GEOLOGICAL SURVEY CIRCULAR 161

COMPILATION OF FIELD METHODS USED IN GEOCHEMICAL PROSPECTING BY THE U. S. GEOLOGICAL SURVEY

By H. W. Lakin, Hy Almond, and F. N. Ward

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GEOLOGICAL SURVEY
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COMPILATION OF FIELD METHODS USED IN GEOCHEMICAL PROSPECTING BY THE U. S. GEOLOGICAL SURVEY

INTRODUCTION

The field methods described in this report are those currently used in geochemical prospecting by the U. S. Geological Survey. Some have been published, others are being processed for publication, while others are still being investigated. The purpose in compiling these methods is to make them readily available in convenient form. The methods have not been thoroughly tested and none is wholly satisfactory. Research is being continued.

These methods, developed to meet the needs of geochemical prospecting, (Hawkes, 1950), possess speed, simplicity, and a moderate amount of accuracy. Each method permits as many as 25 to 30 determinations in an ordinary day. Separations and other chemical operations are held to a minimum, and in as far as possible, the required apparatus is restricted to common laboratory equipment. Moreover, the methods are designed to give positive tests for background material (see table 1) and results within 30 to 50 percent of the correct value for materials containing abnormal amounts of the element.

Two types of colorimetric procedures are used in the methods of estimation. The first type used in the methods for the determination of zinc, lead, molybdenum, tungsten and heavy metals, is extraction of an aqueous solution whereby a colored solution of the desired constituent is obtained in an immiscible solvent. The intensity or shade of the color is proportional to the quantity of the metal present. The second type of colorimetric procedure, used in the methods for the determination of copper, nickel, cobalt, and silver, is a confined spot test procedure. A colored precipitate is obtained in a fixed area, the intensity of the color being a function of the quantity of the metal present.

Both methods of estimation have advantages and disadvantages. The extraction procedures require a minimum amount of simple and easily assembled equipment; the confined spot test procedures require one moderately expensive piece of equipment. The extraction procedures require a great deal of shaking of solvent with aqueous solution to effect extraction, and are therefore subject to a large personal factor; they also require the preparation of comparison standards with each group of samples analyzed. The spot test procedures are simpler to perform and the standards as well as the spots obtained by the test are semipermanent.

The useful range of both extraction and confined spot methods depends on the minimum concentration of the element in solution giving a positive test (hereafter designated sensitivity, and on the concentration of the element which produces a maximum color. As concentrations can be conveniently expressed in micrograms per milliliter, each method is characterized by a minimum number of micrograms per milliliter required to give a test, and by a maximum number of micrograms per milliliter, beyond which color differences are not perceptible. Because the quantity of a constituent present in a test solution is proportional to the size of the sample, by trial and error the weight of the sample can be increased until the concentration in the test solution of the constituent being determined is sufficient to give a positive test. However, the extent to which the sample size can be increased, while the volume of the sample solution is held constant, is limited. When the ratio of the weight of the solution in which the sample is dissolved to the weight of the sample exceeds about 50, several things may happen. For example, if 0.1 g of sample is dissolved in 2.5 ml of solution--ratio of weight of solution to weight of sample is 25--salts of the major constituents may precipitate as the solution cools. Silica may separate, and frequently salts resulting from the neutralization on the acid or alkaline attack of the sample may crystallize. Such difficulties impose a practical limit to the ratio of the weight of sample solution to the weight of sample. This ratio and the sensitivity of the reaction determine the smallest concentration of a given constituent which can be estimated by these field methods. The concentration of the element producing a maximum color governs the largest concentration of the given element which can be determined by these methods except as one takes smaller aliquots. The reliability of results obtained on the latter types of materials is largely dependent on the accuracy with which smaller aliquots can be measured.

Special Reagents and Apparatus

Before the methods are presented, a brief discussion of some important reagents and special apparatus is desirable. A more complete discussion of the reagents will be found in the excellent treatises of Feigl (1946, 1949), Flagg (1948), Sandell (1950), Welcher (1948), and Wenger and Duckett (1948). All of the special apparatus and reagents (analytical grade) are commercially available.

Special Reagents

Dithizone (diphenylthiocarbazone), first investigated as an analytical reagent by Hellmut Fischer (1925), is now quite widely used. Sandell (1950, p. 87) and Welcher (1948, Vol. III, p. 463) give in detail very satisfactory accounts of its analytical properties and applications. The violet

Table 1.--Comparison between average metal content of igneous rocks and minimum content detected by field methods described in this compilation.

Metal	Average content of igneous rocks[1] (ppm)	Minimum content detected by field method (ppm)[2]
Zinc	132	50
Nickel	80	15
Copper	70	10
Cobalt	23	10
Molybdenum	2.5 - 15.	1
Lead	16	10
Silver	.1	.2
Tungsten	1.5 - 69.	10

[1]Averages given by Rankama and Sahama in Geochemistry, table 2, 3, pp. 39-40, Chicago, Ill. The University of Chicago Press, 1950.

[2]ppm = parts per million; 1 ppm = 0.0001 percent.

black solid is insoluble in acid solutions, soluble in alkaline solutions and in almost all organic solvents. Carbon tetrachloride, in which dilute solutions of dithizone are green, is the solvent used in the methods described in this compilation.

Dithizone forms internal complex salts with many metals. The so-called dithizonates, can be formed by shaking the carbon tetrachloride solution of dithizone with an aqueous solution of the metal. The dithizonates, usually soluble in the organic solvent, impart to it a violet, red, orange, or yellow color, depending on the metal involved.

Dithizone reacts with about seventeen metals to form colored dithizonates, but its principal use as an analytical reagent has been confined to cobalt, copper, cadmium, bismuth, lead, mercury, silver, thallium, and zinc. The value of the reagent lies in the great sensitivity that can be obtained by its use; the sensitivity of dithizone methods is of the same order as that of spectrographic methods. Specificity for certain elements can be obtained with dithizone by careful control of pH and by use of complex forming agents which sequester other reacting metals.

Two properties of the reagent must be kept in mind when dithizone is used under field conditions. First, the reagent is easily oxidized, particularly when exposed to sunlight and/or heat, and both the color and strength of the solution are modified as a result. It may also be oxidized by certain constituents of the sample solution, as for example, ferric iron in the presence of cyanide and citrate. The oxidation product, diphenylthiocarbodiazone, is soluble in carbon tetrachloride to which it imparts a yellow color, and is insoluble in aqueous solutions. This yellow color may be confused with that of such dithizonates as those of silver, mercury (II), thallium (III), and bismuth; in the determination of copper, zinc, and lead, the presence of the yellow oxidation product in the dithizone solution produces an off-shade color which is difficult to compare with standards. Dithizone, stored in a concentrated form in a dark, cool place is fairly stable. Webb and Millman (1950, p. 7) describe special precautions that must be taken when working with dithizone in a tropical climate.

The second property of the reagent that must be kept in mind is the high sensitivity of dithizone for a large number of elements. Therefore, extreme care must be exercised to prevent contamination. Because a large number of elements react with dithizone, the final extraction must be made in the presence of proper complexing agents and at the proper pH to make the reagent specific for the metal being determined. In the lead determination on page 24, for example, the final estimation is carried out at pH 8.5 in the presence of potassium cyanide to insure specificity.

Dimethylglyoxime, the reagent used in the test for nickel in this paper, is a white crystalline solid, only slightly soluble in water (0.4 g per liter) and soluble in alcohol and acetone. Diehl (1940) has published an extensive discussion on the uses of dimethylglyoxime in analytical chemistry. Dimethylglyoxime reacts with nickel in acid, neutral, and ammoniacal solution to give a bright red, extremely insoluble complex compound. The reagent reacts with palladium in acid solution to yield an acid insoluble yellow compound. Copper (II), cobalt (II) (III), and iron (II) form water soluble colored compounds.

Rubeanic acid (dithiooxamide) is an orange-red crystalline compound, slightly soluble in water, alcohol, and acetone. In ammoniacal solutions, the reagent forms insoluble complex salts with copper, cobalt, and nickel, the colors of which are respectively black, brown, and blue. Copper rubeanate is the only one of these three precipitated from acetic acid solutions--a fact used in the copper test. In strong mineral acid solutions, rubeanic acid yields red crystalline precipitates with palladium and platinum, and a soluble blue compound with ruthenium.

2-nitroso-1-naphthol is a greenish-yellow crystalline solid soluble in hot water and alcohol, and slightly soluble in ether.

Like most of the organic reagents used in analytical chemistry, 2-nitroso-1-naphthol reacts with a number of metals to give relatively insoluble precipitates. It reacts with iron, copper, and zirconium, as well as with cobalt. However, like dithizone, the reagent can be made specific by proper adjustment of pH and the use of complexing agents. Thus in the cobalt test given later, the reagent is made specific for the element by precipitating from an acid solution (pH 6) in the presence of citric acid.

p-Dimethylaminobenzalrhodanine is a red crystalline solid, only slightly soluble in chloroform, benzene, and ether. It is insoluble in water, but dissolves in strong acids imparting a yellow color to the solution.

Although in acid solution the reagent gives red or violet precipitates with silver, mercury, copper(I), gold, and palladium, it is the most satisfactory reagent available for the determination of minute amounts of silver.

Potassium thiocyanate has been used as a reagent for iron, molybdenum, tungsten, rhenium, cobalt, niobium, and bismuth. The formation of a red compound between thiocyanate and iron (III) is the basis of a sensitive test for iron. In the presence of a reducing agent such as stannous chloride, molybdenum in weak acid solution forms an amber-colored complex ion and tungsten in strong acid solution forms a yellowish-green complex ion. Since the products in both cases are extractible with organic solvents, the reaction with thiocyanate followed by an extraction with isopropyl ether is the basis for the molybdenum and tungsten methods.

Special Apparatus

The equipment required for the tests has been simplified as far as possible. To illustrate, test tubes are used for fusions in place of crucibles, for digestions in place of beakers, and with simple volume calibrations in place of volumetric flasks. Pipettes, wash bottles, reagent bottles, graduated cylinders, and test tube racks are also used. In addition to the above equipment and to certain special pieces of apparatus described later, the field methods included in this compilation require a source of heat and some means of measuring the sample. Depending on the accuracy desired, one can measure the sample size volumetrically by means of a calibrated spoon, or gravimetrically by means of a torsion balance. A balance with a sensitivity of 2 mg is adequate for the majority of the methods. A gasoline stove or an alcohol blowtorch can be used as a source of heat for fusions, and either of these or a small portable electric hot plate can be used for the digestions.

Chromograph. The chromograph is a device for making confined spot tests on paper. A detailed description is given by Stevens and Lakin (1949). The device is used to confine areas of definite size on a strip of paper fed through the apparatus and to control automatically the rate of flow of test solution through the confined spot. The rate of flow of test solution through the paper is controlled by the uniform pull of a column of water (and/or filtrate from previous tests) passing through a calibrated capillary. The paper in the form of strips is fed through the apparatus to give a number of confined spots on each strip, the sample number being written on the strip near the corresponding spot.

An early model of the chromograph is shown in figure 1. Two all-glass chromographs mounted in a portable case are shown in figure 2. The essential features of the chromograph are (1) filter head and filter base between which the test paper is secured, (2) a three-way stopcock connecting the filter base to the adjustor bulb and, or, the settling bottle, (3) a settling bottle fitted with three pieces of capillary tubing to provide a choice of outlets. The critical dimensions are (1) the inside diameter of the passage through the filter head and filter base which fixes the diameter of the confined spot, (2) the length of the column of water supported above the capillary, and (3) the internal diameter and length of the capillary. The height of the water column and the diameter and length of the capillary control the rate of flow of the test solution through the reagent paper. In the chromograph the diameter of the spot has been set at 0.25 in., and the height of the column of water at 9 in. The lengths of precision-bore capillary tubing with an inside diameter of 0.0065 in. have been set at 0.75, 1.5, and 2.25 in. to provide rates of flow of 100, 200, and 300 sec. for passage of 0.2 ml of solution without paper in the apparatus.

The methods so far developed using the chromograph employ three types of precipitation reactions.

1. With reagent papers. The paper is impregnated with a slightly soluble reagent which reacts with the sample solution, causing the ion sought to be precipitated. The solubility of the reagent must be such that it acts as an efficient precipitant without being completely removed during the passage of the solution. The determinations of copper and nickel in soils, to be described, are examples.

2. With reagents added to the solution. The reagent solution is added to the test solution on an untreated paper in the chromograph head. The solutions are mixed by bubbling air up through the paper by means of the adjustor bulb. The precipitate formed by the reaction is collected on the confined area of untreated paper, by reversing the stopcock and allowing the solution to flow through the capillary. The determination of cobalt in soils and rocks is an example of this type.

3. With previously formed precipitate. The previously formed precipitate is dispersed and the dispersion is transferred to the chromograph head containing untreated paper. The precipitate is collected on the paper by opening the stopcock and allowing the solution to pass through the capillary. The determination of silver in soils is an example of this type.

The colored spots obtained by these methods are relatively stable and serve as a semipermanent record of the results obtained. A standard series

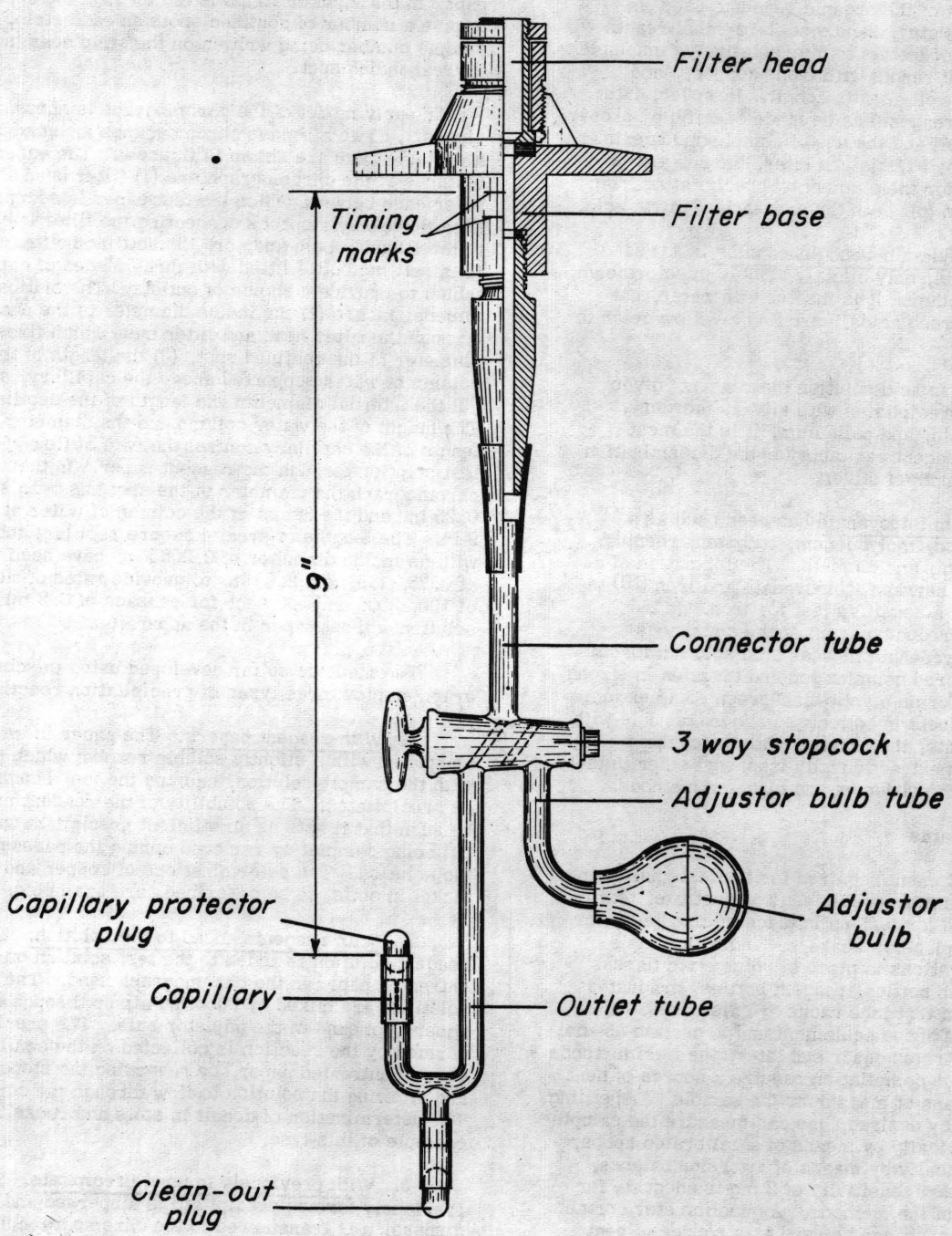

Figure 1.--Original plastic model of chromograph.

of spots is used to compare with the spots obtained on samples in much the same manner as a standard series of colored solutions are used to evaluate the sample solutions in visual colorimetry. However, the semipermanent nature of the confined spots makes frequent preparation of standards unnecessary.

Stevens Extraction Stick. (Extractor for removing soluble constituents in chemical analysis. Patent applied for by Rollin E. Stevens.) Filtrations and extractions are made with a Stevens extractor. This device is made as follows: A medium porosity, fritted disc is fused in one end of a pyrex glass tube 170 mm long and 7 mm inside diameter; a number 13 ground glass joint provided with a number 13 stopper is fused on the other end. The tube is calibrated at 2, 5, and 10 ml. A modified extractor can be easily made by constricting the glass tube near one end and packing the resulting small bulb with fine borosilicate glass fiber to serve as a filtering medium. In the molybdenum and tungsten procedures the simple extractor requires only cork stoppers; other procedures using strong, oxidizing acids require the ground-glass stopper.

To make extractions with the extractor, the solvent and the extractor are placed in a test tube containing the sample or a fusion of the sample, with the filter end of the extractor pointing downward. See figure 3. The liquid in the test tube is then brought to a boil. Bumping is eliminated, at first by the release of air bubbles from the expansion of the air within the extractor, and later by the filter, which causes a continuous and gentle release of the superheated liquid from the many surfaces. While the solvent is boiling the sample is maintained in suspension and continuous motion, thus promoting better extraction. Evaporation of the solvent during boiling is largely prevented by a close fit of the extractor to the open end of the test tube. These features permit boiling for long periods without attention. When the extraction of the sample is completed, the heat is removed from the test tube and contents. As the tube cools, the contraction of the air remaining in the extractor causes the solution to flow through the filter into the extractor. Thus a filter extract is obtained by steps that are essentially automatic.

