survey are discussed here. This is not to imply that omitted items are unsatisfactory.

A:3a SAMPLE CONTAINERS

Factors that are pertinent in selecting containers used to collect and store water samples are resistance to solution and breakage, efficiency of closure, size, shape, availability, and cost. Preferences for one type of container over another are varied, and selection is guided largely by experience, supposition of the possible effect of the container on the water sample, and use of containers in the individual laboratories. No adequate study of all factors has been made.

Hard rubber, polyethylene and perhaps other plastics, and some types of borosilicate glass are believed to be suitable on the basis of experience within the Survey and the reports of others in water chemistry. A limited investigation, conducted by the Survey, of the relative merits of four common types of bottles showed that storage in Pyrex and polyethylene did not significantly alter the silica, sodium, total alkalinity, chloride, and boron content, or the specific conductance, pH, or hardness of the water during a storage period of about 5 months, although some investigators have avoided Pyrex because of suspected contamination from the boron in the glass. Glass bottles marketed under the name "No-Sol-Vit" added boron to the samples but were otherwise satisfactory. The increase in silica content of water stored in soft-glass bottles (citrate of mag-

nesia type) was significant after 2 or 3 weeks. Prolonged storage in these bottles also increased decidedly the sodium content and hardness of the water. The chemical type and concentration of the stored water apparently has a definite influence on the rate and nature of materials dissolved. Much additional research is required before the findings will be conclusive. The American Society for Testing Materials (1954, p. 134) does not recommend soda-lime glass bottles as sample containers unless they are coated internally with paraffin.

Before use, all new bottles must be thoroughly cleansed, filled with water, and allowed to soak several days. The soaking removes much of the water-soluble material from the container surface.

The Geological Survey uses 4-ounce to 1-gallon bottles for sample collection. A sample of 1 or 2 liters is usually sufficient for the normal routine chemical analysis. Excluding containers for samples in which dissolved gases or constituents particularly affected by atmospheric gases are to be determined, the bottle design is immaterial. Nevertheless, uniformity within any one organization has definite operational advantages. The standard BOD (biochemical-oxygen demand) bottle with pointed stopper, which prevents entrapment of air bubbles in the bottle, should be used to collect samples that are to be analyzed for dissolved oxygen, carbon dioxide, cyanide, sulfides, and, probably, oxygen consumed. If the sample is supersaturated with carbon dioxide, a pressure-seal bottle is preferable.

Because of their design and construction material, some bottles are more satisfactory for transporting water than others. The bottle must be resistant to impact and to internal pressure, which is increased by expansion of the water or by release of dissolved gases at elevated temperatures. Well-sealed fragile bottles of liquid when shipped by air may not withstand the large differential pressures or freezing temperatures in the rarefied atmosphere. In respect to fragility alone, polyethylene bottles are more satisfactory than glass. However, samples in polyethylene bottles must be protected from compression, else the liquids may be squeezed out around the threads of the cap.

Samples subjected to freezing temperatures are very likely to be lost through breakage of glass bottles but are retained by polyethylene. However, this advantage may sometimes be more apparent than real. The chemical analysis of a previously frozen sample is always suspect because the original chemical character may not be completely reconstructed after the sample thaws. Although the analysis of the previously frozen sample is usually of some value,

the use of plastic bottles does not lessen the necessity for protecting samples from freezing.

The closures for sample containers should be glass, well-washed rubber, tin-wrapped cork, or inert plastics. Many of the common screw caps have waxed-paper or cork liners that are unsatisfactory. Corrodible metal should not be used. Pliable sheet plastic is often used to protect samples from contamination by direct contact with rubber stoppers, but this precaution is rarely necessary for the usual chemical constituents determined. No practical, completely gas-tight closure has been developed, but the efficiency of the seal is very important in the selection of caps and stoppers. The bottle seal must remain tight during transport to prevent spillage and gain or loss of gas. Some caps differ in their sealing capacity; shallow hard-plastic caps are notoriously susceptible to loosening during transport, but the deeper caps are somewhat better in that respect. Various types of stoppers have been used satisfactorily. The success with stoppers is largely dependent on the shape of the bottle neck and stopper and on the composition of the stopper. The flexibility of polyethylene permits a tight seal that withstands vibration. A practical, tight closure that the Survey has used is the patented stopper commonly associated with "citrate of magnesia" bottles. This stopper is permanently attached to the bottle neck and clamps firmly on a rubber washer, an advantage that may outweigh the disadvantage of solubility of the bottle when the time of contact between sample and bottle can be limited.

A:3b APPARATUS FOR SAMPLING WATER THAT CONTAINS NONVOLATILE CONSTITUENTS UNSUSCEPTIBLE TO AERATION

Depth-integrating samplers and point samplers are used in the collection of water for determination of nonvolatile constituents and those unsusceptible to aeration. The depth-integrating samplers consist only of a mechanism for holding and submerging the bottle. When the bottle is lowered at a uniform rate, water is admitted throughout the vertical profile. Hence the sampler must be sufficiently heavy to submerge the bottle in swift water. The method of securing the bottle to the sampler should require a minimum of manipulation. Belt-and-buckle devices are generally avoided because of the difficulty in handling such items in cold weather. Some of the depth-integrating samplers used by the Survey are shown in figure 1.

Point samplers are used to collect water at a specific depth below the water surface and may be very simple or complex in construction. The principal types are shown in figure 2. Sampler A is used only for collecting water samples from the bed of a stream or lake. The cork is tied to the suspension line in such a way that a

FIGURE 1.—Depth-integrating samplers.

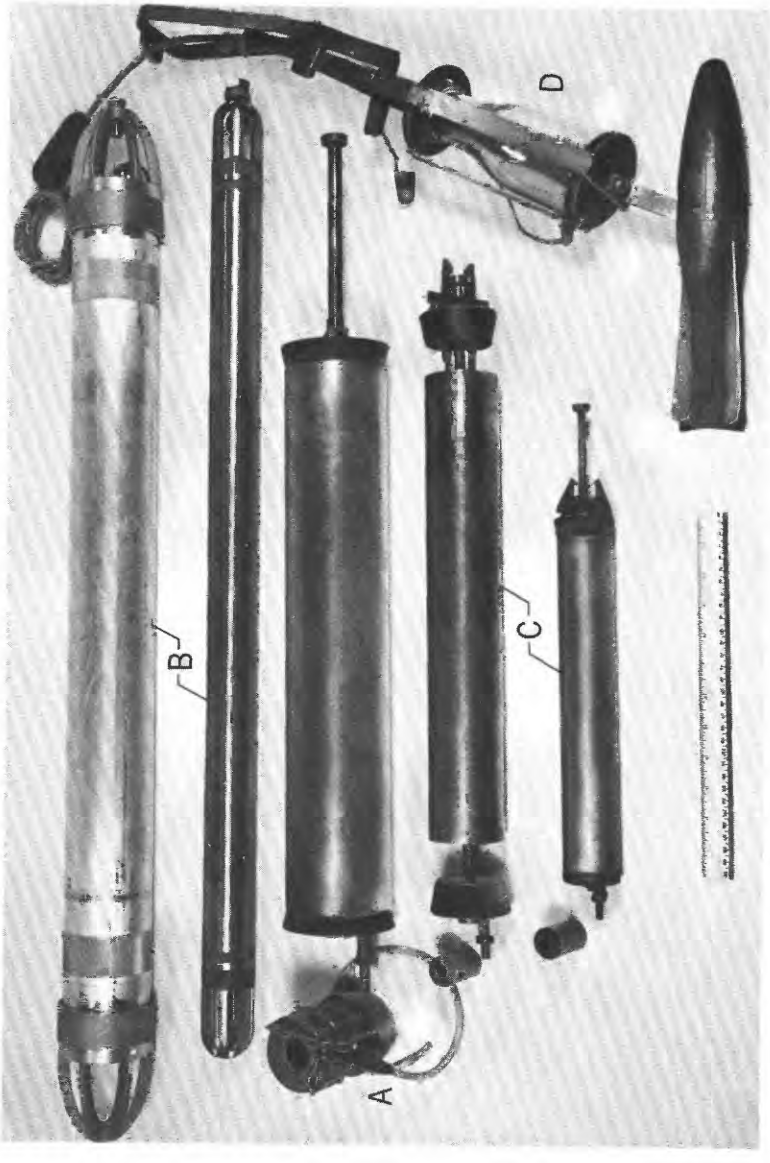

FIGURE 2.—Point samplers. *A*, Bottom sampler; *B*, Ball-valve; *C*, Foerst; *D*, Colorado River.

sharp pull on the line will remove the cork and allow the bottle to fill. In operation the bottle is corked and then thrown into the water with an excess of line; when the bottle comes to rest on the bed, the suspension line is jerked, removing the cork. The bottle is allowed to fill in place and then stoppered when it is withdrawn from the water. Sampler B is a ball-valve type and was designed for the collection of ground-water samples at any desired depth. When the desired depth is reached, the sampler is filled by raising and lowering several times in rapid succession, which opens the ball valves at either end and traps the water. The 1-gallon sampler is 3 inches in diameter and the 1-quart size about 1½ inches. Sampler C, the Foerst sampler, is used to collect surface-water samples from a given depth and has been used with some success to sample water from wells. The sampler is lowered to the desired depth in the open position; then the messenger weight, which trips the closing mechanism, is run down the suspension line. The messenger weight must meet the triggering device on the top of the sampler squarely. Hence a set of messenger weights drilled to accommodate suspension lines of different diameters permits the use of the sampler with a wide variety of ropes and cables. The Foerst sampler is available in 4 sizes: 400-ml capacity, 2 inches in diameter; 1,200-ml capacity, 2½ inches in diameter; 2,000-ml capacity, 3¼ inches in diameter; and 3,000-ml capacity, 3¾ inches in diameter. The samplers are constructed of brass and thus resist corrosion. Sampler D is used exclusively in sampling surface waters. It is lowered with stopper in place; the messenger weight then pulls the stopper and the bottle is raised to the surface open.

Detachable weights are useful with practically all samplers. Appreciable weight is necessary in excess of that required to submerge the bottle. In moving water, inadequately weighted samplers drift with the current and tend to ride on the water surface at the end of the suspension line. Added weight also decreases the angle between the suspension line and the vertical, thereby increasing the accuracy of the depth measurement.

A:3c APPARATUS FOR SAMPLING WATER THAT CONTAINS DISSOLVED GASES AND CONSTITUENTS SUSCEPTIBLE TO AERATION

The collection and handling of samples for the determination of dissolved-gas content and constituents susceptible to aeration require special equipment and careful technique. The sampler assembly for determining dissolved-oxygen content and biochemical-oxygen demand described by the American Public Health Association and others (1955, p. 250) or a modification thereof, is generally accepted as the standard apparatus for sampling open water. This sampler

provides for a threefold displacement of water in the sample bottle without aeration. Although this apparatus is efficient, satisfactory samples can be collected by other methods. A nonaerated sample collected in a Foerst sampler can be transferred by means of a tube connected to the outlet valve projecting into the bottom of the sample bottle. Twofold or threefold displacement of water in the bottle is recommended (see fig. 3).

FIGURE 3.—Apparatus for sampling water that contains dissolved gases and constituents susceptible to aeration.

Rather elaborate instructions are given by the American Society for Testing Materials (1954) for collecting samples from closed systems, and those procedures or modifications thereof can be used. Often a sample can be collected satisfactorily by running the water through a tube to the bottom of the bottle and using twofold or threefold displacement. The water should be run in slowly to minimize agitation and the resultant excessive aeration or loss of gas.

The samples are generally collected in narrow-mouthed biochemical-oxygen-demand bottles that have pointed glass stoppers to

avoid entrapment of air in the sample. Unfortunately this type of stopper does not provide a seal that permits much transporting or handling of the sample unless the container in which the sample is transported exerts pressure on the stopper. "Citrate-of-magnesia" bottles (see sec. A:3a) can be pressure sealed without entrapment of air bubbles and, consequently, are used frequently for transporting samples for the determination of dissolved gases and constituents susceptible to aeration.

A:3d SAMPLER SUSPENSION APPARATUS

Sashcord with or without a wire core is the most common means of suspending depth-integrating samplers (fig. 4). When long lengths of line are required, commercially available clothesline reels (fig. 4*A*) are useful. These reels also have a locking device, which facilitates use with point samplers. Figure 4*B* shows a versatile assembly with which the exact depth can be read from a depth indicator on the reel; different weights can be interchanged as required by the current. In use the crane is tipped forward against the bridge rail. Modified booms having similar elements can be used from boats.

A:4 SAMPLING INSTRUCTIONS

A:4a SAFETY PRECAUTIONS

Water samples are collected under a wide range of conditions, and the work is not without some hazard. A knowledge of the hazards involved and means by which they can be minimized should be helpful in preventing accidents and in providing greater safety for sample collectors. Surface-water samples are collected from bridges, docks, cableways, and boats, and by wading, or through ice. Inability to swim and difficulty in freeing oneself of burdensome equipment if suddenly plunged into deeper water are perhaps the most serious hazards in taking samples from streams, lakes, and reservoirs. The collection of ground-water samples has its own perils, primarily in connection with pumping equipment, snakebite, and unfriendly dogs. Dangers include loose or rotten well coverings and entanglement with belts and drive shafts. Many wells are surrounded by heavy brush which makes an attractive habitat for snakes, particularly during dry, hot months. High boots will reduce the likelihood of snakebites considerably, as most bites are below the knee. Beating the grass and proceeding cautiously will give the snakes an opportunity to glide away instead of striking.

Wading.—Wading is one of the easiest methods to collect samples from many streams and also affords the collector the best opportunity to "size up" the flow and decide where to collect the samples. Rubber boots or breast-high waders are standard equipment. A

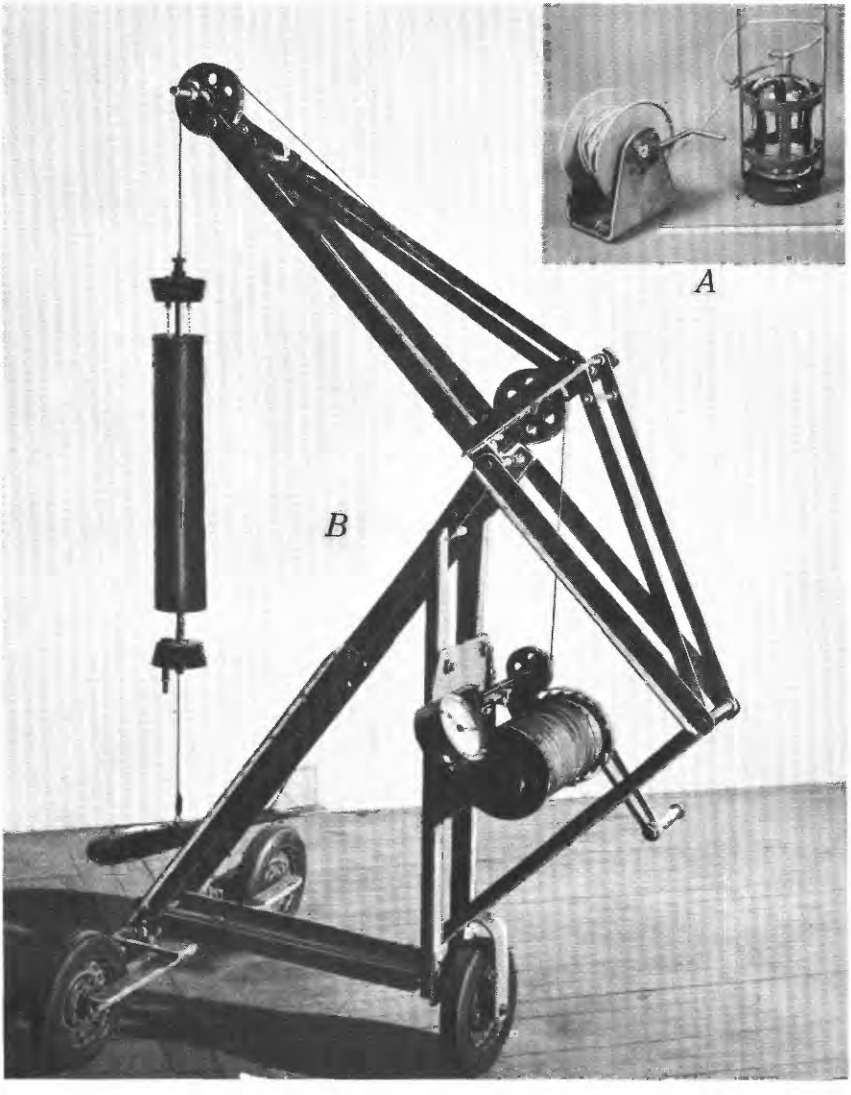

FIGURE 4.—Sampler suspension apparatus. *A*, Hand assembly for shallow water; *B*, crane assembly for deep water.

wading rod or similar probing instrument is essential to safe wading. By probing ahead, the collector can estimate the current and locate holes, benches, and even quicksand. In shallow water the most satisfactory method of extricating oneself from quicksand is to fall flat on the bed and crawl to firmer ground; in deep water one's effective weight in the sand can be lessened by swimming

motions. In a swift sandy-bottom stream or where the bottom is covered with ooze, the wader may find that his feet slowly sink into the bottom if he stands in one position too long. Lake or pond bottoms may be more treacherous than the beds of flowing streams.

A general rule of thumb is that wading should not be attempted if the depth of the water in feet multiplied by the water velocity in feet per second equals 10 or more, but this criterion must be modified by many factors peculiar to the site and to the season of the year. The depth as related to the velocity of water that can be waded safely is closely associated with the body weight. If the wader has any uncertainty about his ability to wade a stream, he should attach a rope or tag line securely to the bank. An extra change of clothing is advisable if much wading is to be done, particularly during the colder months.

Bridges.—Traffic is the most serious hazard when working from bridges. Sometimes the bridges have walkways for pedestrian traffic or catwalks suspended at the side or beneath the bridge, but more often than not the collector must work in the traffic lanes. If necessary to interfere with traffic, suitable arrangements with local authorities should be made in advance. Warning signals and signs of various kinds are some protection when sampling from a bridge, and approval for their use is generally granted by local traffic officers. Commonly used signals include flags, signs, red lanterns, and blinking red lights. For some reason motorists respect certain signals more than others. For night work a blinking red light is usually more effective than other warning signals. Elevating the light several feet above the top of the car is effective in congested traffic; this affords some warning to drivers whose vision might be obstructed by preceding vehicles.

On highway bridges that have particularly heavy traffic, and when cranes are used to handle sampling equipment, 1 lane of traffic may be blocked off by placing a barricade and suitable lights or "1–lane–traffic" signs on both bridge approaches. For additional protection, the car or truck may be parked in one lane and between the collector and oncoming traffic. After all the prescribed traffic warnings are installed the collector still must keep an eye on approaching vehicles—there are always drivers unwilling to cooperate.

When working on railroad bridges a knowledge of train schedules is essential, and at no time should the collector use equipment that cannot be removed quickly.

A hazardous condition in which the sampler is likely to inflict serious injury on others exists at bridges over navigable streams.

Boat operators cannot see the small suspension line until they are almost ready to collide with it, and the sample collector frequently cannot see a small boat approaching. Red pennants attached to the suspension line or to an independent line in the same location are recommended.

High-tension powerlines strung close to the bridge are also dangerous. If it is necessary to sample repeatedly from a bridge that has hazardous powerlines, a warning sign should be painted on some part of the bridge structure directly above the hazard.

Cableways.—The principal hazards of cableways are not the possibility of their structural failure, but rather those that attend the operation of the cable car. Proper instruction of inexperienced personnel in cable-car operation may prevent many accidents. Before releasing a car from its mooring, check the car pullers; in some districts the puller is left in the car and in others it may be carried as a part of field equipment. Also check the brake lining attached to the car puller; this lining is used to scotch the sheaves and hold the car stationary while the sample is collected. Once the car is rolling free on the cable, no attempt should be made to retard its speed by use of hands or car puller until it has slowed almost to a standstill. Some of the later model cable cars are equipped with brakes. If there is any danger of the car continuing across the stream and crashing into the cable mooring on the opposite bank, the sample collector should ease the car out from the landing platform with the car puller or brake and never allow the car to run free.

Boats.—Water samples are often collected from boats. The degree of hazard involved is generally dependent on the selection and operation of the boat. Lifejackets are essential equipment.

Much of the hazard in sampling large streams, lakes, and reservoirs is related to the seaworthiness of the craft and to changing weather. A sampling trip in a small boat begun on mirror-calm water can suddenly develop into a perilous expedition if the wind comes up and large waves form. Only an experienced man can judge the roughness in the center of the reservoir from the breeze on the shore. In many parts of the country the wind often follows a rather definite pattern during any 24-hour period, depending on the season of the year. For example: During the summer and early fall in the Great Plains area, the water is generally calm in the early morning, the wind rises about midmorning, reaches its peak in the afternoon, and dies shortly before sunset. Other regions have their own wind patterns. It is always advisable to

check the weather forecast before planning an extended sample-collection trip on a large lake or reservoir. All work should be done at a safe distance from spillways, "glory holes," and other areas of water discharge.

Boat operations on streams during floods is particularly hazardous, and, where measurements by boat are required, the services and equipment of skilled local personnel should be utilized where possible. Not only must the boatman cope with the fast current, but he must be on the alert for shallows and for floating and submerged drift. Floating ice is very dangerous; even when no danger to the boat is involved, changes in wind, current, or tide may shift the position of ice floes in such a way as to cut the boat off from the shore. On navigable waters in fog it may be necessary to stop the motor at intervals to listen for other vessels.

The good boatman checks such items as oars, life preservers, buoyancy tanks, lights, motor performance, gasoline supply, and spare parts (particularly shear pins) and inspects the boat for leaks before he leaves the dock. He loads the equipment so as to provide the most efficient operation of the boat and installs his booms where the danger of capsizing or swamping the boat will be at a minimum.

Ice.—Samples are sometimes collected through ice at considerable risk. A hole of sufficient diameter to collect a sample from a bridge may be broken in thin ice by dropping a weight attached to a handline. But if the ice is thick, or no bridge is present, it may be necessary to venture out on the ice. The ice in a stream is likely to be of variable thickness, and the strength of the ice cannot be estimated from the apparent thickness near the edges. In advancing across an ice-covered stream it is advisable to test the ice with a sharp blow of an ice chisel every few steps. A few inches of new snow on top of ice can conceal dangerous places that would be visible if there was no snow. Work from ice during breakups is particularly hazardous. Moving blocks of ice are as destructive to sampling equipment as other debris. Vehicles should not be driven over ice-covered bodies of water.

First aid.—By definition, first aid is the immediate and temporary care of an injured or suddenly ill person until a doctor can be obtained; it is not a substitute for competent medical attention. Each field party should be supplied with a standard first-aid kit and first-aid manual. "First Aid Guide," published in 1954 by the U.S. Department of Agriculture, Forest Service, and sold by the U.S. Government Printing Office is a satisfactory manual.

A:4b COLLECTION OF REPRESENTATIVE SAMPLES

After the sampling site and frequency of sampling have been established, certain precautions must be exercised to insure that the samples collected are representative.

If only one sample of surface water is collected in the cross section of the stream it should be collected near the center of flow. The center of flow may or may not correspond with the midpoint of the stream. The single sample should also be depth integrated by lowering and raising the bottle vertically at a uniform rate from water surface to bottom, taking care not to get excessive amounts of bed material in the sample. Samples should not be collected from ponded or sluggish water or coves near the bank. Many water gages are located in pools upstream from natural or manmade low obstructions to flow, called controls. If there is no flow over the control this fact should be noted on the sample bottle.

A representative sample can be collected through a hole in the ice only with difficulty. The hole will often fill with slush or chips that rarely have the same dissolved-mineral characteristics of the water beneath the ice. Ice should be excluded from the water sample either by clearing the hole or by collecting the sample below the ice. Information on means and conditions of collection should be noted on the sample bottle.

When a ground-water sample is collected to determine the chemical characteristics of the water in the aquifer adjacent to the well, the water in the gravel pack, well casing, and distribution system between the aquifer and the point of collection should be displaced several-fold before the sample is collected. Water-quality data serve many other uses in ground-water studies, and the collector's techniques for special purposes may differ appreciably from the standard procedure. The important point is that the collector must know the volumes involved in the water system and have a reasonable idea of what the sample represents.

Precautions in the collection of special samples are discussed in section A : 4d.

All bottles should be rinsed with the water to be sampled before the sample for analysis is collected. Sufficient air space should be left in glass bottles to allow for expansion of the water at increased temperatures; polyethylene bottles may be completely filled.

A:4c TABULATION OF SAMPLE DATA

The importance of describing in writing the source of the sample and conditions under which it was collected cannot be overem-

phasized. A water analysis is of limited value if unaccompanied by detailed information on what the sample represents. Field notes are extremely valuable in project-type investigations of water quality, but they can easily be misplaced or lost. Field notes never should take the place of detailed information accompanying the sample from point of collection to finished analysis tabulation.

The Geological Survey records the sample description in two ways. Small soft-glass bottles, of 12-ounce capacity and less, are usually etched on the outside, and the information is written directly on the etched surface with a lead pencil. Standard sample tags, which provide space for sufficient detail to describe most samples, are used for other types of containers (fig. 5 and 6). The tag for ground-water samples is numbered 9–016 and that for surface-water samples is numbered 9–070.

Surface water.—The minimum data required for most surface-water samples are:

Name of the water body
Location of the station or site
Point of collection
Date of collection
Time of collection
Gage height or water discharge
Temperature of the water
Name of collector
Weather and other natural or manmade conditions that may assist in interpreting water quality

Many surface-water samples are collected at stream-gaging stations operated by the Geological Survey. The exact name used by the Survey for the stream-gaging station must be recorded. One common and extremely troublesome example of carelessness is the use of "at," "near," "above," or "below" in disagreement with the official name of the station. If the sampling station is at or within 1 mile of a surface-water gaging station, the name of the water body and location can be noted simply; for example, "Colorado River near Glenwood Springs, Colo., at gage" or "Colorado River near Glenwood Springs, Colo., 100 yards above gage." If any tributaries or other influents enter the stream between the sampling point and the gage, this fact should be recorded under "Remarks." (See fig. 5.)

When a station is established for the collection of surface-water samples on a routine basis where water-discharge data are not compiled, this station is given an official name, in a manner similar to the designation of a stream-gaging station. Where the sampling site is more than 1 mile from the gage or routine sampling station,

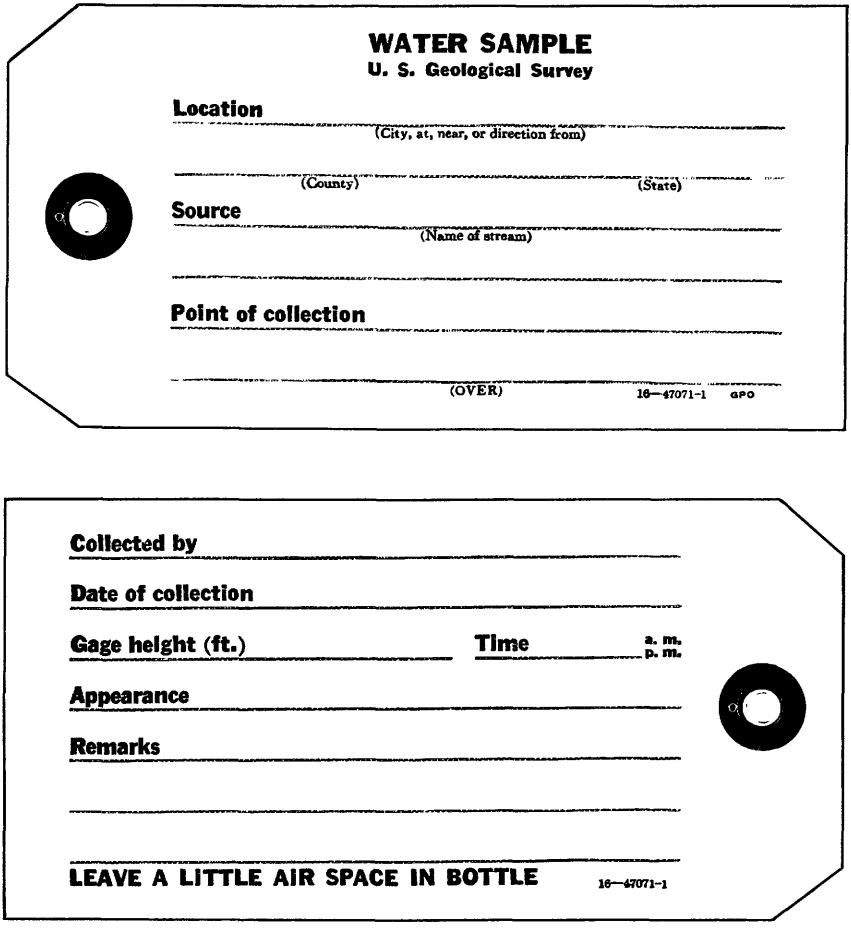

FIGURE 5.—Tag for surface-water sample.

the information given for the location of a site should be complete and clear enough for a person to locate readily the exact sampling site on suitable maps and to return to the location. For example, if the following sites were not at regular stations they would be described as "Republican River at Cambridge, Nebr., at bridge on State Highway 47, ½ mile south of Cambridge, Furnas County, ¼ mile upstream from Medicine Creek" or, if the site is not at a bridge, "Supply Canal (Tri-County Diversion) near Maxwell, Nebr., at Parshall flume, sec. 28, T. 13 N., 29 W., Lincoln County." If topographic maps are available and if there are no distinguishing landmarks (such as a Parshall flume), the location of the site should

be pinpointed to within a quarter-quarter section. Sketches of the sampling station in respect to roads, buildings, and the surrounding area are often desirable.

The quality of surface water may be far from uniform throughout the water body. For this reason the location of the sampling site must be clearly defined.

"Point of collection" refers to the spot within the cross-sectional plane of the stream where the sample is collected. When only one sample is collected from a stream it is usually obtained from the center of flow, and the sample should be so marked. If more than one sample is collected, all should be designated by station numbers. Station numbers, unless otherwise indicated, are the distance, in feet, from a predetermined reference point on one of the banks. Many station numbers are painted on bridge railings, but some are determined by a tagline or other measure stretched across the stream. A notation accompanying the sample should tell where the sample was collected in relation to the banks. The abbreviations "LEW" and "REW" for the left and right edges of the water, respectively, are used to code this information. For example, the coded notation "Sta. 25′, LEW 5′, REW 65′" tells that the stream was 60 feet wide at the time of sampling and that the sample was collected 20 feet from the left edge of the water. The left edge is on the left side as one faces downstream.

A series of stations in an unchanging direction on a stream, lake, or reservoir constitute a range line (RL). Range lines are usually located in respect to bench marks or readily apparent topographic or cultural features. In establishing a range line, consideration should be given to the permanence of the landmarks. It is very disconcerting to establish a range line in relation to a red barn and a tall tree and then return to the area later and find that someone has repainted or torn down the barn and cut down the tree. Stations along a range line should be noted as directed in the preceding paragraph wherever possible. A transit mounted on shore and two-way communication can be used to keep the boat on the range line. Orientation along a range line on a lake or reservoir may be more difficult than on a stream. Long taglines can be used but they are not practical when the distance is long or when they are a hazard to navigation. The position of the boat can be located accurately by triangulation, but this method requires two or more transits on shore, a shore party, and means of communication. Another method is to lay out 2 markers a known distance apart on shore and read the marker-boat-marker angle with a sextant; angles greater than 30° and less than 130°

are more accurate for plotting. Plotting of this information is simplified when one marker is on the range line. Less precise methods include time of travel at a uniform rate, stadia distances, and visual estimation. On estimating distances by sight it is often easier to record distances in reference to the nearest shore than in reference to the point of origin. If a bottom profile is available along the range line, or if soundings have been made on a previous trip, the sampling station can sometimes be located with sufficient accuracy by soundings; of course, depths must be corrected for changes in water-surface elevation. This identical-depth technique is limited to bodies of water that have had little change in bottom profile during the period since the last sampling. These are only a few of the methods available for station location in lake and reservoir surveys.

If more than 1 sample is collected in the vertical profile at 1 station, the depth at which the sample is collected below the water surface, as well as the total depth of water, should be recorded. Therefore, to locate adequately the point of collection the coded notation accompanying the sample may read "RL 2, LEW 10′, Sta. 125′ REW 500′, depth 4′ in 53′ of water."

"Time of collection" should include a.m., p.m., 12:00 m (noon) or 12:00 p.m. (midnight), if military time is not used. The use of daylight saving time is always a cause of uncertainty and confusion. Consequently, notations of standard time on the samples are desirable. Any recorded daylight saving time must be clearly marked as such.

"Gage height" (water level) should always be recorded if a water-discharge measuring station is nearby. The stream discharge can be computed from this gage height and suitable rating tables or curves. At sites other than water-discharge measuring stations it may be necessary to compute an approximate discharge from data at other stations in the general area or to make a measurement or estimate of discharge. Estimated, measured, or computed discharge entered in the space on the tag provided for gage height should be clearly noted as such, in order that it will not be confused with verified, factual information. When a measurement is made, the discharge is recorded on the sample bottle or tag in the field and noted "unchecked." A manual of methods and practices used by the Geological Survey to gage streams has been prepared by Corbett and others (1943). Water-surface elevation of impounded water at time of sampling should be recorded.

Descriptions of turbidity and color of sediment and water are particularly helpful if there is any question of chemical or phys-

ical change between the time the sample was collected and when it was received in the laboratory. Other information pertinent to the physical characteristics of the sample at the time of collection or to conditions under which the sample was collected can be noted as "Remarks." If the water has been treated, the treatment should also be described here, if possible.

Ground water.—Ground-water sampling sites are somewhat more difficult to locate and to identify than surface-water sites, and the use of ground-water analyses requires more information. In quality-of-water work, springs and seeps are considered as ground water. Minimum data required for most ground-water samples include:

Geographical and legal location
Depth of well
Diameter of well
Length of casing and position of screens
Method of collection (source)
Point of collection
Water-bearing formation(s)
Water level
Yield of well in normal operation
Water temperature
Principal use of the water
Name of collector
Date of collection
Appearance at time of collection
Weather or other natural or manmade factors that may assist in interpreting chemical quality

When recording the data on the sample-bottle tag (fig. 6), the collector should differentiate between those that he has determined himself and those that are reported by the owner or well driller.

"Geographical and legal location" ("location" on fig. 6) refers to the nearest town and the direction and distance therefrom; county and State should also be included. Geographical locations give the general area only and are of little help in locating one well in the presence of many.

Legal descriptions of the sampling site and well-numbering systems used by the Geological Survey are not standardized throughout the United States. In areas surveyed by the General Land Office the most logical designations, and those used in many areas, are related to townships north and south of base lines, ranges east and west of principal meridians, sections, and quarter-quarter sections. The standard tag for ground-water samples, No. 9–016, includes space for this type of location. It also has a space designated as "Field No." where other location descriptions can be

shown. Multiple wells on farms and ranches are not uncommon. Sketches of the location of the sampled well to fence lines, buildings, and topography are very helpful. Some owners do not object to numbering the wells with a permanent mark on the pump or structure.

"Method of collection," designated by the ambiguous term "Source" on standard tags now in use, refers to the description of the well and equipment relating to means of taking the sample, such as motor-pumped well, windmill, hand-pumped well, flowing well, spring, seep, and sample obtained with a bailer.

"Diameter," other than for uncased wells, refers to the diameter of the submerged casing and not to the diameter of the gravel

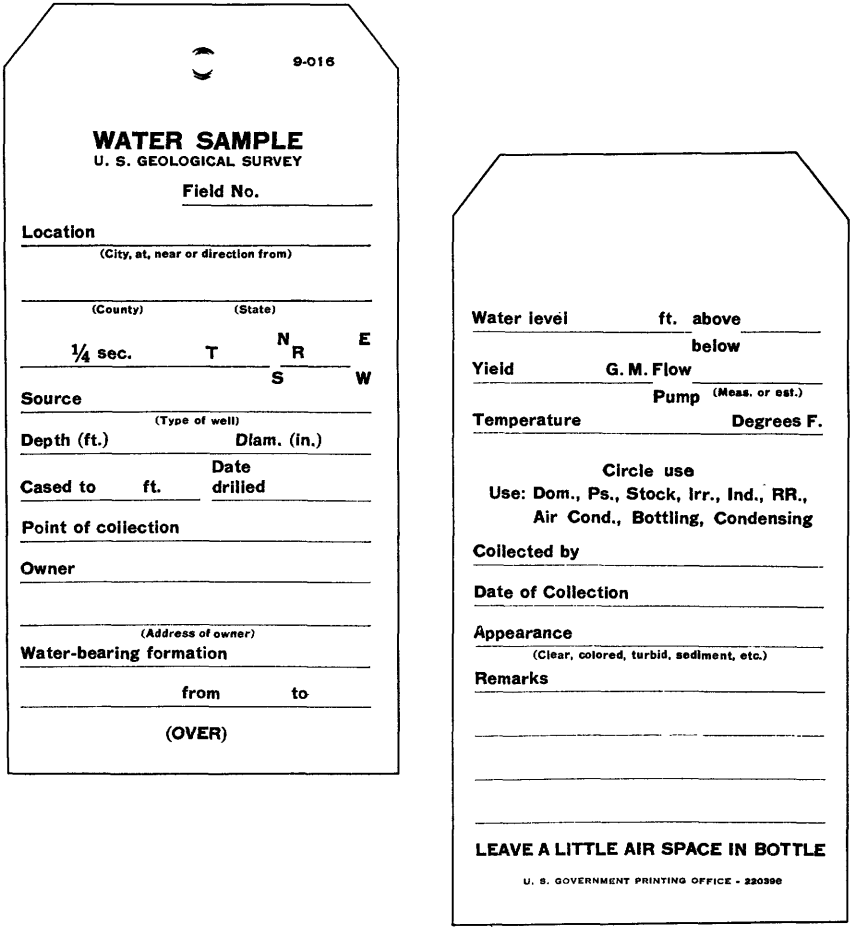

FIGURE 6.—Tag for ground-water sample.

pack or hole drilled when the well was put in. However, the diameter of the gravel pack may be included as additional information. Diameters and lengths of telescoped casings should be given in order from top to bottom.

"Point of collection" concerns the location in the water distribution system where the sample was collected. Inasmuch as ground water can change appreciably in chemical quality as it passes through the distribution system, any points of collection other than at the pump should be described in detail under "Remarks." A sketch of the distribution system is helpful.

"Water-bearing formation" refers to the principal aquifer or aquifers that discharge the water. The geologic name of the aquifers, not just sandstone, limestone, sand, and gravel, should be recorded if definitely known. If a certain aquifer is believed to be the source of the water but some uncertainty remains, the aquifer name is listed and followed by a question mark. The question mark must be retained on all tabulations until the correctness of the aquifer name is substantiated. If further investigation disproves the original assumption, the original notation should be changed.

Water levels are commonly measured to the nearest hundredth of a foot from a convenient measuring point on or near the well structure; the same point is always used and is described in the well schedule. Because the measuring point may be above or below the land surface, it should be clearly stated on the tag whether the recorded water level is in relation to the land surface or a measuring point. When a well is pumped, the water level may be substantially different from the "static" or nonpumping level. Therefore, the reported information should indicate whether the water level represents pumping or nonpumping conditions. It may be advisable to indicate the length of time the pump has been operating and the discharge rate.

The turbidity, color, and sediment content of the sample at the time of collection should be recorded under "Appearance." Rusty water suggests that the casing or distribution system is the source of the iron. A sample containing an appreciable amount of iron or manganese in solution may be colorless and clear at the time of collection, but these metals may oxidize and precipitate after the sample is collected.

A:4d SPECIAL TREATMENTS, PRESERVATIVES, AND FIXATION

Many of the heavy-metal ions normally present in only trace amounts in natural waters may not remain in the water sample until it is analyzed because of such chemical and physical reactions

as oxidation, reduction, precipitation, adsorption, and ion exchange. Coprecipitation may also reduce the concentrations of these constituents in solution. Many commonly used methods for the separation and isolation of traces of substances involve coprecipitation and adsorption processes. Iron is a particularly troublesome component in natural water because of its tendency to precipitate from solution and to coprecipitate other metal ions.

Although most water chemists recognize the chemical and physical forces that remove metals from solution, the literature provides very little specific information on preferable techniques for collection, storage, and preservation of samples for the determination of hydrolyzable metals. Most authoritative manuals recommend a minimum of lapsed time between sample collection and analysis. This is a valid recommendation but one which laboratories of the Geological Survey can seldom follow because of the distance between laboratories and many sampling sites. Measures other than speed must be taken. The Geological Survey has not conducted extensive research on the problem, but an analysis probably will be more representative of the water at the time of collection if a separate sample of water is taken for the determination of aluminum, chromium, copper, iron, lead, manganese, and zinc. The sample should be freed of its sediment and acidified to about pH 3.5 with glacial acetic acid (0.5 ml per 100 ml maximum) at the time of collection. Inasmuch as acetic acid stimulates the growth of molds, it may be necessary to add a little formaldehyde (0.2 ml per 100 ml) to retard growth. The presence of the acid also tends to stabilize the original valence state of the metals. Although not an ideal preservative, this acidification minimizes precipitation as well as adsorption on the container. Even collection of a separate clear sample, and, later, drastic acidification in the laboratory, is preferable to determination of the trace metals in alkaline water that has been stored for some time.

The determination of other constituents requires specific fixatives or preservatives. These techniques, without exception, merely retard the natural processes of change in composition, and the sample should be analyzed as soon after collection as possible. Recommended treatments are described below.

Ammonia nitrogen.—The percentage concentrations of the various components of the nitrogen cycle are rapidly changed by the biologic activity of organisms common in natural waters. Chloroform (5 ml per liter of sample) inactivates the organisms and fixes the nitrogen-cycle components.

Chlorine residual.—Samples to be analyzed for chlorine residual should not be stored, as the chlorine content of a water sample decreases rapidly. Exposure to sunlight or other strong light, and agitation, will further reduce the amount of chlorine present.

Dissolved oxygen.—Immediately after collection, the dissolved oxygen in a sample should be converted to an equivalent amount of free iodine, which is more stable in solution than oxygen. The sample is normally collected in a 300-ml BOD bottle, with a minimum of aeration (see sec. A:3c). Water temperature must be taken at the time of collection if the percentage of saturation is to be computed.

Suspended solids in high concentration may adsorb appreciable quantities of iodine in acid solution and they should be removed by coagulation with aluminum sulfate (alum) as follows: Collect the sample in a 500-ml glass-stoppered bottle using the same precautions as for the BOD bottles; add 10 ml of 10 percent alum solution and 1–2 ml of concentrated ammonium hydroxide; mix by inversion and allow the floc and suspended material to settle; decant the supernatant into a BOD bottle until it overflows.

If the sample is clear, or after it has been clarified, proceed with the following treatment.

1. Add 1 ml KF solution below the liquid surface of the sample in a BOD bottle.
2. Add 2 ml $MnSO_4$ solution below the liquid surface.
3. Add 2 ml alkaline-iodide sodium azide reagent below the liquid surface.
4. Stopper and mix by inversion. Allow the precipitate to settle and then repeat the mixing and settling processes.
5. Add 2 ml concentrated H_2SO_4 by allowing the acid to run down the neck of the bottle.
6. Mix by gentle inversion until solution is complete.

In the absence of interferences described in section D:28a–1, titration of the released iodine can be postponed for 48–72 hours if the treated sample is refrigerated. Instructions for preparation of reagents are given in section D:28a–1.

Nitrate nitrogen.—Although routine nitrate determinations are usually made on an untreated sample at the time of the regular analysis, treatment with chloroform is recommended if the exact quantity of nitrate in the sample at the time of collection is required (see "Ammonia nitrogen").

Nitrite nitrogen.—See "Ammonia nitrogen."

Oils and waxes.—Samples for the determination of oils and waxes should be collected in a separate bottle and fixed with 2 ml of concentrated HCl per liter to inhibit bacterial action, which may

decompose oils and waxes. Care should be taken that the sample is representative. It is very difficult to obtain a representative sample from surface water because the material is seldom, if ever, uniformly distributed.

Organic nitrogen.—See "Ammonia nitrogen."

Orthophosphate.—The conversion of organic phosphorus to orthophosphate is largely the result of microbiologic action. Chloroform (5 ml per liter of sample) inactivates the organisms and stabilizes the organic phosphorus-orthophosphate system.

Phenolic material.—It has been shown that phenolic materials in solution are rapidly destroyed by the biologic activity of organisms common in natural surface waters. Copper sulfate (2 g per liter of sample) has been found to be an effective preservative for a few days. Refrigeration can be used as an additional measure.

Selenium.—Very little information is available on the stability of selenium in aqueous solutions. Selenium is much more prevalent in bottom deposits of undrained lakes and the sea than it is in water above these deposits. This fact leads to the conclusion that selenium tends to precipitate from solution, possibly by reaction with iron salts, or to be adsorbed by some stream sediments (Trelease and Beath, 1949). If appreciable delay in analysis is anticipated the sample should be filtered at the time of collection and acidified.

Sulfide.—Water containing dissolved sulfides readily loses hydrogen sulfide, particularly if the pH of the sample is low. Oxygen destroys sulfides by oxidation, particularly if the pH of the sample is high. Aeration of the sample should therefore be avoided (see sec. A:3c). Two grams of zinc acetate per liter of water will fix the sample for several days. Acid water must be neutralized before addition of the zinc acetate.

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SECTION B. HANDLING OF WATER SAMPLES BEFORE ANALYSIS

The Geological Survey is confronted with problems of handling and storing water samples that do not prevail in most public and private laboratories. There is usually only one laboratory within a State of group of several States. In each area the efficient handling of samples should be considered both in respect to the validity of the analytical results and the cost of transportation and storage.

B:1 TIME BETWEEN SAMPLE COLLECTION AND ANALYSIS

The effect of bottle composition in changing the quality of water samples during storage is discussed in section A:3a. The samples are also subject to changes not attributable to bottle composition. The general relations of the time between collection and analysis to the validity of the analytical results as being representative of the water quality at the time of collection are well presented by the American Public Health Association and others (1955) as follows:

> In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results. For certain constituents and physical values, immediate analysis in the field is required in order to obtain dependable results, because the composition of the sample may change before the sample arrives at the laboratory.
>
> Some determinations are more likely to be affected than others by storage of samples prior to analysis. Certain cations are subject to loss by adsorption or ion exchange upon the walls of glass containers. These include iron, copper, aluminum, manganese, trivalent chromium, and zinc. Temperature changes very quickly; pH may change significantly in a matter of minutes; dissolved gases may be lost (O_2, CO_2, H_2S, Cl_2, CH_4) or gained (O_2, CO_2). Determinations of temperature, pH, and dissolved gases should always be carried out in the field, because changes are almost inevitable by the time the samples reach the laboratory. With changes in the pH-alkalinity-carbon dioxide balance, calcium carbonate may precipitate and cause a decrease in the values for calcium and for total hardness. Iron and manganese form readily soluble compounds in their lower (reduced) valence states, and relatively insoluble compounds in their higher (oxidized) valence states; therefore these cations may precipitate out, or may dissolve out of a sediment, depending upon the redox potential of the sample. Microbiological activity may be responsible for changes in the nitrate-nitrite-ammonia balance, for decreases in phenols and in BOD, or for the reduction of sulfate to sulfide. Any residual chlorine is converted to chloride. Sulfide, sulfite, ferrous iron, iodide, and cyanide may

be lost through oxidation. Color, odor, and turbidity may increase, decrease, or change in quality. Sodium, silica, and boron may be leached out of the glass container. Hexavalent chromium may be reduced to the trivalent state. This list is by no means all-inclusive. It is clearly impossible to prescribe absolute rules for the prevention of all possible changes . . . to a large degree the dependability of water analyses must rest upon the experience and good judgment of the analyst.

Even the concentrations of the more stable dissolved constituents may vary during prolonged storage, and a lapse of more than 3 months between collection and analysis is not recommended. Once opened, the sample should be analyzed as rapidly as possible. Changes in water quality are greatly accelerated after the bottle seal has been broken. Composite samples should be prepared immediately before analysis.

Although equilibrium between sediment and dissolved material can be assumed for the time of collection, this is no assurance that the same equilibrium will be maintained during storage. Solutions of the sediment, ion exchange, or other chemical reactions that affect the chemical composition of the sample are all possible. But little definite information is available on the problem; much more work must be done before substantial conclusions can be made.

B:2 SAMPLE-BOTTLE CASES

Sample-bottle cases commonly used by the Geological Survey are shown in figure 7. Cork or rubber stoppers may jar loose unless the bottles are packed in a shipping case that exerts pressure on the stopper. Containers should be marked clearly "Liquid in Glass" and "Keep from Freezing."

B:3 SAMPLE STORAGE

It is a wise practice to check and tighten the seals of bottles as the samples are put on the storage shelves. High temperatures should be avoided. Stored samples should be left undisturbed, as much of the suspended material will settle on standing, and they should be protected from light, which accelerates photochemical processes that may alter the chemical composition of the sample. Growth of algae in stored samples is particularly troublesome.

B:4 PREPARATION OF COMPOSITE SAMPLES

When samples are collected at frequent intervals at a station, analysis of each individual sample would be prohibitive in cost and for many streams would result in needless duplication. Consequently, the compositing of several samples into a single sample for chemical analysis is a common practice. This is solely a pro-

FIGURE 7.—Sample-bottle shipping cases.

cedure of expediency, and the chemist realizes that in so doing the chemical characteristics peculiar to each individual sample are not identifiable in the composite. Likewise, it should be recognized that for some streams even the analysis of daily samples would not adequately define the changes in stream quality. The length of the composite period is always a compromise between the cost of analysis and the desire to determine the quality pattern of the stream in minute detail. Early studies indicated that periods of approximately 10 consecutive days were optimum; small variations in quality were smoothed out, but major changes were still shown by 36 composite samples per year. For each month, three composite samples were regularly prepared by mixing together equal quantities of daily samples collected from the 1st to the 10th, 11th to the 20th, and the remainder of the month.

In the 1930's, changes in compositing methods were brought about by the general acceptance and use of specific conductance as an approximate indication of the total concentration of ionized material in solution. Although generally holding to the principle of 10-day periods, split composites were made on the basis of total dissolved mineral content as indicated by measurements of conductivity of the daily samples, supplemented by other easily obtained information such as concentration of chloride, river stage, weather conditions, appearance of sample, and previous history of the stream. This modification is now used by many laboratories and is recommended in preference to a fixed time interval of compositing samples because it affords the chemist more discretion in deciding which changes in concentrations are significant and worthy of more intensive study.

Short of continuous measurement of all constituents, there are 2 fundamental categories of data application which can be met by 2 different methods of compositing—the time-weighted metnod and the water-discharge-weighted method. One area of data application requires knowledge of the chemical composition, as concentration per unit volume, of only a fraction of the total flow. Analyses of time-weighted composites provide information on the quality of water available for uniform-quantity withdrawal, such as municipal or industrial diversions and domestic uses, or on the effect of water as an environment, such as the effect of water quality on growth of crops or on plant and animal life. The preparation of time-weighted composites simulates these uses of the water, and therefore chemical analyses of such composites are best suited for consideration of these problems.

The other field of data application requires consideration of the whole stream as a dynamic agent transporting and capable of receiving material. Whereas the total quantities of water and dissolved matter that pass the cross section on the stream are irrelevant to the problems of uniform withdrawal and environment, they are vital to problems of solute transport (dissolved load). Knowledge of solute transport of a stream is essential to most quantitative considerations of water quality such as the geologic processes of erosion of rocks and soils and modification of landforms, the quantity of pollutants entering a stream or the capacity of the stream for safely receiving a quantity of waste material, the salt balance on irrigated lands, the action of evapotranspiration on land or in streams or reservoirs, and the anticipated quality of the water if impounded. Analyses of discharge-weighted composites supply information applicable to such problems.

No single method of compositing provides data applicable to all problems confronting the chemical-quality hydrologist, and he must be cognizant of the effects of the compositing method on the analytical results and be so guided in the application of the data. When there is doubt about which method to use, the decision must be based on the ability to extract or compute from the data the type of information that may be required for understanding the stream's water quality and for utilization of the water.

Theoretically, for either method of compositing, all samples for a major period such as a year could be included in one composite. Actually this cannot be done because changes in quality occur during storage of samples and because data representative of water quality during much shorter periods are needed. Fluctuations in quality during the sampling interval influence the degree to which the analysis of a composite is representative of the stream. It is improbable that any one sample taken during a period of fluctuating quality can possibly represent the mean concentration for all dissolved constituents because the factors controlling the concentration of the individual constituents are not identical. For example, the time of mean calcium concentration may not coincide with that of mean sodium or nitrate concentration. Also, the ability to choose in advance the time at which the mean for the interval could be sampled is even less likely. Consequently, the probability that a composite analysis represents the streamflow becomes a statistical problem of sampling, controlled by both the range of fluctuations and the number of samples included in the composite.

Both methods of compositing leave appreciable latitude in the number of composites that can be made per year. No hard and fast

rules for compositing can be set forth because of the differences in range and the rapidity of fluctuations in the quality of different streams and because of the diversity of purposes for which chemical-quality investigations are conducted. The following suggestions are presented as a *general guide* but are *by no means mandatory*, and their application should be tempered by the chemical characteristics of the streams at the particular sampling station and by the significance of the observed variations in quality to present and anticipated use of the water-quality record. The number of composites per year should not ordinarily be greater than 40 or less than 20. Analyses of less than 20 composites per year are usually insufficient to define adequately the water-quality pattern of the stream unless the chemical characteristics are exceptionally stable, such as may be true below a reservoir. The cost of running more than 40 analyses per year increases the overall station-operation cost appreciably, and there is always some question as to whether the more detailed information justifies the additional expenditure. No single composite should cover more than a 30-day period. Suggestions regarding selection of compositing periods are presented in the detailed discussion of each compositing method.

B:4a TIME-WEIGHTED COMPOSITE SAMPLES

If the chemical analysis of a composite sample of a stream is made primarily to determine the average concentration of chemical constituents in the water that flowed past the sampling station during the period, the composite should theoretically be obtained by continuously diverting and thoroughly mixing a constant volume of streamflow. To the extent that the individual samples define the water quality during the compositing period, satisfactory time-weighted composites can be prepared by combining volumes that are proportional to the sampling interval for each individual sample. The sampling interval is the length of time that a sample represents; generally it is half the time between the time the preceding sample and the following sample were taken. At many sampling stations one sample is collected each day at approximately the same time of day; therefore, the sampling intervals and the volume of the samples taken are constant.

In preparation of time-weighted composites the compositing periods are selected on the basis of observed differences in water quality exhibited by some single characteristic or group of readily determined characteristics of the individual samples, such as specific conductance, pH, or chloride. The purpose of utilizing conductance or other characteristics in defining the limits of the compositing period is to provide a composite that contains only water of some-

what similar chemical characteristics. The compositing period represents a period during which it is assumed that no large changes in composition have occurred. As a flexible guide to the selection of compositing periods it is suggested that the composite include only those consecutive daily samples whose individual conductances are within ±15 percent of average conductance for the group. Any percentage other than 15 can be used to keep the number of composites per year within the optimum range. A knowledge of stream characteristics at the sampling station is essential for compositing and can be gained only through experience. As the chemist learns more of the chemical behavior of the streams in his area, his judgment in selecting compositing intervals will improve.

The degree to which time-weighted composites are representative of the stream during the compositing period is not dependent on the degree to which each sample represents the arithmetic mean concentration of each individual constituent for the sampling interval, but rather on the extent to which the algebraic sum of the positive and negative deviations of the individual sample concentrations from the true mean concentration for the individual sampling intervals approaches zero.

B:4b DISCHARGE-WEIGHTED COMPOSITE SAMPLES

If the chemical analysis of a composite sample of a stream is made primarily to determine the concentration of chemical constituents in the total volume of water that flowed past the sampling station during the compositing period, the composite should theoretically be obtained by continuously diverting and thoroughly mixing a constant fraction of streamflow. Practically, sampling must be periodic rather than continuous, but the volume of each individual sample that goes into the composite can be varied in proportion to the rate of discharge at the time of sampling. To the extent that the products of dissolved material in the individual samples and the discharge rates define the load of dissolved material carried by the stream during the compositing period, satisfactory discharge-weighted composites can be prepared from individual samples by combining volumes that are proportional to the stream discharge at the time of sampling. If the individual samples have different sampling intervals, the volume to be taken from an individual sample should be proportional to the product of the sampling interval and the water discharge at the time of sampling.

The preparation of discharge-weighted composites requires water-discharge data for the time of sampling. At sampling stations where the relations between water stage and discharge are stable, the water discharge can be determined by using the gage height at

the time of sampling and a stage-discharge rating table or curve. More precise discharge data are desirable for a shifting stream, where significant error is incurred by the use of stage-discharge tables or curves. The required data on streams that have shifting controls or instructions for the computation of provisional instantaneous discharges satisfactory for compositing purposes can be obtained from the district offices of the Surface Water Branch of the Water Resources Division.

When samples are composited according to discharge, the subdivision into compositing periods usually has little effect on the computed total tonnages (loads) of mineral constituents for a period of a month or a year. The accuracy of computed tonnages is not increased by the use of short compositing periods nor by breaking compositing periods when abrupt changes in specific conductance occur. However, the chemical-quality records serve many purposes, and much additional factual information concerning the water-quality characteristics of the stream is provided by the judicious selection of compositing periods.

Both specific conductances, or other readily determined characteristics of water quality, and water discharges representative of the individual samples are used as a guide in determining when to end one compositing period and begin another. When combined, these factors often aid the chemist in anticipating changes in chemical composition which might not be evident from either alone. Specific conductance also aids in selecting individual samples to represent high and low concentrations. However, of the two variables discharge and conductance, the former is given somewhat more consideration than the latter in the selection of compositing periods. A knowledge of the chemical-quality characteristics throughout the water-discharge range permits construction of a reliable chemical-concentration rating curve based on water discharge as the independent variable. Inasmuch as the selected compositing period has little effect on the validity of computed loads, these periods are chosen primarily to show the relation of concentration to water discharge. Consequently, the compositing period should represent a limited range of water discharge. As a flexible guide it is suggested that the composite sample include only those consecutive samples whose corresponding instantaneous discharges are within ± 25 percent of the mean instantaneous discharges for the group. Any percentage other than 25 can be used to limit the number of composites per year to a feasible level (see sec. B:4). If the stage-discharge relation of the stream is known to shift appreciably, and if the water discharge must be taken from a rating curve, one com-

positing period should be ended and another begun at times of radical change in discharge. A shift in the stage-discharge relation during the compositing period upsets the ratio of the computed provisional discharges to true discharges, and correct proportional quantities will not be taken for the composite. These shifts usually are caused by changes in stream velocities that result in scour and fill of the stream channel at the gaging-station control. The tonnage figure is computed later from the true-discharge figures supplied by the Surface Water Branch and not from the provisional discharges used to make the composite.

The degree to which a discharge-weighted composite represents both the average concentration in the total mass of water passing the sampling station and the load of each and all determined constituents transported during the compositing period is dependent on the degree to which the summation of the individual products of concentration of constituents and water discharge approach the true average concentration and loads of the whole volume of water that flowed past the station. Deviations of individual-sample concentrations from the mean concentration or deviations of instantaneous discharge used in the compositing process from mean discharge for the sampling interval do not in themselves affect the validity of the analysis of the composite. This is true because, as with time-weighted composites, the validity of an average is proportional to the extent to which the algebraic sum of the positive and negative errors approaches zero and not on the magnitude of the individual errors.

B:5 REMOVAL OF TURBIDITY

Every water chemist has been confronted with turbid samples. All natural-water samples contain varying amounts of ionized and nonionized constituents in true solution, less finely divided material in colloidal suspension, and coarser readily separable material. The analytical statement will tend to represent the total ionic concentration in the fraction of the total sample taken for analysis regardless of whether the constituent is in solution or suspension. Inasmuch as the suspended material often contains ions determined in the analysis, the reported concentrations are dependent on the separation of the solution and solid phases. A filtration assembly made of transparent plastic and designed by the Geological Survey is shown in figure 8.

Most authoritative compilations of analytical procedure recognize the significance of finely divided material in suspension but omit specific instructions for its separation from the water. Comparable analytical results demand that the water-quality sample taken for

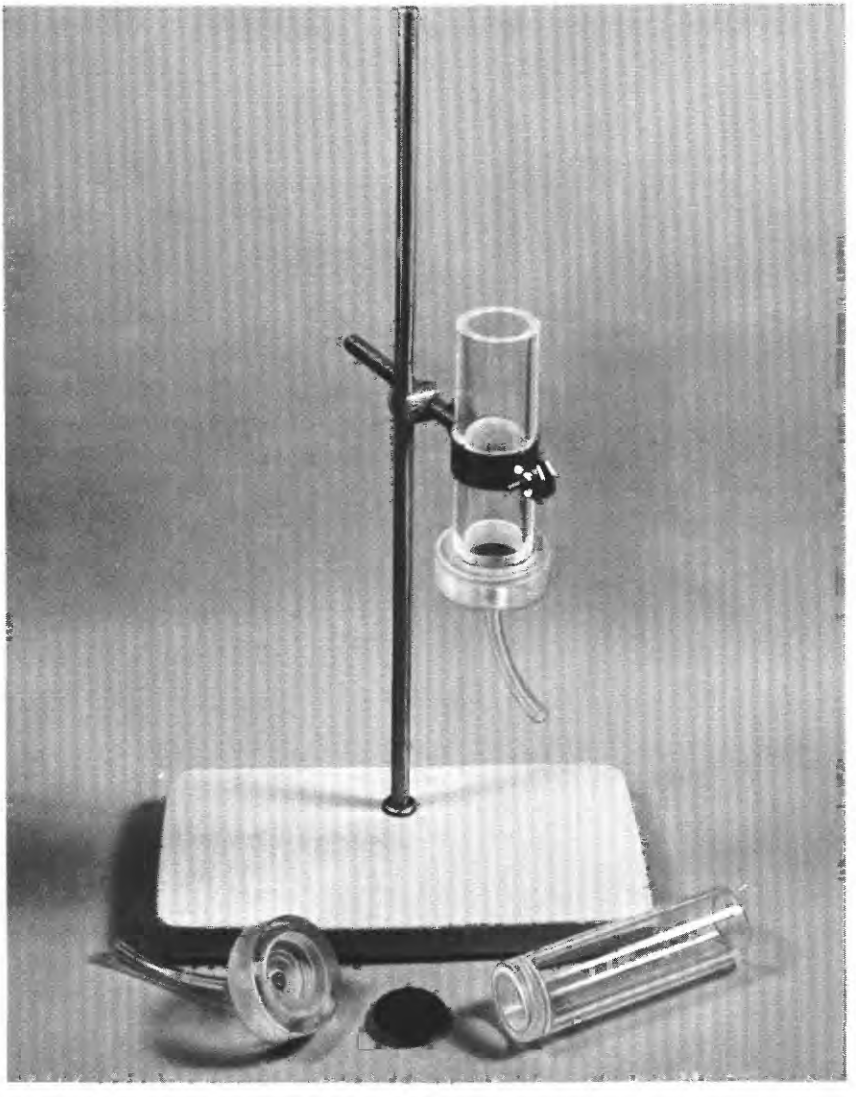

FIGURE 8.—Sample-filtration assembly.

chemical analysis be defined in terms of the maximum particle size of the suspended material. The specific method of separation should produce a minimum of change in the concentrations of the constituents in solution. No ideal method for removing solids exists, but tests have indicated that filtration through the commercially available cellulose acetate membrane has a minimum of undesirable qualities compared with other available methods. As a matter of

convenience, the maximum particle size of suspended material can be limited to that which passes by gravity through a filter whose retention rating is 0.5 microns. This specification does not imply that all settled solids should be resuspended before filtration, nor does it imply that obviously clear samples should be filtered. Determinations of pH, alkalinity, and(or) acidity should be made before filtration in the laboratory because these characteristics are related to the gas content of the sample.

REFERENCE

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

SECTION C. ANALYSIS OF WATER SAMPLES

In analysis of water the chemist is confronted with a wide variety of complex aqueous solutions. Most water in streams, lakes, and ground-water reservoirs probably contains most of the elements, although many are present in only extremely small quantities. The scope of analyses by the Geological Survey is generally limited by the significance of a constituent in relation to the other dissolved material and to the usability of the water, and by the precision of the analytical methods used.

C:1 ANALYTICAL TECHNIQUES IN WATER ANALYSIS

Water analysis may be termed "microchemistry with macro-volumes" because all determinations require the quantitative determination of either milligram or microgram quantities or fractions thereof. Techniques by which the water analysis is made include gravimetric, volumetric, spectrophotometric, and flame-photometric procedures.

Gravimetric techniques in water analysis are generally tedious and time consuming because of the usual necessity for precipitation, filtration, washing, ignition, and weighing. Volumetric analysis is usually more rapid than gravimetric analysis if the titrant reagent is specific for the constituent; the sensitivity and(or) precision may also exceed that of a gravimetric analysis for some determinations. Progress in instrument development, particularly during the last decade, has provided the water analyst with truly precision instruments in spectrophotometers and flame photometers. Spectrophotometric methods are well suited to water analysis because small quantities of substances can often be determined readily and accurately. The differences in techniques of individual analysts are also minimized. The accuracy and precision of flame-photometric determinations of the alkali metals surpass the available gravimetric method, and the time required is much less.

C:1a SPECTROPHOTOMETRY

Colorimetric determinations based on visual estimation of color have long been used in water analysis, but the widespread application of colorimetric analysis in the refined form of instrumental spectrophotometry is a relatively new development. Because of its youth, the terminology of spectrophotometry is in a confused state. The system of terminology used in this report follows that recom-

mended by the National Bureau of Standards (1947), a system which was derived as a compromise of several recognized terminologies.

C:1a–1 TERMINOLOGY AND PROCEDURES

In the practical application of spectrophotometric analysis, only three terms need to be considered in detail. These are the fundamental term "transmittance" and the two terms "transmittancy" and "absorbancy" which are derived from it. Transmittance is defined by the equation:

$$T=\frac{I_2}{I_1}$$

where

T=transmittance,
I_1=radiant energy incident upon the first surface of the sample, and
I_2=radiant energy leaving the sample.

The term "transmittance" relates to the rectilinear transmission of homogeneous radiation through a homogeneous, isotropic, nonmetallic medium having plain, smooth, parallel surfaces. In analytical practice the transmittance is not measured. The quantity that is indirectly measured is a ratio of the transmittance of the sample solution to the transmittance of the solvent (or blank) solution. The name "transmittancy" is given to this ratio. It is seen from the following relation that transmittancy (T_s) can be measured directly in a spectrophotometer.

$$T_s=\frac{T \text{ sample}}{T \text{ solvent}}=\frac{I_2 \text{ sample}}{I_2 \text{ solvent}}$$

where

T=transmittance, and
I_2=radiant energy leaving the sample.

It should be noted that the transmittancy relation is correct only if the reflection and absorption losses at the cell windows are insignificant. These conditions are met in normal applications of visible-light spectrophotometry in water analysis.

The third term of importance and the one most generally used in absorptiometric work is "absorbancy," which is simply the negative logarithm of the transmittancy.

$$A_s=-\log_{10}T_s=\log_{10}\frac{1}{T_s}$$

In the preparation of spectrophotometric curves of light-intensity ratio plotted against concentration, it is preferable, for convenience, to use absorbancy as the basis of the plot. Under these conditions a system that conforms to Beer's law gives a straight-line plot, and the commonly used colorimetric systems that do not conform will usually show only a moderate curvature. Extreme curvature, when the curve

is plotted on the basis of absorbancy data, is sometimes a sign that the system is not sufficiently stable for analytical purposes. Semicolloidal suspensions of colored substances often give extreme curvatures. When transmittancy data are used for plotting, a curve is always obtained unless semilogarithmic coordinates are used. The modern spectrophotometers have an absorbancy calibration as well as the conventional "percent transmission" or "percent transmittance," and it is increasingly prevalent practice to use the absorbancy scale. The relations between transmittancy and absorbancy plots for potassium permanganate solutions at three wavelengths are illustrated by Mellon (1950, p. 95, figs. 2, 3).

