# NOTES ON PRACTICAL WATER ANALYSIS

BY

## W. D. COLLINS

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# ILLUSTRATION

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## INTRODUCTION

The directions given below are intended to show the methods used in the United States Geological Survey for the analysis of waters of moderate mineral content in order to learn their suitability for industrial use. The analyses so made give little or no indication of the sanitary condition of the waters, and they do not involve the determination of some of the rarer constituents of natural waters. The methods must be modified for some waters of unusual composition.

The methods have been selected from long-established procedures for the different determinations, and their details have been chosen as best adapted for use in a laboratory which is planned and equipped to make such analyses and in which no other chemical work is done. Different details might be selected for use under other conditions. The selections necessarily agree closely with those made by organizations that have published standard[1] or official[2] methods for water analysis.

These notes are intended for the use of those who have had experience in analytical work and may wish to know the methods used for the water analyses published by the United States Geological Survey. It is assumed that the reader is familiar with the standard procedures of volumetric and gravimetric analysis, and therefore it is not necessary to direct that a crucible shall be cooled in a desiccator before weighing or that the volumetric glassware and the weights used shall be calibrated. Some directions that may seem equally simple have been included because certain minor details that have a real effect on the reliability of a water analysis appear to be overlooked by some analysts.

Directions as to the volumes of solution in which the precipitations are made must be taken merely as suggestions for average conditions. For success the analyst must keep in mind the quantities of the substances dissolved in the solution at hand. A reagent added to produce a precipitate must be in sufficient excess to make the precipitate properly insoluble. The excess must not be so great as to

[1] Am. Pub. Health Assoc., Standard methods for the examination of water and sewage, 5th ed., 1923.
[2] Assoc. Official Agricultural Chemists, Official and tentative methods of analysis, 2d ed., revised to July, 1924, pp. 83–112, 1925.

interfere with subsequent treatment of the filtrate, and care is necessary to avoid the addition of undesirable quantities of impurities through the use of too great an excess of a reagent. If a solution is too concentrated the precipitate will retain undue amounts of the soluble substances that should be in the filtrate. If the volume is too great the solubility of the precipitate will introduce errors or else too large a quantity of the precipitant must be used to give the proper concentration for the best precipitation. By keeping these considerations in mind it is easy to tell whether a precipitation should be made in a volume of 200 cubic centimeters or 20 cubic centimeters. Considerations of the same kind govern the washing of precipitates, for which precise directions can not be given.

Analyses are reported in parts per million of the radicles determined. Portions of the samples for the different determinations are measured in cubic centimeters at room temperature. The error involved in the assumption that a cubic centimeter of water that contains less than 3,000 parts per million of dissolved solids weighs 1 gram is usually considerably less than the probable error of most of the determinations and is much too small to have any effect on the practical use of the analysis.

For practical use quantities of less than 1 part per million of the ordinary mineral constituents of a water have little or no significance, with the exception of iron. In general the error in the determination of a single constituent is likely to be about 1 per cent of the quantity determined. These considerations lead to the arbitrary rule that no decimals are reported for quantities of 10 parts per million or more, one decimal figure is given for quantities from 1 to 10, and two decimal figures for quantities less than 1.

### SAMPLES

The size of sample required may be from a gallon to a pint, according to the concentration of the water. Usually a gallon is most satisfactory. It is desirable that the samples be collected in bottles of resistant glass,[3] and this precaution is necessary if more than a few days is to elapse between the collection and the analysis of the sample. Bottles sold for other uses may be good enough for water samples, but some may give up to a sample more mineral matter than was in the water at its source.

Analysis of the mineral content of a water should be started within a month of the collection of the sample, even if it is in a good bottle. Some waters will be apparently unchanged after three months in storage. Those containing sodium bicarbonate or else very little dis-

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[3] Collins, W. D., and Riffenburg, H. B., Contamination of water samples with material dissolved from glass containers: Ind. and Eng. Chemistry, vol. 15, pp. 48–49, 1923.

solved mineral matter are much more likely to attack the glass container than the waters high in calcium sulphate or sodium chloride.

It is essential that the condition of the water as regards precipitated iron be noted at the time of collection. Few surface waters carry much over 0.1 part per million of iron in solution unless they are acid. Ground waters may have several parts per million of iron that will be precipitated on contact with the oxygen of the air. This iron is in the water in the ground and must be reported with the dissolved material, even though it is precipitated when the analysis is made.

If the water contains hydrogen sulphide, precautions must be taken to permit a correct determination of sulphate in the laboratory. Usually the best way is to collect a small extra sample in a bottle or several bottles containing solid cadmium chloride free from sulphate. The cadmium sulphide remains unaffected and can be filtered out and treated by the method used in steel works for the determination of sulphur in steel when the steel is dissolved in acid and the evolved hydrogen sulphide is collected in a solution of a cadmium salt. The result for hydrogen sulphide will probably be less accurate than if the water were titrated with iodine at its source but will be better than if the determination were made on a sample as received without any treatment at the time of collection.

The filtrate from the cadmium sulphide will give a correct figure for the sulphate in the water at its source. All the other determinations may be made on the larger sample with the precautions mentioned in the directions for titration of chloride. Very rarely a sample contains alkaline sulphides, which make the determination of bicarbonate unreliable.

A sample may have a noticeable odor of hydrogen sulphide although it contains barely 1 part per million of the gas. The analysis of the mineral content of such a water is practically unaffected by the hydrogen sulphide, which may be completely oxidized by the time the sample reaches the laboratory.

## REAGENTS AND APPARATUS

Reagents used in water analysis should be at least up to the standards proposed by the Committee on Analytical Reagents of the American Chemical Society.[4] It is desirable to use better reagents in some of the work. All reagents must be tested with reference to the determinations in which they are to be used.

The main source of error from reagents is in the determination of the alkalies. Barium chloride and barium hydroxide may contain

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[4] Recommended specifications for analytical reagent chemicals : Ind. and Eng. Chemistry, vol. 17, p. 756, 1925 ; vol. 18, pp. 636, 759, 1926 ; vol. 19, p. 645, 1927.

more sodium than is permissible. Ammonium carbonate may have too much nonvolatile material, and ammonium hydroxide is likely to introduce alkali salts into the analysis. The impurities in ammonium hydroxide nearly all come from the action of the reagent on the glass of the container. Many laboratories are now preparing ammonium hydroxide by absorbing in cold water ammonia gas from cylinders of liquid ammonia. Where large quantities are used there may be some saving in cost by this procedure, but the greatest saving comes from the improved quality due to the shorter time for action on the glass container as compared with the time required for the shipment and storage of the reagent in bottles. Some laboratories prepare small quantities of the reagent by distillation of the commercial reagent ammonium hydroxide with absorption in cold water.

Distilled water for use in the analysis of the mineral content of waters does not have to be up to the standard of the ammonia-free water used in sanitary analyses, but care must be taken that it does not take up material from containers in which it may be kept.

Solutions of reagents should not be kept long. Many must be made up fresh for each set of analyses. Volumetric solutions must be checked from time to time.

Evaporations are best made in platinum unless enough nitrate and chloride are present in acid solutions to dissolve some of the metal. It is obvious that care must be taken to use resistant glass vessels throughout, and it is well to note that acid solutions usually attack glass much less than alkaline solutions.

Throughout the directions the acids and ammonium hydroxide used are to be of full strength unless dilution is specified. The customary convention is followed of indicating dilution of 1 volume of strong acid with 2 volumes of water as "(1+2)."

## PRELIMINARY EXAMINATION [5]

Unless the composition of the water is known approximately it is worth while to make a preliminary examination so that the most advantageous quantity of water may be taken for evaporation. The preliminary examination includes the final determinations of alkalinity, chloride, and nitrate, with turbidimetric estimations of sulphate and calcium. A determination of hardness by the soap method may replace or supplement the determination of calcium.

### ALKALINITY (BICARBONATE, CARBONATE, HYDROXIDE, ACIDITY)

The alkalinity should be determined promptly after the sample bottle is opened. Exposure to the air permits absorption of carbon

[5] Collins, W. D., and Foster, M. D., Preliminary examination of water samples: Ind. and Eng. Chemistry, vol. 15, p. 1078, 1923.

dioxide, which changes the relations of hydroxide, carbonate, and bicarbonate. If an excess of carbon dioxide is present it may be lost, sometimes even to the precipitation of calcium carbonate. With some samples it is necessary to titrate the alkalinity and take out the sample to be evaporated for the determination of calcium and magnesium at the same time in order to avoid the error that would be introduced if time were given for precipitation of calcium carbonate.