The extractors may be used as filters for cold solutions by applying suction to the open end with a rubber ear syringe.

Huff antibump test tube. The Huff (1951) antibump test tube shown in figure 4 is another device used to prevent bumping during the extraction of a soil or rock sample with acid. With the round end of the test tube (13 by 100 mm) drawn to a point, Huff found that the extractant boils in the tip before the main mass becomes superheated, thus preventing bumping. Heat can be applied by either a flame or a hot plate.

Apparatus for preparation of metal-free water. Very pure water must be used in trace analysis because the quantity of a metal in the water used as solvent may exceed the quantity of metal in the sample. In the methods presented here the ratio of the weight of water used to the weight of sample is very great. For example, in the heavy metals test described on page 13, the ratio of water to sample is 2200 to 1. In this method, if no precautions were taken to purify the water used, 0.001 ppm of metal in the water would appear as 2.2 ppm in the sample. Huff (1948) has reported 1.52 ppm zinc, 0.01 ppm copper, and 0.03 ppm lead in the tap water of the Denver, Colo. Public Supply. If such water were used in the above test, the contamination would result in an error of 3,300 ppm of zinc, 22 ppm of copper, and 66 ppm of lead. Obviously ordinary tap water should not be used.

Several small resin demineralizers now commercially available are satisfactory for preparing metal-free water. However, since resin demineralizers remove only ionized impurities such as sodium, calcium, zinc, lead, sulfate, and bicarbonate, and do not remove bacteria or organic impurities, water reasonably free of organic materials should be used, such as a public water supply.

Digestion and fusion rack. This piece of apparatus, shown in figure 5, is used to support eight test tubes over a gasoline stove. The rack consists of two disks of sheet steel 115 mm in diameter welded to a central supporting rod, 200 mm long. Each disk has eight holes for test tubes; the holes in the bottom disk are smaller, so that the test tubes cannot slip through, but large enough to permit the ready flow of heat.

Fusion rack (used in Mo and W methods). This rack, designed to support three culture tubes at any desired angle over the flame of a gasoline stove, is shown in figure 6. The design of the rack permits the operator to rotate as well as to raise and lower each tube independently. It consists of an iron band 100 mm in diameter, 25 mm wide and 2 mm thick, three supporting rods with spring clamps pivoted at the upper ends, held in a vertical position in a slot through an "L" shaped member riveted to the outer side of the iron band. A set screw normal to the slot permits adjustment of height of the rods.

Sieves. In the analysis of materials for trace constituents contamination must be kept to the minimum. Almost all the sieves currently available on the market are made of brass, and often solder has been used to fasten the screen. Sieves containing brass or solder cannot be used in preparing samples for determination of traces of copper, zinc and lead. The following types have been used in our work:

(a) Iron sieve. 2 mm mesh iron screen in an iron holder having an outside diameter of 100 mm.
(b) Aluminum sieve. 80 mesh silk bolting cloth in an aluminum holder with outside diameter of 100 mm. Stainless steel bolting cloth has been used in place of the silk bolting cloth. It is stronger and preferable if free of the constituents being determined.

An aluminum receiver which fits both (a) and (b) is desirable.

The sieve and sieve holder are shown in figure 7.

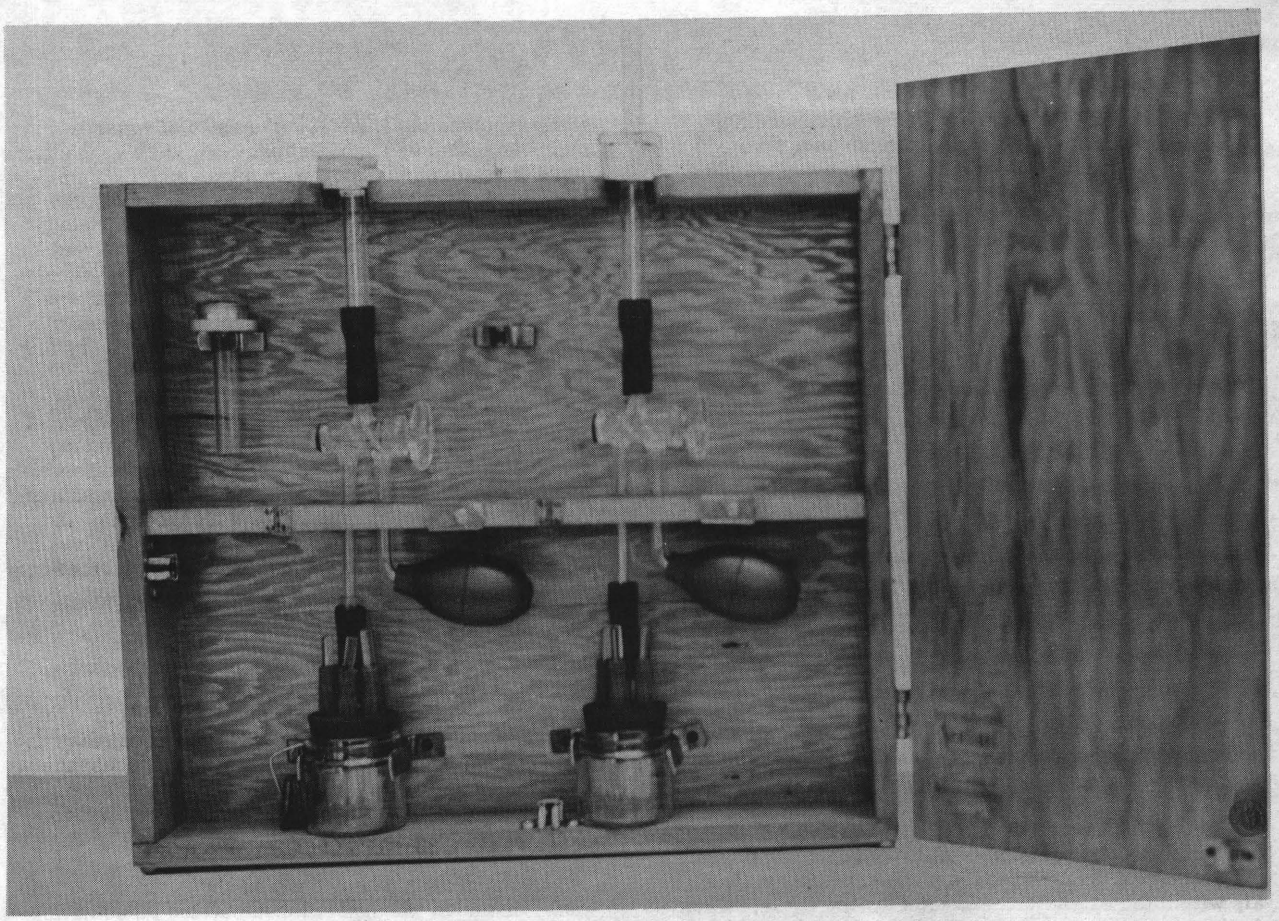

Figure 2. --Kit containing two all glass chromographs.

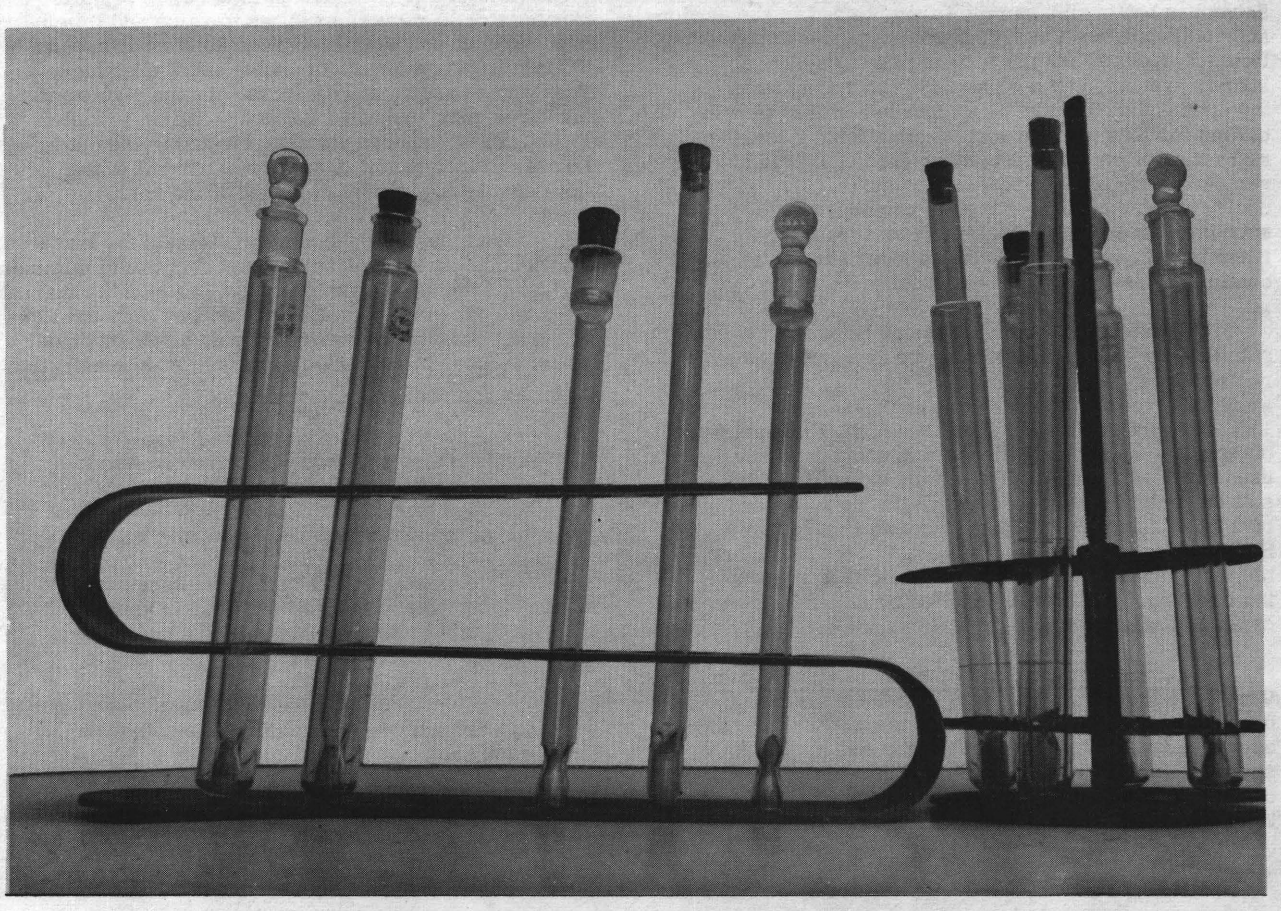

Figure 3. --Stevens Extraction Stick.

Toxicity of Reagents

Most reagents used in analytical chemistry are poisonous. However, when the analyst is cautioned about the toxicity of a specific reagent it is because of some special property of the reagent, such as volatility, which makes handling the reagent especially hazardous. For example, potassium cyanide is extremely poisonous and reacts with acid to produce a volatile, lethal gas (HCN). Hydrofluoric acid is another example of a substance with a property which makes handling dangerous. If it is allowed to remain in contact with the skin more than two to three minutes, it produces an exceedingly painful burn, the pain persisting for two days or more. The vapors are also toxic.

The reagents discussed below are mentioned especially because their use involves certain special hazards.

Carbon tetrachloride

Carbon tetrachloride is one of the most toxic of the common solvents. Carbon tetrachloride poisoning results in liver and kidney damage and may be fatal. Since the maximum allowable concentration in the air is 40 ppm (Elkins, 1950), carbon tetrachloride should never be used in a poorly ventilated room. If a large quantity of carbon tetrachloride is spilled, the windows should be opened and the room vacated until cleared of the fumes. The majority of fatalities have resulted from acute exposures while using the reagent as a cleaner in a confined space or from the products formed by pyrolysis of the reagent which may occur when fire extinguishers filled with carbon tetrachloride are used.

Amyl alcohol

Fatal poisonings from amyl alcohol have been reported. The harmful effects are irritation and narcosis, but these are usually transitory. The maximum allowable concentration in the air is 50 ppm. If the precautions listed for carbon tetrachloride are applied in the use of amyl alcohol, no harmful effects are likely to result. One should remember, however, that amyl alcohol is inflammable.

Isopropyl ether

Very little is known regarding the toxic effects of isopropyl ether. It is reasonable to assume that this ether is somewhat more toxic than diethyl ether, but being less volatile is less dangerous to use. If the same precautions are followed as in the use of carbon tetrachloride, no harm should result. Like amyl alcohol, isopropyl ether is inflammable.

Potassium cyanide

Potassium cyanide is exceedingly poisonous; a very small amount taken internally is fatal. Therefore, never draw a potassium cyanide solution into a pipette by mouth; always wash immediately after handling potassium cyanide or its solutions.

Acidification of cyanide produces a lethal gas (HCN). Never store potassium cyanide near acids. Exercise meticulous care to avoid any possible contact of the salt or its solution with acids that may result from breakage in transport. Never add potassium cyanide solutions to an acid solution or acidify solutions containing cyanide. Always wash vessels thoroughly in which the reagent has been used.

Hydrofluoric acid

Almost all of the people likely to use the methods in this compilation know of the vicious burns that result from contact with hydrofluoric acid, but may not be aware of the fact that the fumes are corrosive and poisonous. The generally accepted maximum allowable concentration for an 8-hr day is 3 ppm by volume in air. A concentration of 50 ppm or more may be fatal in 30 to 60 min. (See Manual Sheet H-10. Hydrofluoric acid -- aqueous and anhydrous--handling and discharge of containers. Manufacturing Chemist's Association, Inc., Washington, D. C.) Therefore, a good draft away from the operator is essential. Use in the field should be in the open with the operator on the windward side of the burner. Caution: An analyst using hydrofluoric acid should wash his hands frequently with copious amounts of water.

Purification of Reagents

Although special attention must always be given to purification of water used in trace analysis ("Special Apparatus"), reagent chemicals also must be checked for purity, and a high reagent blank avoided. Dithizone methods are particularly susceptible to error due to high reagent blanks.

Solutions prepared from solid reagents are most conveniently purified by extraction with a carbon tetrachloride solution of dithizone. The procedure for this type of purification is to be found in the instructions for preparing specific reagents. The salts used in fusions (potassium bisulfate, sodium carbonate, sodium chloride, and potassium nitrate) are usually sufficiently pure to give satisfactory results, nevertheless, each batch should be checked by running a blank on the reagent. Fluxes giving a high reagent blank should be rejected, as purification is tedious.

Hydrochloric and nitric acids are usually very low in heavy-metal content and frequently can be used without purification. If necessary, they may be purified by distillation from a pyrex still. Hydrofluoric acid may be freed from lead according to the method of Rosenqvist (1942) as follows:

Add 10 ml of 10 percent strontium chloride to one kilogram of concentrated hydrofluoric acid, allow the precipitate to settle, and again add 10 ml of strontium chloride solution. Allow the precipitate to settle and decant the supernatant liquid through a filter paper in a hard rubber or plastic funnel. In this manner lead is removed from the acid by coprecipitation of lead fluoride with strontium fluoride.

Pure ammonium hydroxide is easily obtained by saturating metal-free water, cooled in an ice bath, with ammonia from a tank. The change in

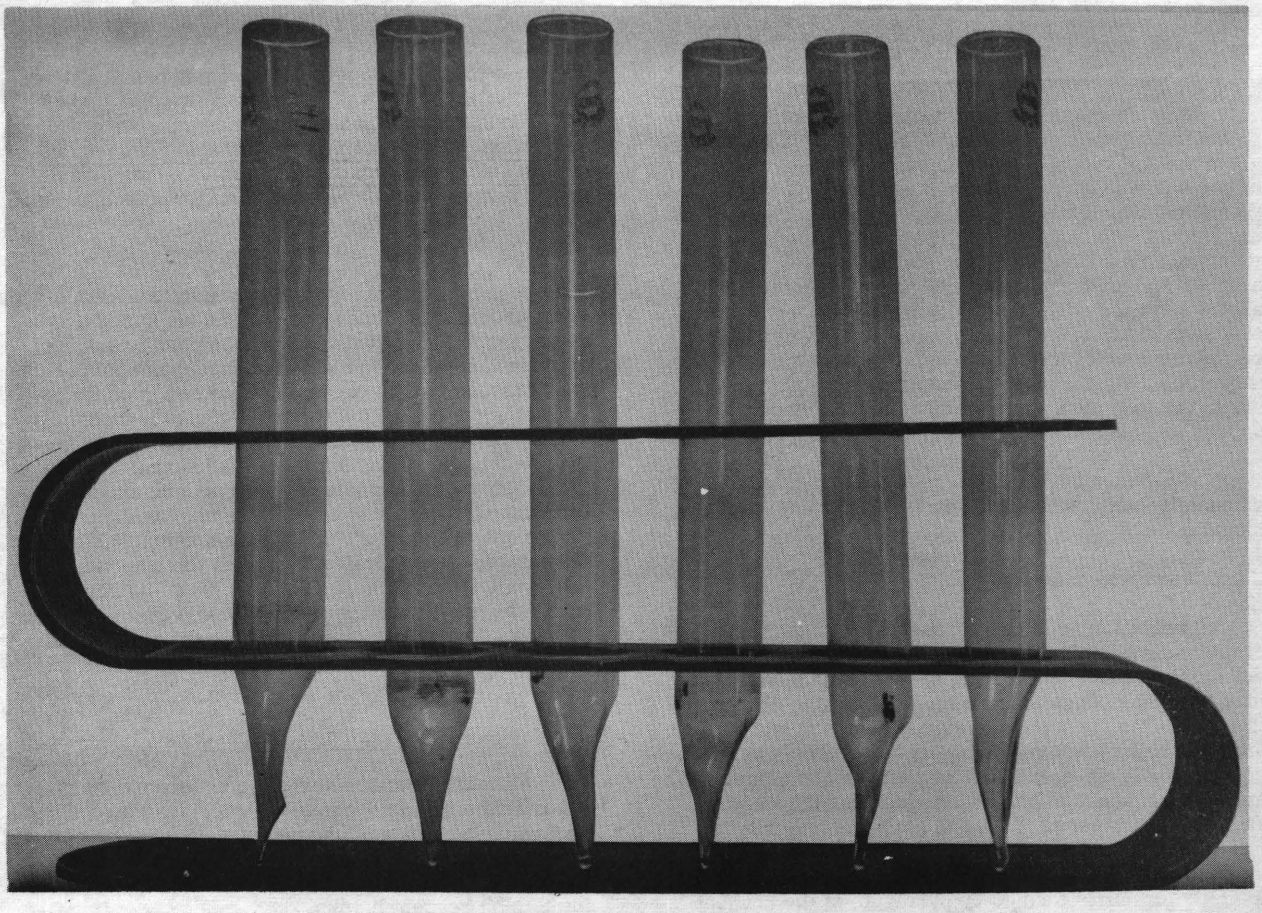

Figure 4. --Huff antibump test tube.