Several other terms for light absorption are given in the literature and are still found on the printed scales of some photometers. "Optical density" is often used. Sometimes optical density is the same as absorbancy, and sometimes it represents absorbancy multiplied by 10. "Extinction" is sometimes used, as is "percent extinction." Even a few purely arbitrary scales have been used.

The fundamental expression that correlates the light-absorption reading of the instrument with the concentration of the light-absorbing constituent in the solution is Beer's law. The law is expressed by several mathematical formulations, and the derivation of each may be found in standard texts. One of the simplest statements of Beer's law is in the terminology recommended by the National Bureau of Standards (1947):

$$A_s = a_s bc$$

where

a_s = "absorbancy index,"
b = thickness of the cell,
c = concentration, and
A_s = scale reading.

Since the terms a_s and b are constant for a given analytical system and a given absorption cell, it is apparent that A_s is directly proportional to c.

The relation demonstrated by Beer's law is very useful and apparently is rather generally true for solutions of a single colored constituent and when no chemical reaction is involved. But in analytical practice many colorimetric systems show deviations from the law. Most apparent failures of Beer's law are due to chemical or instrumental properties. Some of the chemical effects responsible for departure are:

1. Small changes in pH acting on a pH-sensitive color system. Most organic indicators are weak acids or bases and consequently they are pH sensitive.
2. Temperature effect. A rise in temperature of a color system generally causes the absorption peak to shift toward the red.

3. Change in refractive index with concentration.
4. Equilibria displacement with concentration change.
5. Reciprocal interaction of the absorbing constituents. This is characteristic of dithizone and other reagents.
6. Salt effect. This applies mainly to absorbing solutions of electrolytes, but the effect is sometimes present even if the absorber is not an electrolyte.

The major instrumental cause of deviations from Beer's law is the use of an impure spectral band for illumination of the sample. If the spectral band covers an area where the absorbancy curve of the constituent shows a sharp change with wavelength, a deviation will appear. By using the narrowest possible spectral band, this effect is minimized. The analyst is referred to standard texts for a complete explanation of this effect.

A second frequent source of instrumental deviations from Beer's law is a nonlinear photometer unit in the spectrophotometric instrument. If either the photocells, amplifying unit, or indicating unit do not respond linearly to a variation in light intensity, a deviation from Beer's law will be evidenced. Most commonly such effects originate in aging photocells and can be remedied by replacing the photocell. It should be emphasized that the common practice of making determinations by comparison (by comparing the sample against a blank) is no protection against nonlinear amplification of the signal. The effects do not "cancel out."

An important consideration in the use of spectrophotometric instruments is the absorbancy range within which the particular instrument will give accurate readings. The relative-error relation of a spectrophotometer is expressed by the curve shown in figure 9, from which it is apparent that the best accuracy is attained in the absorbancy region from approximately 0.1 to 1.0. Theoretically, the point of minimum relative error is approximately 37-percent transmittancy, which is 0.43 on the absorbancy scale. When filter photometers and simple spectrophotometers are used, it is necessary to observe the above limitations if the measurements are to be acceptably accurate. Absorbancy measurements above 1.0 should not be taken; dilution of the sample, or a similar expedient, should be used to bring the reading down into the reliable area. At the other end of the range, it is frequently impossible to avoid taking measurements in the area of poor accuracy; however, enrichment of the sample is sometimes possible and should be practiced when convenient.

The situation with respect to accuracy is somewhat different with instruments such as the Beckman B and DU spectrophotometers that have a stepwise variable-sensitivity adjustment. By use of

the higher sensitivities for reading dense solutions the accuracy is much improved, and readings up to approximately 2.5 can be taken. The flat part of the error curve in figure 9 is extended on the left side to higher absorbancy values by this device. However, the variable-sensitivity adjustment gives no improvement in the very low absorbancy region at the right side of figure 9.

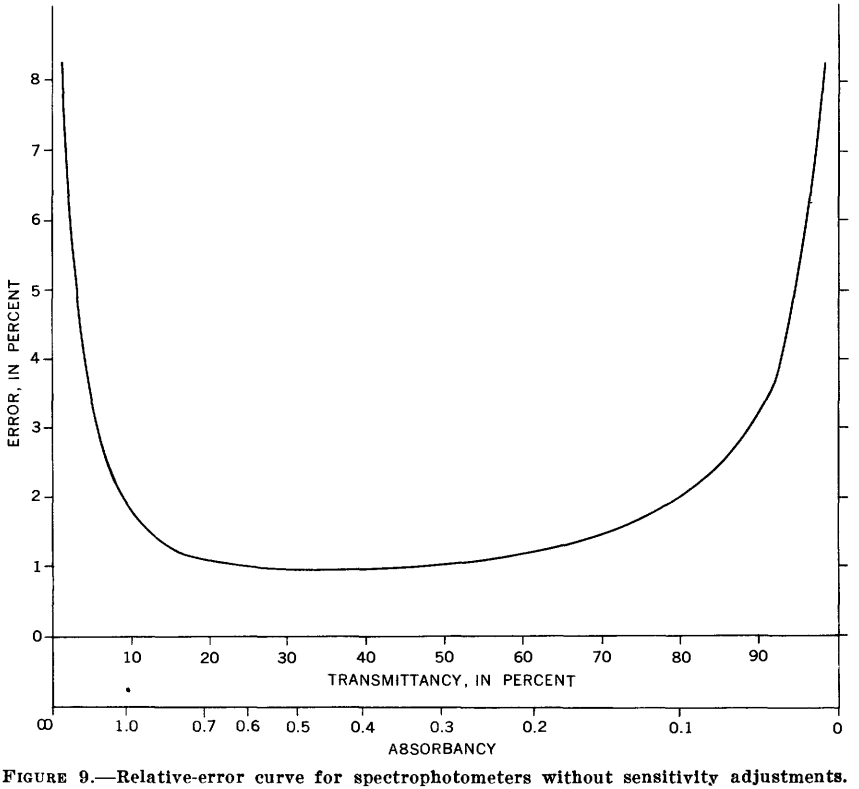

FIGURE 9.—Relative-error curve for spectrophotometers without sensitivity adjustments.

C:1a–2 APPLICATIONS OF SPECTROPHOTOMETRY TO WATER ANALYSIS

The mass application of instrumental spectrophotometry to water analysis has erected rapid advances in the determination of trace metals in water. In analyses for trace metals, a point of major importance is the sensitivity of determination. In this respect the spectrophotometer is superior to the polarograph, and for certain metals it is also superior to the spectrograph. Only the fluorimeter possesses a generally higher inherent sensitivity, but at the present time the application of fluorimetry to different types of analytical problems is limited.

In spectrophotometric determinations in water analysis it is generally desirable to attain maximum sensitivity. This confers several

advantages besides the obvious one of extending the determination to the lower concentration ranges: The interferences of other ions can be minimized, the effect of natural color and turbidity in the water sample can often be made insignificant, and a small volume of sample can be used. The use of a highly sensitive reagent permits dilution of the sample to a point where interfering ions are rendered innocuous. The necessary dilution can be simply and automatically made by adding a large volume of dilute reagent to the sample, as opposed to the more common practice in other types of analysis of adding a small volume of fairly concentrated reagent. An example of this principle is the Eriochrome Cyanine R fluoride determination, in which 25 ml of a dilute reagent is added to 10 ml of the water sample, thus diluting the sample to minimize the interference of phosphate, aluminum, and other ions.

The same principle applies to minimizing the effect of turbidity and color. The natural color and turbidity in many water samples show a significant absorbancy at the wavelengths used in a number of determinations, and this effect requires either compensation or elimination. In some cases it is possible to select a spectrophotometric reagent of such high sensitivity that the absorbancy of the sought constituent will exceed the arbsorbancy of the natural color and turbidity by a very large factor. If this factor is as high as 50 for a particular determination, the error introduced by the natural color and turbidity will be only 2 percent, and in routine work no compensation would be required. Several of the spectrophotometric determinations described in this manual, notably the chromate and phosphate determinations, will normally give an absorbancy reading considerably higher than 50 times the absorbancy of the natural coloring matter in the water sample. In other procedures, such as the aluminum determination, the absorbancy of the color and turbidity may be as high as that contributed by the analytical system. Thus, correction for color and turbidity is very rarely required for chromate and phosphate, but correction is frequently required for aluminum. A knowledge of the relative sensitivity for the sought constituent as compared to the natural color and turbidity in the sample is necessary to the application of spectrophotometric methods. Sufficient data are given in each procedure so that the analyst can approximate the extent of this anticipated interference in the application of selected methods.

Sensitivity is a word that is used loosely, and it is important to identify the type of sensitivity under consideration. The sensitivity of a method depends on both the chemical phase of the determination

and the instrumental phase. Generally, the chemical phase provides the major differentiation of the sought constituent against the "background," although the instrument used to analyze and measure the system also contributes. The type of sensitivity under consideration is that which improves the absorbancy of the sought constituent relative to the background absorbancy, which is made up of the absorbancy of interfering ions, natural color, and turbidity. Merely increasing the optical path of the absorption cell does not improve the relative sensitivity of the sought constituent against the background because the absorbancy of both is increased proportionately. To obtain a useful improvement in the sensitivity it is necessary to select an analytical method that will provide a greater absorbancy for the sought constitutent without simultaneously raising the background value.

While maximum sensitivity is usually desirable for water analysis, the more sensitive analytical systems are more subject to contamination effects, and their use requires careful technique. Laboratory glassware will contribute lead and possibly other metals. In all sensitive lead determinations it is necessary to boil the glassware in dilute nitric acid to remove surface lead. Pyrex glassware is still the mainstay of the trace-metals laboratory, although polyethylene, polystyrene, and other types of plastic equipment are available for reactions that do not require heat. Stainless steel, aluminum, copper, and nickel beakers are available and might well be used more extensively for special contamination problems. In some tests the one or more metals contributed by the metal beaker might be less of an interference than the several metals extracted from glass.

A more serious source of interference in sensitive work is the reagents. Only reagents of the highest purity should be used, but even these will show some impurity if the test is sufficiently sensitive. Therefore, it is always advisable to use the minimum amount of reagent that accomplishes the objective. For example, there is no point in using 10 g of sodium acetate to buffer a solution if 1 g will buffer adequately. For some determinations the special spectroscopic-purity reagents, such as those supplied by the Johnson Matthey Co., can be used to advantage. Distilled water is another source of metallic contamination, but it can usually be satisfactorily cleaned up by the ion-exchange resins. In general, contamination should not be a major difficulty in spectrophotometric work.

The end result of analysis is affected not only by changes and impurities in the reagents but by instrumental variations as well (instrument maintenance is discussed in sec. C:2d). An overall check on the performance of each component, instrumental and

chemical, that enters into the determination of the final result is desirable. This can best be done by running standards at frequent intervals. For some determinations where the variations seem to be particularly pronounced and uncontrollable, it may be necessary to run a series of standards with each set of analytical determinations, as with the dianthrimide determination of boron. This method will be of no benefit in controlling purely random variations, for which there is no effective control. But if the absorbancy shows a slow and comparatively small consistent change from day to day, it is valid to run standards each day as a means of correcting for small departures from the calibration curve. A calibration curve is normally made up of a comparatively large number of points, with the mean curve drawn through them. Thus the small random errors in the individual determinations tend to average out. Such a calibration curve made of many points has an inherent reliability superior to that of the 1 or 2 standards that would be run with each set of determinations to check the curve. Therefore, these "checking" standards should be run simply to detect changes in the calibration curve. Absorbancy values should not be calculated on the basis of just one standard. The proper procedure is to prepare a new calibration curve if it is found that the single standard has revealed an actual shift in the absorbancy calibration curve.

In the consideration of the significance of sensitivity in spectrophotometric water analysis, the effect of natural color and turbidity has been mentioned. This is a recurring problem and should be considered in detail. Waters containing high concentrations of humic matter, such as swamp water, have an intense yellow color. Iron, especially in the form of the colloidal oxide, gives a yellow-tan color. These two colors are common and cannot be distinguished by visual inspection. Both give similar absorbancy curves. Curve A in figure 10 shows the absorbancy-wavelength curve of swamp water from Dade County, Fla., that contained a very high concentration of organic matter. The color reading on the Hellige scale is 140. This curve is characteristic of water that appears yellow tan to the eye. Curve B shows the absorbancy curve of a water that contained colloidal iron. The reading on one Hellige scale was 45. The similarity between the curve for organic coloring matter and the curve for iron is obvious.

Curves A and B illustrate a very important phenomenon in spectrophotometric water analysis. The interference of the "normal" natural color is much greater in the blue region of the spectrum. Therefore, there is a very definite advantage to using analytical systems that absorb in the yellow-red region. This is one reason why

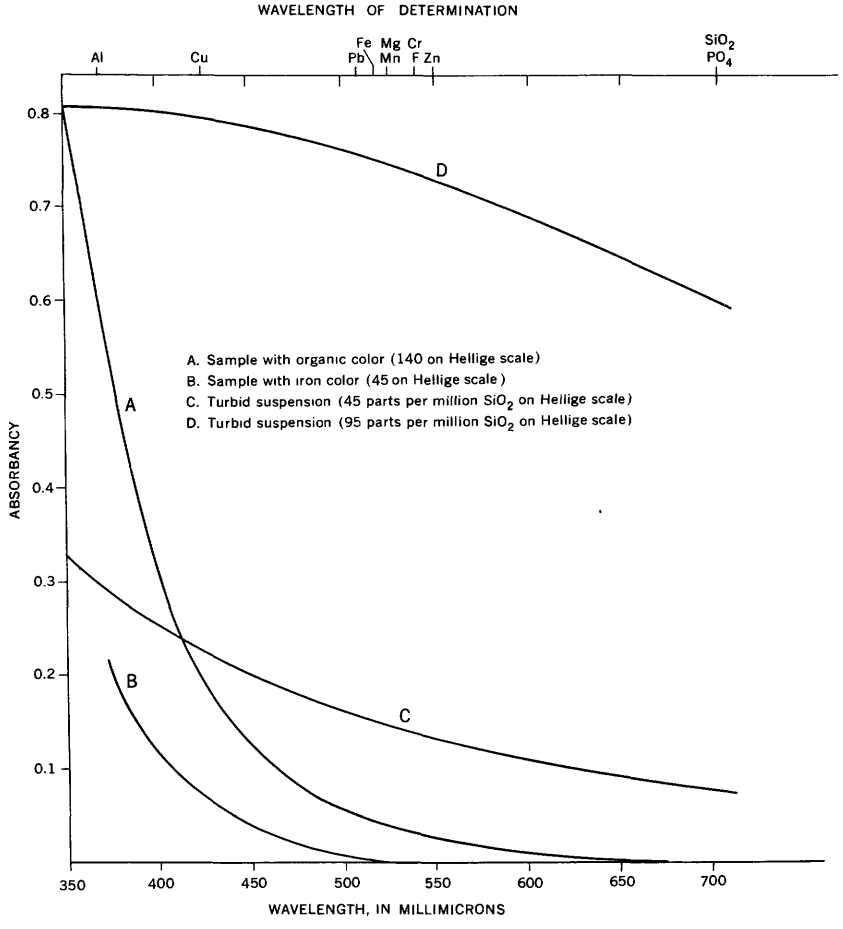

FIGURE 10.—Absorbancy curves for colored and turbid samples. Absorbancy readings were taken with Beckman B spectrophotometer, using 40-mm absorption cells.

most of the spectrophotometric methods in this manual utilize wavelengths of 500 mμ or greater. Methods that require measurement in the blue region are included only when their merits are sufficient to outweigh the detrimental effect of high color intereference; the ferron determination of aluminum is an example.

The color curves in figure 10 permit estimation of the approximate interference that the "normal" type of yellow color in a water sample will give at the wavelength of a particular determination. When the effect of color is not too great, a correction could be made on this basis. This method could be applied only to samples with the familiar yellow-tan color indicating humic matter and iron oxide. For samples containing colored industrial wastes, petroleum products, and other material with "abnormal" colors, new curves would have

to be prepared. Where a laboratory is analyzing colored waters of consistent composition on a routine basis, it would be profitable to prepare color-correction tables for each spectrophotometric method, thereby eliminating the necessity to include the color-compensation step in each analysis. The approximate effect of the interference of the natural color represented by curve A in several spectrophotometric determinations is given below:

	Wavelength ($m\mu$)	*Error* (*ppm*)
Al	370	+0.6
Cu	425	+.3
Fe	520	+.1
F	540	−.15
PO_4	700	+.001

The effect of natural color may be compensated in several ways, of which four are described below.

1. Subtraction of natural-color absorbancy.—Determine absorbancy of the test sample, A_{ts}, against the blank specified for the procedure. Determine absorbancy of the natural-color sample, A_{ncs}, against distilled water using the same spectrophotometric conditions as for the test sample. The difference is the corrected absorbancy, A_s. Use A_s to obtain concentration values.

The test sample is the water sample with color developed as outlined in the analytical procedure.

The natural-color sample can be prepared in two ways. The most general method is to take the same volume of sample water as was used for the test sample. Treat it exactly as the test sample with one exception: do not add the indicator reagent. Instead add an equal volume of indicator solvent, usually dilution water. The second method uses color- and turbidity-correction solutions, which are simply shortcuts of the above general procedure. These solutions combine the significant reagents into one solution, so that a single addition of reagent suffices. The color-correction solutions are not applicable in every case. The full procedure is usually a little more reliable.

The subtraction method is the most generally applicable correction method. It can be applied to turbidity corrections as well as natural color. The method fails where the indicator reagent reacts with or affects the natural color or turbidity in the water sample or where the effects of the other reagent on the test sample and natural-color sample are not essentially identical. The latter qualification relates more to turbidity than color, and filtration of excessively turbid samples may be required.

2. Direct compensation.—The direct-compensation procedure is illustrated by the cuprethol copper determination. All the reagents except cuprethol, the indicator, are added to the sample. The sample is placed in the spectrophotometer and the absorbancy is set to zero by adjusting the slit width. This step eliminates the natural absorbancy of the water. The indicator reagent is then added. The color is developed and the correct absorbancy is read directly from the scale. This procedure is not of general utility and can be applied only when conditions are right. One requirement is that the absorbancy curve should have only a shallow slope in the operating region.

3. Bleaching.—If the indicator reagent reacts with the material that gives the sample its natural color, the resulting color must be removed by bleaching. One example of such a reaction is the periodate determination of manganese. Periodate oxidizes manganese to permanganate, developing the familiar pink color. Periodate also partially oxidizes the organic coloring matter in the water and changes the natural color. Therefore, compensation by means of a natural-color sample will not be correct. In the permanganate test the procedure is to develop the color in the test sample and determine the absorbancy. A few crystals of sodium nitrite are then added to the sample. This destroys the permanganate color immediately but does not affect the organic matter. The color contribution of the organic matter can now be directly measured. It is subtracted from the absorbancy of the test sample to obtain the corrected absorbancy.

4. Removal of color material.—The color material is sometimes removed with conventional activated-carbon or alumina treatments. The method is mentioned only to cite its limitations. Gross contamination from impurities in activated carbon is an ever-present possibility. Furthermore, the carbon will adsorb trace metals and can completely change the content of trace metals in the sample. Alumina is less likely to be a source of contamination, but it will take up trace metals just as avidly as activated carbon. These two methods cannot be used for sensitive analyses. The acceptable procedures for removing color are chemical oxidations with nitric acid, hydrogen peroxide, and similar agents.

Curves C and D in figure 10 show how the effect of natural turbidity varies with wavelength. Curve C represents a turbidity of 45 ppm SiO_2, and curve D represents 95 ppm SiO_2; both measurements are on the Hellige scale. The suspensions used to prepare the curves were of barium sulfate with 10 ppm sulfate in C and 40 ppm in D. Suspension C was of fine particles, and D was of coarser

particles. The shape of the two curves is influenced by the particle size in the way that would be predicted by Rayleigh's equations for light scattering. A turbid suspension not only absorbs light but scatters it as well, and the scattered-light losses are indicated as absorbancy by the spectrophotometer. Suspension C shows a higher relative scattering in the blue region, as would be predicted, because of its smaller particle size. The significant observation for both curves is that the absorbancy effect of the relatively high turbidity in C is greater over most of the spectrum than the very high color represented by curve A. Only in the extreme blue end of the spectrum, at wavelengths less than 400–425 mμ, does the interference of natural color normally exceed that of turbidity. The approximate interferences of the 2 turbid suspensions in the 5 determinations cited previously are as follows:

	Wavelength (*mμ*)	*Error*	
		C (*45 ppm* SiO_2) (*ppm*)	*D* (*95 ppm* SiO_2) (*ppm*)
Al	370	+0. 3	+1. 0
Cu	425	+. 3	+1. 2
Fe	520	+. 3	+1. 2
F	540	−. 3	−1. 2
PO_4	700	+. 08	+. 5

Fortunately, most natural-water samples are less turbid than the suspension represented by curve C; however, some streams carry such a fine suspension of clay that the water appears opaque when collected. For these samples the spectrophotometric methods of correction for turbidity, treating it the same as natural color, are not satisfactory, and the turbidity must be removed. To date only one generally acceptable method for removing such turbidity has been found; this is filtration through membrane filters such as the cellulose acetate type supplied by the Millipore Co. (See sec. B:5.) Centrifuging is often useful, but it is less efficient than membrane filters for fine particles. Good results can sometimes be obtained by filtering the sample through a fine filter paper, such as Whatman 42, that will remove a large part of the turbidity. The residual turbidity in the sample is then corrected for by the same methods as for color.

The difficulty in removing turbidity is to avoid upsetting the trace-metal ionic relations in the sample. While it is not known that any single method accomplishes this objective ideally, it is known that some methods are better than others. The methods cited above, while not ideal, are acceptable. Some methods are not acceptable because of the high possibility of gross contamination of the sample or gross change of the sample by adsorption of constituents on the

filtering medium. The methods that cannot be used in spectrophotometric work are:

1. Filtration through Berkefeld tubes and similar porous porcelain or diatomaceous-earth filters.
2. Filtration with the aid of charcoal or alumina.
3. Filtration with the aid of filter pulp unless it has been established that the pulp does not significantly adsorb the particular constituent being determined.

Filtration through fritted-glass discs is probably safe from the standpoint of adsorption losses, but it is always necessary to guard against contamination by carryover from previous filtrations with these units. Another method is the addition of large quantities of salts to the sample to neutralize the charges on the particles and cause their coagulation. What effect this procedure may have on trace metals has not been investigated, but it is obvious that contamination may occur because of the high concentration of salt that must be added.

It is impossible to specify procedures for the correction of turbidity that will fit all field conditions. Through familiarity with waters of the area the analyst will be able to identify the appropriate method for eliminating errors resulting from turbidity. Often no correction will be necessary. In other cases it will be possible to empirically prepare correction tables or curves for the streams. It should be necessary only occasionally to apply lengthy physical or chemical procedures.

C:1b FLAME PHOTOMETRY

Flame photometry is closely related to spectrographic analysis, and many of the concepts of that field carry over into flame photometry. The essential difference between the two forms of analysis is the temperature of the source used to excite spectral emission of the sample. The gas-and-air or gas-and-oxygen flames are much cooler than the spark and arc sources used in spectrography. Hence, in this manual, flame photometry is limited to the easily excited metals—sodium, potassium, and lithium.

Selection of the fuel to be used in flame-photometric work is important, as the nature of the fuel affects not only the emissivity of the sought metal but also affects the interferences that show up in the measurement of the metal. For example, in the Perkin Elmer flame photometer the interference of calcium in the barium determination is approximately seven times greater with the propane flame than with the acetylene flame. The situation is reversed in the interference of sodium on potassium, where the propane flame is superior. Generally, the hotter flame is the more sensitive flame,

and it will permit the determination of more elements. Strontium can be determined with the Perkin Elmer flame photometer using the acetylene flame, but not with propane flame. In a few cases, perhaps because of a lower flame background in the desired wavelength region, the lower temperature flame gives superior sensitivity. For the analysis of sodium, potassium, and lithium in the Perkin Elmer 52–C instrument, the propane flame is preferred because sensitivity is adequate, and the propane flame is less noisy and gives a lower background than the acetylene flame. The acetylene flame offers some advantage with the Beckman instrument, but the optimum flame temperatures for determination of different elements are not identical.

Flame photometers can be operated by either the internal-standard or direct-intensity method. The former method is the "tried and true" standby of spectrographic work and is generally preferred, although accurate results can be obtained by the direct-intensity method if four conditions are essentially fulfilled:

1. The instrument is electronically stable and gives reproducible readings as a photometer.
2. The flame can be precisely and reproducibly controlled. This means fine gas and air adjustments that will hold their settings.
3. The interference of foreign elements can be compensated by reference to graphs or other techniques inasmuch as the presence of the matrix constituent tends to reduce the mutual enhancements and quenching effects between elements.
4. The sample is fed to the flame in a constant and reproducible rate.

While the same four conditions must be stabilized to a reasonable degree in the internal-standard flame photometer, only condition 1 is as critical as with the direct-reading type. Successful direct-reading flame photometers, such as the Beckman flame attachments, are characterized by precisely machined atomizers and flame orifices and fine gas controls that give more precise pressure adjustment than the ordinary regulator.

Although internal-standard flame photometers are more reliable for day-to-day operation, the direct-reading instruments are inherently more sensitive. In the internal-standard instruments the value indicated on the meter is the difference between the signal from the sought element and the internal-standard element; the difference, of course, is always less than the full signal measured with the direct-reading instrument. Most internal-standard instruments have provision to switch over to direct-intensity operation when conditions require.

One of the common phenomena of spectrography that is also encountered in flame photometry is the mutual enhancement and depression (more often the former) of emission between two or more

metals. This phenomenon is not associated with the overlapping of lines. The most frequent manifestation is the enhancement that sodium gives to potassium readings. This effect is said to be eliminated by various "radiation buffers" which are made up of a high concentration of salts. Whether these radiation buffers do everything claimed for them is open to doubt, and, furthermore, they have a bad tendency to clog the atomizer. The sodium-potassium enhancement is completely eliminated by using lithium as the internal standard. With the flame attachments for Beckman models DU and B, the effect of sodium enhancement of potassium emission can be eliminated by adding sufficient sodium to standards and samples to obtain the maximum, or "saturation," enhancement; for practical work this is attained at a sodium concentration of 500 ppm.

In general, the curves obtained with flame photometers do not show the day-to-day reproducibility that one expects from a spectrophotometric calibration curve. It is good practice to prepare a new curve each time the flame photometer is used by running 4 or 5 standards along with the samples. If experience shows that the instrument is relatively stable, then it should be satisfactory to simply prepare a curve for the day. The practice of "bracketing" the samples with standards has been rather extensively employed. Some of the more erratic instruments require this procedure as a routine matter. In bracketing, the approximate sodium and potassium concentration is estimated (by calculation, past experience with samples of similar water, or by a preliminary run), and standards with concentrations slightly less and slightly greater than the unknown are prepared. The readings of all three solutions are taken as nearly simultaneously as possible (it may be necessary to take several readings and average the results), and then the value of the unknown is found by simple proportion. Inasmuch as flame-photometer calibration curves are generally not linear, it is apparent that the standards have to be fairly close to the unknown if the simple proportion calculation is to be valid. A more suitable method, and one which does not require as many standards, is to prepare a series of celluloid curves representing the mean curve obtained with the instrument for each of the several operating ranges. These "master" curves can be arranged to rotate about an origin or move upscale or downscale to fit the instrument fluctuations as determined from the standards. Concentrations can be read directly from these curves. It should be noted that flame-photometer curves do not have a general configuration common to all elements. The shape of the curve varies with each element and may show linearity, an increase in slope at higher concentrations, or, most frequently, a tendency to level off at higher concentrations.

The Beckman photomultiplier attachment for the spectrophotometer has considerably extended the range of flame analysis in the blue and green region of the spectrum. Although the sensitivity continues down into the ultraviolet, this region is not of maximum utility because the flame background is likely to be excessive. However, in the region from approximately 400 to 600 mμ, which contains sensitive lines of strontium, calcium, and sodium, the photomultiplier attachment presents possibilities for expanding the scope of flame-photometric analysis.

C:2 INSTRUMENTS

Water analysis as performed today requires the use of several measuring devices. Some determinations, such as specific conductance, can be made only with instruments. The water analyst has a wide variety of measuring devices to choose from, and the choice is rightly guided by the scope of the analytical scheme and the accuracy and precision desired. In this section, discussion is limited to the minimum of instruments required by the Geological Survey to make the determinations included in this manual with the precision and accuracy required.

The selection of a given commercial product has been based largely on the adequacy of the instruments for fulfilling the needs, durability, cost, maintenance requirements, and advantages of semi-standardization throughout the many laboratories of the Geological Survey. The ultimate in accuracy or current refinement is not heavily overweighted in choosing the instrument. Instead, the selection has been guided to a considerable degree by the experiences of the different laboratories—a unit is purchased by one laboratory, evaluated, and the findings made known to other laboratories.

C:2a CONDUCTIVITY METERS

Specific conductance is determined by using a Wheatstone bridge in which a variable resistance is adjusted so that it is equal to the resistance of an unknown solution between two platinized electrodes. The null point is detected by an a-c galvanometer or a cathode-ray tube. Alternating current is necessary to prevent polarization of the electrodes. Direct current produces gas bubbles on the electrodes that greatly increase the resistance and change the concentration of the electrolyte in the vicinity of the electrodes. The electrodes are coated with a thin layer of amorphous platinum, which tends to adsorb gases and catalyzes their reunion, thereby minimizing polarization.

The electrode cell may be either the dip or pipet type. The pipet cells are generally more satisfactory for routine laboratory use because they require a smaller volume of water for the determination, the

water can be drawn directly from a narrow-mouth sample bottle without transferring it to another container, the total time for the determination is less, and there is less mechanical agitation of the water sample. Dip cells are preferable for fieldwork.

Conductivity meters differ in their design, construction, and suitability for waters of different ionic concentration, although they are fundamentally the same in operating principle. The Geological Survey must determine the specific conductance of waters that range widely in concentration. A satisfactory instrument should handle samples having specific conductances in the range of 0 to 100,000 micromhos; the results should be reproducible and accurate to within 3 percent of the true value.

Cell polarization is particularly troublesome when the specific conductance of highly mineralized waters is determined. Polarization varies directly with the amount of current that flows between the electrodes and inversely with the frequency of the current. High input voltage to the bridge or low resistance of the cell (concentrated water) is conducive to polarization. The cell resistance can be increased by increasing the cell constant (see sec. D:37). The selection of the cell constant is, however, limited by the accuracy and sensitivity of the bridge for measuring very high and low resistances. In addition, the current frequency should not be excessively high because a-c resistance is a complex function of frequency; at frequencies necessary to avoid polarization completely, the differences between a-c resistance and d-c resistance may be appreciable unless the cell has been very carefully designed to minimize this difference. Therefore, the ideal single apparatus for the measurement of conductivity throughout a wide range would necessarily incorporate practical compromises between low input voltage, high cell constant, high current frequency, and(or) the accuracy and sensitivity of the bridge for measuring extreme resistances and at high current frequencies.

For many years a bridge fabricated within the Geological Survey has been used successfully for the determination of specific conductances ranging from about 25 to 3,500 micromhos. The essential elements of this bridge are a variable resistance, 0 to 9,999 ohms in steps of 1 ohm, with a multiplying factor of 0.001 to 1,000 for widening the range of the resistance box; an a-c pointer-type galvanometer which supplies current for the bridge circuit at 6 v and has a sensitivity of 1 μa (microampere) per mm scale division; and an insulating transformer, 115 to 115 v, 60 cycles, 50 va. This bridge is used with a pipet cell (cell constant approximately 0.3 reciprocal cm). Above about 3,500 micromhos the determined specific conductances are lower than the true values by more than 3 percent,

and the percentage of error increases gradually as the ionic concentration of the water increases.

Several combinations of bridges and commercially available cells have been investigated. The line-operated Serfass Model RCN 15 bridge has proved satisfactory for routine laboratory determinations when used as a resistance-measuring device and with a pipet cell having a constant of 0.3 reciprocal cm (see "Wheatstone bridge method," sec. D:37a–1). Current frequency of either 60 or 1,000 cycles per second can be selected. The lower frequency is preferable for measuring the high resistances of very dilute solutions such as distilled water, but the higher frequency is preferable for most natural water. The Serfass instrument also incorporates an a-c bridge with an input voltage of 3; a vacuum-tube amplifier; a cathode-ray-tube null detector; a scale of about 14 inches in length, logarithmically graduated from 0.5 to 1.5, which permits direct reading of resistances to 2 significant figures and interpolation of the third figure; and an adjustment knob that varies resistance ratios from 1 to 100,000 in 6 steps, each representing a factor of 10. Other assemblies comparable in accuracy and reproducibility throughout the 0 to 100,000 micromho range would be equally suitable.

Direct-reading conductivity meters are commercially available, but none investigated by the Geological Survey gave results comparable in accuracy to the resistance method described in section D:37a–1. Two potential sources of error are inherent to the direct-reading meters; first, they must either have a cell constant of exactly 1.0 or some type of cell-constant-adjustment mechanism; second, the temperature of the solution must either be exactly 25°C or the temperature must be compensated for manually or automatically. However, some direct-reading conductivity meters have been used satisfactorily for tests when the accuracy requirements are not stringent.

C:2b BALANCES

Either manually operated or automatic balances that are sensitive and accurate to 0.1 mg in the 0- to 100-g range are suitable for water analysis. A large-capacity balance sensitive to 0.1 g is also useful for less accurate weighings.

C:2c pH METERS

pH meters measure the electrical potential between two suitable electrodes immersed in the solution to be tested. The reference electrode assumes a constant potential, and the indicating electrode assumes a potential dependent on the pH of the solution. Electrode potential is the difference in potential between the electrode and the solution in which it is immersed. The calomel electrode,

which is a widely used reference electrode in water analysis, consists of a mercury-calomel rod immersed in a saturated solution of potassium chloride; this electrode has a potential of +0.246 v. Electrical connection with the sample is provided through porous fiber sealed into the immersion end. A glass electrode is normally used as an indicating electrode. The glass electrode has several features that recommend it for pH measurements. Among the most important are that it is not affected by oxidizing or reducing substances in the sample and that it can be used in turbid and(or) colloidal suspensions. The basic design is a silver-silver chloride or mercury-mercurous chloride electrode immersed in a solution of known pH and the whole completely sealed in glass.

The mechanism by which the glass membrane responds to hydrogen-ion activity is not thoroughly understood, but it probably involves absorption of hydrogen ions on both sides of the membrane proportionally to the activity of the hydrogen ions in solution. The cell for measuring the pH of a solution is of the following type:

$$\underbrace{\mathrm{Ag^{\circ}:AgCl} \,\|\, \text{Solution of known pH} \,;\, \text{Glass membrane} \,;\, \text{Solution of unknown pH} \,\|\, \mathrm{Hg^{\circ}:HgCl}}_{\text{Glass electrode}}$$

The voltage of the glass electrode is a logarithmic function of the difference in hydrogen-ion activity of the solutions on either side of the glass membrane. To measure this voltage an electron-tube voltmeter is used because the resistance of the glass membrane is so great.

pH meters differ in their design, construction, and applicability to all phases of water analysis in which the instrument is used. Desired features in a line-operated pH meter are built-in voltage regulator, accuracy of ±0.05 pH, calibration for wide pH range with 1 buffer solution, stability of calibration, built-in temperature-compensating mechanism, durable electrodes, and a design that permits insertion of the electrodes, stirrer, and a buret into a suitable vessel for titrations. For pH determinations in the field the instrument should also be rugged and compact.

C:2d SPECTROPHOTOMETERS

Most spectrophotometric instruments used in water analysis are designed for operation in the visual region of the spectrum. Although some work has been done with phenols in the ultraviolet region, and a considerable amount of infrared-absorption study of organic pollutants is reported in the literature, the major application of spectrophotometers is still in the visual region, and the following discussion is limited to instruments of this type.

Every spectrophotometer contains four major components: the light source, the monochromator, the absorption-cell unit, and the

photometer unit. The major factor that controls the quality and the price of the instrument is the monochromator system, which may be an optical filter, a diffraction grating, or a prism. The optical-filter type is the simplest and is satisfactory for many routine analytical applications. In the use of filter photometers, the primary consideration is the quality of the filters, a factor that varies over a wide range. While there is no standard method of specifying the characteristics of optical filters, the use of "half-intensity" band widths is fairly common. The principle of the system is illustrated in figure 11. Curve A on figure 11 is for a typical broad-band glass filter, Corning 5874. The half-intensity band pass (*a*) for this filter is approximately 55 mμ, which is about the maximum that can be tolerated in a useful filter for photometric analysis. By combining several filters into a single unit, the band pass can be narrowed to 10 or 20 mμ. To select the simple filter components for such a com-

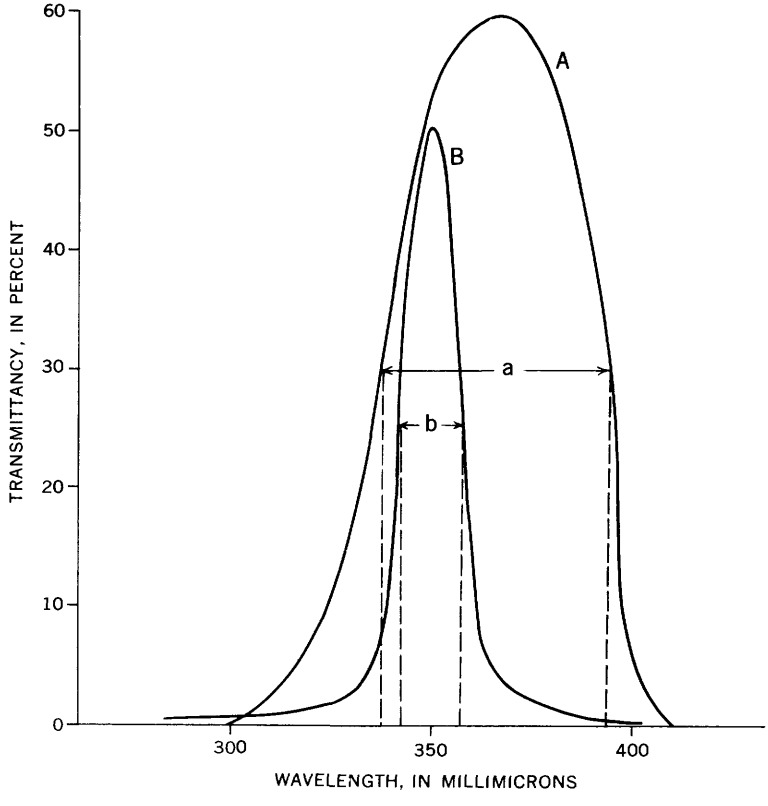

FIGURE 11.—Comparative energy transmission of filters. Curve A is for a Corning 5874 glass filter, which has a half-intensity band pass (*a*) of 55 mμ, and curve B is for a Photovolt interference filter with a half-intensity band pass (*b*) of 10 mμ.

bination, a manufacturer's catalog that gives the transmittance curves for the individual filters is very useful. Sometimes, filter combinations seriously attenuate the light intensity. To overcome this problem, interference filters can be used. These are mirror devices wherein the desired spectral region is isolated by multiple reflections that cancel out all but the required region. They can be made very sharp and in almost any wavelength. Curve B (fig. 11) is for an interference filter manufactured by the Photovolt Corp. The half-intensity band pass (b) is less than 10 mμ. Similar filters having a peak transmission accurate to ± 1 mμ can be obtained in any wavelength from 400 to 840 mμ. Other sources for interference filters are the Baird Instrument Co. and Farrand Optical Co.

Diffraction gratings are extensively used in the Coleman instruments and are also used in the Bausch and Lomb spectronic photometer. The latter is a very ruggedly made and serviceable instrument and has a band pass of 20 mμ. This value is comparable to the isolation achieved with high-grade optical filters. The major recommendation of diffraction-grating instruments is their linear dispersion, which gives a constant band pass throughout the spectrum at a fixed slit width. For routine analytical applications, interest in this feature is mainly academic, but it has some advantages in research-type instruments.

A variety of spectrophotometers is used by the Geological Survey, but the most common is the prism type, as represented by the Beckman B spectrophotometer. The dispersion of a prism is nonlinear, being much greater at the blue end of the spectrum than at the red. It is important for every operator of this instrument to realize that when the slit-width setting for a particular determination is increased to compensate for changes in a reagent solution, a drop in output of a photocell, or for some other reason, the band pass at the operating wavelength is simultaneously widened. In a few determinations where the wavelength of the absorption system is critical, this broader band pass could cause a shift in the analytical calibration with possibly an increase of curvature. Such an adverse effect would be the exception rather than the rule, because at normal operating wavelengths the band pass is so narrow as to be safely within the requirements of most colorimetric systems. For example, at 500 mμ with a slit width of 0.2 mm, the band pass is only 3 mμ. For some research applications it is necessary to know the band pass of the instrument throughout the wavelength spectrum for various slit widths. These data for the Beckman instrument may be obtained from the half-intensity band-width curves on page 6 of the Beckman Bulletin 291–A.

In selecting the sample absorption cells for use in the photometer, it is necessary to consider the wavelength at which the determinations will be made. Almost any type of glass is suitable at wavelengths above 400 mμ. Pyrex cells can be used successfully for the aluminum determination at 370 mμ, but the transmission drops off rapidly below this region. Corex-window cells can be used at wavelengths down to approximately 300 mμ. Below this region silica-window cells must be used.

Open-top absorption cells are preferred for routine work, as stoppered-orifice cells are too cumbersome and often trap air bubbles. Only sintered- or fused-joint cells should be used. Cement in joints will sometimes react with reagents to give false colors. Plastic cells should not be used. Rectangular cells are preferred for critical work because they do not require the critical centering necessary for cylindrical cells. Several types of rectangular open-top cells may be obtained from suppliers of photometric equipment. Absorption cells can be made to special order in a variety of shapes and dimensions. Many of the colorimetric methods described in this manual give data applicable to rectangular cells of 40-mm optical depth. The cell carriage of the Beckman B spectrophotometer will not accept these cells. However, it is relatively easy to make a carriage that will accommodate the 40-mm or larger cell. A drawing of one such carriage for the 40-mm cell is shown in figure 12.

After the light passes through the filter system and the absorption cell, it is received on the photoreceptor and is converted into electrical energy. There are three major classes of photosensitive devices, each with distinctive characteristics with which the operator should be familiar. These are the barrier-layer cell, the vacuum phototube, and the photomultiplier tube. Diagrams of the three types are shown in figure 13. The barrier-layer cell is the type generally used in the less expensive photometers because it requires no power supply and puts out a comparatively high current that will operate a meter without further amplification. Barrier-layer cells are relatively stable and rugged. The output of the barrier-layer cell cannot be easily amplified, and consequently it is necessary to use the second type of cell, the vacuum phototube, for the measurement of low light values. This cell consists of a semicylindrical cathode with a coating of cesium-cesium oxide or other photoemissive metal and a central wire anode. When light strikes the cathode, electrons are emitted from the surface and are drawn to the anode, which is maintained at a positive potential. The microampere current so obtained develops a voltage across a high resistance; the voltage is fed to the grid of an amplifier tube. A development of the vacuum phototube is the

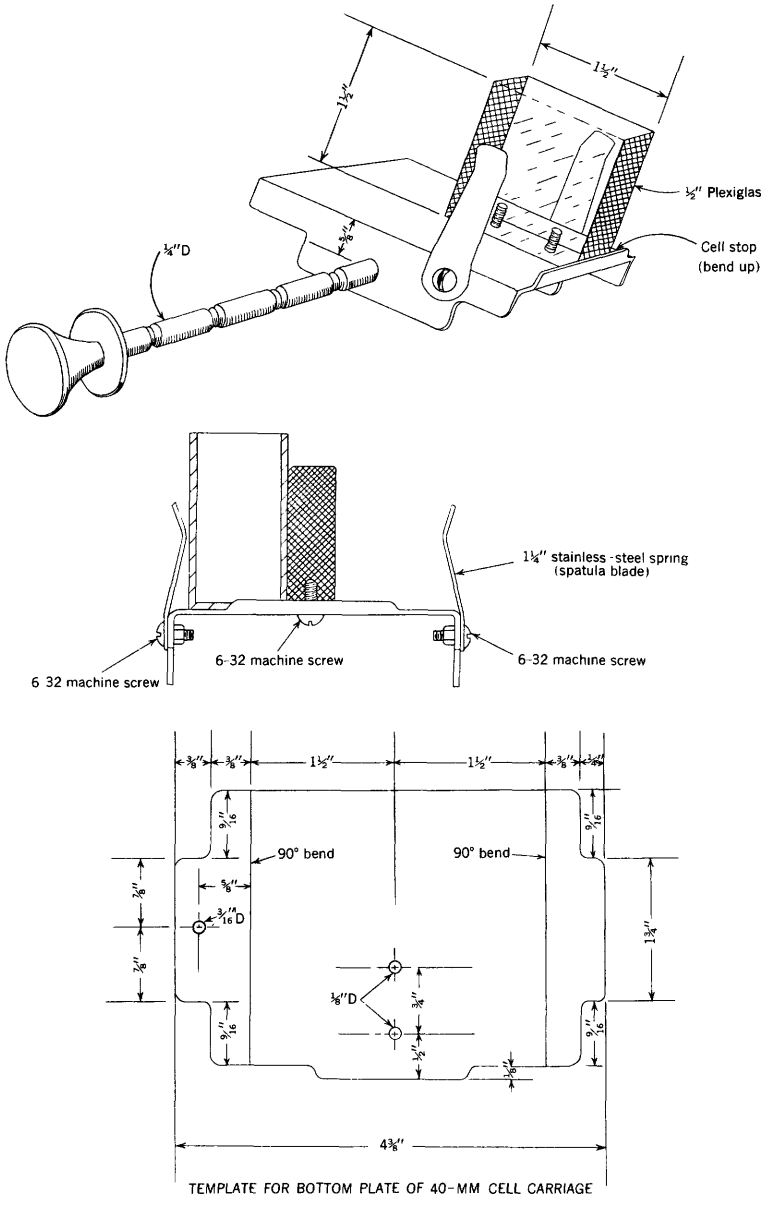

FIGURE 12.—Forty-millimeter cell carriage for Beckman Model B spectrophotometer.

photomultiplier tube, in which the current is enormously amplified within the tube itself. The emission from the cathode circles through a chain of 10 positive dynodes and is amplified at each one. The major disadvantages of the photomultiplier tube are the necessity

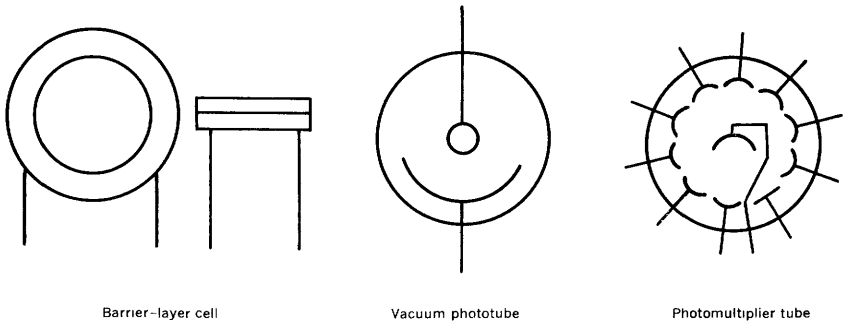

FIGURE 13.—Schematic representation of photocells.

for high voltages (1,000 v) and a tendency toward instability. They vary greatly in individual characteristics, and in critical applications they must often be selected from several tested for certain specific characteristics.

In general, the output of all three types of photoreceptors is approximately linear within their appropriate working ranges. But for critical work the linearity of the tube output (and amplifier) must be checked and a correction curve plotted. As the tubes age, the output falls, and curvature may become pronounced.

All photocells show a marked variation of response with wavelength. The wavelength-response curves for the various types of photocells can be found in a bulletin entitled "Phototubes, Cathode Ray and Special Tubes" and published by the Radio Corporation of America.

Most of the spectrophotometric methods in this manual are designed for use with the Beckman B spectrophotometer because this instrument is common to all laboratories of the Geological Survey. Except for aluminum and fluoride, all of the colorimetric determinations described in this manual can also be made with the Bausch and Lomb spectronic instrument. The sensitivity of the Bausch and Lomb is approximately half that of the Beckman B, however, because the maximum absorption-cell depth is only 22 mm as compared to the 40-mm depth usually specified for the modified Beckman B. The Beckman instrument will accept special cells as long as 70 mm for determinations in which maximum sensitivity is required. For field analysis the Photovolt Lumetron 401 has been used. The Lumetron is a simple and fairly rugged instrument that will operate from a 6-v storage battery as well as 110-v a-c current. Many of the simpler colorimetric determinations can be performed with this instrument without excessive loss of sensitivity as compared to the Beckman B.

For the most successful and general application of spectrophotometry in water analysis, the instruments should meet certain requirements, some of which are more exacting than the normal requirements of colorimetric work. A list of the features of the ideal water-analysis spectrophotometer for laboratory and field use is given below. No single instrument meets all the requirements, but a combination of instruments may approach the ideal specifications.

1. Useful-wavelength range from approximately 350 mμ to 900 mμ.
2. Provision to use long absorption cells (40 mm or longer) when necessary.
3. Suitable for field use. This means specifically a rugged construction and operation from a 6-v storage battery.
4. Suitable for spectrotitration.
5. Narrow band pass when required, and a light source and photocell combination of sufficient sensitivity so that dense filters or narrow slits may be used.
6. Provision to shift the absorbancy scale by stepwise adjustment so that solutions of high absorbancy may be set to "zero." This is a very useful device in many analyses.
7. Readily available electronic, optical, and mechanical components for replacement. Reasonable freedom from breakdown under laboratory conditions and a satisfactory repair service and policy on the part of the manufacturer.
8. Availability of a few common attachments such as fluorescence-measuring adaptors and turbidity adaptors is desirable but not necessary.
9. Reasonable facility of operation.
10. Good voltage regulation and general stability.
11. Sufficiently rugged and well made to hold its adjustments through the normal rigors of routine laboratory service.

In theory, all spectrophotometers of the same type should be expected to give the same reading for the absorbancy of a given solution under fixed conditions of wavelength and band pass. In actual practice this ideal is not realized. The disagreement between high-quality spectrophotometers in the measurement of absorbancy is much greater than the disagreement between analytical balances in the measurement of mass. The spectrophotometer is a more complex instrument. Many more components contribute to the result than in a simple, direct device like a balance. Spectrophotometric instruments require careful handling and close adjustment if they are to perform properly. Two major phases of spectrophotometer function require frequent checking: the wavelength setting and the absorbancy scale. In any laboratory that uses spectrophotometers on a routine basis, a regular schedule for testing these two scales should be set up on a definite periodic basis.

Wavelength-scale calibrations can be tested by two relatively simple methods:

1. Emission sources of known wavelength: Helium discharge tubes, the mercury arc, and the sodium-flame spectrum can be used as sources of known lines for testing the accuracy of a spectrophotometer wavelength scale. Inex-

pensive discharge tubes suitable for the purpose can be obtained from several suppliers of photometric equipment. This is the most accurate method for testing a wavelength scale.

2. Didymium filter: Mellon (1950) reports that the National Bureau of Standards has tested the Corning No. 5120 didymium glass (3.0-mm thickness) and has never found any certain variation in the positions of the wavelength maxima in the absorption curve for this glass. Therefore, it is concluded that this didymium glass would make a satisfactory standard for checking the wavelength scale of spectrophotometers used in routine work. This method is inferior to the use of line sources but should be sufficiently accurate for instruments used in routine work. The prominent absorption maxima in the wavelength region between 400 and 808 mμ are as follows:

441.0	684.8
475.5	743.5
528.7	745
585.0	808

The second periodic check of importance is the accuracy of the photometric scale, which may show considerable variation depending upon the condition of the phototubes and the amplifier. Neutral filters of known transmittance have been used for checking the scales. Standards that are probably superior in a practical sense are the calibrated color glasses issued by the National Bureau of Standards (Gibson and Balcom, 1947, p. 601). These filters of known transmittance cover the wavelength region from 400 mμ to 750 mμ and simulate the properties of colored solutions. Tables of spectral absorbancy throughout the wavelength region 350 mμ to 750 mμ for a standard solution of copper sulfate are given by Mellon (1950). Similar tables are given for cobalt ammonium sulfate and potassium chromate. If it is desired simply to check the linearity of the absorbancy scale, this may be done by determining the absorbancy of successive dilutions of a colored solution known to follow Beer's law. Cobalt ammonium sulfate in sulfuric acid solution gives a good spectral absorption range for such linearity tests.

Some of the routine aspects of spectrophotometric maintenance, such as cleaning the slits and keeping the optics in alinement, have not been considered here. These subjects are discussed in detail in the manufacturer's handbook supplied with each instrument, and reference is made to these for further information.

C:2e FLAME PHOTOMETERS

Both the internal-standard type and the direct-reading type of flame photometer are in use by the Geological Survey. The former is represented by the Perkin Elmer 52–C instrument and the latter by the Beckman B and DU flame attachments. These relatively expensive instruments were put into use by the Survey several years ago, and there are now some less expensive filter-type flame photom-

eters on the market that may be entirely adequate for sodium and potassium determinations.

Before making a final decision on the type of flame equipment to be purchased, it is essential to obtain information on the type of fuel permitted by fire-control regulations. Acetylene and hydrogen tanks are not allowed in some places.

Attention should be given to the quality of the auxiliary equipment purchased for use with the flame photometers. For example, it is pointless to purchase the best instrument available and use it with an inefficient, erratic air compressor, for example. If an air compressor is necessary, the unit should have more than adequate capacity so that a constant pressure is maintained. The manufacturers will supply information as to preferred air compressors to go with their units. Filtering of the air may be very important in some areas; some instruments come equipped with a trap for this purpose. Additional purification and control can be achieved by installing ahead of the trap an air-purifier cartridge that is especially effective for removing suspended oil droplets from the air. Purification is usually no problem with instruments that require only bottled oxygen, because the bottled gas is generally sufficiently pure for direct use.

Flame photometers in general are less stable than spectrophotometers because the light source in the flame photometer is much less stable. The only means of stabilizing this component is by careful control of the flame adjustments. This practice, of course, is not completely successful. To avoid introducing still further fluctuation, the most careful attention should be given to voltage regulation and the photocells, which are most likely to contribute electronic instability. Considerable change in calibration curves is not uncommon after the substitution of new phototubes.

C:2f WATER-COLOR COMPARATORS

Color comparators are used to measure the color of the water in terms of the color of platinum-cobalt solutions of known concentration. However, colored glass discs individually calibrated to correspond with the colors on the platinum scale have generally replaced solutions in the laboratory, and their use is recognized as standard practice.

A rather long optical depth of solution is desirable for making a comparison because the observed intensity of the color is proportional to the depth of the solution. Satisfactory comparison of the water sample and standard can be made if long equal-length cylinders of sample and distilled water are illuminated from the bottom and viewed from the top of a lightproof housing. The more refined

instruments bring the beams of light to focus on a single split field in the eyepiece.

Commercial color comparators used in laboratories of the Geological Survey must permit color differentiation to the degree listed for reporting color units (see sec. D:13a–1) and must give results comparable to those obtained with platinum-cobalt standards.

C:2g TURBIDIMETERS

Newell (1902) defined the standard for turbidity as

> . . . a water which contains 100 parts of silica per million in such a state of fineness that a bright platinum wire 1 millimeter in diameter can just be seen when the center of the wire is 100 millimeters below the surface of the water and the eye of the observer is 1.2 meters above the wire, the observation being made in the middle of the day, in the open air, but not in sunlight, and in a vessel so large that the sides do not shut out the light so as to influence the results. The turbidity of such water shall be 100.

A turbidity rod calibrated for use under these conditions was designed by the Geological Survey and used for many years. However, because of the large number of variables that must be controlled to measure accurately the turbidity of a water body or sample, a simpler method was needed to measure the same characteristic as defined by the standard for turbidity. The Jackson candle turbidimeter made it possible to determine turbidity in the laboratory and simplified the measurement somewhat. Since shortly after the turn of the century the Jackson turbidimeter has been considered by most water chemists to be the referee instrument for the turbidity determination, although uniform results still required control of several variables. More recently, other instruments simpler in operation and more sensitive to small differences in turbidity have been marketed. The advertisement for some of these instruments has stated that the results are comparable to the Jackson turbidimeter. Experimentation has shown that the nature of the suspended material has a bearing on the degree of similarity of the results.

The Geological Survey now uses the Hellige turbidimeter as a standard turbidity-measuring instrument, not primarily because of the instrument's superiority but because of its sensitivity for measurements of low turbidity and because of the need for results that are reproducible and comparable between the different laboratories. Operation of the Hellige turbidimeter is based on the comparison of the intensity of a beam of light passing through the solution with the Tyndall effect produced from the lateral illumination of the sample by the same light source.

The slit width that controls the amount of light passing up through the solution is controlled by a knob on the side of the instrument. This knob is calibrated in arbitrary units, and the readings from the

knob are converted to parts per million turbidity by means of appropriate curves, which are supplied by the manufacturer. The transmitted light is viewed as a circle of light in a field of Tyndall light. (See sec. D: 40a–1.)

C:2h PHOTOMETRIC TITRATION ASSEMBLIES

Interest in photometric titration devices in analytical chemistry is increasing. This is another manifestation of the accelerating movement toward eliminating subjective factors in analysis. Automatic titrators are used extensively by industry, but they have not proved satisfactory in the low-concentration levels characteristic of water analysis, and they are quite expensive. For these reasons, spectrotitrators—standard spectrophotometers or filter photometers with titration adaptors—are used. Spectrotitrators also probably permit a wider range of application than the automatic devices because the latter are based on potentiometric principles and can be utilized only when the analytical system gives the required potential difference. Probably there are more colorimetric systems of analytical value than there are potentiometric systems.

Two spectrotitration assemblies have been developed by the Geological Survey: a research type for the Beckman B spectrophotometer and a routine-analysis type for the Photovolt Lumetron 401. Both are shown on figure 14. The principal application of the latter instrument is in the titration of calcium with Na_2EDTA (disodium dihydrogen ethylenediamine tetraacetate) where murexide is used for the indicator. The murexide end point, which is difficult for many analysts to detect visually, gives a very decisive response in the spectrotitrator. Spectrotitration in this instrument differs from visual titration technique mainly in the use of a concentrated titrant solution. This is necessary to minimize the volume change during the titration. A microburet is used. In general, the monochromaticity requirements for spectrotitrations are considerably less than for colorimetric measurements. Filter photometers can almost always be used.

One other type of instrumental titrator is the relatively new high-frequency titration system which requires no electrodes. The principle involves loading the tank circuit of an oscillator with the titration solution. Usually the oscillator coil surrounds the titration beaker. As the ionic composition of the solution varies during the titration, the gain of the tank circuit varies correspondingly, and in the end-point region a major shift takes place which is observed on a meter. This method of detecting the end point would seem to present the most general application. Although development in this field will probably be rapid, the present instruments do not provide the sensitivity necessary for general application in water analysis.

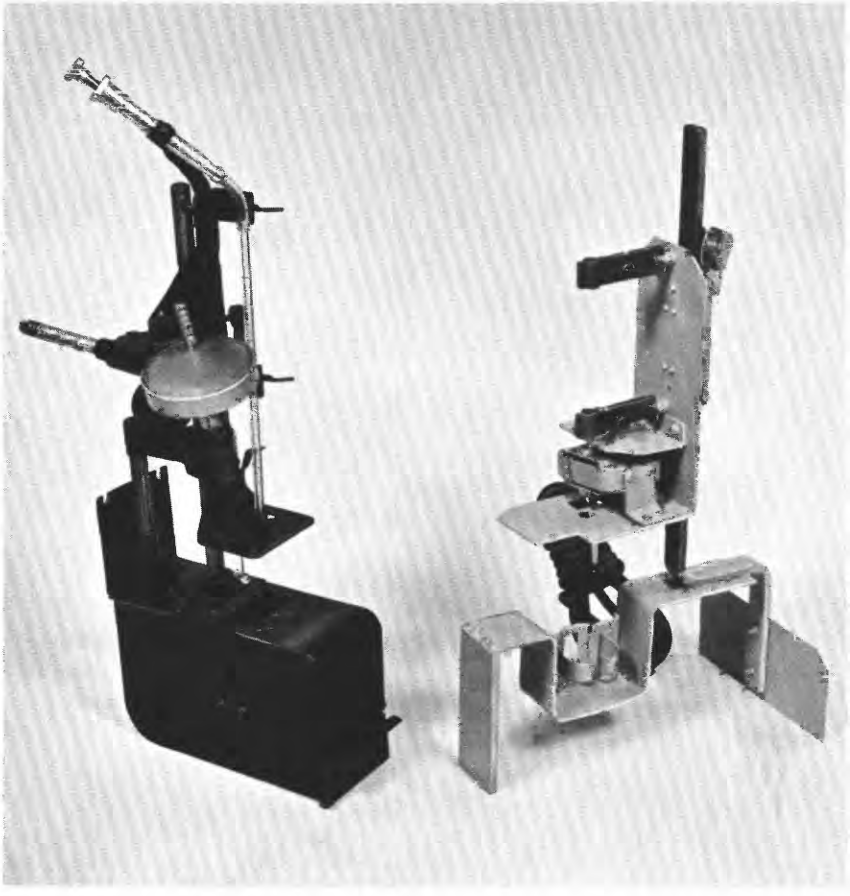

FIGURE 14.—Photometric titration assemblies.

C:3 GLASSWARE AND OTHER CONTAINERS USED IN THE LABORATORY

Laboratory vessels serve three functions: storage of reagents, measurement of solution volumes, and confinement of reactions. Soft-glass containers are usually relatively soluble and therefore are not recommended for storage of many reagents. Even Pyrex, which is a borosilicate glass, is not completely inert, particularly to alkalis. The Corning Glass Co. Alkali-Resistant (Boron-Free) laboratory glassware and T. C. Wheaten and Co. No-Sol-Vit bottles are reported by the manufacturers to be more chemically durable than soft-glass containers. Standard solutions of silica, boron, and the alkali metals are usually stored in polyethylene bottles. Some strong solvents and strong mineral acids (such as H_2SO_4) will attack polyethylene

readily. In the instructions for preparations of solutions referred to in this manual it is assumed that the solutions will be stored in Pyrex bottles unless otherwise specified.

Vessels for measuring solutions differ in their accuracy of calibration. By common usage, accurately calibrated glassware for precise measurements of volume has become known as volumetric glassware. This group encompasses volumetric flasks, volumetric pipets, and accurately calibrated burets. Volumetric glassware used in laboratories of the Geological Survey is calibrated to contain or deliver volumes accurate to within the tolerances specified by the National Bureau of Standards (1941). These specifications are given in the table on the following page. Glassware certified by manufacturers to meet specifications of the National Bureau of Standards has been found to be satisfactory. Less accurate types of glassware include serological pipets, graduated cylinders, and Nessler tubes.

Silicone solutions have appeared on the market that are advertised to coat the glass and thereby prevent wetting of the glass by aqueous solutions. These products have not been approved by the National Bureau of Standards (1941) and are not recommended for laboratory use of volumetric glassware for several reasons. Volumetric flasks and pipets are calculated to contain and deliver the correct volume when the bottom of the normal meniscus coincides with the calibration line; coating of the glass distorts the meniscus. Furthermore, experience has shown that deterioration of the coating causes excessive adherence of the solution to the side of the vessel and inaccurate delivery. Once the coating material is on the glass it is very difficult to remove.

Pyrex containers are more universally used than any other as containers for reactions because of their relative inertness and thermal properties. Nessler tubes and absorption cells (spectrophotometric) are often used for colorimetric reactions to eliminate the necessity of transferring solutions before determining the color intensity.

Treatment of the water sample or reaction of the solution that involves evaporation can usually be carried out in glass, porcelain, or platinum dishes. Platinum is superior to the other materials if the weight of the residue must be determined accurately because the weight of platinum vessels is very constant.

Glassware and porcelain can be cleaned with soap, synthetic detergents, organic solvents, dichromate cleaning solution or aqua regia (25 percent v/v conc HNO_3 in conc HCl). Aqua regia will attack platinum, but 50 percent hydrochloric acid is an effective cleaning agent. Material that does not dissolve in 50 percent hydrochloric acid usually can be removed by rubbing with fine sea sand.

TABLE 1.—*Tolerances for volumetric glassware*

[Abridged from National Bureau of Standards, 1941]

Capacity (ml) less than and including—	Limit of error (ml)
Graduated flasks	
25	0. 03
50	. 05
100	. 08
200	. 10
300	. 12
500	. 15
1, 000	. 30
2, 000	. 50
Transfer pipets	
2	0. 006
5	. 01
10	. 02
30	. 03
50	. 05
100	. 08
200	. 10
Burets [1]	
2	----
5	0. 01
10	. 02
30	. 03
50	. 05
100	. 10

[1] *Limits of error are of total or partial capacity. Customary practice is to test the capacity of 5 intervals*

Although platinum is one of the most resistant metals, it is not completely inert and is subject to embrittlement. The following precautions are recommended: Never put solutions containing tin, mercury, or lead in a reducing environment in platinum; if the free metal should be formed it will alloy with the platinum, especially if heated. Do not heat mixtures of hydrochloric acid with oxidizing substances such as nitrate or manganese dioxide; ferric chloride in hydrochloric acid attacks platinum appreciably. Place hot platinum vessels on a refractory material; never on a cold metal surface or on a dirty surface. Use clean platinum-tipped tongs to handle hot

platinum vessels. Coarse crystal growth and embrittlement can be caused by unnecessarily prolonged heating at high temperatures, heating under reducing conditions, and heating phosphates or sulfates in the presence of organic compounds. Embrittlement can be counteracted by rubbing the platinum ware with moistened sea sand. Gentle rubbing with sea sand cold-works the metal and breaks down the crystal structure. Detailed instructions for the care and use of platinum ware are distributed by manufacturers of these vessels and are described in textbooks of quantitative analysis.

C:4 CHOICE OF ANALYTICAL METHODS

Several analytical methods may be listed for the determination of a single constituent in the section of this manual that deals with methods of analysis. The laboratory methods are generally the more accurate, but useful approximations and screening tests are also included. Screening tests may be either a means of approximating concentrations for the selection of the proper sample volume for a laboratory determination or they may be tests that are sufficiently accurate in only a low-concentration range. For example, the tetramethyldiaminodiphenylmethane test for manganese is a screening test that is rapid and accurate in low-concentration ranges; if the concentration of manganese is within the range of this test, it is not then necessary to perform the more laborious regular procedure.

A choice of laboratory methods is also given for the determination of some constituents to provide the analyst with the means for checking dubious results and to permit a flexible laboratory scheme. Most procedures are subject to some interferences, but seldom are two methods subject to the same interferences. No method is designated as a referee method in which the results obtained are the ultimate in accuracy or by which the adequacy of other methods can be gaged. However, the method listed first in each group of methods is generally preferred because of its applicability to most water samples, its advantages in required time, its accuracy, or its comparative simplicity.

C:5 EXPLANATION OF TERMINOLOGY

Specific terminology is used in describing the analytical techniques. Some that are an integral part of the instructions are described below.