Titrate 50 cubic centimeters of the sample with 0.01639 normal sulphuric acid, using as indicators phenolphthalein and either methyl orange or methyl red. If methyl red is used air free from carbon dioxide must be bubbled through the water during the titration; the calculations are the same as with methyl orange.

Let A represent the number of cubic centimeters of acid used in the phenolphthalein titration and B the additional acid used in the methyl orange titration.

For most natural waters A is zero, the total alkalinity is due to bicarbonate, and the quantity of bicarbonate ($HCO_3$) in parts per million is $20 \times B$.

If A is greater than zero and less than B the alkalinity is due to carbonate and bicarbonate, and the water contains no hydroxide. The carbonate ($CO_3$) is $19.67 \times A$, and the bicarbonate ($HCO_3$) is $20 \times (B-A)$.

If A is greater than B the water contains no bicarbonate. The carbonate ($CO_3$) is $19.67 \times B$, and the hydroxide is $5.574 \times (A-B)$.

The strength of the acid was chosen to facilitate the calculation of bicarbonate without the use of tables or calculating instruments. The factors used for carbonate and hydroxide may well be rounded off to three or even two figures for most analyses.

For waters that contain only small quantities of dissolved mineral matter the estimation of alkalinity is likely to introduce the largest error in the analysis. It is possible to evaporate large volumes of water for the main analysis and for the determination of chloride, but the alkalinity must be determined on about the same volume of sample regardless of the quantity of mineral matter in the water. After practice the analyst can check titrations with methyl orange and find twice as much bicarbonate in 100 cubic centimeters as in 50 cubic centimeters. It is worth while to try this, or to titrate a volume of about 50 cubic centimeters of water containing different quantities of sodium carbonate, in order to learn the exact shade that corresponds to the correct end point.

Some waters are acid to methyl orange. If the acidity is due to free mineral acids and the water contains little iron or aluminum the free acid may be titrated with sodium hydroxide, using methyl orange indicator, and reported as free sulphuric or hydrochloric acid. In practically all acid natural waters, however, the acidity is due to

sulphates of iron and aluminum, and the titration is not so simple. Titration at boiling temperature with sodium hydroxide and phenolphthalein indicator will give approximately the sum of the acidity due to free mineral acids and that due to sulphates of iron and aluminum. The latter may be calculated from determinations of iron and aluminum.

Some colored waters seem to contain in equilibrium with th  ases organic acids that do not appear as alkalinity in the titration with methyl orange and therefore leave the analysis out of balance.

### CHLORIDE

For the chloride determination titrate 25 cubic centimeters with a silver nitrate solution of which 1 cubic centimeter corresponds to 0.5 milligram of chloride radicle, using potassium chromate indicator. The titration is best made in yellow light or with the use of yellow goggles. Each analyst must determine his own correction for the end point. An average correction is 0.1 cubic centimeter for a volume of 25 cubic centimeters. The accuracy of the figure for the end point may be estimated by making several successive titrations in the same solution, removing the red tint each time by the addition of 1 cubic centimeter of a standard sodium chloride solution. Such small increases in volume will not affect the quantity of silver nitrate needed to produce the end point, and the successive quantities of chloride should require the same volume of silver nitrate. The total volume at the end of three or four titrations will exceed three or four times the amount used in the successive titrations by the amount necessary to produce the tint adopted as the end point.

If the chloride is more than 100 parts per million take a smaller sample and dilute to 25 cubic centimeters; if less than 5 parts per million concentrate a larger volume to 25 cubic centimeters, taking care to avoid absorption of chloride by the sample during evaporation and washing down the sides of the vessel before titration.

If the sample contains hydroxide add standard sulphuric acid till it is just acid to phenolphthalein; if it is acid add sodium carbonate till it is slightly alkaline to methyl orange or litmus. If hydrogen sulphide is present remove it by passing pure air through the sample or by boiling. A small quantity of hydrogen sulphide may disappear on exposure to the air for a short time.

It is possible to buy silver nitrate sufficiently pure to make the standard solution by weighing out 2.3955 grams of dry crystals and making up to a liter. It is well to crush the crystals before drying. The solution may be checked against a solution made from pure fused sodium chloride, but it is generally possible to get the silver nitrate purer than the sodium chloride.

The indicator solution is made by dissolving 50 grams of potassium chromate in a liter of water, adding enough silver nitrate to precipitate a small amount of silver chromate, and filtering or decanting after the solution has stood in the dark for a day. The quantity of indicator solution used affects the sharpness of the end point, and the same quantity must be used for each titration and for the determination of the correction for the end point. From 0.25 to 0.50 cubic centimeter is satisfactory in titrating a volume of 25 cubic centimeters.

## NITRATE
### (See correction p. 262)

Nitrate is best determined by the phenoldisulphonic acid method.[6] To prepare the phenoldisulphonic acid solution dissolve 25 grams of pure white phenol in 150 cubic centimeters of concentrated sulphuric acid, add 75 cubic centimeters of fuming sulphuric acid (15 per cent $SO_3$), stir well, and heat for two hours at about 100° C.

Evaporate 50 cubic centimeters of the sample to dryness and at the same time evaporate measured volumes of a standard solution of potassium nitrate to make standards for comparison. These should have from 0.015 to 0.15 milligram of nitrate radicle, $NO_3$. Remove the dishes from the bath as soon as dry, or better just before, so that the last few drops may evaporate as the dishes cool. When the sample and standards are cool add to each 1 cubic centimeter of the phenoldisulphonic acid and rub thoroughly with a glass rod. Dilute cautiously with water, allow to cool, and add an excess of ammonium hydroxide to develop the yellow color. Compare in Nessler tubes with or without a colorimeter. If the quantity of nitrate is less than 0.015 milligram the comparison may be made best in the porcelain dishes. If care is taken to have the treatment identical it is safe to prepare the standards after development of color in the samples. This practice saves the preparation of standards that are not needed. If the sample evaporated contains much over 0.15 milligram of nitrate evaporate a smaller sample and develop the color to compare with the standards.

Experience in the routine examination of several thousand samples and the results of many tests of the method have shown the necessity for the above directions as to the preparation of standards, and the use of a fresh smaller sample rather than dilution when too intense color is obtained. The relation of the intensity of color to the quantity of nitrate is not absolute over an indefinite range, and serious errors may be introduced in the determination of high nitrates by assuming strict proportionality.

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[6] Chamot, E. M., and Pratt, D. S., A study on the phenolsulphonic acid method for the determination of nitrates in water: Am. Chem. Soc. Jour., vol. 31, pp. 922–928, 1909; vol. 32, pp. 630–637, 1910.

In a laboratory where sanitary analyses are not made it is simplest to use ammonium hydroxide to develop the color. This helps keep the stock moving through the reagent bottles and does not call for an extra reagent, which must be kept if potassium hydroxide solution is used. The latter solution is not satisfactory to keep in stock on account of its rapid action on bottles.

### SULPHATE (BY TURBIDITY)

For the turbidimetric estimation of sulphate take a clear sample of 10 cubic centimeters in a test tube and prepare in other test tubes standards made from distilled water and enough standard sulphuric acid solution to give from 0.1 to 0.3 milligram of $SO_4$ in 10 cubic centimeters. Add to each tube 1 cubic centimeter of acidified barium chloride solution (10 grams of $BaCl_2.2H_2O$ and 5 cubic centimeters of hydrochloric acid of specific gravity 1.20 in 100 cubic centimeters), shake vigorously and compare after 10 minutes. The comparison is best made by looking down through the tubes against a dark background. If the sulphate is more than 30 or 35 parts per million take a smaller sample and dilute to 10 cubic centimeters.