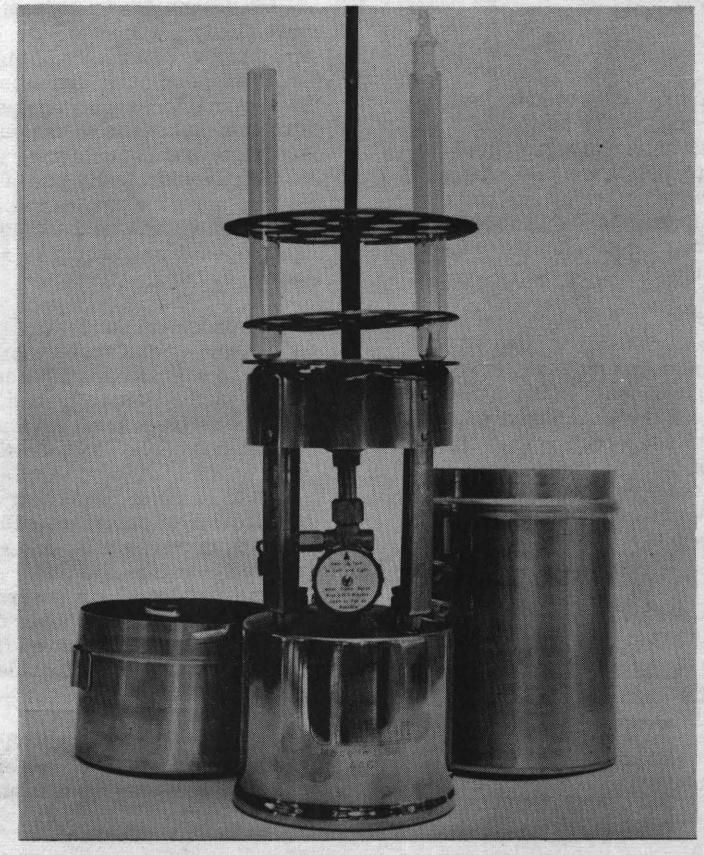

Figure 5. --Digestion and fusion rack.

weight of the receiver indicates the concentration of the solution.

Carbon tetrachloride of reagent quality is usually satisfactory. Distillation in a pyrex still in the presence of calcium oxide will give a product free of heavy metals.

METHODS OF ANALYSIS

Explanatory Notes

The plan is to present the minimum information required to perform properly each determination; a brief introduction, a list of reagents and apparatus, and a concise statement of the procedure are given. While there are occasional warnings for critical operations, the purpose is to present direct instructions that can be followed by a relatively untrained operator. Those interested in the reactions involved, the interfering elements, and the comparative accuracy should refer to the original papers from which these methods were taken.

In order to reduce unnecessary repetition, a section on the preparation of the sample for analysis is inserted before the methods for soils and rocks. Subsequently it is assumed that a proper sample of soil, rock, or sediment has been prepared and therefore the directions for the analysis of such material start with a given weight of the finely ground sample. On the other hand, no consistent plan is followed in the preparation of samples of vegetation where the preparation of the sample is an integral part of each procedure.

The aqueous solutions listed under "Reagents and apparatus" are identified by listing the solute and its approximate concentration in terms of percent, normality, or dilution; for example, sodium citrate, 50 percent, acetic acid, 2 N, or hydrochloric acid, 1+2. Detailed instructions for preparing solutions designated by percent or normality follow in each case. The designations 50 percent and 2 N do not imply exact concentrations. The concentration expressed in terms of dilution, such as hydrochloric acid, 1+2, means that the reagent is prepared by mixing 1 volume of concentrated hydrochloric acid and 2 volumes of metal-free water.

Water used in the preparation of reagents, in dilutions and as a wash liquid, is metal-free water whether specified or not. The importance of metal-free water is discussed under "Special Apparatus."

All of the apparatus required for each method is listed, but no consistent effort has been made to specify the amount of apparatus required to work efficiently since the size of the job to be done and the facilities available are the determining factors. However, lists of reagents required for 1,000 determinations with each method are given as an appendix.

Determination of Heavy Metals in Water

A complete description of the method and its applications are given by Huff (1948). According to Huff, the sensitivity of the test permits the detection of 0.002 ppm of zinc, 0.01 ppm of lead, and 0.01 ppm of copper in a 50 ml sample. Waters high in heavy metals can be analyzed by reducing the size of the sample taken for analysis. Organic matter in the water tends to cause stable emulsions to form between the carbon tetrachloride and water. These emulsions and zinc contamination are the most serious interferences encountered in the use of the method. Although reagents of exceptional purity are required, only simple equipment is needed and the test can be made in a few minutes in the field. Thus the geologist can test water samples as he collects them and follow leads without delay.

Reagents and apparatus

Acetic acid 2 N, dilute 114 ml of glacial acetic acid to 1 liter with metal-free water.

Acetic acid 1 N, dilute 50 ml of 2 N acetic acid to 100 ml with metal-free water.

Sodium acetate 2 N, dissolve 164 g CH_3COONa in metal-free water and dilute to 1 liter

Acetate buffer, Mix nine parts 2 N sodium acetate with one part 2 N acetic acid. Purify by shaking with successive portions of 0.016 percent dithizone solution until the organic layer remains green.

Ammonium hydroxide 2 N, dilute 127 ml concentrated NH_4OH 1 liter with metal-free water.

Dithizone (diphenylthiocarbazone), 0.016 percent weight per volume. Dissolve 0.08 g of dithizone in 500 ml of reagent-grade carbon tetrachloride. Since sunlight and heat decomposes the reagent, solutions should be stored in paper-wrapped, glass-stoppered, pyrex bottles and kept cool.

Dithizone, 0.0016 percent weight per volume. Dilute 10 ml of 0.016 percent dithizone solution to 100 ml with reagent-grade carbon tetrachloride. When working at temperatures over 70F, prepare a fresh solution every 4 hr.

Potassium cyanide, 1 percent. Dissolve 1 g KCN in 2 ml water. Add 2 drops of 0.016 percent dithizone solution. Extract excess dithizone from potassium cyanide solution with small portions of chloroform until no green dithizone appears in the chloroform phase. Dilute to 100 ml with metal-free water. Shake with carbon tetrachloride and discard the organic layer. Caution: Very poisonous! See "Toxicity of Reagents."

Sodium thiosulfate 2 N. Dissolve 25 g of $Na_2S_2O_3 \cdot 5H_2O$ in metal-free water and dilute to 100 ml. Purify by shaking with successive portions of 0.016 percent dithizone solution.

Metal-free water. Pass tap water through a resin demineralizer. See "Special Apparatus."

Zinc standard, 0.01 percent in 0.1 N HCl. Dissolve 0.01 g of reagent-grade zinc in 100 ml of 0.1N HCl. One ml of this solution contains 100 micrograms of zinc. Less concentrated standard solutions are prepared by dilution.

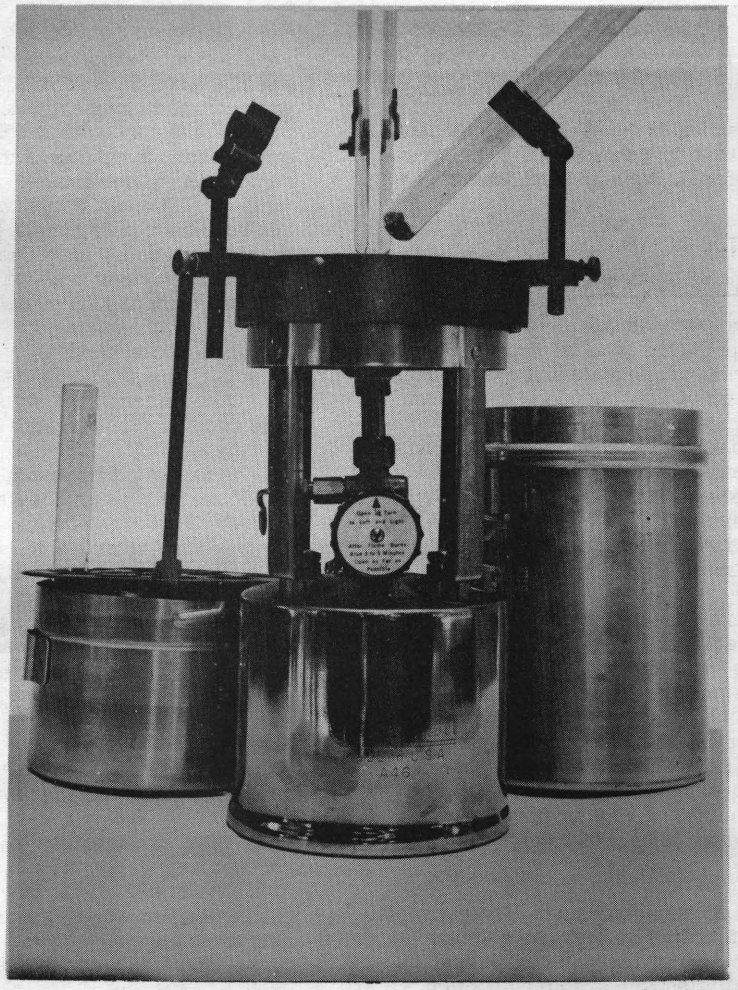

Figure 6. --Fusion rack.

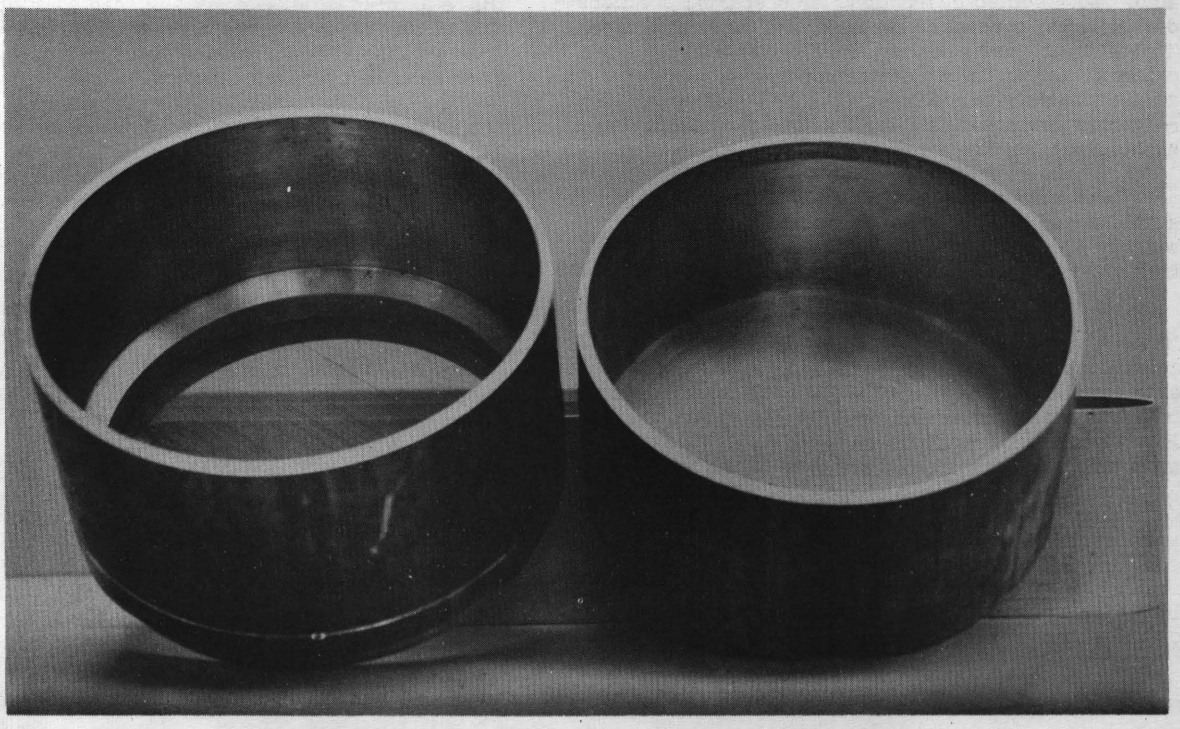

Figure 7. --Aluminum sieve and holder.

Thymol blue indicator 0.04 percent. Dissolve 0.04 g of the sodium salt in 100 ml water.

4 graduated cylinders, 100 ml, glass-stoppered, pyrex.

1 graduated cylinder, 5 ml, pyrex.

1 separatory funnel, 125 ml, Squibb type, glass-stoppered, pyrex.

6 dropping bottles, 30 ml, flat top.

pH meter, Beckman Model G, or suitable indicator papers for determining acidity of water samples.

Procedure

Transfer 50 ml of the water sample to a 100 ml glass-stoppered, graduated cylinder. Add 5 drops of the buffer solution, 5.0 ml of 0.0016 percent dithizone solution and shake vigorously for 1 min. If the color of the dithizone solution is red after the initial shaking, clean the cylinder and repeat the analysis using a smaller volume of sample. Repeat until a mixed color (red metal-dithizonate plus unreacted green dithizone) is obtained; determine quantity of heavy metals present expressed as Zn by reference to table 2, column 3.

If the dithizone remains apparently unchanged add 2 drops of thymol blue indicator, ammonium hydroxide until the indicator changes from yellow to blue, then 1 additional drop of ammonium hydroxide. Shake again for 15 sec. Estimate visually by referring to table 2, column 3, mono-color range pH about 9.

Table 2.--Description of colors with heavy metals test on standard solutions (according to Huff)

Acidity of extraction	Micrograms of metal in 50 ml solution	Color of dithizonate in strong, white transmitted light*			
		Zinc	Copper	Lead	1:1:1 mixture of Zn, Cu, Pb
Mixed color range; pH of about 5.5 obtained with acetate buffer.	20			Light purplish red	
	15			Light red purple	Light purplish red
	10	Light purplish red	Strong purplish red	Pale purplish blue	
	7				
	5		Pale purple	Light blue green	Light red purple
	4	Light red purple	Pale purplish blue		
	3	Light purple	Light blue green		Pale blue
	2	Pale blue	Light bluish green	Light bluish green	Light blue green
	1	Light blue green	Light green		Light bluish green
	1/2	Light bluish green			
	0	Light green	Light green	Light green	Light green
Mono-color range; pH of about 9.0 obtained by adding ammonium hydroxide to mixed color test.	1	Strong pink	Moderate pink	Moderate pink	Strong pink
	1/2	Weak pink	Faintest color detectable	Faintest color detectable	Weak pink
	1/10	Faintest color detectable	Colorless	Colorless	Faintest color detectable
	0	Colorless	Colorless	Colorless	Colorless

*Color identification based upon Munsell notation. See Munsell Book of Color, Standard Edition, Munsell Color Co., Inc., Baltimore, Md., 1929, and Judd, D. B. and Kelly, K. L., Method of designating colors, National Bureau Standards Research Paper 1239, Sept., 1939. It may be noticed that in the mixed color range the colors all have about the same value but vary in hue and chroma, the intermediate hues being distinctly grayish while the end members have strong chroma; in the mono-color range the hue remains constant while the chroma and value change as the colors become fainter.

Because the reagent is very sensitive, the analysis is extra-ordinarily susceptible to contamination; it is advisable to keep all apparatus scrupulously clean and always make check determinations.

In the course of prospecting it may be desirable to identify the metal or metals producing the positive tests. The supplemental tests, the procedures of which are given in table 3, permit the separation of copper, lead, and zinc; other metals may cause interference, but it is likely that many of these occur only in very small amounts in natural waters.

Table 3.--Supplemental determinations for heavy metals in water (according to Huff)

Metals	Producedure	Significance of color
Copper group	Repeat as in the general test with the same volume of sample but using 1 ml of 1.0 N acetic acid instead of the acetate buffer. A mixed color after shaking indicates presence of the copper group. Add more sample and shake to change all dithizone to metal dithizonates.	Copper-Purplish red Silver--Yellow Mercury--Orange (I) to orange yellow (II) Bismuth--Orange yellow Gold--Yellow (flocs) Palladium--Dark violet Platinum (II)--Green carbon tetrachloride layer; violet or violet-red aqueous layer Thallium (III)--Yellowish red (reaction not complete)
Zinc group	Repeat the test as before adding both buffer and 5 ml of 2.0 N purified sodium thiosulfate solution. A mixed color after shaking indicates presence of the zinc group. Add more sample and shake to change all dithizone to metal dithizonates.	Zinc--Red Tin (II)--Red (not stable) Palladium--Dark violet (reaction slow) Cadmium--Red (pH of 8 or over)
Lead group	Repeat the test as before, after adding 5 drops of 2.0 N ammonium hydroxide followed by 1 ml of a 1 percent purified potassium cyanide solution instead of the buffer. Any color left after shaking, other than a pale yellow dithizone oxidation product, indicates presence of the lead group. Oxidation of the dithizone can be decreased by preliminary addition of a little hydroxylamine hydrochloride.	Lead--Red Tin (II)--Red (optimum pH 6-9; not stable) Bismuth--Orange red Thallium (I)--Red (pH of 9 or over)
Other metals	Detectable with simple field test but removed by any of the procedures given above. Must be isolated by other methods.	Cobalt--Violet (optimum pH 7-9) Nickel--Brown (weakly basic solution) Iron (II)--Violet red (pH 6-7 only) Manganese--Brown flocs (pH about 11) Indium--Red (optimum pH 5-6) Thallium (III)--Yellowish red (pH 3-4 only)

Preparation of soils and rocks for analysis

Simplicity in all steps of the analysis is required for rapid tests. As these chemical methods are only moderately accurate, large samples and elaborate sample preparation are not justified. Any simplification of the sampling procedure that will provide a small satisfactory sample is desirable.