Dilution water for adjustment of sample volume or preparation of reagent solutions, unless otherwise specified, shall be distilled water whose pH is between 5.8 and 7.2 and whose impurity as measured by specific conductance at 25°C shall not exceed 8.0 micromhos.

Redistilled water shall be prepared by redistillation of dilution water from Pyrex apparatus. It shall have a specific conductance

at 25°C of 1.5 micromhos or less. Redistilled water should be stored in resistant glass (Corning Glass Co. Alkali-Resistant glass No. 7280) or polyethylene bottles and should be prepared fresh frequently.

Metal-free water shall be distilled water that has been passed through a suitable acid-charged cation-exchange resin and that conforms to the pH and other requirements of dilution water.

Carbon dioxide-free water shall be prepared by boiling and cooling dilution water immediately before use. It shall have a pH between 6.2 and 7.2.

Ammonia-free water shall be distilled water that has been freed of ammonia by shaking with Folin's ammonia permutit and that conforms to the pH and other requirements of dilution water.

In the instructions for making the analysis and preparing the solutions, significant figures are utilized to define the accuracy of weights and measures. Weighings will be accurate to the last figure shown. For example: A mass designated as 4.532 g must be weighed accurately to ±0.0005 g, whereas a mass designated as 4.5 g must be weighed accurately to only ±0.05 g.

Required accuracy for measurement of volume in the analysis and preparation of reagents is shown similarly. Standard solutions are always prepared in and measured from volumetric glassware. The significant figures given for such measurements are in practical agreement with the tolerance limits (see sec. C:3), and the word "approximately" indicates that the volume or weight needs to be within only ±5 percent of that prescribed. For example: "Add 2.00 ml of reagent" shows that a volumetric pipet must be used for the addition, but "add 2 ml" or "add 1.5 ml" shows that a serological pipet may be used; "dilute to 1,000 ml" shows that a volumetric flask is essential, but "dilute to approx 1 liter" permits the volume to be between 950 and 1,050 ml.

The chemistry of most water-analysis procedures is such that they are applicable over a restricted concentration range. To get a satisfactory amount of the constituent into the reaction and still maintain the correct proportions of sample and reagents, the analyst may have to concentrate a large volume of sample or dilute a small sample to the proper volume. Concentration limits of the procedures are given in the instructions to aid the analyst in the selection of the proper sample volume. The highest accuracy in most determinations is obtained if the largest convenient sample volume is selected, because the factor for converting the weight of the constituent in the test sample to parts per million is smaller if a larger volume of sample is used. Most of the analytical methods

are designed for dilute solutions, and, therefore, concentration by evaporation is rarely required. Evaporation should be kept to a minimum because of the danger of contamination during the long exposure to the atmosphere and because sparingly soluble salts may precipitate.

Obviously, selection of a test-sample volume can be carried to extremes for the sake of dubious accuracy. Therefore, parenthetical quantities are used to designate the accuracy normally desired. For example: "Measure a sample containing less than 0.5 mg SiO_2 (10.00 ml max)" indicates that a 10-ml sample will give the desired accuracy in the 0.00- to 0.50-mg range and that a larger sample is unnecessary.

All test samples and standard solutions are measured with volumetric glassware (see sec. C:3). Test-sample volumes less than 5 ml should not be measured directly because the calibration of 1-ml and 2-ml pipets is not as precise as that of the larger volume pipets. Less error is incurred if a suitable sample dilution is prepared and part of this dilution taken for the test sample. Although the glassware is calibrated to deliver a specific volume at 20°C, the error in measurement incurred by pipeting samples at room temperature is insignificant for water analysis. One gram of pure water (H_2O) is contained in 1.002 ml at 20°C and in 1.007 ml at 38°C; the maximum error in volume that will result from temperature differences is only 0.5 percent. Brine samples unstable at room temperature cannot be measured in the usual way. The brine may be heated to bring precipitated material into solution and the test measured approximately into a tared weighing bottle and weighed accurately. Calibrated pycnometers used with a constant-temperature bath are preferable for measuring test-sample volumes of heavy stable brines when highest accuracy is required; these bottles, normally calibrated at 20°C, should not be used with brines that are unstable at this temperature.

Chemicals used in standard and reagent solutions shall conform with the specifications for purity of the American Chemical Society (1950 and subsequent revisions) when such specifications exist. Chemicals not contained in this compilation shall be of commonly accepted reagent purity. Primary standards (solid) for acidimetry, alkalinity, and oxidation-reduction reactions may be obtained from the National Bureau of Standards or from chemical manufacturers marketing products of comparable purity. Primary standard solutions are prepared fresh in duplicate for each standardization of volumetric solutions.

C:6 SCHEME OF ANALYSIS

The validity of the analytical statement and the time required for analysis are affected by the order in which constituents are determined and by the manner in which the sample is treated. The following discussion concerns only the group of constituents and measurements included in the "complete analysis" normally made by most of the laboratories of the Geological Survey and does not include the determinations of volatile materials or constituents readily changed by aeration or bacterial action.

Constituents and measurements most susceptible to change are determined first. The pH and relative proportions of the alkalinity and acidity components are related to the gas content of the sample and are the least stable. Filtration may alter the gas content of the sample. Hence, pH and alkalinity or acidity of the unfiltered sample should be determined immediately after the bottle is uncapped. Composite samples should not be prepared far in advance of analysis.

The specific conductance gives an indication of the total ionic concentration of the sample and is, therefore, useful in the selection of the volume of sample to be taken for the individual determinations. The specific conductance is not affected by moderate turbidity and can be determined from either a raw or filtered sample.

If the sample requires clarification (see sec. B:5), a sufficient volume should be filtered at one time to provide samples for all remaining determinations. This has two advantages: less time is required for one filtration than for several individual filtrations, and if any solution or exchange of ions is progressing at the sediment-water interface, an early separation is desirable. The single filtrate provides identical water for analysis, whereas there is no assurance that individual filtrations at different times would provide identical samples.

A loss of carbon dioxide from solution converts bicarbonate to carbonate. Calcium carbonate, which is only sparingly soluble, often precipitates soon after a bottle is uncapped. Precipitation of calcium carbonate affects the validity of the pH, alkalinity, specific-conductance, calcium, titrated-hardness, and dissolved-solid values. Consequently, test-sample volumes for determination of calcium, hardness, and dissolved solids should be withdrawn soon after the bottle is opened. All samples should be inspected visually for evidences of calcium carbonate precipitation when received in the laboratory. If precipitation is evident, the analytical statement will not represent the chemical character of the sample at the time of collection unless special techniques are used. Proper handling of such samples requires special treatments and may involve the

omission of some determination from the analysis. Selected constituents and measurements, even calcium and total alkalinity, can be determined with a reasonable degree of accuracy. The selected special treatment will depend on the nature of the precipitate and the constituents that are considered most important in the analysis.

Other constituents and measurements can be determined in any order. Time is important, however, and the analysis should be carried to completion without undue delay. It has been observed that, because of changes in chemical composition of the water, the validity of the analytical statement often decreases as the time consumed in the analysis increases. All required determinations should be made within 1 week after the sample is opened.

C:7 SIGNIFICANT FIGURES FOR REPORTING RESULTS

The significant figures used by the Geological Survey in reporting the results of analysis are the result of a compromise between precision of the measurement, importance of this precision to the use of the analytical data, and the obvious advantages of some semblance of uniformity in tables of analyses.

One of the commonly used methods, which applies only to the expression of the precision of a determination, is to include all certain digits and the first (and only the first) doubtful digit. This method has one obvious disadvantage: Published data so reported may not be interpreted to mean the same thing by all users of the data. Possible confusion and misinterpretation is minimized if the tabulated analytical results represent the certainty of the reported results within reasonable limits. In analytical results published by the Survey, the last digit may not be absolutely accurate in all analyses, but it is a figure that can be used with a good degree of confidence in most applications of water-analysis data.

The precision of procedures for water analysis cannot be measured in absolute terms of either concentration or percentage, nor is it desirable to do so for practicable purposes. Generally, more precise measurements are required when the concentration of a constituent is low than when the concentration is high. For example, in potable water supplies the difference between 1.0 and 1.5 ppm of fluoride is very important, but the difference between 10.0 and 10.5 ppm is not significant, although the absolute error is the same. Neither is percentage of error a good gage of the precision of the analysis. For example, an absolute error of ± 0.01 ppm is an error of 100 percent when the concentration of the constituent is only 0.01 ppm.

Another factor that complicates the problem of designating precision of analysis is the inherent tendency of most analytical

determinations to vary in accuracy throughout the concentration range of the constituent in a manner that is akin neither to absolute nor percentage quantities. Consequently, the Survey's rules for rounding off and reporting significant figures are somewhat arbitrary. However, the individual procedures contain a general statement as to the precision of the method in the concentration range most frequently found in water analysis in routine laboratory operations.

The importance of the accurate determination of minute quantities of a constituent to the usability of the water has also influenced the selection of significant figures. Water-quality data are used for a vast variety of purposes. Water analysts have endeavored to design and use analytical methods sufficiently sensitive to meet the requirements of exacting users of water-quality information. The precision of a few methods and their ability to measure low concentrations accurately are far superior to present needs. However, when such precision and sensitivity are available with no additional effort on the part of the analyst, the results are determined and reported to the smallest concentration increment that can be obtained.

Instructions for reporting analytical results are given in "Analytical procedures" (sec. D) for each constituent and property.

Chemical equivalents per million are computed by multiplying the reported concentration of the individual constituents in parts per million, by the reciprocal of their combining weights. The reciprocal factors of the more commonly determined constituents are given in table 2. Equivalents per million (epm) as reported by the Geological Survey are numerical expressions of parts per million and for uniformity are carried to two decimal places regardless of the magnitude of the parts-per-million value; the significant figures shown in no way reflect the accuracy and precision of the measurement as do the parts-per-million values.

TABLE 2.—*Factors for converting parts per million to equivalents per million*

[1954 atomic weights]

Ion	*Sum of atomic weights*	*Multiply ppm by—*	*Ion*	*Sum of atomic weights*	*Multiply ppm by—*
Al^{+3}	26. 98	0. 11119	K^{+1}	39. 100	0. 02558
Br^{-1}	79. 916	. 01251	Li^{+1}	6. 940	. 14409
Ca^{+2}	40. 08	. 04990	Mg^{+2}	24. 32	. 08224
Cl^{-1}	35. 457	. 02820	Mn^{+2}	54. 94	. 03640
CO_3^{-2}	60. 011	. 03333	Mn^{+4}	54. 94	. 07281
F^{-1}	19. 00	. 05263	Na^{+1}	22. 991	. 04350
Fe^{+2}	55. 85	. 03581	NO_3^{-1}	62. 008	. 01613
Fe^{+3}	55. 85	. 05372	OH^{-1}	17. 0080	. 05880
H^{+1}	1. 0080	. 99206	S^{-2}	32. 066	. 06237
HCO_3^{-1}	61. 019	. 01639	SO_4^{-2}	96. 066	. 02082
I^{-1}	126. 91	. 00788	Zn^{+2}	65. 38	. 03059

C:8 EVALUATION OF THE ACCURACY OF ANALYTICAL RESULTS

Some errors are practically unavoidable in analytical work. Errors may result from the reagents, from the limitations of the method or instruments employed, or even from impurities in distilled water. The analyst's skill and general judgment have a direct bearing on the accuracy of the analytical statement. After the chemical analysis of the water sample has been completed, there are several ways by which the validity of the results can be evaluated. No one method of checking gives conclusive proof of the accuracy of the determinations, but the process of checking may bring to light some dubious results or may suggest some additional constituents of the sample that were not considered in the analysis.

C:8a CHEMICAL BALANCE

One of the most commonly used procedures for checking water analyses is a balancing of the chemical equivalents of the major ions. Since water is a chemically balanced system, the sum of the equivalents of cations in solution equals the sum of the anions. If all of the predominant ions have been determined, the equivalents per million should be in reasonable balance.

The hydrogen-ion content of acid water is included in the balance. The hydrogen-ion concentration is approximated from the pH of the sample,

$$\mathrm{pH} = \log \frac{1}{a_{H^{+1}}}$$

or

$$a_{H^{+1}} = 10^{-\mathrm{pH}}$$

where the base of hydrogen is the effective concentration (activity) of hydrogen ions. The calculated pH of standard solutions of sulfuric acid has been compared with determined pH, and the agreement is good up to 2.0 ppm H (pH 2.70). Reproducibility and accuracy of ± 0.1 epm H^{+1} is the best that can be anticipated under normal operating conditions and with most waters. Considerable possible error is introduced in converting pH to hydrogen-ion concentration because of the effect of other ions on the activity of the hydrogen ion.

pH	*epm* H^{+1}	*pH*	*epm* H^{+1}
4.25–3.85	0.1	2.95	1.1
3.80–3.60	.2	2.90	1.3
3.55–3.50	.3	2.85	1.4
3.45–3.40	.4	2.80	1.6
3.35–3.30	.5	2.75	1.8
3.25–3.20	.6	2.70	2.0
3.15	.7	2.65	2.2
3.10	.8	2.60	2.5
3.05	.9	2.55	2.8
3.00	1.0	2.50	3.2

pH meters determine the activity of the hydrogen ion as distinguished from concentration. The chemist is referred to the work of Kolthoff and Laitinen (1941) for a full discussion of the subject.

Multivalent ions present difficulties in the ionic balance unless the ionic states are differentiated by the analysis. Fortunately, these ions are present in only minor amounts in many waters and rarely influence the ionic balance appreciably. Orthophosphates may occur in water as PO_4^{-3}, HPO_4^{-2}, and H_2PO^{-1}; the proportion of each of these ions is related to the pH of the water. The PO_4^{-3} ion occurs only above about pH 9.3. Because natural waters practically never attain this pH, a general assumption can be made that the PO_4^{-3} ion is not present in natural waters. For the purpose of ionic balance, the proportion of HPO_4^{-2} and $H_2PO_4^{-1}$ present can be calculated from the pH relation as shown in table 3. The data in table 3 are based on work of Sorensen as reported by Clark (1928) and from Rieman, Neuss, and Naiman (1942, p. 323). Review and checking of this table with work by others is in order. However, limited use of this table has provided at least reasonably good analytical balance for samples with a high orthophosphate content. Other forms of phosphorus cannot be differentiated in this manner, nor are suitable methods available for the other multivalent ions.

TABLE 3.—*Orthophosphate mixtures as related to pH*

pH	HPO_4 (*percent*)	H_2PO_4 (*percent*)	*pH*	HPO_4 (*percent*)	H_2PO_4 (*percent*)
4.5	0	100. 0	7.0	61. 0	39. 0
4.6	. 5	99. 5	7.1	66. 5	33. 5
4.7	. 5	99. 5	7.2	72. 0	28. 0
4.8	1. 0	99. 0	7.3	76. 5	23. 5
4.9	1. 0	99. 0	7.4	80. 5	19. 5
5.0	1. 5	98. 5	7.5	84. 0	16. 0
5.1	1. 5	98. 5	7.6	87. 0	13. 0
5.2	2. 0	98. 0	7.7	89. 5	10. 5
5.3	2. 5	97. 5	7.8	91. 5	8. 5
5.4	3. 0	97. 0	7.9	93. 0	7. 0
5.5	3. 5	96. 5	8.0	94. 5	5. 5
5.6	4. 5	95. 5	8.1	95. 5	4. 5
5.7	6. 0	94. 0	8.2	96. 5	3. 5
5.8	8. 0	92. 0	8.3	97. 0	3. 0
5.9	9. 5	90. 5	8.4	98. 0	2. 0
6.0	12. 5	87. 5	8.5	98. 5	1. 5
6.1	15. 5	84. 5	8.6	98. 5	1. 5
6.2	19. 0	81. 0	8.7	99. 0	1. 0
6.3	23. 0	77. 0	8.8	99. 0	1. 0
6.4	27. 0	73. 0	8.9	99. 0	1. 0
6.5	32. 0	68. 0	9.0	99. 5	. 5
6.6	37. 5	62. 5	9.1	99. 5	. 5
6.7	43. 5	56. 5	9.2	99. 5	. 5
6.8	49. 5	50. 5	9.3	100. 0	. 0
6.9	55. 5	44. 5			

Dissociation also must be considered in balancing analyses. Many of the determinations, particularly those for the heavy metals, do not differentiate between dissociated and undissociated constituents. Constituents that hydrolyze to give undissociated products determined along with the ionized forms in the analysis cannot be included directly in the ionic balance. Published dissociation constants give some indication of the possible ionized concentration, but complete confidence cannot be placed in these values when considering complex solutions such as natural water.

The deviations from balance can be expressed in terms of absolute quantities or as a percentage of the total ionic concentration. Obviously, the analyst must use some type of sliding scale to evaluate the significance of the deviations for water of different concentrations. With careful work and a comprehensive analysis of the sample, it is customary for the deviation between equivalents per million of cations and anions not to exceed 1 or 2 percent of the total concentration for analyses of waters with more than about 150 ppm of dissolved solids. A deviation of up to 3 percent may result from the accumulation of small unavoidable errors in the analysis of water containing about 100 ppm of dissolved solids and about 5 percent for waters with as little as 25 or 30 ppm.

Chemical balance is only an indication of the gross validity of the analysis. Very large errors in the determination of minor constituents can go unnoticed; neither are compensating errors detected. Conclusions that can be drawn from deviations in anion and cation balance are usually negative. Large deviations indicate either a large error in one or more determinations or the presence of some undetermined constituent, but a good balance is not conclusive evidence that each of the determinations is accurate nor that all constituents have been determined. Chemical balance is one tool for evaluating the validity and comprehensiveness of an analysis but must not be a goal for the analyst.

C:8b RELATION OF RESIDUE ON EVAPORATION TO CALCULATED DISSOLVED SOLIDS

Comparison of the residue on evaporation and dissolved solids calculated from the analytical statement is a rough check of the comprehensiveness of an analysis (see sec. D:36a–2). Several important factors have a bearing on this comparison. First, the residue on evaporation might contain appreciable amounts of organic and some inorganic materials that are not determined in the analysis. Second, water of hydration may also be contained in the residue. Ignition loss is sometimes determined as a rough estimate of the water of hydration and combustible organic materials. The

calculated dissolved solids is usually between the value obtained as residue on evaporation and the residue on evaporation minus the ignition loss. Third, volatile solids which are determined in the course of the analysis may be lost during evaporation. If volatile solids are lost, the residue on evaporation may be less than the calculated value. Fourth, the alkalinity determination is influenced by weak-acids residuals other than carbonate and bicarbonate. Phosphate, borate, and silicate, measured collectively as alkalinity and reported as carbonate and bicarbonate, may be redetermined individually in specific analyses. If so, the solids determined by calculation may be higher than by evaporation. Other factors such as the behavior of acid waters and iron compounds during evaporation also complicate the relation between residue on evaporation and the calculated dissolved solids.

C:8c SPECIFIC-CONDUCTANCE RELATION

For most natural waters of mixed type the specific conductance, in micromhos, multiplied by a factor of 0.65 ± 0.1 approximates the residue on evaporation in parts per million. This does not approach an exact relation because the conductance of a solution is dependent on the type and total quantity of ions in solution. More precise relations can be developed for specific water types. The factor of 0.65 is applicable only with comparatively dilute solutions and usually increases as the total dissolved-salt content exceeds 2,000 to 3,000 ppm. For waters that contain appreciable concentrations of free acid, caustic alkalinity, or sodium chloride, the factor may be much less than 0.65. The factor for some other specific types of water may be higher. Nonionized silica will also disturb the ratio of residue on evaporation to conductance. With similar limitations, the specific conductance divided by 100 approximates the equivalents per million of anions or cations. This relation is particularly helpful in detecting the location of error (in anions or cations) as well as for estimating the comprehensiveness of an analysis.

Rossum (1949, p. 631) proposed a method for checking analyses that is based on a comparison of the specific conductance of dilute solutions with the summation of the added increments of conductance contributed by each determined ion in solution. This procedure is known as the diluted-conductance method. The sample is diluted with redistilled water until the conductance of the solution is between 90 and 120 micromhos. This observed conductance is recorded. The exact dilution ratio, D, is then computed as follows:

$$D = \frac{\text{volume of sample + volume of redistilled water}}{\text{volume of sample}}$$

Next, the conductance of the redistilled water, K_w, is determined and the true diluted conductance, K_d, is calculated:

$$K_d = \text{observed diluted conductance} - (D-1)K_w$$

The diluted conductance is then compared with the summation of the conductances of the determined ions.

Diluted-conductance factors for ions commonly found in water

[After Rossum, 1949]

Ion	*Micromhos per meq per liter at 25° C.*	*Micromhos per mg per liter at 25° C.*
Bicarbonate	43. 6	0. 715
Calcium	52. 0	2. 60
Carbonate	84. 6	2. 82
Chloride	75. 9	2. 14
Magnesium	46. 6	3. 82
Nitrate	71. 0	1. 15
Potassium	72. 0	1. 84
Sodium	48. 9	2. 13
Sulfate	73. 9	1. 54

The American Public Health Association and others (1955) recommends that a recheck of the chemical analysis is advisable if the diluted conductance differs by more than 2 percent from the sum of the conductances of the determined ions. This degree of accuracy may be somewhat excessive for routine water analysis unless the dilutions are made with extreme care.

The diluted-conductance method of checking is not applicable to waters whose initial conductance are less than 90 micromhos, or to samples whose pH values are not between 6 and 9, or to samples that contain appreciable quantities of ions not listed in the above table. The conductance contributed by hydrogen and hydroxyl ions is greater than that by other common ions.

This method of checking is a little more time consuming than chemical balance, but it does have the advantage of considering all of the ions in solution. A good check by the diluted-conductance method is conclusive proof that no major ion has been omitted from the determination.

C:8d INTERRELATION OF CONSTITUENTS OF WATER FROM THE SAME SOURCE

As samples from the same source repeatedly come through the laboratory, the analyst begins to recognize patterns of water quality. These may be the relation of calcium to bicarbonate, sodium to chloride, or other relations that appear to hold true. When the determined values deviate significantly from previously observed relations the analyst is immediately suspicious of the analytical results and may elect to make some checks. The apparent departure from the expected may be the result of manipulative errors, such as

recording incorrect test-sample volume, buret readings, or weights or transposing figures. Checks of these and similar points are usually made first, followed by redetermination of the questionable measurement when indicated, before assuming that the unexpected value represents an actual change in water quality. This method of evaluating an analysis must be used judiciously because some marked deviation from normal relations can be expected occasionally, and an attempt to reproduce a relation may in actuality result in an erroneous analysis. The most valid analytical value should be the one finally accepted and not necessarily the one that most closely approaches the analysis of a previous sample.

C:8e METHOD FOR CHECKING PARTIAL ANALYSES

Much has been said here about checking the validity of comprehensive analyses, but little help has been given for verifying results when only a few of the constituents are determined. There is no simple adequate method for checking a partial analysis. A recovery test can be run by adding a known quantity of constituent to the sample and repeating the analysis. The results are not always conclusive, however; a fraction of the constituent that missed detection in the first analysis might also be missed in the second. Interrelations of constituents in water from the same source and relations of certain constituents to specific conductance or water discharge may be helpful as guides, but the ability of the analyst is the only good control.

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SECTION D. ANALYTICAL PROCEDURES

D:1 ACIDITY

The acidic properties are attributable to the presence of mineral acids, uncombined dissolved gases, organic acids, and salts of strong acids and weak bases. Hydrolyzable salts of iron and aluminum of mine and industrial origin are common sources of acidity. The analyst should differentiate between acidity as a property of a solution and as a total concentration of acids. In terms of the dissociation theory, an acid is any compound which on dissociation produces hydrogen ions. To determine the concentration of a specific acid compound requires titration with a base to a practical end point at which all hydrogen ions that can be produced by the compound have been neutralized. This end point is normally taken as the inflection point, or points, on the titration curve. The inflection points differ with the acid compound, hence it is impossible to determine accurately the acid concentration of different hydrolyzable salts or mixtures by titration to a single predetermined end point. Total acid compounds might be estimated by titrating to the last inflection point on a sodium hydroxide curve, provided that this point is readily recognizable. Acidity, on the other hand, is the property of a solution attributable to the presence of an excess of hydrogen ions over hydroxyl ions, and the acidity value is a measure of the strong base required to adjust the hydrogen and hydroxyl ions to equivalency. Acid compounds may exist at the equivalence point, pH 7.0, without producing hydrogen ions in solution.

Three determinations of acidity are given, each of which measures a different group of contributors to acidity. Total acidity (see sec. D:1a) shows the total stream acidic potential. The immediate-acidity (see sec. D:1b) determination measures the existing acidity from all causes plus that immediately available from uncombined dissolved gases when titrated with a standardized base. Potential free acidity (see sec. D:1c) represents the existing acidity from all causes and includes that which may develop from acid-producing salts but excludes that from uncombined gases. The difference between the total acidity and potential free acidity is an indication of the acidity that can be developed from uncombined gases. Similarly, the difference between total acidity and immediate acidity is

an estimate of the acidity that can be developed through oxidation and (or) hydrolysis of acid-producing salts. Combined, the three determinations are useful for approximating the nature of the acid-causing components. Determinations of acidity are among the least reliable in water analysis in respect to accuracy and reproducibility of results.

The acidity of water is significant to the operation of water-treatment plants and waste-disposal systems. High acidity, particularly that due to strong acids, contributes to the corrosiveness of the water.

D:1a TOTAL ACIDITY

Total acidity is the capacity of a water containing a compound or compounds, with or without hydrolysis, for neutralizing base to pH 7.0. Basicity is the counterpart of total acidity.

D:1a-1 VOLUMETRIC METHOD

Principle of determination

The volumetric determination of total acidity measures the total capacity of the water to neutralize base to pH 7.0, irrespective of the time involved for the reactions to reach equilibrium at pH 7.0. This capacity includes the combined effect of free mineral acids, dissolved gases, buffer systems, and combined equilibrium products of hydrolysis at pH 7.0. The acidity is determined by titrating the water with a standardized strong base. Often, total acidity is due primarily to carbon dioxide or other dissolved gases. Hence, customary precautions should be taken to minimize the loss of these gases before they are chemically combined with the titrant base.

If the water contains principally free mineral acids, the total acidity can be titrated rather accurately. If hydrolyzable salts are present the titration is complicated by the degree and rate of hydrolysis. For example:

$$Fe_2(SO_4)_3 + 6H_2O \rightleftarrows 2Fe(OH)_3 + 6H^{+1} + 3SO_4^{-2}$$

The addition of sodium hydroxide shifts the hydrolysis equilibrium toward the right, thereby liberating more hydrogen ions. Hydrolysis proceeds slowly in the cold as the basic titrant is added to the solution, and the time involved for the hydrolysis to reach equilibrium at pH 7.0 may be infinite. Heating of the sample hastens hydrolysis.

The sample is titrated rapidly in the cold to pH 7.0; the free mineral acids have now been neutralized and all the dissolved gases that are going to react at this pH have been combined. Then the solution is heated. Boiling is to be avoided because of the excessive loss of dissolved gases. The sample is allowed to cool before com-

pleting the titration to avoid upsetting the pH-temperature relations. Heating may increase the pH slightly if no hydrolyzable salts are present. Such increase in pH is probably due to the loss of uncombined carbon dioxide at pH 7.0 and hence has no bearing on the capacity of the water to neutralize base. When pH increases during heating, the titrant volume required by the cold solution is used in the computation. If the carbon dioxide concentration of the water is high, the end point of the cold titration will not be sharp because of the buffering effect of the bicarbonate-carbonic acid system.

The procedure given here has been used for the determination of total acidity in waters that contain mine-drainage products and some industrial pollutants. The procedure may not be universally applicable to all types. The total-acidity determination is one of the least reliable in water analysis in respect to accuracy and reproducibility of results. If the sample contains no materials acting as buffers at the end point, reproducibility and accuracy of ± 0.05 ppm H^{+1} can be expected. Unfortunately, this condition seldom prevails, and usually the reproducibility and accuracy are appreciably less.

Apparatus and reagents

pH meter
Electric hotplate
Sodium hydroxide, 0.0248*N*, 1.00 ml≅0.025 mg H^{+1}

Procedure

For precise work the sample for the determination of total acidity should be collected as directed in sec. A:3c and the analysis should proceed as soon as possible after the collection of the sample.

1. Pipet a volume of sample containing less than 1.0 mg H^{+1} (50.0 ml max) into into a 150-ml beaker.
2. Rapidly titrate the solution with 0.0248*N* NaOH (1.00 ml≅0.025 mg H^{+1}) to pH 7.0.
3. Heat the solution to 80°–90°C (do not boil) and maintain this temperature for 2 min.
4. Cool the solution to approximately room temperature.
5. Continue the titration to pH 7.0. Disregard any pH increase during the heating period.

Calculations

$$\text{ppm Total acidity } (H^{+1}) = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{ml titrant} \times 0.025$$

Report total-acidity concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Sodium hydroxide, 0.0248*N*, 1.00 ml≈0.025 mg H^{+1}: Dilute 12 ml 2*N* NaOH with carbon dioxide-free water to approx 1 liter. Standardize the solution against primary standard potassium acid phthalate as follows: Lightly crush 3–4 g of the salt to a fineness of approx 100 mesh and dry for 1 or 2 hr at 120°C. Dissolve about 2 g, accurately weighed to the nearest milligram, in carbon dioxide-free water and dilute to 500.0 ml. Titrate 50.0 ml of the solution with the NaOH to pH 8.6.

$$\text{Normality of alkali} = \frac{\text{g } KHC_8H_4O_4 \text{ in 50.0 ml} \times 4.8967}{\text{ml alkali}}$$

Store the 0.0248*N* base in a tightly capped polyethylene bottle.

Sodium hydroxide, 2*N*: Cover approx 100 g NaOH sticks with water until the surface coating is dissolved. Discard the supernatant fluid and immediately dissolve the remaining NaOH (about 80 g) in approx 1 liter of carbon dioxide-free water. Store the base in a tightly capped polyethylene bottle.

D:1b IMMEDIATE ACIDITY

Immediate acidity is the capacity of a water containing a compound or compounds, with or without hydrolysis, for rapidly neutralizing base to pH 7.0. The only difference between immediate acidity and total acidity is the degree of oxidation and hydrolysis proceeding during the analysis.

D:1b–1 VOLUMETRIC METHOD

The volumetric method is similar in substance to D 1067–51 T, ASTM[1] (1954, p. 171–173) Manual on Industrial Water.

Principle of determination

Immediate acidity is determined by rapid titration with a standardized strong base in the cold to minimize the effect of oxidation and hydrolysis in producing hydrogen ions.

Apparatus and reagents

pH meter

Sodium hydroxide, 0.0248*N*, 1.00 ml≈0.025 mg H^{+1}

Procedure

For precise work the sample for the determination of immediate acidity should be collected as directed in sec. A: 3c and analysis should proceed as soon as possible after the collection of the sample.

1. Pipet a volume of sample containing less than 1.0 mg H^{+1} (50.0 ml max) into a 150-ml beaker.
2. Rapidly titrate the solution with 0.0248*N* NaOH (1.00 ml≈0.025 mg H^{+1}) to pH 7.0.

[1] American Society for Testing Materials.

Calculations

$$\text{ppm Immediate acidity } (H^{+1}) = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{ml titrant} \times 0.025$$

Report immediate-acidity concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Sodium hydroxide, 0.0248*N*, 1.00 ml≃0.025 mg H^{+1}: Dilute 12 ml 2*N* NaOH with carbon dioxide-free water to approx 1 liter. Standardize the solution against primary standard potassium acid phthalate as follows: Lightly crush 3–4 g of the salt to a fineness of approx 100 mesh and dry for 1 or 2 hr at 120°C. Dissolve about 2 g, accurately weighed to the nearest milligram, in carbon dioxide-free water and dilute to 500.0 ml. Titrate 50.0 ml of the solution with the NaOH to pH 8.6.

$$\text{Normality of alkali} = \frac{\text{g } KHC_8H_4O_4 \text{ in 50.0 ml} \times 4.8967}{\text{ml alkali}}$$

Store the 0.0248*N* base in a tightly capped polythylene bottle.

Sodium hydroxide, 2*N*: Cover approx 100 g NaOH sticks with water until the surface coating is dissolved. Discard the supernatant fluid and immediately dissolve the remaining NaOH (about 80 g) in approx 1 liter of carbon dioxide-free water. Store the base in a tightly capped polyethylene bottle.

D:1c POTENTIAL FREE ACIDITY

Potential free acidity is the capacity of a water containing a non-volatile compound or compounds, with or without hydrolysis, for neutralizing base to pH 7.0.

D:1c–1 VOLUMETRIC METHOD

Principle of determination

The sample is heated to drive off uncombined gases and to oxidize and (or) hydrolyze acid-producing salts (sec. D:1a). Boiling is essential for complete expulsion of uncombined dissolved gases.

Apparatus and reagents

pH meter
Hotplate
Sodium hydroxide, 0.0248*N*, 1.00 ml≃0.025 mg H^{+1}

Procedure

1. Pipet a volume of sample containing less than 1.0 mg H^{+1} (50.0 ml max) into a 150-ml beaker.
2. Heat the sample to boiling and continue boiling for 2 min. Vigorous stirring may be used to hasten the removal of dissolved gases.
3. Cool the solution to approximately room temperature.
4. Titrate the degassed sample with 0.0248*N* NaOH to pH 7.0.

Calculations

$$\text{ppm Potential free acidity } (H^{+1}) = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{ml titrant} \times 0.025$$

Report potential free-acidity concentrations of <10 ppm to 1 decimal place, of between 10 and and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Sodium hydroxide, 0.0248*N*, 1.00 ml≈0.025 mg H^{+1}: Dilute 12 ml 2*N* NaOH with carbon dioxide-free water to approx 1 liter. Standardize the solution against primary standard potassium acid phthalate as follows: Lightly crush 3–4 g of the salt to a fineness of approx 100 mesh and dry for 1 or 2 hr at 120°C. Dissolve about 2 g, accurately weighed to the nearest milligram, in carbon dioxide-free water and dilute to 500.0 ml. Titrate 50.0 ml of the solution with the NaOH to pH 8.6.

$$\text{Normality of alkali} = \frac{\text{g } KHC_8H_4O_4 \text{ in } 50.0 \text{ ml} \times 4.8967}{\text{ml alkali}}$$

Store the 0.0248*N* base in a tightly capped polyethylene bottle.

Sodium hydroxide, 2*N*: Cover approx 100 g NaOH sticks with water until the surface coating is dissolved. Discard the supernatant fluid and immediately dissolve the remaining NaOH (about 80 g) in approx 1 liter of carbon dioxide-free water. Store the base in a tightly capped polyethylene bottle.

REFERENCE

American Society for Testing Materials, 1954, Manual on industrial water: Spec. Tech. Pub. 148–A.

D:2 ALKALINITY

Alkalinity is the capacity of a water containing a compound or compounds, with or without hydrolysis, for neutralizing strong acid to pH 4.5. The determination of alkalinity is a measure of the excess basic constituents over the amount necessary to balance the strong acid constituents. Alkalinity in water is caused primarily by the presence of bicarbonates, carbonates, and hydroxides. The relative concentrations of hydroxide, carbonate, and bicarbonate are a function of the temperature, pH, and concentration of other dissolved solids. The chemist is referred to the work of Langelier (1946, p. 169) for a full discussion of the equilibria involved. Minor acid radicals such as borates, phosphates, and silicates also add to the alkalinity of the water.

Because the alkalinity of many waters is primarily a function of the carbonate, bicarbonate, and (or) hydroxide content, the alkalinity determination is sometimes taken as an indication of the concentration of these constituents. Such values are maximums and include titratable weak acid radicals. Perhaps the effect of phosphate can be corrected for by utilizing the relations given in sec. C:8a, but the Geological Survey has not had sufficient experience with the correction to recommend it universally. No suitable methods for correcting for the other acid radicals are available.

Carbonates and bicarbonates are common to most waters because of the abundance of carbonate minerals in nature and because carbon dioxide, which helps dissolve them and other minerals, is readily available. Direct contribution to alkalinity by hydroxides is rare in nature, and the presence of hydroxides can usually be attributed to water treatment or to contamination.

The U.S. Public Health Service (1946) recommends the following limitations on alkalinity of drinking and culinary water on carriers subject to Federal quarantine regulations:

1. The phenolphthalein (CO_3) alkalinity (calculated as $CaCO_3$) should not be greater than 15 ppm + 0.4 × total alkalinity.
2. The normal carbonate alkalinity should not exceed 120 ppm.
3. If excess alkalinity is produced by chemical treatment, the total alkalinity (calculated as $CaCO_3$) should not exceed the hardness by more than 35 ppm.

The alkalinity, in equivalents per million, in excess of the alkaline earths has a bearing on the suitability of a water for irrigation (Eaton, 1954). If this excess alkalinity, termed "residual sodium carbonate," exceeds 2.5 epm the water is generally not suitable for irrigation; water containing 1.25 to 2.5 epm is marginal, and that containing less than 1.25 epm is probably safe (U.S. Salinity Laboratory Staff, p. 81).

D:2a–1 POTENTIOMETRIC METHOD

The potentiometric method is similar in substance to that in part I, APHA [2] (1955, p. 35–37) Standard Methods, and D 1067–51 T, ASTM (1954, p. 172–175) Manual on Industrial Water.

Principle of determination

Alkalinity is determined by titrating the water sample with a standard solution of strong acid. The equivalency, or end points, of the titration are selected as the inflection points in the titration of Na_2CO_3 with H_2SO_4. The carbonate end point is taken as pH 8.2 and the bicarbonate as pH 4.5. The following reactions occur:

$$CO_3^{-2} + H^{+1} \rightarrow HCO_3^{-1} \text{ (titration to pH 8.2)}$$

$$\left.\begin{aligned} HCO_3^{-1} \text{ (from } CO_3^{-2}) + H^{+1} &\rightarrow H_2O + CO_2 \\ HCO_3^{-1} \text{ (natural)} + H^{+1} &\rightarrow H_2O + CO_2 \end{aligned}\right\} \text{(titration to pH 4.5)}$$

The presence of hydroxide is indicated if the carbonate titrant volume exceeds the bicarbonate titrant volume.

For waters that contain only small quantities of dissolved mineral matter, the determination of alkalinity is likely to introduce the largest error in the analysis. Reproducibility of results between duplicate samples cannot be expected to be better than about 2 percent. As discussed in sec. C:6, alkalinity is very susceptible to change between time of collection and analysis. Changes occur more rapidly after the sample bottle is opened. The total-alkalinity value is probably somewhat more stable than the relative values of the common alkalinity components. Unless a gross error is made in the initial determination of alkalinity, it is seldom advisable to try to check the results if several days have elapsed since the bottle was first opened. In some water the alkalinity may change appreciably in a few hours.

Additional information on the principle of the determination is given by Collins (1928).

Apparatus and reagents

Titration assembly, consisting of pH meter, medium-speed mechanical stirrer, and 50-ml buret.

Sulfuric acid, 0.01639*N*, 1.00 ml≈1.00 mg HCO_3^{-1}

Procedure

Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way.

1. Pipet a volume of sample containing less than 40 mg alkalinity as HCO_3^{-1} (50.0 ml max) into a suitable beaker.
2. Insert beaker in titration assembly and record the pH.
3. Start the stirrer and proceed immediately with the titration.
4. Record the titrant volume at pH 8.2 and 4.5.

[2] American Public Health Association and others.

Calculations

$$\text{ppm Alkalinity as } CaCO_3 = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times 0.82 \times \text{ml titrant}$$

$$\text{ppm } OH^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times [(\text{ml to pH } 8.2) - (\text{ml to pH } 4.5)] \times 0.2788$$

$$\text{ppm } CO_3^{-2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times [(\text{ml to pH } 8.2 \times 0.9835) - (\text{ppm } OH^{-1} \times 3.527)]$$

$$\text{ppm } HCO_3^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times [(\text{ml pH } 8.2 \text{ to } 4.5) - (\text{ml to pH } 8.2)]$$

Report alkalinity concentrations of <999 ppm to whole numbers and of >999 ppm to 3 significant figures only.

Preparation of reagents

Sulfuric acid, 0.01639*N*, 1.00 ml≏1.00 mg HCO_3^{-1}: Add 0.5 ml conc H_2SO_4 (sp gr 1.84) to 950 ml water. (The titrant is stable for several months if protected from ammonia fumes and is usually prepared in larger quantities.) After the solution has been thoroughly mixed, standardize it by titrating 25.00 ml Na_2CO_3 (1.00 ml≏1.00 mg HCO_3^{-1}) to pH 4.5.

Sodium carbonate, 1.00 ml≏1.00 mg HCO_3^{-1}: Dissolve 0.8686 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 ml.

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

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D:3 ALUMINUM

Aluminum forms complex alumino silicates, and combined with other metals these alumino silicates are among the most abundant minerals in the earth's crust. Yet aluminum is usually only a minor constituent in water. It is highly resistant to removal by solution during weathering and remains behind persistently during the process of rock decomposition in the form of clay minerals in the soil and anhydrous minerals in shale and similar sediments. Aluminum is amphoteric and can exist as the natural cation or aluminate anion. However, the normal buffer system in natural water tends to maintain the pH between 5 and 9, in which range disassociated aluminum or aluminate ions will usually not be present in appreciable quantities. Waters of normal pH may contain as much as 10 ppm of aluminum in the colloidal form. Aluminum ions form strong complexes with organic matter, sulfate, and fluoride. This tendency stabilizes high concentrations of aluminum in some waters.

No evidence has been found to prove that aluminum is harmful to human beings (California State Water Pollution Control Board, 1952, 1954, p. 174). It is of little importance in irrigation waters, although very high concentrations could be toxic to some crops. Aluminum compounds in water in concentrations as low as 0.05 ppm may cause trouble in industries such as laundries and mineral-water plants.

D:3a–1 FERRON-ORTHOPHENANTHROLINE METHOD

Principle of determination

Ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) reacts with aluminum to give a complex that absorbs light in the ultraviolet range. A true solution rather than an absorption lake is involved. Color development is complete immediately. Normal temperature variations do not affect the reaction.

The method is subject to significant interference from iron, but this effect can be greatly minimized by adding an iron-complexing agent. Orthophenanthroline is ideal for the purpose and has the additional advantage that iron may be simultaneously determined. A correction for iron must still be made, but it is comparatively small.

Several other metals and anions show small interference effects, but only manganese, lead, cobalt, and fluoride show sufficiently

pronounced effects to require correction. Beryllium minimizes the interference of fluoride. The relative interfering effects of certain constituents are indicated by the following results obtained in solutions containing 1.00 ppm of aluminum:

Constituent	*Parts per million*	Al *found (ppm)*
Mg	40	1. 04
Mg	80	1. 09
Zn	5	1. 05
Mn	5	1. 17
Mn	10	1. 28
F	1	. 94
F	2	. 90
F	5	. 80

Orthophosphate up to 5 ppm and residual chlorine up to 5 ppm do not interfere. Natural color and turbidity interfere in the aluminum determination, and a correction is usually required.

Interferences are relatively rare in the associated orthophenanthroline iron determination. Orthophenanthroline is generally considered specific for iron. Copper may interfere if the pH goes above 6, but this will not happen if the pH buffer is in good condition. Natural color and turbidity have a measurable but not excessive effect.

Occasionally, small negative absorbancy values are obtained in the aluminum determination due to colorless-complex formation with calcium. This is harmless, as a reading is always obtained if aluminum is present.

In the analytical sequence, manganese and fluoride should be determined before aluminum so that the necessary corrections may be applied. These corrections are derived from the data in the above table of interferences. They apply with accuracy only at the 1-ppm-aluminum level. However, because concentrations of interfering ions are generally not greatly in excess of aluminum in most waters, the equation holds with satisfactory accuracy for general analytical purposes. If a highly precise aluminum determination is desired in waters containing high concentrations of interfering ions, it is suggested that empirical corrections be made by adding similar concentrations of the interfering ions to an appropriate aluminum standard and measuring the resulting absorbancy change.

Additional information on the principle of the determination is given by Davenport (1949) and by Smith and Richter (1944).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

	Al	Fe
Wavelength, mμ	370	520.
Cells, mm	40	40.
Phototube	Blue-sensitive	Blue-sensitive.
Filter	Blue	None.
Blank	Metal-free water, plus reagents.	Metal-free water, plus reagents.
Initial sensitivity setting	2	2.
Slit width (approx), mm	1.0	0.1.

The following absorbancies have been observed for iron and aluminum:

mg Fe	Absorbancy 370 mμ	Absorbancy 520 mμ
0.025	0. 07	0. 51
.050	. 125	1. 02
.075	. 185	1. 53
.100	. 25	1. 95
.125	. 305	2. 33

mg Al	Absorbancy (370 mμ)
0. 025	0. 64
. 050	1. 14
. 075	1. 60

Potassium alum, 1.00 ml=0.010 mg Al^{+3}
Iron chloride, 1.00 ml=0.004 mg Fe
Hydroxylamine-hydrochloric acid reagent
Ferron-orthophenanthroline reagent
Sodium acetate, 35 percent

Procedure

Samples for the determination of aluminum should be collected in accordance with directions given in sec. A : 4d.

1. Pipet a volume of sample containing not more than 0.075 mg Al^{+3} or 0.10 mg Fe (25.00 ml max) into a 50-ml beaker and adjust the volume to 25.0 ml.
2. Prepare a metal-free water blank and sufficient standards, and adjust the volumes to 25.0 ml.
3. Add 2.0 ml $NH_2OH \cdot HCl$ reagent and let stand 30 min to permit complete reduction of the iron to ferrous iron. If precipitated iron is to be determined, the standing time is prolonged until all iron is in solution (overnight standing is a good practice).
4. Add 5.00 ml ferron-orthophenanthroline reagent and stir.
5. Add 2.0 ml $NaC_2H_3O_2$. Stir and let stand at least 10 min but not more than 30 min before taking a reading of the color.
6. Determine the absorbancy of the test sample and standards against the blank at 370 mμ and 520 mμ and, when necessary, make corrections for water color as directed in sec. C : 1a–2, method 1; 2.0 ml $NaC_2H_3O_2$ is added to the color-correction blank.

Calculations

1. Determine the mg Fe in the test sample from a plot of absorbancies at 520 mμ of standards containing known amounts of the constituent.

2. $\text{ppm Fe} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg Fe in sample}$

3. Determine the apparent mg Al^{+3} in the test sample from a plot of absorbencies at 370 mμ of standards containing known amounts of the constituent.

4. $\text{Apparent ppm } Al^{+3} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{apparent mg } Al^{+3} \text{ in sample}$

5. ppm Al^{+3}=apparent ppm Al^{+3} − 0.12 ppm Fe − 0.04 ppm Mn + 0.05 ppm F^{-1}.

Report aluminum concentrations of <10 ppm to 1 decimal place and of >10 ppm to 2 significant figures only.

Preparation of reagents

Potassium alum, 1.00 ml=0.010 mg Al^{+3}: Dissolve 1.758 g $AlK(SO_4)_2 \cdot 12H_2O$ in metal-free water. Add 0.5 ml $CHCl_3$ and dilute to 1,000 ml with metal-free water. Dilute 25.00 ml of this solution to 250.0 ml with metal-free water.

Iron chloride, 1.00 ml=0.004 mg Fe: Dilute 10.00 ml $FeCl_3$ (1.00 ml=0.400 mg Fe) to 1,000 ml with metal-free water, containing 1 or 2 drops of conc HCl (sp gr 1.19).

Iron chloride, 1.00 ml=0.400 mg Fe: Weigh out 0.400 g analytical-grade iron wir which has been cleaned in dilute HCl, rinsed, and dried. Dissolve in a minimum of dilute HCl and dilute to 1,000 ml.

Hydroxylamine-hydrochloric acid reagent: Dissolve 100 g $NH_2OH \cdot HCl$ in metal-free water. Add 40 ml conc HCl (sp gr 1.19). Add 1 g $BeSO_4 \cdot 2H_2O$. Dilute to approx 1 liter with metal-free water.

Ferron-orthophenanthroline reagent: Add 0.5 g ferron and 1.0 g of orthophenanthroline to approx 1 liter metal-free water. Stir for several hours until the maximum solution is obtained. The ferron will not always dissolve completely. Allow any solids to settle out and decant the clear supernate for use.

Sodium acetate, 35 percent: Dissolve 350 g anhydrous $NaC_2H_3O_2$ in metal-free water and dilute to approx 1 liter.

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D:4 ARSENIC

Arsenic compounds are present naturally in some waters, but the occurrence of quantities detrimental to health is rare. Weed killers, insecticides, and many industrial effluents contain arsenic and are potential sources of water pollution. The U.S. Public Health Service (1946) states that the maximum concentration of arsenic in drinking and culinary water on carriers subject to Federal quarantine regulations must not exceed 0.05 ppm. The lethal dose for animals is believed to be about 20 mg per animal pound (Miller and Byers, 1935, p. 456). Concentrations of 2–4 ppm of arsenic are reported not to interfere with the self-purification of streams (Rudolphs and others, 1944, p. 222).

D:4a–1 GUTZEIT-VOLUMETRIC METHOD

Principle of determination

The arsenic is distilled from the sample as arsine (fig. 15), and its concentration determined by oxidation-reduction reactions and volumetric titration. The optimum pH for the reaction in the receiver tube is 7.0–9.5. The reactions that occur in the determination are as follows:

In distillation flask—

$$As_2O_3 + 6\,H_2 \rightarrow 2\,AsH_3 + 3\,H_2O$$

In receiving tube—

$$2\,AsH_3 + 12\,HgCl_2 + 3\,H_2O \rightarrow 12\,HgCl + As_2O_3 + 12\,HCl$$

On addition of 20 percent KI—

$$12\,HgCl + 24\,KI \rightarrow 6\,Hg^{\circ} + 6\,K_2HgI_4 + 12\,KCl$$

On addition of 0.001*N* I_2—

$$6\,Hg^{\circ} + As_2O_3 + 8\,I_2 + 12\,KI + 2\,H_2O \rightarrow 6\,K_2HgI_4 + As_2O_5 + 4\,HI$$

On back titration of excess iodine with standard As_2O_3—

$$As_2O_3 + 2\,I_2 + 5\,H_2O \rightarrow 2\,H_3AsO_4 + 4\,I^{-1} + 4\,H^{+1}$$

Lead acetate in the distillation apparatus removes all sulfides and sulfur dioxide, which would otherwise interfere with the determination. Antimony is not separated from arsenic and may interfere. The dimensions of the apparatus (fig. 15) should conform closely with that prescribed by Cassil and Wickmann (1939); otherwise, additional refluxing may be required to carry the arsine over quantitatively. The apparatus should be dismantled and cleaned and new lead acetate plugs inserted at the beginning of each day's work, but a large number of determinations can be made consecutively without cleansing or flushing the distillation apparatus. Excess lead acetate should be

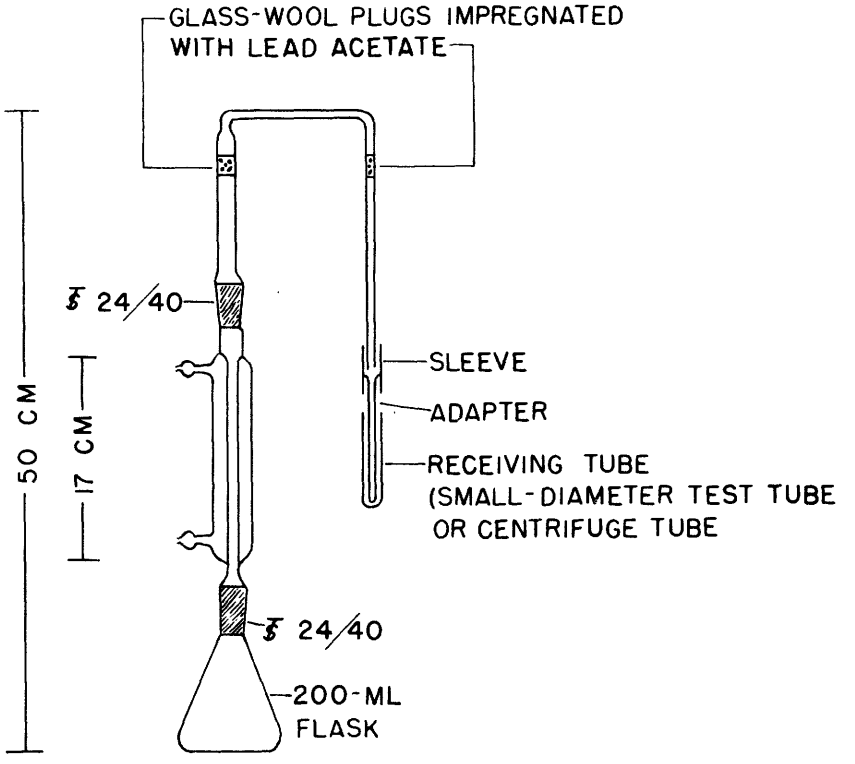

FIGURE 15.—Arsine generator for the isolation of arsenic.

blown out of the plugs with air before making the determinations. The thermometer may be suspended within the condenser, or a flask with a thermometer well may be used.

With the listed apparatus, results are reproducible and accurate to ±0.002 mg.

Apparatus and reagents

Arsine generator (fig. 15)
Hotplate
Buret, 5-ml, graduated in 0.01 ml
Glass wool
Lead acetate, 10 percent
Mercuric chloride, 1.6 percent
Hydrochloric acid, conc (sp gr 1.19)
Potassium iodide, 15 percent
Stannous chloride, 40 percent in conc HCl
Zinc, granulated, low in As
Potassium iodide, 20 percent
Iodine, 0.001*N*
Buffer solution
Starch indicator, 1 percent
Arsenous oxide, 1.00 ml=0.050 mg As_2O_3

Procedure

1. Pipet 1.0 ml $HgCl_2$ into the receiving tube of the generator and insert the tube in the reflux assembly so that the tip of the delivery tube is below the surface of the solution.
2. Allow the hotplate to heat.
3. Pipet a volume of sample containing less than 0.07 mg As (100.0 ml max) into the 250-ml liberation flask.
4. Add rapidly, and with mixing, 10 ml conc HCl, 5 ml 15 percent KI, 1 ml $SnCl_2$, and 4–5 g Zn. Connect the flask immediately to the reflux condenser.
5. Continue refluxing 5 min after the temperature *of the solution* has reached 95°C.
6. Disconnect the receiving tube and adapter.
7. Precipitate and redissolve the red HgI_2 with a few drops of 20 percent KI. Note: If much As is present, the solution will contain a white or pale-yellow precipitate. This precipitate will not be dissolved with the KI.
8. Add 5.00 ml 0.001*N* I_2 through the adapter and mix well. All precipitates should dissolve and the solution still retain the iodine color.
9. Add 2.0 ml buffer solution through the adapter and mix. Connect a small rubber bulb to the adapter and wash down the sides of the tube.
10. Add a few drops of 1 percent starch and titrate the excess I_2 with As_2O_3 (1.00 ml=0.050 mg As_2O_3). Record the titrant volume to the nearest 0.01 ml.
11. Determine a reagent blank by taking 100 ml dilution water through the procedure given above.

Calculations

Calculations take into consideration the fact that in the AsH_3 liberation and subsequent reactions—

$$1\ As_2O_3 \rightleftarrows 6\ Hg^\circ$$
$$6\ Hg^\circ \rightleftarrows 8\ I_2$$

and on titration of excess I_2—

$$1\ As_2O_3 \rightleftarrows 2\ I_2$$

1. Determine the arsenic and iodine equivalents by titrating in the receiver tube 3.00 ml 0.001*N* I_2 with As_2O_3 (1.00 ml=0.05 mg As_2O_3) in the presence of 2.0 ml buffer and 0.5 ml starch.

$$\frac{\text{ml } I_2}{\text{ml } As_2O_3} = \text{iodine equivalent in titration}$$

$$\frac{\text{ml } As_2O_3}{\text{ml } I_2} \times \frac{0.050}{4} = \text{mg } As_2O_3 \rightleftarrows 1.00 \text{ ml } I_2 \text{ in reaction (arsenic equivalent)}$$

2. Calculate ml I_2 not consumed in back titration:

$$\text{ml } As_2O_3 \times \text{iodine equivalent} = I_{2(t)}$$

3. Calculate ml I_2 used in the reaction:

$$I_{2(i)} - I_{2(t)} = I_{2(r)}$$

4. Calculate mg As distilled:

$$I_{2(r)} \times \text{As equivalent} = \text{mg } As_2O_3$$

5. $$\text{ppm As} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} (\text{mg } As_2O_3 - \text{mg blank}) \times 0.7574$$

Report arsenic concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Lead acetate, 10 percent: Dissolve 10 g $Pb_2(C_2H_3O_2)_3OH$ in water, make just acid to litmus, and dilute to approx 100 ml.

Mercuric chloride, 1.6 percent: Dissolve 1.6 g $HgCl_2$ and 0.05 g gum arabic in water and dilute to 100 ml.

Potassium iodide, 15 percent: Dissolve 15 g KI in water and dilute to approx 100 ml.

Stannous chloride, 40 percent in conc HCl: Dissolve 40 g $SnCl_2 \cdot 2H_2O$ in approx 100 ml conc HCl (sp gr 1.19).

Potassium iodide, 20 percent: Saturate approx 75 ml boiling water with KI. Add a crystal of I_2 and allow KI to recrystallize in the refrigerator. Filter off the crystals with suction and wash once with alcohol. Dry the crystals overnight in a 180°C oven to sublime the excess I_2. Dissolve 20 g recrystallized KI in water and dilute to approx 100 ml.

Iodine, 0.001*N*: Dilute 5.00 ml 0.02*N* I_2 to 100.0 ml. This dilution of reagent is relatively unstable, and its arsenic equivalent in the reaction and iodine equivalent in the backtitration should be determined each day. To determine these equivalents add 3.00 ml 0.001*N* I_2, 2.0 ml buffer, and 0.5 ml starch solution to a receiving tube; titrate with As_2O_3 (1.00 ml=0.050 mg As_2O_3) (see calculation 1). Store the 0.001*N* I_2 in a glass-stoppered bottle protected from light.

Iodine, 0.02*N*: Dissolve 2.54 g I_2 and 12 g KI in water and dilute to 950 ml before standardizing. Standardize against primary standard As_2O_3 as follows: Dissolve approx 0.04 g As_2O_3 weighed accurately to 0.0001 g in 10 ml 1*N* NaOH. Add 15 ml 1*N* H_2SO_4 and mix. Add 50 ml 4 percent $NaHCO_3$. Titrate slowly with I_2 solution, maintaining constant agitation until most of the I_2 has been reacted (0.04 g As_2O_3 requires approx 40 ml 0.02*N* I_2). Add starch solution for indicator and continue the titration until the initial pink coloration just passes to clear blue. Deduct from the volume of iodine consumed the amount required to produce the same color in a solution composed of the reagents added to 40 ml of freshly boiled and cooled water in which 5 g KI has been dissolved.

$$\text{Normality of } I_2 = \frac{\text{g } As_2O_3 \times 20.220}{\text{ml } I_2}$$

Store in a glass-stoppered bottle protected from light.

Arsenous oxide, 1.00 ml=0.050 mg As_2O_3: Dilute 50.00 ml As_2O_3 (1.00 ml=1.00 mg As_2O_3) to 1,000 ml. This solution is the basic standard for the arsenic determination.

Arsenous oxide, 1.00 ml=1.00 mg As_2O_3: Dry 1–2 g Mallinckrodt AR Primary Standard As_2O_3 at least 1 hr at 110°C. Dissolve 1.000 g As_2O_3 in 25 ml 20 percent NaOH saturated with CO_2; dilute to 1,000 ml with water. Prepare the 20 percent NaOH by dissolving 20 g NaOH pellets in approx 100 ml water. Saturate the NaOH solution with CO_2 from a CO_2 generator; filter off the Na_2CO_3, if any.

Starch indicator, 1 percent: Triturate 1 g soluble starch with a little water and add the suspension slowly to approx 100 ml boiling water. Store in a glass-stoppered bottle in a refrigerator.

Buffer solution: Dissolve 10 g $Na_2HPO_4 \cdot 12H_2O$ in water and dilute to approx 100 ml.

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D:5 BARIUM

Many mineral salts of barium are soluble, but barium sulfate is very insoluble. Consequently barium ions will be quickly precipitated from waters containing sulfate. Barium salts are used in dyeing, paint, and some explosives manufacture, and in tanning operations. Barium in measurable quantities is generally limited to certain types of brines and industrial wastes and to normal waters whose sulfate content is extremely low. Barium is not determined in normal waters having a sulfate concentration greater than 2 ppm.

The U.S. Public Health Service (1946) states that salts of barium, which have a deleterious physiological effect, must not be added to drinking and culinary water on carriers subject to Federal quarantine regulations.

D:5a–1 GRAVIMETRIC METHOD

The gravimetric method is recommended for waters whose barium content is greater than 10 ppm and for brines and industrial wastes when the complexometric method fails (see sec. D:5a–2).

Principle of determination

Barium is precipitated from acid solution as the sulfate, ignited, and weighed. Calcium and strontium also form slightly soluble sulfates and may precipitate with the barium sulfate. Iron, aluminum, and manganese may be occluded by the barium sulfate and contaminate the precipitate. There is always the possibility of silica coprecipitating. These possible interferences are particularly significant when the amount of barium is small, but they are eliminated or sufficiently minimized if the gravimetric barium determination is made on the filtrate from the gravimetric calcium determination (see sec. D:8a–3, procedure 13). Coprecipitation of other ions in the filtrate with barium sulfate are other sources of error in the determination; they are classics in quantitative analysis and are discussed in detail by Kolthoff and Sandell (1952) and Hillebrand and Lundell (1929, p. 486–505).

When the barium concentration in the original water samples is less than 10 ppm, the quantity of barium sulfate precipitate is so small that results obtained by the gravimetric method may be in appreciable error. The accuracy and reproducibility of results are dependent on the quantitative removal of strontium and on the amount of coprecipitation of foreign ions with barium sulfate. With careful work the results may be accurate and reproducible to 0.25 mg.

Apparatus and reagents

Steam bath
Porcelain crucibles
Muffle furnace
Hydrochloric acid, conc (sp gr 1.19)
Sulfuric acid, 5 percent v/v
Sulfuric acid, conc (sp gr 1.84)

Procedure

1. Dilute or concentrate the filtrate from the gravimetric calcium determination (see sec. D: 8a–3, procedure 13) to a convenient volume. Take an aliquot containing more than 1 mg Ba^{+2} for the determination.
2. Concentrate the aliquot to about 50 ml by evaporation.
3. Transfer the concentrate to a casserole and evaporate to dryness.
4. Decompose the ammonium salts by heating over an open flame.
5. Take up the residue with hot water.
6. Add 5–10 drops conc HCl.
7. Filter off any insoluble material through Whatman No. 42 paper.
8. Wash the insoluble material 3 times with hot water and combine the washings with the filtrate.
9. Dilute to approx 100 ml if necessary.
10. Heat the filtrate to boiling and add sufficient 5 percent H_2SO_4 to precipitate the barium and to provide a small excess.
11. Digest the precipitate overnight on a steam bath.
12. Quantitatively transfer the precipitate to Whatman No. 42 filter paper. The beaker should be scrubbed at least 3 times with a rubber policeman.
13. Wash the beaker and precipitate with hot water until a sample of the filtrate will develop no turbidity with $AgNO_3$.
14. Slowly ignite the precipitate in a tared porcelain crucible over a low, oxidizing flame until the filter paper is reduced to white ash.
15. Transfer the crucible to the muffle furnace and ignite at 800°C for 1 hr.
16. Cool the crucible in a desiccator and weigh.
17. After weighing, add 1 drop conc H_2SO_4. Fume off and reweigh. The weighings in steps 16 and 17 should be identical. A discrepancy indicates probable coprecipitation of chlorides, and the weight taken in step 17 should be used in the calculation.
18. If the purity of the $BaSO_4$ in respect to calcium and strontium is questionable, dissolve the precipitate completely in the crucible in 5 ml hot conc H_2SO_4. Cool and pour into 50 ml water and dilute to 100 ml. Digest for 1 hr on the steam bath, filter and wash with a little hot water, ignite, and weigh (Hillebrand and Lundell, 1929).

Calculations

$$\text{ppm } Ba^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } BaSO_4 \times 0.5884$$

Report barium concentrations of <10 ppm to 1 decimal place of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

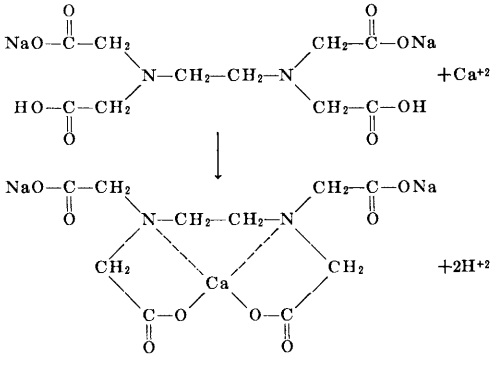
Sulfuric acid, 5 percent v/v: Mix 50 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 1 liter.

D:5a–2 COMPLEXOMETRIC METHOD

The complexometric method is applicable to most natural and treated waters whose barium content ranges from 0 to 10 ppm. The method fails conspicuously at times with acid or polluted waters that contain excessive amounts of heavy metals.

Principle of determination

Barium is determined by the difference between the titrant volume of disodium dihydrogen ethylenediamine tetraacetate (Na_2EDTA) required by an untreated sample and a sample from which barium has been precipitated as barium sulfate. Na_2EDTA forms a slightly ionized colorless stable complex with the alkaline earths. A solution of Eriochrome Black T dye is bright blue in the absence of alkaline earths but with them forms a deep red complex which has a higher ionization constant than the Na_2EDTA complex. Hence by using Eriochrome Black T as an indicator, the alkaline earths can be titrated with Na_2EDTA. For example, with calcium:



Barium titrates approximately stoichiometrically with calcium. The optimum pH for the reaction is 10.4 or higher.

The determination is not strictly quantitative because coprecipitation errors are involved in the precipitation of barium, especially in the presence of strontium. Interferences of heavy metals with the Na_2EDTA titration (see sec. D:17a–1) are not significant to the barium determination because their net effect may be assumed to be identical in both samples. Interference of heavy metals with detec-

tion of the end point, however, may cause an error in the determination of barium unless this interference is removed. Precision is improved if the end point is compared with a color blank of dilution water plus reagents.

Results obtainable are generally accurate and reproducible to ±0.1 mg in the 0–10 ppm range.

Apparatus and reagents

Titration assembly: Some analysts prefer to use conventional lighting and hand stirring. Others have reported better results by using a visual titration assembly consisting of motor-driven stirrer, 25-ml buret, white-porcelain-base buret holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from behind the beaker and in the plane of vision.

Photometric-titration assembly, optional (see sec. C: 2h)

Hydroxylamine hydrochloride, 3 percent

Ammonium hydroxide, conc (sp gr 0.900)

Sodium cyanide, 2.5 percent

Eriochrome Black T indicator solution

Na_2EDTA, 1.00 ml≏1.00 mg $CaCO_3$

Sulfuric acid, 5 percent v/v

Sodium sulfate, 10 percent

Procedure

1. Pipet a volume of sample containing less than 0.5 mg Ba^{+2} (50.00 ml max) into a 150-ml beaker and adjust the volume to approx 50 ml.
2. Insert the beaker in the titration assembly and start stirrer.
3. Add 1 ml 3 percent $NH_2OH \cdot HCl$.
4. Add 1 ml conc NH_4OH. (If NH_4OH not tightly stoppered it tends to lose strength; weak NH_4OH will not buffer the solution to the necessary pH.)
5. Add 2 ml 2.5 percent NaCN (*CAUTION*—deadly poison). NaCN may be eliminated unless the presence of interfering metals decreases the sharpness of the end point.
6. Add 2.0 ml Eriochrome Black T indicator.
7. Titrate with Na_2EDTA (1.00 ml≏1.00 mg $CaCo_3$) until blue or purple swirls begin to show. The end point is reached when all traces of red and purple have disappeared and the solution is clear blue in color. The detection of the end point may be facilitated by comparison of the titration solution with a color blank prepared of metal-free water and the reagents.
8. Record the titrant volume (ml_t) to the nearest 0.05 ml.
9. Measure approx 75 ml sample into a 150-ml beaker.
10. Add 1.5 ml 5 percent H_2SO_4.
11. Add 1.5 ml 10 percent Na_2SO_4.
12. Mix and allow the sample to stand several hours for the $BaSO_4$ to settle.
13. Pipet a volume of clear supernatant identical with that taken in step 1 and adjust the volume to approx 50 ml.
14. Treat the sample as directed in steps 2–8, with the exception of adding 2 ml NH_4OH in step 4. The additional NH_4OH is required to neutralize the acid added in step 10.