### CALCIUM (BY TURBIDITY)

For the turbidimetric estimation of calcium take a clear sample of 10 cubic centimeters in a test tube and prepare in other test tubes standards of equal volume. Add to each tube 1 cubic centimeter of dilute glacial acetic acid $(1+1)$ and shake well; add 1 cubic centimeter of potassium oxalate solution containing 0.2 gram of $K_2C_2O_4$, shake, and compare after 10 minutes. The calcium chloride solution used for standardizing the soap solution for hardness determinations makes convenient standards. From 0.5 to 3.0 cubic centimeters of the calcium chloride solution will make standards of 10 cubic centimeters corresponding to 4 to 24 parts per million of calcium. If the sample contains more than 24 parts per million of calcium a smaller quantity is taken for the determination and diluted to 10 cubic centimeters.

### HARDNESS (BY SOAP)

The determination of hardness by Clark's soap method [7] has been found satisfactory for ordinary waters [8] if the directions are followed carefully in every detail.

Prepare the standard calcium chloride solution by dissolving 0.2 gram of pure calcite or other dry calcium carbonate in a little dilute

[7] Clark, Thomas, The examination of water for towns for its hardness and for the incrustation it deposits on boiling: Chem. Gazette, vol. 5, p. 100, 1847.

[8] Collins, W. D., and Foster, M. D., Preliminary examination of water samples: Ind. and Eng. Chemistry, vol. 15, p. 1078, 1923.

hydrochloric acid, taking care to avoid loss by spattering. Remove the excess of acid by several evaporations and make to 1 liter.

Prepare a stock soap solution by dissolving 100 grams of shredded dry pure olive oil castile soap in 1 liter of 80 per cent ethyl alcohol or 50 per cent methyl alcohol. It is necessary to use alcohol that has not been denatured. Many soaps not made with olive oil can not be used for this solution. Potassium oleate for the solution may be made from potassium carbonate and lead plaster, or from the hydroxide and oleic acid.

Adjust the strength of the soap solution by the exact procedure that is to be used in titrating the waters. Dilute 20 cubic centimeters of the standard calcium chloride solution to 50 cubic centimeters with distilled water that has been freshly boiled and cooled. To the diluted solution in a bottle of about 250 cubic centimeters capacity add soap solution from a burette, 0.2 to 0.5 cubic centimeter at a time. A bottle of square cross section is most convenient for the test. Shake vigorously after each addition of soap solution. The titration is completed when a permanent lather persists for 5 minutes over the whole surface of the water when the bottle is on its side. Adjust the soap solution by the addition of alcohol till exactly 6.40 cubic centimeters is required to produce the permanent lather as described.

Table 1 gives the hardness as found by Clark for different volumes of soap solution. The figures for less than about 1.5 cubic centimeters of soap solution do not check with results obtained in tests of the method in the Geological Survey. Above this point the agreement has been all that could be expected for such a method.

TABLE 1.—*Total hardness, in parts per million of CaCO₃, indicated by 0.0 to 7.9 cubic centimeters of soap solution when 50 cubic centimeters of the sample is titrated* [a]

| Cubic centimeters of soap solution | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | | | | | | | | 0.0 | 1.6 | 3.2 |
| 1 | 4.8 | 6.3 | 7.9 | 9.5 | 11.1 | 12.7 | 14.3 | 15.6 | 16.9 | 18.2 |
| 2 | 19.5 | 20.8 | 22.1 | 23.4 | 24.7 | 26.0 | 27.3 | 28.6 | 29.9 | 31.2 |
| 3 | 32.5 | 33.8 | 35.1 | 36.4 | 37.7 | 39.0 | 40.3 | 41.6 | 42.9 | 44.3 |
| 4 | 45.7 | 47.1 | 48.6 | 50.0 | 51.4 | 52.9 | 54.3 | 55.7 | 57.1 | 58.6 |
| 5 | 60.0 | 61.4 | 62.9 | 64.3 | 65.7 | 67.1 | 68.6 | 70.0 | 71.4 | 72.9 |
| 6 | 74.3 | 75.7 | 77.1 | 78.6 | 80.0 | 81.4 | 82.9 | 84.3 | 85.7 | 87.1 |
| 7 | 88.6 | 90.0 | 91.4 | 92.9 | 94.3 | 95.7 | 97.1 | 98.6 | 100.0 | 101.5 |

[a] Recalculated in Sutton's "Volumetric analysis" from the original table by Thomas Clark, printed in a circular and reprinted in Chem. Gazette, vol. 5, pp. 100–106, 1847.

Titrate 50 cubic centimeters of the sample with the soap solution exactly as directed for the standardization. If the hardness of the sample is over 100 parts per million take a smaller volume and dilute to 50 cubic centimeters. Use the appropriate factor for multiplication of the hardness taken from the table.

Hardness is not usually determined in the preliminary examination if an analysis is to be made.

## RESULTS OF PRELIMINARY EXAMINATION

The preliminary examination may give all the information that is needed about a particular sample. The work outlined above will frequently satisfy the analyst that a sample is practically identical with another for which a complete analysis is at hand. If the water is known to come from a place where high-calcium limestone predominates, as in most parts of Florida, it is safe to assume that practically all the hardness is due to calcium, and if either the hardness or calcium has been determined the other is known approximately. If the water comes from typical dolomite half the hardness will be due to calcium and half to magnesium.

If hardness is determined a rough figure for sodium and potassium together may be calculated. It will be the quantity of sodium which must be taken with the hardness to balance the acid radicles. The figure will be affected by any error in the determination of hardness and the estimation of sulphate.

The best quantity of water to take for evaporation is indicated by the preliminary examination. For most practical analyses a liter or half a liter is enough to evaporate for analysis of the residue. In order to obtain a convenient weight of silica it is generally well to evaporate the whole volume in one dish and divide the filtrate into two parts after separation of the silica. The most satisfactory quantity of calcium for titration with permanganate is from 10 to 20 milligrams. As little as 1 or 2 milligrams can be determined by careful manipulation, and as much as 40 milligrams can be titrated easily. It is convenient to weigh as oxide 100 or 200 milligrams of calcium. Almost any quantity of sulphate from 2 or 3 to 400 milligrams can be handled easily. It is most satisfactory to have between 50 and 100 milligrams of mixed chlorides of sodium and potassium. More than 250 milligrams may give less accuracy on account of loss by occlusion with the precipitates removed in the purification and loss by decrepitation in heating. Less than 10 milligrams requires careful attention to prevent loss and is likely to have an undue percentage of contamination from the reagents used.

The preliminary determinations of sulphate and calcium or hardness may sometimes show errors in the regular analysis that come from incorrect calculation, a mistake as to the quantity of water taken, or some other accident that introduces an error much greater than possible normal errors of analysis.

## TURBIDITY

The commonly accepted standard for measurement of turbidity is that proposed by Hazen and Whipple,[9] as follows:

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

Practically all measurements of slightly turbid waters are made by comparison with dilutions of a standard suspension. Pear's precipitated fuller's earth which has been dried and sifted through a 200-mesh sieve may be weighed out to make the standard suspension. One gram in 1,000 cubic centimeters of water will produce a turbidity of about 1,000. A 1 to 10 dilution of this standard should have a turbidity of 100 measured by the platinum-wire method. If slightly in error the suspension may be adjusted to the standard by the addition of water or fuller's earth as required.

The turbidity rod described by Hazen and Whipple may be used in the field. The Jackson turbidimeter or a similar instrument should be used in the laboratory for the measurement of turbidities greater than about 100. Each observer must calibrate the graduations on the tube of the turbidimeter by use of a standard suspension of silica or other insoluble material. If the turbidity to be measured is much over 500 the sample should be diluted with clear water for the measurement and the measured turbidity multiplied by the factor corresponding to the dilution.

For the measurement of turbidity of filter effluents and other clear waters it is necessary to use a more sensitive method, such as that proposed by Baylis.[10] The apparatus used can be purchased from dealers or may be made according to the directions given with the description of the method.

## SUSPENDED MATTER

To determine suspended matter filter a measured volume of the well-shaken sample through asbestos in a Gooch crucible, dry at 180° C., and weigh. If the suspended matter is so finely divided as to pass through any asbestos mat that permits water to pass at a

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[9] Measurement of turbidity and color: U. S. Geol. Survey Div. Hydrography Circ. 8, 1902.
[10] Baylis, J. R., Turbidimeter for accurate measurement of low turbidities: Ind. and Eng. Chemistry, vol. 18, p. 311, 1926.

reasonable rate, it is not possible to obtain a thoroughly satisfactory result for suspended matter. A part of the sample may be completely clarified by the use of a filter of the Berkfeldt type or by adding alumina cream and filtering through paper. The difference between the residue on evaporation of samples of the unfiltered and the clear water is sometimes taken as a measure of the suspended matter. This result is affected by the errors of drying and weighing the two residues, and the errors are likely to be different for the two determinations.