In any particular area the minimum size of sample required to give satisfactory results should be determined experimentally. An example of this is found in the work of Hawkes and Lakin (1949) in Tennessee. They collected a series of bulk samples (about 500 g) and compared the analyses of these with those of grab samples (about 5 g). The results showed that 5 g samples were just as satisfactory as samples 100 times larger. Another type of a simplified sampling procedure was used by Lovering and others (1950). These workers demonstrated that dry sieving of soil and alluvium samples through an 80-mesh sieve gave satisfactory subsamples for the study of the dispersion of copper from the San Manuel copper deposit. This procedure greatly reduces the size of the sample and eliminates the need for grinding.

When no modification in sampling can be employed to reduce the sample size, the following general procedures are recommended for the preparation of the sample.

Soils.--Dry the sample, break up clods with a wood rolling pin and pass the sample through a 2 mm mesh sieve. Pour the sieved soil in a pile on heavy wrapping paper, mix thoroughly, quarter, discard opposite quarters, and repeat the process until a sample of 3 to 5 g remains. Pulverize this small subsample in a mullite mortar to an impalpable powder. From this powdered sample take the amount required for the analysis.

Rocks.--Break the rock fragments into small chips with a Plattner diamond mortar, and pass the sample through a 2 mm mesh sieve, crushing the portion that fails to pass the sieve until the entire sample has passed through the coarse sieve. Mix thoroughly and quarter down as in soils to a subsample of 3 to 5 g. Pulverize this small sample in a mullite mortar to an impalpable powder for analysis.

Determination of Heavy Metals in Soil or Sediment

Huff (1951) has described this procedure, and has discussed the reactions involved in the method as well as its usefulness in geochemical prospecting.

The test is designed to detect as little as 50 ppm and as much as 10,000 ppm of heavy metals expressed as zinc equivalents. The test is most sensitive for zinc and least sensitive for lead. Four methods of preparing the sample solution are described in order of increasing rigor of attack on the sample. If representative samples are treated by all four digestion methods, the digestion method best suited for a particular study can be selected; in general, it will be the quickest method which gives satisfactory results. The test is easy to make and only simple apparatus and reagent-grade chemicals are required to make 60 to 80 tests per man day in a make-shift field laboratory. The test has been used in reconnaissance studies.

Reagents and apparatus

Dithizone (diphenylthiocarbazone), 0.016 percent weight per volume. Dissolve 0.08 g of dithizone in 500 ml of reagent-grade carbon tetrachloride. Since sunlight and heat decompose the reagent, solutions should be stored in paper-wrapped, glass-stoppered, pyrex bottles and kept cool.

Dithizone, 0.0016 percent weight per volume. Dilute 10 ml of 0.016 percent dithizone solution to 100 ml with reagent-grade carbon tetrachloride. When working at temperatures over 70F, prepare a fresh solution every 4 hr.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Concentrated nitric acid, approximately 69 percent (constant-boiling). Purify by distilling in an all-pyrex still.

Dilute nitric acid, 1+7.

Hydrofluoric acid, approximately 48 percent. A.C.S. analyzed grade.

Sodium acetate, 25 percent. Dissolve 250 g of anhydrous sodium acetate, or 415 g of $NaC_2H_3C_2 \cdot 3H_2O$, in water; and purify by shaking in a large separatory funnel with dithizone stock solution. Remove traces of dithizone by shaking with pure carbon tetrachloride. Dilute to 1.0 liter.

Ammonium fluoride, 10 percent. Prepare by dissolving 100 g of ammonium fluoride in water; purify as with sodium acetate, and dilute to 1.0 liter. Keep in a pyrex bottle.

Buffer solution, containing 5 percent sodium acetate and 1 percent ammonium fluoride. Prepare as needed by diluting 200 ml of 25 percent sodium acetate solution and 100 ml of 10 percent ammonium fluoride solution to 1.0 liter.

Standard zinc solution, 0.01 percent in approximately 0.1 N hydrochloric acid. Dissolve reagent-grade zinc in a slight excess of hydrochloric acid and dilute to volume. Before use, dilute with pure water and a little additional acid to a 0.001 percent solution (10 micrograms of zinc per ml).

Huff antibump tubes. See "Special Apparatus."

Digestion tube rack. The digestion tubes can be held conveniently in a wooden frame having a series of 13-mm holes spaced with centers about an inch apart.

1 pipette, 0.1 ml, graduated in hundredths of a ml.

Lucite spoon, a lucite bar with a cavity of 0.25 ml, 7 mm diameter, 6.5 mm deep, drilled near one end.

1 graduated cylinder, 100 ml, glass-stoppered, pyrex.

1 beaker, 250 ml.

3 graduated cylinders, 5 ml, pyrex.

1 separatory funnel, 125 ml.

1 serological pipette, 10 ml, graduated in tenths of a ml.

1 serological pipette, 5 ml, graduated in tenths of a ml.

1 alcohol lamp, small.

1 hot plate, electrical, 110 volt a-c, variable temperature control heating surface 6 by 6 in.

12 platinum dishes, flat-bottomed dishes, without rim, about 20 mm in diameter and 10 mm high.

1 platinum wire, 75 mm long.

1 polyethylene wash bottle, 250 ml.

Colorimetric tubes. 25 by 200 mm glass culture tubes, with a screw cap. Mark the tubes with a stylus at volumes of 5, 10, 20, and 40 ml. Glass-stoppered, graduated pyrex cylinders are a satisfactory substitute for the colorimetric tubes.

Procedure

Digestion: Four different digestion methods are described below which represent four distinct steps of increasing rigor of digestion. By the use of all four digestion methods on representative samples the digestion method best suited for use for a particular study can be selected; in general, the best method will be the quickest method that gives satisfactory results. Instructions for the digestions are as follows:

A. Place a scoopful of the ground sample in an antibump tube, add 4 ml of dilute nitric acid and heat over an alcohol lamp. Maintain at or near the boiling point for 10 min.

B. Place a scoopful of the ground sample in an antibump tube, add 4.0 ml of dilute nitric acid and boil slowly and continuously on a hot plate for 1 hr. Dilute with water to 4.0 ml and mix by shaking.

C. Place a scoopful of the ground sample in an antibump tube, add 1 ml concentrated

nitric acid, and heat on a hot plate (low heat) overnight without boiling; heat further the following morning (high heat) until about one-half the acid is boiled away. Dilute to 4.0 ml and mix by shaking.

D. Place a scoopful of sample in a 5 ml platinum dish, add 2 ml hydrofluoric acid and 2 ml concentrated nitric acid, mix with a platinum rod. Heat on a hot plate at about 35 C to 40 C until dry. Cool and add 2 to 5 drops of concentrated nitric acid, heat to dryness again. Add 10 drops of concentrated nitric acid and 10 drops of water and heat. Wash the contents into a tube with water and dilute to 4 ml.

Each of the four digestion methods leaves the sample dissolved in nitric acid of about the same concentration. When the sample solution cools, the solid residue settles to the bottom of the digestion tube, leaving a clear yellowish solution. Aliquots of this are pipetted for the estimation.

Estimation.--Place 5.0 ml of the dilute dithizone solution in a clean colorimetric tube, add 35 ml of the buffer solution, 0.2 ml of the sample solution, and shake for 30 sec. Compare the color of the carbon tetrachloride layer with the color of similar layers prepared by using zinc standards or with the colors listed in table 3 to determine the metal content of the sample (expressed as zinc equivalents, that is zinc plus one-half copper plus one-fourth lead). If the carbon tetrachloride layer is red or nearly red, clean the tube, using distilled water and dithizone solution. Repeat the determination using a smaller aliquot of the sample solution to obtain a mixed color (red metal dithizonate plus unreacted green dithizone), so that the concentration can be read from table 4. The color differences are most sensitive near the purplish, midpoint of the range, and this range should be used for greatest accuracy.

Do not use more than 0.2 ml of the sample solution for the determination. The procedure is designed so that samples containing 50 or 100 ppm total heavy metal, a normal background concentration, will give a slight positive test and any concentrations higher than this background will be easily distinguishable. The test, as described, is not suitable for determining heavy-metal contents in the range below 50 to 100 ppm, the normal background range. It is advisable to make many repeat determinations and to run blanks on the reagents frequently to avoid error by contamination. If any check determinations are to be omitted, omit those for "background" samples.

Determination of Zinc in Soils

The field method for zinc in soils and rocks given below is described more fully by Lakin, Stevens, and Almond (1949). In the authors' experience about 85 percent of the values obtained by the field method are within ± 40 percent of those obtained by careful laboratory analysis. The method, as described, is applicable to samples containing 50 to 1000 ppm of zinc. Under the conditions of the test, the reaction of copper with dithizone is largely prevented. However, if the copper content of a sample is ten times that of zinc, the zinc value may be as much as 75 percent greater than its true value. Care must be exercised to avoid contamination, since erratic results are often due to zinc contamination of the test tubes, pipettes, or reagent solutions. Under favorable conditions up to 60 determinations per man day can be made. The apparatus is simple and portable. The chemicals required for the test are readily available and, except for carbon tetrachloride, are not hazardous. The method has been used widely in geochemical prospecting.

Reagents and apparatus

Potassium bisulfate. Analytical grade ground to fine powder in a porcelain mortar.

Water. Pass tap water through a resin demineralizer. See "Special Apparatus."

Sodium acetate, 2 N. Dissolve 164 g CH_3COONa and dilute to 1 liter with metal-free water.

Acetic acid, 2 N. Dilute 114 ml of glacial acetic acid to 1 liter with metal-free water.

Acetate buffer. Mix 5 volumes of 2 N sodium acetate with 2 volumes of 2 N acetic acid, and remove reacting heavy metals by shaking with 0.01 percent dithizone solution.

Dithizone solution, 0.01 percent weight per volume. Dissolve 0.01 g in 100 ml of reagent-grade carbon tetrachloride. Store in cool, dark place.

Dithizone solution, 0.0025 percent weight per volume. Dilute 25 ml of 0.01 percent solution to 100 ml with reagent-grade carbon tetrachloride.

Sodium thiosulfate. Dissolve 50 g of $Na_2S_2O_3 \cdot 5H_2O$ in 100 ml of water. Remove reacting heavy metals by shaking with 0.01 percent dithizone solution.

Standard zinc solution. 0.01 percent in about 0.1 N hydrochloric acid. Dissolve 0.1 g reagent-grade 30-mesh zinc in concentrated hydrochloric acid and dilute to 1 liter. One ml of this solution contains 100 micrograms of zinc. Prepare dilute solution containing 20 micrograms per ml from the standard solution.

20 pyrex culture tubes, 18 by 150 mm, marked at 3, 10, and 11 ml.

20 pyrex culture tubes, 16 by 150 mm, marked at 5 ml.

1 serological pipette, 5 ml, fitted with stopcock at upper end.

1 graduated cylinder, 100 ml, or other suitable device in which to support pipette.

Lucite spoon, a lucite bar with cavity of 0.05 ml, 4 mm diameter, 4 mm deep, drilled near one end.

Lucite spoon, a lucite bar with cavity of 0.25 ml, 7 mm diameter, 6.5 mm deep, drilled near one end.

Table 4.--Descriptive chart of color of dithizone solution for determination of heavy metals, expressed as zinc equivalents according to Huff

Aliquot (ml)	Volume dithizone solution	Green (ppm)	Blue green (ppm)	Blue (ppm)	Purple (ppm)	Red purple (ppm)	Purplish red (ppm)	Red (ppm)
0.2	5	0	50	100	150	200	250	300 or more
.2	5	0	100	200	300	400	500	600 or more
.05	5	0	200	400	600	800	1,000	1.200 or more
.025	5	0	400	800	1,200	1,600	2,000	2,500 or more
.0125	5	0	800	1,600	2,500	3,500	4,000	5,000 or more
.0125	10	0	1,800	3,500	5,000	7,000	9,000	10,000 or more

Mullite mortar and pestle, outside diameter of mortar, 75 mm.

2 sieves, 2 mm mesh iron screen and 100 mesh cloth, see "Special Apparatus."

1 camel's-hair brush, length of brush part, 18 mm.

1 small spatula, zinc free, length of blade, 50 mm.

1 digestion and fusion rack. See "Special Apparatus."

1 gasoline stove.

Procedure

Preparation of Sample Solution. --Fill a lucite spoon, capacity 0.05 ml, with soil by tightly pressing the prepared soil into the spoon with a small flexible spatula. Wipe the outside of the spoon level with the spatula, and tap into a pyrex (18 by 150 mm) culture tube. Add one spoonful (0.25 ml) of powdered potassium bisulfate to the soil sample and place in the digestion and fusion rack. Place the rack with seven test tubes containing soils and one reagent blank on the gasoline stove and heat for about 10 min or until the soil is essentially decomposed. If necessary, add a little more potassium bisulfate to effect the desired fusion. Remove, allow to cool, add 3 ml of water to each sample, and heat again until a milky suspension is obtained. Prolonged or too violent heating will cause excessive bumping and should be avoided. Add 7 ml of the acetate buffer solution and 1 ml of the sodium thiosulfate solution to each sample, stopper with a clean cork, shake thoroughly, and set aside to allow the suspension to settle and the solution to cool.

Estimation. --This step is essentially a titration. Place 5 ml of the 0.0025 percent dithizone solution in a pyrex culture tube (16 by 150 mm). Add measured volumes (1.0, 1.5, 2.0, 3.0, and 8.0 ml) of the solution prepared from a soil sample to the dithizone solution and shake vigorously for 1 min between each addition, using a clean cork to close the test tube. Sufficient sample solution has been added when the color of the carbon tetrachloride layer matches a standard containing 5 micrograms of zinc, prepared as follows: Add 20 micrograms of zinc to the reagent blank carried through the fusion process, dissolve and buffer as above, and shake one-fourth of the solution with 5 ml of 0.0025 percent dithizone solution. Make new color standards every 30 min because the color fades rapidly.

The added increments of the sample solution correspond to zinc content of the soil samples as follows:

Milliliter of sample solution required to match standard	Probable zinc content (ppm)	Reported group value (ppm)
1.0	1000 and up	1000+
1.5	700 - 1000	800
2.0	400 - 700	500
3.0 to 8.0	100 - 400	300
excess of 8.0 ml	under 100	100

Chromographic Determination of Nickel in Soils and Rocks

This field method for the determination of nickel in soils and rocks, together with an illustration of its use, is given by Stevens and Lakin (1949). The method may be used without modification on samples ranging from 30 to 2000 ppm in nickel content. In the authors' experience about 85 percent of the results are within $\pm$ 40 percent of those obtained by spectrophotometric analysis. A strip of dimethylglyoxime reagent paper is inserted in the chromograph and the sample solution allowed to filter through the paper at a controlled rate. Nickel in the test solution reacts with the dimethylglyoxime in the paper to form a red precipitate, the intensity of the color being a function of the quantity of the metal present. Copper and cobalt also react under the conditions of the test to give water-soluble complex compounds and relatively large amounts may interfere by removing the reagent from the paper. The method is easy to perform and with adequate equipment, 40 or more determinations can be made per man day. To work effectively, four to six chromographs should be provided. The confined spots obtained by the method serve as semipermanent records of the tests performed. The method is suitable for rapid analysis of large numbers of samples where a high degree of accuracy is not needed.

Reagents and apparatus

Potassium Bisulfate. Analytical quality is satisfactory provided the same lot is used to make the standard series. Pulverize before using.

Sodium citrate solution, 13.3 percent. Dissolve 133 g in 500 ml of metal-free water and dilute to one liter.

Ammonium hydroxide, concentrated C. P. grade.

Litmus paper, red.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Dimethylglyoxime solution, 2 percent. Dissolve 2 g of dimethylglyoxime in 100 ml of acetone. Prepare as needed.

Reagents and apparatus

Potassium Bisulfate. Analytical quality is satisfactory provided the same lot is used to make the standard series. Pulverize before using.

Sodium citrate solution, 13.3 percent. Dissolve 133 g in 500 ml of metal-free water and dilute to one liter.

Ammonium hydroxide, concentrated C. P. grade.

Litmus paper, red.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Dimethylglyoxime solution, 2 percent. Dissolve 2 g of dimethylglyoxime in 100 ml of acetone. Prepare as needed.

Dimethylglyoxime Reagent Paper. Dip sheets of no. 50 Whatman filter paper into a 2 percent solution of dimethylglyoxime in acetone at a rate faster than the spread of solvent through the paper. Pauses must be avoided, as they cause uneven distribution of the reagent on the paper by allowing the solvent to spread through the paper without the reagent. When the paper is dry, repeat the process. Discard the outer edges of the paper and cut the dry reagent paper into strips 7/16 in wide. The reagent paper is stable for several months. For more detail on preparation of reagent papers, see Clarke and Hermance (1938).

Chromograph. See "Special Apparatus."

Balance. Torsion, capacity 120 g, sensitivity 2 mg.

Gasoline stove.

Lucite spoon. A lucite bar with cavity of 0.50 ml (10 mm diameter, 6.5 mm deep) drilled near one end.

Culture tubes. Borosilicate glass, 18 by 150 mm, marked at 2.5, 3.0, and 5 ml.

1 pipette, 0.5 ml, graduated in tenths of a ml.

Filter paper, Whatman no. 50. Large sheets, 50 cm diameter.

Ear syringes, adult size.

Stevens Extraction Sticks. See "Special Apparatus."

Standard nickel solution, 0.01 percent. Dissolve 0.01 g of pure nickel in 10 ml of 6 N nitric acid. Dilute to 100 ml with water.

Preparation of standard spots

The colors obtained on the confined spots are affected by the presence in the solution of modifier ions such as iron and aluminum. It is therefore necessary to prepare the standard spots used for comparison from solutions that contain the ions that will be present in the unknown solutions to be analyzed.

Soil solution. --Fuse in a pyrex beaker 7 g of soil, selected for exceedingly low nickel content, with 35 g of potassium bisulfate. Cool, add 27 g of sodium citrate and 100 ml of metal-free water, and digest on a steam bath until the cake is disintegrated. Cool, dilute to 200 ml, and filter through Whatman no. 50 filter paper.

Standard nickel test solutions. --Prepare a series of standard nickel test solutions by adding appropriate volumes of a standard solution of nickel from a microburette to 3 ml of the soil solution. Add ammonium hydroxide until a piece of litmus paper in the solution turns blue. Dilute to 5 ml. The series of nickel test solutions should vary from 0.30 micrograms Ni/ml (corresponding to 15 ppm Ni in 0.1 g of soil sample) to 40 micrograms Ni/ml (corresponding to 2,000 ppm Ni).