Calculations

$$\text{ppm } Ba^{+2} = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml sample}} \times \left[ml_t - \left(\frac{ml_{Ba}}{0.96} \right) \right] \times 1.37$$

where ml_t = titrant volume for the first titration and
ml_{Ba} = titrant volume after barium is removed.

Report barium concentrations of <10 ppm to 0.1 ppm, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Hydroxylamine hydrochloride, 3 percent: Dissolve 30 g $NH_2OH \cdot HCl$ in metal-free water and dilute to approx 1 liter.

Sodium cyanide, 2.5 percent (*CAUTION*—NaCN is a deadly poison and the reagent solution must be so marked): Dissolve 2.5 g NaCN in metal-free water and dilute to approx 100 ml.

Eriochrome Black T indicator solution: Dissolve 0.40 g Eriochrome Black T in 100 ml metal-free water and dilute to approx 1 liter with 95 percent ethyl alcohol. This indicator is stable for at least 2 months. The Eastman reagent product has been found to be satisfactory.

Na_2EDTA, 1.00 ml≏1.00 mg $CaCO_3$: Dissolve 3.720 g Na_2EDTA, which has been dried overnight in an H_2SO_4 desiccator, in metal-free water and dilute to 1,000 ml. Check the titer of the reagent by titrating 25.00 ml $CaCl_2$ (1.00 ml≏1.00 mg $CaCO_3$) as described in the procedure for sample analysis. This Na_2EDTA solution is identical to that used in the hardness determination (Sec. D: 17a–1)

Calcium chloride, 1.00 ml≏1.00 mg $CaCO_3$: Suspend 1.000 g $CaCO_3$, dried at 180°C for 1.0 hr before weighing, in approx 600 ml metal-free water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 ml.

Sulfuric acid, 5 percent v/v: Mix 5 ml conc H_2SO_4 (sp gr 1.84) with metal-freee water and dilute to approx 100 ml.

Sodium sulfate, 10 percent: Dissolve 10 g Na_2SO_4 in metal-free water and dilute to approx 100 ml.

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D:6 BORON

The boron content in most surface waters seldom exceeds 1 ppm, but some ground waters, particularly those affected by igneous rocks, may contain appreciably more boron. The form or forms in which boron exists in natural waters is not known with certainty and may not be uniform for all waters; hence, the boron content is reported as elemental boron.

In normal concentrations, boron in drinking water is not regarded as a hazard to humans, but the boron content of water to be used for irrigation is highly important. Boron is an essential plant nutrient, but the presence of as little as 1 ppm has been known to injure citrus trees and walnut and bean crops, while waters containing more than 2 ppm will in time cause trouble with many common crops (U.S. Salinity Laboratory Staff, 1954, p. 81).

D:6a-1 DIANTHRIMIDE METHOD

The dianthrimide method is susceptible to high concentrations of oxidizing or reducing material and dissolved organic matter but is not affected by buffering solutions or high concentrations of total salts. It is satisfactory for most natural waters.

Principle of determination

Boron when heated with 1,1′-dianthrimide in concentrated sulfuric acid gives a colored complex (Ellis, Zook, and Baudisch, 1949, p. 1345–1348). The color change ranges from greenish-yellow to blue. The reaction producing the blue color depends on the nature of the vessel in which the reaction occurs, the temperature and duration of heating, and the concentration of reagent and of boron. In platinum vessels, the reagent is unstable and darkens with no blue-color formation. Maximum color development is obtained after the reaction has proceeded for 3 hours at 90°C.

Traces of moisture precipitate the reagent and interfere in the determination; therefore, precautionary measures given in the procedure must be followed explicitly. Nitrate and bicarbonate interfere with color development unless removed. Removal as nitric acid and carbon dioxide by evaporation of the sample in the presence of sulfuric acid is employed. Organic matter in high concentrations chars and causes a discoloration of the complex, but this interference is easily recognized; small quantities of organic material cause no trouble. Some success in removal of the organic-material interference has been obtained by heating the sample in the presence of hydrogen peroxide for 1–2 hours, but it is essential that all nascent oxygen be volatilized before the dianthrimide is added to the sample.

When peroxide digestion is used, the final color complex should be compared with standard boron solutions similarly treated. Oxidizing and reducing constituents also interfere. In cleaning glassware avoid the use of chromic-sulfuric acid.

Some boric acid is probably volatilized during the evaporation of the sample in the presence of sulfuric acid. Prolonged heating, or temperatures higher than that recommended, volatilize an excessive amount of boron and decrease the sensitivity of the test. The loss of boron is proportional to the boron content of the sample or standard, hence such loss in no way affects the linearity of the color development if the heating is uniform. Nonlinearity of the concentration-versus-absorbancy curve can result from weak reagents. The two standards in step 2 of the procedure act as a check on linearity of the reaction and suitability of the working reagent.

With the listed apparatus, results are generally accurate and reproducible to ± 0.0001 mg.

Apparatus and reagents

Oven, 90°C: Uniformity of temperature throughout the oven is imperative. Fisher Isotemp ovens have been found to be satisfactory.

Stoppers to fit absorption cells: Teflon or polyethylene are satisfactory, rubber can be used with caution, glass-stoppered cells are preferable.

Spectrophotometer, Beckman Model B:

Wavelength: 620 mμ
Cells: 23-mm or 25-mm optical depth
Phototube: Blue-sensitive
Blank: Dilution water carried through the procedure with the sample
Initial sensitivity setting: 2
Slit width: 0.6 mm (approx)
The following absorbancies have been observed:

mg B	*Absorbancy*
0.001	0.26
.002	.52
.005	1.30

Sodium tetraborate, 1.00 ml=0.001 mg B.

Sulfuric acid, conc (sp gr 1.84)

1,1′-dianthrimide, working reagent

Procedure

1. Pipet a volume of sample containing less than 0.005 mg B (5.00 ml max) into the absorption cell and adjust volume to 5.0 ml.
2. Prepare a blank of redistilled water and sufficient standards and adjust volumes to 5.0 ml.
3. Add 1.0 ml conc H_2SO_4 and mix by swirling the contents of the cell.
4. Evaporate overnight in an oven at 90°C. At the end of the evaporation, the solution volume should be between 1.0 and 0.5 ml.
5. Add 5.0 ml dianthrimide working reagent, and mix by swirling the contents of the cell.

6. Incubate for 3.0 hr at 90°C.
7. Cool and immediately dilute with 10.0 ml conc H_2SO_4.
8. Mix thoroughly but carefully with a stirring rod. The contents must not be spattered on the upper walls of the cell.
9. Stopper the cells but do not let the stopper come in contact with the acid contents.
10. Remove all traces of acid, reagent, and fingerprints from the exterior surface of the cell.
11. Determine the absorbancy of the sample and standards against the blank.

Calculations

1. Determine the mg B in the sample from a plot of absorbancies of standards containing known amounts of the constituent.

2. $\text{ppm B} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg B in sample}$

Report boron concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Sodium tetraborate, 1.00 ml=0.001 mg B: Dilute 10.00 ml $Na_2B_4O_7$ (1.00 ml=0.100 mg B) to 1,000 ml with redistilled water. Store in a plastic bottle.

Sodium tetraborate, 1.00 ml=0.100 mg B: Dissolve approx 10 g $Na_2B_4O_7 \cdot 10H_2O$ in redistilled water at 50°–60°C. Recrystallize by placing in refrigerator for several hours. Dry by removing the water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8813 g in redistilled water and dilute to 1,000 ml. Store in plastic bottle.

1,1′-dianthrimide, working reagent: Dilute 1 volume of stock reagent to 20 volumes with conc H_2SO_4 (sp gr 1.84). The reagent is stable for long periods of time if the container is sealed with sealing wax and is kept in a refrigerator.

1,1′-dianthrimide, stock reagent: Dissolve 200 mg in 50 ml conc H_2SO_4 (sp gr 1.84). The reagent is stable for long periods if the container is sealed with sealing wax and is kept in a refrigerator.

D:6a–2 POTENTIOMETRIC METHOD

The potentiometric method is similar in substance to part IB, APHA (1955, p. 46–49) Standard Methods, and method 73a, U.S. Salinity Laboratory Staff (1954, p. 140–141) Handbook 60.

The method is susceptible to buffering agents and high concentrations of dissolved minerals but is not particularly affected by the presence of organic material.

Principle of determination

Boric acid with an ionization constant of 5.5×10^{-10} cannot be titrated directly with base. However, certain polyhydroxy organic compounds, such as mannitol, form complex acids with boric acid that are much stronger than boric acid itself. The quantity of alkali required to titrate the complex acid back to the initial pH of the boric acid is a

measure of the boron present (Foote, 1932). The following reactions are involved:

$$C_6H_{14}O_6 + H_3BO_3 \rightarrow C_6H_{12}O_4 \cdot BO_3H + 2H_2O$$
$$C_6H_{12}O_4 \cdot BO_3H + NaOH \rightarrow C_6H_{12}O \cdot \cdot BO_3Na + H_2O$$

The pH of the water is adjusted to 7.00 with sulfuric acid and (or) sodium hydroxide, and mannitol is then added. The liberated hydrogen ion is backtitrated to 7.00 pH with standard sodium hydroxide (Wilcox and Hatcher, 1947). The pH meter with glass electrode is used.

The method is particularly susceptible to the effects of buffering systems. The water is freed of carbon dioxide by acidification and boiling. Iron, aluminum, and probably most of the weak ions that tend to buffer the solution interfere to some extent unless removed. Phosphate reacts with mannitol, though not quantitatively. The reliability of the results generally decreases in proportion to the total concentration of the dissolved material.

With careful treatment, results with dilute alkaline waters and in the absence of buffering action may be accurate and reproducible to ±0.005 mg but are appreciably less with most natural waters. Results are not reliable with acid waters that contain hydrolyzable salts.

Apparatus and reagents

Water bath for cooling
pH meter
Electric stirrer: The stirrer should adequately mix the solution but should not aerate it excessively. Magnet-type stirrers are recommended.
Buret, 10–ml
Methyl orange indicator
Sulfuric acid 1*N*
Sodium hydroxide, 0.5*N*, carbonate-free
Sulfuric acid, 0.02*N*
Mannitol
Sodium hydroxide, 0.0231*N*, 1.00 ml=0.25 mg B

Procedure

1. Measure a volume of sample containing less than 1 mg B (250 ml max) into a 600–ml beaker and adjust the volume to 250 ml.
2. Add 2–3 drops methyl orange.
3. Acidify with 1*N* H_2SO_4.
4. Bring to boil and stir cautiously for 3 or 4 min, then vigorously for 1 min to expel CO_2. If the sample reverts to the alkaline color during the boiling period, adjust the pH with 1*N* H_2SO_4 to the acid color.
5. Cover the Sample with a watch glass and rapidly cool to room temperature in a water bath. The cooling should not require more than 30 min.
6. Insert the beaker in the titration apparatus and start the stirrer.
7. Adjust the pH to 7.00 with 0.5*N* NaOH, 0.002*N* H_2SO_4, and 0.0231*N* NaOH. The indicator needle of the pH meter should be steady and not drift from the reading of pH 7.00.

8. Record the buret reading to 0.01 ml.
9. Add approximately 5 g mannitol. If boron in the form of boric acid is present, the pH will drop to some value below 7.00.
10. Titrate rapidly back to the initial pH of 7.00 with 0.0231*N* NaOH. Use caution near the end point to permit a slight lag in the pH-meter response.
11. When the indicator needle remains steady at pH 7.00 for at least 10 sec, record the volume of NaOH used to the nearest 0.01 ml.
12. Determine a blank correction for the reagents by carrying 250 ml carbon dioxide-free water through the complete procedure. The normal blank is 0.06 ± 0.01 ml.

Calculations

$$\text{ppm B} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times [f(\text{ml NaOH} - \text{ml blank})] \times 0.25$$

where f = factor for 0.0231*N* NaOH.

Report boron concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Methyl orange indicator: Dissolve 0.05 g methyl orange in water and dilute to approx 100 ml.

Sulfuric acid, 0.02*N*: Dilute 20 ml 1*N* H_2SO_4 to approx 1 liter.

Sulfuric acid, 1*N*: Mix 28 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 1 liter.

Sodium hydroxide, 0.5*N*, carbonate-free: Prepare a saturated solution of NaOH in alkali-resistant flask (Corning No. 728). Stopper and let stand until the Na_2CO_3 precipitates. Titrate a portion of supernatant liquid with 1*N* H_2SO_4 and dilute to proper strength with carbon dioxide-free water. Store the solution in a stoppered polyethylene bottle.

Sodium hydroxide, 0.0231*N*, 1.00 ml≈0.25 mg B: Dilute 46 ml 0.5*N* NaOH to 950 ml with carbon dioxide-free water. Standardize by titrating solutions containing 0.25, 0.50, and 1.00 mg B which have been carried through the complete procedure for the determination of boron. Despite the usual precautions, the normality of this dilute base is not very stable and a factor should be computed every 2 or 3 weeks. Use the following equation to calculate the factor (f) for the 0.0231*N* NaOH:

$$f = \frac{\text{ml theoretical titration}}{\text{ml actual titration} - \text{ml blank}}$$

The normal blank is 0.06±0.01 ml. Accepted f values are 0.9–1.1. Protect the solution from carbon dioxide by means of a soda lime tube.

Sodium tetraborate, 1.00 ml = 0.010 mg B: Dilute 100.0 ml $Na_2B_4O_7$ (1.00 ml = 0.100 mg B) to 1,000 ml with redistilled water. Store in plastic bottle.

Sodium tetraborate, 1.00 ml=0.100 mg B: Dissolve approx 10 g $Na_2B_4O_7 \cdot 10H_2O$ in redistilled water at 50°–60°C. Recrystallize by placing in refrigerator for several hours. Dry by removing the water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8813 g in redistilled water and dilute to 1,000 ml. Store in plastic bottle.

D:6a–3 CARMINE METHOD

The carmine method is similar in substance to part IA, APHA (1955, p. 45–46) Standard Methods, and method 73b, U.S. Salinity Laboratory Staff (1954, p. 142) Handbook 60.

The method finds maximum utility for waters whose boron content exceeds 1 ppm or when the precision required does not exceed 0.1 ppm.

Principle of determination

In acid solution, boron forms a colored complex with carmine. The color change is from red to blue. Maximum color development requires approximately 1 hr, but the color intensity decreases thereafter. The fading is proportional to the boron content and is therefore not consequential if standards are run simultaneously with the sample. Special attention must be given to the time element because the fading is rather rapid, approx 25 percent or more reduction in intensity between 1.0 and 2.0 hr. The optimum range for the procedure on undiluted or unconcentrated samples is 0.5–10 ppm of boron. Samples containing less than 0.5 ppm must be concentrated by special evaporation. The concentration is carried out in strong alkaline solution to prevent the loss of volatile boric acid.

Ammonium, molybdenum, cerium, chloride, calcium, magnesium, sodium, and potassium are reported not to interfere. Strong ammonia fumes affect the reagent. Silica interferes, but the interference is independent of the silica concentration and dependent on the boron concentration. With 0.5 ppm of boron the determined value may be about 20 percent high in the presence of 5 or 30 ppm of silica. At lower boron levels the effect is variable. Fluoride, nitrate, and phosphate contribute some interference but to a lesser degree.

With the listed apparatus, results are reproducible to ± 0.0005 mg in the 0.002- to 0.020-mg range. Accuracy is dependent on effect of interfering substances.

Additional information on the principle of determination is given by Hatcher and Wilcox (1950).

Apparatus and reagents

Steam bath

Spectrophotometer, Beckman Model B:

Wavelength: 600 mμ
Cells: 25-mm optical depth
Phototube: Blue-sensitive
Blank: Dilution water carried through the procedure with the sample

Initial sensitivity setting: 2
Slit width: 0.1 mm (approx)
The following absorbancies have been observed:

mg B	*Absorbancy*
0.005	0.24
.010	.48
.015	.70
.020	.93

Sodium tetraborate, 1.00 ml=0.010 mg B
Sodium hydroxide, 2 percent
Hydrochloric acid, 5 percent v/v
Hydrochloric acid, conc (sp gr 1.19)
Sulfuric acid, conc (sp gr 1.84)
Carmine solution, 0.05 percent

Procedure

1. Pipet a volume of sample containing between 0.001 and 0.020 mg B (2.00 ml max) into a 150-ml flask. If the sample contains less than 0.5 ppm B, take a 2.00-ml aliquot of sample concentrated as follows:
   a. Pipet an accurately measured volume of sample (100 ml max) into an evaporating dish.
   b. Add 1 ml 2 percent NaOH.
   c. Evaporate on a steam bath to dryness.
   d. Take up the residue, triturate in 5.00 ml 5 percent HCl with a rubber policeman, and centrifuge to obtain a clear solution.
2. Prepare a blank and sufficient standard and adjust volume to 2.0 ml.
3. Add 2 drops conc HCl.
4. Add 12 ml conc H_2SO_4, mix, and allow to cool for at least 30 min.
5. Add 10 ml 0.05 percent carmine solution and mix.
6. Allow the solution to stand approx 1 hr.
7. Determine the absorbancies of the sample and standards against the blank and when necessary make corrections for water color as directed in sec. C: 1a–2, method 1.

Calculations

1. Determine the mg B in the sample from a plot of absorbancies of standards containing known amounts of the constituent.

2. $$\text{ppm B} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg B in sample}$$

Report boron concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Sodium hydroxide, 2 percent: Dissolve 2 g NaOH in water and dilute to approx 100 ml.

Hydrochloric acid, 5 percent v/v: Mix 50 ml conc HCl (sp gr 1.19) with water and dilute to approx 1 liter.

Sodium tetraborate, 1.00 ml=0.010 mg B: Dilute 100.0 ml $Na_2B_4O_7$ (1.00 ml=0.100 mg B) to 1,000 ml with redistilled water. Store in plastic bottle.

Sodium tetraborate, 1.00 ml=0.100 mg B: Dissolve approx 10 g $Na_2B_4O_7 \cdot 10H_2O$ in redistilled water at 50°–60°C. Recrystallize by placing in a refrigerator for several hours. Dry by removing water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8813 g in redistilled water and dilute to 1,000 ml. Store in plastic bottle.

Carmine solution, 0.05 percent: Suspend 0.50 g carmine in 1,000 ml conc H_2SO_4 and mix with a mechanical stirrer until solution is complete. The stain certified by the Biological Stain Commission has been used satisfactorily.

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D:7 BROMIDE

Bromide is a very minor element in the earth's crust and is normally present in natural waters in only minute quantities. Measurable amounts may be found in some streams that receive industrial wastes, and some natural brines may contain rather high concentrations.

D:7a-1 OXIDATION METHOD

The oxidation method is similar in substance to D 1246–53 T, ASTM (1954, p. 260–263) Manual on Industrial Water.

Principle of determination

The determination of bromide involves the determination of bromide and iodide collectively and then the determination of iodide alone; bromide is calculated by difference. Bromide and iodide are oxidized to bromate and iodate, respectively, by hypochlorite, and the excess hypochlorite is subsequently decomposed with sodium formate (Kolthoff and Sandell, 1952, p. 585–605).

$$3\ OCl^{-1}+Br^{-1}\rightarrow BrO_3^{-1}+3Cl^{-1}$$
$$3\ OCl^{-1}+I^{-1}\rightarrow IO_3^{-1}+3Cl^{-1}$$

Iodine equivalent to the combined iodate and bromate is then liberated by addition of potassium iodide to an acid solution.

$$BrO_3^{-1}+6I^{-1}+6H^{+1}\rightarrow 3I_2+3H_2O+Br^{-1}$$
$$IO_3^{-1}+5I^{-1}+6H^{+1}\rightarrow 3I_2+3H_2O$$

The liberated iodine is then titrated with standard thiosulfate using starch as the indicator.

$$I_2+2S_2O_3^{-2}\rightarrow S_4O_6^{-2}+2I^{-1}$$

Iodide alone is determined by oxidation to iodate with bromine in a buffered solution. Iodine equivalent to the iodate is then liberated from added potassium iodide and titrated with thiosulfate as in the combined determination.

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interferences are removed by preliminary treatment with calcium oxide.

Results are accurate and reproducible to ± 0.05 mg.

Apparatus and reagents

Iodine flasks, 250-ml
Buret, 10-ml
Calcium oxide, anhydrous powder
Sodium chloride, crystals
Methyl red indicator solution, 0.01 percent
Hydrochloric acid, 50 percent v/v

Potassium hypochlorite, 4.4 percent
Calcium carbonate, powder
Sodium formate, 50 percent
Sodium molybdate, 0.85 percent
Potassium fluoride, crystals
Potassium iodide, crystals
Sulfuric acid, 20 percent v/v
Sodium thiosulfate solution, 0.010*N*
Starch indicator, stable
Sodium acetate solution, 16.5 percent
Acetic acid, 12.5 percent v/v
Bromine water, saturated

Procedure

1. Remove soluble iron manganese, and organic matter by adding a slight excess of CaO to approx 400 ml of sample, shake, let stand about 1 hr, and filter through dry paper. Discard the first 75 ml of filtrate.
2. For the combined Br^{-1} and I^{-1} determination pipet a volume of the filtrate containing less than 5.0 mg Br^{-1} and I^{-1} (100.0 ml max) into a 250-ml iodine flask and adjust the volume to approx 100 ml.
3. Prepare a blank of approx 100 ml water and carry it through the procedure with the sample.
4. Add sufficient NaCl to produce a 3.0-g Cl^{-1} content in the sample.
5. Add a drop of 0.01 percent methyl red indicator, and neutralize the solution with 50 percent HCl.
6. Add 10 ml 4.4 percent KClO.
7. Add 0.5 ml 50 percent HCl.
8. Add sufficient $CaCO_3$ to produce an excess of approx 0.1 g.
9. Heat the solution to boiling and maintain this temperature for about 8 min.
10. Reduce the excess KClO by adding 2 ml 50 percent $NaCHO_2$, taking precautions to wash down the sides of the flask with a small amount of hot water. Keep the solution hot for an additional 8 min.
11. Cool and add several drops of 0.85 percent Na_2MoO_4.
12. If any iron precipitates at this point, add 0.5 g $KF \cdot 2H_2O$.
13. Add approx 1 g KI.
14. Add 10 ml 20 percent H_2SO_4.
15. Let stand 5 min in the dark.
16. Titrate the liberated I_2 with 0.010*N* $Na_2S_2O_3$, adding 2–3 ml starch indicator as the end point is approached. Disregard the return of the blue color after the end point has been reached.
17. For the I^{-1} determination, pipet a volume of filtrate (step 1) containing less than 5.0 mg I^{-1} (100.0 ml max) into a 250-ml iodine flask and adjust the volume to approx 100 ml.
18. Prepare a blank of 100.0 ml water and carry through the procedure with the sample.
19. Add a drop of 0.01 percent methyl red indicator and make the solution just acid with 20 percent H_2SO_4.
20. Add 15.0 ml 16.5 percent $NaC_2H_3O_2$.
21. Add 5.0 ml 12.5 percent $HC_2H_3O_2$.
22. Add sufficient bromine water to produce a light-yellow color, mix, and allow to stand 5 min.

23. Reduce the excess Br_2 by adding 50 percent $NaCHO_2$ until the yellow tinge in the sample disappears, then add an excess of 1 ml.
24. Wash down the sides of the flask with a small amount of water and blow out Br_2 vapors with a syringe and a glass tube inserted through the mouth of the flask.
25. If any iron precipitates at this point, add 0.5 g $KF \cdot 2H_2O$.
26. Add approx 1 g KI.
27. Add 10 ml 20 percent H_2SO_4.
28. Let stand 5 min in the dark.
29. Titrate the liberated I_2 with 0.010*N* $Na_2S_2O_3$, adding 2–3 ml starch indicator as the end point is approached. Disregard the return of the blue color after the end point has been reached.

Calculations

1. $\text{epl } Br^{-1}+I^{-1}=\frac{1{,}000}{\text{ml sample}}\times\frac{0.01}{6}\times(\text{ml}_t-\text{ml blank})$
2. $\text{epl } I^{-1}=\frac{1{,}000}{\text{ml sample}}\times\frac{0.01}{6}\times(\text{ml}_{I^{-1}}-\text{ml blank})$
3. $\text{ppm } Br^{-1}=\frac{1}{\text{density}}\times 79.916\times[\text{epl}(I^{-1}+Br^{-1})-\text{epl } I^{-1}]$

where epl=equivalents per liter,
ml_t=titrant volume for combined determination,
$\text{ml}_{I^{-1}}$=titrant volume for I^{-1} determination.

Report bromide concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Sodium chloride crystals: In addition to conforming to American Chemical Society specifications, these shall also be free from I^{-1}, IO_3^{-1}, Br^{-1}, and BrO_3^{-1}. The NaCl can be tested for IO_3^{-1} and BrO_3^{-1} by dissolving about 0.1 g in 5 ml water, acidifying with 1 or 2 drops conc H_2SO_4 (sp gr 1.84), and adding 2–3 ml starch solution. Immediate appearance of blue color indicates presence of IO_3^{-1} or BrO_3^{-1}, slow color formation is caused by atmospheric oxidation.

Methyl red indicator, 0.01 percent: Dissolve 0.01 g water-soluble methyl red in approx 100 ml water.

Hydrochloric acid, 50 percent v/v: Mix 50 ml conc HCl (sp gr 1.19) with water and dilute to approx 100 ml.

Potassium hypochlorite, 4.4 percent: Dissolve 6.2 g KOH in approx 100 ml water, then saturate the solution with bromine-free Cl_2 while continually cooling and stirring. Store in glass-stoppered actinic-glass bottle. Prepare fresh daily.

Sodium formate, 50 percent: Dissolve 50 g $NaCHO_2$ in hot water and dilute to approx 100 ml. Prepare fresh daily.

Sodium molybdate, 0.85 percent: Dissolve 1.0 g $Na_2MoO_4 \cdot 2H_2O$ in water and dilute to approx 100 ml.

Potassium fluoride crystals, $KF \cdot 2H_2O$.

Potassium iodide crystals, IO_3^{-1}-free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 ml water, acidifying with 1 or 2 drops conc H_2SO_4, and adding 2–3 ml starch indicator. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

Sulfuric acid, 20 percent v/v: Mix 200 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 1 liter.

Sodium thiosulfate solution, 0.010*N*: Dilute 100.0 ml 0.1*N* $Na_2S_2O_3$ to 950 ml with carbon dioxide-free water and standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 hr at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 ml. Pipet 25.00 ml of the KIO_3 into a 250-ml iodine flask, then add successively 75 ml water and 0.5 g KI crystals. After solution is complete add 10 ml 20 percent H_2SO_4. Allow the stoppered flask to stand 5 min in the dark, then titrate with $Na_2S_2O_3$ using 2 ml starch indicator as the end point is approached (light straw color).

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{ml } Na_2S_2O_3}$$

Sodium thiosulfate, 0.1*N*: Dissolve 25.0 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water, add 1 g Na_2CO_3, and dilute to 1,000 ml.

Sodium acetate solution, 16.5 percent: Dissolve 273.5 g $NaC_2H_3O_2 \cdot 3H_2O$ in water and dilute to 1,000 ml.

Acetic acid, 12.5 percent v/v: Mix 125 ml glacial $HC_2H_3O_2$ (sp gr 1.049) with water and dilute to 1,000 ml.

Bromine water, saturated: Add to approx 250 ml of water slightly more liquid Br_2 than will dissolve when shaken. Store in a glass-stoppered actinic-glass bottle.

D:7a–2 BROMINE DISPLACEMENT METHOD

The bromine-displacement method is only semiquantitative and finds maximum utility as a screening or field test.

Principle of determination

Chlorine water oxidizes the bromide to elemental bromine, which is concentrated and extracted with carbon disulfide or carbon tetrachloride (ASTM, 1954, p. 93).

$$2Br^{-1} + Cl_2 \rightarrow Br_2 + 2Cl^{-1}$$

The amount of color developed in the globule of carbon disulfide (or tetrachloride) depends on the relation between the amount of chlorine water added and the amount of bromide present. For each concentration of bromide, there is an optimum amount of chlorine water that develops the deepest color. Therefore, to develop the deepest color in the unknown, it is necessary to add the chlorine water stepwise, 0.10 ml at a time, until the maximum color in the samples has been developed. The point of maximum color development is best detected if duplicate sets of unknowns and standards are prepared and one set is kept one step behind the other.

Apparatus and reagents

Potassium bromide solution, 1.0 ml=1.0 mg Br^{-1}
Carbon disulfide or carbon tetrachloride
Chlorine water

Procedure

1. Measure 10 ml of the sample into a test tube.
2. Prepare stepwise standards containing, in a 10.0-ml volume, from 0.5–4.0 mg of Br^{-1} as KBr (1.00 ml KBr solution=1.00 mg Br^{-1}), in increments of 0.5 mg.
3. Add 1.0 ml CS_2 or CCl_4 and 1 ml chlorine water to liberate the bromine.
4. Shake well.
5. After 15 min compare the color of the globule of CS_2 or CCl_4 with that of the globules in standards.

Calculations

$$\text{ppm } Br^{-1} = \frac{1{,}000}{\text{ml sample}} \times 1.0 \times \text{ml standard}$$

Preparation of reagents

Chlorine water: Saturate a small volume of water with Cl_2.
Potassium bromide solution, 1.0 ml=1.0 mg Br^{-1}: Dissolve 1.49 g KBr in water and dilute to 1,000 ml.

REFERENCES

American Society for Testing Materials, 1954, Manual on industrial water: Spec. Tech. Pub. 148–A.
Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis: New York, MacMillan Co.

D:8 CALCIUM

Calcium is dissolved from practically all rocks but is usually found in greater quantities in waters leaching deposits of limestone, dolomite, gypsum, or gypsiferous shale. Waters associated with granite or silicious sand may contain less than 10 ppm of calcium. Many waters from limestone areas contain 30 to 100 ppm, and waters that traverse gypsiferous shale may contain several hundred ppm.

Calcium imparts the property of hardness to water and when present with alkalinity or sulfate may cause boiler scale. A little calcium carbonate is desirable in water used domestically because of the protective coating that it may form in the pipes. A high ratio of calcium to sodium is desirable in water used for irrigation because calcium flocculates the soil colloids and tends to maintain good soil structure and permeability.

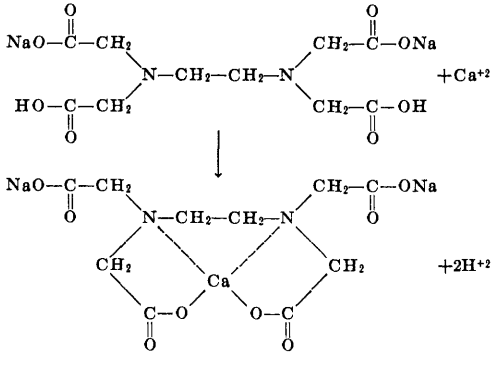
D:8a-1 COMPLEXOMETRIC METHOD

The complexometric method is similar in substance to part IC.4, APHA (1955, p. 118) Standard Methods; D 1126–53 T, ASTM (1954, p. 254) Manual on Industrial Water; and method 7, U.S. Salinity Laboratory Staff (1954, p. 94) Handbook 60.

The method is applicable to most natural waters but may fail in the analysis of brines or some acid or polluted waters that contain excessive amounts of heavy metals.

Principle of determination

Disodium dihydrogen ethylenediamine tetraacetate (Na_2EDTA) forms a slightly ionized, colorless, stable complex with calcium ions. Murexide is dark purple in the absence of calcium, but with calcium forms a light-salmon-colored complex which has an ionization constant higher than the Na_2EDTA complex. Hence, by using murexide as an indicator, a solution containing calcium ions may



be titrated with Na_2EDTA. The optimum pH of the titration is 10.4 or above.

The salt, Na_2EDTA, reacts with iron, manganese, copper, zinc, lead, cobalt, nickel, barium, strontium, calcium, magnesium, and several other metals. Murexide reacts with strontium but not with magnesium or barium; however, the end point in the presence of strontium is sluggish, and the titration is not strictly stoichiometric. Barium does not titrate as calcium but affects the indicator in some unknown way so that no end point, or at best a poor end point is obtained. Barium can be removed by prior precipitation with sulfuric acid. The interference of heavy metals is minimized by the addition of hydroxylamine and cyanide, which reduce and (or) complex the metals. Concentrations of 5 ppm of iron and 10 ppm of manganese can be tolerated.

The interference of heavy metals is relatively easy to detect because of the typical end point. Conventional methods of hydroxide and sulfide treatment can be used, if necessary, to remove these metals from solution before titration. Magnesium in high concentrations may precipitate as magnesium hydroxide, but the precipitation is not significant unless the photometric-titration assembly is used to determine the end point.

The results are generally accurate and reproducible to ± 0.025 mg in the 1-mg range and to ± 0.05 mg in higher concentrations.

Additional information on the principle of determination is given by Banks (1952, p. 484).

Apparatus and reagents

Visual titration apparatus consisting of a motor-driven stirrer, 25-ml buret, white-porcelain-base buret holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from the side and at about 90° from the line of vision.

Photometric-titration assembly, optional (see sec. C: 2h)

Buret, 25-ml

Hydroxylamine hydrochloride, 3 percent

Sodium hydroxide, 2*N*

Sodium cyanide, 2.5 percent

Murexide, dry mixture

Na_2EDTA, 1.00 ml=0.50 mg Ca^{+2}

Procedure

1. Pipet a volume of sample containing less than 10 mg Ca^{+2} (50.0 ml max.) into a 150-ml beaker and adjust the volume to approx 50 ml.
2. Insert beaker in titration assembly and start stirrer.
3. Add 1 ml 3 percent $NH_2OH \cdot HCl$.
4. Add 1 ml 2*N* NaOH.

5. Add 1 ml 2.5 percent NaCN (*CAUTION*—deadly poison).
6. Add 0.2 g murexide indicator and proceed immediately with the titration.
7. Titrate with Na_2EDTA (1.00 ml≏0.50 mg Ca^{+2}) until purple swirls begin to show. The end point is reached when the sample color changes from salmon to orchid purple. At the end point, the addition of a small increment of titrant will not cause a deepening of the purple color.
8. Determine a blank correction by similarly treating 50 ml metal-free water. The normal blank correction is 0.05 or 0.10 ml.

Calculations

$$\text{ppm } Ca^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times (\text{ml titrant} - \text{ml blank}) \times 0.5$$

Report calcium concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Hydroxylamine hydrochloride, 3 percent: Dissolve 30 g $NH_2OH \cdot HCl$ in metal-free water and dilute to approx 1 liter.

Sodium hydroxide, 2*N:* Dissolve 80 g NaOH in 800 ml water. Cool and dilute to approx 1 liter.

Sodium cyanide, 2.5 percent (*CAUTION*—NaCN is a deadly poison and the reagent must be so marked.) Dissolve 25 g NaCN in water and dilute to approx 1 liter.

Murexide, dry mixture: Mix thoroughly 1.0 g ammonium purpurate with 200 g sucrose. Eastman reagent-grade product has been found to be satisfactory. Provide the bottle with a dispensing spoon of 0.2-g capacity.

Na_2EDTA, 1.00 ml≏0.50 mg Ca^{+2}: Dissolve 4.65 g Na_2EDTA, which has been dried overnight in an H_2SO_4 desiccator, in metal-free water and dilute to 1,000 ml. (The titrant is stable for several months and is usually prepared in larger quantities.) Standardize the titrant by titrating 25.00-ml $CaCl_2$ solutions (1.00 ml=0.40 mg Ca^{+2}) as described in the procedure for sample analysis.

Calcium chloride, 1.00 ml=0.40 mg Ca^{+2}: Suspend 1.000 g $CaCo_3$, dried at 180°C for 1.0 hr before weighing, in approx 600 ml metal-free water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 ml.

D:8a–2 PERMANGANIMETRIC METHOD

The permanganimetric method is similiar in substance to part IB, APHA (1955, p. 51–52) Standard Methods.

Principle of determination

Calcium is precipitated as the oxalate; the calcium oxalate is then dissolved and titrated in acid media with a standard solution of potassium permanganate. The following reactions are involved:

$$Ca^{+2} + C_2O_4^{-2} \rightarrow CaC_2O_4$$
$$5C_2O_4^{-2} + 2MnO_4^{-1} + 16H^{+1} \rightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

The presence of magnesium increases the solubility of calcium oxalate appreciably, as a consequence of the formation of a complex mag-

nesium oxalate which withdraws oxalate ions. The effect may be counteracted by the addition of a large excess of oxalate. Heavy metals interfere unless removed by hydroxide and (or) sulfide precipitation (see sec. D:8a–3). Barium and strontium also form insoluble oxalates. Calcium can be separated from small quantities of barium (3–4 mg or more) by double precipitation, but strontium interference cannot be eliminated in this manner. Precipitation of calcium oxalate from acid solution followed by hot digestion minimizes the effects of most coprecipitation and provides a precipitate of nearly theoretical composition.

The first few drops of permanganate react slowly with oxalic acid, but after a small amount of manganous salt has been formed the reaction proceeds almost instantaneously. If the water is low in calcium the initial increments of permanganate should be added with care to prevent overshooting the end point. In hot acid solutions permanganate is slowly decomposed with the evolution of oxygen; therefore, too rapid titration with insufficient stirring may cause an error. In addition, the permanganate tint at the end point can be expected to fade in time.

Results are generally accurate and reproducible to ± 0.1 mg.

Apparatus and reagents

Steam bath
Hotplate
Buret, 50-ml
Methyl orange indicator solution, 0.05 percent
Hydrochloric acid, conc (sp gr 1.19)
Ammonium oxalate, 5 percent
Ammonium hydroxide, conc (sp gr 0.900)
Ammonium hydroxide, 1 percent v/v
Sulfuric acid, 25 percent v/v
Potassium permanganate, 0.0499*N*, 1.00 ml≏1.00 mg Ca

Procedure

1. Pipet a volume of sample containing less than 40 mg Ca (100.0 ml max) into a 250-ml beaker and adjust the volume to approx 100 ml.
2. Acidify to methyl orange with conc HCl.
3. Heat the solution nearly to boiling. While hot, add 10 ml 5 percent $(NH_4)_2C_2O_4$ slowly and with constant stirring.
4. Add conc NH_4OH with constant stirring until CaC_2O_4 begins to precipitate. Do not make the solution alkaline at this point.
5. While the mixture is still acid to methyl orange, digest for 0.5 hr on a steam bath.
6. Slowly add conc NH_4OH to make the solution just alkaline to methyl orange and then 2–5 drops in excess.
7. Allow the precipitate to digest on the steam bath for another 2 hr.

8. By decantation rinse the beaker and precipitate at least 4 times with 5- to 10-ml portions of hot 1 percent NH_4OH, pouring the rinses through Whatman No. 40 filter paper.
9. Carefully unfold the filter paper and quantitatively wash any precipitate back into the original beaker with a minimum of hot water.
10. Dissolve and rinse any remaining precipitate on the filter paper into the beaker with 2 successive 10-ml portions of warm 25 percent H_2SO_4. Rinse the paper 3 times with hot water and collect the rinsings in the original beaker.
11. Heat the solution 55°–60°C and, while hot, titrate to the first pink tint that persists for 30 sec.

Calculations

$$\text{ppm } Ca^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{ml titrant}$$

Report calcium concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Methyl orange indicator solution 0.05 percent: Dissolve 0.50 g methyl orange in water and dilute to approx 1 liter.

Ammonium oxalate, 5 percent: Dissolve 50 g $(NH_4)_2C_2O_4$ in water and dilute to approx 1 liter.

Ammonium hydroxide, 1 percent v/v: Mix 10 ml conc NH_4OH (sp gr 0.900) with water and dilute to approx 1 liter.

Sulfuric acid, 25 percent v/v: Mix 250 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 1 liter.

Potassium permanganate, 0.0499*N*, 1.00 ml$\simeq$1.00 mg Ca^{+2}: Heat 500 ml $KMnO_4$ stock solution to boiling and filter it through asbestos fiber or fritted glass. Dilute to 950 ml and standardize against primary standard $Na_2C_2O_4$ as follows: Dry 0.5 g of the salt at 105°C for 1 hr. Dissolve approx 0.1 g, accurately weighed to 0.1 mg, in 50 ml water and 20 ml 25 percent H_2SO_4.

$$\text{ml } KMnO_4 \text{ required} = \frac{\text{mg } Na_2C_2O_4}{3.3434}$$

Add, from a buret, 90 percent of required $KMnO_4$ to the oxalate solution and heat to 55°–60°C. Continue the titration slowly and with constant stirring until a faint pink color persists for 30 sec. For practical work, no blank correction is required. Store the standardized $KMnO_4$ solution in a light-proof bottle.

Potassium permanganate, stock solution: Dissolve 3.25 g $KMnO_4$ in water and dilute to 1,000 ml. Store the solution in a dark place for at least 1 week to permit precipitation of manganous salts.

D:8a–3 GRAVIMETRIC METHOD

The gravimetric method is similar in substance to D 511–52, ASTM (1954, p. 245) Manual on Industrial Water.

This method is normally used in the analysis of brines, some acid waters, and concentrated industrial wastes.

Principle of determination

Calcium is precipitated as calcium oxalate, ignited to calcium oxide, and weighed. The following reactions are involved:

$$Ca^{+2} + C_2O_4^{-2} \rightarrow CaC_2O_4$$

$$CaC_2O_4 \xrightarrow{\Delta} CaCO_3 + CO$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

The possible error caused by coprecipitation of silica is eliminated if the calcium is determined on the filtrate from the gravimetric silica determination.

The presence of magnesium increases the solubility of calcium oxalate very appreciably as a consequence of the formation of a complex of magnesium oxalate which withdraws oxalate ions. The effect may be counteracted by the addition of a large excess of oxalate. Heavy-metal ions which also form slightly soluble salts are removed by precipitation as the hydroxides. Manganese is precipitated as the sulfide. When only a few milligrams of barium is present in the sample volume, double precipitation suffices to separate the calcium from it. Strontium also precipitates as the oxalate, and its interference is not eliminated by double or triple precipitation. Strontium is frequently present in brines, and the completeness of its precipitation as strontium oxalate requires further study. Probably the strontium should be subtracted from the gravimetrically determined calcium value, but the Geological Survey has not yet found a completely satisfactory method for determining strontium in all types of water. Until such a method is developed, the reported value for calcium may also include some strontium. Recognized coprecipitations with calcium oxalate are minimized by diluting a sample about fifteenfold. Interferences in some brines and industrial wastes may present special problems of separation. The analyst is referred to Hillebrand and Lundell (1929, p. 486–505) for detailed discussion of chemistry and technique of the determination.

Calcium oxide is very hygroscopic and special attention should be given to the desiccant over which the ignited residue is cooled. Freshly charged alminum oxide, freshly ignited calcium oxide, or concentrated sulfuric acid are satisfactory drying agents. Calcium oxide is a better drying agent than calcium chloride, hence the latter is unsatisfactory. To insure a completely anhydrous residue, the calcium oxide is weighed, ignited, and reweighed, until 2 successive weighings are comparable.

If suitable precautions are taken to minimize the effect of interferences, the results may be accurate and reproducible to ± 0.5 mg.

Apparatus and reagents

Hotplate
Platinum crucible
Muffle furnace, 1,000°C
Bromthymol blue, 1 percent
Ammonium hydroxide, conc (sp gr 0.900)
Ammonium sulfide, 20 percent
Hydrochloric acid, conc (sp gr 1.19)
Ammonium oxalate, 4 percent
Ammonium hydroxide, 50 percent v/v
Ammonium oxalate, 0.1 percent
Hydrochloric acid, 20 percent v/v

Procedure

1. Dilute or concentrate the filtrate from the gravimetric silica determination (see sec. D:34a–2, procedure 8) to a convenient volume. Pipet an aliquot containing less than 250 mg Ca into a 1,000 ml beaker and adjust the volume to approximately 800 ml.
2. Add 2 drops 1 percent bromthymol blue.
3. Neutralize the solution to the green color with conc NH_4OH. Some silica may precipitate along with the iron and aluminum.
4. Add 1 ml 20 percent $(NH_4)_2S$ to precipitate the manganese and allow the mixture to stand 1–2 hr.
5. Filter off the precipitates through Whatman No. 40 filter paper, retaining the filtrate.
6. Wash the beaker and precipitate several times with distilled water that contains a few drops of conc NH_4OH.
7. Discard the residue and combine the filtrate and washings.
8. Acidify the filtrate with conc HCl and add a 10-drop excess.
9. Warm on a hotplate but do not bring solution to a boil.
10. While hot, add with constant stirring approx 100 ml warm 4 percent $(NH_4)_2C_2O_4$.
11. Add with constant stirring 50 percent NH_4OH dropwise until the color changes from yellow to blue.
12. Remove the mixture from the hotplate and allow it to digest for 1 hr.
13. Quantitatively collect the precipitate on Whatman No. 40 filter paper and rinse the beaker and precipitate 4 times with cold 0.1 percent $(NH_4)_2C_2O_4$. Retain the combined filtrate and washings for the gravimetric barium and magnesium determinations.
14. Carefully unfold the filter paper and wash the precipitate back into the original beaker with hot water. Dissolve any precipitate remaining on the paper with 50 ml 20 percent HCl, collecting the washings in the original beaker. Rinse the paper 3 times with hot water, collecting the rinsings in the original beaker. When dissolving the precipitate give particular attention to the folds in the filter paper.
15. Repeat steps 9 through 13.
16. Wash the precipitate 3 times with cold water containing 3 drops conc NH_4OH.
17. Slowly ignite the precipitate in a tared platinum crucible over a low oxidizing flame until the filter paper is reduced to white ash.
18. Transfer the crucible to the muffle furnace and ignite at approx 1,000°C for 0.5 hr or until the precipitate is white.

19. Cool the crucible in a desiccator and weigh. Ignite and weigh to constant weight.

Calculations

$$\text{ppm } Ca^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg CaO} \times 0.7147$$

Report calcium concentrations of <999 ppm to whole numbers and of >999 ppm to 3 significant figures only.

Preparation of reagents

Bromthymol blue, 1 percent: Triturate 1.0 g bromthymol blue with 1.6 ml 0.1*N* NaOH and dilute to approx 100 ml with water.

Ammonium sulfide, 20 percent: Dissolve 20 g $(NH_4)_2S$ in water and dilute to approx 100 ml.

Ammonium oxalate, 4 percent: Dissolve 40 g $(NH_4)_2C_2O_4$ in water and dilute to approx 1 liter.

Ammonium hydroxide, 50 percent v/v: Mix 50 ml conc NH_4OH (sp gr 0.900) with water and dilute to approx 100 ml.

Ammonium oxalate, 0.1 percent: Dissolve 1 g $(NH_4)_2C_2O_4$ in water and dilute to approx 1 liter.

Hydrochloric acid, 20 percent v/v: Mix 200 ml conc HCl (sp gr 1.19) with water and dilute to approx 1 liter.

D:8a–4 TURBIDIMETRIC METHOD

The turbidimetric estimation of calcium is a semiquantitative test useful in fieldwork and in selecting the proper sample volume for quantitative determinations.

Principle of determination

The turbidity of precipitated calcium oxalate is compared with the turbidity of standard calcium solutions similarly treated.

Apparatus and reagents

Test tubes, 10-ml graduations

Calcium chloride, 1.0 ml = 0.1 mg Ca^{+2}

Acetic acid, 50 percent v/v

Potassium oxalate, 5 percent

Procedure

1. Pipet a volume of sample containing less than 0.2 mg Ca (10.0 ml max) into a graduated test tube and adjust the volume to 10 ml.
2. Prepare a blank and sufficient standards and adjust the volumes to 10 ml.
3. Add 1 ml 50 percent $HC_2H_3O_2$.
4. Add 1 ml 5 percent $K_2C_2O_4$ and mix well.
5. Allow the mixture to stand for 10 min; then resuspend the precipitate.
6. Compare the turbidity of the sample with the turbidities of the standards.

Calculations

$$\text{ppm } Ca^{+2} = \frac{1{,}000}{\text{ml sample}} \times \text{mg Ca standard}$$

Preparation of reagents

Calcium chloride, 1.0 ml=0.1 mg Ca^{+2}: Suspend 0.2497 g $CaCO_3$ in 600 ml water. Dissolve with a minimum of dilute HCl and dilute to 1,000 ml.

Acetic acid, 50 percent v/v: Mix 50 ml glacial $HC_2H_3O_2$ (sp gr 1.049) with water and dilute to approx 100 ml.

Potassium oxalate, 5 percent: Dissolve 5.0 g $K_2C_2O_4$ in water and dilute to approx 100 ml.

REFERENCES

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D:9 CARBON DIOXIDE

Carbon dioxide is a respiration product of aquatic plants and animals and is one of the byproducts of aerobic and anaerobic decomposition of organic matter. Acids from natural sources or pollution liberate carbon dioxide from bicarbonate. Most of the carbon dioxide in water is from these sources. Air contains only about 0.04 percent carbon dioxide, and the concentration in water in equilibrium with air will approach 0.7 ppm. Streams are normally rather low in carbon dioxide, but some ground waters contain large quantities in their natural environment.

Carbon dioxide in drinking water is not physiologically important to man and livestock, but it has a marked effect on fish. Tolerances differ widely with the species, dissolved oxygen, and other chemical properties of the water. Of waters of the United States that support good fish fauna, 50 percent have less than 1.5 ppm and 95 percent have less than 5 ppm (California State Water Pollution Control Board, 1952, 1954, p. 205–206). Free carbon dioxide contributes to the corrosiveness of the water and is likely to damage calcareous building material such as cement. It has been recommended that concrete be coated if it is in contact with water containing 20 ppm carbon dioxide (Terzaghi, 1949, p. 136).

D:9a–1 CALCULATION METHOD

The calculation method is applicable to most unpolluted water whose dissolved-solids content does not exceed 500 ppm, or at the most 800 ppm. References are given to ways of extending the range of application somewhat. Carbon dioxide should not be calculated for waters whose pH is not essentially a function of the carbonate-carbon dioxide system only; this would probably exclude some highly colored waters and others containing appreciable quantities of organic or inorganic acids from natural or cultural sources.

Principle of determination

Equations for the calculation of carbon dioxide are derived from 3 well-known mass-law equations and 1 stoichiometric equation as follows:

$$\frac{[H^{+1}]\times HCO_3^{-1}}{H_2CO_3}\times K_1' = 4.54\times 10^{-7} \quad (1)$$

$$\frac{[H^{+1}]\times CO_3^{-2}}{HCO_3^{-1}} = K_2' = 5.61\times 10^{-11} \quad (2)$$

$$[H^{+1}]\times[OH^{-1}] = K_w' = 1.00\times 10^{-14} \quad (3)$$

K_1' and K_2' are apparent constants applicable for normal water having a dissolved-solids concentration of less than 500 ppm.

$$\text{Alkalinity}+[H^{+1}]=2CO_3^{-2}+HCO_3^{-1}+[OH^{-1}] \tag{4}$$

where alkalinity is titratable equivalents of base per liter (to pH 4.5).

From equation 2:

$$CO_3^{-2}=\frac{K_2'\times HCO_3^{-1}}{[H^{+1}]}. \tag{5}$$

From equations 3 and 4:

$$CO_3^{-2}=\frac{\text{Alkalinity}+[H^{+1}]-HCO_3^{-1}-\frac{K_w'}{[H^{+1}]}}{2}. \tag{6}$$

Equating equations 5 and 6:

$$\frac{\text{Alkalinity}-HCO_3^{-1}+[H^{+1}]-\frac{K_w'}{[H^{+1}]}}{2}=\frac{K_2'\times HCO_3^{-1}}{[H^{+1}]}. \tag{7}$$

Solving for HCO_3^{-1}:

$$HCO_3^{-1}+2\left(\frac{K_2'\times HCO_3^{-1}}{[H^{+1}]}\right)=\text{alkalinity}+[H^{+1}]-\frac{K_w'}{[H^{+1}]}$$

and

$$HCO_3^{-1}=\frac{\text{alkalinity}+[H^{+1}]-\frac{K_w'}{[H^{+1}]}}{1+\frac{2K_2'}{[H^{+1}]}} \tag{8}$$

From equation 1:

$$H_2CO_3=\frac{[H^{+1}]}{K_1'}\times HCO_3^{-1}$$

$$=\frac{[H^{+1}]}{K_1'}\times\frac{\text{alkalinity}+[H^{+1}]-\frac{K_w'}{[H^{+1}]}}{1+\frac{2K_2'}{[H^{+1}]}}. \tag{9}$$

In order that CO_2 may be expressed in parts per million:

$$\text{ppm } CO_2=\text{moles } H_2CO_3\times 44{,}011 \text{ (or } 4.4\times 10^4)$$

$$\text{equiv. per liter alkalinity}=\frac{1}{61{,}019}\times\text{ppm alkalinity as } HCO_3^{-1}$$

$$=1.64\times 10^{-5}\text{ alkalinity as } HCO_3^{-1}$$

Evaluating the constants and expressing alkalinity as ppm HCO_3^{-1}:

$$\text{ppm } CO_2=\frac{4.4\times 10^4}{4.54\times 10^{-7}}[H^{+1}]\times\frac{\text{ppm alkalinity as } HCO_3^{-1}\times 1.64\times 10^{-5}+[H^{+1}]-\frac{10^{-14}}{[H^{+1}]}}{1+\frac{11.22\times 10^{-11}}{[H^{+1}]}}$$

$$=9.70\times 10^{10}[H^{+1}]\times\frac{\text{ppm alkalinity as } HCO_3^{-1}\times 1.64\times 10^{-5}+[H^{+1}]-\frac{10^{-14}}{[H^{+1}]}}{1+\frac{11.22\times 10^{-11}}{[H^{+1}]}} \tag{10}$$

The values for constants K_1', K_2', and K_w' are affected by other dissolved minerals and become greater as the total salt concentrations increase because of the diminution of activities of the various ions (Moore, 1939, p. 51–65). The numerical values of the constants given are satisfactory for practical purposes for waters having less than 800 ppm of dissolved solids; 500 ppm has been recommended by some investigators. To compute apparent constants from the constants at zero ionic strength (the values given in handbooks), the analyst is referred to the works of Langelier (1936, p. 1500–1521) and Larson and Buswell (1942, p. 1667–1678).

Between pH 6 and 9 some of the terms of equation 10 become insignificant and can be eliminated for practical purposes. The $[H^{+1}]$ in the numerator of the second half of the equation becomes relatively insignificant above a pH of about 5. The $10^{-14}/[H^{+1}]$ is also insignificant at a pH of less than 9; however, the possible carbon dioxide concentration at a pH of 9 and higher is so small that little error is incurred by eliminating this term from any computations. As pH decreases, the denominator of the second half of the equation approaches 1 and is 1 for all practical purposes in the acid and neutral range. The $2\,K_2'/[H^{+1}]$ term becomes significant at elevated pH's, and its elimination would result in a rather high percentage error at and above about pH 9. Nevertheless, it can be eliminated because the absolute error (ppm) is very small. Therefore, in a pH range of 6 to 9, equation 10 may be simplified to:

$$\text{ppm } CO_2 = \frac{4.4\times10^4}{4.54\times10^{-7}}[H^{+1}]\times1.64\times10^{-5}\text{ ppm alkalinity as } HCO_3^{-1}$$

$$= 1.589\times10^6[H^{+1}]\times\text{ppm alkalinity as } HCO_3^{-1}$$

Additional information on the principle of the determination is given by De Martini (1938, p. 85).

Apparatus and reagents

Titration assembly consisting of pH meter and medium-speed stirrer
Sulfuric acid, 0.01639*N*: 1.00 ml≃1.00 mg HCO_3^{-1}

Procedure

Samples for the determination of carbon dioxide should be collected as directed in sec. A: 3c, and the determination should be made as soon after collection as possible. (See discussion of changes of pH-alkalinity-carbon dioxide balance in sec. B: 1.).

1. Pipet a volume of sample containing less than 40 mg alkalinity as HCO_3^{-1} (50.0 ml max) into a suitable beaker.
2. Insert the beaker in the titration assembly and record the pH to the nearest 0.1.
3. Start the stirrer and titrate immediately to pH 4.5.

Calculations

1. ppm Alkalinity as $HCO_3^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{ml titrant}$

2. ppm CO_2 can be calculated directly from the complete equation 10 under "Principle of determination". Between pH 6.0 and 9.0:

$$\text{ppm } CO_2 = 1.589 \times 10^6 [H^{+1}] \times \text{ppm alkalinity as } HCO_3^{-1}.$$

For convenience a table has been prepared in which the term $1.589 \times 10^6 [H^{+1}]$ has been evaluated for each 0.1 pH unit between 6.0 and 9.0

pH	$1.589 \times 10^6 [H^{+1}]$	pH	$1.589 \times 10^6 [H^{+1}]$	pH	$1.589 \times 10^6 [H^{+1}]$
6.0	1. 589	7.0	0. 159	8.0	0. 016
6.1	1. 262	7.1	. 126	8.1	. 013
6.2	1. 003	7.2	. 100	8.2	. 010
6.3	. 796	7.3	. 080	8.3	. 008
6.4	. 633	7.4	. 063	8.4	. 006
6.5	. 503	7.5	. 050	8.5	. 005
6.6	. 399	7.6	. 040	8.6	. 004
6.7	. 317	7.7	. 032	8.7	. 003
6.8	. 252	7.8	. 025	8.8	. 003
6.9	. 200	7.9	. 020	8.9	. 002
				9.0	. 002

Report carbon dioxide concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Sulfuric acid, 0.01639*N*, 1.00 ml≏1.00 mg HCO_3^{-1}: Add 0.5 ml conc H_2SO_4 (sp gr 1.84) to 950 ml water. (The titrant is stable for several months if protected from ammonia fumes and is usually prepared in larger quantities.) After the solution has been thoroughly mixed, standardize it by titrating 25.00 ml Na_2CO_3 (1.00 ml≏1.00 mg HCO_3^{-1}) to pH 4.5.

Sodium carbonate, 1.00 ml≏1.00 mg HCO_3^{-1}: Dissolve 0.8686 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 ml.

REFERENCES

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D:10 CHLORIDE

Most naturally occurring chlorides are very soluble. Chloride concentration in natural waters ranges widely from less than 1 ppm in some waters to many thousand ppm in some brine. Chloride is the major anion in most brines of the United States. The discharge of some industrial wastes into streams or ground-water reservoirs may considerably increase their chloride content. Human and animal excreta are high in chloride and nitrogenous material. In water supplies, the presence of abnormal concentrations of the two together is indicative of possible pollution by human or animal wastes.

A high concentration of chloride imparts a salty taste to the water but the threshold of detection varies with individuals. Although for drinking purposes, water with a chloride content of 1,000 ppm may be physiologically safe, the U.S. Public Health Service (1946) recommends that the concentration not exceed 250 ppm in water on carriers subject to Federal quarantine regulations.

Chlorides may accelerate corrosion in pipes, boilers, and other fixtures (Taylor, 1949). Magnesium chloride when heated releases hydrochloric acid which is highly corrosive. Many crops may be injured by waters containing excessive quantities of chloride. Chloride is generally about twice as toxic to crops as sulfate (Eaton, 1954).

D:10a-1 VOLUMETRIC METHOD

The volumetric method is similar in substance to part IB, APHA (1955, p. 60) Standard Methods, and D 512–49, ASTM (1954, p. 220–222) Manual on Industrial Water.

The procedure is recommended for waters whose chloride concentration is less than 2,000 ppm and can be used satisfactorily for measuring chloride concentrations up to 5,000 ppm.

Principle of determination

In the well-known Mohr method for determination of chloride, use is made of the fact that in the titration of sodium chloride with silver nitrate, the solution is saturated with silver chloride at the equivalence point and contains equal concentrations of silver and chloride ions. Addition of an excess of silver precipitates silver chloride, whose solubility decreases with an excess of either silver or chloride ions. When potassium chromate is used as an indicator, the chromate ion combines with the excess silver to form very slightly soluble red silver chromate. The following reactions occur:

$$Ag^{+1} + Cl^{-1} \rightarrow AgCl$$

$$2\ Ag^{+1} + CrO_4^{-2} \rightarrow Ag_2CrO_4$$

The pH for the titration should be between 7.0 and 10.5. In an acid medium, the sensitivity of the method is decreased; the second ionization constant of chromic acid is small, and therefore the chromate ion reacts with hydrogen ions.

$$CrO_4^{-2} + H^{+1} \rightleftarrows HCrO_4^{-1}$$

The solution should not be too alkaline because silver hydroxide might then precipitate before the silver chromate (Collins, 1928). Calcium carbonate can be used to adjust the pH of acid waters without danger of making the solution too alkaline. Detection of the end point is facilitated by illuminating the titration with yellow light or by viewing the titration through yellow goggles or a filter.

Iodide and bromide titrate stoichiometrically as chloride. Phosphate, sulfide, and cyanide interfere. Sulfide and cyanide can be removed by acidifying and boiling the sample, then adjusting the pH with calcium carbonate. Hydrogen sulfide can often be removed simply by passing pure air through the sample. Sulfite interferes but can be oxidized readily to sulfate with hydrogen peroxide.

Two strengths of silver nitrate are provided. The dilute titrant is recommended if the chloride concentration is less than 5 mg in a 50- or 25-ml sample. The end point with the dilute silver nitrate is not as sharp as with the concentrated titrant; therefore, the concentrated silver nitrate is recommended if the chloride concentration is greater than 200 ppm. In high-chloride waters, the voluminous precipitate masks the end point, and the maximum chloride concentration that can be titrated satisfactorily is about 50 mg. Sample dilution can be carried only so far before the dilution factor decreases the precision and accuracy considerably. If a 10-ml sample were taken, 0.1 ml silver nitrate (1.00 ml≏5.00 mg Cl^{-1}) is equivalent to 50 ppm of chloride. Sample volumes less than 10 ml are not recommended.

The results are usually accurate and reproducible to ±0.05 mg when the dilute silver nitrate (1.00 ml≏0.50 mg Cl^{-1}) is used. When the concentrated silver nitrate (1.00 ml≏5.00 mg Cl^{-1}) is used, accuracy and reproducibility of ±2–3 percent can be expected.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 303–309).

Apparatus and reagents

Yellow light (a yellow bulb or yellow filter is suitable)
Buret, 25-ml
Potassium chromate indicator solution
Silver nitrate, 1.00 ml≏5.00 mg Cl^{-1}
Silver nitrate, 1.00 ml≏0.50 mg Cl^{-1}

Procedure

1. Pipet a volume of sample containing less than 50 mg Cl^{-1} (50.0 ml max) into a porcelain evaporating dish and adjust the volume to approx 50 ml.
2. Add 10 drops K_2CrO_4 indicator.
3. With constant stirring, titrate with $AgNO_3$ until the pink-red Ag_2CrO_4 persists for 10–15 sec.
4. Determine a blank correction by similarly treating 50 ml dilution water. The normal blank correction with $AgNO_3$ (1.00 ml≏0.50 mg Cl^{-1}) is 0.05 or 0.10 ml. No blank correction is required with the stronger titrant.

Calculations

$$\text{ppm } Cl^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times (\text{ml titrant} - \text{ml blank}) \times (\text{mg } Cl^{-1} \text{ per ml titrant})$$

Report chloride concentrations of <10 ppm to 1 decimal place of between 10 and 999 ppm to whole numbers and of >999 ppm to 3 significant figures only.

Preparation of reagents

Potassium chromate indicator solution: Dissolve 50 g K_2CrO_4 in approx 1,000 ml water. Add $AgNO_3$ (1.00 ml≏0.50 mg Cl^{-1}) until a small amount of red Ag_2CrO_4 precipitates. Put aside in dark for 24 hr and filter to remove the Ag_2CrO_4.

Silver nitrate, 1.00 ml≏0.50 mg Cl^{-1}: Dilute 100 ml $AgNO_3$ (1.00 ml≏5.00 mg Cl^{-1}) to 1,000 ml. Check the titer of the reagent by titrating 10.00 ml NaCl (1.00 ml=1.00 mg Cl^{-1}). Store in a lightproof bottle.

Silver nitrate, 1.00 ml≏5.00 mg Cl^{-1}: Pulverize approximately 30 g $AgNO_3$ crystals in a mortar and dry at 105°–120°C. Browning of the crystals indicates reduction to Ag° owing to the high heating temperatures or presence of impurities. Dissolve 23.96 g dried $AgNO_3$ in water and dilute to 950 ml before standardizing. Standardize by titrating 25.00 ml NaCl (1.00 ml= 1.00 mg Cl^{-1}) diluted to approx 50 ml. Store in a lightproof bottle.

Sodium chloride, 1.00 ml=1.00 mg Cl^{-1}: Fuse NaCl in a platinum dish and cool. Dissolve 1.6484 g of the fused NaCl in water and dilute to 1,000 ml.

D:10a–2 GRAVIMETRIC METHOD

The gravimetric procedure is recommended for industrial wastes that contain substances that interfere with the Mohr titration and for waters whose chloride content exceeds 5,000 ppm. Although the volumetric method can be used in the range of 2,000–5,000 ppm, results obtained by the gravimetric procedure are usually more accurate and reproducible than those obtained by the volumetric method.

Principle of determination

Chloride is precipitated as silver chloride. Best results are obtained if the precipitate weighs between 250 and 500 mg (approx 65–125 mg Cl^{-1}). The optimum silver nitrate concentration in the precipitation reaction is 0.05 g per liter. For routine analysis a

moderate excess of silver nitrate can be tolerated, but an unnecessarily large excess should be avoided.

Precipitation is complete almost immediately after addition of the silver nitrate, but digestion is needed to flocculate the colloidal silver chloride into a filterable mass. The presence of nitric acid and heat hastens the flocculation. When exposed to light, silver chloride slowly decomposes to silver and chlorine, the silver remaining dispersed in the precipitate and the chlorine escaping from the crystals. Excessive exposure to light during precipitation and digestion phases of the determination may also precipitate free silver from the silver nitrate. The precipitate collected on filter paper cannot be ignited satisfactorily because the carbon and reducing gases formed in burning off the paper reduce some of the silver chloride to free silver.

Anions that form silver salts insoluble in nitric acid, such as bromide, iodide, cyanide, and sulfide, also precipitate with the silver chloride. Cyanide and sulfide can be removed from the water by acidifying and boiling. High concentrations of heavy metals may interfere, but such concentrations are seldom found except in some industrial wastes.

The results are generally accurate and reproducible to ±0.5 mg.