## COLOR

The measurement of color is usually made by the method described by Hazen.[11] The standard color of 500 is prepared by dissolving 1.245 grams of potassium chloroplatinate ($K_2PtCl_6$), containing 0.5 gram of platinum, and 1 gram of crystallized cobalt chloride ($CoCl_2.H_2O$), containing about 0.25 gram of cobalt, in water with 100 cubic centimeters of concentrated hydrochloric acid, and diluting to 1 liter with distilled water. Comparison is made with dilutions of this standard or with colored disks that have been calibrated against standard color solutions.

## PRECIPITATED IRON

When iron precipitates from a clear sample after exposure to the air make a separate determination of the precipitated iron. With some samples it is satisfactory to shake vigorously and then pour out quickly a definite quantity to be filtered. The iron often precipitates on the walls of the container and can not be distributed throughout the sample by shaking. In this event the whole sample must be filtered and the iron dissolved from the glass with hydrochloric acid.

Dissolve the iron from the filter paper, add the solution of iron from the container, and make to a definite volume. Determine the iron colorimetrically as thiocyanate and calculate to parts per million from the volume of the sample filtered and the original volume in the container if solution from the walls is necessary.

## RESIDUE ON EVAPORATION (TOTAL DISSOLVED SOLIDS)

For determination of the residue on evaporation, or total dissolved solids, measure out the volume of filtered sample required for the main analysis and evaporate to dryness in platinum on the steam bath. Silica or porcelain dishes may be used, but the results are less satisfactory than with platinum. Dry the dish and contents one hour

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[11] Hazen, Allen, Am. Chem. Jour., vol. 12, pp. 427–428, 1892.

at 180° C. and weigh. The weight obtained is often reported as "total dissolved solids," and for most waters of moderate mineral content this is reasonably accurate.

Occasionally a sample will increase in weight while on the balance pan. It must then be dried again and weighed more quickly. Sometimes it is necessary to make the determination of total solids or residue by evaporating and drying in a small bottle with a glass stopper that can be inserted for the weighing.

## LOSS ON IGNITION

Determine the loss on ignition by weighing the dish after heating 3 minutes in a "radiator," which consists of a nickel dish with cover and a triangle to support the platinum dish out of direct contact with the radiator. The full heat of a Bunsen burner is used. The residue may be ignited carefully over a small free flame, but it is more difficult to obtain consistent results without the use of the "radiator."

Some surface waters with high color require much more heating than is directed above in order to burn off all the carbon. For such water the loss on ignition may be a rough indication of the quantity of dissolved organic matter. The loss for other waters may be chiefly water that was not removed by the heating at 180° C.

For most samples the only value of the determination of loss on ignition is to afford a check on the residue on evaporation and another reference point for comparison of the sum of the determined constituents, which obviously ought to come between the residue on evaporation and the residue on ignition.

## SILICA

The first step in the separation of silica from the residue on evaporation in platinum of a sample that contained more than 2 milligrams of nitrate as $NO_3$ is to transfer the residue to a porcelain or silica dish with water and a small quantity of dilute hydrochloric acid. If the sample was not evaporated in platinum or contained less than 2 milligrams of nitrate take up the residue with water and add cautiously 1 cubic centimeter of hydrochloric acid (1+1). Evaporate to dryness. Moisten the residue with a few drops of hydrochloric acid and take up with hot water. If the sample contains much calcium and sulphate it may be difficult to dissolve all of the calcium sulphate from the dish. Sometimes the successive portions of hot water used amount to as much as the original volume of the sample, even with the addition of several cubic centimeters of hydrochloric acid. Filter and wash with hot water, collecting the filtrate and wash water in a volumetric flask (usually 100 or 200 centimeters).

Ignite the precipitate in a platinum crucible and weigh. Add two or three drops of sulphuric acid and a few cubic centimeters of hydrofluoric acid, heat gently to volatilize the acids; then ignite and weigh. The loss is silica ($SiO_2$). The nonvolatile residue should not be as much as 0.0005 gram. A larger quantity may come from calcium sulphate that was not dissolved when the residue was taken up in water and acid, or from suspended silt that was not completely filtered out before the evaporation.

Mix the filtrate thoroughly and divide into two equal portions unless the preliminary examination has shown the desirability of some other division. One part will serve for the determination of iron, calcium, and magnesium; the other for sulphate and alkalies.

## IRON

To determine iron heat to boiling one portion of the filtrate from the silica and add ammonium hydroxide in slight excess. If only a few drops of acid was used in taking up the residue on evaporation, add 1 cubic centimeter of hydrochloric acid (1+1) to redissolve the precipitate and again make alkaline with ammonium hydroxide. Allow to stand on the steam bath for half an hour, filter, and wash. Dissolve the precipitate with hydrochloric acid and water, using the equivalent of 1 cubic centimeter of strong acid. Add 1 cubic centimeter of strong nitric acid, mix and make to a convenient volume of 50 to 100 cubic centimeters. Prepare standards of the same volume containing from 0.05 to 0.4 milligram of iron and the quantities of acid used for the sample. Add 5 cubic centimeters of 2 per cent ammonium thiocyanate to the sample and standards and compare at once. The color is affected by temperature and by the concentration of reagents in the solution.

## ALUMINUM

The determination of aluminum is not worth while in the ordinary practical analysis. If it must be made one of the special methods for aluminum should be used. The practice of weighing the ammonium hydroxide precipitate and reporting as aluminum oxide the difference between this weight and the iron oxide calculated from the determination of iron generally gives incorrect results. This procedure is, however, satisfactory for the analysis of waters high in iron and aluminum, such as the seepage from shale beds and many mine waters. The quantity of iron may be large enough to make it desirable to determine the iron by titration with permanganate or dichromate after fusion of the ignited oxides with sodium bisulphate.

## CALCIUM

For the determination of calcium add to the filtrate from the iron precipitation an excess of ammonium oxalate or oxalic acid. From 5 to 10 cubic centimeters of saturated ammonium oxalate solution is usually enough. Too little will permit the precipitation of magnesium or even fail to precipitate all the calcium. Too much interferes with the subsequent precipitation of magnesium. If the amount of calcium is very small a considerable excess of the oxalate is necessary to start the precipitation. Add hydrochloric acid till the solution is clear and heat to boiling. Add ammonium hydroxide drop by drop with constant stirring till the calcium begins to precipitate. Allow to stand on the steam bath for about half an hour with the precipitate partly down and the solution still acid to methyl orange. Add ammonium hydroxide to make the solution alkaline to methyl orange and allow to stand on the steam bath two or three hours more. Filter, then wash by decantation three times with dilute ammonium hydroxide (0.2 to 0.5 per cent $NH_3$) and twice with hot water. As much as possible of the precipitate should be kept in the beaker, because it is much more easily dissolved there than from the paper. Dissolve the precipitate from the paper into the beaker in about 20 cubic centimeters of hot sulphuric acid (1+3) and hot water to make to about 75 cubic centimeters. Titrate hot with permanganate solution of such strength that 1 cubic centimeter corresponds to 1.0 milligram of calcium. The permanganate solution is best standardized against Bureau of Standards sodium oxalate.

Care is necessary to insure complete removal from the filter paper of the strong oxalate solution in which precipitation took place and at the same time to avoid dissolving too much calcium oxalate. If too much of the precipitate reaches the paper its complete solution is difficult.

The calcium oxalate precipitate may be ignited and weighed as oxide. If this is done the washing of the precipitate may all be done with water containing a little ammonium oxalate.

## MAGNESIUM

To determine magnesium add to the filtrate from the calcium 5 to 10 cubic centimeters of a 10 per cent solution of ammonium phosphate or sodium and ammonium phosphate, clear the solution with hydrochloric acid, and cool in ice water. Add ammonium hydroxide slowly with stirring till the solution is alkaline to methyl orange. Stir occasionally during half an hour or an hour, add an excess of 10 or 20 cubic centimeters of ammonium hydroxide, and allow to stand overnight. Filter and wash with 2 to 3 per cent ammonium hydroxide.