Make confined spot tests with 0.2 ml of each of the standard test solutions, using dimethylglyoxime reagent paper. Mount the series of spots on the edge of a cardboard chart and cover with cellophane tape. Label each spot with the figure of parts per million of nickel to which it corresponds. Prepare new standards with each new batch of reagent paper.

Procedure

Preparation of sample solution. --Fuse 0.1 g of soil with 0.5 g (or one 0.5 ml lucite spoonful) of potassium bisulfate in a culture tube until a dull-red quiescent melt is obtained. As the tube cools, rotate to allow the molten meterial to crystallize in a thin layer on the walls of the tube. To the cooled tube add 3 ml of 13.3 percent sodium citrate solution and boil until the melt disintegrates. Cool, add concentrated ammonium hydroxide until a piece of litmus paper in the solution turns blue, and dilute to 5 ml with water. Place a Stevens Extraction Stick in the test tube containing the sample solution, insert a deflated rubber ear syringe into the top of the extraction stick and allow to stand until a sufficiently large aliquot has filtered.

Determination of nickel. --Place a strip of dimethylglyoxime reagent paper in the reagent-paper slot of a chromograph. With the stopcock turned to connect the adjustor bulb with the connector tube, press the rubber adjustor bulb to force the water up the tube to the upper timing mark, then close the stopcock. Tighten the metal coupling to press the glass pipe filter head firmly against the reagent paper. Place 0.2 ml of the filtered sample solution in the bottom of the filter head. Turn the stopcock to join the connector tube with the medium capillary. When all of the solution has drained through the reagent paper, turn the stopcock to join the adjustor bulb to the connector tube. Raise the filter head sufficiently high so that it is well clear of the reagent paper. Draw the reagent-paper strip through the reagent-paper slot until the spot is clear of the filter head, and write the sample number on the reagent paper adjacent to the spot. Readjust the liquid column to the level of the upper timing mark and proceed as before with the next sample solution. When the spots are dry, compare them with standard spots on the chart.

Storage of test spots. --Place the strip of reagent paper containing the test spots, when they are

dry, on a slightly longer piece of cellophane tape, with spots face down against the adhesive, and mount the strip on a page of the notebook. Spots stored in this way have undergone no apparent changes in more than 2 yr.

Chromographic Determination of Copper in Soils and Rocks

This method is described by Stevens and Lakin (1949). It is another example of the confined spot technique in which the chromograph is used. (See "Special Apparatus.") Two sources of error inherent in the method tend to give low results. These are the incomplete attack of the sample by the bisulfate fusion and occasional excessive precipitation of alums from the aqueous solution of the fusion. Nevertheless the method gives satisfactory results on soil and rock samples ranging from 10 to 1500 ppm in copper content. Forty or more determinations can be made per man day and the results are usually well within ± 40 percent of those obtained by spectrophotometric methods. It is useful for the rapid analysis of large numbers of samples provided that great accuracy is not required. It has been used in geochemical prospecting.

Reagents and apparatus

Potassium bisulfate. See "Determination of Nickel."

Sodium citrate solution, 13.3 percent. Dissolve 133 g in 500 ml of metal-free water and dilute to 1 liter.

Ammonium hydroxide, concentrated C. P. grade.

Litmus paper, red.

Acetic acid, 50 percent. Dilute 25 ml of C. P. glacial acetic acid to 50 ml with metal-free water.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Rubeanic acid (dithiooxamide) 2 percent. Dissolve 2 g of rubeanic acid in 100 ml of acetone. Prepare as needed.

Rubeanic acid reagent paper. Dip sheets of no. 50 Whatman filter paper into a 2 percent solution of rubeanic acid in acetone at a rate faster than the spread of solvent through the paper, to prevent uneven distribution of the reagent on the paper. Remove, blot between clean sheets of blotting paper, and allow to dry. Repeat the process. Discard the outer edges of the paper, and cut the dry reagent paper into strips 7/16 in. wide. Use care in handling the reagent paper since the amount of copper on one's fingers is usually sufficient to react with the rubeanic acid on the reagent paper and produce a black print of copper rubeanate. The reagent paper is stable for several months. For more detail on preparation of reagent papers, see Clarke and Hermance (1938).

Standard copper solution, 0.01 percent. Dissolve 0.2 g of clear uneffloresced crystals of $CuSO_4.5H_2O$ in water, add enough sulfuric acid to make the final acidity about 0.1 and dilute to 500 ml. One ml of this solution contains 100 micrograms.

Apparatus. --Identical to that used for determination of nickel.

Preparation of standard spots

The color obtained on the confined spot with rubeanic acid is suppressed by the presence of modifier ions in the solution such as iron and aluminum. It is therefore necessary to prepare the standard spots used for comparison from solutions that contain the ions that will be present in the unknown solutions to be analyzed.

Soil solution. --Follow exactly the same procedure as in nickel method, using a soil exceedingly low in copper content.

Standard copper test solutions. --Prepare a series of standard copper test solutions by adding appropriate volumes of a standard solution of copper from a microburette to 3 ml of the soil solution. Add ammonium hydroxide until a piece of litmus paper in the solution turns blue. Dilute to 5 ml with metal-free water and add one ml of 50 percent acetic acid. The series of copper test solutions vary from 0.167 micrograms of Cu/ml (corresponding to 10 ppm Cu in 0.1 g of soil) to 25 micrograms of Cu/ml (corresponding to 1500 ppm Cu in 0.1 g of soil). The copper content of the standard test solution series should be made so that successive standards differ by about 30 percent.

Make confined spot tests with 0.2 ml of each of the standard test solutions, using rubeanic acid reagent paper. Mount the series of spots on the edge of a cardboard chart and cover with cellophane tape. Label each spot with the figure of parts per million of copper to which it corresponds. Prepare new standards with each new batch of reagent paper.

Procedure

Preparation of sample solution. --Fuse 0.1 g of soil with 0.5 g (or a 0.5 ml lucite spoonful) of potassium bisulfate in a culture tube (18 by 150 mm) until a dull-red quiescent melt is obtained. As the tube cools, rotate it to allow the molten material to crystallize in a thin layer on the walls of the tube. To the cooled tube add 3 ml of 13.3 percent sodium citrate solution and boil until the melt disintegrates. Cool, add ammonium hydroxide until a piece of litmus paper in the solution turns blue, dilute to 5 ml with water, and add 1 ml of 50 percent acetic acid solution. Place a Stevens Extraction Stick in the test solution, insert a deflated rubber ear syringe into the top of the extraction stick and allow to stand until a sufficiently large aliquot has filtered.

Determination of copper. --Make a confined spot test with 0.2 ml of the sample solution in a chromograph containing rubeanic acid reagent paper in the manner described for the nickel determination. When the spots are dry, compare with the chart of standard copper rubeanate spots. To preserve the spots for future reference, place the dry strip of reagent paper containing the test spots on a slightly longer piece of cellophane tape, with the spots faced downward against the adhesive and mount the strip on a page in a notebook.

Determination of Cobalt in Soils and Rocks

The following directions for the determination of cobalt in soils and rocks were given by Almond and Bloom (1951). The method as described is suitable to determine the cobalt content of soils containing from 10 to 400 ppm. Generally a value reported by the field method is dependable to within ± 40 percent of the value obtained by a laboratory procedure. The acidity of the sample solution must be carefully adjusted to prevent interference by iron and to assure complete precipitation of the cobalt compound. Cobalt is precipitated with 2-nitroso-1-naphthol reagent in the chromograph, and after filtration the confined spot thus obtained is compared with a standard series of confined spots. A large body of data can be collected within a short span of time since about 25 determinations can be completed per man day. The method has been successfully used in geochemical prospecting.

Reagents and apparatus

2-Nitroso-1-naphthol, 0.01 percent. Dissolve 0.01 g of 2-nitroso-1-naphthol in 100 ml of water to which 4 drops of 1 N NaOH solution have been added.

Sodium hydroxide, 1 N. Dissolve 40 g NaOH in water and dilute to 1 liter.

Potassium bisulfate, C. P. grade. Pulverize.

Sodium citrate solution, 50 percent. Dissolve 50 g $Na_3C_6H_5O_7 . 5\ 1/2\ H_2O$ in water and dilute to 100 ml.

Litmus paper, red.

Borate buffer solution, pH about 6.5. Dissolve 19 g $Na_2B_4O_7 . 10\ H_2O$ in 1 liter of water. Add 17 ml 1+1 hydrochloric acid.

Sulfuric acid 1 N. Add 28.5 ml concentrated sulfuric acid to about 500 ml of water and dilute to 1 liter.

Cobalt standard solution, 0.01 percent. Dissolve 0.04 g $CoCl_2 . 6H_2O$ in water, add 1 ml of 1+1 hydrochloric acid and dilute to 100 ml. Prepare more dilute solutions from this stock solution.

Water. Pass tap water through resin demineralizer. See "Apparatus."

Gasoline stove.

Fusion and digestion rack. See "Special Apparatus."

Stevens Extraction Sticks. See "Special Apparatus."

Culture tubes. 16 by 150 mm, pyrex, calibrated at 10 ml.

Balance. A torsion balance with a sensitivity of 2 mg is satisfactory.

Ear syringes, 6, rubber, adult size.

Pipettes. 2 - 0.5 ml, serological
2 - 2. ml, volumetric
2 - 5. ml, volumetric

Filter paper. Whatman no. 50, cut in 7/16 in. strips.

Mullite mortar and pestle. Outside diameter of mortar, 75 mm.

Chromograph. See "Special Apparatus."

Preparation of standard spots

Prepare a series of spots representing 10 to 400 ppm of cobalt in the soil as follows: To a series of 0.1 g cobalt-free soil samples, add 0, 1, 3, 5, 8, 10, 20, and 40 micrograms of cobalt from the standard cobalt solution. Evaporate to dryness over a steam bath. Add the flux, fuse and prepare standards spots by the procedure below. Mount the dry spots on the edge of a cardboard with cellophane tape and label as ppm in the soil on the basis of a 0.1 g sample.

Procedure

Mix 0.1 g of finely ground soil or rock sample with 0.4 g pulverized potassium bisulfate in a pyrex culture tube and fuse for 5 min. Cool, rotating the tube so that the melt solidifies in a thin layer on the sides of the tube. Add 5 ml of the sodium citrate solution and digest in a boiling water bath until the melt disintegrates. Add a small piece of litmus paper and 1 N sodium hydroxide dropwise until the paper turns blue. Add 2 ml of borate buffer, then sufficient 1 N sulfuric acid to make the solution acid to litmus. Dilute to 10 ml with metal-free water. Place a Stevens Extraction Stick in the culture tube and apply suction to the upper end of stick with an ear syringe. Insert a strip of filter paper in reagent-paper slot of the chromograph, tighten the metal coupling to press the glass pipe filter head firmly against the filter paper, and adjust the water level to the base of the connector tube. Transfer 0.2 ml of the filtered sample solution to the filter head of the chromograph and add 0.1 ml of the 2-nitroso-1-naphthol reagent. Squeeze the rubber adjustor bulb and open the stopcock to connect the filter head with the bulb, and squeeze the bulb until the water column rises to the upper timing mark. Turn the stopcock into position so that drainage takes place through the slow capillary. After filtration is complete, add 1 drop of 1 N sulfuric acid, to the colored spot and drain again. Remove the filter head, write the sample number adjacent to the spot on the paper, remove the strip of paper and allow the spot to dry. Compare the spot with the standards. Wash and dry the chromograph parts that come in contact with the filter paper to remove traces of the acid. With samples containing more than 400 ppm, dilute an aliquot of the sample solution and prepare another spot.

Determination of Molybdenum in Soils and Rocks

A more complete discussion of the method is given by Ward (1951a). The procedure given below can be used without modification to determine from 1 to 32 ppm of molybdenum in soils and rocks. Data given in the original publication shows that duplicate determinations on soils containing less than 10 ppm of molybdenum agree within 1 ppm. A carbonate fusion and a subsequent aqueous leaching removes practically all the iron and other elements which form insoluble hydroxides. Tungsten interference

is prevented by the addition of tartrate to the test solution. An isopropyl ether extraction separates molybdenum from the remaining elements which interfere. The field method is essentially a "test tube" method for the determination of trace quantities of molybdenum in soils and rocks. The minute amount of molybdenum obtained from a 0.025 g sample of soil or rock reacts under reducing conditions with thiocyanate to form an amber-colored complex ion which rarely is visible in the relatively large aqueous solution. The complex ion is, however, more soluble in certain organic solvents than in the aqueous solution and can be extracted by and concentrated in a very small volume of isopropyl ether. If the extraction is carried out in an ordinary test tube, the ether separates as a shallow layer over the aqueous sample solution. As little as 0.005 microgram of molybdenum per ml of aqueous solution can be determined. The simplicity of the method as well as the speed--30 or more molybdenum determinations per man day--makes this method a valuable tool in the hands of the modern prospector.

Reagents and apparatus

Flux, a mixture of equal parts by weight of sodium carbonate and potassium nitrate, ground to pass an 80-mesh silk bolting cloth sieve, thoroughly mixed, and passed through sieve again.

Sodium tartrate, reagent quality.

Potassium thiocyanate, 5 percent. Dissolve 10 g of KSCN in 200 ml of water.

Stannous chloride, 10 percent. Dissolve 10 g of $SnCl_2.2H_2O$ in 100 ml of 2 N hydrochloric acid. Add tin to improve the stability. Prepare fresh solutions at weekly intervals.

Standard molybdenum solution, 0.01 percent. Dissolve 0.075 g of pure MoO_3 in 1 N NaOH, dilute with water, add 1 N hydrochloric acid until solution is just acid, and dilute to 500 ml with water. This solution contains 100 micrograms of Mo per ml.

Standard molybdenum solution, 0.0001 percent. Prepare daily at least 1 hr before use, by adding 1 ml of the 0.01 percent solution to 50 ml of water and diluting to 100 ml.

Hydrochloric acid, concentrated C. P. grade.

Potassium nitrate, 1 N. Dissolve 10 g of KNO_3 in 100 ml of water.

Isopropyl ether. Practical or C. P. grades are suitable provided peroxides are absent. Unless specially packaged, all dry ethers on standing tend to form explosive peroxides. Peroxides of isopropyl ether interfere with the molybdenum method. To test for peroxides, shake 5 ml of ether with 5 ml of an acidified aqueous solution of potassium iodide. If the iodide solution shows more than a faint yellow color, due to free iodine produced by the peroxides, the ether contains appreciable quantities of peroxides and should not be used. Shake peroxide-free ether with 1/10 its volume of equal amounts of stannous chloride and potassium thiocyanate solutions on the day during which it is to be used.

Phenolphthalein indicator, 1 percent. Dissolve 1 g of phenolphthalein in 100 ml of alcohol.

Lucite spoon, a lucite bar with cavity of 0.25 ml (7 mm diameter, 6.5 mm deep) drilled near one end.

Mullite mortar and pestle, outside diameter of mortar, 75 mm.

1 sieve, 80 mesh. See "Special Apparatus."

1 camel's-hair brush, length of brush part, 18 mm.

1 small spatula, length of blade, 50 mm.

1 pyrex volumetric flask with stopper, 100 ml.

20 pyrex culture tubes, 16 by 150 mm, marked at 5 ml.

Pyrex culture tubes, 16 by 150 mm, unmarked. One is required for each determination.

3 serological pipettes, 1 ml, calibrated in tenths of a ml.

2 serological pipettes, 1 ml, calibrated in hundredths of a ml.

1 serological pipette, 10 ml, calibrated in tenths of a ml.

1 test tube rack, capacity at least 20 tubes.

1 digestion and fusion rack. See "Special Apparatus."

Balance, torsion, with sensitivity of 2 mg.

Stevens Extraction Sticks. See "Special Apparatus."

1 Gasoline stove.

Water, metal-free. Pass tap water through resin demineralizer. See "Special Apparatus."

Cork stoppers, for the culture tubes.

1 fusion rack. See "Special Apparatus."

Procedure

Preparation of sample solution.--In the mullite mortar mix thoroughly 0.1 g of the finely ground sample with 0.5 g of the flux. Transfer the mixture to an unmarked culture tube and tap gently to dislodge the sample from the side of the tube. Heat and rotate the tube in the fusion rack over the gasoline stove to effect fusion. Usually, 4 to 5 min are required; by the time all the sample has been attacked, the tube is filled with brown fumes from the nitrate decomposition. After the fusion is complete, remove the tubes from the fusion rack, place in a test-tube rack and allow to cool. While the tubes are cooling, fill the top of the metal case of the gasoline stove about half full with water. Insert the digestion and fusion rack in water bath. Place on the stove and bring the water to a boil. Pipette 4 ml of metal-free water

into each tube and place in the boiling water. After 3 min insert a corked Stevens Extraction Stick into the culture tube and let the tube remain in the boiling water bath for 3 min or until air bubbles are escaping freely from the lower end of the stick. Remove the culture tube from the water bath and place in a test tube rack to cool. As the system cools, a clear filtrate from the aqueous extraction of the fused mass is drawn into the extractor. Transfer a 1 ml aliquot of the filtrate representing 0.025 g of soil, to a clean calibrated culture tube. Add 1 drop of indicator and 1 N hydrochloric acid drop by drop, until the red color of the solution disappears. Avoid an excess. Dissolve one 0.25 ml lucite spoonful (0.2 g) of sodium tartrate in the solution and add water to the 5 ml mark.

Preparation of standards.--Pipette the appropriate volume of the 0.0001 percent standard solution into culture tubes as follows:

Standard	Volume of standard required milliliter	Molybdenum content micrograms
a	0.03	0.03
b	.05	.05
c	.08	.08
d	.15	.15
e	.20	.20
f	.30	.30
g	.40	.40
h	.50	.50
i	.65	.65
j	.80	.80

To each tube add 0.5 ml of 1 N potassium nitrate, and one 0.25 ml lucite spoonful of sodium tartrate. Add about 2 ml of water and shake to effect a clear solution. Dilute to 5 ml with water.

Estimation.--To the sample solution and to each standard, add 0.5 ml of concentrated hydrochloric acid and shake to liberate carbon dioxide. Add 0.3 ml of 5 percent potassium thiocyanate and 0.5 ml of stannous chloride reagent with shaking after each addition. Allow the solution to stand for 1/2 to 1 min, add 0.3 ml of isopropyl ether and shake vigorously. Place a cork in each tube to prevent evaporation of the ether. View the amber-colored organic layer against a white background and compare with standard solutions. Multiply the number of micrograms of molybdenum found in the sample aliquot by 40 to convert the results to ppm.