Apparatus and reagents

Steam bath
Gooch crucible with asbestos- or glass-fiber mat
Suction filtration apparatus
Oven, 180°C
Nitric acid, conc (sp gr 1.42), Cl^{-1}-free
Nitric acid, 0.1 percent v/v
Silver nitrate, 5 percent

Procedure

1. Pipet a volume of sample containing between 65 and 125 mg Cl^{-1} into a 250-ml beaker and adjust the volume to approx 100 ml.
2. Add 5–6 drops conc HNO_3.
3. Heat solution nearly to boiling.
4. With constant stirring, slowing add 5 percent $AgNO_3$ until no more Cl^{-1} is precipitated.
5. Digest the mixture on a steam bath until the precipitate flocculates and settles, leaving a clear supernatant solution.
6. Test the supernatant solution with 1 drop 5 percent $AgNO_3$ to insure complete precipitation.
7. Place the mixture in the dark and allow it to stand overnight.
8. Collect the precipitate quantitatively in a tared Gooch crucible.
9. Wash the beaker and precipitate with small amounts of 0.1 percent HNO_3, until the washings give no test for silver with dilute HCl.
10. Dry the crucible and precipitate at 180°C to constant weight. Record the precipitate weight to the nearest 0.0001 g.

Calculations

$$\text{ppm } Cl^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg AgCl} \times 0.24737$$

Report chloride concentrations >999 ppm to 3 significant figures only.

Preparation of reagents

Nitric acid, 0.1 percent v/v: Mix 1 ml conc HNO_3 with water and dilute to approx 1,000 ml.

Silver nitrate, 5 percent: Dissolve 5.0 g $AgNO_3$ in water and dilute to approx 100 ml.

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

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U.S. Public Health Service, 1946, Drinking water standards: U.S. Public Health Service Repts., v. 61, no. 11.

D:11 CHLORINE RESIDUAL

Residual chlorine includes "free available chlorine" and "combined chlorine." Chlorine hydrolyzes immediately in water.

$$Cl_2 + H_2O \rightarrow HOCl + H^{+1} + Cl^{-1}$$

$$HOCl \rightleftarrows H^{+1} + OCl^{-1}$$

Through common usage the term "free available chlorine" is recognized to include HOCl and OCl^{-1} and "combined available chlorine" to include chloramines and other chloro derivatives (APHA, 1955, p. 62–81). Both free and combined chlorine may be present together. Results are reported in terms of chlorine (Cl_2).

Chlorination is used in the treatment of many public water supplies and sewage effluents. Industrial processes, particularly those that use bleaching operations, may discharge free or combined chlorine to watercourses. Chlorine is unstable in solution; strong light accelerates its dissipation.

It is generally agreed that the small amounts of residual chlorine that are present in palatable drinking water are not harmful; low concentrations of chlorine are reported to be toxic to fish, but the degree to which chlorine is harmful is dependent on pH, temperature, dissolved oxygen and synergism and antagonism of other pollutants (California State Water Pollution Control Board, 1952, 1954, p. 212).

Industrial water supplies are often chlorinated to control bacteria and other slime-producing organisms. Residual chlorine may cause taste in processed foods (Kohman, 1923). Concentrations not exceeding 2.0 ppm are recommended for the manufacture of fine paper. In concentrations normally found, chlorine is not reported to be injurious to land crops.

D:11a-1 ORTHOTOLIDINE-ARSENITE METHOD

The orthotolidine-arsenite method is similar in substance to part ID, APHA (1955, p. 72–73) Standard Methods.

Principle of determination

In dilute solution, hydrolyzed chlorine oxidizes orthotolidine to give a yellowish-brown complex. The color developed is compared with that of standards or standardized colored-glass discs. Other free halogens react quantitatively. The reaction is practically instantaneous with free available chlorine but proceeds more slowly with the combined forms. This differential in reaction rates is utilized in differentiating between the two. Arsenite inhibits the reaction but does not reverse it.

The pH must be below 1.3 for proper color development, and the ratio of orthotolidine to chlorine should be at least 1 to 3. The reac-

tion is temperature sensitive, the precision of the test increasing with decreasing temperature. A reaction temperature of less than 20°C is recommended.

Iron, manganese, nitrite, algae, and lignocellulose interfere and increase the color. The effect of these interferences is evaluated by development of color in presence of arsenite and compensated for in the calculations.

Reproducibility of results is dependent on close adherence to prescribed procedure, temperature, and relative concentrations of free and combined available chlorine. Reproducibility of ±0.0001 mg chlorine may be achieved with less than 0.0005 mg and ±0.0003 mg in the 0.005- to 0.01-mg range.

Apparatus and reagents

Hellige Aqua Tester with standard color discs covering range of 0.00–0.10 ppm, 0.1–1.0 ppm, and 1.0–2.0 ppm.
Sodium arsenite, 5 percent
Orthotolidine reagent

Procedure

Because of its instability, residual chlorine should be determined immediately after collection of the sample. (See sec. A:4d.)

1. Pipet equal volumes of sample containing less than 0.01 mg residual chlorine as Cl_2 (50.0 ml max) into 3 flasks and adjust the volumes to 50 ml.
2. To the first flask add 0.5 ml 5 percent $NaAsO_2$ and mix. Add 5.0 ml orthotolidine, mix rapidly, and immediately compare the color in the "Aqua-tester." The value observed is the blank correction (B_1) for the free available chlorine.
3. Make a second observation on the contents of the first flask 5.0 min after addition of the orthotolidine. This value is the blank correction (B_2) for the total available chlorine.
4. To the second flask add 5.0 ml orthotolidine. Mix quickly and immediately add 0.5 ml $NaAsO_2$. Immediately compare the color. The observed value (A) is the free available chlorine plus effect of interfering substances that react rapidly.
5. To the third flask add 5.0 ml orthotolidine, mix, and compare the color after 5.0 min. The observed value (OT) is the total residual chlorine plus the effect of interfering substances that react in 5.0 min.

Calculations

$$\text{ppm Total residual chlorine} = \frac{1}{\text{density}} \times \frac{50}{\text{ml sample}} (OT - B_2)$$

$$\text{ppm Free available chlorine} = \frac{1}{\text{density}} \times \frac{50}{\text{ml sample}} (A - B_1)$$

$$\text{ppm Combined available chlorine} = \frac{1}{\text{density}} \times \frac{50}{\text{ml sample}} [(OT - B_2) - (A - B_1)]$$

Report chlorine concentrations of <0.10 ppm to 2 decimal places and of >0.10 ppm to 2 significant figures only.

Preparation of reagents

Sodium arsenite, 5 percent: Dissolve 5.0 g $NaAsO_2$ in water and dilute to approx 100 ml.

Orthotolidine reagent: Dissolve 1.35 g orthotolidine hydrochloride in approx 450 ml water. Add this solution with constant stirring to a solution of 375 ml conc HCl (sp gr 1.19) and 125 ml water. Dilute to 1,000 ml. Store in amber or actinic bottle and protect from light. The reagent is stable for 6 months.

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

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Kohman, E. F., 1923, The effect on canned foods of industrial wastes in the water supply: Natl. Canners Assoc. Circ. 4–L.

Technical Association of the Paper and Pulp Industry, 1948, Specifications for chemical process water for fine paper manufacture: Tech. Assoc. Paper and Pulp Industry Standards, E-60D, s–48, corrected.

D:12 CHROMIUM

Few if any waters contain chromium from natural sources. Hexavalent chromium salts are used in metal pickling and plating, anodizing aluminum, and in the manufacture of paints, dyes, explosives, ceramics, paper, and many other substances. Trivalent chromium salts are used as mordants in textile dyeing, in the ceramic and glass industries, and in photography. Chromium is a corrosion inhibitor and may be present in treated cooling waters. Waste products from many of these activities may contain chromium.

The U.S. Public Health Service (1946) states that the concentration of hexavalent chromium shall not exceed 0.05 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations; no limit is given for the trivalent form. The toxicity of chromium salts to aquatic life differs widely with the species, temperature, pH, valence of chromium, and other factors. (California State Water Pollution Control Board, 1952, 1954.)

D:12a HEXAVALENT CHROMIUM

D:12a-1 DIPHENYLCARBAZIDE METHOD

The diphenylcarbazide method determines only the hexavalent chromium.

Principle of determination

In acid solution diphenylcarbazide forms with hexavalent chromium a soluble red-violet product that absorbs light at 540 mμ. The formula for the colored substance is not known. For all practical purposes the reaction is specific for chromium; metallic interference almost never occurs. Iron, mercury, and molybdenum in concentrations as high as 100 ppm show only a small effect. Vanadium should not be present in concentrations exceeding 4 ppm. The effect of water color is small, and color up to 50 can be tolerated. The pH of the reaction is not critical; solutions differing in pH from 0.7 to 1.3 give identical colors. The color of the chromium-diphenylcarbazide product changes slightly with time but for practical purposes it can be considered to be stable. The chromium color develops almost instantly and is stable, whereas vanadium color develops instantly and then fades rapidly. If the original vanadium concentration is less than 4 ppm, no color persists after 10 min.

Results are reproducible and accurate to ±0.0002 mg.

Additional information on the principle of the determination is given by Sandell (1950, p. 260–268).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 540mμ
Cells: 10-mm optical depth
Phototube: Blue-sensitive
Blank: Metal-free water plus reagents
Initial sensitivity setting: 1
Slit width: 0.1 mm (approx)
The following absorbancies have been observed:

mg Cr	*Absorbancy*
0.01	0.7
.02	1.2
.03	1.7
.045	2.5

Potassium chromate, 1.00 ml=0.10 mg Cr^{+6}.
Sulfuric acid, 6.5 percent v/v
Diphenylcarbazide reagent

Procedure

Samples for the determination of chromium should be collected and treated as directed in sec. A :4d.

1. Pipet a volume containing less than 0.03 mg Cr^{+6} (10.00 ml max) into a 50-ml beaker and adjust the volume to 10.0 ml with metal-free water.
2. Prepare a blank of metal-free water and sufficient standards, and adjust the volumes to 10.0 ml with metal-free water.
3. Add 1.0 ml 6.5 percent H_2SO_4 and mix.
4. Add 0.5 ml diphenylcarbazide reagent and mix.
5. Allow to stand 10 min.
6. Determine the absorbancy of the sample and standards against the blank and when necessary make correction for water color as directed in sec. C: 1a–2.

Calculations

1. Determine the mg Cr^{+6} in the sample from a plot of absorbancies of standards containing known amounts of the constituent.
2. $$\text{ppm } Cr^{+6} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } Cr^{+6} \text{ in sample}$$

Report hexavalent chromium concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Potassium chromate, 1.00 ml=0.10 mg Cr^{+6}: Dissolve 0.3734 g K_2CrO_4 dried overnight in H_2SO_4 desiccator in metal-free water and dilute to 1,000 ml.

Sulfuric acid, 6.5 percent v/v: Add 6.5 ml conc H_2SO_4 (sp gr 1.84) to metal-free water and dilute to 100 ml.

Diphenylcarbazide reagent: Dissolve 0.2 g diphenylcarbazide and 1.0 g phthalic anhydride in approx 200 ml ethyl alcohol. This reagent is stable for several weeks; slight discoloration may be noted but this does not impair the usefulness of the reagent.

D:12b CHROMIUM

D:12b–1 PERMANGANATE-AZIDE METHOD

Principle of determination

Total chromium is determined by oxidizing trivalent chromium to the hexavalent state with potassium permanganate prior to diphenylcarbazide color development (see sec. D: 12a–1). The excess oxidant is destroyed with sodium azide.

Attention should be given to the glassware used, because scratched glassware may adsorb chromium. Any glassware cleaned with chromic acid cleaning solution should be recleansed with hydrochloric acid to remove the last traces of chromium.

Additional information on the principle of the determination is given by Saltzman (1952, p. 1016) and Lieber (1956, p. 295–299).

Apparatus and reagents

Steam bath

Spectrophotometer, Beckman Model B:

Wavelength: 540 mμ
Cells: 10-mm optical depth
Phototube: Blue-sensitive
Blank: Metal-free water plus reagents
Initial sensitivity setting: 1
Slit width: 0.1 mm (approx)
The following absorbancies have been observed:

mg Cr	*Absorbancy*
0.01	0.7
.02	1.2
.03	1.7
.045	2.5

Potassium chromate, 1.00 ml=0.10 mg Cr^{+6}
Sulfuric acid, 6.5 percent v/v
Diphenylcarbazide reagent
Trivalent chromium, 1.00 ml=0.002 mg Cr^{+3}
Sulfuric acid, 0.5*N*
Potassium permanganate, 0.1*N*
Sodium azide, 5 percent
Ammonium hydroxide, 50 percent v/v

Procedure

Samples for the determination of chromium should be collected and treated as directed in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.30 mg Cr (50.0 ml max) into a 250-ml Erlenmeyer flask and adjust the volume to approx 50 ml.
2. Prepare a blank of metal-free water and sufficient standards and adjust the volumes to approx 50 ml with metal-free water.
3. Add 10 ml 0.5*N* H_2SO_4 and mix.
4. Add approx 0.5 ml 0.1*N* $KMnO_4$.
5. Heat on steam bath for 20 min. If color disappears, add more $KMnO_4$ to maintain a slight excess.

6. Remove from steam bath, and while warm add 5 percent NaN_3 dropwise until $KMnO_4$ color disappears. Allow about 10 sec between each drop of NaN_3; 3 to 5 drops are usually sufficient.
7. Promptly cool to room temperature in a cold-water bath.
8. Add 0.75 ml 50 percent NH_4OH and dilute to 100.0 ml.
9. Pipet a 10.00-ml aliquot into a 50-ml beaker and proceed as directed in sec. D: 12a–1. The color correction is not made.

Calculations

1. Determine the mg Cr in the aliquot from a plot of absorbancies of standards containing known amounts of the constituent.
2. $$\text{ppm Cr} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \frac{\text{ml sample}}{\text{ml aliquot}} \times \text{mg Cr in aliquot}$$

Report chromium concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Potassium chromate, 1.00 ml=0.10 mg Cr^{+6}: Dissolve 0.3734 g K_2CrO_4 dried overnight in H_2SO_4 desiccator in metal-free water and dilute to 1,000 ml.

Sulfuric acid, 6.5 percent v/v: Add 6.5 ml conc H_2SO_4 (sp gr 1.84) to metal-free water and dilute to 100 ml.

Diphenylcarbazide reagent: Dissolve 0.2 g diphenylcarbazide and 1.0 g phthalic anhydride in approx 200 ml ethyl alcohol. This reagent is stable for several weeks; slight discoloration may be noted but this does not impair the usefulness of the reagent.

Trivalent chromium, 1.00 ml=0.002 mg Cr^{+3}: Dissolve 0.2263 g $K_2Cr_2O_7$ in metal-free water and dilute to 1,000 ml. Pipet 5.00 ml into an Erlenmeyer flask. Add approx 15 mg Na_2SO_3 and 0.5 ml conc HNO_3 (sp gr 1.42). Evaporate to dryness gently; strong heating reoxidizes the Cr. Add 0.5 ml conc HNO_3 and again evaporate to dryness to destroy any excess sulfite. Take up in 1 ml conc HNO_3 with warming and dilute to 200.0 ml with metal-free water.

Sulfuric acid, 0.5*N*: Mix 13.9 ml conc H_2SO_4 (sp gr 1.84) with metal-free water and dilute to approx 1 liter.

Potassium permanganate, 0.1*N*: Dissolve 0.32 g $KMnO_4$ in approx 100 ml metal-free water. Allow to stand several days and decant or filter through medium-porosity fritted glass.

Sodium azide, 5 percent: Dissolve 5 g NaN_3 in approx 100 ml metal-free water.

Ammonium hydroxide, 50 percent v/v: Mix 50 ml conc NH_4OH (sp gr 0.900) with water and dilute to 100 ml.

REFERENCES

California State Water Pollution Control Board, 1952, Water quality criteria: Pub. no. 3.

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U. S. Public Health Service, 1946, Drinking water standards: U. S. Public Health Service Repts., v. 61, no. 11.

D:13 COLOR

The color of water as considered herein is that due only to substances in solution. Color in water may be of natural mineral, animal, or vegetable origin. It may be caused by metallic substances, humus material, peat, algae, weeds, or protozoa. Industrial wastes may also color water. Color may range from zero to several hundred units.

In domestic water, color is undesirable from aesthetic considerations and because it may dull clothes or stain food and fixtures. The U.S. Public Health Service (1946) states that the color shall not exceed 20 units in drinking and culinary water on carriers subject to Federal quarantine regulations. Color is undesirable in water for many industries, particularly food processing, laundering, ice manufacturing, bottled beverage, photographic and textile (California State Water Pollution Control Board, 1952, 1954, p. 226–228).

D:13a–1 COMPARISON METHOD

Principle of determination

The color of the water is compared to that of glass colored discs which have been calibrated to correspond to the platinum-cobalt scale of Hazen (1892, p. 427–428). The unit of color is that produced by 1 mg of platinum per liter. The Hazen scale is usually satisfactory for most waters, but the hues and shades of some waters may not easily be compared with standards. If the hue of the water does not compare with that of the standard there is very little that can be done about it, other than to visually compare the optical densities of the sample and standard. A minimum of dilution of highly colored water is recommended because the color of the diluted sample often is not proportional to the dilution.

Turbidity causes the observed color to be higher than the true color, but there apparently is some disagreement as to the magnitude of the effect of turbidity. One authoritative source states that "Even a slight turbidity causes the apparent color to be noticeably higher than the true color" (APHA, 1955, p. 87), whereas another states that "The color of water with low turbidity is substantially the same as that of clear water" (California State Water Pollution Control Board, 1952, 1954, p. 226–228). The removal of turbidity is the most recurrent problem in the determination of color. Color is removed by adsorption on suspended material, and filtration of the sample through paper and other media which pass the water through a membrane of concentrated sedimentary material tends to decolorize the water. Centrifuging is preferable to filtration through any media for turbidity removal, but centrifuging

is not completely effective if the water contains very finely divided particles. Flocculation of the dispersed particles with a strong electrolyte has been proposed (Lamar, 1949, p. 726). The electrolytic method is effective for removing turbidity, but the process of flocculation is also often used to decolorize some waters. The flocculation method may have some application but is probably not suitable for every type of color in water.

The color in some highly colored waters may have a tendency to fade and (or) precipitate on standing. Biological changes during storage may also affect the color. Consequently the color determination should be made within a reasonable period of time after the sample is collected.

Because of the many complicating factors involved, the determination of color is one of the least precise in water analysis. No statements on the accuracy and reproducibility of the tests can be made.

Apparatus

Hellige Aqua Tester (see sec. C : 2f).

Procedure

1. Fill one instrument tube with the sample of water, level, insert the glass plug making sure that no air bubbles are trapped, and insert the tube into the Aqua Tester.
2. Use distilled water in the second tube as a blank.
3. The color comparison is made by revolving the disc until the color of the two tubes matches. Waters that have colors greater than 70 should be diluted.

Calculations

The color is read directly from the matching color standard, and the proper dilution factor is applied. Report color as follows:

Color unit	*Record units to nearest—*
1–50	1
51–100	5
101–250	10
250–500	20

REFERENCES

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D:14 COPPER

Most copper minerals are relatively insoluble, and little copper found in water is of natural origin. The presence of copper in more than trace amounts can usually be attributed to corrosive action of water on copper pipes, to industrial wastes, or to the use of copper salts for the control of algae and other aquatic growths.

Copper imparts a disagreeable metallic taste to water. As little as 1.5 ppm can usually be detected, and 5 ppm can render the water unpalatable. Copper is not considered to be a cumulative systemic poison like lead and mercury; most copper ingested is excreted by the body and very little is retained. The pathological effects of copper are controversial, but it is generally believed very unlikely that humans could unknowingly ingest toxic quantities from palatable drinking water. The U. S. Public Health Service (1946) recommends that copper should not exceed 3.0 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations. The toxicity to aquatic organisms differs significantly not only with the species but also with the chemical and physical characteristics of the water, such as temperature, hardness, turbidity, and carbon dioxide content (California State Water Pollution Control Board, 1952, p. 230).

Copper is undesirable in water used for canning foods (Weckel, 1942) and for metal-plating baths (Irenas, 1946). Although copper is an essential or beneficial plant nutrient, crops differ widely in their tolerances. Low concentrations have been found to be injurious to orange seedlings, flax, sugar beets, tomatoes, and barley, but high concentrations had no effect on oats or kale (California State Water Pollution Control Board, 1952, p. 230).

D:14a-1 DIETHYLDITHIOCARBAMATE SPECTROPHOTOMETRIC METHOD

Principle of determination

Copper reacts with the substituted carbamate, dihydroxyethyldithiocarbamic acid, to give a stable colored complex, which is a true solution. With freshly prepared reagents, the color development is instantaneous. If copper is determined infrequently, preparation of fresh carbon disulfide and diethanol-amine solutions is recommended for each set of samples. Refrigerated reagents are sufficiently stable for about 1 month.

Nickel, cobalt, and bismuth also give colored solutions with the reagents, but these metals must be present in concentrations 20 times that of copper to equal the copper color. At the wavelength used, the absorbancy of natural color in the water is appreciable, and a color correction is often necessary. Iron reacts with the reagent to give a color of less intensity than copper. This inter-

ference is eliminated by complexing iron with citrate and compensating for the slight yellow color of the iron-citrate complex.

With the listed apparatus, results are usually accurate and reproducible to ±0.002 mg.

Additional information on the principle of the determination is given by Sandell (1950, p. 309).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 425 mμ
Cells: 40-mm optical depth
Phototube: Blue-sensitive
Blank: Metal-free water plus reagents
Initial sensitivity setting: 2
Slit width: 0.2 mm (approx)
The following absorbancies have been observed:

mg Cu	*Absorbancy*
0.0125	0.33
.0250	.66
.0375	.98
.0500	1.31

Copper solution, 1.00 ml=0.005 mg Cu
Nitric acid, 5 percent v/v
Sodium citrate, 10 percent
Ammonium hydroxide, conc (sp gr 0.900)
Dihydroxyethyldithiocarbamic acid

Procedure

Samples for the determination of copper should be treated as directed in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.05 mg Cu (25.00 ml max) into a 50-ml beaker and adjust the volume to 25.0 ml with metal-free water.
2. Prepare a blank of 25.0 ml metal-free water and sufficient standards and adjust volumes to 25.0 ml with metal-free water.
3. Add 1.0 ml 5 percent HNO_3.
4. Add 1.0 ml 10 percent $Na_3C_6H_5O_7$.
5. Add 1.0 ml conc NH_4OH. Stir the solutions vigorously.
6. Add 1.0 ml dihydroxyethyldithiocarbamic acid and mix well.
7. When necessary, make corrections for water color and iron as directed in sec. C: 1a–2, method 2, to obtain true sample absorbancy.

Calculations

1. Determine the mg Cu in sample from a plot of absorbancies of standards containing known amounts of constituent.

2. $$\text{ppm Cu} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg Cu in sample}$$

Report copper concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Copper solution, 1.00 ml=0.005 mg Cu: Dilute 5.00 ml Cu (1.00 ml=1.00 mg Cu) to 1,000 ml with metal-free water containing 1 or 2 drops conc HNO_3 (sp gr 1.42).

Copper solution, 1.00 ml=1.00 mg Cu: Dissolve 1.00 g Cu in a minimum of dilute HNO_3 and dilute to 1,000 ml with metal-free water.

Nitric acid, 5 percent v/v: Mix 5 ml conc HNO_3 (sp gr 1.42) with metal-free water and dilute to approx 100 ml.

Sodium citrate, 10 percent: Dissolve 10 g $Na_3C_6H_5O_7$ in metal-free water and dilute to approx 100 ml.

Dihydroxyethyldithiocarbamic acid: Just before use, mix equal volumes of 0.32 percent CS_2 and 3.6 percent diethanol-amine.

Carbon disulfide, 0.32 percent v/v: Dissolve 0.32 ml CS_2 in ethyl alcohol and dilute to 100 ml. Store in refrigerator.

Diethanol-amine, 3.6 percent v/v: Dissolve 3.6 ml diethanol-amine in ethyl alcohol and dilute to 100 ml. Store in refrigerator.

REFERENCES

California State Water Pollution Control Board, 1952, Water quality criteria: Pub. no. 3.

Irenas, Z., 1946, The significance of water in the plating room: Water Pollution Abs. 19 [August].

Sandell, E. B., 1950, Colorimetric determination of trace metals: New York, Interscience Publishers.

U. S. Public Health Service, 1946, Drinking water standards: U. S. Public Health Service Repts., v. 61, no. 11.

Weckel, K. G., 1942, Watch your water supply — it affects food quality: Water Pollution Abs. 15 [March].

D:15 DENSITY

Density is the mass of any substance per unit volume at a designated standard temperature. Density should not be confused with specific gravity, which is a mass-to-mass relation.

The density value has some use in industries that utilize brines and whose basic unit of concentration of dissolved material is density. Density is used primarily by the chemist in the computation of parts per million for highly mineralized waters. In the analysis, weight per sample volume is determined, and these values must be converted to parts per million. Parts per million by definition is the weight of dissolved material per 1 million equal weights of solution (milligrams per kilogram). Therefore the determined concentration of each constituent is divided by the density to give the correct parts per million. This computation is made before rounding the results.

A dissolved-materials content of 1,000 ppm increases the density of the solution by slightly less than 1 g per kg, or less than 0.1 percent; the exact amount is dependent on the nature of the solid material. Consequently differences in density are not significant to the chemical analysis unless the total concentration of dissolved solids exceeds about 5,000–10,000 ppm. The Geological Survey has arbitrarily selected 7,000 ppm as the dividing line. If the dissolved-solids content is less than 7,000 ppm it is assumed that exactly 1 ml of solution weighs exactly 1 g; if it exceeds 7,000 ppm the density is determined and used in the computation of parts per million for all constituents. If determination of dissolved solids is not included in the scope of the analysis, a specific conductance of 10,000 is then taken as the differentiating measurement.

D:15a–1 GRAVIMETRIC METHOD

Principle of determination

The density determination is based on the weight of a carefully measured volume of solution at a given temperature. Densities are determined at 20° C, the same temperature at which volumetric glassware is calibrated to deliver a given weight of pure water.

Results are accurate and reproducible to ±0.0005 g.

Apparatus

Weighing bottle: 50+–ml capacity

Volumetric pipet, 50–ml, calibrated. The actual volume delivery of the pipet is determined by weighing a delivered volume of dilution water at 20°C. The volume is obtained from relative-density tables in handbooks. Alternatively, a 50–ml pycnometer can be used; it must be calibrated also.

Procedure

1. Adjust the temperature of the sample to 20.0°C.
2. Rapidly withdraw a sample and transfer it to a tared weighing bottle.
3. Stopper the bottle immediately to prevent water loss by evaporation.
4. Weigh the solution to the nearest 0.1 mg.

Calculations

$$\text{Density} = \frac{\text{g sample}}{\text{ml sample}}$$

If a constant-temperature bath is not available, the determination can be made at the sample temperature and a correction applied for the departure from 20°C. The temperature is recorded with an accurate thermometer, and the relative density for that temperature obtained from a table. The density result is then corrected by the factor:

$$\frac{\text{Relative density (20°C)}}{\text{Relative density (test temp in °C)}}$$

Report density to 3 decimal places in terms of grams per milliliter at 20°C.

D:16 FLUORIDE

Unlike chlorides, fluorides are only sparingly soluble and are present in most natural waters in only small amounts. Calcium fluoride (fluorite) is the principal source of fluoride, but there are some other complex fluoride-bearing minerals. The element is often characteristic of waters from deep strata and is frequently found in salt water from oil wells and in water from areas that have been subjected to recent vulcanism. Fluorides are used as insecticides, disinfectants, preservatives, and for a few other purposes in industry. They are seldom found in large quantities in industrial wastes, except as the result of spillage.

Pathological changes in man attributable to fluoride absorption are in the nature of ostosis. Large quantities of fluoride are toxic, but it has been reported that adults may safely drink 2 gallons per day of water containing 10 ppm of fluoride (Smith, 1944, p. 1293). Daily intakes of about 15–20 mg of fluoride over a period of several years are required to induce chronic fluorosis in an adult man (California State Water Pollution Control Board, 1952, p. 256). Excessive quantities in drinking water during calcification may cause discoloration in the teeth of children; adults are not affected. Available evidence indicates that water containing less than 1.0–0.9 ppm of fluoride seldom causes mottling of children's teeth, and the literature describing the beneficial effect of 0.88–1.5 ppm in drinking water as an aid in the reduction of tooth decay in children is abundant. The U. S. Public Health Service (1946) states that the concentration of fluoride shall not exceed 1.5 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations.

Manufacturers of products for internal consumption generally limit the fluoride content of water to about 1.0 ppm. In normal concentrations it is not significant in irrigation; it is generally concluded that the fluoride content of irrigation water has no consistent influence on the fluoride content of plants. The effect of fluoride on livestock is similar to that on humans (California State Water Pollution Control Board, 1952, p. 256).

D:16a–1 ZIRCONIUM-ERIOCHROME CYANINE R METHOD

The Zirconium Eriochrome Cyanine R method is a much modified version of the procedure of Megregian (1954, p. 1161).

Principle of determination

In acid solution, zirconium reacts with Erichrome Cyanine R to form a red complex ion. Fluoride forms a more stable complex with zirconium (ZrF_6^{-2}) and withdraws zirconium from the organic complex to produce a bleaching effect. Eriochrome Cyanine R

shows a decided specificity to zirconium. Under the experimental conditions the dye does not give a color with titanium or beryllium, two metals which react with many other zirconium agents. Aluminum reacts to give a positive interference that is easily eliminated. This is accomplished by allowing the solution to stand for at least 2 hr before making color comparison. Up to 10 ppm can be tolerated.

Analytical conditions are not overly critical. The pH is controlled at a highly acid level by the addition of 1.7 ml of concentrated hydrochloric acid to each sample. This assures that high concentrations of bicarbonate or other alkaline ions will not affect the pH significantly. Sulfate interferes but is removed in the procedure by precipitation as barium sulfate. Overnight standing is usually required to assure complete settling of barium sulfate before making color comparison. The clarification of the sample can be accelerated by centrifuging if the fluoride result is desired immediately. Filtration should not be used.

Residual chlorine, chromate, and probably other strong oxidants attack the indicator. The susceptibility to attack varies with batches of indicator. Stannous chloride is used to eliminate chromate and chlorine interference. Chromium, cadmium, and nickel, in concentrations of less than 5 ppm, do not interfere in the lower fluoride range. When the fluoride concentration exceeds 1.0 ppm, larger quantities of these metals can be tolerated. Ten ppm iron, zinc, lead, cyanide and phosphate, cause no appreciable interference if the sample is allowed to stand overnight.

The determination shows "salt effect"; the sensitivity is depressed by 5 to 10 percent at a dissolved-solids concentration of 10,000 ppm. The effect of the usual type of color is not serious. A color of 70 on the Hellige scale is equivalent to an absorbancy error of only 0.005 in the spectrophotometric measurement. Thus, it appears that color correction will not often be necessary.

The quality of batches of Eriochrome Cyanine R from different sources differs very significantly, and it is necessary to test the reagent each time it is prepared. The individual absorbancy curves show corresponding differences, and the sensitivity of fluoride between reagents may differ by 20 percent.

The method has rather good tolerance for temperature differences. For most purposes, operating at room temperature without other precautions is satisfactory.

With listed apparatus, results are accurate and reproducible to ± 0.0005 mg in the lower ranges and approx 0.001 mg in the higher fluoride range.

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 540 mμ
Cells: 40-mm optical depth
Phototube: Blue-sensitive
Blank: Dilution water plus reagents
Initial sensitivity setting: 3
Slit width: 0.3 mm (approx)
The following absorbancies have been observed:

mg F^{-1}	*Absorbancy*
0.00	1.50
.01	1.15
.02	.82
.03	.56

Sodium fluoride, 1.00 ml=0.010 mg F^{-1}
Stannous chloride reagent, 2 percent
Indicator solution

Procedure

If the sample contains an excessive amount of interfering materials, the fluoride should be isolated by distillation (see sec. D:16a–3).

1. Pipet a volume of sample containing less than 0.03 mg F^{-1} (10.00 ml max) into a 50-ml centrifuge tube or test tube.
2. Prepare a blank and sufficient standards, and adjust the volumes to 10.0 ml.
3. If chromate, residual chlorine, or other strong oxidizing agents are present in the sample, add 0.1 ml 2 percent $SnCl_2$ and let the solution stand for 10 min.
4. Add 25.0 ml indicator.
5. Allow the solution to stand overnight for barium sulfate to settle.
6. Decant approx 25 ml pure supernatant solution, taking care not to disturb the precipitate.
7. Determine the absorbancy of the test sample and standards against the blank, and when necessary make correction for water color as directed in sec. C:1a–2, method 1.

Calculations

1. Determine mg F^{-1} in test sample from a plot of absorbancies of standards containing known amounts of constituent.

2. $$\text{ppm } F^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } F^{-1} \text{ in sample}$$

Report fluoride concentrations of <1 ppm to 0.1 ppm and of >1 ppm to 2 significant figures only.

Preparation of reagents

Sodium fluoride, 1.00 ml=0.010 mg F^{-1}: Dissolve 0.2210 g NaF in water and dilute to 1,000 ml in metal-free water. Dilute 100.0 ml of this stock solution to 1,000 ml.

Stannous chloride reagent, 2 percent: Dissolve 1 g $SnCl_2 \cdot 2H_2O$ in 10 ml conc HCl (sp gr 1.19) and dilute to approx 50 ml.

Indicator solution: To about 300 ml metal-free water add 20.0 ml 0.9 percent Eriochrome Cyanine R and 10.0 ml 0.2 percent $ZrO(NO_3)_2 \cdot 2H_2O$ in acid. Add 70 ml conc HCl (sp gr 1.19) and 4 g $BaCl_2$. Dissolve and dilute to 1,000 ml. The solution is consumed rapidly and a larger volume is normally prepared.

Eriochrome Cyanine R, 0.9 percent: Dissolve 1.80 g tested Eriochrome Cyanine R in water and dilute to 200 ml. The National Aniline product labeled "Alizarol Cyanone RC" has been used successfully. With other products, a precipitate sometimes forms when the indicator solution is prepared.

Zirconyl nitrate, 0.2 percent in acid: Dissolve 0.40 g $ZrO(NO_3)_2 \cdot 2H_2O$ in 200 ml 50 percent HCl v/v.

D:16a–2 ZIRCONIUM-ALIZARIN METHOD

The zirconium-alizarin method is similar in substance to part ID, APHA (1955, p. 105–107) Standard Methods, and method 85, U.S. Salinity Laboratory Staff (1954, p. 147) Handbook 60.

Principle of determination

In acid solution, zirconium reacts with alizarin red S to form a reddish-violet lake. Upon addition of fluoride ion to the zirconium red lake, the more stable fluorozirconate complex ion, ZrF_6^{-2}, is formed. If the amount of zirconium and alizarin is carefully controlled, the amount of zirconium removed by fluoride subtracts from the reddish-complex color. The reaction simultaneously liberates free alizarin sulfonic acid which is yellow in acid solution. With increasing fluoride, the color change is from reddish violet to yellow green. The bleaching effect of the fluoride in the sample is compared visually with that in standard solutions. As the color approaches yellow green, the test is less sensitive; the method is most useful when the sample volume contains less than 0.10 mg of fluoride, but the range can be extended a little higher. The reaction requires several hours to reach equilibrium, and the rate is somewhat dependent on temperature. Color comparison can be made at the end of 1 hr if the reagent was added to the sample and standards within 2 min and uniform temperature is maintained.

The interference of 20 mg of calcium, 20 mg of magnesium, 100 mg of sodium, 20 mg of potassium, and 30 mg of nitrate is negligible; even higher concentrations would cause very little trouble. Up to 1.5 mg of iron does not interfere seriously, but larger amounts cannot be tolerated; 2.5 mg of manganese does not interfere. Free residual chlorine interferes but can be removed by adding sodium arsenite. Several other ions common to water interfere; some give high results and others low. Aluminum gives a negative error because of the formation of aluminum-fluoride complex, which withdraws fluoride from the reaction of zirconium. The magnitude of the interference is dependent on the quantity of both alluminum and

fluoride, but the percentage of fluoride complexed is approximately constant for a given concentration of aluminum. The ratio taken from the graph shown below (fig. 16) and multiplied by the apparent fluoride concentration will give the actual fluoride content. For fluoride concentrations not exceeding 0.10 mg and aluminum concentrations not exceeding 0.05 mg, the maximum variable errors will not exceed −0.01 mg of fluoride.

In the presence of 1.0 mg of aluminum, the ratio of actual to apparent fluoride concentration is 2.8. The interference of 0.05 mg of aluminum does not exceed the equivalent of 0.01 mg of fluoride. Hexavalent chromium causes a positive error, but 0.05 mg can be tolerated if the color comparison is made 1 hr after addition of the reagent, but only 0.01 mg of chromium can be tolerated when readings are taken between 7 and 18 hr. The interference of orthophosphate and hexametaphosphate is lessened if the reaction is allowed to go 7–18 hr; 0.20 mg can be tolerated. Below pH 4.5, hydrogen ion gives positive errors but the effect can be eliminated by raising the pH of the sample to 4.5–6.0 with sodium hydroxide.

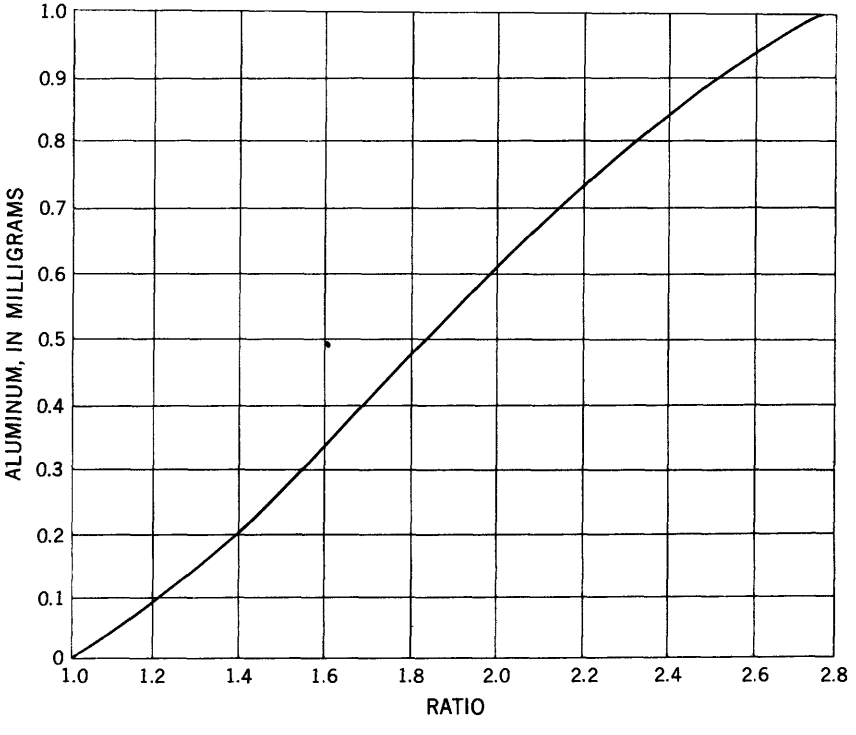

FIGURE 16.—Variation of the ratio of actual to apparent fluoride content with aluminum content.

Sulfate increases the fluoride reading, while chloride and alkalinity decrease it. These effects are substantially additive, and corrections taken from the following table can be applied to the apparent fluoride concentration. Alkalinity in excess of 10 mg of calcium carbonate can be neutralized with an equivalent quantity of nitric acid.

Corrections for fluoride determination

[mg Actual F=mg apparent F+value indicated]

Concentration of foreign ion	mg per 100 ml		
	Sulfate	Chloride	Alkalinity as $CaCO_3$
10	−0. 002		0. 005
20	−. 002	0. 002	. 011
30	−. 003	. 003	. 017
40	−. 006	. 004	. 023
50	−. 009	. 006	. 028
60	−. 011	. 007	
100	−. 018	. 012	
200		. 018	

Turbidity interferes with color precipitation, as does the natural color of the water to a lesser extent. Turbid water should be filtered through the Millipore filter membrane. Most quantitative filter papers are washed with hydrofluoric acid and can add fluoride to the sample. The effect of color can be partly compensated for by placing a tube of distilled water below the sample and an equal volume of water treated with acid below the standard and by making a color comparison through both tubes.

When color and turbidity do not interfere with color comparison, results are generally accurate and reproducible to ±0.01 mg.

When interfering substances are present in significant amounts, distillation of the fluoride from the sample as hydrofluosilicic acid (see sec. D:16a–3) followed by reaction with zirconium-alizarin reagent is preferable to corrections of apparent fluoride concentration.

Additional information on the principle of the determination is given by Lamar and Drake (1955, p. 563–572).

Apparatus and reagents

Color comparator, 3-hole, that permits longitudinal viewing of the contents of the tube.

Nessler tubes, low form, matched

Sodium arsenite, 1.0 ml≡1.0 mg Cl_2

Acid indicator reagent

Sodium fluoride, 1.00 ml=0.010 mg F^{-1}

Procedure

If the sample contains an excessive quantity of interfering materials, the fluoride should be isolated by the distillation procedure (see sec. D:16a–3).

1. Measure a volume of sample containing less than 0.12 mg F^{-1} (100.0 ml max) into Nessler tubes and adjust the volume to 100 ml.
2. Neutralize residual chlorine with $NaAsO_2$ (1.0 ml≏1.0 mg Cl_2), adding 0.1 ml in excess.
3. Prepare a blank and sufficient standards, and adjust the volumes to 100 ml.
4. Add 10.0 ml acid indicator reagent and mix.
5. Allow the solutions to stand 7–18 hr and visually compare the color of the sample with that of standards in the comparator.

Calculations

1. Correct the apparent F^{-1} concentration for sulfate, chloride, and alkalinity as required from figure 16 and the table shown under "Principle of determination."

2. $$\text{ppm } F^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \left(\begin{matrix}\text{corrected mg } F^{-1} \\ \text{in sample}\end{matrix}\right)\left(\begin{matrix}\text{aluminum} \\ \text{correction ratio}\end{matrix}\right)$$

Report fluoride concentrations of <1 ppm to 0.1 ppm and of >1 ppm to 2 significant figures only.

Preparation of reagents

Acid indicator reagent: Add 25.0 ml $ZrO(NO_3)_2$ solution to approx 100 ml water. With constant stirring, slowly add 25.0 ml alizarin solution and dilute to approx 450 ml with water and mix well. Add 500 ml 2.1*N* H_2SO_4 and dilute to 1,000 ml with water. Allow the indicator to stand approx 1 hr before use. Storage in a lightproof bottle increases the stability of the indicator. If the indicator precipitates on standing, shake it thoroughly before use.

Zirconyl nitrate (or zirconyl chloride): Dissolve 1.84 g $ZrO(NO_3)_2 \cdot 2H_2O$ or 2.22 g $ZrOCl_2 \cdot 8H_2O$ in water and dilute to 250 ml. Turbid solutions should not be filtered.

Alizarin red S: Dissolve 0.37 g alizarin monosodium sulfonate in water and dilute to 250 ml.

Sodium arsenite, 1.0 ml≏1.0 mg Cl_2: Dissolve 0.916 g $NaAsO_2$ in water and dilute to 500.0 ml.

Sodium fluoride, 1.00 ml=0.010 mg F^{-1}: Dissolve 0.2210 g NaF in water and dilute to 1,000 ml. Dilute 100.0 ml of this stock solution to 1,000 ml.

D:16a–3 ISOLATION OF FLUORIDE BY DISTILLATION

The isolation of fluoride by distillation is similar in substance to part IA, APHA (1955, p. 99–101) Standard Methods.

Principle of determination

The alkalized sample is concentrated to a small volume to facilitate quantitative steam distillation. After acidification, silver sulfate is added to prevent distillation of chloride as hydrochloric acid and the fluoride is microdistilled as hydrofluosilicic acid.

Apparatus and reagents

Distillation assembly consisting of steam-generating assembly, fluoride-distillation section, and a distillate-receiving flask. (See fig. 17.)

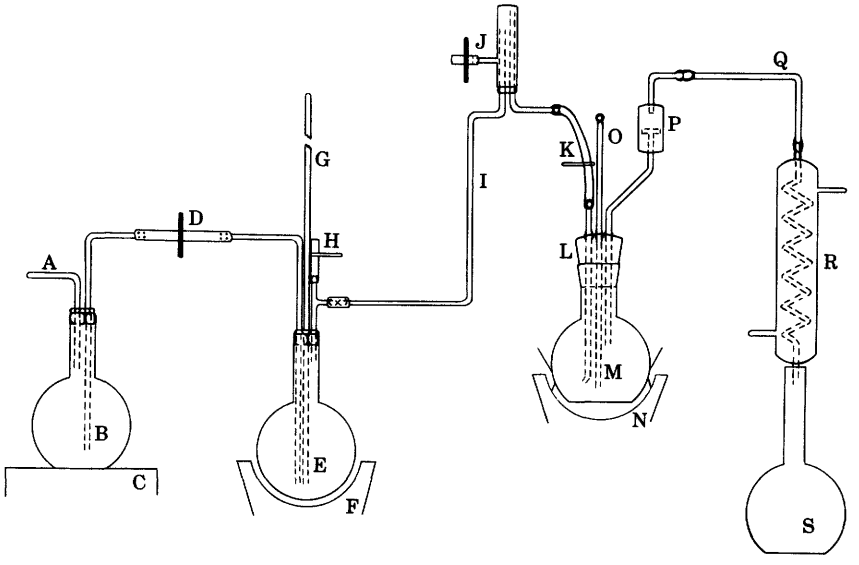

FIGURE 17.—Distillation apparatus for the isolation of fluoride.

A. Pressure-control tube.
B. Hot-water reservoir, 1 liter.
C. Hotplate.
D. Hot-water-supply tube clamp.
E. Steam generator flask, 1 liter.
F. Heating mantle.
G. Pressure-relief tube.
H. Steam-regulation tube with Hoffman clamp.
I. Glass steam line (asbestos covered).
J. Steam trap (asbestos covered), with clamp on relief-water drain.
K. Steam-inlet tube, with Hoffman clamp.
L. Fluoride-distillation flask adapter.
M. Fluoride-distillation flask, 300 ml.
N. Heating mantle with asbestos shield.
O. Thermometer, 250° C.
P. Trap.
Q. Condenser adapter.
R. Condenser.
S. Distillate-receiving flask, 200 ml.

Phenolphthalein indicator solution
Sodium hydroxide, pellets
Sulfuric acid, conc (sp gr 1.84)
Silver sulfate, powder

Procedure

1. Measure 200.0 ml of sample into the fluoride distillation flask (*M*).
2. Add a few drops of phenolphthalein indicator solution and make alkaline with NaOH. Insert some glass beads to prevent bumping.
3. Concentrate sample by evaporation to a volume of 15–20 ml. If solution tends to bump at this point, add more glass beads.
4. Cool the concentrated sample, and acidify with a few drops of conc H_2SO_4.
5. Add a slight excess of Ag_2SO_4 powder.
6. Disconnect steam-inlet tube (*K*), and in its place insert a long-stemmed separatory funnel containing 20 ml conc H_2SO_4.

7. Turn condenser on.
8. Slowly introduce 20 ml conc H_2SO_4 into distillation flask (*M*). Before removal of funnel, wash tip of funnel in flask.
9. Reconnect steam-inlet tube (*K*) to flask.
10. Pass steam through assembly by opening valve on steam trap (*J*) and closing valve on steam-regulating tube (*H*). Adjust clamp so that a pressure of 20–40 cm is maintained in the steam-generator pressure-relief tube (*G*). The distilled water in the steam generator should be made slightly alkaline with NaOH.
11. Apply even heat to distillation flask (*M*). Use an asbestos pad, and do not allow heat to be applied around sides of flask above solution.
12. Maintain a temperature of 135°–140°C in sample by means of the steam flow and heat applied to the flask.
13. Collect a sufficient volume of distillate to fill a 200-ml volumetric flask. The distillate should be free of interferences.
14. Continue as directed in sec. D : 16a–1 or 2.

Preparation of reagents

Phenolphthalein indicator solution: Dissolve 2.5 g phenolphthalein in approx 500 ml 50 percent ethyl alcohol. Neutralize with 0.02*N* NaOH.

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

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D:17 HARDNESS

Hardness of water is the property attributable to the presence of alkaline earths. Calcium and magnesium are the principal alkaline earths in natural waters, whereas strontium and barium are usually present only in small quantities.

Hardness of water results from the solution of alkaline-earth minerals from the soil and rocks, or the minerals may enter from direct pollution by wastes. Calcium and magnesium carbonates (limestone and dolomite) are prevalent in the earth's crust but are only sparingly soluble in pure water. Water that contains carbon dioxide or other acidic constituents readily dissolves carbonate minerals; in the presence of carbon dioxide the carbonates are converted to the more soluble bicarbonates.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

Many waters with a hardness of less than 200–300 ppm may derive practically all of their alkaline earths from carbonate rocks. Gypsiferous shale and evaporites often contain large quantities of more soluble sulfates and chlorides of calcium and magnesium, and waters that traverse these deposits may have a hardness of several hundred parts per million or more.

Hard water is not generally believed to have harmful effects on man, although the relation to urinary concretions is controversial. Hard water decreases the sensitivity of fish to toxic metals (California State Water Pollution Control Board, 1952, 1954, p. 265–267), but experiments with calves and chicks have indicated that those supplied with hard water develop somewhat better than those supplied with distilled water.

Hardness in conjunction with other chemical properties, such as acidity and other polyvalent cations, is an indication of the soap-consuming power of the water. Soap will not cleanse or lather until these constituents have either been neutralized or precipitated as insoluble salts of the fatty acids. Hard water is recognized by the curd formed with soap. Carbonates and some sulfates of the alkaline earths are sparingly soluble and tend to precipitate on evaporation; heating converts bicarbonate to carbonate, which precipitates calcium and magnesium carbonate in boilers, pipes, cooking vessels, etc. Calcium sulfate is also relatively insoluble and in addition to silica may comprise a portion of many incrustations found in the home or in industry.

Hardness limitations for water used in steam generation are very exacting and only 2 ppm or less is generally considered per-

missible in feed water for boilers operating at 400 psi or more. The tolerances of process water differ from one industry to another and range from less than 10 ppm to several hundred (California State Water Pollution Control Board, 1952, 1954, p. 265–267). Hard water is usually superior to soft water for irrigation, and it is often stated that hard water makes soft soil and soft water makes hard soil. (See significance of calcium and sodium in secs. D:8 and D:35, respectively.)

D:17a HARDNESS

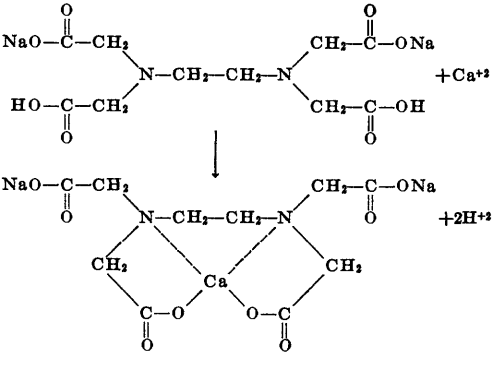
D:17a–1 COMPLEXOMETRIC METHOD

The complexometric method is similar in substance to part IC, APHA (1955, p. 112–117) Standard Methods; D 1126–53 T, ASTM (1954, p. 253–254) Manual on Industrial Water; and method 7, U.S. Salinity Laboratory Staff (1954, p. 94–95) Handbook 60.

The procedure is applicable to most natural and treated waters, but the method fails conspicuously at times with acid or polluted waters that contain excessive amounts of heavy metals.

Principle of determination

Disodium dihydrogen ethylenediamine tetraacetate (Na_2EDTA) forms a slightly ionized colorless stable complex with alkaline earth ions. The indicator Eriochrome Black T is bright blue in the absence of alkaline earths, but with them forms a deep red complex which has a higher ionization constant than the Na_2EDTA complex. Hence, by using Eriochrome Black T as an indicator, the alkaline earths can be titrated with Na_2EDTA. For example, with calcium, the reaction is:



All alkaline earths titrate approximately stoichiometrically. The titration should proceed immediately upon addition of the indicator, as the color of the solution will fade upon standing. The optimum pH of the titration is 10.4 or above.

The salt Na_2EDTA also reacts with iron, manganese, copper, lead, cobalt, zinc, and nickel. Heavy-metal interferences can usually be eliminated by complexing the metals with cyanide. In the presence of cyanide, the procedure can be used with undiluted samples for analysis of water having metal concentrations as high as 10 ppm iron, 10 ppm copper, 10 ppm zinc, 10 ppm lead.

The higher oxidation states of manganese above Mn^{+2} react rapidly with the indicator to form discolored oxidation products. Hydroxylamine hydrochloride reagent is used to reduce manganese to the divalent state. The divalent-manganese interference can be removed by addition of 1 or 2 small crystals of potassium ferrocyanide.

In the presence of high aluminum concentrations, a characteristic effect will be observed as the end point is approached. The blue color that indicates that the end point has been reached will appear and then on short standing will revert to red. This reversion should not be confused with the gradual change that normally takes place in the titrated sample several minutes after the titration has been completed. Although it has been stated that the titration cannot be used in the presence of excessive amounts of heavy metals, it should be pointed out that most heavy metal interference can be alleviated by applying conventional separations described in quantitative-analysis texts such as Hillebrand and Lundell (1929, p. 487).

Results are accurate and reproducible to ± 0.1 mg.

Additional information on the principle of the determination is given by Goetz, Loomis, and Diehl (1950) and Botha and Webb (1952).

Apparatus and reagents

Titration assembly: Some analysts prefer to use conventional lighting and hand stirring. Others have reported better results by using visual-titration assembly consisting of a motor-driven stirrer, 25–ml buret, white porcelain base buret holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from behind the beaker and in the plane of vision. The photometric titration assembly described in sec. C: 2h may also be used.

Buret, 25–ml

Hydroxylamine hydrochloride, 3 percent

Ammonium hydroxide, conc (sp gr 0.900)

Sodium cyanide, 2.5 percent

Potassium ferrocyanide, crystals

Eriochrome Black T indicator solution

Na_2EDTA, 1.00 ml = 1.00 mg $CaCO_3$

Procedure

1. Pipet a volume of sample containing less than 25 mg hardness (50.00 ml max) into a 150–ml beaker and adjust the volume to approx 50 ml.
2. Insert the beaker in the titration assembly and start the stirrer.
3. Add 1 ml 3 percent $NH_2OH \cdot HCl$.
4. Add 1 ml conc NH_4OH (if NH_4OH is not tightly stoppered it tends to lose strength, and 1 ml of weak NH_4OH will not buffer the solution to the desired pH).
5. Add 2 ml 2.5 percent NaCN (*CAUTION*—deadly poison). NaCN may be eliminated if copper, zinc, lead, cobalt, and nickel are entirely absent and if the sample contains less than 0.25 mg Fe and 0.025 mg Mn.
6. If manganese is present, add 1 or 2 small crystals $K_4Fe(CN)_6 \cdot 3H_2O$. Stir and wait at least 5 min until the $Mn_2Fe(CN)_6$ precipitates.
7. Add 2.0 ml Eriochrome Black T indicator.
8. Titrate with Na_2EDTA (1.00 ml≏1.00 mg $CaCO_3$) until blue or purple swirls begin to show. The end point is reached when all traces of red and purple have disappeared and the solution is clear blue in color. The detection of the end point may be facilitated by comparison of the titration solution with a color-free blank prepared of metal-free water and the reagent.

Calculations

$$\text{ppm Hardness as } CaCO_3 = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{ml titrant}$$

Report hardness of <1,000 ppm to whole numbers and of >1,000 ppm to 3 significant figures only.

Preparation of reagents

Hydroxylamine hydrochloride, 3 percent: Dissolve 30 g $NH_2OH \cdot HCl$ in metal-free water and dilute to approx 1 liter.

Sodium cyanide, 2.5 percent (*CAUTION*—NaCN is a deadly poison and the reagent solution must be so marked): Dissolve 2.5 g NaCN in metal-free water and dilute to approx 100 ml.

Eriochrome Black T indicator solution: Dissolve 0.40 g Eriochrome Black T in 100 ml metal-free water and dilute to approx 1 liter with 95 percent ethyl alcohol. This indicator is stable for at least 2 months. The Eastman reagent product has been found to be satisfactory.

Na_2EDTA, 1.00 ml≏1.00 mg $CaCO_3$: Dissolve 3.72 g Na_2EDTA, which has been dried overnight in an H_2SO_4 desiccator, in metal-free water and dilute to 1,000 ml. The reagent is stable for several weeks and a larger volume is usually prepared. Check the titer of the reagent by titrating 25.00 ml $CaCl_2$ (1.00 ml≏1.00 mg $CaCO_3$), as described in the procedure for sample analysis.

Calcium chloride, 1.00 ml = 1.00 mg $CaCO_3$: Suspend 1.000 g $CaCO_3$, dried at 180°C for 1.0 hr before weighing, in approx 600 ml metal-free water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 ml.

D:17a–2 CALCULATION METHOD

Principle of determination

Hardness is computed from the individual determinations of the alkaline earths. The procedure does not require the determination of each constituent because of the interference of strontium

and barium in the calcium determination. Strontium is included in the calcium values determined by any of the methods given in sec. D:8. Its inclusion is not strictly stoichoimetric or quantitative, but for practical purposes can be assumed to be so. Barium interferes with detection of the complexometric calcium end point. Hence, a good end point is a reasonable indication that barium is not present in significant quantities. When barium is present in significant quantities it should be determined separately by the procedure given in sec. D:5 and included in the calculated hardness. Some barium may be included with calcium in the single-precipitation permanganimetric calcium determination (sec. D:8a–2). Therefore, if much barium is present and this method is used for calcium, double precipitation is recommended.

Calculations

$$\text{ppm Hardness as } CaCO_3 = (\Sigma \text{ epm } Ca+Mg+Ba) \times 50.05$$

Report hardness of less than 1,000 ppm to whole numbers and of more than 1,000 ppm to 3 significant figures only.

D:17b CARBONATE AND NONCARBONATE HARDNESS

The hardness caused by the alkaline-earth equivalent of the alkalinity in a water is called carbonate hardness, and the remainder, if any, noncarbonate hardness. These terms approximate the terms "temporary hardness" and "permanent hardness," which are based on the fact that upon boiling hard water the bicarbonate is decomposed and most of the calcium corresponding to the bicarbonate is precipitated as calcium carbonate. The consumption of soap by water of a given hardness is normally the same whether the hardness is caused by carbonate or noncarbonate hardness.

D:17b–1 CALCULATION METHOD

Carbonate and noncarbonate hardness are computed from the hardness and alkalinity determinations. No negative values are reported. However, "negative noncarbonate hardness" will counteract "positive noncarbonate hardness" in a mixture of two or more waters. Hence in all calculations of averages concerned with a mixture of waters for which two or more analyses are available, carbonate and noncarbonate hardness of the mixture must be computed from the average hardness and average alkalinity and not by averaging the noncarbonate hardnesses of the individual samples.

Calculations

$$\text{ppm Noncarbonate hardness as } CaCO_3 = 50.05 \text{ (epm hardness} - \text{epm alkalinity)}$$

Computed "negative noncarbonate hardness" is reported as "0." Report noncarbonate hardness of $<1{,}000$ ppm to whole numbers and of $>1{,}000$ ppm to 3 significant figures only.

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

American Society for Testing Materials, 1954, Manual on industrial water: Spec. Tech. Pub. 148–A.

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Hillebrand, W. F., and Lundell, G. E. F., 1929, Applied inorganic analysis: New York, John Wiley and Sons, Inc.

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D:18 IODIDE

Iodide, like bromide, is a minor element in the earth's crust and is normally present in natural waters in only minute quantities. Measurable amounts may be found in some streams that receive industrial wastes, and some natural brines may contain rather high concentrations.

D:18a-1 OXIDATION METHOD

The oxidation method is similar in substance to D 1246–53 T, ASTM (1954, p. 260–263) Manual on Industrial Water, and U.S. Salinity Laboratory Staff (1954) Handbook 60.

Principle of determination

Iodide in a buffered solution is oxidized with bromine to iodate, and the excess bromine is subsequently removed with sodium formate (Kolthoff and Sandell, 1952, p. 585–605).

$$I^{-1}+3Br_2+3H_2O \rightarrow IO_3^{-1}+6HBr$$

Iodine equivalent to the iodate is then liberated by addition of potassium iodide to an acid solution.

$$IO_3^{-1}+5I^{-1}+6H^{+1} \rightarrow 3I_2+3H_2O$$

The liberated iodine is then titrated with standard thiosulfate, using starch as the indicator.

$$I_2+2S_2O_3^{-2} \rightarrow S_4O_6^{-2}+2I^{-1}$$

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interference is removed by preliminary treatment with calcium oxide.

Results are accurate and reproducible to ± 0.02 mg.

Apparatus and reagents

Iodine flasks
Buret, 10-ml
Calcium oxide, anhydrous powder
Methyl red indicator, 0.01 percent
Sulfuric acid, 20 percent v/v
Sodium acetate, 16.5 percent
Acetic acid, 12.5 percent v/v
Bromine water, saturated
Sodium formate, 50 percent
Potassium fluoride, $KF \cdot 2H_2O$, crystals
Potassium iodide, crystals
Sulfuric acid, 20 percent v/v
Sodium thiosulfate solution, 0.010*N*
Starch indicator, stable

Procedure

1. Remove soluble iron, manganese, and organic matter by adding a slight excess of CaO to approx 400 ml of sample, shake, let stand about 1 hr, and filter through dry paper. Discard the first 75 ml of filtrate.
2. Pipet a volume of the filtrate containing less than 5.0 mg I^{-1} (100.0 ml max) into a 250-ml iodine flask and adjust the volume to approx 100 ml.
3. Prepare a blank of approx 100 ml water and carry it through the procedure with the sample.
4. Add 1 drop 0.01 percent methyl red indicator and barely acidify with 20 percent H_2SO_4.
5. Add 15.0 ml 16.5 percent $NaC_2H_3O_2$.
6. Add 5.0 ml 12.5 percent $HC_2H_3O_2$.
7. Add sufficient Br_2 water to produce a light-yellow color, mix, and allow to stand 5 min.
8. Reduce the excess Br_2 by adding 50 percent $NaCHO_2$ until the yellow tinge in the sample disappears, then add an excess of 1 ml.
9. Wash down the sides of the flask with a small amount of water and blow out Br_2 vapors with a syringe and a glass tube inserted through the mouth of the flask.
10. If any iron precipitates at this point, add 0.5 g $KF \cdot 2H_2O$.
11. Add approx 1 g KI.
12. Add 10 ml 20 percent H_2SO_4.
13. Let stand 5 min in the dark.
14. Titrate the liberated I_2 with 0.010*N* $Na_2S_2O_3$, adding 2–3 ml of starch indicator as the end point is approached. Disregard the return of the blue color after the end point has been reached.

Calculations

$$\text{ppm } I^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times 21.15 \times [(\text{ml titrant} - \text{ml blank}) \times N]$$

where N = normality of thiosulfate.

Report iodide concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Methyl red indicator, 0.01 percent: Dissolve 0.01 g water-soluble methyl red in approx 100 ml of water.

Sodium acetate, 16.5 percent: Dissolve 273.5 g $NaC_2H_3O_2 \cdot 3H_2O$ in water and dilute to 1,000 ml.

Acetic acid, 12.5 percent v/v: Mix 125 ml glacial $HC_2H_3O_2$ (sp gr 1.049) with water and dilute to 1,000 ml.

Bromine water, saturated: Add to approx 250 ml water slightly more liquid Br_2 than will dissolve when shaken. Store in a glass-stoppered actinic-glass bottle.

Sodium formate, 50 percent: Dissolve 50 g $NaCHO_2$ in hot water and dilute to approx 100 ml. Prepare fresh daily.

Potassium iodide crystals, IO_3^{-1} free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 ml water, acidifying with 1 or 2 drops conc H_2SO_4 (sp gr 1.84), and adding 2–3 ml starch indicator. Immediate appearance of

a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

Sodium thiosulfate solution, 0.010*N:* Dilute 100.0 ml 0.1*N* $Na_2S_2O_3$ to 950 ml with carbon dioxide-free water and standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 hr at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 ml. Pipet 25.00 ml of the KIO_3 into a 250-ml iodine flask, then add successively 75 ml water and 0.5 g KI crystals. After solution is complete, add 10 ml 20 percent H_2SO_4. Allow the stoppered flask to stand 5 min in the dark, then titrate with $Na_2S_2O_3$ using 2 ml starch indicator as the end point is approached (light straw color).

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{ml } Na_2S_2O_3}$$

Sodium thiosulfate, 0.1*N:* Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water. Add 1 g Na_2CO_3 and dilute to approx 1,000 ml.

D:18a–2 STARCH METHOD

The starch method is extremely sensitive and is useful for the determination of trace quantities of iodide. It is also useful as a screening test or semiquantitative test in higher concentrations to select the proper sample volume for method D: 18a–1.

Principle of determination

Iodide is oxidized to iodate with bromine water (ASTM, 1954, p. 93).

$$I^{-1} + 3Br_2 + 3H_2O \rightarrow IO_3^{-1} + 6HBr$$

The excess bromine is then neutralized with phenol, and the iodate is then reacted with added iodide to produce 6 atoms of iodine for each atom of iodide originally present:

$$IO_3^{-1} + 5I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O$$

The blue color developed by the iodine with starch is compared visually by that developed in standard solutions of iodide.

Bromide does not interfere, but any agent that will oxidize iodide to iodine will interfere.

The test as usually run in test tubes is sensitive to ±0.0002 mg, but the use of Nessler tubes or other means to increase the optical viewing depth can increase the sensitivity proportionally.

Apparatus and reagents

Test tubes, matched, Pyrex
Boiling-water bath
Potassium iodide, 1.00 ml=0.10 mg I^{-1}
Sulfuric acid, 10 percent v/v
Bromine water
Phenol, solid
Potassium iodide, 5 percent
Starch indicator, stable

Procedure

1. Pipet a volume of sample containing less than 0.02 mg I^{-1} into a test tube and adjust the volume to 10.0 ml.
2. Prepare a blank of dilution water and standards containing known amounts of I^{-1} (0.02 mg max) in a 10.0–ml volume.
3. Add 1 drop 10 percent H_2SO_4.
4. Add bromine water dropwise until a slight excess has been added, as indicated by a yellowish color.
5. Heat gently over a flame or immerse in a boiling-water bath for 5 min.
6. Add a few crystals of phenol and shake until the yellow Br_2 color is entirely discharged. A white precipitate of tribromophenol may form if too much Br_2 water was added in step 4.
7. Add 1.0 ml 5 percent KI.
8. Add 1.0 ml starch indicator solution.
9. Compare the color of the sample with that of the standards.

Calculations

$$\text{ppm } I^{-1} = \frac{1{,}000}{\text{ml sample}} \times 0.1 \times \text{ml standard}$$

Preparation of reagents

Potassium iodide, 1.00 ml=0.10 mg I^{-1}: Dissolve 0.131 g KI, dried overnight in a sulfuric acid desiccator, in water and dilute to 1,000 ml.

Bromine water: Add sufficient Br_2 to approx 100 ml dilution water to produce about 1 ml excess. Store in a dark bottle protected from light. Commercial preparations of bromine water are satisfactory.

Sulfuric acid, 10 percent v/v: Mix 10 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 100 ml.

Potassium iodide, 5 percent: Dissolve 5 g KI in water and dilute to approx 100 ml.

REFERENCES

American Society for Testing Materials, 1954, Manual on industrial water: Spec. Tech. Pub. 148–A.

Kolthoff, I. M. and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis: New York, Macmillan Co., 3d ed.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkali soils: U.S. Dept. Agriculture, Agriculture Handb. 60.

D:19 IRON

Iron is one of the most abundant minerals in the earth's crust. It occurs in the dark-colored silicate minerals of igneous rocks and as sulfides and oxides. In sandstone, iron oxide and iron hydroxide are often present as cementing materials. Iron is also present as oxides and sulfides in shale. Some of the common humic complexes causing color in water may also be iron bearing.