Ignite in a porcelain crucible and weigh as magnesium pyrophosphate. Report as magnesium (Mg), which is 21.84 per cent of the precipitate

If the quantity of magnesium is very small it is well to evaporate the filtrate from the calcium to dryness and remove the bulk of the ammonium salts by heating and gentle ignition. The residue is taken up with a little hydrochloric acid and hot water, the solution is filtered, and the magnesium is precipitated with phosphate and ammonium hydroxide in small volume. A small precipitate comes down much more promptly under these conditions.

## SULPHATE

To determine the sulphate add, if necessary, enough hydrochloric acid to acidify slightly the portion of the filtrate from the silica reserved for the determination of sulphate and alkalies. Heat to boiling and slowly add 5 to 8 cubic centimeters of hot 10 per cent barium chloride solution, with constant stirring. Allow to stand overnight or till the precipitate settles rapidly after stirring. Filter, wash thoroughly, ignite the precipitate, and weigh. Report as sulphate ($SO_4$), which is 41.14 per cent of the weight of barium sulphate.

## SODIUM AND POTASSIUM

To determine sodium and potassium heat the filtrate from the sulphate determination in a volume of 100 to 200 cubic centimeters, add an excess of ammonium hydroxide and an excess of a fresh solution of ammonium carbonate, and heat till the precipitate becomes crystalline and settles well. Slow clearing of the solution is often due to lack of sufficient ammonium carbonate or hydroxide. Filter out, wash thoroughly, and reject the precipitated calcium and barium carbonates. With samples containing very large quantities of alkalies with much calcium and barium it may be worth while to dissolve the carbonates and reprecipitate them in order to avoid loss of alkalies, but the quantity held by the precipitate under normal conditions is negligible.

Evaporate the filtrate to dryness, then heat gently to drive off ammonium salts and just below redness to remove the last traces. Take up in a small volume of hot water, and add a slight excess of freshly prepared barium hydroxide solution. Heat to boiling, filter, and wash. Heat the filtrate, add an excess of ammonium hydroxide and ammonium carbonate, filter, and wash. Evaporate the filtrate to dryness, drive off the ammonium salts, take up in a little hot water, filter and add ammonium hydroxide and ammonium carbonate. If a precipitate appears, filter and repeat the treatment. When no precipitate is produced by the ammonium hydroxide and carbonate,

filter into a small platinum, porcelain, or silica dish suitable for weighing, cautiously add an excess of hydrochloric acid, evaporate to dryness, drive off the ammonium salts, heat just below redness, cool, and weigh. It is easy to volatilize potassium and sodium chlorides when small quantities are spread thinly over a dish. It is necessary to heat sufficiently to remove all the ammonium salts and water. Repeat the heating and weighing to constant weight, taking care not to volatilize any potassium or sodium chloride. Take up the mixed chlorides in a few cubic centimeters of water and filter through a small filter paper. Wash thoroughly and reserve the filtrate for the determination of potassium. Place the filter paper in the dish, dry, burn the paper carefully, gently ignite, and weigh. The difference between the last two weights is the weight of the sodium and potassium chlorides.

### POTASSIUM [12]

For the determination of potassium add to the solution of mixed chlorides in a small evaporating dish 1 drop of hydrochloric acid and a slight excess of platinic chloride over the amount needed to combine with the potassium. It is not necessary to add enough to combine with the sodium. For average waters it may be assumed that approximately one-fourth the weight of mixed chlorides is potassium chloride. The determination should be carried on in a place free from fumes of ammonia that might be absorbed by the solutions and be precipitated by the platinic chloride. Evaporate on the steam bath nearly to dryness. Remove from the bath and allow the last few drops of water to evaporate as the dish is cooling to room temperature. When cool and dry add a few cubic centimeters of 80 per cent alcohol. Grind the residue in the alcohol with a flattened glass rod and allow to stand half an hour with occasional grinding to insure extraction of all the sodium platinic chloride from the insoluble potassium platinic chloride. Decant through a small filter paper and repeat the extraction two or three times till the alcohol in contact with the precipitate is no longer yellow. Transfer the precipitate to the filter paper and wash with 80 per cent alcohol. The yellow color of the solution shows that enough platinic chloride was added. If the solution is not yellow there is probably some potassium chloride still in solution, and it will be necessary to evaporate the filtrate to dryness to remove the alcohol and then repeat the treatment with platinic chloride. If the alcohol contains other organic matter it may be necessary to ignite the residue to prevent reduction

[12] Hicks, W. B., A rapid modified chloroplatinate method for the estimation of potassium: Jour. Ind. Eng. Chemistry, vol. 5, p. 650, 1913. Wells, R. C., Bailey, R. K., and Fairchild, J. G., Note on the Hicks method of determining potassium: Ind. and Eng. Chemistry, vol. 16, p. 935, 1924.

and precipitation of platinum by the organic matter. Dissolve the contents of the filter paper in hot water and make to a volume of about 50 cubic centimeters. Add one or two drops of hydrochloric acid and a piece of metallic magnesium weighing from 20 to 50 milligrams. Allow to stand covered on the steam bath for about two hours, adding a few drops more of acid if necessary to insure complete solution of the magnesium. Filter through a small paper, wash thoroughly, ignite, and weigh the reduced platinum. The filtrate with the excess of platinic chloride is saved in a platinum residue bottle. The ignited metallic platinum is saved in the same or another bottle, and when enough is collected the total residue is reworked into a solution of platinic chloride which is made to a known strength. Usually the strength is indicated on the label as the weight of potassium chloride corresponding to 1 cubic centimeter of the solution.

The weight of potassium is 40.05 per cent of the weight of the metallic platinum.

## SODIUM

To determine sodium subtract from the weight of the mixed chlorides the weight of potassium chloride corresponding to the platinum from the potassium platinic chloride. This is 76.37 per cent of the weight of the platinum. The remainder is sodium chloride, of which 39.34 per cent is sodium.

Only a small error is introduced in most analyses by ignoring the potassium and calculating the sodium corresponding to the total weight of the chlorides. Report as sodium and potassium, although it would be more accurate to use the expression "sodium plus ¾ potassium."

## MANGANESE

Manganese is rarely present in quantity sufficient to affect the balancing of the analysis or to interfere with any of the regular determinations. It may, however, be desirable to determine even a very small quantity on account of possible trouble it may cause in the use of the water. It is most satisfactory to make the determination on a separate sample by the well-known bismuthate method, modified for use with water samples.[13]

To 100 cubic centimeters of water or a sample small enough to contain less than 1 milligram of manganese, add 10 cubic centimeters of dilute nitric acid (1+3) and 1 cubic centimeter of concentrated sulphuric acid, and heat in a beaker on a hot plate until most of the sulphuric acid has been driven off. Cool and take up with about 50

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[13] Collins, W. D., and Foster, M. D., The determination of manganese in water by the sodium bismuthate method: Ind. and Eng. Chemistry, vol. 16, p. 586, 1924.

cubic centimeters of water and 20 cubic centimeters of dilute nitric acid through which air has been bubbled to remove oxides of nitrogen. Add 0.10 gram of sodium bismuthate, stir for one or two minutes, allow the excess of bismuthate to settle, and filter through an alundum crucible or a Gooch crucible with a mat of ignited asbestos which has been washed with permanganate solution and water. Dilute the filtrate to a definite volume and compare with standards. To prepare the standards measure out appropriate volumes of standard permanganate solution, add to each the quantity of nitric acid used for the sample, and make to the same volume.

## CHECKS AND CALCULATIONS

The reliability of an analysis may be checked by the calculations described below.