Determination of Lead in Soils and Rocks

The procedure for the determination of traces of lead in soils is based on the method used by Almond and Morris (1951). A nitric acid digestion has been found to dissolve lead more completely than the extraction used by Almond and Morris and is recommended here. A 0.1 g sample is suitable for determination of lead in samples ranging from 10 to 1000 ppm. The lead estimation is made with dithizone in the presence of cyanide as a complexing agent for other reacting metals. The oxidation product formed when an aqueous solution is shaken with dithizone in the presence of citrate, iron (III) and cyanide is a major source of error, but this is avoided in part by diluting the aliquot and by using freshly prepared dithizone. Duplicate samples can be determined to within 20 percent and generally the value reported differs from a careful laboratory determination by less than 50 percent. About 35 samples can be determined per man day. The method has been used in geochemical prospecting.

Reagents and Apparatus

Potassium cyanide, 10 percent. Dissolve 50 g KCN in 75 ml water and shake successively with small portions of 0.01 percent dithizone solution until the final carbon tetrachloride layer is green. Extract the excess dithizone dissolved in the aqueous layer with successive portions of chloroform and discard the chloroform. The final extraction should be colorless. Dilute the solution to 500 ml with metal-free water.

Potassium cyanide, 0.1 percent. Add 50 ml metal-free water to 100 ml graduated cylinder, add about 1 ml of the 10 percent potassium cyanide solution to cylinder and make the volume up to 100 ml with water. Insert stopper and shake. Caution: Potassium cyanide is exceedingly poisonous; a very small amount taken internally is fatal. Therefore, never transfer a potassium cyanide solution with a pipette; always wash hands immediately after handling the reagent and its solutions.

Acidification of cyanide solutions produces a lethal gas (HCN). Never store near acids. Exercise meticulous care to avoid any possible contact of the salt or its solution with acids resulting from breakage in transport. Never acidify solutions containing cyanide. Always wash thoroughly vessels in which the reagent has been used.

Ammonium citrate solution, 10 percent. Dissolve 100 g $(NH_4)_2HC_6H_5O_7$ in about 400 ml metal-free water. Shake with successive portions 0.01 percent dithizone solution until the carbon tetrachloride phase is green. Extract the excess dithizone dissolved in the aqueous phase by shaking with successive portions of chloroform and discard the chloroform. The final extract should be colorless. Dilute the aqueous phase to 1 liter.

Ammonium hydroxide, 1 N. Dilute 70 ml concentrated ammonia with water to 1 liter.

Dithizone (diphenylthiocarbazone), 0.01 percent weight per volume. Dissolve 0.01 g dithizone in 100 ml carbon tetrachloride.

Dithizone, 0.001 percent. Dilute 10 ml of the 0.01 percent dithizone with carbon tetrachloride to 100 ml. Prepare daily and keep in a pyrex bottle covered with a dark-colored paper.

Standard lead solution, 0.01 percent. Dissolve 0.016 g dry lead nitrate in 100 ml of solution containing 1 drop of concentrated nitric acid. This solution contains 100 micrograms lead per ml.

Standard lead solution, 0.001 percent. Add 10 ml 0.01 percent to about 50 ml 1 N nitric acid and make up to 100 ml with 1 N nitric acid. This solution contains 10 micrograms lead per ml.

Nitric acid, concentrated.

Nitric acid, 1+3, add 1 volume concentrated acid to 3 volumes water.

Water. Pass tap water through a resin demineralizer. See "Special Apparatus."

Thymol blue indicator, 0.04 percent. Dissolve 0.04 g of the sodium salt in 100 ml water.

Digestion and fusion rack. See "Special Apparatus."

Mullite mortar and pestle, diameter of mortar, 75 mm.

Balance, torison, sensitivity, 2 mg.

1 gasoline stove.

Sieve, 80 mesh. See "Special Apparatus."

1 serological pipette, 0.1 ml, graduated in hundredths of a ml.

1 serological pipette, 1 ml, graduated in tenths of a ml.

1 serological pipette, 5 ml, graduated in tenths of a ml.

2 volumetric pipettes, 5 ml.

1 volumetric pipette, 10 ml.

30 pyrex culture tubes, 18 by 150 mm, marked at 2 and 10 ml.

6 graduated cylinders, glass-stoppered, 100 ml.

3 separatory funnels, Squibb type, 125 ml.

30 Stevens Extraction Sticks. See "Special Apparatus."

Procedure

Extraction.--Place 0.1 g of the finely ground sample in a pyrex test tube. Prepare eight samples at a time. Add 2 ml of 1+3 nitric acid. Allow time for effervescence from carbonates to cease. Place a Stevens Extraction Stick in the test tube and boil gently for 30 min. Cool. The solution filters into the extractor during cooling.

Estimation of lead.--Transfer the filtered solution to a clean culture tube and dilute with water to 10 ml mark. Shake and transfer a 5 ml aliquot to a 125 ml pyrex separatory funnel. Add 5 ml of 10 percent ammonium citrate, 2 drops of thymol blue indicator and sufficient 1 N ammonium hydroxide to turn the solution distinctly yellow. Add 10 percent potassium cyanide until the entire solution just turns blue (pH about 8.5). Add 5 ml of 0.001 percent freshly prepared dithizone solution and shake gently for 5 sec. Drain the carbon tetrachloride (lower) phase into a 100 ml glass-stoppered pyrex graduated cylinder containing 10 ml of 0.1 percent potassium cyanide solution. Shake the mixture for 3 sec. The unreacted dithizone is now in the aqueous phase while the pink lead dithizonate is in the carbon tetrachloride phase. From standards similarly prepared, estimate the amount of lead present.

One microgram of lead gives a weak but perceptible pink, corresponding to 20 ppm lead in the original sample, and more than 3 micrograms is difficult to estimate visually. If the first aliquot does not give a color in the suitable range, repeat using larger or smaller aliquots until a readable color is obtained.

Determination of Silver in Soils and Rocks

The procedure given below for the determination of traces of silver in soils and rocks is described in detail by Almond, Stevens and Lakin (1951). With a 0.5 g sample from 0.2 to 20 ppm of silver can be estimated. The noble metals, as well as mercury and copper (I) also react with the reagent, but the method minimizes these interferences. Mercury is eliminated with organic matter by igniting the sample. Nitric acid, the digesting agent, oxidizes copper to copper (II), and has poor solvent action on gold.

Silver is separated from the colored ions in nitric acid solution by collecting the silver salt of p-dimethylaminobenzalrhodanine at the interface of an amyl alcohol aqueous extract, and then discarding the aqueous extract. This silver precipitate, in a dispersed state is filtered through the chromograph to form a confined spot. The intensity of the confined spot remaining on the filter paper is a measure of the silver content of the original soil. About 20 samples can be analyzed per man day. Generally duplicate samples can be determined within 40 percent. The method is suitable for geochemical prospecting.

Reagents and Apparatus

Ammonium citrate, 25 percent. Dissolve 25 g ammonium citrate, $(NH_4)_2HC_6H_5O_7$, in metal-free water and dilute to 100 ml. Shake with amyl alcohol in a 250 ml separatory funnel and allow to stand 4 hr. Drain the citrate from the solids in the interface and discard the amyl alcohol and solids. Repeat the process until no solids appear in the interface.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Nitric acid, concentrated. C. P. grade.

Ammonium hydroxide, concentrated, C. P. grade.

Acetic acid, glacial, C. P. grade.

p-Dimethylaminobenzalrhodanine, 0.05 percent. Dissolve 0.05 g in 100 ml of glacial acetic acid.

Amyl alcohol, B. P. 136-138 C.

Ethyl alcohol, 95 percent, U. S. P.

Standard silver solution A, 0.01 percent. Dissolve 0.016 g of silver nitrate, dried at 110 C, in 100 ml of 1 N ammonium hydroxide.

Standard silver solution B, 0.001 percent. Transfer 10 ml solution A to a 100 ml volumetric flask containing about 50 ml 1 N ammonium hydroxide and dilute to volume with 1 N ammonium hydroxide. Shake thoroughly.

Standard silver solution C, 0.0001 percent. Transfer 10 ml solution B to a 100 ml volumetric flask containing about 50 ml 1 N ammonium hydroxide and dilute to volume with 1 N ammonium hydroxide. Shake thoroughly.

100 Stevens Extraction Sticks. See "Special Apparatus."

20 separatory funnels. 60 ml, Squibb.

6 glass chromographs. See "Special Apparatus."

100 pyrex culture tubes, 16 by 150 mm.

1 gasoline stove.

Electric hot plate, 110V a-c, variable temperature control, 6 by 6 in. heating surface.

Munktell Swedish filter paper, no. OA. Cut in strips 7/16-in. wide.

Balance, a torsion balance, sensitivity 2 mg.

40 porcelain crucibles, no. 0., high form.

Litmus paper, blue.

1 serological pipette, 1 ml, graduated in tenths of a ml.

1 serological pipette, 10 ml, graduated in tenths of a ml.

3 graduated cylinders, 5 ml, pyrex.

1 graduated cylinder, 10 ml, pyrex.

Digestion and fusion rack. See "Special Apparatus."

Mullite mortar and pestle, outside diameter of mortar, 75 mm.

Sieve, 80 mesh. See "Special Apparatus."

1 wash bottle, 250 ml, polyethylene.

1 pyrex glass rod, 150 mm in length.

Preparation of standard spots

Prepare a series of spots representing values ranging from 0 to 24 ppm as follows: Label eight no. 0 crucibles, a to h, inclusive, and to each add 0.5 g finely ground silver-free soil and roast 10 min. Cool. To each crucible add standard solution B or C, in the quantities indicated below. Evaporate to dryness. Add 10 ml concentrated nitric acid to each crucible and prepare standard spots as directed in the procedure given below. Spot "b" represents 0.2 ppm silver in a sample, since 0.1 microgram of silver has been added to a 0.5 g sample.

Sample	Add Standard B milliliter	Add Standard C milliliter	Micrograms silver added
a	--	--	0.0
b	--	0.1	.1
c	--	.3	.3
d	--	.6	.6
e	.1	---	1.0
f	.3	---	3.0
g	.6	---	6.0
h	1.2	---	12.0

Mount the series of spots on the edge of a cardboard chart and cover with cellophane tape. Label each spot with the value in parts per million of silver to which it corresponds.

Procedure

Preparation of sample solution. --Place a 0.5 g soil or rock sample, ground to pass an 80-mesh sieve, in a no. 0 porcelain crucible. Heat for 10 min at about 800 C (dull red heat). Cool and add 10 ml concentrated nitric acid. Place on a hot plate covered with a sheet of asbestos paper. Set at very low heat (40 C to 50 C.) so that about 1 1/2 ml of acid remains after 12 hr of digestion. Allow the sample to digest on the hot plate overnight. Transfer the sample and nitric acid to a 16 by 150 mm culture tube, and wash the soil remaining in the crucible into the tube with concentrated nitric acid using a volume of about 1/2 ml. Rinse the crucible again with 1/2 ml of water and add to the contents of the culture tube. Insert a firmly stoppered Stevens Extraction Stick into the test tube and place in a digestion and fusion rack. Place the rack on the gasoline stove and digest for 10 min. Remove the culture tube from the heat. When cool, the solution is in the extractor.

Separation and estimation of silver. --Transfer the filtered solution from the Extraction Stick to a 60 ml separatory funnel containing 10 ml metal-free water. Rinse the extractor with 10 ml water and combine the washings with the original extract in the

separatory funnel. Add 3 ml of 25 percent ammonium citrate solution, shake to mix, and make the solution alkaline to litmus by adding ammonium hydroxide dropwise. Test frequently by alternately dipping a glass rod into the solution and touching it to a fresh piece of litmus paper. Add 5 ml of glacial acetic acid and 0.1 ml of 0.05 percent p-dimethylaminobenzalrhodanine, and mix thoroughly. Allow to cool. Add 3 ml amyl alcohol, shake for 30 sec and allow to stand for 30 min to permit the phases to separate. Drain until about 1/2 ml of the aqueous (lower) phase remains, add about 1 ml of water and drain again until about 1/2 ml of aqueous phase remains. Add 1 ml ethyl alcohol and shake to disperse the precipitate. Place a strip of filter paper in the slot in the head of the chromograph and tighten the coupling to seal the filter paper between the two sections of pipe. Adjust the water column to the upper timing mark and transfer the contents of the separatory funnel to the head of the chromograph. Open the fast capillary of the chromograph and turn the stopcock so that the drainage is through the capillary. When filtration is complete, remove the paper from the chromograph, write the number of sample adjacent to the spot and mount the dry spots in the analyst's notebook with cellophane tape. Compare the dried spot on the filter paper with a standard series of spots. After the analysis is complete, wash the separatory funnel with nitric acid, rinse four times with tap water and finally with metal-free water to remove traces of ethyl alcohol. Carefully clean the glass filter head of the chromograph similarly.

Determination of Tungsten in Soils

A more complete discussion of the method is given by Ward (1951b). The procedure given below can be used without modification on soils containing 20 to 400 ppm of tungsten; however, if the size of the aliquot taken for the estimation is varied, the method can be used on soils containing 10 to 800 ppm of tungsten. The results obtained by the field method on 12 out of 14 representative soil samples are within ± 40 percent of those obtained by a laboratory method. An aqueous extraction of the carbonate fusion separates tungsten from iron, titanium, and other elements which form insoluble hydroxides. Later, an isopropyl ether extraction of the acidified sample solution under reducing conditions and in the presence of an alkali thiocyanate serves to separate tungsten from small amounts of tantalum, uranium, phosphorus, boron, and from as much as 1,000 micrograms of vanadium. Although copper reacts with thiocyanate to form the insoluble cuprous thiocyanate, the reaction causes no interference in the field method. Although large amounts of molybdenum interfere with the field method, a higher acid concentration bleaches the color of the molybdenum thiocyanate and prevents that interference. This field method is essentially a "test tube" method which requires a minimum amount of reagents and simple equipment. With a little practice the average individual can determine the tungsten content of as many as 30 soil samples per day in temporary quarters and under a wide range of conditions. The field method should prove useful in geochemical prospecting programs.

Reagents and Apparatus

Flux, a mixture by weight of 5 parts sodium carbonate, 4 parts sodium chloride, and 1 part potassium nitrate, ground to pass an 80-mesh silk bolting cloth sieve, thoroughly mixed, and passed through the sieve again.

Potassium thiocyanate, 25 percent. Dissolve 25 g KSCN in water and dilute 100 ml.

Hydrochloric acid, concentrated. C.P. grade

Stannous chloride. Dissolve 10 g $SnCl_2.2H_2O$ in concentrated hydrochloric acid and dilute to 100 ml with the acid.

Standard tungsten solution, 0.01 percent. Solution A. Dissolve 0.09 g $Na_2WO_4.2H_2O$ in water and dilute to 500 ml. The solution contains 100 micrograms of tungsten per ml.

Standard tungsten solution, 0.0005 percent. Solution B. Because the concentration decreases on standing, one should prepare it daily by diluting 5 ml of solution A with water to 100 ml and mixing thoroughly.

Isopropyl ether. Practical or C. P. grades are suitable provided peroxides are absent. Unless specially packaged, all dry ethers on standing tend to form explosive peroxides. Peroxides of isopropyl ether interfere with the tungsten method. To test for peroxides shake 5 ml of ether with 5 ml of an acidified aqueous solution of potassium iodide. If the iodide solution shows more than a faint yellow color, due to free iodine produced by the peroxides, the ether contains appreciable quantities of peroxides and should not be used. Shake peroxide-free ether with 1/10 its volume of equal amounts of stannous chloride and potassium thiocyanate solutions on the day during which it is to be used.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Mullite mortar and pestle, outside diameter of mortar, 75 mm.

1 sieve, 80-mesh. See "Special Apparatus."

1 camel's-hair brush, length of brush part, 18 mm.

1 pyrex volumetric flask with stopper. 100 ml.

20 pyrex culture tubes (16 by 150 mm), marked at 5 ml.

Pyrex culture tubes (16 by 150 mm), unmarked. One is required for each determination.

1 serological pipette, 1 ml, calibrated in hundredths of a ml.

1 serological pipette, 2 ml, calibrated in tenths of a ml.

2 serological pipettes, 5 ml, calibrated in tenths of a ml.

1 test tube rack, capacity 20 tubes.

Balance, torsion, sensitivity 2 mg.

Stevens Extraction Sticks. See "Special Apparatus."

1 portable gasoline stove.

1 fusion rack. See "Special Apparatus."

1 water bath. The top of the gasoline stove container filled with water to about 2/3 of its capacity is an excellent water bath.

1 digestion and fusion rack. A round rack fitting inside the top of the gasoline stove container and holding 16 tubes was used. See "Special Apparatus."

Cork stoppers no. 5 for the culture tubes.

1 thermometer, 0 to 110 C.

Procedure

Preparation of sample solution. Weigh out 0.25 g of the finely ground soil and transfer to a culture tube. Tap the tube gently to dislodge sample from the sides and add 1.25 g of flux. Mix the sample and flux by alternately rotating and tapping the tubes. Place the tube in the fusion rack over the gasoline stove and allow the contents to fuse 5 to 6 min. Rotate the tube occasionally to insure a thorough attack of the sample. After the fusion is complete, remove the tube from the rack and allow to cool. Pipette 5 ml of metal-free water into the tube, and place the tube in a boiling water bath. After 3 min insert a corked Stevens Extraction Stick into the culture tube and let the tube remain in the boiling water bath for 3 min or until air bubbles are escaping freely from the lower end of the extraction stick. Remove the culture tube from the water bath and place in a test-tube rack to cool. As the system cools, a clear filtrate from the aqueous extraction of the fused mass is is drawn into the extractor. Transfer a 1 ml aliquot of the filtrate, representing 0.05 g of soil, to a clean culture tube and add water to make the volume up to the 5 ml mark.

Preparation of standards. --Prepare a series of standard solutions by pipetting the required volumes of standard solution B into separate culture tubes and adding water to the 5 ml mark.