Because iron is readily precipitated as the hydroxide, it seldom is one of the major constituents in water. The metal occurs in water in both the ferrous and ferric state. Ferrous iron is unstable in solution in the presence of oxygen.

$$2Fe^{+2}+4HCO_3^{-1}+H_2O+\tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3+4CO_2$$

If the sample is subjected to a strong reducing environment the reaction is reversed, and the solution may contain large quantities of ferrous iron. In the 6–8 pH range the amount of ferric iron in true solution is theoretically limited to the solubility of ferric hydroxide, about 4×10^{-10} to 5×10^{-6} ppm. At lower pH values, the solubility is greatly increased. Most of ferric iron in apparent solution in alkaline water is believed to be principally in the colloidal form (Kolthoff and Sandell, 1952, p. 617).

Concentrations greater than 1 ppm of iron are rare in alkaline surface water. However, higher concentrations are common in ground water and acid surface water.

Iron in concentrations much greater than 0.20 ppm is objectional in waters for public supply. The U.S. Public Health Service (1946) recommends that the sum of iron and manganese in drinking and culinary water on carriers subject to Federal quarantine regulations not exceed 0.3 ppm. These limits are not based on toxicity but on esthetic and taste considerations. Iron tends to stain laundry and porcelain, and also it can be tasted in concentrations higher than about 0.5–1.0 ppm. Livestock is sensitive to the taste of iron and may not drink water with a high iron content. Ninety-five percent of the waters that support good fish fauna in the United States have 0.7 ppm or less of iron (Ellis, 1937).

Industries' tolerance for iron varies, but concentrations exceeding 1–2 ppm are generally not satisfactory (California State Water Pollution Control Board, 1952, p. 277). It has been established that iron in irrigation water is of no practical significance to plant growth or soil texture.

D:19a IRON

The category "iron" includes ferric and ferrous iron in the ionized form and in suspension as the colloidal hydroxide. In all probability

the iron bound in the common humic complexes is also determined. Ferrous iron in solution at time of analysis can be determined by the procedure modification given in sec. D: 19b–1, and ferric iron can be computed as the difference.

D:19b–1 BIPYRIDINE METHOD

Principle of determination

The bipyridine determination utilizes the reaction between ferrous iron and 2,2′-bipyridine that yields a red complex. Hydroxylamine hydrochloride reduces ferric iron to ferrous. The color develops immediately and is stable for several hours. The color intensity is independent of pH in the range 3 to 10.

Copper reacts with bipyridine at pH values greater than 6, but the method embodies pH adjustment to about 5.5 where copper does not show appreciable interference. Silver and bismuth must be absent. The procedure can be used with undiluted samples for analysis of water having metal and anion concentrations as high as:

	Ppm		*Ppm*
Sb	20	Hg	1
Cd	50	Ni	2
Cr	20	Sn	20
Co	10	W	10
Cu	10	Zn	10

Interfering anions must be limited to the following concentrations:

	Ppm		*Ppm*
CN	10	PO_4	20
CrO_4	20	P_2O_7	20

At 520 mμ, the wavelength used in the determination, the natural color of the water contributes a measurable absorbancy and must be corrected for if the color exceeds about 50 units. This applies only to the "normal" type of yellow color found in water.

With the listed apparatus, results are accurate and reproducible to ±0.005 mg.

Additional information on the principle of the determination is given by Moss and Mellon (1942, p. 862–865).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 520 mμ
Cells: 40-mm optical depth
Phototube: Blue-sensitive
Blank: Metal-free water plus reagents
Initial sensitivity setting: 1
Slit width: 0.1 mm (approx)

The following absorbancies have been observed:

mg Fe	*Absorbancy*
0.0125	0.265
.0250	.540
.0500	1.070
.1000	2.140

Iron chloride, 1.00 ml=0.004 mg Fe
Bipyridine, 0.2 percent
Hydroxylamine-hydrochloric acid reagent
Sodium acetate, 35 percent

Procedure

Samples for the determination of iron should be treated as directed in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.10 mg Fe (25.00 ml max) into a 50-ml beaker and adjust the volume to 25.0 ml with metal-free water.
2. Prepare a blank of metal-free water and sufficient standards, and adjust the volumes to 25.0 ml.
3. Add 1.0 ml 0.2 percent bipyridine solution. Color development at this stage indicates the presence of ferrous iron.
4. Add 2.0 ml hydroxylamine-hydrochloric acid reagent, mix, and allow the solution to stand 0.5 hr.
5. Add 2.0 ml 35 percent $NaC_2H_3O_2$ and mix.
6. Determine the absorbancies of the test sample and standards against the blank and, when necessary, make correction for water color as directed in sec. C: 1a–2, method 1, to obtain true sample absorbancy.

Calculations

1. Determine mg Fe in sample from a plot of absorbancies of standards containing known amounts of constituent.

2. $$\text{ppm Fe} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg Fe in sample}$$

Report iron concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Iron chloride, 1.00 ml=0.004 mg Fe: Dilute 10.00 ml $FeCl_3$ (1.00 ml=0.400 mg Fe) to 1,000 ml with metal-free water containing 1 or 2 drops of conc HCl (sp gr 1.19).

Iron chloride, 1.00 ml=0.400 mg Fe: Weigh out 0.400 g analytical-grade iron wire which has been cleaned in dilute HCl, rinsed, and dried. Dissolve in a minimum of dilute HCl and dilute to 1,000 ml.

Bipyridine, 0.2 percent: Dissolve 1.0 g α,α'-dipyridyl in metal-free water and dilute to approx 500 ml.

Hydroxylamine-hydrochloric acid reagent: Dissolve 100 g $NH_2OH \cdot HCl$ in metal-free water. Add 40 ml conc HCl (sp gr 1.19). Add 1 g $BeSO_4 \cdot 2H_2O$. Dilute to approx 1 liter with metal-free water.

Sodium acetate, 35 percent: Dissolve 350 g $NaC_2H_3O_2$ in metal-free water and dilute to approx 1 liter.

D:19b FERROUS AND FERRIC IRON

The determined values of ferrous and ferric iron may not be truly representative of the sample at the time of collection because the oxidation states of iron are not completely stabilized by the preservative treatment prescribed in sec. A: 4d.

D:19b–1 BIPYRIDINE METHOD

The method distinguishes between ferrous and ferric iron in solution at the time of analysis but does not distinguish between the ionized and nonionized ferric iron.

Principle of determination

Ferrous bicarbonate is relatively soluble in water, as is ferrous hydroxide. Therefore, the ferrous iron remains in solution in many natural waters and can be determined by direct reaction with bipyridine in the pH range 3–10 without addition of reductant.

The chemistry of the procedure, interferences, and reagents, are identical to those described in sec. D: 19a–1.

Apparatus and reagents

Spectrophotometer, Beckman Model B:
Wavelength: 520 mμ
Cells: 40-mm optical depth
Phototube: Blue-sensitive
Blank: Metal-free water plus reagents
Initial sensitivity setting: 1
Slit width: 0.1 mm (approx)
The following absorbancies have been observed:

mg Fe	*Absorbancy*
0. 0125	0. 265
. 0250	. 540
. 0500	1. 070
. 1000	2. 140

Iron chloride, 1.00 ml=0.004 mg Fe
Bipyridine, 0.2 percent
Hydroxylamine-hydrochloric acid reagent
Sodium acetate, 35 percent

Procedure

Samples for the determination of ferrous iron should be treated as directed in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.1 mg Fe^{+2} (25.00 ml max) into a 50-ml beaker and adjust the volume to 29.0 ml with metal-free water.
2. Prepare a blank of metal-free water and sufficient standards, and adjust the volumes to 25.0 ml.
3. Add 1.0 ml bipyridine solution.

4. Treat the blank and standards *only* as follows:
   (a) Add 2.0 ml hydroxylamine-hydrochloric acid reagent, mix, and allow the solution to stand 0.5 hr.
   (b) Add 2.0 ml 35 percent $NaC_2H_3O_2$ and mix.
5. Determine the absorbancies of the test sample and standards against the blank, and, when necessary, make correction for water color as directed in sec. C: 1a–2, method 1, to obtain true sample absorbancy.

Calculations

1. Determine mg Fe^{+2} in sample from a plot of standards containing known amounts of the constituent.

2. ppm $Fe^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg Fe in sample}$

3. ppm Fe^{+3} = ppm Fe [sec. D: 19a–1] − ppm Fe^{+2}

Report iron concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Iron chloride, 1.00 ml=0.004 mg Fe: Dilute 10.00 ml $FeCl_3$ (1.00 ml=0.400 mg Fe) to 1,000 ml with metal-free water, containing 1 or 2 drops conc HCl (sp gr 1.19).

Iron chloride, 1.00 ml=0.400 mg Fe: Weigh out 0.400 g analytical-grade iron wire which has been cleaned in dilute HCl, rinsed, and dried. Dissolve in a minimum of dilute HCl and dilute to 1,000 ml.

Bipyridine, 0.2 percent: Dissolve 1.0 g α,α'-dipyridyl in metal-free water and dilute to approx 500 ml.

Hydroxylamine-hydrochloric acid reagent: Dissolve 100 g $NH_2OH \cdot HCl$ in metal-free water. Add 40 ml conc HCl (sp gr 1.19) and dilute to approx 1 liter.

Sodium acetate, 35 percent: Dissolve 350 g $NaC_2H_3O_2$ in metal-free water and dilute to approx 1 liter.

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Moss, M. L., and Mellon, M. G., 1942, Colorimetric determination of iron with 2,2′-bipyridyl and with 2,2′,2″-terpyridyl: Indus. and Eng. Chemistry, Anal. Ed., v. 14.

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D:20 LEAD

Lead is only a minor element in most natural waters, but industrial or mine and smelter effluents may contain relatively large amounts of lead. Many of the commonly used lead salts are water soluble. Lead acetate is used in printing and dyeing operations; lead chloride and sulfate are used in the manufacture of some paints; lead nitrate is used in photography, dyeing, engraving, and in the manufacture of certain explosives.

Lead is a cumulative poison to humans and animals, but the individual sensitivity differs. Lead does not have to be in solution to be toxic. Reports on human tolerance for lead vary widely, but the U.S. Public Health Service (1946, p. 12) states that lead shall not exceed 0.1 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations. The maximum safe concentration for animal watering has been reported to be 0.5 ppm (Pierse, 1938, p. 145). The toxicity of lead to fish results from a film of coagulated mucus which forms over the gills and causes suffocation. The toxicity to fish is decreased by water hardness; 50 ppm of calcium has destroyed the toxic effect of 1.0 ppm lead (Ohio River Valley Water Sanitation Commission, 1950).

D:20a-1 DITHIZONE METHOD

Principle of determination

Dithizone forms an insoluble red chelated complex with lead in basic solution. The complex is insoluble in water but soluble in chloroform or carbon tetrachloride. The color of the complex in organic solvent changes from green to red, depending on the quantity of lead present.

The procedure is extremely sensitive. so much so that measurable amounts of lead are often picked up from glassware and reagents. All glassware must be soaked and rinsed with dilute nitric acid. If the analysis is made frequently it is advisable to reserve certain cleansed glassware for lead determinations. Reagents used in large quantities must be repeatedly extracted with a carbon tetrachloride solution of dithizone until all lead is removed. Some batches of dithizone may require purification; when necessary the reagent can be purified by the ammonia-extraction method (Sandell, 1944). A reagent blank is carried through the procedure to compensate for the lead picked up from other reagents and the glassware.

Double extraction at a rather carefully controlled pH is used to isolate lead from other metals which also react with dithizone. Copper and zinc are often present with lead and are particularly troublesome. In the first extraction, ammonium citrate and cyanide are used to complex many heavy metals; hydroxylamine inhibits the oxidation of dithizone by ferricyanide formed by iron. Copper also oxidizes dithizone in a basic medium, and the color developed with dithizone is bleached if the combined concentration of copper and zinc exceeds 0.02 mg. The color of the first dithizone extract is seldom, if ever, suitable for color comparison. The lead dithizone complex from the first extraction is then decomposed with dilute nitric acid, and the lead is taken up in the aqueous phase. This procedure separates lead from iron and copper whose dithizonate is more appreciably decomposed by acid. The pH of the aqueous phase is then adjusted, and the lead complexed with dithizone.

With listed apparatus and reagents, results are usually accurate and reproducible to about ± 0.002 mg.

Additional information on the principle of the determination is given by Sandell (1944, p. 283–284) and Clifford (1943, p. 26–53).

Apparatus and reagents

Separatory funnels, 100- to 125-ml capacity, washed free of lead with dilute HNO_3.
Spectrophotometer, Beckman Model B:

Wavelength: 510 mμ
Cells: 10-mm optical depth; plastic cells are unsatisfactory because they are attacked by the organic solvent.
Phototube: Blue-sensitive
Blank: Metal-free water
Initial sensitivity setting: 1
Slit width: 0.11 mm (approx)
The following absorbancies have been observed:

mg Pb	*Absorbancy*
0.00	0.11
.01	.71
.02	1.30

Lead nitrate, 1.00 ml=10.0 mg Pb
Lead nitrate, 1.00 ml=0.002 mg Pb
Ammonium citrate, 50 percent
Hydroxylamine hydrochloride, 20 percent
Thymol blue indicator solution, 0.04 percent
Ammonium hydroxide, conc (sp gr 0.900)
Potassium cyanide, 10 percent
Dithizone, 0.005 percent in CCl_4
Ammonia-cyanide reagent, 10 percent
Nitric acid, 1 percent

Procedure

Samples for determination of lead should be collected and treated as directed in sec. A : 4d.

1. Pipet a volume of sample containing less than 0.020 mg Pb (50.0 ml max) into a separatory funnel and adjust the volume to 50 ml with metal-free water.
2. Prepare a blank of 50.0 ml metal-free water and sufficient standards, and adjust volumes to 50 ml.
3. Add 10 ml 60 percent $(NH_4)_3C_6H_5O_7$.
4. Add 2 ml 20 percent $NH_2OH \cdot HCl$.
5. Add 10 drops 0.04 percent thymol blue indicator solution and make alkaline with conc NH_4OH.
6. Add 4 ml 10 percent KCN (*CAUTION*—use hood).
7. Carefully adjust the pH of the solution to 8.5–9 (green color) with 1 percent HNO_3 (*CAUTION*—use hood).
8. Immediately extract the solution with 5-ml portions of the dithizone solution, draining off each extract into another separatory funnel until the lead is completely removed and the dithizone retains its original green color.
9. Remove the lead from the combined CCl_4 extracts by shaking the mixture with 20 ml 1 percent HNO_3. Discard the CCl_4 layer.
10. Dilute the samples and standards to 50.0 ml with 1 percent HNO_3.
11. Add 4.0 ml 10 percent ammonia-cyanide reagent.
12. Add 5.0 ml dithizone and immediately shake for 1 min.
13. Transfer part of the CCl_4 layer to the absorption cell and determine the absorbancy of samples and standards against the blank. Water or air bubbles in the CCl_4 can cause serious errors.

Calculations

1. Determine mg Pb in sample from a plot of absorbancies of standards containing known amounts of constituent.

2. $$\text{ppm Pb} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg Pb in sample}$$

Report lead concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Lead nitrate, 1.00 ml=0.002 mg Pb: The reagent should be prepared fresh immediately before use as follows: Dilute 5.00 ml $Pb(NO_3)_2$ (1.00 ml=10.0 mg Pb) to 1,000 ml with metal-free water. Dilute 10.00 ml of this solution to 250.0 ml with metal-free water.

Lead nitrate, 1.00 ml=10.0 mg Pb: Dissolve 15.986 g dry $Pb(NO_3)_2$ in metal-free water and 1 ml lead-free conc HNO_3 (sp gr 1.42) and dilute to 1,000 ml.

Ammonium citrate, 50 percent: Dissolve 50 g $(NH_4)_3C_6H_5O_7$ in approx 100 ml metal-free water. Make the solution ammoniacal (pH 8.5–9) and shake with successive portions of 0.005 percent dithizone until all the lead has been removed (green color in the final dithizone extract). Remove any excess dithizone by extracting with CCl_4.

Hydroxylamine hydrochloride, 20 percent: Dissolve 20 g $NH_2OH \cdot HCl$ in approx 65 ml metal-free water and make the solution alkaline to thymol blue with

conc NH_4OH (sp gr 0.900). Add 5 ml 4 percent sodium diethyldithiocarbamate. After a few minutes extract with successive portions of CCl_4 until no color is developed in the CCl_4 layer when the extract is shaken with a dilute solution of a copper salt. Make the $NH_2OH \cdot HCl$ solution just acid with HCl and dilute to approx 100 ml.

Thymol blue indicator solution: Grind 0.1 g thymol blue with 21.5 ml 0.01*N* NaOH. When solution is complete, dissolve to approx 250 ml with metal-free water.

Potassium cyanide, 10 percent: Dissolve 50 g KCN in metal-free water and dilute to approx 500 ml. Extract the solution with successive small portions of dithizone until all lead has been removed. Extract the dithizone from the aqueous layer with $CHCl_3$.

Dithizone, 0.005 percent: Dissolve 50 mg of diphenylthiocarbazone in approx 1 liter CCl_4. Keep the solution tightly stoppered and store in the refrigerator.

Nitric acid, 1 percent: Dilute 10 ml conc HNO_3 (sp gr 1.42) to approx 1 liter with metal-free water.

Ammonia-cyanide reagent, 10 percent: Dissolve 10 g KCN in approx 500 ml conc NH_4OH (sp gr 0.900). Add 10 g citric acid and dilute to approx 1,000 ml with metal-free water.

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Pierse, R. R., 1938, Some cases of interest met with in practice—chronic lead poisoning [in cows]: Veterinary Rec., v. 50.

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U.S. Public Health Service, 1946, Drinking water standards: U.S. Public Health Service Repts., v. 61, no. 11.

D:21 LITHIUM

Lithium is present in some minerals but is not abundant in nature. From available information, most fresh waters rarely contain lithium concentrations in excess of 10 ppm, but larger quantities may be contained in brines and thermal waters. Lithium is used in metallurgy, medicinal water, and some types of glass and storage batteries. Waste from such industries may contain lithium.

D:21a–1 FLAME-PHOTOMETRIC METHOD

The exact procedure used in the flame-photometric method is governed principally by the design and performance of the particular flame photometer used; hence, no specific directions can be given. See secs. C:1b and C:2e for a discussion of flame photometry and flame photometers. Many helpful suggestions are provided by the manufacturers of the individual instruments.

Report lithium concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

D:22 LOSS ON IGNITION

The loss of weight on ignition of residue on evaporation has frequently been taken as a measure of the organic matter in the water. By subtracting loss on ignition from the residue on evaporation a result for the so-called fixed residue is obtained. For some waters, the loss on ignition may be chiefly water that was not removed by drying at 180°C. In the majority of samples, the only value of the determination is to afford a check on the residue on evaporation and provide another reference point for comparison of the calculated dissolved solids. This latter value should lie somewhere between residue on evaporation and residue after ignition (Collins, 1928, p. 247). (See sec. C: 8b, this report.)

D:22a–1 GRAVIMETRIC METHOD

Apparatus

Radiator, consisting of a nickel dish and cover. A nichrome triangle is placed in the radiator to keep the evaporating dish containing the solids from coming in contact with the sides of the radiator.

Sulfuric acid desiccator.

Procedure

1. Determine the dissolved solids as directed in sec. D: 36a–1.
2. Preheat the radiator with a burner until the center of the bottom is cherry red.
3. Ignite the residue in the covered radiator for 3.0 min.
4. Cool in the sulfuric acid desiccator and weigh.

Calculations

$$\text{ppm Loss on ignition} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times [\text{mg}(R \text{ on } E - \text{mg}(R \text{ on } I)]$$

where

R on E = weight of residue on evaporation, and
R on I = weight of residue after ignition.

Report loss on ignition of $<1{,}000$ ppm to whole numbers and of $>1{,}000$ ppm to 3 significant figures only.

REFERENCE

Collins, W. D., 1928, Notes on practical water analysis: U. S. Geol. Survey Water-Supply Paper 596–H.

D:23 MAGNESIUM

Magnesium is relatively abundant in the earth's crust. Ferromagmasian minerals in igneous rocks and magnesium carbonate in carbonate rocks are generally considered to be the principal sources of magnesium in natural waters. Carbon dioxide plays an important role in the solution of magnesium from both silicate and carbonate minerals. Water associated with granite and silicious sand may contain less than 5 ppm of magnesium, but water from dolomite or limestone rich in magnesium may contain 10–50 ppm. Sulfates and chlorides of magnesium are very soluble, and water in contact with such deposits may contain several hundred parts per million. Magnesium is widely used in industry, and industrial wastes may add appreciable quantities to streams and ground water.

It is not believed that water can contain toxic quantities of magnesium and remain potable. Salts of magnesium act as cathartics and diuretics; the U.S. Public Health Service (1946) recommends that magnesium should not exceed 125 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations. High concentrations of magnesium may cause scouring diseases among livestock, but less than 5,000 ppm is reported to be harmless to cattle that have become accustomed to it (Frens, 1948).

Magnesium imparts the property of hardness to water and is therefore of concern to industrial users of water. Magnesium acts similarly to calcium in that it flocculates soil colloids and tends to maintain good soil structure and permeability, hence it complements calcium in consideration of sodium ratios in irrigation water.

D:23a–1 CALCULATION METHOD

The calculation method is applicable to all waters with which complexometric calcium and hardness determinations can be made satisfactorily.

Principle of determination

Equivalents per million of hardness is calculated from the hardness determination (sec. D:17a–1). The equivalents per million of calcium is subtracted and the remainder multiplied by the equivalent weight of magnesium. Strontium does not interfere because strontium is included almost quantitatively in either the complexometric or permanganimetric calcium determination. Barium interferes with both the complexometric and single-precipitation permanganimetric calcium determination but in different ways. (See sec. D:8.) In the presence of barium, magnesium should be determined by the pyrophosphate method (see sec. D:23a–2).

Nonrounded values of hardness and calcium should be used in the calculation.

With the listed apparatus and reagents, results are accurate and reproducible to about ±0.002 mg.

Calculations

1. $\text{epm Hardness} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml hardness sample}} \times \text{ml titrant} \times 0.01998$

2. $\text{epm } Ca^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml } Ca^{+2} \text{ sample}} \times (\text{ml titrant} - \text{ml blank}) \times 0.5 \times 0.0499$

3. $\text{ppm } Mg^{+2} = 12.16 \times (\text{epm hardness} - \text{epm } Ca^{+2})$

Report magnesium concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

D:23a–2 PYROPHOSPHATE METHOD

The pyrophosphate method is normally used in the analysis of brines, some acid waters, and concentrated industrial wastes in which calcium and hardness cannot be determined satisfactorily by complexometric methods.

Principle of determination

Diammonium hydrogen phosphate precipitates magnesium in ammoniacal solutions; the precipitate is ignited to magnesium pyrophosphate and weighed.

$$Mg^{+2} + NH_4^{+1} + PO_4^{-3} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O$$

$$2MgNH_4PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$$

$MgNH_4PO_4$ is one of the most soluble precipitants in gravimetric analysis. A large excess of ammonium hydroxide serves to quantitatively precipitate the magnesium as the ammonium salt. Magnesium also forms slightly soluble $MgHPO_4$ and $Mg_3(PO_4)_2$, which do not yield pyrophosphate on ignition.

Calcium, strontium, and manganese form sparingly soluble phosphates and must be absent in the precipitation media. Iron and aluminum if present may precipitate as hydroxides, and coprecipitation of silica is a potential source of error. These interferences can be eliminated or sufficiently minimized if the magnesium determination is made on the filtrate of the gravimetric calcium determination. Some magnesium may be lost by precipitation as the phosphate during precipitation of the iron and aluminum in the calcium determination, if the concentration of phosphate and arsenate exceeds that of iron and aluminum. If the original sample

contains an excess of phosphate or arsenate, sufficient iron may be added before precipitation as described in section D:8a–3 to bring down all phosphate and arsenic and leave all magnesium in solution. Coprecipitation of various salts of magnesium, ammonium, different phosphates, chlorides, and oxalates in the presence of a large excess of $(NH_4)_2HPO_4$ and large amounts of ammonium salts is so prevalent that double precipitation is usually required for accurate results. The concentration of ammonium salts is decreased by ignition of the salts in the filtrate from the calcium determination. In the first precipitation, quantitative removal of magnesium is about all that can be achieved. The precipitate is then redissolved with a minimum of acid and the magnesium reprecipitated under conditions more favorable to a precipitate of the theoretical composition uncontaminated by coprecipitants.

Ignition temperature and time are important. If the precipitate is of proper composition it need not be ignited at temperatures above 1,000°–1,050°C. However, the precipitate usually contains a little $Mg(NH_4)_4(PO_4)_2$ which decomposes on ignition to $Mg(PO_3)_2$; 5–10 min final heating at 1,150°–1,200°C will complete the conversion to pyrophosphate. However, pyrophosphate slowly liberates phosphorus pentoxide at 1,200°C, hence heating at the elevated temperature should not be prolonged. Ignition for 30 min at 1,100°C is a practical compromise and is recommended for most water analyses.

Either porcelain or platinum crucibles may be used with proper precautions. Porcelain tends to soften somewhat at 1,100°–1,200°C, and repeated heating at this temperature embrittles the crucible. If porcelain is used it is advisable to allow the crucibles to cool a little before handling them with tongs. Platinum may be used satisfactorily if the precipitate is of normal composition and if the filter paper is adequately ashed before ignition at the high temperature. $MgNH_4PO_4$ can be ignited safely in platinum, but salts that decompose to $Mg(PO_3)_2$ may cause corrosion of the platinum. The filter paper must be ashed completely in an oxidizing atmosphere before ignition to decomposition temperature. Adequate ashing is essential regardless of the crucible composition. Impurities in the precipitate lower the melting point of the pyrophosphate appreciably and may cause a fused mass at temperatures even lower than 1,100°C.

By careful work, results may be accurate and reproducible to ± 0.05. Single precipitation is sometimes used with an attendant decrease in accuracy and reproducibility.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 352–363) and Hillebrand and Lundell (1929, p. 506–516).

Apparatus and reagents

Steam bath
Ice-water bath
Crucibles, platinum or porcelain
Muffle furnace
Hydrochloric acid, conc (sp gr 1.19)
Ammonium phosphate, 10 percent
Ammonium hydroxide, conc (sp gr 0.900)
Methyl orange indicator solution
Hydrochloric acid, 1 percent v/v
Ammonium hydroxide, 8 percent v/v

Procedure

1. Dilute or concentrate the filtrate from the gravimetric Ca^{+2} determination (see sec. D: 8a–3, procedure 13) to a convenient volume. Take an aliquot containing less than 60 mg Mg^{+2} for the determination.
2. Evaporate the solution to dryness on a steam bath and decompose the ammonium salts by gentle ignition.
3. Take up the residue in approx 100 ml water containing several drops of conc HCl.
4. Place the beakers in the ice bath.
5. Add 10 ml 10 percent $(NH_4)_2HPO_4$.
6. Add conc NH_4OH slowly and with vigorous stirring until the solution is alkaline to methyl orange and until a precipitate begins to form.
7. Stir occasionally for ½ hr.
8. Add 15 ml conc NH_4OH and stir vigorously.
9. Allow the mixture to stand overnight.
10. Filter the supernatant solution through Whatman No. 42 filter paper, but retain as much precipitate as possible in the beaker.
11. Quantitatively return the precipitate to the beaker by washing the filter paper 3 times with 10-ml portions of warm 1 percent HCl. Adjust the volume to approx 100 ml with water.
12. Place the beaker in the ice bath.
13. Add 2–3 ml $(NH_4)_2HPO_4$.
14. Add conc NH_4OH slowly and with vigorous stirring until the solution is alkaline to methyl orange and the precipitate begins to form.
15. Add 5 ml conc NH_4OH and stir vigorously.
16. Allow the mixture to stand for at least 4 hr.
17. Quantitatively collect the precipitate on Whatman No. 42 filter paper.
18. Rinse the beaker and precipitate 3–5 times with 5- to 10-ml volumes of 8 percent NH_4OH.
19. Transfer the precipitate and filter to the crucible.
20. Completely ash the filter paper over an oxidizing flame. Heat the crucible gently at first and gradually increase the heat as the ashing proceeds.
21. Ignite the crucible and contents at 1,100°C for 0.5 hr.
22. Cool in a desiccator and weigh. Record the weight to the nearest 0.0001 g.

Calculations

$$\text{ppm } Mg^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } Mg_2P_2O_7 \times 0.2185$$

Report magnesium concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Ammonium phosphate, 10 percent: Dissolve 100 g $(NH_4)_2HPO_4$ in water and dilute to approx 1 liter.

Hydrochloric acid, 1 percent v/v: Mix 10 ml conc HCl (sp gr 1.19) with water and dilute to approx 1 liter.

Ammonium hydroxide, 8 percent v/v: Mix 80 ml conc NH_4OH (sp gr 0.900) with water and dilute to approx 1 liter.

Methyl orange indicator solution: Dissolve 0.05 g methyl orange in water and dilute to approx 100 ml.

D:23a–3 ERIOCHROME BLACK T METHOD

The Eriochrome Black T method is not applicable to waters containing more than 100 ppm magnesium because of the small sample volumes required.

Principle of determination

Eriochrome Black T reacts with calcium, magnesium, strontium and other metals, especially zinc, copper, manganese, and aluminum, to give a red color. The sensitivity for a particular metal varies greatly with the pH. When the alkaline-earth metals alone are considered, the indicator can be made specific for magnesium with relative ease. The color development with magnesium is good in the pH range from 9.5 to 12. Calcium and strontium do not give appreciable color until the pH rises to about 11. Calcium gives a much more intensive color than strontium; barium does not react at any pH value. Zinc, copper, manganese, and possibly other metals react over a broader pH range than magnesium. The reaction is specific for magnesium only in the absence of these metals.

For optimum reaction conditions the pH is adjusted to 10.8, at which point calcium interferes appreciably. This interference is eliminated by the use of a silicate-oxalate buffer. The oxalate complexes calcium and the silicate complexes aluminum. Permissible concentrations of other interfering ions are as follows:

	Ppm		*Ppm*
Copper	1	Calcium	100
Zinc	1	Orthophosphate	20
Iron	10	Citrate	10
Manganese	2	Residual chlorine	10
Aluminum	20	Beryllium	5

With listed apparatus, results are accurate and reproducible to ±0.005 mg.

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 520mμ
Cells: 10-mm corex
Phototube: Blue-sensitive
Blank: Distilled water plus reagents
Initial sensitivity setting: 2
Slit width: 0.5 mm (approx)
The following absorbancies have been observed:

mg Mg	*Absorbancy*
0.025	0.54
.050	1.02
.075	1.50
.100	1.88
.125	2.00

Test tubes, glass-stoppered, graduated at 50 ml
Magnesium sulfate, 1.00 ml=1.00 mg Mg^{+2}
Ammonium hydroxide, 2 percent v/v
Eriochrome Black T reagent
Silicate-oxalate buffer

Procedure

1. Pipet a volume of sample containing less than 0.100 mg Mg^{+2} (5.00 ml max) into a glass-stoppered test tube and adjust the volume to 5.0 ml.
2. Prepare a blank of dilution water and sufficient standards, and adjust the volumes to 5.0 ml.
3. Add 1.0 ml 2 percent NH_4OH.
4. Add 20 ml Eriochrome Black T reagent. Run the solution down the side of the tube so that the reagent forms a layer on top of the sample.
5. Dilute to 50 ml with silicate-oxalate buffer.
6. Invert the stoppered test tubes several times until complete homogeneity, as evidenced by the absence of striations in the alcohol-water mixture, is achieved. Allow to stand at least 15 min but no longer than 30 min.
7. Determine the absorbancy of the test sample and standards against the blank, and when necessary make correction for water color as directed in sec. C: 1a–2, method 1, to obtain the true sample absorbancy.

Calculations

1. Determine the quantity of Mg^{+2} in the sample from the plot of absorbancy of standards containing known amounts of the constituent.

2. $$\text{ppm } Mg^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } Mg^{+2} \text{ in sample}$$

Report magnesium concentrations of <10 ppm to 1 decimal place and of >10 ppm to 2 significant figures only.

Preparation of reagents

Magnesium sulfate, 1.00 ml=1.00 mg Mg^{+2}: Ignite $MgSO_4 \cdot H_2O$ in a muffle furnace at 300°C for 2 hr. Cool in a stoppered bottle in a sulfuric acid desiccator. Rapidly weigh a little more than 4.95 g into a tared weighing bottle. Return the bottle to the muffle furnace at low heat for ½ hr. Cool and adjust the salt weight to 4.950 g. Quantitatively transfer the dry salt to a 250-ml beaker. Cautiously add water and immediately cover; the hydration of the salt is rather violent. Add 1 or 2 drops conc HCl (sp gr 1.19), a few drops of $CHCl_3$, and dilute to 1,000 ml.

Ammonium hydroxide, 2 percent: Dilute 2 ml conc NH_4OH (sp gr 0.900) to approx 100 ml.

Eriochrome Black T reagent: Mix 0.40 g Eriochrome Black T with 100 ml dilution water and dilute to approx 1 liter with 95 percent ethyl alcohol.

Silicate-oxalate buffer: Dissolve 1.0 g $Na_2SiO_3 \cdot 9H_2O$ in 500 ml water. Dissolve 1.5 g $Na_2C_2O_4$ in approx 200 ml water. Mix the 2 solutions and dilute to 1,000 ml.

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D:24 MANGANESE

Manganese is much less abundant in nature than iron and is usually present in lower concentrations. Manganese may exist in natural waters in the bivalent or quadrivalent state. Manganous bicarbonate is relatively soluble but oxides readily to the quadrivalent form. Manganese dioxide and tetrahydroxide are nearly insoluble, and manganese in water under aerobic environment is probably carried primarily as a colloidal suspension. The reducing environment in bottom muds of lakes and reservoirs may promote solution of manganese from sediments. Manganese from natural sources seldom exceeds 1 ppm in water.

Waters containing less than 0.1 ppm seldom prove troublesome as public supplies, but those containing more than 0.5 ppm are reported to form objectionable deposits on cooked food, laundry, and plumbing fixtures. In concentrations that do not cause unpleasant taste, manganese is not regarded to be toxicologically significant. The U.S. Public Health Service (1946, p. 13) recommends that the concentration of iron and manganese combined not exceed 0.3 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations.

Tolerances for manganese in industrial water supplies are generally very low (less than 0.2 ppm), particularly for textile dyeing, food processing, distilling and brewing, paper, plastics, and photography. Manganese stimulates the growth of *Crenothrix* and similar organisms that are troublesome in wells and water-supply systems. Crop tolerances to manganese differ widely; concentrations ranging from 0.5 to 500 ppm have been reported to be harmful (California State Water Pollution Control Board, 1952, 1954, p. 291–292).

D:24a-1 PERMANGANATE METHOD

The Permanganate method is quite sensitive and specific for manganese but does not distinguish the forms in which manganese was originally present in the water.

Principle of determination

Manganese may be oxidized by several oxidizing agents such as sodium bismuthate, ammonium persulfate with silver nitrate, and potassium periodate. Preference is usually given potassium periodate. In hot-acid solution, periodate oxidizes manganese as follows:

$$2Mn^{+2} + 5IO_4^{-1} + 3H_2O \rightarrow 2MnO_4^{-1} + 5IO_3^{-1} + 6H^{+1}$$

Phosphoric acid is needed in solution to prevent the possible precipitation of the periodates or iodates of manganese and to decolorize ferric iron (Kolthoff and Sandell, 1952, p. 681).

Few interfering ions affect the accuracy. No interference is offered by 500 ppm of chloride, 5 ppm of organic material as sugar, 436 ppm of methyl orange alkalinity, 100 ppm of ammonium salts as nitrogen, or 5 ppm of iron. Higher concentrations of chloride may reduce the permanganate. High concentrations of organic matter not oxidized by the nitric acid treatment may be attacked by the permanganate and the color thereby bleached. Charred organic material imparts a brownish tint to the solution. Interference of high concentrations of chloride and organic matter can be minimized by first evaporating the sample almost to dryness in the presence of hydrogen peroxide and a few drops of sulfuric acid. The concentrate is then diluted in a little water before step 3 of the procedure. The interference of organic matter can also be minimized by increasing the digestion time with nitric acid, or by the addition of an excess of potassium periodate. The evaporation is best carried out on a hotplate as the acid mixture tends to bump and spatter when concentrated over a flame.

Accuracy and reproducibility of results depend on the other constituents in solution. With the listed apparatus results may be reproducible and accurate with normal water to ± 0.003 mg in the lower concentration range. With high permanganate color the final dilution error may amount to 2–3 percent.

Additional information on the principle of the determination is given by Sandell (1950, p. 312–314).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 525 mμ
Cells: 40-mm optical depth
Phototube: Blue-sensitive
Blank: Dilution water plus reagents
Initial sensitivity setting: 1
Slit width: 0.2 mm (approx)
The following absorbancies have been observed:

mg Mn	*Absorbancy*
0.05	0.31
.10	.63
.25	1.59

Graduated cylinder, 25-ml
Manganous sulfate, 1.00 ml=0.010 mg Mn
Nitric acid, conc (sp gr 1.42)
Phosphoric acid, 85 percent
Potassium periodate, crystals

Procedure

Samples for the determination of manganese should be collected and treated as directed in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.25 mg Mn (100.0 ml max) into a 250-ml Erlenmeyer flask.
2. Prepare a blank of metal-free water and sufficient standards, and adjust the volumes to approx 100 ml.
3. Add 5 ml conc HNO_3.
4. Concentrate to approx 10 ml by boiling.
5. Cool and add 5 ml conc HNO_3.
6. Add 5 ml 85 percent H_3PO_4.
7. Boil for 3–5 min but do not allow any part of the bottom of the flask to become dry. If there is any evidence of charred organic materials, continue the digestion until the solution clears.
8. Add 10 ml dilution water.
9. Add approx 0.3 g KIO_4 and boil until maximum MnO_4^{-1} color is produced; 3 min is usually sufficient. Add a little more KIO_4 to check completeness of the color development.
10. Cool the solution and decant into a 25-ml graduated cylinder. Wash the contents of the flask with several small portions of water and decant as before, taking care not to transfer any crystals of KIO_4 into the graduate. Adjust the volume to 25 ml.
11. Determine the absorbancy of the test sample and standards against the blank, and when necessary make correction for water color as directed in sec. C: 1a–2, method 3, to obtain true sample absorbancy.

Calculations

1. Determine mg Mn in sample from a plot of absorbancies of standards containing known amounts of the constituent.

2. $$\text{ppm Mn} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg Mn in sample}$$

Report manganese concentrations of <1 ppm to 1 decimal place and of >1 ppm to 2 significant figures only.

Preparation of reagents

Manganous sulfate, 1.00 ml=0.010 mg Mn: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 hr at 180°C. Dissolve 0.275 g in metal-free water containing 1 ml conc H_2SO_4 (sp gr 1.84) and dilute to 1,000 ml. Dilute 100.0 ml of this intermediate solution to 1,000 ml with metal-free water.

D:24a–2 TETRABASE METHOD

The tetrabase method is rapid, but it is limited for quantitative purposes to very low manganese levels, 0.02 ppm and below. Hence, the method is essentially a screening test to identitfy those samples that require quantitative determination by the method described in sec. D: 24a–1. It can, however, be used to estimate up to 0.1 ppm manganese.

Principle of determination

Permanganate and manganese dioxide react with tetramethyldiaminodiphenylmethane (Arnold's base, tetrabase) to give an intensely blue oxidation product. With manganese concentrations above about 0.02 ppm, the oxidation continues to a higher stage where a somewhat more stable yellow color is developed, but the stability of this color is not satisfactory for quantitative purposes. The method requires careful adjustment of the pH which is provided by the buffer. A short standing period eliminates negative tests.

Strong oxidizing agents interfere; persulfate, chromate, peroxide, and vanadate must be absent. However, false positive tests due to unsuspected oxidizing agents are rarely obtained. The method will tolerate residual chlorine up to 4 ppm. Chloride in concentrations up to 1,000 ppm does not interfere.

Additional information on the principle of the determination is given by Gates and Ellis (1947, p. 537) and Harry (1931, p. 434T).

Apparatus and reagents

Manganous sulfate, 1.00 ml=0.010 mg Mn
Manganous sulfate, 1.00 ml=0.00002 mg Mn
Test tubes, approx 1-cm diameter
Ammonium hydroxide, 0.5 percent
Potassium periodate, saturated solution
Sodium acetate buffer
Tetrabase solution

Procedure

Samples for the determination of manganese should be treated as directed in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.00002 mg Mn (1.00 ml max) into a test tube.
2. Prepare a blank of metal-free water, and sufficient standards, and adjust the volumes to 1.0 ml.
3. Add 1 drop 0.5 percent NH_4OH.
4. Add 2 drops saturated KIO_4 solution, and mix.
5. Add 1 drop sodium acetate buffer. Mix and let stand for at least 30 sec.
6. Add 1 drop tetrabase solution and mix.
7. Immediately compare the color of the sample with that of the standards. The color is stable for only 2 or 3 min.

Calculations

$$\text{ppm Mn} = \frac{1{,}000}{\text{ml sample}} \times \text{mg Mn}$$

Record the manganese concentration of the sample to 2 decimal places.

Preparation of reagents

Manganous sulfate, 1.00 ml=0.00002 mg Mn: Dilute 2.00 ml Mn (1.00 ml=0.010 mg Mn) to 1,000 ml.

Manganous sulfate, 1.00 ml=0.010 mg Mn: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 hr at 180°C. Dissolve 0.275 g in metal-free water containing 1 ml conc H_2SO_4 (sp gr 1.84) and dilute to 1,000 ml. Dilute 100.0 ml of this intermediate solution to 1,000 ml with metal-free water.

Ammonium hydroxide, 0.5 percent: Mix 1.00 ml conc NH_4OH (sp gr 0.900) with water and dilute to approx 200 ml.

Sodium acetate buffer solution: Dissolve 10 g $NaC_2H_3O_2$ in approx 75 ml metal-free water. Add 3.0 ml glacial $HC_2H_3O_2$ (sp gr 1.049) and dilute to approx 100 ml. The pH of this solution is 4.8.

Tetrabase solution: Dissolve approx 10 mg tetramethyldiaminodiphenylmethane in approx 100 ml acetone. The solution is stable for about 2 weeks.

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D:25 NITROGEN

Nitrogen makes up about 78 percent by volume of normal air at 20°C, and therefore water in equilibrium with air will contain about 15.6 ppm of dissolved nitrogen gas. Gaseous nitrogen is inert and not important in water chemistry, but the combined forms of nitrogen are. Although ammonia, nitrite, and nitrate are highly soluble, natural waters contain only small quantities, usually less than 10 ppm. Legumes take nitrogen from the atmosphere and fix it in the soil as nitrate. Most plant, animal, and bacterial life require nitrogen, and this nitrogen is constantly being converted from one form to another by tissue synthesis, metabolism, and decomposition. Bacteria are very important in converting the forms of nitrogen because some obtain their energy for life from these chemical reactions.

Both organic and inorganic nitrogen in water may result from the leaching of soils and rocks, from fertilizers, normal decomposition of plants and animals, sewage, industrial effluents, and living organisms.

D:25a AMMONIA NITROGEN

Ammonia nitrogen includes nitrogen in the form of NH_3 and NH_4^{+1}. As a component of the nitrogen cycle, it is often present in water, from natural causes, but usually in only small amounts. Ammonia is used in some water-treatment processes. More than 0.1 ppm usually indicates organic pollution (Rudolph, 1931).

There is no evidence that ammonia nitrogen in water is physiologically significant to man or livestock. Fish, however, cannot tolerate large quantities. The toxicity to fish is directly related to the amount of undissociated ammonia in solution; hence, the toxicity is dependent on the pH of the water. Ammonia decreases the ability of hemoglobin to combine with oxygen, and the fish suffocate. Although the tolerances of fish differ, 2.5 ppm of ammonia nitrogen is considered harmful in the 7.4–8.5 pH range (Ellis, Westfall, and Ellis, 1946).

The low concentrations of ammonia in natural waters are of little industrial significance, except that ammonium salts are destructive to concrete made from portland cement.

D:25a-1 NESSLERIZATION METHOD

The Nesslerization method is similar in substance to part IB, APHA (1955, p. 142–147) Standard Methods.

The method is the most sensitive of those given in this manual and is recommended for determination of low concentrations of less than 2 ppm.

Principle of determination

Ammonia is distilled from a buffered solution, and an aliquot of the distillate is then nesslerized. Essentially, nesslerization is the reaction between potassium mercuric iodide and ammonia which forms a red-brown complex of mercuric ammonobasic iodide:

$$HgI_2 \cdot 2KI + NH_3 \rightarrow Hg(NH_2)I + 2KI + HI$$

High concentrations of calcium (>250 ppm) interfere in the distillation by combining with the phosphate of the buffer and thereby lowering the pH. More than the prescribed amount of buffer can be added to maintain a pH of 7.4 ± 0.2, or the buffer can be added first and then the pH adjusted with sodium hydroxide. Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the interference of the metals is eliminated by the distillation. Sulfide can be precipitated in the distillation flask with a little lead carbonate. Several amines, organic chloramine, acetone, aldehydes, and other undefined organic compounds are reported to form off-colors or a turbidity with Nessler reagent (APHA, 1955, p. 142–147). These compounds would normally be expected only in wastes or in grossly polluted waters, but when present in troublesome quantities, the procedure described in sec. D:25a–2 is recommended for the determination of ammonia nitrogen.

All glassware should be rinsed with ammonia-free water.

With the listed apparatus, results are accurate and reproducible to ± 0.01 mg nitrogen.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 633–635).

Apparatus and reagents

Kjeldahl distillation apparatus, 1,000-ml flask
Graduated cylinders, 50-ml
Spectrophotometer, Beckman Model B:
Wavelength: 425 mμ
Cells: 40-mm optical depth
Phototube: Blue-sensitive
Blank: Ammonia-free water plus reagent
Initial sensitivity setting: 1
Slit width: 0.3 mm (approx)
The following absorbancies have been observed:

mg N	*Absorbancy*
0.02	0.24
.04	.47
.06	.70
.10	1.16

Phosphate buffer, 0.5*M*
Ammonium chloride, 1.00 ml=1.00 mg N
Ammonium chloride, 1.00 ml=0.010 mg N
Nessler reagent

Procedure

Samples for the determination of ammonia nitrogen should be treated as directed in sec. A: 4d.

1. Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace with Nessler reagent (*CAUTION*—deadly poison).
2. Measure a volume of sample containing less than 1.0 mg ammonia nitrogen (500 ml max) into the distillation flask and adjust the volume to approx 500 ml with ammonia-free water.
3. Add 10 ml phosphate buffer.
4. Immediately distill at a rate of not more than 10 ml nor less than 6 ml per minute; catch the distillate in a 200-ml volumetric flask.
5. Collect approx 190 ml of distillate, dilute to 200.0 ml with ammonia-free water, and mix.
6. Pipet an aliquot of distillate containing less than 0.1 mg ammonia nitrogen (50.00 ml max) into a graduate and adjust the volume to 50.0 ml with ammonia-free water.
7. Prepare a blank of ammonia-free water, sufficient standards, and adjust the volumes to 50.0 ml.
8. Add 1.0 ml Nessler reagent (*CAUTION*—deadly poison) and mix.
9. Allow the solutions to stand at least 10 min but not over 30 min.
10. Determine absorbancy of test sample and standards against the blank.

Calculations

1. Determine quantity of NH_3 (as N) in aliquot from a plot of absorbancies of standards containing known amounts of constituent.

2. $$\text{ppm Ammonia nitrogen as N} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \frac{\text{ml distillate}}{\text{ml aliquot}} \times \left(\frac{\text{mg N in}}{\text{aliquot}}\right)$$

   $$\text{ppm Ammonia nitrogen as } NH_4^{+1} = \text{ppm as N} \times 1.288$$

Report ammonia nitrogen concentrations of <1 ppm to 2 decimal places and of between 1 and 10 ppm to 2 significant figures only.

Preparation of reagents

Phosphate buffer, 0.5*M*: Dissolve 14.3 g KH_2PO_4 and 90.1 g $K_2HPO_4 \cdot 3H_2O$ in ammonia-free water and dilute to approx 1 liter.

Ammonium chloride, 1.00 ml=0.010 mg N: Dilute 10.00 ml NH_4Cl (1.00 ml=1.00 mg N) to 1,000 ml with ammonia-free water. Prepare fresh.

Ammonium chloride, 1.00 ml=1.00 mg N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 ml.

Nessler reagent (*CAUTION*—$HgCl_2$ is a deadly poison and the reagent must be so marked): Dissolve 61.75 g KI in approx 250 ml ammonia-free water. Cautiously add a sufficient quantity of a cold solution of $HgCl_2$, which has been saturated by boiling with an excess of the salt, to make the color a permanent bright red (about 400 ml); avoid an excess of $HgCl_2$. Dissolve the red precipitate by adding 0.75 g KI. Add 150 g KOH dissolved in 250 ml ammonia-free water and dilute to 1,000 ml. Allow the precipitate to settle and use the supernatant liquid.

D:25a–2 TITRATION METHOD

The titration method is recommended for the determination of ammonia nitrogen concentrations of above 2 ppm and for water containing substances that interfere with the Nessler reaction.

Principle of determination

Ammonia is distilled from a strongly alkalized sample and collected in boric acid. The ammonia is then titrated with standard acid. Cyanides may interfere by hydrolyzing to ammonia in presence of hot alkali:

$$CN^{-1}+2H_2O \rightarrow HCOO^{-1}+NH_3$$

This interference can, however, be greatly reduced if mercury salts are added before the alkali (Feigle, 1947, p. 183). Undissociated mercuric cyanide is stable to alkali.

Results are accurate and reproducible to ± 0.1 mg nitrogen.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 633–635).

Apparatus and reagents

Kjeldahl distillation apparatus, 500-ml flasks
Buret, 25-ml
Boric acid, 2 percent
Sodium hydroxide, 10*N*
Bromcresol green-methyl red indicator solution
Sulfuric acid, 0.0357*N*, 1.00 ml≈0.50 mg N

Procedure

Samples for the determination of ammonia nitrogen should be treated as directed in sec. A : 4d.

1. Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace with Nessler reagent (*CAUTION*—deadly poison).
2. Prepare a reagent blank of approx 250 ml ammonia-free water and carry it through the distillation procedure.
3. Pour approx 50 ml 2 percent H_3BO_3 into a 250-ml receiving flask. The tip of the delivery tube must be below the surface of the acid.
4. Measure a volume of sample containing less than 10 mg N (250.0 ml max) into the distillation flask, and adjust the volume to approx 250 ml.
5. Add 5 ml 10*N* NaOH.
6. Digest the solution over low heat for at least 15 min.
7. Gradually increase the heat and collect approx 100 ml distillate. Check the last drops of the distillate with litmus paper to be sure that no more NH_3 is coming over.
8. Titrate blank and sample with 0.0357*N* H_2SO_4 to identical colors, using 1.0 ml mixed indicator.

Calculations

$$\text{ppm Ammonia nitrogen as N} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times 0.5 \times (\text{ml titrant} - \text{ml blank})$$

$$\text{ppm Ammonia nitrogen as } NH_4^{+1} = \text{ppm as N} \times 1.288$$

Report ammonia nitrogen concentrations of between 1 and 99 ppm to 2 significant figures and of >100 ppm to 3 significant figures only.

Preparation of reagents

Boric acid, 2 percent: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to approx 1 liter.

Sodium hydroxide, 10*N*: Dissolve 400 g NaOH in ammonia-free water and dilute to approx 1 liter.

Bromcresol green-methyl red indicator solution: Dissolve 0.3 g bromcresol green and 0.1 g methyl red in approx 500 ml methyl alcohol.

Sulfuric acid, 0.0357*N*, 1.00 ml≈0.50 mg N: Mix 1.3 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 950 ml before standardization. Standardize by titrating 25.00 ml 0.0357*N* Na_2CO_3 to pH 4.5.

Sodium carbonate, 0.0357*N*: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 ml.

D:25a–3 TEST-PAPER METHOD

The test-paper method is a qualitative screening test which is useful in detecting relatively large quantities of ammonia nitrogen.

Principle of determination

Ammonia is liberated from the sample by treatment with strong alkali and heat, and is detected by litmus paper. The sensitivity of the test is dependent primarily on the quality and age of the test paper. As little as 0.1 ppm has been detected with fresh litmus paper, but as much as 1 ppm has not been detected by other batches of paper. The sensitivity of the paper should be checked with standard ammonium solutions before the test is used. Cyanides interfere as with procedure D:25a–2.

Additional information on the principle of the determination is given by Feigle (1947, p. 183).

Apparatus and reagents

Test tubes, 25-mm

Sodium hydroxide, 10*N*

Litmus paper, red

Procedure

1. Carefully measure approximately 25-ml sample into the test tube so as to leave the neck of the tube dry.
2. Add 2 ml 10*N* NaOH well below the neck of the tube.
3. Immediately loop a piece of moist litmus paper below a stopper and insert stopper in the tube.
4. Mix the contents of the tube by swirling.
5. Place the tube in a water bath at 70°–80°C for 5 min.
6. A positive test is indicated by color change of the litmus.

Preparation of reagents

Sodium hydroxide, 10*N*: Dissolve 40 g NaOH in water and dilute to approx 100 ml.

D:25b NITRATE NITROGEN

Nitrate is usually the most prevalent form of nitrogen in water because it is the end product of the aerobic decomposition of organic nitrogen. Nitrate from natural sources is attributed to the oxidation of nitrogen of the air by bacteria and to the decomposition of organic material in the soil. Fertilizers may add nitrate directly to water resources. Nitrate concentrations range from a few tenths to several hundred parts per million, but in unpolluted water seldom exceed 10 ppm. Nitrate and chloride are major components of human and animal wastes, and the occurrence of abnormally high concentrations of both constituents suggests possible pollution of the water resources.

Cyanosis due to methemoglobinemia may occur in infants whose drinking or formula water contains a high concentration of nitrates. The nitrates, when ingested, are converted to nitrites in the digestive system of some infants. The nitrite ion oxidizes hemoglobin to methemoglobin and thereby causes cyanosis. It is widely recommended that water containing more than 10–20 ppm of nitrate, expressed as nitrogen, should not be used in infant feeding (Comly, 1945).

Nitrates in large amounts are injurious to the dyeing of wool and silk and are undesirable in fermentation processes (California State Water Pollution Control Board, 1952, p. 301). At least 2 ppm of nitrate prevents intercrystalline cracking of steel in steam boilers.

D:25b-1 PHENOLDISULFONIC ACID METHOD

The phenoldisulfonic acid method is similar in substance to part IB, APHA (1955, p. 149–151) Standard Methods.

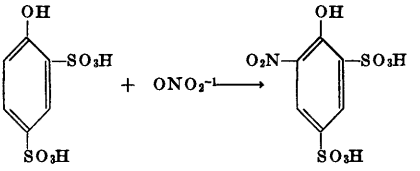
Because of its sensitivity, the method is applicable for the determination of low nitrate concentrations, generally less than 30 ppm. It is not recommended for brines and other waters that contain more than 5,000 ppm of chloride or 0.2 ppm of nitrite.

Principle of determination

The water is evaporated to dryness and the residue mixed with 1,2,4-phenoldisulfonic acid in the cold. Ammonium hydroxide is added until the nitrated sulfonic acid ring is converted to the yellow ammonium salt (see next page).

All acid samples must be neutralized or made slightly basic before evaporation to prevent loss as volatile nitric acid. Some samples lose nitrate rapidly if the heating is prolonged. Hence, the evaporation is carried almost to dryness on a steam bath; then the dish is removed from the bath and the remaining moisture allowed to evaporate.

1.



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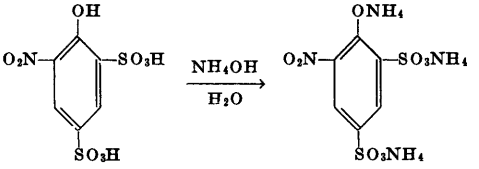


Chloride interferes by forming oxides of nitrogen in a strong acid solution, but reports of the permissible quantities differ widely; as little as 10 ppm is reported by one authority to interfere. Chloride can be precipitated with silver sulfate, but the use of this salt presents its own problems. If an excess of silver sulfate is used, the unprecipitated silver ion produces an off color and (or) turbidity. As a practical compromise between potential chloride error and silver error, chloride is not removed unless the quantity in the volume of sample exceeds about 1 mg. The precision with which the silver sulfate can be measured is limited; therefore, it is not advisable to attempt to remove less than 0.1–0.2 mg of chloride from the sample volume. The inherent manipulative difficulties of voluminous precipitate and large volumes of filtrate decrease the accuracy of the determination, and for this reason the maximum volume of silver sulfate is generally limited to about 25ml. Nitrite in excess of 0.2 ppm erratically increases the apparent nitrate concentrations. Colored materials that physically modify the color system should be absent; the sample can be decolorized with alumina suspension.

Time is an important factor in the determination. Once the procedure is started it should be carried through to the development of the color with a minimum of delay between steps. The color is stable for several hours.

With the listed apparatus and reagents and in absence of interfering substances, results are generally accurate and reproducible to ± 0.005 mg of NO_3^{-1} (0.001 mg N). For some water the error may be appreciably greater.

Additional information on the principle of the determination is given by Chamot and Pratt (1909, 1911) and Taras (1950, p. 1020).

Apparatus and reagents

Evaporating dishes, porcelain
Steam bath
Graduated cylinders, 50-ml

Spectrophotometer, Beckman Model B:
Wavelength: 410 mμ
Cells: 40-mm optical depth
Phototube: Blue-sensitive
Blank: Dilution water carried through the procedure
Initial sensitivity setting: 2
Slit width: 0.2 mm (approx)
The following absorbancies have been observed:

mg NO_3	*Absorbancy*
0.08	0.66
.16	1.31

Silver sulfate, 1.00 ml≏1.00 mg Cl^{-1}
Aluminum hydroxide suspension
Potassium nitrate, 1.00 ml=0.016 mg NO_3^{-1}
Phenoldisulfonic acid
Ammonium hydroxide, conc (sp gr 0.900)

Procedure

If distribution of nitrogen in the nitrogen cycle is to be determined, the sample should be treated as directed in sec. A: 4d. Highly colored water may be decolorized with aluminum hydroxide suspension.

1. Pipet a volume of sample containing less than 0.16 mg NO_3^{-1} (10.00 ml max) into a small evaporating dish.
2. If the Cl^{-1} in the test sample exceeds about 1.0 mg, precipitate all but 0.1–0.3 mg Cl^{-1} with appropriate volume of Ag_2SO_4 (1.00 ml≏1.00 mg Cl^{-1}). Cover the dish and set aside in a dark place overnight to obtain a filterable mass of precipitate, or the precipitate can be immediately flocculated with aluminum hydroxide suspension. Filter the suspension through Whatman No. 42 filter paper and thoroughly wash the precipitate with hot water, combining the filtrate and washings.
3. Prepare a blank and sufficient standards, and adjust the volumes to 10 ml.
4. Evaporate almost to dryness on a steam bath.
5. Within the next 5 min add 1.0 ml phenoldisulfonic acid to the cooled dry residue.
6. Immediately grind the residue and acid.
7. Cautiously dilute to approx 20 ml and mix.
8. Add dropwise and with constant stirring conc NH_4OH until full color is developed, then add approx 1 ml excess.
9. Transfer the solution to a graduate, dilute to 50.0 ml, and mix.
10. Determine the absorbancies of test sample and standards against the blank.

Calculations

1. Determine quantity of NO_3^{-1} in test sample from a plot of absorbancies containing known amounts of the constituent.
2. $$\text{ppm } NO_3^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } NO_3^{-1} \text{ in sample}$$

   $$\text{ppm Nitrate as N} = \text{ppm } NO_3^{-1} \times 0.226$$

Report nitrate (NO_3^{-1}) concentrations of <10 ppm to 1 decimal place and of >10 ppm to 2 significant figures only.

Preparation of reagents

Silver sulfate, 1.00 ml≈1.00 mg Cl^{-1}: Dissolve 4.3972 g Ag_2SO_4, dried overnight over H_2SO_4, in water and dilute to 1,000 ml. Check the titer by titrating 25.00 ml NaCl (1.00 ml=1.00 mg Cl^{-1}) using K_2CrO_4 indicator (see sec. D:10a–1). Store in lightproof bottle.

Sodium chloride, 1.00 ml=1.00 mg Cl^{-1}: Dissolve 1.6484 g NaCl, which has been dried at 900°C for ½ hour, in water and dilute to 1,000 ml.

Aluminum hydroxide suspension: Dissolve 125 g $KAl(SO_4)_2 \cdot 12H_2O$ or $NH_4Al(SO_4)_2 \cdot 12H_2O$ in approx 1 liter water. Precipitate $Al(OH)_3$ by cautiously adding conc NH_4OH (sp gr 0.900). Wash the precipitate by successive additions of water and decantation until the washes contain less than 0.04 ppm NO_3^{-1}. Keep the solution basic during the washing.

Potassium nitrate, 1.00 ml=0.016 mg NO_3^{-1}: Dissolve 2.6100 g KNO_3, dried overnight over H_2SO_4, in water and dilute to 1,000 ml. Dilute 10.00 ml of this intermediate solution to 1,000 ml.

1,2,4–phenoldisulfonic acid: (*CAUTION*—use hood). Dissolve 113.5 g phenol (¼-lb bottle) by placing the bottle in warm water. Pour the dissolved phenol slowly and with constant stirring into 766 ml conc H_2SO_4 (sp gr 1.84). Slowly add 255 ml fuming H_2SO_4 (20 percent SO_3) and stir well. Heat the mixture 2 hr on a steam bath. Care must be taken in the preparation of phenoldisulfonic acid to be sure that only 1,2,4–acid and not ortho or para mono acids are produced. The ortho and para acids give many side reactions with nitrate.

D:25b–2 REDUCTION METHOD

The reduction method is recommended for water that contains more than about 30 ppm of nitrate or more than 5,000 ppm of chloride or 0.2 ppm of nitrite.

Principle of determination

Nitrate is reduced to ammonia by aluminum and zinc in alkaline solutions. The ammonia is distilled, collected in boric acid, and titrated with standard acid.

The sample must be free of ammonia or ammonium salts. The residue from the ammonia nitrogen determinations (see sec D:25a–1) can be used, or the ammonia can be volatilized from a fresh sample buffered to pH 7.4. Nitrite also is reduced to ammonia during the digestion, and the results must be corrected for significant quantities of nitrite. Nitrogenous organic matter is not readily decomposed in hot alkali and adds little, if any, nitrogen to a measured quantity of nitrate.

The reduction is not instantaneous, and recovery may not be quantitative if the digestion time is insufficient.

Results are accurate and reproducible to ±0.1 mg N (0.5 mg NO_3^{-1}).

Additional information on the principle of the determination is given by the Association of Official Agricultural Chemists (1945).

Apparatus and reagents

Kjeldahl distillation apparatus, 500-ml flask

Buret, 25-ml

Phosphate buffer (see sec. D : 25a–1)
Boric acid, 2 percent
Devarda alloy
Sodium hydroxide, 10*N*
Sulfuric acid, 0.0357*N*, 1.00 ml≈0.50 mg N
Bromcresol green-methyl red indicator solution

Procedure

If the distribution of nitrogen in the nitrogen cycle is to be determined, samples for the determination of nitrate should be treated as directed in sec. A : 4d.

1. Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace of ammonia when tested with Nessler reagent (*CAUTION*—deadly poison).
2. Dilute the residue of the ammonia nitrogen distillation (see sec. D : 25a–1) to a convenient volume and transfer an aliquot containing less than 50 mg nitrate and nitrite combined (250 ml max) to a Kjeldahl flask and adjust the volume to approx 250 ml, or buffer a suitable volume of sample to pH 7.4 with phosphate buffer and evaporate to approx 20 percent of the original volume to drive off ammonia nitrogen; cool and adjust the volume to approx 250 ml with ammonia-free water.
3. Pour approx 50 ml 2 percent H_3BO_3 into a 250-ml receiving flash. The tip of the delivery tube must be below the surface of the acid.
4. Add approx 3 g Devarda alloy.
5. Add 5 ml 10*N* NaOH down the side of the flask and immediately connect the flask to the distillation apparatus.
6. Mix the contents of the flask by swirling.
7. Digest the solution over low heat for about 15 min.
8. Gradually increase the heat and collect approx 100 ml distillate.
9. Prepare a reagent blank of approx 250 ml ammonia-free water and carry it through the distillation procedure.
10. Titrate the blank and the sample with 0.0357*N* H_2SO_4 to identical colors, using 1.0 ml mixed indicator.

Calculations

$$\text{ppm Nitrate as N} = \left[\frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times 0.5\ (\text{ml titrant} - \text{ml blank})\right] - \left(\frac{\text{ppm } NO_2^{-1}}{\text{as N}}\right)$$

$$\text{ppm } NO_3^{-1} = \text{ppm as N} \times 4.427$$

Report nitrate (NO_3^{-1}) concentrations of <999 ppm to whole numbers and of >999 ppm to 3 significant figures only.

Preparation of reagents

Boric acid, 2 percent: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to approx 1 liter.

Bromcresol green-methyl red indicator solution: Dissolve 0.3 g bromcresol green and 0.1 g methyl red in approx 500 ml methyl alcohol.

Sodium hydroxide, 10*N*: Dissolve 400 g NaOH in ammonia-free water and dilute to approx 1 liter.

Sulfuric acid, 0.0357N, 1.00 ml≈0.50 mg N: Mix 1.3 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 950 ml before standardization. Standardize by titrating 25.00 ml 0.0357*N* Na_2CO_3 to pH 4.5.

Sodium carbonate, 0.0357*N*: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 ml.

D:25c NITRITE NITROGEN

Nitrite is unstable in the presence of oxygen and is, therefore, absent or present in only minute quantities in most natural waters under aerobic conditions. The presence of nitrite in water is sometimes an indication of organic pollution.

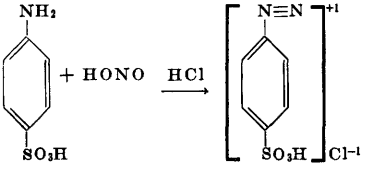
Recommended tolerances of nitrite in domestic water supplies differ widely. A generally accepted limit is 2 ppm, but as little as 0.1 ppm has been proposed (California State Water Pollution Control Board, 1952, p. 303). Nitrite is undesirable in water used in dyeing wool and silk and in brewing.

D:25c–1 DIAZOTIZATION METHOD

Principle of determination

The diazotization method is based on a diazotization reaction with nitrite and sulfanilic acid followed by coupling with alpha napthylamne.

1.



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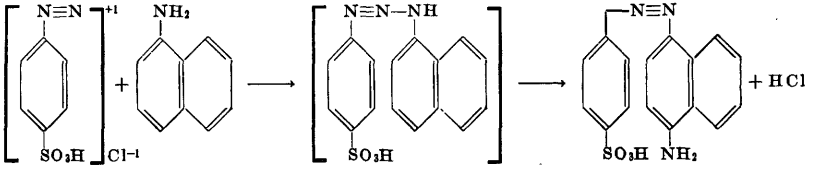

Red azo dye

The development of the azo dye is affected by several variables including temperature, pH, standing time, and the degree of purity of the reagents. In addition, the azo dye is photosensitive, and, therefore, the solutions must be shielded from direct sunlight during the development of the color. Ordinary artificial light usually has no effect, although close fluorescent lamps may be detrimental. The effect of pH is probably the most significant. The diazotization step requires strong acid, while the coupling step proceeds best at moderate acidities. Therefore, at the completion of the diazotization stage, sodium acetate is introduced to raise the pH. At room temperature, the diazotization requires about 3 min for practical

completion. After 10 min, the diazotization product shows significant decomposition.