### RESIDUE ON EVAPORATION AND SUM OF DETERMINED CONSTITUENTS

For a calcium carbonate water of moderate concentration the residue on evaporation should be about the same as the sum of the determined constituents if the bicarbonate is divided by 2.03 to convert it to the corresponding carbonate that remains on evaporation. If the water is high in calcium and sulphate the residue is likely to be decidedly greater than the sum. If the water contains much nitrate and chloride with only a moderate quantity of sodium the residue may be less than the sum. Samples have been analyzed after they had stood in bottles so long that appreciable quantities of silicate were dissolved. Some of the alkalinity that was reported as carbonate and bicarbonate, or possibly hydroxide, was really silicate. All the silica was reported as such, and therefore the sum exceeded the weight of the residue by the amount of carbonate calculated as the equivalent of the alkalinity due to silicates.

### ERROR OF BALANCE OF BASES AND ACIDS

The determinations described in the previous pages cover all the constituents ordinarily found in natural waters in appreciable quantities. The titration of alkalinity which is reported as bicarbonate, carbonate, or hydroxide is really a measure of the excess of the bases calcium, magnesium, sodium, and potassium over the amounts necessary to balance the strong acid radicles sulphate, chloride, and nitrate. Therefore, the accuracy of the analysis as a whole is indicated by the error of balance of the acids and bases.

In the calculation of the error of balance the silica and iron are usually left out of consideration. The results in parts per million are divided by the combining weights of the respective radicles, giv-

ing the milligram equivalents per kilogram, which are directly comparable. Instead of dividing by the combining weights it is generally more convenient to multiply by their reciprocals as given in the following list of factors for converting analyses in parts per million to milligram equivalents per kilogram:

| | | | |
|---|---|---|---|
| Calcium | 0. 04991 | Bicarbonate | 0. 01639 |
| Magnesium | . 08224 | Sulphate | . 02082 |
| Sodium | . 04348 | Chloride | . 02821 |
| Potassium | . 02556 | Nitrate | . 01613 |
| Carbonate | . 03333 | | |

The use of these factors is illustrated in Table 2, which shows a partial analysis as reported in parts per million and also in milligram equivalents per kilogram. The last column shows the analysis adjusted for graphic representation.

TABLE 2.—*Partial analysis of water from a public supply*

| Constituents | Parts per million | Milligram equivalents per kilogram | |
|---|---|---|---|
| | | As reported | Adjusted to distribute error [a] |
| **Bases:** | | | |
| Calcium (Ca) | 23 | 1. 1480 | 1. 13 |
| Magnesium (Mg) | 5. 4 | . 4441 | . 44 |
| Sodium (Na) | 3. 0 | . 1304 | . 13 |
| Potassium (K) | 1. 4 | . 0358 | . 03 |
| | | 1. 7583 | 1. 73 |
| **Acids:** | | | |
| Bicarbonate radicle (HCO₃) | 70 | 1. 1473 | 1. 17 |
| Sulphate radicle (SO₄) | 20 | . 4164 | . 42 |
| Chloride radicle (Cl) | 3. 3 | . 0931 | . 09 |
| Nitrate radicle (NO₃) | 2. 8 | . 0452 | . 05 |
| | | 1. 7020 | 1. 73 |

[a] See p. 256.

As stated above, the sum of the equivalents of the bases should be equal to the sum for the acids. In the analysis shown in Table 2 the difference is 0.0563, which is 1.6 per cent of the total 3.4603. It is customary to report this error as +1.6 per cent and report as negative the errors of analyses in which the acids are in excess.

The error in this average analysis is seen to amount to more than the total potassium or nitrate and to be the equivalent of more than 1 part per million of calcium or sodium and about 2 parts of chloride or sulphate. It is not at all likely that this total error is concentrated in a single determination. An error up to 2 per cent may result from a summation of small unavoidable errors in the analysis of a water containing about 100 parts per million of dissolved solids. In careful work it is customary to have the error not over 1.0 per

cent in analyses of water with much over 100 parts per million of dissolved solids. The error may be 5 per cent for waters with as little as 25 or 30 parts per million of solids.

The general tendency is toward positive errors. The reagents and distilled water are more likely to introduce calcium, magnesium, and particularly sodium into the analysis than they are to introduce sulphate. The other determinations are made on separate samples to which reagents have not been added other than those used in the actual determination. When the error appears unduly large an examination of the analysis will frequently suggest the single determination that is responsible for most of the error.

### HARDNESS

Report the hardness as the calcium carbonate corresponding to the total calcium and magnesium. Multiply the parts per million of calcium by 2.5 and the magnesium by 4.1. If the milligram equivalents have been calculated the sum of the equivalents for calcium and magnesium may be multiplied by 50 to obtain the total hardness in parts per million.

It is sometimes desirable to show the noncarbonate hardness. This is most easily calculated from the milligram equivalents by subtracting the bicarbonate from the sum of the calcium and magnesium and multiplying the remainder by 50. The noncarbonate hardness may be calculated by multiplying the bicarbonate in parts per million by 0.820 and subtracting the product from the total hardness.

The calculated hardness is generally considered more accurate than the hardness determined by the soap method. The two should, however, agree within about 10 per cent if the soap method has been followed with care. This check will occasionally indicate a gross error in the determination of calcium or magnesium.

### HYPOTHETICAL COMBINATIONS

The disadvantages of expressing analyses in hypothetical combinations so outweigh the slight advantage of this form of expression that the use of such combinations was abandoned many years ago for reports of the United States Geological Survey.

The main advantage of hypothetical combinations as indicating the general character of a water may be had more simply by indicating the predominating basic and acid radicles if the analysis shows that the water contains chiefly the constituents of some one salt. This can best be seen from the equivalents but is not difficult to tell from the analysis in parts per million. If the hypothetical combinations must be reported they may be calculated from the equivalents as explained in the official methods of the Association of

Official Agricultural Chemists.[14] Stabler[15] and Palmer[16] have given methods for making calculations and classifications based on analyses expressed in milligram equivalents per kilogram, for which Stabler used the name "reacting values."

## GRAPHIC REPRESENTATION OF ANALYSES [17]

In recent publications of the United States Geological Survey and for the study of analyses in the laboratory use has been made of diagrams to represent analyses, as shown in Plate 14. The heights of the sections are proportional to the quantities of the constituents as measured in equivalents. Only three patterns are used for each side of the analysis. Unless the quantity of potassium, of nitrate, or of carbonate is exceptional no notice is taken of it. If the quantity is large a horizontal line is drawn through the area representing sodium and potassium, chloride and nitrate, or bicarbonate and carbonate, to show the division, with the potassium, nitrate, or carbonate at the top. Although the diagrams as shown with patterns are cheaper to print, it is easier to make them for laboratory study with colored crayons. A convenient color scheme is as follows: Calcium, red; magnesium, orange; sodium and potassium, yellow; chloride (and nitrate), light green; sulphate, blue; bicarbonate (and carbonate), violet.

Few analyses balance absolutely, and it is necessary to adjust the equivalents to make the two sides of the diagram come to the same height. This is illustrated in Table 2. Half the difference between the totals of the equivalents for bases and for acids is divided proportionally and subtracted from the higher and added to the lower. This method of adjustment makes the greatest changes in the predominating constituents and little change in those present in small quantities.

Since one equivalent of $CaCO_3$ is 50, the coordinates for equivalents represent hardness as $CaCO_3$ in units of 50 parts per million. The total hardness is measured on the diagram to the top of the magnesium. The carbonate hardness is measured to the top of the bicarbonate if this is below the top of the magnesium. In such a

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[14] Assoc. Official Agricultural Chemists, Official and tentative methods of analysis, p. 104, 1925.

[15] Stabler, Herman, The mineral analysis of water for industrial purposes and its interpretation by the engineer: Eng. News, vol. 60, p. 335, 1908; Some stream waters of the western United States, with chapters on sediment carried by the Rio Grande and the industrial application of water analyses: U. S. Geol. Survey Water-Supply Paper 274, pp. 165–181, 1911.

[16] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, 1911.

[17] Collins, W. D., Graphic representation of analyses: Ind. and Eng. Chemistry, vol. 15 p. 394, 1923.

water the distance from the top of the bicarbonate to the top of the magnesium measures the noncarbonate hardness.    If the bicarbonate extends above the magnesium there is no noncarbonate hardness; the water has more alkalinity than hardness and is commonly said to contain sodium bicarbonate or carbonate.    Waters of this type are shown by diagrams 5, 10, and 11 in Plate 14, which represents the analyses in Table 3.