Standard	Volume of solution B required milliliter	Tungsten content micrograms
a	0.2	1
b	.4	2
c	.6	3
d	.8	4
e	1.0	5
f	2.0	10
g	3.0	15
h	4.0	20

Estimation. --Add 4 ml of stannous chloride and 0.5 ml of potassium thiocyanate reagents to the sample solution and to each standard solution. Place the tubes in a water bath maintained at a temperature of 90 C to 95 C for 5 min or until one observes a moderate evolution of hydrogen sulfide. If the altitude causes the water to boil below the specified temperature, allow the tubes to remain in the water bath until hydrogen sulfide evolves freely. Remove the tubes from the water bath, cool, add 0.5 ml of potassium thiocyanate reagent and 0.3 ml of isopropyl ether. Insert a clean cork into the tube and shake 5 sec to extract the tungsten thiocyanate complex ion into the ether. Compare the intensity of the yellowish-green color of the ether layer over the sample solution with that obtained over the standard solution. If the color of the ether layer over the sample is amber instead of yellowish-green, add about 5 ml of concentrated hydrochloric acid and shake to bleach the amber color. Since a small amount of the isopropyl ether dissolves in the aqueous phase during this process, add an additional 0.1 ml of isopropyl ether in order to make valid comparisons.

Multiply the number of micrograms of tungsten found in the aliquot by 20 to convert the results to parts per million. The procedure is suitable for soils containing from 20 to 400 ppm of tungsten; but, if one adjusts the aliquot, he can decrease the lower limit to 10 ppm. The upper limit is determined by the accuracy with which the operator can measure small aliquots. With materials containing more than 0.1 percent of tungsten, the field method of North and Grimaldi (1946) is convenient.

After the analysis is complete, wash and retain the calibrated culture tube and extraction stick for future use. Discard the tube used for the fusion as the action of the flux makes further use impracticable.

Determination of Readily Soluble Copper, Zinc, and Lead in Soils and Rocks: Sulfuric Acid Extraction

The procedure for the determination of traces of copper, zinc, and lead is described by Almond and Morris (1951). A dilute sulfuric acid solution is used to dissolve trace amounts of copper, zinc, and lead from the sample, and dithizone is the reagent used to estimate the three metals separately. The sulfuric acid extraction is used because it is a simple procedure and indications of the content of the three metals in a sample can be obtained from the same sample solution. About 20 samples can be analyzed daily for copper, zinc, and lead. The method is a useful tool for survey work in geochemical prospecting.

Reagents and Apparatus

Potassium cyanide, 10 percent. Dissolve 50 g KCN in 75 ml of water and shake with successive small portions of 0.01 percent dithizone solution until the final carbon tetrachloride layer is green. Extract the excess dithizone in the aqueous layer with successive portions of chloroform, and discard the chloroform. The final extract should be colorless. Dilute to 500 ml.

Potassium cyanide, 0.1 percent. Add 50 ml metal-free water to 100 ml graduated cylinder, add about 1 ml 10 percent solution to cylinder and make volume up to 100 ml with water. Stopper and shake. Caution: Potassium cyanide is exceedingly poisonous; a very small amount taken internally is fatal. Therefore, never transfer a potassium cyanide solution with a pipette; always wash the hands immediately after handling the reagent and its solutions.

Acidification of cyanide solutions produces a lethal gas (HCN). Never store near acids. Use meticulous care to avoid any possible contact of the salt or its solution with acids resulting from breakage in transport. Never acidify solutions containing cyanide. Always thoroughly wash vessels in which the reagent has been used.

Ammonium hydroxide, 1 N. Dilute 70 ml concentrated ammonia to one liter.

Sodium thiosulfate, 50 g $Na_2S_2O_3 . 5H_2O$ in 100 ml water. Remove reacting heavy metals by shaking with 0.01 percent dithizone solution.

Sulfuric acid, 1 N. Add 28.5 ml concentrated sulfuric acid to about 500 ml water and dilute to 1000 ml.

Ammonium citrate solution, 10 percent. Dissolve 100 g $(NH_4)_2HC_6H_5O_7$ in about 400 ml of metal-free water. Shake with successive portions of 0.01 percent dithizone solution until the carbon tetrachloride phase is green. Extract the excess dithizone dissolved in the aqueous phase by shaking with successive portions of chloroform and discard the chloroform. The final extract should be colorless. Dilute the aqueous phase to 1 liter.

Dithizone (diphenylthiocarbazone), 0.01 percent weight per volume. Dissolve 0.01 g dithizone in 100 ml carbon tetrachloride.

Dithizone, 0.001 percent. Dilute 10 ml 0.01 percent dithizone with carbon tetrachloride to 100 ml. Prepare daily and keep in a pyrex bottle covered with a dark-colored paper.

Sodium acetate, 2 N. Dissolve 164 g CH_3COONa in metal-free water and dilute to 1 liter.

Acetic acid, 2 N. Dilute 114 ml glacial acetic acid to 1 liter with metal-free water.

Acetate buffer, pH about 4.75. Mix equal volumes 2 N sodium acetate and 2 N acetic acid and remove traces of zinc by shaking with 0.01 percent dithizone solution.

Thymol blue indicator, 0.04 percent. Dissolve 0.04 g of the sodium salt in 100 ml of metal-free water.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Standard copper solution, 0.01 percent. Dissolve 0.2 g of clear uneffloresced crystals of $CuSO_4 . 5H_2O$ in water, add enough sulfuric acid to make the final acidity about 0.1 N and dilute to 500 ml. One ml of this solution contains 100 micrograms.

Standard zinc solution, 0.01 percent in about 0.1 N hydrochloric acid. Dissolve 0.1 g of reagent-grade 30-mesh zinc in concentrated hydrochloric acid and dilute to 1 liter. One ml of this solution contains 100 micrograms.

Standard lead solution, 0.1 percent. Dissolve 0.16 g of dry lead nitrate in 100 ml of solution acidified with nitric acid. One ml of this solution contains 1,000 micrograms.

Fusion and digestion rack. See "Special Apparatus."

Balance. Sensitivity, 2 mg.

1 gasoline stove.

Sieve, 80-mesh. See "Special Apparatus."

3 serological pipettes, 1.0 ml, graduated in hundredths of a ml.

1 serological pipette, 5.0 ml, graduated in tenths of a ml.

30 pyrex culture tubes, 25 by 200 mm, marked at 30 and 40 ml.

6 graduated cylinders, 100 ml, glass-stoppered pyrex.

3 graduated cylinders, 5 ml, pyrex.

3 separatory funnels, 125 ml, Squibb type, glass-stoppered, pyrex.

Procedure

Extraction. --Place 1 g of the finely ground sample in a culture tube. Prepare eight samples at the same time. Add 30 ml of 1 N. sulfuric acid and reflux for 30 min. Dilute to 40 ml; reflux for an additional 5 min, and allow to cool. Take aliquots directly from the supernatant liquid.

Estimation of copper. --Transfer a 2 ml aliquot of the sulfuric acid solution to a 100 ml glass stoppered pyrex graduated cylinder, containing about 10 ml of water. Add 2 to 3 drops of thymol blue indicator, 1 ml ammonium citrate, then 1 N. ammonium hydroxide until the solution begins to turn yellow. The color should have a pink tinge. If it does not, back titrate with 1 N sulfuric acid until the pink begins to reappear. Add 5 ml of fresh 0.001 percent solution of dithizone and shake for two minutes. Compare the mixed color with those of standard copper solutions. Four micrograms of copper produce a gray; 5 micrograms, a blue; and six micrograms, a purple color in the organic phase. Less than 4 micrograms of copper gives an indecisive color change, whereas more than 6 micrograms produces a color ranging from purple to pink, which is difficult to compare. If the first aliquot does not give a color in the suitable range, repeat using larger or smaller aliquots until a readable color is obtained.

Estimation of zinc. --Transfer 1 ml of the sulfuric acid extract to a 100 ml graduated cylinder containing about 10 ml of water. Add 0.5 ml of ammonium citrate, 2 to 3 drops of thymol blue, and ammonium hydroxide until the indicator turns yellow. Add 1 ml of the sodium acetate buffer and 1 ml of sodium thiosulfate solution. Add 5 ml of 0.001 percent fresh solution of dithizone and shake for 1 min. Estimate the zinc in the carbon tetrachloride phase by the mixed color method. Zinc produces the following colors: 0.5 micrograms, blue green;

1 microgram, blue; 2 micrograms, purple; 3 micrograms, violet; 4 micrograms, or more, purplish red. Use a smaller aliquot if a purplish-red color results, or a larger aliquot if the green remains apparently unchanged.

Estimation of lead. --Transfer 2 ml of the sulfuric acid extract to a 125 ml separatory funnel, containing about 10 ml of water. Add 5 ml ammonium citrate, 2 drops of indicator, and sufficient ammonium hydroxide to turn the solution distinctly yellow. Add 10 percent potassium cyanide until the entire solution just turns blue (pH about 8.5). Add 5 ml of 0.001 percent freshly prepared dithizone solution and shake gently for 5 sec. Drain the carbon tetrachloride phase into a 100 ml graduated cylinder containing 10 ml of 0.1 percent potassium cyanide solution. Shake the mixture for 3 sec. Excess dithizone is now in the aqueous phase and the pink lead dithizonate is in the carbon tetrachloride phase. From standards similarly prepared, estimate the amount of lead present.

One microgram of lead gives a weak but definite pink; more than 3 micrograms is difficult to estimate visually. If the first aliquot does not give a color in the suitable range, repeat using larger or smaller aliquots until the readable color is obtained.

Determination of zinc in plants

This method for the field determination of zinc in fresh plant leaves is described in detail by Reichen and Lakin (1949). The fresh leaves are collected with a leaf punch cutting discs of 1 sq cm. Twenty of the discs are used as a sample. Results are calculated in micrograms per 100 discs. As an approximation for eastern vegetation 2 times micrograms per hundred discs gives parts per million on the dry weight basis. The method is suitable for determining from 50 to 2500 micrograms per 100 discs or roughly 100 to 5000 ppm on air dry basis. Some zinc is lost during the ashing of the leaves, but the loss is not sufficient to impair the use of direct ashing for geochemical prospecting. The zinc losses during ashing are generally less with fresh green vegetation than with air dried vegetation. Apparatus and chemicals are readily available and easily portable. Under favorable conditions, 40 or more determinations can be made per man day. The method may prove useful in geochemical prospecting.

Reagents and apparatus

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Acetate buffer. Dissolve 248 g sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$) in 900 ml of water. Add 11 ml glacial acetic acid and make up to 1 liter. Remove traces of zinc by shaking with successive portions of 0.01 percent dithizone solution until the green color of dithizone persists.

Sodium thiosulfate, 50 g $Na_2S_2O_3 \cdot 5H_2O$ in 100 ml water. Remove reacting heavy metals by shaking with 0.01 percent dithizone solution.

Standard zinc solution, 0.01 percent in about 0.1 N hydrochloric acid. Dissolve 0.01 g reagent-grade 30 mesh zinc in concentrated hydrochloric acid and dilute to 100 ml with water.

Standard zinc solution, 0.0005 percent. Add 2.5 ml 0.01 percent standard zinc solution to 35 ml acetate buffer and 5 ml sodium thiosulfate. Dilute to 50 ml with 1 N hydrochloric acid. This solution should be made fresh daily. One ml contains 5 micrograms of zinc.

Hydrochloric acid, 1 N. Dilute 83.5 ml of concentrated hydrochloric acid to 1 liter with metal-free water.

Dithizone solution, 0.01 percent weight per volume. Dissolve 0.01 g in 100 ml reagent-grade carbon tetrachloride. Store in cool, dark place.

Dithizone solution, 0.0025 percent weight per volume. Dilute 25 ml 0.01 percent solution to 100 ml with reagent-grade carbon tetrachloride.

20 pyrex culture tubes, 18 by 150 mm, marked at 3, 10, and 11 ml.

20 pyrex culture tubes, 16 by 150 mm, marked at 5 ml.

1 test tube rack

1 serological pipette, 5 ml, fitted with stopcock at upper end.

1 graduated cylinder, 100 ml, or other suitable device in which to support pipette.

1 serological pipette, 10 ml, graduated in tenths of a ml.

1 camel's-hair brush.

10 nickel crucibles about 40 mm in diameter and 30 mm high.

1 leaf punch, similar to item no. 2-846 listed by Fisher Scientific Co. The punch cuts a disk 1 sq cm in area.

1 gasoline stove.

Cork to fit both sizes of culture tubes.

Procedure

Place 20 disks (20 sq cm, cut from the leaves of the plant with the leaf punch) in a nickel dish and ash over the flame of the gasoline stove, heating only long enough to burn the sample completely. Transfer the ash to a test tube (18 by 150 mm) and rinse the dish with a little 1 N hydrochloric acid. Dilute to 3 ml with 1 N hydrochloric acid, add 7 ml acetate buffer and 1 ml sodium thiosulfate, stopper with a clean cork, and mix by shaking.

Preparation of standard. --Transfer 5 ml of the 0.0025 percent dithizone solution to a culture tube

(16 by 150 mm). Add 1 ml 0.0005 percent zinc standard and shake for 1 min. Prepare fresh standards every 30 min because the color fades rapidly.

Estimation.--This step is essentially a titration. Place 5 ml of the 0.0025 percent dithizone solution in a culture tube (16 by 150 mm), and add the sample solution in increments of 1 ml, shaking vigorously for 1 min after each addition. Continue the titration until the color of the carbon tetrachloride layer matches as nearly as possible that of the standard. If less than 1 ml of sample solution is needed to match the standard, repeat the titration on a tenfold dilution of the sample solution.

The zinc content of the sample corresponding to the volume of sample solution required in the titration to match the standard is found in table 5.

Table 5.--Zinc content of plants corresponding to various volumes of sample solution

Volume required for closest matching of standard milliliter	Zinc content	
	Micrograms per 100 sq cm fresh material	Approximate micrograms per gram air-dry weight (parts per million)
Original sample solution:		
5	50	100
4	60	120
3	80	160
2	125	250
1	250	500
Diluted sample solution:		
6	400	800
5	500	1,000
4	600	1,200
3	800	1,600
2	1,250	2,500
1	2,500	5,000

Since "Micrograms per area" is a comparatively unfamiliar manner of expressing trace element content of plant material, the calculations are given both in micrograms per gram (parts per million) and in micrograms per 100 sq cm. No accurate conversion from area to weight basis can be made because of the variation in the leaf structure of different kinds of plants; however, for a group of plants collected in the eastern United States, it has been found that multiplying the micrograms per 100 sq cm by 2 will give the approximate micrograms per gram of air dried plant material.

Determination of nickel in plants

A more complete discussion of the method is given by Reichen (1951). Data given in the original publication show that the results obtained by the field method are generally within 30 percent of those obtained by a conventional laboratory procedure. As little as 0.025 percent nickel in plant ash can be determined and with a simple modification 0.003 percent nickel in plant ash can be detected. The ash obtained from fresh plant material is dissolved in dilute hydrochloric acid, and ammonia is added until the pH is 8.8 as indicated by the color of thymol blue. A molybdate solution is added to complex silica and prevents the formation of a gel in the sample solution. The sample solution is allowed to stand for about 15 min to permit calcium citrate to settle, otherwise it collects on the reagent paper and obscures the color of the nickel spots. Large amounts of copper and cobalt interfere by consuming the reagent and in the presence of ferric iron cobalt may form a red-brown precipitate with dimethylglyoxime. As a large excess of citrate is present in the test solution, the latter kind of interference is unlikely. The use of fresh plant material and the collection of the red nickel dimethylglyoxime in a confined spot by means of the chromograph are unique features which contribute to the speed and simplicity of the field method. Since as many as 30 determinations can be made per man day in temporary quarters, the method should be useful to the prospector in reconnaissance programs and in detailed surveys.

Reagents and apparatus

Hydrochloric acid, 1+1.

Sodium citrate, 50 percent. Dissolve 50 g $Na_3C_6H_5O_7 \cdot 5\ 1/2\ H_2O$ in 100 ml of water.

Ammonium hydroxide, concentrated.

Ammonium hydroxide, 1+1, freshly prepared.

Thymol blue indicator, 0.1 percent. Dissolve 0.1 g of the sodium salt in 100 ml of water.

Molybdate solution. Dissolve 1 g MoO_3 in a few ml dilute sodium hydroxide and dilute with water to 100 ml.

Nickel standard solution, 0.01 percent. Dissolve 0.01 g pure nickel in 10 ml 6 N nitric acid. Dilute to 100 ml with water. This solution contains 100 micrograms per ml.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Dimethylglyoxime reagent paper. Dip sheets of no. 50 Whatman filter paper into a 2 percent solution of dimethylglyoxime in acetone at a rate faster than the spread of solvent through the paper. Pauses must be avoided as they cause uneven distribution of the reagent on the paper by allowing the solvent to spread through the paper without the reagent. When the paper is dry, repeat the process. Discard the outer edges of the paper and cut the dry reagent paper into strips 7/16-in. wide. The reagent paper is stable for several months. For more detail on preparation of reagent papers, see Clarke and Hermance (1938).

Chromograph. See "Special Apparatus."

1 gasoline stove.

1 balance. Micro torsion type, capacity 25 mg. A lucite spoon previously calibrated by weighing a measured amount of pulverized plant ash can be used in place of the balance to measure samples.

Pyrex culture tubes, 13 by 100 mm, calibrated at 2 ml.

Filter sticks.--Alundum filter R. A. 225 sealed on end of pyrex glass tube 180 mm long and 7 mm outside diameter.

1 serological pipette, 0.5 ml, calibrated in tenths of a ml.

Rubber bulbs, 10 ml capacity.

1 glass rod, 150 mm, flattened on one end.

Platinum dishes, 60 ml. 60 mm diameter and 30 mm high.

1 pair tongs, platinum tipped.

1 fused quartz grating. For support of platinum dishes over burner.

1 test tube rack.

1 digestion and fusion rack. See "Special Apparatus."

Preparation of standard spots

To a series of test tubes, each containing 0.2 ml of molybdate solution, 0.5 ml sodium citrate and 1 drop of indicator, add respectively 1, 2.5, 5.0, 7.5, 10.0, 15.0, and 20.0 micrograms of nickel. Adjust pH to 8.8 with 1+1 ammonium hydroxide and make volume up to 2 ml. Prepare standard spots by passing a 0.2 ml aliquot of each solution through dimethylglyoxime reagent paper in the chromograph. These spots correspond respectively to 0.010, 0.025, 0.050, 0.075, 0.10, 0.15 and 0.20 percent nickel in the ash for a 10 mg sample.