The common anions, with the exception of iodide, are not known to interfere. Iodide should not exceed 0.1 mg. Lead, zinc, and manganese are considered not to interfere. Copper interferes, and the quantity in the test sample should not exceed 0.05 mg. Disodium ethylenediamine tetraacetate effectively complexes iron to prevent its interference.

With the listed apparatus, results are accurate and reproducible to ± 0.0002 mg of NO_2^{-1}.

Additional information on the principle of the determination is given by Karrer (1950, p. 481–497) and Mellan (1941).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 520 mμ
Cells: 10-mm optical depth
Phototube: Blue-sensitive
Blank: Distilled water plus reagents
Initial sensitivity setting: 1
Slit width: 0.2 mm (approx)
The following absorbancies have been observed:

mg NO_2^{-1}	*Absorbancy*
0.01	0.73
.02	1.40

Na_2EDTA, 0.5 percent
Sulfanilic acid solution, 0.6 percent
Sodium nitrite, 1.00 ml=0.001 mg N
Alpha napthylamine hydrochloride, 0.6 percent
Sodium acetate buffer, 27 percent

Procedure

Samples for the determination of nitrite should be treated as directed in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.02 mg NO_2^{-1} (10.00 ml max) into a small beaker or test tube and adjust the volume to 10.0 ml.
2. Prepare a blank and sufficient standards, and adjust the volumes to 10.0 ml.
3. Add 0.2 ml 0.5 percent Na_2EDTA solution
4. Add 0.2 ml sulfanilic acid and mix.
5. Let stand for 5.0 min.
6. Add 0.2 ml 0.6 percent alpha napthylamine hydrochloride.
7. Add 0.2 ml 27 percent sodium acetate buffer and mix.
8. Allow the liquids to stand at least 10 min and no longer than 20 min.
9. Determine the absorbancies of the test sample and standards against the blank, and, when necessary, make correction for water color as directed in sec. C: 1a–2, method 1.

Calculations

1. Determine quantity of NO_2^{-1} in test sample from a plot of absorbancies containing known amounts of the constituent.

2. ppm $NO_2^{-1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } NO_2^{-1}$ in sample

ppm Nitrite as N = ppm $NO_2^{-1} \times 0.304$

Report nitrite (NO_2^{-1}) concentrations of <1 ppm to 2 decimal places and of >1 ppm to 2 significant figures only.

Preparation of reagents

Na_2EDTA, 0.5 percent: Dissolve 5 g disodium salt in water and dilute to approx 1,000 ml.

Sulfanilic acid (4-aminobenzenesulfonic acid), 6 percent: Dissolve 6 g sulfanilic acid in about 700 ml of hot water. Cool the solution. Add 200 ml conc HCl (sp gr 1.19). Dilute to approx 1,000 ml.

Sodium nitrite, 1.00 ml=0.100 mg N: Dissolve 0.4926 g $NaNO_2$ in water and dilute to 1,000 ml.

Alpha-napthylamine hydrochloride: The commercially available reagent is of variable composition. The reagent should be purchased in small bottles, stored in a desiccator, and kept in the refrigerator. The pure reagent is white and comparatively odorless. If the reagent turns dark, it should be purified by recrystallization before use. To recrystallize 4 or 5 g., dissolve the material in 100 ml boiling water plus 5 ml conc HCl (sp gr 1.19). Add 2 g activated carbon, stir, and filter rapidly through a Buchner funnel fitted with filter paper. Cool in ice and collect the purified crystals. To prepare the solution, dissolve 0.6 g of the amine salt in water, add 1 ml HCl, and dilute to 100 ml.

Sodium nitrite, 1.00 ml=0.001 mg N: Add 1 ml $CHCl_3$ to 10.00 ml $NaNO_2$ (1.00 ml=0.100 mg N) and dilute to 1,000 ml with water. The standard should be used for the preparation of the calibration curve without delay.

Sodium acetate buffer solution, 27 percent: Dissolve 270 g $NaC_2H_3O_2 \cdot 3H_2O$ in water and dilute to approx 1,000 ml.

D:25d ORGANIC NITROGEN

Organic nitrogen includes all nitrogenous organic compounds, such as amino acids, polypeptides, and proteins. It is present naturally in all surface waters as the result of inflow of nitrogenous products from the watershed and the normal biological life of the stream. Effluents of sewage and waste from slaughter houses and chemical plants often contain nitrogen in varying combinations. Organic nitrogen in unpolluted ground water is usually very low.

Organic nitrogen is not pathologically significant but is sometimes an indication of pollution. Organic nitrogen is important to considerations involving aquatic biology.

D:25d–1 KJELDAHL METHOD

The Kjeldahl method is similar in substance to part I, APHA (1955, p. 155–156) Standard Methods.

Principle of determination

Organic nitrogen is degradated to the ammonium ion by digestion with sulfuric acid in the presence of copper sulfate, which acts as a catalyst. The solution is made alkaline with sodium hydroxide, and

the free ammonia is distilled off and Nesslerized. The color developed is proportional to the organic-nitrogen content.

Nitrate and nitrite do not interfere. The effect of ammonium ions and ammonia is strictly additive. Therefore, the organic nitrogen is normally made on the residue of the ammonia nitrogen determination (see sec. D:25a–1). If the residue from the method described in sec. D:25a–2 is used, additional sulfuric acid should be added for the digestion.

Calcium, magnesium, iron, and sulfide interfere with the Nesslerization, but the interference of the metals is eliminated by the distillation. Sulfides can be precipitated in the distillation flask with a little lead carbonate before addition of sodium hydroxide. Several amines, organic chloramines, acetone, aldehydes, and other undefined organic compounds are reported to form off-color or turbidity with Nessler reagent (APHA, 1955, p. 155–156). These compounds would normally be expected only in wastes and polluted waters, but, when present in troublesome quantities, the ammonia can be collected in boric acid and titrated with standard acid rather than nesslerized (see sec. D:25a–2). Cyanides are liberated during acid digestion and do not interfere.

All glassware should be rinsed with ammonia-free water. With the listed apparatus results for organic nitrogen in solution are accurate and reproducible to ±0.02 mg of nitrogen. The adequacy of results for total organic nitrogen in solution and suspension will depend on the completeness of the acid degradation, but will usually approach that obtained with soluble nitrogenous compounds.

Additional information on the principle of the determination is given by Kolthoff and Sandell, 1952, p. 537–538).

Apparatus and reagents

Kjeldahl distillation apparatus, 1,000-ml flask
Graduated cylinders, 50-ml
Spectrophotometer, Beckman Model B:
Wavelength: 425 mμ
Cells: 40-mm optical depth
Phototube: Blue-sensitive
Blank: Ammonia-free water plus reagents
Initial sensitivity setting: 1
Slit width: 0.3 mm (approx)

The following absorbancies have been observed:

mg N	*Absorbancy*
0.02	0.24
.04	.47
.06	.70
.10	1.16

Phosphate buffer, 0.5*M*
Sulfuric acid, conc (sp gr 1.84)
Copper sulfate, 10 percent
Sodium hydroxide, 10*N*
Ammonium chloride, 1.00 ml=0.010 mg N
Nessler reagent

Procedure

Samples for the determination of organic nitrogen should be treated as directed in sec. A : 4d.

1. Free the distillation apparatus of ammonia by boiling ammonio-free water until the distillate shows no trace with Nessler reagent (*CAUTION*—deadly poison).
2. Take the residue of the ammonia nitrogen determination for this determination. Or, buffer a volume of sample containing less than 1.0 mg N (500.0 ml max) to pH 7.4 with phosphate buffer and evaporate to approx 20 percent of original volume to drive off ammonia nitrogen.
3. Cool and add 10 ml conc H_2SO_4.
4. Add 1 ml 10 percent $CuSO_4$.
5. Digest under a hood until copious fumes are given off and the liquid becomes colorless or pale yellow.
6. Cool and dilute to approx 300 ml with ammonia-free water.
7. Add 50 ml 10*N* NaOH cautiously down the side of the flask.
8. Immediately connect the flask to the distillation apparatus and cautiously mix the contents by swirling gently.
9. Distill at a rate of no more than 10 ml nor less than 6 ml per min; catch the distillate in a 200-ml volumetric flask.
10. Collect approx 190 ml distillate, dilute to 200.0 ml with ammonia-free water, and mix.
11. Pipet an aliquot of distillate containing less than 0.1 mg ammonia nitrogen (50.0 ml max) into a graduate and adjust the volume to 50.0 ml with ammonia-free water.
12. Prepare a collorimetric blank of ammonia-free water and sufficient standards, and adjust volumes to 50.0 ml.
13. Add 1.0 ml Nessler reagent (*CAUTION*—deadly poison) and mix.
14. Allow the solutions to stand at least 10 min but not more than 30 min.
15. Determine the absorbancies of the aliquot and standards against the colorimetric blank.

Calculations

1. Determine a reagent blank for each new batch of H_2SO_4 by taking 300 ml ammonia-free water through the entire procedure.

$$\text{mg Reagent blank} = \text{mg N per 10 ml } H_2SO_4 \times \frac{\text{ml aliquot}}{\text{ml distillate}}$$

2. Determine the quantity of nitrogen in the aliquot from a plot of absorbancies of standards containing known amounts of the constituent.

3. $$\text{ppm Organic nitrogen as N} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \frac{\text{ml distillate}}{\text{ml aliquot}} \left[\left(\begin{matrix} \text{mg N in} \\ \text{aliquot} \end{matrix} \right) - \left(\begin{matrix} \text{mg reagent} \\ \text{blank} \end{matrix} \right) \right]$$

Report organic nitrogen concentrations of <1 ppm to 2 decimal places, of between 1 and 10 ppm to 1 decimal place, and of >10 ppm to 2 significant figures only.

Preparation of reagents

Phosphate buffer, 0.5*M*: Dissolve 14.3 g KH_2PO_4 and 90.1 g $K_2HPO_4 \cdot 3H_2O$ in ammonia-free water and dilute to approx 1 liter.

Copper sulfate, 10 percent: Dissolve 10 g $CuSO_4 \cdot 5H_2O$ in ammonia-free water and dilute to approx 100 ml.

Sodium hydroxide, 10*N*: Dissolve 400 g NaOH in water and dilute to approx 1 liter.

Ammonium chloride, 1.00 ml=0.010 mg N: Dilute 10.00 ml NH_4Cl (1.00 ml=1.00 mg N) to 1,000 ml with ammonia-free water. Prepare fresh.

Ammonium chloride, 1.00 ml=1.00 mg N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 ml.

Nessler reagent (*CAUTION*—$HgCl_2$ is a deadly poison and the reagent must be so marked): Dissolve 61.75 g KI in approx 250 ml of ammonia-free water. Cautiously add a sufficient quantity of a cold solution of $HgCl_2$, which has been saturated by boiling with an excess of the salt, to make the color a permanent bright red (about 400 ml); avoid an excess of $HgCl_2$. Dissolve the red precipitate by adding 0.75 g KI. Add 150 g KOH dissolved in 250 ml ammonia-free water and dilute to 1,000 ml. Allow the precipitate to settle and use the supernatant liquid.

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D:26 OILS AND WAXES

Potential contributors of oil to water are engaged in production, transportation, handling, and use of oil and petroleum products, such as ships, oil wells, oil-loading points, refineries, railroads, civic dumps, salvage dumps, garages, and many industries. Some oil in natural waters may be derived from the decomposition of plankton or higher forms of aquatic life (Galtsoff, 1936, p. 550–555). Heavy oils, greases, and waxes are somewhat insoluble in water, but they may be emulsified or saponified by detergents, alkalis, or other chemicals. Oil films interfere with gas exchange, coat bodies of birds and fish, exert a direct toxic action on some organisms as a result of water-soluble components, and interfere with fish-food organisms and the natural food cycle. Oils from surface films become adsorbed on clay particles, settle to the bottom, and remain a source of pollution because they may be stirred up and float again or release toxic principles (Galtsoff, 1936, p. 550–555).

The principal objection to oils in water for domestic use is the resulting disagreeable taste and odor. Aging causes petroleum odors to become musty, probably as a result of biochemical decomposition (California State Water Pollution Control Board, 1952, p. 307).

Oils are detrimental to any industrial process water that is used in food and beverage preparation. The Portland Cement Association (1948) recommends that water used for mixing concrete be free of oil.

Oil pollution is harmful to marine life in at least four ways: through the formation of surface films, by emulsification, by sedimentation and coating of benthal organisms, and by toxic action of water-soluble principles (Gage, 1924, p. 237). Also, oil may affect the taste of fish.

D:26a–1 WET-EXTRACTION METHOD

The wet-extraction method is applicable to waters containing small amounts of oil, grease, wax, and other diethyl ether-soluble substances in solution, suspension, or attached to sediment.

The wet-extraction method is similar in substance to part I 18B, APHA (1946, p. 42) Standard Methods.

Principle of determination

Dissolved or emulsified oils, greases, waxes, and other extractable substances are extracted from water by diethyl ether. The diethyl ether is evaporated and the residue dried and weighed. Volatile oils may be lost in the process.

Apparatus and reagents

Steam bath

Separatory funnel, "No-lub" glassware is recommended (one source of supply is the Scientific Glass Co.)

Diethyl ether

Procedure

Samples for the determination of oils and waxes must be treated in accordance with directions given in sec. A: 4d.

1. Mark the sample bottle at the water-plus-oil line and pour the treated sample into the separatory funnel.
2. Thoroughly wash the sample bottle with ether and add washings to sample in separatory funnel. Extract the sample with a sufficient number (minimum of 2) of 25-ml portions of diethyl ether.
3. The ether extractions are collected in a previously dried and tared evaporating dish or beaker.
4. Evaporate just to dryness on a steam bath.
5. Dry in a desiccator for 1 hr and weigh.
6. Determine the blank correction by weighing the residue of a portion of ether equal to that used for extracting the sample.

Calculations

$$\text{ppm Oils and waxes} = \frac{1{,}000}{\text{ml sample}} \times (\text{mg sample residue} - \text{mg blank})$$

Report oil and wax concentrations of $<1{,}000$ ppm to whole numbers and of $>1{,}000$ ppm to 3 significant figures only.

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D:27 OXYGEN CONSUMED

The oxygen-consumed determination is a measure of the readily oxidizable material in the water and furnishes an approximation of the minimum amount of organic and reducing material present. In reality, the term "oxygen consumed" is defined by the method used for its determination. In the test given below it is defined as the amount of oxygen used by the sample when digested 30 minutes in a boiling-water bath with an excess of potassium permanganate in an acid solution. Oxygen consumed may be correlated with natural-water color or with some carbonaceous organic pollution from sewage or industrial wastes.

Tolerances for oxygen consumed in feed water for low- and high-pressure boilers are 15 and 3 ppm, respectively (Northeast Water Works Association, 1940). Wash water containing more than 8 ppm has been reported to impart a bad odor to textiles; concentrations for water used in beverages and brewing range from 0.5 to 5.0 ppm (California State Water Pollution Control Board, 1952, 1954).

D:27a-1 PERMANGANIMETRIC METHOD

Principle of determination

The sample is acidified and digested with potassium permanganate for 30 minutes in a boiling-water bath, during which time reducing substances are oxidized along with part of the carbonaceous material. The remaining permanganate is reacted with a volume of oxalate equivalent to the permanganate originally added, and the excess oxalate is determined by back titration with permanganate. The permanganate required in the back titration is therefore equivalent to the oxygen consumed. Nitrogen is not oxidized by the permanganate. The carbon in nitrogenous organic materials such as proteins is not as easily oxidized as that in simple carbonaceous materials, and the results may not therefore include the effect of all carbon. Similarly, some organic matter is fairly stable and may not react completely under the conditions of the test. Chloride will partially react with permanganate, and waters containing more than 1,000 ppm of chloride will give significantly higher oxygen-consumed values.

In hot acid solution, permanganate slowly decomposes with the evolution of oxygen, and the blank must be run with the sample to evaluate the decomposition of permanganate; the blank also compensates for any oxidizable material in the acid.

To obtain reproducible results, it is essential that the directions be followed explicitly.

Additional information on the principle of the determination is given by APHA (1946, p. 122–124) and Treadwell and Hall (1935, p. 543).

Apparatus and reagents

Buret, 25-ml
Potassium permanganate, 1.00 ml≏0.100 mg O_2
Sulfuric acid, 25 percent v/v
Sodium oxalate, 1.00 ml≏1.00 ml $KMnO_4$ (1.00 ml≏0.100 mg O_2)

Procedure

1. Pipet a volume of sample containing less oxygen-consuming material than can be oxidized by 7 ml $KMnO_4$ (100.0 ml max) into a 250-ml Erlenmeyer flask and adjust the volume to approx 100 ml.
2. Prepare a blank of approx 100 ml dilution water.
3. Add 10.00 ml $KMnO_4$ (1.00 ml≏0.100 mg O_2).
4. Add 10 ml 25 percent H_2SO_4, and mix.
5. Place the flasks in a boiling-water bath and digest for 30 min. The flasks must be at such depth that the surface of the sample is below the surface of the boiling water throughout the digestion period. This step is critical and determines the reproducibility of the determination. It is essential to maintain constant boiling conditions if determinations between different sets of samples are to be comparable. That is, the water bath should be at full boil before the samples are introduced. The water bath should be large enough to accommodate all the samples plus the blank. Porcelain rings can be placed around the necks of the flasks to weigh them down.
6. Remove the flask from the bath and cool to about 70°C.
7. Immediately add 10.00 ml $Na_2C_2O_4$ (1.00 ml≏1.00 ml $KMnO_4$), and mix.
8. Immediately back titrate with $KMnO_4$ (1.00 ml≏0.100 mg O_2) to the first pink tint that persists for 30 sec. The temperature during the titration should be between 55° and 60°C.

Calculations

$$\text{ppm Oxygen consumed} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times 0.1\ (\text{ml titration} - \text{ml blank})$$

Report oxygen consumed of <10 ppm to whole numbers and of >10 ppm to 2 significant figures only.

Preparation of reagents

Potassium permanganate, 1.00 ml≏0.100 mg O_2: Dissolve 0.40 g $KMnO_4$ in water and dilute to approx 1 liter. Store the solution in the dark for at least 1 week to permit precipitation of manganous salts. Heat the solution to boiling and filter through asbestos fiber or fritted glass. Cool and standardize against primary standard $Na_2C_2O_4$ as follows: Dry about 0.1 g of the salt at 105°C for 1 hr. Dissolve approx 25 mg accurately weighed to 0.1 mg in 50 ml water and 20 ml 25 percent H_2SO_4.

$$\text{ml } KMnO_4 \text{ required} = \text{mg}\frac{Na_2C_2O_4}{0.8376}$$

Add from the buret 90 percent of the required $KMnO_4$ to the oxalate solution and heat to 55°–60°C. Continue the titration slowly and with constant

stirring until a faint pink color persists for 30 sec. For practical work, no blank correction is required. Store the standardized $KMnO_4$ solution in a lightproof bottle. The titer of the $KMnO_4$ solution should be checked frequently.

Sulfuric acid, 25 percent v/v: Mix 250 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 1 liter.

Sodium oxalate, 1.00 ml≅1.00 ml $KMnO_4$: Dissolve 0.8376 g $Na_2C_2O_4$, dried at 105°C for 1 hr in water. Add 1 ml 25 percent H_2SO_4 and dilute to 1,000 ml.

REFERENCES

American Public Health Association and American Water Works Association, 1946, Standard methods for the examination of water and sewage: New York, Am. Public Health Assoc., Inc., 9th ed.

California State Water Pollution Control Board, 1952, Water quality criteria: Pub. no. 3.

Northeast Water Works Association, 1940, Progress report, Committee on Quality Tolerances of Water for Industrial Uses: Northeast Water Works Assoc. Jour., v. 54.

Treadwell, F. P., and Hall, W. T., 1935, Analytical chemistry: New York, John Wiley and Sons, Inc., 8th ed., v. 2.

D:28 OXYGEN DISSOLVED

Oxygen dissolved in water is derived from the air and from the oxygen given off in the process of photosynthesis by aquatic plants. The solubility of oxygen in water is dependent upon the partial pressure of oxygen in air, the temperature of the water, and the mineral content of the water.

Dissolved oxygen in water has no adverse physiological effect and actually increases the palatability of the water (California State Water Pollution Control Board, 1952, p. 241). In general, no minimum concentration of dissolved oxygen required to support fish life has been listed because the oxygen requirements of fish vary with the species and age, with temperature, and concentration of other substances in the water. Ellis believes that under average stream conditions, 3.0 ppm of dissolved oxygen, or less, should be regarded as hazardous or lethal, and that to maintain a varied fish fauna in good condition the dissolved-oxygen concentration should be at least 5.0 ppm (Ellis, 1937). Water supersaturated with dissolved oxygen has been reported as detrimental to fish (American Water Works Association Journal, 1938, p. 1420).

Dissolved oxygen is responsible for many of the corrosion problems in industry. For many industrial uses of water, zero dissolved oxygen would be desirable as a means of inhibiting corrosion.

D:28a-1 ALSTERBERG (AZIDE) METHOD

The Alsterberg (azide) method is similar in substance to part IIB, APHA (1955, p. 160, 255) Standard Methods, and D 888–49 T Non-Referee Method A, ASTM (1954, p. 243–245) Manual on Industrial Water.

This method is applicable to natural waters and most other waters which are not heavily polluted. It is not recommended for samples that contain more than 1 mg per liter of ferrous iron or appreciable quantities of sulfite, thiosulfate, polythionate, hypochlorite, or free chlorine.

Principle of determination

This method is a modification of the Winkler process for the determination of dissolved oxygen, and the principle is the same. The method depends on the formation of a precipitate of manganous hydroxide. The oxygen dissolved in the water is rapidly absorbed

by manganous hydroxide, forming a higher oxide, which may be in the following form:

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2$$

$Mn(OH)_2$ floc acts as a "gathering" agent for oxygen; therefore, the floc is passed twice through the solution to insure quantitative reaction.

Upon acidification in the presence of iodide, iodine is released in a quantity equivalent to the dissolved oxygen present.

$$MnO(OH)_2 + 2KI + H_2O \xrightarrow{H^{+1}} Mn(OH)_2 + I_2 + 2KOH$$

The liberated iodine is then titrated with a standard sodium thiosulfate solution using starch as the indicator.

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^{-1}$$

Oxidizable organic matter consumes iodine and thereby causes low results. This effect of organic matter can be minimized if the liberation of iodine is followed immediately by the titration with thiosulfate. Any readily oxidizable or reducible constituents interfere by reaction with either the iodine or thiosulfate. Oxidizable substances cause low results and reducible substances high results. The magnitude of the net effect is, of course, proportionate to the absolute and relative concentrations of the different interferences.

In the listed procedure, sodium azide eliminates the interference of nitrite, and potassium fluoride overcomes the effect of ferric salts, provided the ferric iron concentration does not exceed 200 mg per liter and there is no delay in titration. The ferrous iron concentration should not exceed 1 mg per liter. High concentrations of suspended solids, which interfere, are removed by alum flocculation as directed in sec. A : 4d.

When the method given is used on water which is not heavily polluted the results are generally reproducible to ±0.01 mg, except that at low concentrations (below 0.1 mg) the error may be ± 50 percent.

Additional information on the principle of the determination is given by Adams, Barnett, and Keller (1943).

Apparatus and reagents

Buret, 25-ml
Alum solution, 6 percent
Potassium fluoride solution, 25 percent
Manganous sulfate solution, 32 percent
Alkaline-iodide sodium azide solution
Sulfuric acid, conc (sp gr 1.84)
Starch indicator, stable
Sodium thiosulfate, 0.025*N*

Procedure

Samples for the determination of dissolved oxygen must be collected and treated as directed in secs. A : 3c and A : 4d.

1. Pipet an aliquot of I_2 solution from the treated sample (see sec. A: 4d) that represents less than 2.0 mg O_2 (200.0 ml max).
2. Titrate the liberated I_2 with 0.025N $Na_2S_2O_3$ to a pale straw color.
3. Add 1–2 ml starch indicator and continue the titration to the first disappearance of the blue color. Subsequent recoloration should be disregarded.

Calculations

1. If the sample has been treated with alum as in sec. A : 4d, correct the sample volume reacted with $MnSO_4$ as follows:

$$\text{ml Sample} = \frac{300 \times \text{ml taken for flocculation}}{\text{ml taken for flocculation} + \text{ml } AlK(SO_4)_2}$$

2. $$\text{ppm } O_2 = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \frac{(\text{ml treated aliquot} + 7)}{\text{ml treated aliquot}} \times \text{ml } Na_2S_2O_3 \times 0.2$$

Report dissolved-oxygen concentration to 1 decimal place.

Preparation of reagents

Alum solution, 6 percent: Dissolve 10 g $AlK(SO_4)_2 \cdot 12H_2O$ in water and dilute to approx 100 ml.

Potassium fluoride solution, 25 percent: Dissolve 40 g $KF \cdot 2H_2O$ in water and dilute to approx 100 ml.

Manganous sulfate solution, 32 percent: Dissolve 48 g $MnSO_4 \cdot 4H_2O$ or 40 g $MnSO_4 \cdot 2H_2O$ or 36 g $MnSO_4 \cdot H_2O$ in water, filter, and dilute to approx 100 ml.

Alkaline-iodide sodium azide solution: Dissolve 1 g NaN_3 in 4 ml water. Add this solution with constant stirring to 95 ml alkaline iodide reagent. The reagent should not give a color with starch indicator when diluted and acidified.

Alkaline-iodide reagent: Dissolve 50 g NaOH or 70 g KOH and 13.5 g NaI or 15 g KI in water and dilute to 100 ml.

Sodium thiosulfate solution, 0.025*N*: Dissolve 6.205 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water, add 1 g Na_2CO_3, and dilute to 1,000 ml. Store the thiosulfate in a glass-stoppered bottle which has been cleaned with dichromate-sulfuric acid cleaning solution and rinsed with hot water. Standardize the $Na_2S_3O_2$ against KIO_3 as follows: Dry approx 1 g KIO_3 for 2 hr at 180°C. Dissolve 0.8918 g in water and dilute to 1,000 ml. Pipet 25.00 ml of the KIO_3 into a 250-ml iodine flask, then add successively 75 ml water and 2 g KI. After solution is complete, add 10 ml 20 percent H_2SO_4. Allow the stoppered flask to stand 5 min in the dark. Titrate with $Na_2S_2O_3$ using 2 ml starch indicator as end point is approached.

$$\text{Normality of } Na_2S_2O_3 = \frac{\text{ml } KIO_3}{\text{ml } Na_2S_2O_3} \times 0.025$$

REFERENCES

Adams, R. C., Barnett, R. D., and Keller, D. E., Jr., 1943, Field and laboratory determination of dissolved oxygen: Am. Soc. for Testing Materials Proc. 43.

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

American Society for Testing Materials, 1954, Manual on industrial water: Spec. Tech. Pub. 148–A.

American Water Works Association Journal, 1938, Water bureau aids poor fish: v. 30.

California State Water Pollution Control Board, 1952, Water quality criteria: Pub. no. 3.

Ellis, M. M., 1937, Detection and measurement of stream pollution: U. S. Dept. Commerce, Bur. Fisheries Bull. 22.

D:29 pH VALUE

The pH of a solution is a measure of the effective hydrogen-ion concentration, or more specifically, the hydrogen-ion activity (a_{H^+}).

$$pH = \log \frac{1}{a_{H^+}}$$

In water solutions, deviations in pH from 7 are primarily the result of the hydrolysis of salts of strong bases and weak acids, or vice versa. Dissolved gases such as carbon dioxide, hydrogen sulfide and ammonia also affect the pH appreciably. The effect of dissolved salts of strong acids and strong bases is slight.

Because carbonates are prevalent in nature, most natural waters of the United States are slightly basic. The overall normal pH range is between 6.0 and 8.0. Industrial wastes on the other hand may be strongly acidic or basic, and the effect on the pH of water resources is largely dependent on the normal buffering capacity of the water.

The pH of potable water is not pathologically significant. Acid water with a pH of less than about 4 usually has a sour taste. The U.S. Public Health Service (1946) states that the maximum pH of treated drinking and culinary water on carriers subject to Federal quarantine regulations should be about 10.6. Optimum pH for fish is between 7.8 and 8.5 while acid water with pH below 4.4 and strong basic waters with pH greater than 8.8 generally causes gill irritation and death (Ellis, 1944). pH in conjunction with other factors affects the corrosion potential of water on metals. For detailed discussion the chemist is referred to the work of Langelier (1946, p. 169). Low pH also increases the corrosive action of water on concrete (Antill, 1937, p. 1803). Extremes in pH cannot usually be tolerated by industry. The optimum pH for irrigation water depends on the type of crops to be grown and on the physical and chemical properties of the soil. Acid soils will tolerate the more alkaline water and some alkaline soils will tolerate the more acid water.

D:29a-1 INSTRUMENT METHOD

The instrument method is similar in substance to part I, APHA (1955) Standard Methods; D E70–52 T ASTM (1954) Manual on Industrial Water; and method 21a, U.S. Salinity Laboratory Staff (1954) Handbook 60.

Principle of determination

See sec. C: 2c for the principles of pH-meter operation.

The pH obtained in the laboratory may not be the same as that of the water at the time it was collected owing to reactions with sediment, hydrolysis, and oxidation taking place within the sample

bottle. Also the pH may change appreciably through loss of dissolved gases, the absorption of fumes in the laboratory, and from the deposition of calcium carbonate or other salts. Therefore, a value more representative of the pH at the time of collection is obtained if the determination is made as soon as the sample bottle is opened.

With the apparatus listed below, results are reproducible to ±0.05 pH.

Apparatus and reagents

Beckman pH meter with glass or saturated calomel electrodes.
Buffer solution, pH 7.00 ± 0.02 at 25°C.

Procedure

1. After an appropriate warmup period, standardize the instrument with the buffer solution at the approximate temperature of the sample.
2. With a minimum of aeration and agitation, measure the pH in accordance with the instrument-manufacturer's instructions.

Calculations

For water having an abnormally high sodium content, a correction may be necessary. This correction will differ with the electrodes, hence the analyst is referred to manufacturer's instructions for the computations necessary.

Report pH of <4.5 to the nearest 0.05 and of >4.5 to 1 decimal place.

D:29a–2 FIELD INSTRUMENT METHOD

Beckman Model N and N–1 and Coleman Model 20 pH meters have been used successfully.

D:29a–3 PAPER METHOD

The method is only semiquantitative and is useful only for fieldwork when high precision is not required. If fresh paper is used, accuracy of about ±0.5 pH can be obtained with the Fisher product.

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

American Society for Testing Materials, 1954, Manual on industrial water: Spec. Tech. Pub. 148–A.

Antill, J. M., 1937, Resistance of concrete to chemical attack: Am. Water Works Assoc. Jour., v. 29.

Ellis, M. M., 1944, Water purity standards for fresh water fishes: U. S. Fish and Wildlife Service Spec. Rept. 2.

Langelier, W. F., 1946, Chemical equations in water treatment: Am. Water Works Assoc. Jour., v. 38.

U.S. Public Health Service, 1946, Drinking water standards: U.S. Public Health Service Repts., v. 61, no. 11.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkali soils: U. S. Dept. Agriculture, Agriculture Handb. 60.

D:30 PHENOLIC MATERIAL

Phenolic material in water resources is invariably the result of pollution. Phenols are widely used as disinfectants and in the synthesis of many organic compounds. Waste products from oil refineries, coke areas, and chemical plants may contain high concentrations. Fortunately, phenols decompose in the presence of oxygen and organic material, and their persistence downstream from point of entry is relatively short lived. The rate of decomposition is dependent on the environment.

Very low concentrations impart such a disagreeable taste to water that it is highly improbable that harmful amounts could be consumed unknowingly. Reported thresholds of detection of taste and odor range from 0.01 to 0.1 ppm. Chlorination of water containing phenols produce chlorophenols, which have much more disagreeable tastes and odor than the parent material. The California State Water Pollution Control Board (1952, p. 320) reports that thresholds of taste and odor for chlorophenols range from 0.001 to 0.02 ppm. The U.S. Public Health Service (1946, p. 361) recommends that phenolic material should not exceed 0.001 ppm, reported as phenol, in drinking and culinary water on carriers subject to Federal quarantine regulations. Concentrations up to 1,000 ppm are not believed to be toxic to animals (Heller and Pursell, 1938, p. 99). Lethal concentrations for fish are related somewhat to the species, time of contact, temperature, and other conditions. Literature on the subject is voluminous. On the basis of compiled data, 5.0 ppm could be expected to be harmful to most fish, whereas 1.0 ppm or less is probably safe (California State Water Pollution Control Board, 1952, p. 320).

Phenols are undesirable in water supplies for food and beverage industries because of the attendant taste and odor problems.

D:30a-1 GIBBS REACTION

Principle of determination

The analytical method given here is not specific for phenol but is a collective determination of some of the simpler monohydroxy aromatic compounds. Because of the higher molecular weights and differences in light-absorbance characteristics of the various other materials determined, the reported value represents the minimum concentration by weight present. Phenolic materials are distilled from the acidified water sample, reacted with 2,6-dibromoquinone chloroimide (Gibbs reagent) in a buffered alkaline solution, and the resulting indigo-type dye extracted with n-butyl alcohol. Temperature and pH play an important role in the Gibbs reaction. A

borate buffer is employed to keep the pH at approximately 9.6. It is important that both samples and standards are at the same temperature during the reaction.

The extraction of the dye with n-butyl alcohol is not strictly quantitative, but is sufficiently linear if the volumes of the aqueous and alcoholic phases are uniform and if the extractions are carried to equilibrium. Although serial extraction quantitatively removes the dye, the color intensity of the combined extracts is always less than that of the first extract; hence serial extraction decreases the sensitivity of the test.

Different phenolic materials produce colors including green, blue green, blue, and purple. Therefore, arbitrary spectrophotometric comparison must be used as it would be difficult to prepare visual standards if the sample contained a complex mixture of phenols, cresols, chlorophenols, etc. The butyl alcohol extracts of the dye formed in Gibbs reaction for different phenolic materials have similar wavelengths of maximum absorbance. Accordingly, a wavelength of 670 $m\mu$ is used, and the results reported on the basis of phenol.

The sensitivity of the reaction is dependent on the batch of dye used. Absorbancies of about 0.4 and 0.8 read in 40-mm cells for 0.01 mg of phenol have been observed with different batches of dye.

With the listed apparatus, results with pure phenol are accurate and reproducible to ± 0.0004 mg. Although good color is developed with Gibbs reagent at somewhat higher concentrations, an extension of the range above 0.030 mg for the determination with mixtures is not recommended.

Additional information on the principle of the determination is given by Ettinger and Ruchhoft (1948) and Ettinger and Kroner (1949).

Apparatus and reagents

Spectrophotometer, Beckman Model B:
- Wavelength: 670 $m\mu$
- Absorption cells: 23-mm, 25-mm, or 40-mm optical depth
- Phototube: Red-sensitive
- Blank: Dilution water plus reagents
- Initial sensitivity setting: 3
- Slit width: 1 mm (approx)

Distillation apparatus, 500-ml, with Graham condenser and ground-glass joint and stopper (Corning No. 3360)
Volumetric flask, 250-ml, glass-stoppered
Incubator, 37°C (optional)
Multiple electrical stirrer or other agitation apparatus
Separatory funnel, 500-ml
Phospboric acid, 10 percent

Methyl orange indicator solution
Pumice
Phenol, 1.00 ml=1.00 mg phenol
Borate buffer solution
Copper sulfate, 0.005 percent
2,6-Dibromoquinone chloroimide solution
n-Butyl alcohol
Sodium sulfate, anhydrous

Procedure

Samples for the determination of phenolic material must be preserved as directed in sec. A:4d, and analysis should proceed as soon as possible after collection.

1. Measure a 250-ml volume of sample into the distillation apparatus.
2. Add 0.7 ml 10 percent H_3PO_4 and 2 drops methyl orange indicator solution. If the sample is still alkaline, add more H_3PO_4 until it is just acid to methyl orange.
3. Add a small quantity of pumice to the flash to inhibit bumping.
4. Collect approx 230 ml distillate in a 250-ml glass-stoppered volumetric flask.
5. Allow the apparatus to cool.
6. Add approx 20 ml dilution water to the distillation flask and distill to the 250.0-ml mark on the receiving flask.
7. Mix the distillate thoroughly, and pipet an aliquot containing less than 0.025 mg phenolic material (200.0 ml max) into a 300-ml Erlenmeyer flask and adjust the volume to approx 200 ml.
8. Prepare a blank of dilution water and sufficient standards. and adjust volumes to approx 200 ml.
9. Bring aliquot, blank, and standards to the same temperature.
10. Add 10 ml borate buffer solution.
11. Add 2 ml 0.005 percent $CuSO_4$.
12. Add 3.0 ml 2,6-dibromoquinone chloroimide solution.
13. Mix well and cover the flasks with inverted beakers.
14. Allow the solutions to stand overnight at room temperature or incubate for 3–5 hr at 37°C.
15. Extract the solutions uniformly with 50.0 ml n-butyl alcohol. Vigorous stirring with an automatic stirrer for 5 min or shaking for 2 min has been found to be satisfactory.
16. Separate the aqueous and solvent phases in a separatory funnel.
17. Clarify the alcoholic extract by shaking it with about 0.5 g anhydrous Na_2SO_4 and centrifuging.
18. Decant the clear dye extract into the absorption cells and determine the absorbancies of the extract of sample and standard against that of the blank.

Calculations

1. Determine the mg phenolic material in the aliquot from a plot of absorbancies of standards containing known amounts of phenol.
2. $$\text{ppm Phenolic material} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \frac{\text{ml distillate}}{\text{ml aliquot}} \times \frac{\text{mg phenolic}}{\text{material}}$$

Report phenolic material concentrations of <0.1 ppm to 3 decimal places and of >0.1 ppm to 2 significant figures only.

Preparation of reagents

Phosphoric acid, 10 percent: Dilute 118 ml of 85 percent H_3PO_4 to approx 1 liter.

Methyl orange indicator solution: Dissolve 0.50 g methyl orange in water and dilute to approx 1 liter.

Phenol, 1.00 ml=0.001 mg phenol: Dilute 10.00 ml phenol (1.00 ml=1.00 mg phenol) to 1,000 ml. Dilute 10.00 ml of this intermediate solution to 100.0 ml. This dilute solution is unstable and should be prepared immediately before use.

Phenol, 1.00 ml=1.00 mg phenol: Dissolve 1.000 g phenol in water and dilute to 1,000 ml. Store in the refrigerator. The strength can be checked as follows: Pipet 50.0 ml of the phenol solution into a 250-ml glass-stoppered bottle containing 25 ml water. Add 50.0 ml 0.1*N* Br_2 and 5 ml conc HCl (sp gr 1.19). Allow to stand in cool water for 15 min with occasional shaking. Add about 1 g KI crystals and shake vigorously. Titrate with 0.100*N* $Na_2S_2O_3$ until the I_2 color disappears. The end point may be checked by adding a few drops of starch solution. The following reactions occur:

$$C_6H_5OH + 3\,Br_2 \rightarrow C_6H_2Br_3OH \downarrow + 3HBr$$

$$Br_2\ (\text{excess}) + 2\,I^{-1} \rightarrow I_2 + 2\,Br^{-1}$$

$$I_2 + 2\,S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2\,I^{-1}$$

Similarly treat a blank of dilution water.

$$\text{mg Phenol per ml} = 0.03134\ (\text{ml blank} - \text{ml sample})$$

If retained for long periods of time, the solution should be standardized once a month.

Bromine, 0.1*N*: Dissolve 2.784 g $KBrO_3$ and about 10 g KBr in water and dilute to 1,000 ml.

Sodium thiosulfate, 0.100*N*: Dissolve 24.820 g $Na_2S_2O_3 \cdot 5\,H_2O$ and 1.5 g $(NH_4)_2CO_3$ in water, add 5 ml $CHCl_3$ as a preservative, and dilute to 1,000 ml. Standardize as follows: To 100 ml water in an Erlenmeyer flask, add 5 g KI, 10 ml 10 percent H_2SO_4, and 25.00 ml 0.100*N* $KH(IO_3)_2$. Titrate with the $Na_2S_2O_3$ using starch near the end point. The following reactions occur:

$$5\,I^{-1} + IO_3^{-1} + 6\,H^{+1} \rightarrow 3\,I_2 + 3\,H_2O$$

$$I_2 + 2\,S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2\,I^{-1}$$

$$\text{Normality } Na_2S_2O_3 = \frac{25.0}{\text{ml } Na_2S_2O_3} \times 0.100$$

Potassium biniodate, 0.100*N*: Dissolve 3.250 g $KH(IO_3)_2$ in water and dilute to 1,000 ml.

Borate buffer solution: Dissolve 6.200 g H_3BO_3 and 7.450 g KCl in approx 1,500 ml water. Adjust with 0.2*N* NaOH (about 450 ml) to such a strength that 5 ml, when added to 100 ml of water, will give a pH of about 9.6. The pH of the buffer will be about 10.

Copper sulfate, 0.005 percent: Dissolve 0.05 g anhydrous $CuSO_4$ in water and dilute to approx 1 liter.

2,6-Dibromoquinone chloroimide solution: Dissolve 0.01 g 2,6-dibromoquinone chloroimide in 5 ml 98 percent ethyl alcohol and dilute to 50 ml with water. This solution is stable for about 30 min.

REFERENCES

California State Water Pollution Control Board, 1952, Water quality criteria: Pub. no. 3.

Ettinger, M. B., and Kroner, R. C., 1949, The determination of phenolic materials in industrial wastes: Industrial Waste Conf., 5th, Purdue Univ., Nov. 30.

Ettinger, M. B., and Ruchhoft, C. C., 1948, Determination of phenol and structurally related compounds by the Gibbs method: Anal. Chemistry, v. 20.

Heller, V. G., and Pursell, Lee, 1938, Phenol-containing waters and their physiological action: Jour. Pharmacology and Experimental Therapeutics, v. 63.

U. S. Public Health Service, 1946, Drinking water standards: U. S. Public Health Service Repts., v. 61, no. 11.

D:31 PHOSPHORUS

Phosphorus is prevalent in nature both in the organic and inorganic form. Because of its role in animal and vegetable metabolism, phosphorus is a cyclic element, similar to nitrogen, in that the combined form is continually changing by decomposition and synthesis. As phosphate, it is present in several common minerals but the concentration in water is limited by the relative insolubility of phosphates of the alkaline earths. Both organic and inorganic phosphorus in water may result from leaching of soil and rocks, and from fertilizer, normal decomposition of plants and animals, sewage, and industrial effluents. Waters that have undergone phosphate treatment for removal of hardness can also add phosphorus to water resources.

In concentrations found in water, phosphorus is not reported to be toxic to man, animals, or fish. However, the element does stimulate the growth of algae, which may cause serious odor problems in public water supplies.

D:31a ORTHOPHOSPHATES

Orthophosphate is the most common ionized form of phosphorus in water and the only one derived from natural sources. Orthophosphates include the three ionization products of phosphoric acid, $H_2PO_4^{-1}$, HPO_4^{-2}, and PO_4^{-3}, whose relative concentrations in water are a function of the pH. PO_4^{-3} does not exist in solutions below a pH of about 9.4; at a pH of approx 6.8, HPO_4^{-2} and $H_2PO_4^{-1}$ are present in equal quantities, while at a pH of about 4.4 most of the orthophosphate is present as $H_2PO_4^{-1}$. See Reiman, Neuss, and Naiman (1942, p. 323), Kolthoff and Sandell (1952, p. 440–441), and sec. C: 8a for ionization of orthophosphate at different pHs.

The various ionization products are not differentiated by the method of analysis, nor are they chemically or physiologically significant to water uses. Hence, the combined orthophosphates are reported in terms of parts per million PO_4. The computation of equivalents per million (epm), however, necessitates consideration of the ionization products; instructions for estimating equivalents per million are given in sec. C: 8a.

D:31a-1 PHOSPHOMOLYBDATE METHOD

As far as is known, the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

Principle of determination

Orthophosphate is converted to phosphomolybdate by acidified ammonium molybdate reagent.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O$$

When phosphomolybdate is reduced with stannous chloride, a strong blue color is developed.

Barium, lead, mercury, and silver interfere by forming a precipitate. Silica gives a pale-blue color that is additive to the phosphate color, and a silica correction is made when necessary. The effect of silica is somewhat dependent on the reagents; therefore, appropriate silica correction should be determined with each batch of reagents. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before the determination. Residual chlorine should be removed by boiling the sample. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6–10 min and fades gradually thereafter. After addition of stannous chloride the color can be measured at the exact predetermined time of maximum color development; or within about 30 min thereafter when the time effect is negligible. The amount of stannous chloride added affects the stability of the color. Using less reductant increases the stability but decreases the range of the test by incomplete reduction.

The stannous chloride solution probably causes more trouble than any other single factor. The reagent must be fresh. The salt hydrolyzes readily and is unstable even in the solid form. Only fresh salts with well defined crystals should be used. The acid solution can be kept in the reduced state for several days by adding a small amount of granulated tin or by using hydroxylamine hydrochloride.

With listed apparatus, results are accurate and reproducible to ± 0.0005 mg.

Additional information on the principle of the determination is given by Ellis, Westfall, and Ellis (1946) and Zinzadze (1935, p. 227).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 700 mμ
Filter: Red
Cells: 40-mm optical depth
Phototube: Red-sensitive
Blank: Dilution water plus reagents
Initial sensitivity setting: 1
Slit width: 0.4 mm (approx)

The following absorbancies have been observed:

mg PO_4	*Absorbancy*
0.010	0.38
.025	.95
.050	1.91

Potassium phosphate, 1.00 ml=0.005 mg PO_4
Molybdate reagent
Stannous chloride, 0.25 percent

Procedure

Samples for the determination of orthophosphate should be treated as directed in sec. A : 4d.

1. Pipet a volume of sample containing less than 0.05 mg PO_4 (25.00 ml max) into a 50-ml beaker and adjust the volume to 25.0 ml.
2. Prepare a blank and sufficient standards, and adjust the volumes to 25.0 ml.
3. Add 1.0 ml molybdate reagent and mix.
4. After 5 and before 10 min add 1.0 ml 0.25 percent $SnCl_2$.
5. After about 30–45 min, determine the absorbancies of test samples and standards against the blank, and when necessary, correct for water color as directed in sec. C : 1a–2, method 1.

Calculations

1. Determine mg PO_4 from a plot of absorbancies of standards containing known amounts of constituent.

2. $$\text{ppm } PO_4 = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } PO_4 \text{ in samples}$$

$$\text{ppm Orthophosphate as P} = \text{ppm } PO_4 \times 0.326$$

Report concentrations of orthophosphates of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Potassium phosphate, 1.00 ml=0.005 mg PO_4: Dilute 50.00 ml potassium phosphate (1.00 ml=0.100 mg PO_4) to 1,000 ml.

Potassium phosphate, 1.00 ml=0.100 mg PO_4: Dissolve 0.1433 g KH_2PO_4, dried overnight over H_2SO_4, in water. Add 2–3 drops chloroform and dilute to 1,000 ml.

Molybdate reagent: Mix equal volumes of 5 percent ammonium molybdate and 20*N* H_2SO_4. The reagent is unstable and should be prepared immediately before use.

Ammonium molybdate, 5 percent: Dissolve 10 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water and dilute to approx 200 ml.

Sulfuric acid, 20*N*: Mix 112 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 200 ml.

Stannous chloride, 0.25 percent: Dilute 20 ml conc HCl (sp gr 1.19) to approx 1 liter. Dissolve 2.5 g $SnCl_2\cdot 2H_2O$ and 10 g $NH_2OH\cdot HCl$ in the dilute acid.

D:31b PHOSPHORUS

The category "phosphorus" includes all forms of phosphorus, both inorganic and organic, that are in solution.

D:31b–1 PHOSPHOMOLYBDATE METHOD

The phosphomolybdate method permits determination of phosphorus in all forms that decompose to yield orthophosphate under the drastic conditions of the test. Methane phosphonic acid is not determined, nor in all probability are other synthetic organic compounds of similar structure.

Principle of determination

Organic material is decomposed by acid digestion, and the phosphorus from this source as well as other phosphates such as metaphosphate, pyrophosphate and polyphosphates are oxidized to orthophosphate. The orthophosphate is then determined by development of the phosphomolybdate blue color as discussed in sec. D:31a–1. Acid retards the development of the blue color; hence, the digested sample is neutralized before ammonium molybdate is added.

Additional information on the principle of the determination is given by Taylor (1937) and Hansen and Robinson (1953, p. 55).

Apparatus and reagents

Steam bath
Graduated cylinders, 100-ml
Spectrophotometer, Beckman Model B:
Wavelength: 700 m_μ
Filter: Red
Cells: 40-mm optical depth
Phototube: Red-sensitive
Initial sensitivity setting: 1
Blank: Dilution water plus reagents
Slit width: 0.4 mm (approx)
The following absorbancies have been observed:

mg PO_4	*Absorbancy*
0.010	0.38
.025	.95
.050	1.91

Hydrochloric acid, conc (sp gr 1.19)
Nitric acid, conc (sp gr 1.42)
Sulfuric acid, 3.6*N*
Phenolphthalein indicator solution
Sodium hydroxide, 1*N*
Sulfuric acid, 0.05*N*
Potassium phosphate, 1.00 ml=0.005 mg PO_4
Molybdate reagent
Stannous chloride, 0.25 percent

Procedure

1. Pipet 100.0-ml sample into a 250-ml Erlenmeyer flask.
2. Add 3.0 ml conc HCl.
3. Add 0.5 ml conc HNO_3.
4. Digest on steam bath for 2–3 hr.
5. Evaporate to approx 50 ml over a small flame.
6. Add 4.0 ml 3.6*N* H_2SO_4

7. Evaporate to approx 3 ml. The acid fumes at this point. Do not let portions of the bottom of the flask become dry.
8. Cool and dilute with approx 20 ml water.
9. Add a drop of phenolphthalein and titrate with 1*N* NaOH to a pale-pink color.
10. Add 0.05*N* H_2SO_4 carefully until the pink color just disappears.
11. Quantitatively transfer the solution to a Nessler tube and dilute to original sample volume.
12. Pipet an aliquot containing less than 0.05 mg PO_4 (25.00 ml max) into a 50-ml beaker and adjust the volume to 25.0 ml.
13. Prepare a blank, sufficient standards and adjust the volumes to 25.0 ml.
14. Add 1.0 ml molybdate reagent and mix.
15. After 5 and before 10 min add 1.0 ml 0.25 percent $SnCl_2$.
16. After about 30–45 min determine the absorbancies of test sample and standards against the blank.

Calculations

1. Determine quantity of PO_4 in test sample from a plot of absorbancies of standards containing known amounts of constituent.

2. $$\text{ppm Phosphorus as } PO_4 = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml aliquot}} \times \text{mg } PO_4 \text{ in sample}$$

$$\text{ppm Phosphorus (P)} = \text{ppm P as } PO_4 \times 0.326$$

Report concentrations of phosphorus as PO_4 of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Sulfuric acid, 3.6*N:* Mix 10 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to 100.0 ml.

Phenolphthalein indicator solution: Dissolve 2.5 g phenolphthalein in approx 500 ml 50 percent ethyl alcohol. Neutralize with 0.02*N* NaOH.

Sodium hydroxide, 1*N:* Dissolve 40 g NaOH pellets in approx 1 liter of water.

Sulfuric acid, 0.05*N:* Dilute 1.4 ml 3.6*N* H_2SO_4 to 100 ml.

Potassium phosphate, 1.00 ml=0.005 mg PO_4: Dilute 50.00 ml KH_2PO_4 (1.00 ml=0.100 mg PO_4) to 1,000 ml.

Potassium phosphate, 1.00 ml=0.100 mg PO_4: Dissolve 0.1433 g KH_2PO_4, dried overnight over H_2SO_4, in water. Add 2–3 drops chloroform and dilute to 1,000 ml.

Molybdate reagent: Mix equal volumes of 5 percent ammonium molybdate and 20*N* H_2SO_4. The reagent is unstable and should be prepared immediately before use.

Ammonium molybdate, 5 percent: Dissolve 10 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water and dilute to approx 200 ml.

Sulfuric acid, 20*N:* Mix 112 ml conc H_2SO_4 (sp gr 1.84) with water and dilute to approx 200 ml.

Stannous chloride, 0.25 percent: Dilute 20 ml conc HCl (sp gr 1.19) to approx 1 liter. Dissolve 2.5 g $SnCl_2\cdot 2H_2O$ and 10 g $NH_2OH\cdot HCl$ in the dilute acid.

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D:32 POTASSIUM

Although potassium is relatively abundant in the earth's crust, the potassium content in natural waters is usually small. Potassium occurs in rocks in a form that is not easily brought into solution. Also, several geochemical processes tend to remove potassium selectively and return it to the solid phase. Most waters contain less than 20 ppm potassium, although several hundred parts per million are occasionally found.

Potassium is essential to animal nutrition, but a concentration of 1,000–2,000 ppm in drinking water is regarded as the extreme limit permissible (Moore, 1950). Potassium in water causes foaming, as does sodium, but apparently it is not otherwise significant in industrial water supplies. Potassium stimulates plankton growth (Lackey and Sawyer, 1946, p. 573) and is reported to be somewhat more toxic to fish and shellfish than is calcium, magnesium, or sodium (Brandt, 1948, p. 9015).

D:32a–1 FLAME-PHOTOMETRIC METHOD

The exact procedure used in the flame-photometric method is governed principally by the design and performance of the particular flame photometer used; hence, no specific directions can be given. See secs. C:1b and C:2e for a discussion of flame photometry and flame photometers. Many helpful suggestions are provided by the manufacturers of the individual instruments.

Report potassium concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

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D:33 SELENIUM

Selenium exists in many forms and is found in many localities. The element is generally more prevalent in the Great Plains and Great Basin than in other parts of the United States. Selenium is normally nonexistent or present only in insignificant quantities in natural waters but does occur occasionally under certain geologic environments. Highly significant is the fact that selenium from plants, sedimentary rocks, soils, and animals may find its way into water resources. Selenium concentrations in water in excess of 0.5 ppm are extremely rare and limited primarily to seepage from seleniferous soils.

It is generally agreed that selenium is a cumulative poison to man and animals; it enters all of the body tissues and is present in all secretions and excretions. Because of its chemical similarity to sulfur, it is taken up nonpreferentially in tissue assimilations and is substituted for sulfur in the proteins. Investigations of selenium pathology to man have been somewhat complicated by difficulty in diagnosis, and it is understandable that recommendations for maximum limits in drinking and culinary waters are conflicting. The U.S. Public Health Service (1946) states that the selenium concentration shall not exceed 0.05 ppm in water on carriers subject to Federal quarantine regulations. Chronic selenium poisoning in livestock is known as "alkali disease," and the acute poisoning as "blind staggers" (Moxon, 1937). Water with 0.4 to 0.5 ppm is not believed to be toxic to livestock; such water may contribute to poisoning, but the selenium content of the feed is a more critical factor (California State Water Pollution Control Board, 1952, 1954, p. 350–351). It is generally agreed that when the selenium content of the air-dried diet exceeds about 5 ppm, symptoms of alkali disease occur.

High concentrations of selenium are toxic to some plants, but most plants can absorb relatively large amounts of selenium from irrigation water or the soil without apparent injury to themselves.

Additional information on the occurrence and significance of selenium is given by Trelease and Beath (1949).

D:33a–1 NORRIS-FAY TITRATION METHOD

Principle of determination

For all practical purposes in water analysis, the method is specific for selenium but does not distinguish between the forms of the element. The sample is concentrated in the presence of sodium

peroxide to remove the interference of organic matter and to provide a workable volume of solution. Volumes throughout the procedure are more critical than for many other determinations in water analysis. Selenium is then distilled from sulfuric acid as the volatile bromide, precipitated as elemental selenium, collected, and oxidized to selenious acid. The selenious acid is titrated with thiosulfate and iodine using the Norris-Fay titration.

$$6H^{+1}+SeO_3^{-2}+4S_2O_3^{-2}\rightarrow S_4SeO_6^{-2}+S_4O_6^{-2}+3H_2O$$

Sulfuric acid is used in the distillation to raise the boiling point of the solution and insure quantitative distillation of selenium bromide. The elemental selenium precipitate is extremely fine, and the steam and ice-bath treatments are designed to coagulate the precipitate to a filterable size; nevertheless, attention must be given to the porosity of the filter. A fine asbestos mat is required with some fritted-glass filters. The Norris-Fay titration works best below 25°C; hence, the solution is cooled in an ice bath before titrating.

With careful work, results are accurate and reproducible to ±0.002 mg. The possibilities of manipulative errors are many, and it is recommended that duplicate samples, one containing a known added amount of selenium, be run.

Additional information on the principle of the determination is given by the Association of Official Agricultural Chemists (1945), Klein (1943), and Norris and Fay (1896).

Apparatus and reagents

Distillation apparatus, 250-ml, all glass, no offsets at joints, thermometer, dipping adapter
Steam bath
Microburet, 5-ml
Ice bath
Fritted-glass suction filter, fine, 22- × 100-mm
Pipet-stirrers, 170-mm long (approx), with medicine-dropper bulbs
Test tubes
Suction flash
Sodium peroxide
Sulfuric acid, conc (sp gr 1.84)
Hydrobromic acid, 40 percent or 48 percent
Hydrobromic acid-bromine solution, conc
Hydrobromic acid-bromine solution, dilute
Hydroxylamine hydrochloride, 10 percent
Phenol, 5 percent
Starch indicator, 0.5 percent
Sodium thiosulfate, 0.001*N*
Iodine, 0.001*N*
Selenium bromide, 1.00 ml=0.010 mg Se
Sulfur dioxide (gas supplied in commercial cylinders is free of selenium)

Procedure

Samples for the determination of selenium probably should be collected and treated in accordance with directions given in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.05 mg Se (100.0 ml max) into the distillation flask.
2. Add sufficient Na_2O_2, usually approx 1 g, to oxidize any organic matter and to make the solution definitely alkaline.
3. Evaporate to about 25 ml on an open flame.
4. Cool and cautiously add 50 ml conc H_2SO_4 and mix.
5. To the cooled mixture, add 30 ml conc HBr-Br_2 solution if the solution was prepared with 40 percent HBr, or 25 ml if 48 percent HBr was used.
6. Distill, slowly at first ,into 10–15 ml 48 percent or 40 percent HBr in a 125-ml Erlenmeyer flask surrounded with cold water. Keep the tip of the adapter below the surface of the HBr until all free Br_2 is distilled. If free Br_2 does not distill first, add more conc HBr-Br_2 solution to the distillation flask. Continue distillation until the temperature of the vapor reaches 200°C. At this point there should be no bromine coloration in the distillation flask or condenser.
7. Rinse the adapter into the receiving flask with water, keeping the volume of the distillate and washings below 75 ml.
8. Pass SO_2 with swirling through the distillate until the Br_2 color disappears and for an additional 30 sec to saturate the solution. (This step should be performed under the hood.)
9. Immediately add 1 ml 10 percent $NH_2OH \cdot HCl$.
10. Place on a steam bath for 30 min.
11. Place in an ice bath for 30 min.
12. Collect the precipitated Se_s in a fritted-glass filter overlaid with a fine asbestos mat.
13. Wash the flask and filter with 3–5 ml water.
14. Remove the last traces of SO_2 from the flask with natural gas or compressed air.
15. Attach a test tube to the filter and dissolve the Se_s in the flask and filter with 3 successive 1-ml portions of dilute HBr-Br_2 solution, sucking the filter dry after each addition. After each addition of HBr-Br_2 solution, start the suction to pull the solution into the filter mat. Allow the solution to remain in the mat for about 1 min before continuing suction.
16. Rinse the flask and filter with three 1.5-ml portions of water using same precautions as with the HBr-Br_2 solution.
17. Detach the test tube and add 3 drops 5 percent phenol to neutralize the Br_2.
18. Using the pipet-stirrer, rinse down the sides of the tube with the solution.
19. Immerse in a hot-water bath for 5 min to complete the neutralization of Br_2 and then in an ice bath for 5 min.
20. Add at least 50 percent excess 0.001*N* $Na_2S_2O_3$ and mix well.
21. Add 3 drops starch and sufficient I_2 to give a strong blue color. If less than 1 ml I_2 is used, add sufficient 0.001*N* $Na_2S_2O_3$ to require 1 ml I_2. Record I_2 added to nearest 0.01 ml.
22. Back titrate with 0.001*N* $Na_2S_2O_3$ to disappearance of blue, adding the last drops in 0.01-ml portions. Record total $Na_2S_2O_3$ used to nearest 0.01 ml.

Calculations

1. The thiosulfate equivalent of the iodine should be checked each time a selenium determination is made. Determine the $Na_2S_2O_3$ equivalent as follows: To 4½ ml water and 3 ml dilute HBr–Br_2 solution in a test tube, add 3 drops 5 percent phenol and heat in a hot-water bath for 5 min. Place in an ice bath for 5 min. Add 3.00 ml I_2 and titrate with 0.001*N* $Na_2S_2O_3$, using starch indicator near the end point.

$$\frac{\text{ml } 0.001N \text{ } Na_2S_2O_3}{\text{ml } I_2} = f = \text{thiosulfate equivalent of the iodine solution}$$

1.00 ml 0.001*N* $Na_2S_2O_3$ is equivalent to 0.0198 mg Se.

2. $$\text{ppm Se} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times [(\text{total ml } Na_2S_2O_3) - (\text{ml } I_2 \times f)] \times 0.0198$$

Report selenium concentrations of <1.0 ppm to 2 decimal places and of >1.0 ppm to 2 significant figures only.

Preparation of reagents

Selenium bromide solution, 1.00 ml=0.010 mg Se: Dilute 10.0 ml selenium bromide solution (1.00 ml=1.00 mg Se) to 1,000 ml with 0.05*N* HBr. Check the acidity by titration with 0.100*N* NaOH. The acidity should not be allowed to fall below 0.05*N*.

Selenium bromide solution, 1.00 ml=1.00 mg Se: Dissolve 0.4084 g H_2SeO_3, dried overnight in a desiccator, in 0.05*N* HBr and dilute to 250.0 ml with 0.05*N* HBr.

Hydrobromic acid, 0.05*N*: Dilute 10 ml 40 percent or 8.5 ml 48 percent HBr to approx 1 liter.

Hydrobromic acid-bromine solution, conc: Mix 10 ml Br_2 with 990 ml 40 percent or 48 percent HBr. Use caution when transferring liquid Br_2. Store in a tightly stoppered bottle. (This should be done under the hood.)

Hydrobromic acid-bromine solution, dilute: To 5 ml 40 percent or 48 percent HBr add 10 ml saturated bromine water and dilute to approx 100 ml.

Hydroxylamine hydrochloride, 10 percent: Dissolve 10 g $NH_2OH \cdot HCl$ in water and dilute to approx 100 ml.

Phenol, 5 percent: Dissolve 5 g phenol in water and dilute to approx 100 ml.

Iodine, 0.001*N*: Dilute 50.00 ml 0.02*N* I_2 to 1,000 ml. Before final dilution, add 20 g KI. Determine the thiosulfate equivalent of the iodine solution before each set of determinations.

Iodine, 0.02*N*: Dissolve 2.54 g I_2 and 12 g KI in water and dilute to 950 ml before standardizing. Standardize against primary standard As_2O_3 as follows: Dissolve approx 0.04 g As_2O_3 weighed accurately to 0.0001 g in 10 ml 1*N* NaOH. Add 15 ml 1*N* H_2SO_4 and mix. Add 50 ml 4 percent $NaHCO_3$. Titrate slowly with I_2 solution, maintaining constant agitation until most of the I_2 has been reacted (0.04 g As_2O_3 requires approx 40 ml 0.02*N* I_2). Add starch solution for indicator and continue the titration until the initial pink coloration just passes to clear blue. Deduct from the volume of iodine consumed the amount required to produce the same color in a solution composed of the reagents added to 40 ml of freshly boiled and cooled water in which 5 g KI has been dissolved.

$$\text{Normality of } I_2 = \frac{\text{g } As_2O_3 \times 20.220}{\text{ml } I_2}$$

Store in a glass-stoppered bottle protected from light.

Sodium thiosulfate, 0.001*N*, 1.00 ml≏0.0198 mg Se: Dilute 10.00 ml 0.100*N* $Na_2S_2O_3$ to 1,000 ml. Before adjusting to final volume, add 5 ml amyl alcohol and shake vigorously. Check the titer of the solution against the standard selenium solution (1.00 ml=0.010 mg Se). Add 3 ml dilute HBr-Br_2 solution to 5.0 ml Se standard. Continue as shown under "Procedure," steps 17–22, and "Calculations."

Sodium thiosulfate, 0.100*N*: Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ and 0.1 g Na_2CO_3 in 950 ml carbon dioxide-free water. Allow the solution to stand for a day before standardizing. Standardize against 0.100*N* $KH(IO_3)_2$ as follows: Dissolve 3.250 g $KH(IO_3)_2$ in water and dilute to 1,000 ml. Dissolve 5 g KI in 100 ml of water. Add 10 ml H_2SO_4 (10 percent v/v) and 25.00 ml 0.100*N* $KH(IO_3)_2$. Titrate with $Na_2S_2O_3$ using starch as indicator near the end point.

Starch indicator, 0.5 percent: Dissolve 0.5 g of soluble starch in 100 ml of water. Heating may hasten solution. Prepare fresh daily.

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D:34 SILICA

Silicon is the most abundant element in igneous rocks and some other types of deposits. Most silica in water is probably derived from the decomposition or metamorphism of silicate minerals rather than from solution of quartz, as quartz is one of the most resistant rock minerals to attack by water. Many waters contain less than 10 ppm of silica; those that drain deposits high in silicate minerals, particularly feldspars, often contain up to 60 ppm; concentrations exceeding 100 ppm are not commonly found. The chemistry of silica in solution is not known with certainty. It is believed that most silica is present in a nonionized form, but ionized silicate(s) is undoubtedly present in some waters.

Silica is not physiologically significant to humans, livestock, or fishes, nor is it of importance in irrigation water.

Most industrial processes tolerate silica in the range normally found, but it is particularly undesirable in boiler feed water. A recommended upper limit for boilers operating at 400 psi or above is 1 ppm. Silica forms a hard coating on steam-turbine blades, and a limiting concentration of 0.1 ppm in the steam has been recommended (Minhoff, 1948, p. 438).

D:34a-1 MOLYBDATE BLUE METHOD

The molybdate blue method is not recommended for normal waters whose silica content is more than 100 ppm.

Principle of determination

Silica in solution as silicic acid or silicate has the property of reacting with ammonium molybdate in an acid medium to form the yellow-colored silicomolybdate complex. The silicomolybdate complex is then reduced by sodium sulfite to form the molybdate blue color.

The possibility of having larger concentrations of so-called unreactive silica is greater in water containing high concentrations of silica than in water with a low silica content. One-hour digestion of a 50-ml sample with 0.2 g of silica-free sodium bicarbonate has been recommended as a means of making all the silica available for reaction with the molybdate reagent (APHA, 1955, p. 186).

Phosphate gives a similar molybdate complex under certain pH conditions. In the following determination, the conditions are such that the phosphate complex is not formed. There is also evidence that hydrogen sulfide and ferric and ferrous iron interfere with the determination. Hydrogen sulfide may be removed by boiling an acidified sample. The addition of disodium dihydrogen ethylenediamine tetraacetate eliminates the effect of high concentrations of

iron and also complexes calcium and prevents precipitation of calcium sulfite.