TABLE 3.—*Analyses of natural and treated waters*

[From published reports]

**Parts per million**

| No. | Source | Total dissolved solids | Silica ($SiO_2$) | Iron (Fe) | Calcium (Ca) | Magnesium (Mg) | Sodium (Na) | Potassium (K) | Bicarbonate radicle ($HCO_3$) | Sulphate radicle ($SO_4$) | Chloride radicle (Cl) | Nitrate radicle ($NO_3$) | Hardness as $CaCO_3$ (calculated) Total | Hardness as $CaCO_3$ (calculated) Noncarbonate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Catskill supply, New York, 1921 | 28 | 2.6 | 0.04 | 4.5 | 1.2 | 1.1 | 0.6 | 11 | 7.7 | 1.0 | 0.49 | 16 | 7 |
| 2 | Washington, D. C., supply, 1921 | 103 | 6.6 | .07 | 23 | 5.4 | 3.0 | 1.4 | 70 | 20 | 3.3 | 2.8 | 80 | 22 |
| 3 | Pittsburgh, Pa., supply, 1920 | 148 | 8.2 | .2 | 28 | 4.8 | 8.5 | | 27 | 60 | 13 | .8 | 90 | 67 |
| 4 | Lake Michigan, Chicago | 183 | 18 | .4 | 36 | 10 | 4.6 | 1.6 | 144 | 10 | 6.0 | 1.8 | 131 | 13 |
| 5 | Long Beach, Calif., supply, 1921 | 246 | 19 | .04 | 6.0 | 1.7 | 78 | 3.9 | 207 | 2.1 | 17 | Trace. | 22 | None. |
| 6 | Mississippi River, St. Louis, Mo., Oct. 22–31, 1906 | 306 | 22 | .08 | 53 | 22 | a 25 | | 236 | 58 | 12 | 1.2 | 223 | 29 |
| 7 | Dayton, Ohio, supply, 1922 | 434 | 10 | .09 | 92 | 34 | 8.2 | 1.4 | 339 | 84 | 9.6 | 13 | 369 | 92 |
| 8 | Raw water for a public supply | 290 | | | 65 | 20 | a 8 | | 240 | 54 | 6.0 | | 244 | 48 |
| 9 | Public supply from No. 8 | 160 | | | 19 | 9.0 | a 16 | | 53 | 64 | 6.0 | | 84 | 41 |
| 10 | Water No. 8 softened by hot lime-soda process | 160 | | | 8.4 | .9 | a 45 | | 70 | 54 | 6.0 | | 25 | None. |
| 11 | Water No. 8 softened by an exchange silicate | 318 | | | Trace. | Trace. | a 121 | | 240 | 54 | 6.0 | | Trace. | None. |

**Milligram equivalents per kilogram**

| No. | Source | Total dissolved solids | Silica ($SiO_2$) | Iron (Fe) | Calcium (Ca) | Magnesium (Mg) | Sodium (Na) | Potassium (K) | Bicarbonate radicle ($HCO_3$) | Sulphate radicle ($SO_4$) | Chloride radicle (Cl) | Nitrate radicle ($NO_3$) | Hardness as $CaCO_3$ (calculated) Total | Hardness as $CaCO_3$ (calculated) Noncarbonate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Catskill supply, New York, 1921 | | | | 0.2246 | 0.0987 | 0.0478 | 0.0153 | 0.1803 | 0.1603 | 0.0282 | 0.0079 | 0.3233 | 0.1430 |
| 2 | Washington, D. C., supply, 1921 | | | | 1.1480 | .4441 | .1304 | .0358 | 1.1473 | .4164 | .0931 | .0452 | 1.5921 | .4448 |
| 3 | Pittsburgh, Pa., supply, 1920 | | | | 1.3976 | .3947 | .3696 | | .4425 | 1.2492 | .3667 | .0129 | 1.7923 | 1.3498 |
| 4 | Lake Michigan, Chicago | | | | 1.7968 | .8224 | .2000 | .0409 | 2.3602 | .2082 | .3662 | .0290 | 2.6192 | .2590 |
| 5 | Long Beach, Calif., supply, 1921 | | | | .2995 | .1398 | 3.3913 | .0997 | 3.3994 | .0437 | .4795 | Trace. | .4393 | None. |
| 6 | Mississippi River, St. Louis, Mo., Oct. 22–31, 1906 | | | | 2.6464 | 1.8092 | 1.0870 | | 3.8680 | 1.2078 | .3385 | .0194 | 4.4546 | .5860 |
| 7 | Dayton, Ohio, supply, 1922 | | | | 4.5920 | 2.7960 | .3565 | .0358 | 5.5562 | 1.7489 | .2708 | .2096 | 7.3880 | 1.8318 |
| 8 | Raw water for a public supply | | | | 3.2443 | 1.6447 | .3385 | | 3.9340 | 1.1243 | .1692 | | 4.8890 | .9550 |
| 9 | Public supply from No. 8 | | | | .9483 | .7401 | .6956 | | .8687 | 1.3325 | .1692 | | 1.6884 | .8197 |
| 10 | Water No. 8 softened by hot lime-soda process | | | | .4193 | .0740 | 1.9565 | | 1.1473 | 1.1243 | .1692 | | .4933 | None. |
| 11 | Water No. 8 softened by an exchange silicate | | | | Trace. | Trace. | 5.2275 | | 3.9340 | 1.1243 | 1692 | | Trace. | None. |

a Calculated.
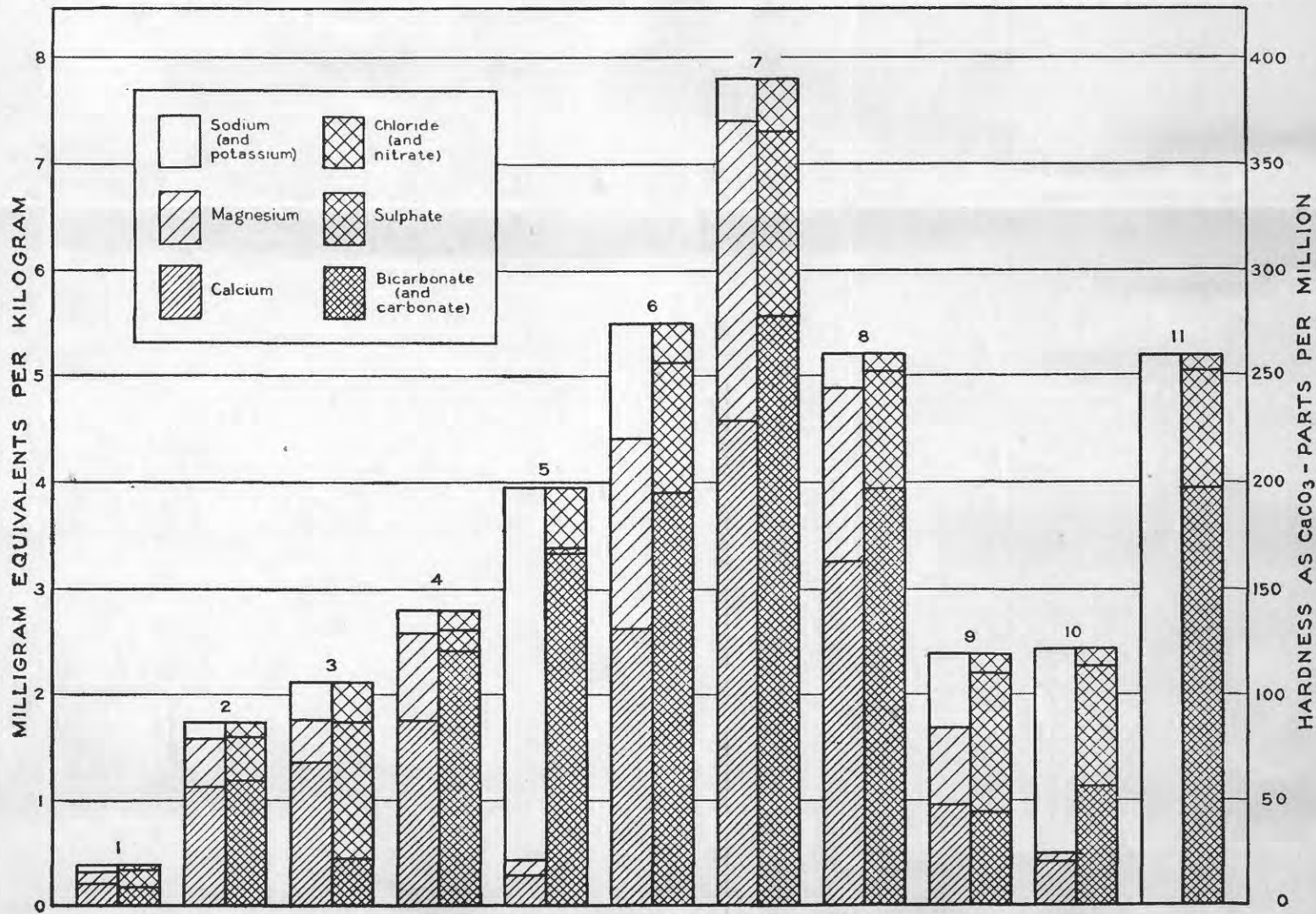
COMPOSITION OF NATURAL AND TREATED WATERS