Procedure

Place the fresh plant material in a platinum dish and ash over the gasoline stove. Stir occasionally during the ashing to facilitate burning. After glowing ceases, remove from the burner and allow the ash to cool. Pulverize the ash with a glass rod and mix thoroughly.

Weigh 10 mg of ash or measure in a spoon and transfer to a calibrated culture tube, add 0.5 ml hydrochloric acid and heat in a boiling water bath for 20 min. Transfer the culture tube to a rack and add 0.2 ml molybdate solution, 0.5 ml sodium citrate, and 1 drop thymol blue. Shake thoroughly and add concentrated ammonium hydroxide until the solution turns yellow. Then add carefully, one drop at a time, the freshly prepared 1+1 ammonium hydroxide to just a true blue. If the flakes of carbon remaining from the ashing cause confusion in seeing the color of the solution, allow the carbon to settle out before adding more ammonium hydroxide. Increase the volume to 2 ml with metal-free water, shake thoroughly and let stand for about 15 min to allow the calcium citrate to precipitate before filtering. To filter, squeeze the air out of a rubber bulb, fit it over the open end of a filter stick and insert the filter stick into the test tube.

Make a confined spot with 0.2 ml of the filtered solution on reagent paper in the chromograph. For details on the operation of the chromograph see page 18, "Chromographic determination of nickel in soils and rocks." Allow the spots to dry and compare with the standard series.

Determination of Molybdenum in Plants

The complete method for determination of molybdenum in plants is given in U. S. Geological Survey Circular 124, (Reichen and Ward, 1951). The method is not designed to detect small differences in the molybdenum content of plants which are caused by such factors as the health of the plant, season, and soil moisture. It is, however, sufficiently accurate to measure differences which are significant in geochemical prospecting. For example, as little as 0.25 microgram or 0.001 percent molybdenum can be determined in plant ash. Since the ashing process is a means of concentrating the nonvolatile constituents of a plant, the estimation of a relatively large quantity of molybdenum is more frequently required than the estimation of a small amount of molybdenum. If a 25 mg ash sample is used, 0.001 to 0.020 percent molybdenum can be determined, and if a 2 mg ash sample is used, as much as 0.25 percent molybdenum can be determined. If the weight of the ash is 10 percent of that of the dry material, 0.25 percent molybdenum in the ash corresponds to 250 ppm in the dry material. With the exception of vanadium, tungsten, and rhenium, the method is practically free from interferences. Under the conditions outlined below as much as 200 micrograms of vanadium in the test solution does not interfere. Moreover, tungsten and rhenium are seldom present in plants in sufficient quantities to cause any

interference. The field method requires, for the most part, simple apparatus and permits the average analyst to make 30 or more determinations per day. Thus, the prospector can obtain the results quickly and economically in the field.

Reagents and apparatus

Hydrochloric acid, concentrated.

Hydrochloric acid, 1 N. Dilute 8.5 ml concentrated acid, sp gr 1.19, to 100 ml with metal-free water.

Ammonium hydroxide, 1 N. Dilute 6.3 ml concentrated ammonium hydroxide, sp gr 0.90, to 100 ml with metal-free water.

Lithium nitrate, solid, reagent-grade.

Potassium nitrate, 10 percent. Dissolve 10 g KNO_3 in water and dilute to 100 ml.

Potassium thiocyanate, 5 percent. Dissolve 5 g KSCN in water and dilute to 100 ml.

Stannous chloride, 10 percent. Dissolve 10 g $SnCl_2 \cdot 2H_2O$ in 100 ml of 2 N HCl. Filter the solution if it is not entirely clear. The addition of tin promotes stability, but fresh solutions should be prepared weekly.

Standard molybdenum solution, 0.01 percent. Dissolve 0.075 g pure MoO_3 in a few ml of dilute NaOH solution, dilute with metal-free water, make slightly acid with hydrochloric acid, and make up to 500 ml with metal-free water. This solution contains 100 micrograms of molybdenum per ml.

Standard molybdenum solution, 0.0002 percent. Dilute 2 ml of the 0.01 percent solution to 100 ml with metal-free water. Prepare a fresh solution daily.

Phenolphthalein, 1 percent. Dissolve 1 g phenolphthalein in 100 ml alcohol.

Water. Pass tap water through resin demineralizer. See "Special Apparatus."

Isopropyl ether. Practical or C. P. grades are suitable provided peroxides are absent. Unless specially packaged, all dry ether on standing tends to form explosive peroxides. Peroxides of isopropyl ether interfere with the molybdenum method. To test for peroxides shake 5 ml of ether with 5 ml of an acidified aqueous solution of potassium iodide. If the iodide solution shows more than a faint yellow color, due to free iodine produced by the peroxides, the ether contains appreciable quantities of peroxides and should not be used. Shake peroxide-free ether with 1/10 its volume of equal amounts of stannous chloride and potassium thiocyanate solutions on the day during which it is to be used.

1 gasoline stove.

1 balance, micro torsion type, capacity 25 mg. A lucite spoon previously calibrated by weighing a measured amount of pulverized plant ash can be used in place of the balance to measure samples.

Pyrex culture tubes, 16 by 150 mm, calibrated at 5 ml.

Dishes, evaporating, 60 ml capacity, platinum.

1 pair platinum tipped tongs.

1 fused quartz grating.

1 test tube rack, capacity 24 culture tubes.

Glass pestle, pyrex glass rod flattened on one end.

Lucite spoon. A lucite bar with a cavity of 0.25 ml, (7 mm diameter, 6.5 mm deep), drilled near one end.

1 serological pipette, 1 ml, graduated in tenths of a ml.

1 serological pipette, 1 ml, graduated in hundredths of a ml.

1 serological pipette, 2 ml, graduated in halves of a ml.

1 serological pipette, 5 ml, graduated in tenths of a ml.

Procedure

Preparation of ash. --Ash the fresh plant material by heating in a platinum dish over the burner. Stir occasionally during the ashing to facilitate burning. After glowing ceases, remove the dish from the burner and allow the ash to cool. Pulverize the ash with a glass pestle and mix thoroughly.

Preparation of sample solution. --Weigh 25 mg of ash and transfer to a calibrated culture tube. Add a spoonful of lithium nitrate (about 0.1 g) and fuse over a low flame holding the mouth of the tube away from the operator. Rotate the tube as the melt cools to form a thin layer on the sides. Dissolve the melt in 1 ml of 1 N hydrochloric acid, add 1 drop of indicator, and add 1 N ammonium hydroxide until the solution is faintly pink. Avoid an excess of ammonium hydroxide. Dilute to 5 ml with water.

Preparation of standards. --Pipette the appropriate volumes of the 0.0002 percent standard solution into separate culture tubes to prepare a series of standard solutions differing by 0.5 microgram over a range from 0 to 5 micrograms. Add 1 ml potassium nitrate solution to each tube and dilute to 5 ml with water.

Estimation. --To both the standards and the plant solutions add 0.6 ml concentrated hydrochloric acid, 0.5 ml potassium thiocyanate solution, and 1 ml stannous chloride solution, shaking after each addition. Let the solutions stand for about 1 min. Make a preliminary comparison of the sample solutions with the 5 microgram standard. Discard any samples which are obviously darker and replace with an aliquot of a 10 mg sample of ash prepared as follows:

Fuse the replacement sample with lithium nitrate and dissolve the melt in 1 N hydrochloric

acid as before. Dilute to 5 ml with water. Pipette 1 ml (2 mg) of this solution into another culture tube, add phenolphthalein, and then 1 N ammonium hydroxide until the solution is faintly pink. Dilute to 5 ml with water, add the concentrated hydrochloric acid, the potassium thiocyanate, and the stannous chloride to this aliquot and proceed as below.

To the standards and the sample solutions add 1 ml freshly saturated isopropyl ether, cork the culture tube and shake for 15 sec. Within 30 min after the extraction, compare the intensity of the amber-colored ether layer over the sample solution with that obtained over the standard solutions. Use a white background to make the comparisons. In order to convert the results to ppm, multiply the number of micrograms of molybdenum found in the 25 mg ash sample by 40 and in the 2 mg aliquot by 500.

APPENDIX

The minimum quantity of reagents to perform 1,000 determinations as well as the desirable stock is listed in the table given below. The desirable stock (column 4) includes the minimum quantity of reagents required and an extra quantity to insure against losses resulting from minor accidents and to permit a reasonable number of repeat determinations. The desirable stock is given in units listed by supply houses. Unless otherwise specified all reagents are analytical grade. Water may be obtained from a public water supply and freed of metals by passing it through a resin demineralizer as directed under "Special Apparatus." The quantity of water listed in the table is the metal-free water needed for the determinations and does not include water for washing.

Reagents required for 1,000 determinations by each method

Method	Reagents	Actual minimun	Desirable Stock
Heavy metals in water	Acetic acid, glacial	6 ml	1/4 lb
	Ammonium hydroxide, conc	30 ml	1/4 lb
	Carbon tetrachloride	10 liters	50 lb
	Dithizone	.16 g	1 g
	Sodium acetate	85 g	1/2 lb
	Thymol blue, sodium salt	.04 g	1 g
	Water, metal-free	10 liters	5 gal
Heavy metals in soil or sediment	Ammonium fluoride	350 g	1 lb
	Carbon tetrachloride	5 liters	2.5 lb
	Dithizone	.08 g	1 g
	Hydrochloric acid, conc	1 ml	1 lb
	Hydrochloric acid, conc (Digestion D)	1 liter	3 lb
	Nitric acid, conc (Digestion A or B)	500 ml	2 lb
	Nitric acid, conc (Digestion C)	1 liter	4 lb
	Nitric acid, conc (Digestion D)	1.75 liters	6 lb
	Sodium acetate	1.75 kg	6 lb
	Water, metal-free	40 liters	20 gal
	Zinc metal	.01 g	1/4 lb
Zinc in soils	Acetic acid, glacial	260 ml	1 lb
	Carbon tetrachloride	5.5 liters	25 lb
	Dithizone	.125 g	1 g
	Hydrochloric acid, conc	1 ml	1 lb
	Potassium bisulfate	250 g	1 lb
	Sodium acetate	820 g	3 lb
	Sodium thiosulfate, $Na_2S_2O_3.5H_2O$	500 g	2 lb
	Water, metal-free	20 liters	10 gal
	Zinc, metal	.1 g	1/4 lb
Nickel in soils and rocks	Acetone	1 liter	2 lb
	Ammonium hydroxide,	1 liter	3 lb
	Dimethylglyoxime	25 g	100 g
	Filter paper, Whatman no.50, sheets diameter 24 cm	1000 sq in.	1 pkg
	Litmus paper, 100 strips per vial	2 vials	6 vials
	Nickel metal	.01 g	1 oz
	Nitric acid, conc	4 ml	1 lb
	Potassium bisulfate	500 g	2 lb
	Sodium citrate	400 g	2 lb
	Water, metal-free	10 liters	5 gal

Reagents required for 1,000 determinations by each method.--Continued

Method	Reagents	Actual minimum	Desirable Stock
Copper in soils and rocks	Acetic acid, glacial	500 ml	2 lb
	Acetone	1 liter	2 lb
	Ammonium hydroxide, conc	1 liter	3 lb
	Copper sulfate, $CuSO_4.5H_2O$	.2 g	1/4 lb
	Filter paper, Whatman no. 50, sheets diameter 24 cm	1000 sq in	1 pkg
	Litmus paper, 100 strips per vial	2 vials	6 vials
	Potassium bisulfate	500 g	2 lb
	Rubeanic acid (dithiooxamide)	25 g	100 g
	Sodium citrate	400 g	2 lb
	Sulfuric acid, conc	2 ml	1 lb
	Water, metal-free	10 liters	5 gal
Cobalt in soils and rocks	Cobalt chloride, $CoCl_2.6H_2O$	.1 g	1 oz
	Hydrochloric acid, conc	30 ml	1 lb
	Litmus paper, 100 strips per vial	2 vials	6 vials
	2-nitroso-1-naphthol	.01 g	5 g
	Potassium bisulfate	400 g	2 lb
	Sodium citrate (U.S.P.VIII), $Na_3C_6H_5O_7.5\ 1/2\ H_2O$	2.5 kg	10 lb
	Sodium hydroxide	120 g	1 lb
	Sodium tetraborate, $Na_2B_4O_7.10H_2O$	57 g	1/4 lb
	Sulfuric acid, conc	.2 ml	1 lb
	Water, metal-free	20 liters	10 gal
Molybdenum in soils and rocks	Ethyl alcohol, 95 percent	100 ml	1 pint
	Hydrochloric acid	700 ml	3 lb
	Isopropyl ether, practical	350 ml	5 lb
	Molybdic anhydride, MoO_3	.075 g	1 oz
	Phenolphthalein	1 g	1 oz
	Potassium iodide	10 g	1 oz
	Potassium nitrate	260 g	1 lb
	Potassium thiocyanate	17.4 g	1/4 lb
	Sodium carbonate	250 g	1 lb
	Sodium hydroxide	1 g	1/4 lb
	Sodium tartrate	232 g	1 lb
	Stannous chloride, $SnCl_2.2H_2O$	60 g	1/4 lb
	Tin metal, mossy	6 g	1/4 lb
	Water, metal-free	20 liters	10 gal
Lead in soils and rocks	Ammonium citrate, $(NH_4)_2HC_6H_5O_7$	500 g	2 lb
	Ammonium hydroxide, conc	350 ml	2 lb
	Carbon tetrachloride	10 liters	70 lb
	Chloroform	1 liter	5 lb
	Dithizone	.2 g	1 g
	Lead nitrate	.16 g	1/4 lb
	Nitric acid, conc	1 liter	7 lb
	Potassium cyanide	500 g	2 lb
	Thymol blue, sodium salt	.04 g	1 g
	Water, metal-free	50 liters	25 gal
Silver in soils and rocks	Acetic acid, glacial	5.1 liters	20 lb
	Ammonium citrate, $(NH_4)_2HC_6H_5O_7$	750 g	2 lb
	Ammonium hydroxide, conc	3.1 liters	12 lb
	n-Amyl alcohol, practical	3 liters	6 kg
	p-dimethylaminobenzalrhodanine	.01 g	1 g
	Ethyl alcohol, 95 percent, U.S.P.	1 liter	3 pints
	Litmus paper, 100 sheets per vial	10 vials	20 vials
	Nitric acid, conc	12 liters	42 lb
	Silver nitrate	.16 g	1 Oz
	Water, metal-free	50 liters	25 gal

Reagents required for 1,000 determinations by each method.--Continued

Method	Reagents	Actual minimum	Desirable stock
Tungsten in soils and rocks	Hydrochloric acid, conc	4.8 liters	12 lb
	Isopropyl ether, practical	360 ml	5 lb
	Potassium iodide	10 g	1 oz
	Potassium nitrate	125 g	1 lb
	Potassium thiocyanate	300 g	1 lb
	Sodium carbonate	625 g	2 lb
	Sodium chloride	500 g	2 lb
	Sodium tungstate, $Na_2WO_4.2H_2O$	.036 g	1 oz
	Stannous chloride, $SnCl_2.2H_2O$	480 g	1 1/4 lb
	Water, metal-free	20 liters	10 gal
Readily soluble copper, zinc and lead in soils and rocks	Acetic acid, glacial	60 ml	1/4 lb
	Ammonium citrate, $(NH_4)_2HC_6H_5O_7$	650 g	2 lb
	Ammonium hydroxide, conc	500 ml	4 lb
	Carbon tetrachloride	20 liters	100 lb
	Chloroform	1 liter	5 lb
	Copper sulfate, $CuSO_4.5H_2O$	.2 g	1/4 lb
	Dithizone	.2 g	1 g
	Hydrochloric acid, conc	4 ml	1 lb
	Lead nitrate	.16 g	1/4 lb
	Nitric acid, conc	4 ml	1 lb
	Potassium cyanide	500 g	2 lb
	Sodium acetate, anhydrous	80 g	1 lb
	Sodium thiosulfate, $Na_2S_2O_3.5H_2O$	500 g	2 lb
	Sulfuric acid, conc	1.2 liters	9 lb
	Thymol blue, sodium salt	.1 g	1 g
	Water, metal-free	100 liters	50 gal
	Zinc metal, 30-mesh	.1 g	1/4 lb
Zinc in plants	Acetic acid, glacial	100 ml	1 lb
	Carbon tetrachloride	5.5 liters	30 lb
	Dithizone	.125 g	1 g
	Hydrochloric acid, conc	400 ml	2 lb
	Sodium acetate, $CH_3COONa.3H_2O$	2 kg	6 lb
	Sodium thiosulfate, $Na_2S_2O_3.5H_2O$	600 g	2 lb
	Water, metal-free	30 liters	15 gal
	Zinc metal, 30-mesh	.01 g	1/4 lb
Nickel in plants	Acetone	1 liter	2 lb
	Ammonium hydroxide, conc	250 ml	1 lb
	Dimethylglyoxime	25 g	100 g
	Filter paper, Whatman no. 50, sheets diameter 24 cm	1000 sq in	1 pkg
	Hydrochloric acid, conc	250 ml	1 lb
	Molybdic anhydride, MoO_3	2 g	1/4 lb
	Nickel metal	.01 g	1 oz
	Nitric acid, conc	4 ml	1 lb
	Sodium citrate (U.S.P. VIII), $Na_3C_6H_5O_7.5\ 1/2\ H_2O$	250 g	1 lb
	Sodium hydroxide	1 g	1/4 lb
	Thymol blue, sodium salt	.1 g	1 g
	Water, metal-free	5 liters	3 gal
Molybdenum in plants	Ammonium hydroxide, conc	65 ml	1 lb
	Ethyl alcohol, 95 percent	100 ml	1 pint
	Hydrochloric acid, conc	900 ml	3 lb
	Isopropyl ether, practical	1.3 liters	10 lb
	Lithium nitrate	100 g	1/2 lb
	Molybdic anhydride, MoO_3	.15 g	1 oz
	Phenolphthalein	1 g	1 oz
	Potassium iodide	10 g	1 oz
	Potassium nitrate	30 g	1/4 lb
	Potassium thiocyanate	32 g	1/4 lb
	Sodium hydroxide	1 g	1/4 lb
	Stannous chloride, $SnCl_2.2H_2O$	12.5 g	1/4 lb
	Tin metal, mossy	6 g	1/4 lb
	Water, metal-free	20 liters	10 gal

[1]Materials listed are for total heavy metals only. Supplemental tests are not included.

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