With the listed apparatus, results are accurate and reproducible to ±0.005 mg below 0.1 mg and to ±0.02 mg near 0.5 mg.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 384–394) and Kahler (1941, p. 536).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 700 mμ
Filter: Red
Cells: 10-mm or 40-mm optical depth
Phototube: Red-sensitive
Blank: Dilution water plus reagents
Initial sensitivity setting: 1
Slit width: 0.8 mm (approx)
The following absorbancies have been observed:

mg SiO_2	*Cell depth (mm)*	*Absorbancy*
0.05	40	0.37
.10	40	.73
.10	10	.19
.20	10	.36
.30	10	.54
.50	10	.90

Sodium silicate, 1.00 ml=0.050 mg SiO_2
Hydrochloric acid, 0.25*N*
Ammonium molybdate, 5 percent
Na_2EDTA, 1 percent
Sodium sulfite, 17 percent

Procedure

1. Pipet a volume of sample containing less than 0.5 mg SiO_2 (10.00 ml max) into 50-ml beaker and adjust the volume to 10.0 ml.
2. Prepare a blank, sufficient standards, and adjust the volumes to 10.0 ml.
3. Add 5 ml 0.25*N* HCl.
4. Add 5 ml 5 percent ammonium molybdate.
5. Add 5 ml 1 percent Na_2EDTA.
6. After 5 min have elapsed following the addition of the molybdate, add 10 ml 17 percent Na_2SO_3.
7. Mix, and allow to stand approx 30 min. The color is stable for several hours after this time.
8. Determine the absorbancy of the test sample and standards against the blank.

Calculations

1. Determine mg SiO_2 in test sample from a plot of absorbancies of standards containing known amounts of the constituent.

2. $$\text{ppm } SiO_2 = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } SiO_2 \text{ in sample}$$

Report silica concentrations of <10 ppm to 1 decimal place and of >10 ppm to 2 significant figures only.

Preparation of reagents

Sodium silicate, 1.00 ml=0.050 mg SiO_2: Stabilize the pentahydrate of approx 3 g $Na_2SiO_3 \cdot 5H_2O$ by placing it in a $CaCl_2$ desiccator for 2–3 hr. Dissolve 1.765 g in water and dilute to 1,000 ml. Dilute 100.0 ml of this intermediate solution to 1,000 ml. The concentration can be checked by the method described in sec. D: 34a–2. Store in a plastic bottle.

Hydrochloric acid, 0.25*N*: Mix 22 ml conc HCl (sp gr 1.19) with water and dilute to approx 1 liter.

Ammonium molybdate, 5 percent: Dissolve 52 g $(NH_4)_6Mo_7O_{24}$ $4H_2O$ in water and dilute to approx 1 liter.

Na_2EDTA, 1 percent: Dissolve 10 g Na_2EDTA in water and dilute to approx 1 liter.

Sodium sulfite, 17 percent: Dissolve 170 g Na_2SO_3 in water and dilute to approx 1 liter.

D:34a–2 GRAVIMETRIC METHOD

The gravimetric procedure is recommended for the analysis of brine and for normal water whose silica content exceeds approx 100 ppm.

Principle of determination

Silica is precipitated by evaporation with strong acid, separated by filtration, ignited, and weighed. If the sample contains much nitrate or other oxidizing agents, the precipitation should not be carried out in platinumware because platinum is readily dissolved by oxidizing agents heated with hydrochloric acid. A porcelain dish is satisfactory, but glass should not be used. The anhydrous residue of the sample is first ignited to burn off the organic material, which might not dissolve in acid and thereby interfere with the determination. The redissolved, or resuspended sample is taken to dryness with hydrochloric acid to dehydrate colloidal silicic acid and convert it to a filterable mass. The digestion in dilute acid extracts the acid-soluble material. This extraction must be quantitative if the filtrate from the silica determination is used in other gravimetric determinations. The acid concentration in the digestion is important because the dilute acid decreases the amount of silica reverting to colloidal form, but concentrated acid increases the reversion.

The actual silica content of the acid-insoluble residue is determined by weighing the residue, volatilizing the silica as fluorosilicate, and subtracting the weight of the nonvolatile residue.

$$SiO_2 + 6HF \rightleftarrows H_2SiF_6 + 2H_2O$$

$$H_2SiF_6 \rightarrow SiF_4 + 2HF$$

The reaction proceeds to the right on heating. Sulfuric acid is added to assure that any iron or aluminum contamination in the precipitate

will be weighed as the oxide in both weighings. Without the addition of sulfuric acid, iron and aluminum would be in the form of chloride in the first residue and fluoride in the second residue. In the presence of sulfuric acid, the contaminating metals are left in the residue as sulfates, which decompose to oxides during ignition.

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$

Inasmuch as the procedure is a single dehydration technique, the results are likely to be slightly low. For quantitative work it is necessary to recover the 1–5 percent of silica that may remain in solution. This may be accomplished readily by determining the silica in the filtrate colorimetrically (see sec. D:34a–1).

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 384–394) and Hillebrand and Lundell (1929, p. 536–546).

Apparatus and reagents

Evaporating dish, porcelain or platinum
Platinum crucibles
Steam bath
Muffle furnace
Hotplate
Hydrochloric acid, 50 percent v/v
Hydrochloric acid, conc (sp gr 1.19)
Sulfuric acid, conc (sp gr 1.84)
Hydrofluoric acid, 48 percent

Procedure

1. Evaporate a volume of sample containing between 0.10 and 0.25 g dissolved material (1,000 ml max) in a platinum dish. The filtrate from the SiO_2 determination is used for the gravimetric determinations of calcium, barium, magnesium, and sulfate, and those requirements will have a bearing on the sample volume taken for the silica determination.
2. Ignite the residue over an open flame or in a radiator. See sec. D: 22a–1.
3. Cautiously wash down the sides of the dish with two 10-ml portions 50 percent HCl followed by enough hot water to bring the solution level at least even with the highest sample level during the initial evaporation.
4. If the sample contains more than about 2 mg NO_3 or other oxidizing agents, quantitatively transfer the solution or mixture to a porcelain dish; if higher concentrations of oxidizing reagents are not present, the following reactions can be carried out in the platinum dish.
5. Evaporate the acid solution to dryness on the steam bath, and leave the dish on the bath for at least 2 hr more.
6. Add 8–10 drops concentrated HCl and wash down the sides of the dish with approx 50 ml water.
7. Cover the dish with a watch glass and extract the acid-soluble material by digesting on a steam bath for 1–2 hr.

8. Quantitatively collect the SiO_2 and other insoluble material on Whatman No. 42 filter paper. Scrub out the dish with a rubber policeman to dislodge the SiO_2, and wash the dish and the precipitate at least 3 times with hot water; retain the combined filtrate and washings for the gravimetric determination of calcium, barium, magnesium, and sulfate.
9. Transfer the residue and filter paper to a platinum crucible.
10. Moisten the paper and residue with 2 or 3 drops conc H_2SO_4.
11. Ignite the paper slowly over a low oxidizing flame.
12. Transfer the crucible to the muffle furnace and ignite at 1,000°C for 0.5 hr.
13. Cool in a desiccator and weigh. Record the weight to the nearest 0.0001 g.
14. Add 2 drops conc H_2SO_4.
15. Add ¼ in. 48 percent HF.
16. Under a hood, volatize the acid and SiF_4 on a hotplate.
17. Reignite in the muffle furnace at 1,000°C for 1.5 hr.
18. Cool in a desiccator and reweigh. Record the weight to the nearest 0.0001 g.

Calculations

$$\text{ppm } SiO_2 = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{loss of weight in mg}$$

Report silica concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Hydrochloric acid, 50 percent v/v: Mix 50 ml conc HCl (sp gr 1.19) with water and dilute to approx 100 ml.

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

Hillebrand, W. F., and Lundell, G. E. F., 1929, Applied inorganic analysis: New York, John Wiley and Sons, Inc.

Kahler, H. L., 1941, Determination of soluble silica in water—photometric method: Indus. and Eng. Chemistry, Anal. Ed., v. 13.

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis: New York, Macmillan Co., 3d ed.

Minhoff, C. E., 1948, Boiler water conditioning to prevent turbine deposits: Petroleum Refiner, v. 27.

D:35 SODIUM

Sodium salts are very soluble, and most sodium leached from the soil or rocks tends to remain in solution. The use of sodium salts is common in industry, and industrial wastes may contain large quantities of the element.

Sodium is not particularly significant in drinking and culinary water except for those persons having an abnormal sodium metabolism; the water supply in some areas contains sufficient sodium to be a factor in the planning of sodium-free diets (National Research Council, 1954). It has been established that more than 50 ppm of sodium plus potassium in boiler water causes foaming. For high-pressure boiler feed water a limiting concentration of 2–3 ppm has been recommended. Water with a high ratio of sodium to calcium plus magnesium is deleterious to soil structure. Sodium tends to disperse the soil colloids with the resultant loss of good tilth and permeability (U.S. Salinity Laboratory Staff, 1954, p. 69–82). The sodium-adsorption-ratio (SAR) is a useful index of the sodium hazard of irrigation water.

$$\mathrm{SAR} = \frac{\text{epm Na}}{\sqrt{\frac{\text{epm Ca} + \text{Mg}}{2}}}$$

D:35a-1 FLAME-PHOTOMETRIC METHOD

The exact procedure used in the flame-photometric method is governed principally by the design and performance of the particular flame photometer used; hence, no specific instructions can be given. See secs. C:1b and C:2e for a discussion of flame photometry and flame photometers. Many helpful suggestions are provided by the manufacturers of the individual instruments.

Report sodium concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

D:35a-2 ZINC URANYL ACETATE METHOD

The zinc uranyl acetate method is not as satisfactory for the determination of low concentrations of sodium as the flame-photometric procedure (see sec. D:35a–1).

Principle of determination

Sodium ion reacts with a concentrated solution containing zinc, uranyl, and acetate ions to precipitate sodium uranyl zinc acetate hexahydrate.

$$\mathrm{Na^{+1} + Zn^{+2} + 3UO_2^{+2} + 9C_2H_3O_2^{-1} + 6H_2O \longrightarrow NaC_2H_3O_2 \cdot Zn(C_2H_3O_2) \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6H_2O}$$

The triple salt would ordinarily be considered a soluble salt. Solubility is 5.85 g per 100 ml, and precipitation is quantitative only in the presence of a very large excess of reagent. The sample volume must be reduced by evaporation to 1–2 ml, and the volume of reagent added must be 10 or 15 times greater.

The zinc uranyl acetate mixture possesses a high degree of specificity for sodium and is one of the more specific among all analytical precipitants. Lithium precipitates quantitatively. Potassium does not interfere. Iron, aluminum, and manganese do not interfere. Certain organic complexing ions such as oxalate and citrate interfere at high concentrations, but only rarely will their effect be found. Other interferences, including phosphate, are at a minimum.

In this determination, the major requirement for good results is good technique. Temperature control is rather important because the solubility of the triple salt varies with temperature. Ideally, the sample should retain the initial temperature of the reagent throughout the standing and filtration period. A rise above normal temperature causes low results and a fall in temperature causes high results. The effect is easily controlled without necessitating thermostatic control.

With careful technique, results are accurate and reproducible to ±2 percent for water containing more than 20 ppm of sodium; in the lower concentration range the error may be appreciable.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952).

Apparatus and reagents

Steam bath

Crucible, fritted-glass, medium porosity. There may be a considerable variation in porosity between individual "medium" filters. A slow filter should be rejected.

Hydrochloric acid, conc (sp gr 1.19)

Zinc uranyl acetate solution, saturated with triple salt

Ethyl alcohol, 95 percent, saturated with triple salt

Acetone, anhydrous

Procedure

1. Pipet a volume of sample containing between 0.25 and 2.5 mg Na^{+1} into a beaker.
2. Add 1 or 2 drops conc HCl and evaporate to dryness on a steam bath.
3. Dissolve the cooled residue in 1 ml water. Add more water if necessary, but note the volume used. A feathery residue of $CaSO_4$ may be tolerated because it usually dissolves in step 4 when the reagent is added.
4. Add zinc uranyl acetate reagent in the ratio of 15 ml reagent to 1 ml residue solution.
5. Allow to stand 1 hr at a fairly constant temperature. Stir occasionally.

6. Filter off the precipitate under suction. Drain the beaker and filter as completely as possible before proceeding to the next step.
7. Transfer the remaining precipitate into the filter crucible with 2-ml portions of saturated alcohol.
8. Wash the precipitate twice with 10-ml portions of saturated alcohol. The washed precipitate should be fine, crystalline, and bright yellow.
9. Wash the approx 10 ml acetone and draw air through for 1 or 2 min.
10. Wipe the outside and inner bottom ring of the crucible with a moist towel if salts have crystallized there. Dry the crucible and precipitate in a desiccator for 1 hr.
11. Weigh the crucible and precipitate.
12. Transfer the crucible to the suction apparatus and dissolve the salt out with warm water. Wash with 10 ml acetone and dry as before and weigh.

Calculations

1. mg Triple salt = (wt crucible and salt) — (wt washed crucible)

2. $$\text{ppm } Na^{+1} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times 0.01495 \times \text{mg triple salt}$$

Report sodium concentrations of <999 ppm to whole numbers and of >999 ppm to 3 significant figures only.

Preparation of reagents

Zinc uranyl acetate solution: Dilute 27 ml glacial acetic acid with 1,000 ml dilution water. Dissolve in this solution 100 g $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, and 300 g Zn $(C_2H_3O_2)_2 \cdot 2H_2O$. On cooling, a precipitate of fine, crystalline triple salt should form due to sodium impurities in the reagent. This salt should be allowed to remain in the bottle to maintain the sodium saturation. If a precipitate does not form, add a few milligrams of NaCl.

Ethyl alcohol, 95 percent, saturated: Saturate the alcohol with the triple salt and allow them to stand in contact at all times. Decant the saturated alcohol just before use.

REFERENCES

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis: New York, Macmillan Co., 3d ed.

National Research Council, 1954, Sodium restricted diets: Pub. 325.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkali soils: U. S. Dept. Agriculture, Agriculture Handb. 60.

D:36 SOLIDS

D:36a DISSOLVED SOLIDS

Theoretically, dissolved solids are the anhydrous residues of the dissolved substances in water. Note that dissolved solid is not a measure of the total weight of dissolved materials as they occur in solution. Neither are dissolved gases of volatile liquids a part of the dissolved solids. In reality, the term "dissolved solids" is defined by the method used in the determination. The methods used by the Geological Survey reflect experience with thousands of water samples of different total concentrations and chemical compositions, and the results obtained are believed to approach closer the theoretical definition than results by other methods.

All salts in solution affect the chemical and physical properties of the water and exert osmotic pressure. Water with several thousand parts per million of dissolved solids is generally not palatable, although those accustomed to highly mineralized water may complain that less concentrated water tastes flat. A change in the source of drinking water more often may cause gastric disturbances than the concentration of dissolved solids in the water itself. The U.S. Public Health Service (1946) recommends that the maximum concentration of dissolved solids not exceed 500 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations but permits 1,000 ppm if no better water is available. Reports of livestock tolerances are extremely variable and range from 3,000 ppm (Colorado Agricultural Experiment Station, 1943) to 15,000 ppm (Heller, 1933). In Montana the following arbitrary limits are used to classify water for livestock: up to 2,500 ppm, good; 2,500–3,500 ppm, fair; 3,500–4,500 ppm, poor; and over 4,500 ppm, unsatisfactory (I. Seghetti, 1951, written communication). The blood of fresh-water fish has an osmotic pressure equal to approximately 6 atmospheres, or about 7,000 ppm of sodium chloride. Although some fresh-water fish are adapted to live in more saline waters, for practical purposes any water that has an osmotic pressure greater than 6 atmospheres can be expected to be lethal.

Industrial tolerances for dissolved solids differ widely, but few industrial processes will permit more than 1,000 ppm. Salinity hazard is an important consideration for irrigation water. The water-uptake relations of plants are controlled by the osmotic-pressure differential between soil solution and the plant solution. A plant cannot draw as much water from a concentrated soil solution as from a dilute soil solution. For most waters that could be

considered for irrigation, the following general relation is applicable:

$$\text{Specific conductance} \times 0.65 \pm 0.1 = \text{dissolved solids}$$

The U.S. Salinity Laboratory Staff (1954) classifies the salinity hazard of irrigation waters, in terms of specific conductance, as follows: Less than 250 micromhos, low; 250–750 micromhos, medium; 750–2,250 micromhos, high; and greater than 2,250 micromhos, very high. However, the satisfactory use of a particular water for irrigation depends on many factors other than water quality, such as soil characteristics, drainage, irrigation practices, and crops grown.

Two methods of determination are given below, but the results obtained are not strictly comparable. The method of determination should be included on the analytical statement.

D:36a–1 RESIDUE-ON-EVAPORATION METHOD

The residue-on-evaporation method is recommended for all waters that contain less than 1,000 ppm dissolved solids and is applicable to all waters regardless of concentration, provided that the residue layer in the evaporating dish is kept sufficiently thin.

Principle of determination

A volume of sample that will yield less than 200 mg residue is evaporated just to dryness on a steam bath. The residue is dried at 180°C for 1.0 hr, cooled in a desiccator, and immediately weighed.

The weight of the residue is limited to 200 mg to insure subjection of all of the residue to the full effects of drying at 180°C. Voluminous residues will often seal over during the evaporation process and even entrap pockets of water that will not be completely driven off during the drying process. Massive residues also give up their water of crystallization more slowly than thin films of residue. The chemical composition of water has a marked effect on the dissolved-solids value obtained, but the percentage of error incurred for any given chemical type of water is independent of the total concentration if the residue film is kept thin.

Bicarbonate is converted to carbonate in the evaporation and drying process. The following other general observations have been reported (Howard, 1933, p. 4). The residues of carbonate-type water that contains considerable magnesium may often be less than would be expected. Residues of calcium and magnesium chloride water can be expected to lose some weight (up to 50 or 100 ppm) during the drying process; however, such loss of weight is usually more than counteracted by water of crystallization tightly held by the salts. Most of the water of crystallization is driven off from sulfates of sodium and magnesium when the residue is heated

at 180°C, but this temperature is insufficient to dehydrate calcium sulfate completely. Residues of water with a high nitrate content may lose as much as 30 ppm on heating.

Inasmuch as many of the salts in the residue are hygroscopic, it is imperative that an efficient desiccant be used. Alumina in which a moisture indicator is incorporated is recommended. Under no circumstances should the dried residues be allowed to stand for long periods of time before weighing.

With listed apparatus, results are generally reproducible to ±0.5–1.0 mg.

Apparatus

Platinum evaporating dishes, 75- to 125-ml capacity, weighing less than 50 g. Platinum is recommended for precise work because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

Steam bath

Oven, 180°C, uniform temperature throughout

Procedure

1. Pipet a volume of sample containing 10–200 mg (500 ml max) into a tared platinum dish.
2. Evaporate the sample just to dryness on a steam bath.
3. Dry in the oven at 180°C for 1.0 hr.
4. Cool in desiccator and immediately weigh. Record the weight to the nearest 0.0001 g.

Calculations

$$\text{ppm Dissolved solids} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg residue}$$

Report dissolved-solids concentrations of <1,000 ppm to whole numbers and of >1,000 ppm to 3 significant figures only.

D:36a–2 CALCULATION METHOD

Comparison of dissolved-solids concentration obtained by the residue-on-evaporation and calculation methods is discussed in sec. C:8b.

Principle of determination

The concentrations of all determined solid constituents are converted mathematically into the forms in which they would normally exist in an anhydrous residue. These quantities are then summarized.

The calculation method is applicable only to those analyses that are complete for all practical purposes. The chemist can never be certain of the completeness of the analysis, but for most alkaline waters other than brines the determination of silica, iron, calcium, magnesium, sodium, potassium, alkalinity, sulfate, chloride, and

nitrate is sufficient. The wide range of metals possible in acid water precludes assumptions as to the completeness of the analysis. If the water is grossly polluted it is usually necesary to determine the nitrogen components (see sec. D: 25), and perhaps estimate the carbonaceous material, before assuming ᵖ relatively complete analysis. Concentration of carbonaceous material can be estimated by redissolving the residue on evaporation and treating it with several successive portions of hydrogen peroxide. The difference in weight between the nonoxidized residue and the oxidized residue is an indication of the carbonaceous solids. The estimated carbonaceous solids are not included in the calculated dissolved solids but are one measure of the differences to be expected between dissolved solids determined by residue on evaporation and by calculation.

The conversion of the analytical statement to the forms in which the constituents would normally exist in an anhydrous residue involve many variables that are not known. It is assumed that all bicarbonate in solution will exist as carbonate in the residue.

$$2HCO_3^{-1} \rightarrow CO_3^{-2} + CO_2 + H_2O$$

Therefore, the bicarbonate in solution is divided by 2.03 to give its equivalent weight as carbonate in the residue. If the bicarbonate alkalinity includes other ions (see sec. D: 2), the calculated dissolved solids will include these constituents twice. However, occurrence of such errors of significant magnitude is relatively rare. For some constituents, such as boron, arsenic, phosphate, and selenium, the ionic states in solution are not known, much less the forms that the elements will take in the anhydrous residue. Heavy metals may be present in solution either as cations or as colloidal hydroxides, and their forms in the anhydrous residues cannot be predicted either. Consequently, when summarizing the constituents, all material is arbitrarily assumed to be present in the theoretical anhydrous residue in the same form as reported in the analysis, with the exception of bicarbonate. Dissolved solids calculated by the Geological Survey include all determined material usually existing in solid form at normal temperature and pressure.

The accuracy and reproducibility of the results are dependent on the completeness of the analysis and on the validity of each reported constituent concentration.

Calculations

1. Convert reported bicarbonate to carbonate.

$$\text{ppm } CO_3^{-2} = \frac{\text{ppm } HCO_3^{-1}}{2.03}$$

2. Add all determined dissolved-solid material reported in the analytical statement.

Report dissolved-solids concentrations of <1,000 ppm to whole numbers and of >1,000 ppm to 3 significant figures only.

D:36b SUSPENDED SOLIDS

Suspended solids are those that can be separated from the sample by filtration. The determined value is fairly representative of the sample but does not accurately represent the suspended-sediment concentration of the stream; suspended-solids values should not be confused with sediment concentration, which is the more accurate measure of material in suspension.

Note that suspended solids are reported as milligrams per liter of mixture, whereas all other concentrations determined by methods in this manual are reported as weight per million weights of clear solution (see sec. B:5). Suspended-solids concentrations reported in relation to weight of clear solution would be meaningless; furthermore, parts per million based on the weight of mixture would be misleading in that the different bases are not differentiated. Milligrams per liter accurately describes what is measured, and the reported value is sufficient for uses of the measurement.

D:36b–1 FILTRATION METHOD

The filtration method is similar in substance to part IIB, APHA (1955, p. 271) Standard Methods, and D 1069–54 T, method B–c, ASTM (1954, p. 323) Manual on Industrial Water.

Principle of determination

The precision and accuracy of the determination and the significance of the values obtained usually do not warrant the collection of a separate sample. If the suspended material is sufficiently settled to leave a clear supernatant solution for analysis, the suspended-solids determination can be postponed until test samples have been withdrawn for other determinations. The sample bottle is marked at the original waterline, and the volume of water removed for any chemical analysis is replaced by dilution water. This treatment is not recommended if a significant quantity of material is removed with the test samples.

The sample is mixed well and a suitable volume quickly poured off into a graduated cylinder. Withdrawal must be rapid to get a representative sample, and no attempt should be made to take an exact volume. The suspended solids are collected in a Gooch crucible and the insoluble material dried and weighed. A glass-fiber filter-paper circle is preferable to an asbestos mat because it withstands washing better.

Apparatus and reagents

Gooch crucible
Glass-fiber filter-paper circle
Suction filtration apparatus
Oven, 110°C

Procedure

1. Mix the suspension well, and rapidly pour off a suitable volume into a graduated cylinder.
2. Record the volume.
3. Quantitatively collect the insoluble materials on the mat in a tared Gooch crucible.
4. Wash the insoluble material sparingly with dilution water.
5. Dry the crucible overnight at 110°C.
6. Cool in a desiccator and weigh.

Calculations

$$\text{mg Suspended solids per liter} = \frac{1{,}000}{\text{ml mixture}} \times \text{mg residue}$$

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

American Society for Testing Materials, 1954, Manual on industrial water: Spec. Tech. Pub. 148–A.

Colorado Agricultural Experiment Station, 1943, Mineral tolerances in livestock drinking water: 56th Ann. Rept.

Heller, V. G., 1933, The effect of saline and alkaline waters on domestic animals: Oklahoma Agr. and Mining Coll. Expt. Sta. Bull. 217.

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Indus. and Eng. Chemistry, Anal. Ed., v. 5.

U.S. Public Health Service, 1946, Drinking water standards: U.S. Public Health Service Repts., v. 61, no. 11.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkali soils: U. S. Dept. Agriculture, Agriculture Handb. 60.

D:37 SPECIFIC CONDUCTANCE

The specific conductance of an electrolyte is the reciprocal of specific resistance and is expressed in mhos. Specific resistance is the resistance, in ohms, of a column of solution 1 cm long and 1 sq cm in cross section. In most waters, the conductance is so low that micromho is used as the unit of expression. The specific conductance is a measure of the ability of the water to carry an electric current and is therefore an indication, within rather wide limits, of the ionic strength of the solution.

Many natural waters in contact only with granite, silicious sand, well-leached soil or other difficultly soluble material have a conductance of less than 50 micromhos. Specific conductance of most waters in the Eastern United States is less than 1,000 micromhos, but in the arid western parts of the country, a specific conductance of more than 1,000 micromhos is common. Some saline lakes and brines may even reach several hundred thousand micromhos.

D:37a-1 WHEATSTONE BRIDGE METHOD

Principle of determination

Specific conductance is determined by using a Wheatstone bridge in which a variable resistance is adjusted so that it is equal to the resistance of the unknown solution between platinized electrodes of a standardized conductivity cell. The fraction of the current carried through the solution is a function of the relative velocities with which the different ions move; ions differ widely in their velocity and in their effect on conductance (see sec. C: 8c). Kohlrausch has shown that at infinite dilution, ions behave independently and that in this range the conductance-concentration relations of electrolytes of identical percentage composition is practically linear. However, as the concentration of the electrolyte increases, interionic attraction decreases the conductance per unit mass of electrolyte. This change in electric conductance of strong electrolytes with concentration is explained by the Debye-Hückel theory of interionic attraction.

$$\Lambda = \Lambda_o - a\sqrt{c}\ \Lambda_o - b\sqrt{c}$$

where

Λ = equivalent conductance,
Λ_o = equivalent conductance at infinite dilution,
c = concentration, and
a and b = theoretical constants.

For practical purposes the relation between specific conductance and concentration is linear below about 10,000 micromhos.

The temperature of the electrolyte affects the ionic velocities and consequently the conductance. Conductance increases about 2 per-

cent per degree centigrade, which is about the same as the temperature coefficient of viscosity of water. Specific conductance at 25°C is reported.

In determining the specific conductance, it would be troublesome to prepare a cell having electrodes exactly 1 sq cm in area and exactly 1 cm apart. However, it is not necessary to do this because it is possible to determine a factor called the cell constant (C). The cell constant is determined experimentally with a standard solution of known conductance. A 0.00702N potassium chloride solution has a specific conductance of 0.001000 mhos at 25°C. The relation between resistance (R), cell constant (C), and specific conductance (K) is shown in the following equation, where K is known and R is determined.

$$RK=C$$

Thus, if the resistance of the cell when filled with 0.00702N KCl is, for example, 350 ohms, the cell constant would be 0.35 for the conductivity cell used. If the conductivity cell having a cell constant of 0.35 is filled with the sample of water at 25°C and the observed resistance is 865 ohms, the specific conductance of the sample could be derived from the cell-constant equation.

$$\frac{C}{R}=K$$

or, by substituting values from the example,

$$\frac{0.35}{865}=0.000405 \text{ mhos at } 25°\text{C}.$$

Unless a constant-temperature room or bath is available, adjustment of temperature (T) to exactly 25° C is difficult. For most work, specific conductance is computed from the following equation:

$$\text{Micromhos}=\frac{R \text{ of } 0.00702N \text{ KCl at } T \text{ of sample measurement}\times 1{,}000}{R \text{ of the sample}}$$

New conductivity cells should be cleaned and the electrodes platinized before using. Subsequently they should be cleaned and replatinized whenever the readings become erratic or indistinct or inspection shows that any platinum black has flaked off. One platinization will usually suffice for a period of several months. To platinize the electrodes, clean them in chromic acid solution and rinse thoroughly in several changes of water. Place the electrodes in a solution of chloroplatinic acid and lead acetate (dissolve 3 g H_2PtCl_6 in 10 ml of water to which 20 mg of $Pb(C_2H_3O_2)_2$ is added; commercial platinizing solutions are also available). Connect the electrodes with 2 dry cells (1½ volts each) in parallel

and reverse the direction of the current once a minute for 6 minutes, or until the shiny platinum surface is covered. Avoid deposition of amorphous platinum on the electrodes. Repeat the electrolytic process using 10 percent sulfuric acid to remove chlorine. When not in use the cell should be kept immersed in distilled water.

The accuracy and reproducibility of results obtainable are dependent to a large extent on the type of bridge used but may approach ±2–3 percent with this equipment. Close attention to temperature is essential for reliable work.

Additional information on the principle of the determination is given by Getman and Daniels (1946, p. 390–396) and Scofield (1932).

Apparatus and reagents

Wheatstone bridge (see sec. C : 2a for discussion of conductivity meters)
Conductivity cell (see sec. C : 2a)
Thermometer, 0°–50°C, graduated in 0.1°
Potassium chloride, 0.00702*N*

Procedure

The manufacturer's instructions for operation of the bridge should be followed explicitly. A constant-temperature room or bath at 25°C simplifies temperature consideration. Where such facilities are not available, the sample should be brought to approximately room temperature before the determination. However, a group of samples standing in the laboratory are seldom at exactly the same temperature because of the influence of drafts, sunlight, radiators, ovens, open flames, etc. Whether the conductance determination is made in the field or laboratory, the temperature of each sample should be determined at the time of measurement.

1. Prepare a graph of resistance of 0.00702*N* KCl throughout the operating temperature range.
2. Rinse the cell with sample.
3. Measure the resistance of the sample and record the temperature at the time of measurement. Record temperature to the nearest 0.1°C.
4. Determine the resistance of 0.00702*N* KCl at the temperature at which the sample resistance was measured from the graph prepared in step 1.

Calculations

$$\text{Specific conductance (micromhos)} = \frac{R \text{ of } 0.00702N \text{ KCl}}{R \text{ of sample}} \times 1{,}000$$

where R = resistance in ohms.

Record conductivities of <1,000 micromhos to whole numbers and of >1,000 to 3 significant figures only.

Preparation of reagents

Potassium chloride, 0.00702*N*: Dry approx 1 g KCl in an oven at 180°C for 1 hr and cool in a desiccator. Dissolve 0.5232 g in water and dilute to 1,000 ml.

REFERENCES

Getman, F. H., and Daniels, Farrington, 1946, Outlines of physical chemistry: New York, John Wiley and sons, Inc., 7th ed.

Scofield, C. S., 1932, Measuring the salinity of irrigation waters and of soil solutions with the Wheatstone bridge: U.S. Dept. Agriculture Circ. 232.

D:38 SULFATE

Sulfate is dissolved from most sedimentary rocks. Large quantities may be derived from beds of gypsum, sodium sulfate deposits, and some types of shale. Water from mines may be high in sulfate as a result of oxidation of pyrite. Organic material containing sulfur adds sulfate to the water as a phase of the sulfur cycle. Sulfate is discharged in many industrial waste products. In natural waters, concentrations range from a few parts per million to several thousand parts per million.

Salts of sulfate are saline cathartics and a quantity equal to that in 1 liter of water containing 1,000–2,000 ppm sulfate constitutes an average dose. The U.S. Public Health Service (1946) recommends that the sulfate concentration not exceed 250 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations. There is some report of a detrimental effect of sulfate to livestock, but it also seems to offset in part the toxicity of selenium toward cattle (Hurd-Karrer, 1934, 1935, p. 289).

The sulfate content of water is not very critical in many industrial processes. The significance is also somewhat dependent on the character of the cations (California State Water Pollution Control Board, 1952, p. 377–378). It is less toxic than chloride to crops.

D:38a-1 VISUAL THORIN METHOD

Principle of determination

Thorin reacts with barium to give a red color. The intensity of the color is dependent on pH, indicator concentration, and nature of the solvent. The color is more intense in organic media than in water solutions. The color reaction can be utilized to titrate sulfate directly with barium chloride by adding a large volume of organic solvent to the sample and titrating in this mixed medium. The color development is also highly dependent on the nature of the organic solvent; dioxane is superior to either ethyl or methyl alcohol when the end point is detected visually. The initial color of thorin in the dioxane-water medium is yellow, and the change in the end point is to pink. The color change is enhanced when the solution is viewed through a pale-blue filter such as a didymium glass filter or glass-blowers' goggles.

The optimum pH for the titration is about 2.5, which permits the use of the method for the analysis of many water samples without danger of precipitation of some salts in the organic media. Thorin reacts with many metals, including calcium; therefore, it is necessary to remove all metal ions by cation exchange prior to titration. Phosphate interferes somewhat by coprecipitation; with 100 ppm of

sulfate, 10 and 20 ppm of phosphate give a positive error of about 2 and 3 percent, respectively. Color may interfere with the detection of the end point, and the method described in sec. D: 38a–2 is recommended for highly colored water.

Two strengths of barium chloride and thorin are provided, but there is a rather wide overlap in application. The dilute titrant and indicator are recommended if the sulfate content of the sample is less than 5 mg. The concentrated titrant and indicator give better results in the higher concentration ranges.

Results are accurate and reproducible to ±0.02 mg in the 0–5 mg range and ±1–2 percent for higher concentrations.

Apparatus and reagents

Ion-exchange columns, charged with Amberlite IR–120 and operating on the hydrogen cycle. The column should be at least 10 in. long to assure complete exchange in moderately concentrated water. Highly mineralized water and brine require a longer column. Experience has shown that a strong acid solution (HCl 30 percent v/v) is required to get uniformly satisfactory regeneration. The frequency of regeneration depends on the mineral content of the samples; with average water, regeneration after 3 or 4 passes is sufficient.

Pale-blue filter: A didymium filter or glass-blowers' goggles have been used satisfactorily.

Titration assembly with a white porcelain base and fluorescent light.

Buret, 25-ml

Sodium hydroxide, 0.05*N*

Thorin indicator, 0.04 percent

Thorin indicator, 0.1 percent

1,4 dioxane: The grade labeled "purified" is usually satisfactory, but distillation from glass may be required if the blank titration is excessive.

Barium chloride, 1.00 ml≏0.500 mg SO_4^{-2}

Barium chloride, 1.00 ml≏1.00 mg SO_4^{-2}

Procedure

1. Rinse the ion-exchange column with 20–30 ml of sample and discard the rinse water. (This portion can be checked for calcium if desired.)
2. Pass a sufficient volume of sample through the exchanger to provide 25–30 ml of effluent for the determination.
3. Pipet a volume of effluent containing less than 25 mg SO_4^{-2} (25.00 ml max) into a 150-ml beaker and adjust the volume to approx 25 ml. The dissolved-solids content should not exceed 125 mg for the high-range titration or 50 mg for the low range.
4. Adjust the pH to between 2.2 and 5 with 0.05*N* NaOH if necessary.
5. Add 50 ml dioxane.
6. Add 1.0 ml thorin indicator.
7. Titrate with $BaCl_2$ to the point where the color changes suddenly from yellow to orange when viewed through the filter. On titrating sulfate concentrations of less than 10 ppm, the end point will appear and then fade on stirring. At the true end point the color persists for several minutes.

Calculations

When $BaCl_2$, 1.00 ml≏0.50 mg SO_4^{-2}, and 0.04 percent thorin indicator are used: The titration is not strictly linear below 5 mg SO_4^{-2}, and the SO_4^{-2} concentration is determined by reading from a graph prepared by titrating standards. The following titrant volumes have been required:

mg SO_4^{-2}	*ml*
0.00	0.05
.25	.55
1.25	2.50
2.50	4.95
5.00	9.90

$$\text{ppm } SO_4^{-2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } SO_4^{-2}$$

When $BaCl_2$, 1.00 ml≏1.00 mg SO_4^{-2}, and 0.1 percent thorin indicator are used:

$$\text{ppm } SO_4^{-2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{ml } BaCl_2$$

Report sulfate concentrations of <10 ppm to 1 decimal place, between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Sodium hydroxide, 0.05*N*: Dissolve 2.0 g NaOH in water and dilute to approx 1 liter.

Thorin indicator, 0.04 percent: Dissolve 0.20 g of thorin in water and dilute to 500 ml.

Thorin indicator, 0.1 percent: Dissolve 0.5 g of thorin in water and dilute to 500 ml.

Barium chloride, 1.00 ml≏1.00 mg SO_4^{-2}: Dissolve 2.130 g anhydrous $BaCl_2$, dried overnight in an oven at 180°C, in water and dilute to 1,000 ml. This concentration is not strictly stoichiometric but has been determined empirically. Check the titer by titrating standard SO_4^{-2} solutions as directed in the procedure.

Barium chloride, 1.00 ml≏0.50 mg SO_4^{-2}: Dissolve 1.085 g anhydrous $BaCl_2$, dried overnight in an oven at 180°C, in water, and dilute to 1,000 ml.

Sodium sulfate, 1.00 ml=1.00 mg SO_4^{-2}: Dissolve 1.4787 g Na_2SO_4, dried for 2 hr at 180°C, in water, and dilute to 1,000 ml.

D:38a–2 SPECTROPHOTOMETRIC THORIN METHOD

The spectrophotometric thorin method is useful for waters whose sulfate content does not exceed 200 ppm and for waters with high color that interferes with the visual detection of the end point in the visual thorin method (see sec. D:38a–1).

Principle of determination

The chemistry of the determination is similar to that in section D:38a–1, with the exception that the preferable titration medium consists of 80 percent ethyl alcohol instead of 66 percent dioxane. The

pH is adjusted to and maintained at 5 by a sodium acetate buffer. The end point of the titration is detected instrumentally.

With listed apparatus, results are accurate and reproducible to ±0.005 mg, which is comparable in terms of parts per million to that for the visual thorin method (see sec. D:38a–1).

Apparatus and reagents

Ion-exchange column (see sec. D:38a–1)

Absorption cells, 50-mm. The cement in some cells reacts with thorin to give a red color. Cells should be tested for thorin reaction, and those that give a red color in 10–15 min should be rejected.

Spectrophotometric-titration assembly (see sec. C:2h).

Spectrophotometer, Beckman Model B:

Wavelength: 520 mμ
Phototube: Blue-sensitive
Initial sensitivity setting: 1
End point: At 0.20 absorbancy

Buret, 10-ml

Solvent-indicator solution

Barium chloride, 1.00ml≏0.20 mg SO_4^{-2}

Procedure

1. Rinse the ion-exchange columns with 20–30 ml of sample and discard the rinse (this portion can be checked for the presence of calcium if desired).
2. Pass sufficient sample through the exchanger to provide a 10-ml effluent for the determination.
3. Pipet a volume of sample containing less than 1 mg SO_4^{-2} and 10 mg dissolved solids (10.00 ml max) into a 50-mm absorption cell and adjust the volume to 10.0 ml.
4. Add 40 ml solvent-indicator solution.
5. Start the stirrer and set the absorbancy to 0.100.
6. Titrate with $BaCl_2$, (1.00 ml≏0.20 mg SO_4^{-2}) to an absorbancy of 0.20, which is stable for 30 sec.
7. Determine a blank correction by titrating dilution water. The blank is constant throughout the concentration range of the method. A blank of 0.05 ml has been used.

Calculations

$$\text{ppm } SO_4^{-2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times 0.2 \times (\text{ml titrant} - \text{ml blank})$$

Report sulfate concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 to 3 significant figures only.

Preparation of reagents

Solvent-indicator solution: Dissolve 0.025 g thorin (the Hach Chemical Co. product has been used satisfactorily), 0.5 g anhydrous sodium acetate in 10 ml of water. Add the solution to 1,000 ml of 95 percent ethyl alcohol. Add 12 ml glacial $HC_2H_3O_2$ (sp gr 1.049) and mix.

Barium chloride, 1.00 ml≏0.20 mg SO_4^{-2}: Dissolve 0.434 g anhydrous $BaCl_2$, dried for 1 hr at 180°C, in water, and dilute to 1,000 ml.

D:38a–3 GRAVIMETRIC METHOD

The gravimetric method is similar in substance to part IA, APHA (1955) Standard Methods; D 516–49, ASTM (1954) Manual on Industrial Water; and method 83, U.S. Salinity Laboratory Staff (1954) Handbook 60.

Principle of determination

Sulfate is precipitated as barium sulfate, and the precipitate is ignited and weighed. Precipitation is carried out in acid media to prevent precipitation of barium carbonate, hydroxide, and phosphate, which are insoluble in alkaline media. Hydrochloric acid has the effect of promoting the formation of coarse crystals. The acid concentration is not important as long as it does not exceed 0.05*N*. The precepitation should be made at boiling temperature because the tendency toward supersaturation decreases at the higher temperatures. According to Kolthoff and Sandell (1952, p. 322–336):

> Barium sulfate provides a notorious example of a precipitate subject to contamination through the action of coprecipitation phenomena. Since the determination of sulfate is of great practical importance, a great deal of attention has been paid to the problem of obtaining a pure precipitate of barium sulfate, and hundreds of papers on the subject are to be found in the literature. In spite of the immense amount of work that has been done, the determination of sulfate remains one of the less accurate determinations of quantitative analysis.

The analyst is referred to authoritative texts, such as Kolthoff and Sandell (1952) and Hillebrand and Lundell (1929), for detailed discussions of potential errors involved. In water analysis the effect of coprecipitation is largely dependent on the character and concentration of the other solutes. Small quantities of ferrous iron, magnesium, zinc, and aluminum may be present. Calcium, ferric iron, and nitrate should not be present in appreciable amounts. Even though some of these constituents may be coprecipitated with the barium sulfate, prolonged digestion of the precipitate in the mother liquor at elevated temperatures makes for a precipitate approaching theoretical composition. Silica may also be precipitated from the hot acid solution. The interference of silica is eliminated if the sulfate is determined on the filtrate from the gravimetric silica determination (see sec. D:34a–2). An alternative method that minimizes silica interference involves treatment of the ignited residue (procedure 9) in a platinum crucible with hydrofluoric acid and a few drops of concentrated sulfuric acid, followed by reignition.

Best results are obtained if the weight of the precipitate is between 0.025 and 0.150 g, about 10–60 mg of sulfate. With careful work, results are reproducible to ± 0.2 mg; the accuracy is dependent on the purity of the precipitate.

Apparatus and reagents

Steam bath or hot plate
Porcelain crucibles
Muffle furnace
Methyl orange indicator solution
Hydrochloric acid, conc (sp gr 1.19)
Barium chloride, 10 percent
Filter-paper pulp

Procedure

1. Dilute or concentrate filtrate from the gravimetric silica determination (see sec. D : 34a–2, procedure 8) to a convenient volume. Pipet an aliquot containing between 10 and 60 mg SO_4^{-2} into a 400-ml beaker and adjust the volume to approx 200 ml.
2. Acidify to methyl orange with conc HCl and add a few drops in excess.
3. Heat the acidified aliquot to boiling and while hot add slowly dropwise, and with constant stirring, 10 ml hot 10 per cent $BaCl_2$.
4. Cover the beaker with a watchglass and digest on the steam bath or hotplate (do not boil) for 2–3 hr, or preferably overnight.
5. Mix in a small quantity of filter-paper pulp and let stand for 1 hr on steam bath or hotplate.
6. Filter hot through Whatman No. 42 filter paper.
7. Quantitatively transfer the precipitate to the filter paper and wash thoroughly, scrubbing out the beaker *several times* with a rubber policeman and rinsing with hot water several times. The filtrate from the last washing should contain no chloride when tested with $AgNO_3$.
8. Slowly ignite the precipitate in a tared crucible over a low oxidizing flame until the filter paper is reduced to a white ash.
9. Transfer the crucible to the muffle furnace and ignite at approx. 800°C for 1.0 hr.
10. Cool in a desiccator and weigh.

Calculations

$$\text{ppm } SO_4^{-2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } BaSO_4 \times 0.4115$$

Report sulfate concentrations of <10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of >999 ppm to 3 significant figures only.

Preparation of reagents

Methyl orange indicator solution: Dissolve 0.05 g methyl orange in water and dilute to approx 100 ml.

Barium chloride, 10 percent: Dissolve 100 g $BaCl_2$ in water and dilute to approx 1 liter.

D:38a–4 TURBIDIMETRIC METHOD

The turbidimetric test is limited to rough approximations of sulfate. Its maximum utility is as a laboratory aid in the selection of proper sample size for the determinations described in secs. D : 38a–1, –2, –3, and as a field test for the approximation of sulfate when accuracy requirements are low.

Principle of determination

Sulfate is precipitated as barium sulfate, and the resultant turbidity is compared with that produced in standards of known concentration.

Apparatus and reagents

Test tubes
Sodium sulfate, 1.0 ml=0.10 mg SO_4
Barium chloride, acidified, 10 percent

Procedure

1. Pipet a volume of sample containing less than 0.25 mg SO_4^{-2} (10.0 ml max) into a test tube and adjust volume to 10.0 ml.
2. Prepare sufficient standards in the 0.00- to 0.25-mg range and adjust the volume to 10.0 ml.
3. Add 1.0 ml 10 percent $BaCl_2$.
4. Shake vigorously and allow suspensions to stand 10 min.
5. Compare the turbidity of the sample with that of the standards. Comparison is best made by looking down through the tubes against a black background.

Calculations

$$\text{ppm } SO_4^{-2} = \frac{1{,}000}{\text{ml sample}} \times \text{mg } SO_4^{-2} \text{ in standard}$$

Preparation of reagents

Sodium sulfate, 1.0 ml=0.10 mg SO_4^{-2}: Dissolve 0.148 g Na_2SO_4 in water and dilute to 1,000 ml.

Barium chloride, acidified, 10 percent: Dissolve 10 g $BaCl_2$ in water, add 5 ml conc HCl (sp gr 1.19), and dilute to approx 100 ml.

REFERENCES

American Public Health Association and others, 1955, Standard methods for the examination of water, sewage, and industrial wastes: New York, Am. Public Health Assoc., Inc., 10th ed.

American Society for Testing Materials, 1954, Manual on industrial water: Spec. Tech. Pub. 148–A.

California State Water Pollution Control Board, 1952, Water quality criteria: Pub. no. 3.

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Kolthoff, I. M., and Laitinen, H. A., 1941, pH and electro titrations: New York, John Wiley and Sons, Inc.

U.S. Public Health Service, 1946, Drinking water standards: U.S. Public Health Service Repts, v. 61, no. 11.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkaki soils: U.S. Dept. Agriculture, Agriculture Handb. 60.

Sulfide occurs in water as a result of bacterial and chemical processes. It usually is present as hydrogen sulfide. Variable amounts may be found in waters receiving sewage, and (or) industrial wastes, such as from tanneries, paper mills, chemical plants, and gas manufacturing work (California State Water Pollution Control Board, 1952, p. 271–272).

Waters containing sulfides, especially hydrogen sulfide, may be considered undesirable because of their odor. The U.S. Public Health Service (1946) states that water on carriers subject to Federal quarantine regulations shall have no objectionable taste or odor. The toxicity to aquatic organisms differs significantly with the species.

D:39a–1 IODOMETRIC METHOD

This iodometric method does not differentiate the forms in which the sulfide exists in solution. The procedure is recommended for use on water containing more than about 0.5 ppm of sulfide.

Principle of determination

Sulfide is reacted with an excess of iodine in acid solution, and the remaining iodine is then determined by titration with sodium thiosulfate using starch as an indicator (Kolthoff and Sandell, 1952, p. 585–605).

$$S^{-2} + I_2 \xrightarrow{H^{+1}} S + 2I^{-1}$$

$$I_2 + 2S_2O_3^{-2} \xrightarrow{H^{+1}} S_4O_6^{-2} + 2I^{-1}$$

A blank is treated with exactly the same amount of iodine and titrated with sodium thiosulfate. The sulfide concentration is calculated from the difference between the volume of thiosulfate required for the blank and the volume used for the sample.

Reducing substances such as sulfites and heavy-metal ions will use up iodine and therefore contribute positive errors. Oxygen and other oxidants may react with hydriodic acid to liberate iodine and thus contribute negative errors.

When the sulfide concentration is below 0.05 mg, the method is accurate to only ±50 percent. Above 0.05 mg of sulfide the accuracy improves as the sulfide concentration increases, and, at 5 ppm of sulfide, the results are reproducible to ±0.05 mg.

Apparatus and reagents

Buret, 10-ml.
Iodine solution, 0.010*N*
Hydrochloric acid, conc (sp gr 1.19)
Sodium thiosulfate solution, 0.010*N*
Starch indicator, stable

Procedure

Samples for the determination of sulfide should be collected with a minimum of aeration and agitation as directed in sec. A:3c and treated in accordance with directions given in sec. A:4d.

1. Vigorously shake the sample to mix the contents thoroughly. Immediately pipet a volume of sample with ZnS in suspension containing less than 1.5 mg S (100.0 ml max) into a 250-ml Erlenmeyer flask and adjust the volume to approx 100 ml.
2. Prepare a blank of approx 100 ml water and carry it through the procedure with the sample.
3. Add 10.00 ml 0.010*N* I_2.
4. Without delay add 10 ml conc HCl.
5. Immediately titrate the excess I_2 with 0.010*N* $Na_2S_2O_3$, adding 2–3 ml starch indicator as the end point is approached.

Calculations

$$\text{ppm } S^{-2} \text{ as } H_2S = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times 0.1704 \times \begin{pmatrix} \text{ml blank titrant} \\ -\text{ml sample titrant} \end{pmatrix}$$

Report sulfides concentrations of <10 ppm to 1 decimal place and of >10 ppm to 2 significant figures only.

Preparation of reagents

Iodine solution, 0.010*N*: Dissolve 6 g iodate-free KI, in approx 25 ml water. Add 1.2691 g resublimed I_2. When solution is complete, dilute to 1,000 ml. Standardize with 0.010*N* $Na_2S_2O_3$ using starch as indicator.

$$\text{Normality of } I_2 = \frac{0.010 \times \text{ml } Na_2S_2O_3}{\text{ml } I_2}$$

Sodium thiosulfate, 0.010*N*: Dissolve 2.482 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water and dilute to 1,000 ml with carbon dioxide-free water. Standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 hr at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 ml. Pipet 25.00 ml KIO_3 solution into 250-ml Erlenmeyer flask, then add successively 75 ml water and 0.5 g iodate-free KI. After solution is complete, add 10 ml conc HCl (sp gr 1.19). Allow the stoppered flask to stand 5 min in the dark and titrate with $Na_2S_2O_3$ using starch indicator as end point is approached (light straw color).

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{ml } Na_2S_2O_3}$$

Potassium iodide, iodate-free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 ml water, acidifying with 1 or 2 drops conc H_2SO_3 (sp gr 1.84) and adding 2–3 ml starch indicator. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

REFERENCES

California State Water Pollution Control Board, 1952, Water quality criteria: Pub. no. 3.

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis: New York, Macmillan Co., 3d ed.

U.S. Public Health Service, 1946, Drinking water standards: U.S. Public Health Service Repts., v. 61, no. 11.

D:40 TURBIDITY

Turbidity is the optical property of a suspension with reference to the extent to which the penetration of light is inhibited by the presence of insoluble material. Turbidity is a function of both the concentration and particle size of the suspended material. Although it is reported in terms of parts per million of silica, it is in no way synonymous with the weight of sediment per unit volume of water. The standard for turbidity (Newell, 1902) is

> . . . a water which contains 100 parts of silica per million in such a state of fineness that a bright platinum wire 1 millimeter in diameter can just be seen when the center of the wire is 100 millimeters below the surface of the water and the eye of the observer is 1.2 meters above the wire, the observation being made in the middle of the day, in the open air, but not in sunlight, and in a vessel so large that the sides do not shut out the light so as to influence the results. The turbidity of such water shall be 100.

This definition in effect describes the size of the particles to be used as standard solutions. With this size particle, and only this size, 1 ppm silica (turbidity) is equal to 1 ppm silica (weight).

The U.S. Public Health Service (1946) recommends that the turbidity not exceed 10 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations. Some species of fish require clear water, but others thrive in somewhat turbid water. In general, turbidity adversely affects fish production by excluding light and thereby interfering with the growth of plants important in the fish-food cycle (California State Water Pollution Control Board, 1952, 1954, p. 226–228). Turbid water is abrasive to pipes, pumps, and turbine blades. In process water, turbidities much more than 1 ppm are not tolerated by several industries, but others permit up to 50 ppm or higher.

D:40a–1 HELLIGE TURBIDIMETER

Principle of determination

The optical phenomena which cause the opalescent or "milky" appearance of a fine suspension are light scattering and absorption. Which of the two effects predominates in a particular case depends upon the size and the concentration of the particles. Inasmuch as the subjective reaction to these phenomena cannot be accurately duplicated by means of the turbidimeters on the market at the present time, it is quite possible to find instrumental measurements of this property at variance with the observers' visual reaction. Sometimes an instrumental measurement will designate one sample as having higher turbidity than a second sample, whereas the observers' reaction will be the reverse.

At the present time the property called turbidity is defined by the instrument used for its measurement. While the basic instrument is considered to be the Jackson candle turbidimeter, there are many other instruments in use. Readings from one to the other are not universally comparable. While all the common visual instruments, including the Jackson device, utilize both the absorption and scattering effect in making the measurement, there is wide variation in the degree to which each effect predominates in the various instruments. In order to achieve uniformity consistent with convenience, the Hellige turbidimeter has been selected as the basis for the turbidity measurement herein described. See sec. C: 2g for a description of the Hellige turbidimeter.

Apparatus and reagents

Turbidimeter, Hellige

Illumination bulbs and calibration curves. New bulbs should be calibrated against standards prepared by the manufacturer and not against laboratory-prepared suspensions of fuller's earth or other similar material.

Procedure

Meticulous cleanliness of the sample containers and all parts of the instrument is mandatory, and the manufacturer's instructions in the operation and maintenance of the instrument should be followed explicitly.

Calculations

Determine the turbidity of the sample from appropriate calibration curves. Report turbidity as follows:

Turbidity (as ppm SiO_2)	*Record to the nearest—*
0–1	0.1
1–10	1
11–100	5
101–400	10
401–700	50
≧701	100

REFERENCES

California State Water Pollution Control Board, 1952, Water quality criteria: Pub. no. 3.

——— 1954, water quality criteria: Pub. no. 3, Addendum no. 1.

Newell, F. H., 1902, Measurement of turbidity and color: U.S. Geol. Survey, Div. Hydrography Circ. 8.

U.S. Public Health Service, 1946, Drinking water standards: U.S. Public Health Service Repts., v. 61, no. 11.

D:41 VISCOSITY

Viscosity is a characteristic property of fluids. It may be described in simple terms as an internal friction or an internal resistance to motion and is defined as the tangential force in dynes that must be exerted between 2 parallel layers, 1 sq cm in area and 1 cm apart, in order to maintain a velocity of streaming of 1 cm per sec of 1 layer past the other (Glasstone, 1946, p. 95–155). Such a fluid would have a velocity of 1 poise (dynes per cm^2 per sec). A more common term for reporting viscosity is the centipoise, which is 1/100 of a poise. Since the viscosity of water is approximately 1 centipoise at 20°C, it seems desirable to report viscosity in centipoises at 20°C.

The experimental methods for the determination of viscosity are based on the fundamental equation of viscosity derived by J. L. M. Poiseville in 1844

$$\eta = \frac{\pi r^4 t p}{8VL}$$

relating the coefficient of viscosity, η, to the volume, V, of gas or liquid which will flow through a narrow tube of L length and r radius in t time when under the influence of p driving pressure (Glasstone, 1946).

D:41a–1 BROOKFIELD VISCOMETER

Principle of determination

The principle upon which the Brookfield viscometer operates is the measurement of the drag produced upon a spindle rotating at a definite constant speed while immersed in the sample. The torque on the spindle rotating at constant speed is measured by a cilibrated spring. Viscosity changes appreciably with changes in temperature; therefore, the viscosity should be measured at constant or controllable temperature.

When measuring viscosities within the range of 0–10 centipoises, the results are reproducible to ±0.02 centipoises.

Apparatus

Brookfield Viscometer, model LV with UL adapter

Procedure

Follow the instructions and procedure that the manufacturer issues with the viscometer.

Calculations

Report viscosity to 0.01 centipoise at 20°C.

REFERENCE

Glasstone, Samuel, 1946, The elements of physical chemistry: New York, D. Van Nostrand Co., Inc.

D:42 ZINC

Zinc is abundant in rocks and ores but is only a minor constituent in natural water because the free metal and its oxides are only sparingly soluble. In most alkaline surface and ground waters it is present only in trace quantities, but more may be present in acid water. Chlorides and sulfates of zinc are highly soluble. Zinc is used in many commercial products, and industrial wastes may contain large amounts.

Zinc in moderate concentrations is not known to have adverse physiological effects on man or stock, but zinc salts give water an unpleasant astringent taste and form a greasy film on boiling water (Howard, 1923, p. 411). The U.S. Public Health Service (1946, p. 13) recommends that the concentration of zinc not exceed 15 ppm in drinking and culinary water on carriers subject to Federal quarantine regulations. Small quantities of zinc are toxic to various aquatic animals and plants. The element may also have such a toxic action on purifying bacterial flora of streams as to present serious sewage pollution problems. The concentration of 0.3 ppm is toxic to some fresh-water fish (Ellis, Westfall, and Ellis, 1946). High concentrations of zinc are reported to be detrimental to some crops (Kelly and Brown, 1938).

D:42a–1 DITHIZONE EXTRACTION METHOD

The dithizone extraction method is similar in substance to part IA (tentative), APHA (1955, p. 212–214) Standard Methods.

Principle of determination

Zinc forms a keto complex with dithizone. This complex is soluble in carbon tetrachloride or chloroform and imparts a bright-red color to the solution. Many other metals react the same way with dithizone as does zinc. At a pH of 4.0–5.5 sodium thiosulfate largely prevents the reaction of copper, mercury, silver, gold, bismuth, lead, and cadmium with dithizone while allowing the reaction of zinc to proceed. In the presence of much nickel or cobalt, potassium cyanide can be used as the complexing agent.

The reaction may not go to completion because the presence of thiosulfate also retards the reaction between zinc and dithizone. Therefore, the determination is to some extent empirical, and it is essential to adhere to directions as to volumes, time of extraction, pH, etc. Even analytical-grade reagents often contain sufficient zinc to be detected by the procedure. Instructions are given for extraction of prepared reagents with dithizone before use. Some

batches of dithizone may require purification; when necessary, the reagent can be purified by the ammonia extraction method (Sandell, 1950). Zinc may also be dissolved from glassware and some stopcock grease. All glassware should be rinsed with dilute nitric acid before use. Dithizone and dithizonates decompose rapidly in a strong light. Hence, samples and standards should be carried through the procedure simultaneously, and the color comparison should be made before an undue lapse of time.

In the absence of excessive quantities of other metals that react with dithizone at the pH of the test, results are accurate and reproducible to ±0.0005 mg.

Apparatus and reagents

Matched test tubes, glass-stoppered
Separatory funnels, 125-ml
Zinc chloride, 1.00 ml=0.010 mg Zn^{+2}
Hydrochloric acid, 0.05*N*
Sodium hydroxide, 0.05*N*
Methyl orange indicator solution
Acetate buffer solution
Sodium thiosulfate, 25 percent
Dithizone, 0.001 percent in CCl_4

Procedure

Samples for the determination of zinc should be treated in accordance with directions given in sec. A: 4d.

1. Pipet a volume of sample containing less than 0.005 mg Zn^{+2} (50.0 ml max) into a separatory funnel and adjust the volume to 50 ml with metal-free water.
2. In separatory funnels, prepare a blank and sufficient standards, and adjust the volumes to 50 ml with metal-free water.
3. Adjust the sample and standards with 0.05*N* HCl and 0.05*N* NaOH until they are just acid to methyl orange.
4. Add 25 ml acetate buffer.
5. Add 5 ml 25 percent $Na_2S_2O_3$, and mix.
6. Add 5.0 ml 0.001 percent dithizone.
7. Extract by shaking vigorously for 2.0 min.
8. Withdraw the CCl_4 layer into a glass-stoppered test tube and stopper tightly to prevent loss of solvent.
9. Compare the sample and standards by viewing transversely against a white background. The color changes from green to red with increasing concentrations of zinc. Record the zinc concentration of the sample to the nearest 0.0005 mg Zn^{+2}.

Calculations

$$\text{ppm } Zn^{+2} = \frac{1}{\text{density}} \times \frac{1{,}000}{\text{ml sample}} \times \text{mg } Zn^{+2} \text{ in sample}$$

Report zinc concentrations of <1 ppm to 2 decimal places and of >1 ppm to 2 significant figures only.

Preparation of reagents

Zinc chloride, 1.00 ml=0.010 mg Zn^{+2}: Dilute 10.00 ml $ZnCl_2$ (1.00 ml=0.10 mg Zn^{+2}) to 100.0 ml with metal-free water. Prepare immediately before using.

Zinc chloride, 1.00 ml=0.10 mg Zn^{+2}: Dissolve 0.100 g reagent-grade Zn^0 (30-mesh) in a slight excess of dilute HCl and dilute to 1,000 ml with metal-free water.

Hydrochloric acid, 0.05*N*: Dilute 4.2 ml conc HCl (sp gr 1.19) to approx 1 liter with metal-free water.

Sodium hydroxide, 0.05*N*: Dissolve 2.0 g NaOH in metal-free water and dilute to approx 1 liter with metal-free water.

Methyl orange indicator solution: Dissolve 0.5 g methyl orange in water and dilute to approx 1 liter.

Acetate buffer solution: Mix equal volumes of 2*N* $NaC_2H_3O_2$ and 2*N* $HC_2H_3O_2$. Remove heavy metals by repeated extraction with 0.005 percent dithizone until the CCl_4 remains green. Rinse out the dithizone by extracting with CCl_4.

Sodium acetate, 2*N*: Dissolve 136 g $NaC_2H_3O_2 \cdot 3H_2O$ in 500 ml metal-free water.

Acetic acid, 2*N*: Dilute 57 ml glacial $HC_2H_3O_2$ to 500 ml with metal-free water.

Dithizone, 0.005 percent in CCl_4. Dissolve 12.5 mg diphenylthiocarbazone in approx 250 ml CCl_4. Stopper tightly and store in the refrigerator.

Sodium thiosulfate, 25 percent: Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in approx 100 ml metal-free water. Extract repeatedly with 0.005 percent dithizone until the CCl_4 remains green. Rinse out the dithizone by extracting with CCl_4.

Dithizone, 0.005 percent in CCl_4. Dissolve 12.5 mg diphenylthiocarbazone in 1 liter CCl_4. Stopper tightly and store in the refrigerator.

D:42a–2 DIRECT COLOR-COMPARISON METHOD

The method is not as specific for zinc as D:42a–1 but is more rapid if copper is also determined.

Principle of determination

In a buffered solution, zinc forms a red keto complex with dithizone in acetone. Sodium thiosulfate inhibits the interference of other metals that react with dithizone. Sodium citrate is used to complex iron, which oxidizes dithizone. The keto complex is soluble in water-acetone media, and no extraction is required.

Copper also forms a complex which absorbs light in the same range as the zinc complex. The absorbancy of the zinc and copper complexes determined collectively are corrected for that attributable to copper.

In the absence of other interfering metals, results are accurate and reproducible to ±0.0005 mg.

Additional information on the principle of the determination is given by Sandell (1950, p. 87–113).

Apparatus and reagents

Spectrophotometer, Beckman Model B:

Wavelength: 550 mμ
Cells: 40-mm optical depth, cylindrical
Phototube: Blue-sensitive
Initial sensitivity setting: 3
Slit width: 0.3 mm (approx)

The following absorbancies have been observed:

mg Zn	*Absorbancy*
0.001	0.068
.002	.133
.004	.260
.008	.515

Zinc chloride, 1.00 ml=0.004 mg Zn^{+2}
Sodium thiosulfate, 25 percent
Acetate-citrate composite solution
Acetone
Dithizone, 0.05 percent in acetone
Copper solution, 1.00 ml=0.010 mg Cu^{+2}

Procedure

Samples for the determination of zinc should be collected in accordance with directions given in sec. A: 4d.

1. Determine the copper content of the sample by the procedure described in sec. D: 14a–1.
2. Pipet a volume of sample containing less than 0.01 mg Zn^{+2} (10.00 ml max) into a 50-ml beaker and adjust the volume to 10.0 ml with metal-free water.
3. Prepare a blank and sufficient standards, and adjust the volumes to 10.0 ml with metal-free water.
4. Add 1.0 ml 25 percent $Na_2S_2O_3$ and mix.
5. Add 1.0 ml acetate-citrate composite solution and mix.
6. Add 10.0 ml acetone and mix.
7. Add 2.0 ml 0.05 percent dithizone and mix.
8. Cover the beakers to minimize evaporation.
9. Immediately determine the combined absorbancy of the test sample and standards against the blank, and when necessary make correction for water color as directed in sec. C: 1a–2, method 1.
10. Prepare a correction curve for copper contributing to absorbancy by treating standard solutions by the procedure given above.

Calculations

1. Correct absorbancy for that attributable to copper.

$$A_{Zn}=A_{Zn+Cu}-A_{Cu}$$

2. Determine quantity of Zn^{+2} in test sample from a plot of corrected absorbancies of standards containing known amounts of constituent.

3. $$\text{ppm } Zn^{+2}=\frac{1}{\text{density}}\times\frac{1{,}000}{\text{ml sample}}\times\text{mg } Zn^{+2} \text{ in sample}$$

Report zinc concentrations of <1 ppm to 2 decimal places and of >1 ppm to 2 significant figures only.

Preparation of reagents

Sodium thiosulfate solution, 25 percent: Dissolve 250 g $Na_2S_2O_3 \cdot 5H_2O$ in metal-free water and dilute to approx 1 liter. Extract with dithizone in CCl_4 until titrant shows no evidence of zinc.

Acetate-citrate composite solution: Dissolve 340 g $NaC_2H_3O_2 \cdot 3H_2O$ in metal-free water, add 1.5 g $Na_3C_6H_5O_7 \cdot 2H_2O$, and dilute to 1,000 ml. Extract with dithizone in CCl_4 until titrant shows no evidence of zinc.

Dithizone reagent, 0.05 percent: Dissolve 0.100 g diphenylthiocarbazone in 200.0 ml acetone. This reagent must not be refrigerated (dithizone will precipitate at low temperatures).

Zinc chloride, 1.00 ml=0.0004 mg Zn^{+2}: Dilute 10.00 ml $ZnCl_2$ (1 ml=0.10 mg Zn^{+2}) to 250.0 ml with metal-free water. Dilute 10.00 ml of this intermediate solution to 100.0 ml with metal-free water. Prepare immediately before using.

Zinc chloride, 1.00 ml=0.10 mg Zn^{+2}: Dissolve 0.1000 g reagent-grade Zn° (30-mesh) in a slight excess of dilute HCl. Dilute to 1,000 ml with metal-free water.

Copper solution, 1.00 ml=0.010 mg Cu^{+2}: Dissolve 0.0100 g Cu° in a minimum of dilute HNO_3 and dilute to 1,000 ml with metal-free water.

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[Boldface entries indicate water properties; boldface numbers, beginning of their major description]