Numbers refer to analyses in Table 3

The type of water most widely used for public and private supplies in the United States is the calcium bicarbonate water in which calcium, magnesium, and bicarbonate make up the greater part of the dissolved mineral matter. Typical waters of this kind are shown in diagrams 2, 4, 6, 7, and 8. Bicarbonate waters of very low mineral content like No. 1 are likely to have the other acid radicles together amount to more than the bicarbonate.

Many natural waters have dissolved enough gypsum to make calcium and sulphate the predominating radicles. The only calcium sulphate water shown in Plate 14 is No. 3, which owes most of its sulphate to contamination of river water with acid wastes from coal mines. The sulphuric acid has been neutralized by the water with reduction of alkalinity.

Here and there throughout the United States natural waters are found with high alkalinity and comparatively little calcium or magnesium. No. 5 is a typical sodium bicarbonate water,[18] although many such waters contain more sodium bicarbonate and less calcium and magnesium. Some waters that have much more calcium and magnesium than sodium still have more bicarbonate than the combined calcium and magnesium and so may be said to contain sodium bicarbonate. They are, however, as much calcium bicarbonate waters as Nos. 4 or 6.

Diagram 9 shows the results obtained by treatment of water No. 8 for a public supply. The sulphate is increased because of the use of aluminum sulphate to produce a precipitate that will settle well and assist in clarification of the water. Lime is added to cause precipitation of calcium and magnesium as carbonate and hydroxide. The sulphate from the aluminum sulphate would increase the noncarbonate hardness but for the fact that soda ash (sodium carbonate) is added to decrease the noncarbonate hardness. The water as delivered has a total hardness of less than 100 parts per million and about the same noncarbonate hardness as before treatment. Complications in the treatment due to delayed precipitation of the calcium carbonate have led to adoption of recarbonation of waters treated by this process, as described recently by C. P. Hoover.[19]

Diagram 10 shows the result of treatment of a water like No. 8 by the hot lime-soda softening process. The hardness is reduced to about 25 parts per million, but the excess of sodium carbonate added brings the total quantity of dissolved material to about the same as in No. 9.

Diagram 11 shows the result of treating water No. 8 with an exchange silicate water softener. The calcium and magnesium are al-

[18] Collins, W. D., and Howard, C. S., Natural sodium bicarbonate waters in the United States: Ind. and Eng. Chemistry, vol. 19, p. 623, 1927.

[19] Hoover, C. P., Recarbonation of softened water: Ind. and Eng. Chemistry, vol. 19, p. 784, 1927.

most entirely replaced by sodium, but the acid radicles are unaffected, and the total quantity of dissolved mineral matter is about the same as before treatment.

## SHORT METHODS AND PARTIAL ANALYSES

It has been found in the Geological Survey and in some other laboratories where large numbers of analyses have been made that most of the rapid methods are not generally superior in speed, reliability, or accuracy to the somewhat old-fashioned standard analytical procedures outlined above. Some of the shorter methods serve well for special routine work where the operator can acquire the necessary skill to obtain consistently accurate results, but for the ordinary laboratory it is usually more satisfactory to shorten the regular methods.

As already stated, the preliminary examination will sometimes give all the information needed about a sample. The total hardness may be determined fairly accurately by the soap method and divided into carbonate and noncarbonate hardness from the determination of bicarbonate. A rough figure for sodium may be calculated, as noted on page 244. The sum of the milligram equivalents of the acids minus the milligram equivalents of the total hardness gives the number of equivalents of alkalies, which may be multiplied by 23 to give the sodium. This figure includes any error in the hardness and the much greater probable error of the sulphate determined by turbidity. A rough figure for the dissolved solids may be calculated by adding the constituents as determined and calculated, assuming all the hardness to be due to calcium and converting the bicarbonate to carbonate by dividing by 2.03. About the same result can be obtained for an estimate of the total dissolved solids by the following equation, in which the formulas stand for the parts per million of the various acid radicles as determined.

$$\text{Dissolved solids} = HCO_3 - \tfrac{1}{6}HCO_3 + SO_4 + 0.4SO_4 + Cl + 0.6Cl$$

Starting from the complete practical analysis as outlined in the text, the first and most common saving is the omission of the determination of potassium. The total weight of mixed chlorides is calculated to sodium, and the error so introduced is not great in an ordinary water with 100 to 500 parts per million of solids. If the quantity of sodium and potassium together is much less than 10 parts per million the percentage error introduced may be appreciable. This shortening of the work still leaves available the check of balancing the analysis.

The next step in saving is usually the entire omission of the determination of alkalies. This saves much time. It also leaves the analysis without a real check. A number can be calculated for alkalies as sodium. The sum of the milligram equivalents of the acid radicles minus the sum for calcium and magnesium gives a number which should give the sodium in parts per million when multiplied by 23. It includes, however, the algebraic sum of all the errors in the determination of acids and of calcium and magnesium. A rough check on the calcium and magnesium is furnished by the soap hardness, and a still more rough check on the whole analysis by comparison of the sum of the constituents with the residue on evaporation. The latter results may differ considerably in a very good analysis, so that the check is not very helpful.

If something more than a preliminary examination is desired and the time available or the value of the information to be obtained does not justify a complete analysis, the preliminary examination may be supplemented by determinations of calcium, magnesium, and sulphate, and the determinations of residue, silica, iron, sodium, and potassium may be omitted. A volume of 100 to 250 cubic centimeters of the sample is filtered if necessary, and the calcium is precipitated and determined as in the regular analysis. Magnesium is determined in the filtrate. In another portion of 100 to 250 cubic centimeters the sulphate is precipitated and determined as usual. Sodium is calculated. If time is important the calcium may be filtered about one hour after precipitation; the magnesium precipitate may be brought into condition for filtering within three or four hours after precipitation by vigorous stirring or shaking. Careful precipitation of the sulphate and sufficient heating after precipitation will make its filtration feasible after a few hours. Thus a sort of analysis can be completed the day it is started, and if no serious error is made the results may be of as much practical value as a complete accurate analysis. They will, however, be without any check except that made by comparing the hardness calculated from the calcium and magnesium with the hardness determined by the soap method.

In the hands of an experienced analyst the short cuts are often very useful, but the incomplete partial analyses can never give the confidence that goes with an analysis in which all the constituents present in appreciable quantities have been determined.

## CORRECTION FOR DETERMINATION OF NITRATE
### (See p. 241)

If a water contains more than 30 parts per million of chloride, the chloride must be removed by silver-sulfate solution before determination of the nitrate, or a smaller sample must be taken so that the chloride in the sample evaporated will not be more than the equivalent of the amount in 50 cubic centimenters of a water containing 30 parts per million of chloride.

The silver-sulfate solution is made by dissolving 4.397 grams of silver sulfate, free from nitrate, in 1 liter of water. One cubic centimeter of this solution is equivalent to 1 milligram of chloride. Enough should be added to the sample taken for the nitrate determination to precipitate all but about 0.1 milligram of chloride. A little alumina cream is added; the sample is stirred very thoroughly and after standing a few minutes is filtered and the precipitate washed a little with distilled water. The filtrate is treated in the usual way for the nitrate determination. The silver sulfate and alumina cream must be tested to insure freedom from nitrate.