Methods of Analysis of Irrigation Waters

[See the introductory notes at the beginning of chapter 6.]

(70) Collection of Irrigation Water Samples

The minimum quantity of water required for the ordinary chemical analysis is about one-half gallon (1.9 liters). In special cases, larger quantities may be necessary.

Care should be taken to obtain a representative sample. Satisfactory samples of some waters can be obtained only by mixing several portions collected at different times, the details as to collection and mixing depending on local conditions. Samples from wells should be collected after the pump has been running for some time, and samples from streams should be taken from running water.

In general the shorter the elapsed time between collection and analysis of a sample, the more reliable will be the analytical data. Changes resulting from chemical and biological activity may alter the composition of the sample. No satisfactory method for sterilizing a water sample to prevent bacterial action has been proposed.

References

American Public Health Association and American Water Works Association (1946, *p. 1*).

(71) Records, Reports, and Expression of Results

At the time of collection, a label, bearing a short identifying description, should be attached to the bottle. Additional information can be recorded on a "Collector's Description of Water Sample" form as shown. One item not specifically called for on this form, but often of importance, is the elevation above sea level of an appropriate reference point at the well. When this is known, it is possible to refer the water level in the well to sea level. This value may be useful in quality-of-water studies. The importance of an accurate and complete description, especially as regards location, cannot be overemphasized.

Two other blank forms used at the Laboratory in connection with the analyses of water samples are shown on pages 138 and 139. The laboratory work sheet is used for recording the original data obtained from the chemical analysis. One such sheet is used for each sample. A laboratory number is assigned which, with the description from the "Collector's Description of Water Sample," is entered at the top of the page. Upon completing and recording each separate determination, the analyst enters his initials and the date.

For purposes of uniformity, the following rules for reporting analytical results are used:

pH.—Report to the nearest 0.1 unit.

ELECTRICAL CONDUCTIVITY ($EC \times 10^6$ at 25° C.).—Report to the nearest 0.1 when less than 100, and to 3 significant figures for values above 100.

DISSOLVED SOLIDS.—Report in parts per million (p. p. m.) to the nearest whole number, but not more than 3 significant figures.

BORON.—Electrometric titration method; report to the nearest 0.01 p. p. m. when less than 10 p. p. m. boron, and to 3 significant figures above 10 p. p. m. boron.

Colorimetric method; report to the nearest 0.1 p. p. m. boron but not more than 2 significant figures.

SILICA.—Report in p. p. m. SiO_2 to nearest whole number, but not more than 3 significant figures.

FLUORIDE.—Report to the nearest 0.1 p. p. m. fluoride or to the nearest 0.01 meq./l.

CATIONS AND ANIONS.—Report to the nearest 0.01 meq./l. up to 100, and to 4 significant figures if above 100 meq./l.

(72) Electrical Conductivity

Remarks

Electrical conductivity is commonly used for indicating the total concentration of the ionized constituents of a natural water. It is closely related to the sum of the cations (or anions) as determined chemically, and it usually correlates closely with the total dissolved solids. It is a rapid and reasonably precise determination that does not alter or consume any of the sample.

Apparatus

Wheatstone bridge, alternating current, suitable for conductivity measurements. This may be a 1,000-cycle a. c. bridge with telephone receivers, a 60-cycle a. c.

UNITED STATES DEPARTMENT OF AGRICULTURE

Agricultural Research Service
Soil and Water Conservation Research Branch
United States Salinity Laboratory
Riverside, California

COLLECTOR'S DESCRIPTION OF WATER SAMPLE

Collector's No. __________; Lab. No. __________; Date __________; Collector ______________________________

Name and/or owner ____

____
Spring, Stream, Lake, Well? (circle one)

____
County — Miles—distance nearest town — USGS sheet

Location _______ ¼, Sec. _______; T _______ _______; R _______ _______; ______________________
Distance and direction from section corner or landmark

Other description ____

Depth _______; Depth to upper perforation _______; Casing diameter ______________________

Discharge __________; Static level __________; Draws down to ______________________

Temp. __________ ° C. or °F.; Odor ____________; Gas ____________; Color ______________________

Use: Irrig., Municipal, Ind., Stock, Domestic ______________________________

Approximate acreage served, crops ______________________________

Condition or symptoms of land or crops ______________________________

Owner's opinion of water quality ______________________________

Collector's remarks ______________________________

____

____

Report to: ______________________________

____

____

(Please draw a map on the reverse side, if necessary, to show the exact location of the sampling site).

259525 O - 54 - 10

Water sample No._______. Description:

pH	Dissolved Solids	Boron	Sum of Cations
Conductivity at 25°C.			Sum of Anions
T°C.			$\frac{EC\times10^6}{Anions}$
$\frac{k}{R}$ = ____			Percent Na
$EC\times10^6$ @ 25° C.	D.S. p.p.m.	B p.p.m.	
Calcium	Magnesium	Sodium	Potassium
Ca meq./l.	Mg meq./l.	Na meq./l.	K meq./l.
Carbonate and Bicarbonate	Sulfate	Chloride	Nitrate
CO_3 meq./l. HCO_3 meq./l.	SO_4 meq./l.	Cl meq./l.	NO_3 meq./l.
			Received laboratory:
			Analysis completed:
			Reported:
			Reported to:

UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Service

Division of Soil and
Plant Relationships

U. S. Salinity Laboratory
Rubidoux Unit
Riverside, California

REPORT OF WATER ANALYSIS

Description

Conductivity, $EC \times 10^6 @ 25^{\circ}C$.		Dissolved Solids: tons per acre-foot	
		parts per million	
Percent Sodium		Hydrogen-ion activity (pH)	
Boron (B) parts per million		Silica (SiO_2) parts per million	

Cations	Milligram equivalents per liter	Parts per million	Anions	Milligram equivalents per liter	Parts per million
Calcium (Ca)			Carbonate (CO_3)		
Magnesium (Mg)			Bicarbonate (HCO_3)		
Sodium (Na)			Sulfate (SO_4)		
Potassium (K)			Chloride (Cl)		
			Fluoride (F)		
			Nitrate (NO_3)		
Sum		X X X	Sum		X X X

Analyzed by:

Reported by:

Reported to:

bridge with an a. c. galvanometer, or one of the newer bridges employing a cathode ray tube as the null indicator.

Conductivity cell, either pipet or immersion type, with platinized platinum electrodes. The cell constant should be approximately 1.0 reciprocal centimeter. New cells should be cleaned with chromic-sulfuric acid cleaning solution, and the electrodes should be platinized before use. Subsequently, they should be cleaned and replatinized whenever the readings become erratic or when an inspection shows that any of the platinum black has flaked off. The platinizing solution contains platinum chloride, 1 gm.; lead acetate, 0.012 gm.; in 100 ml. water. To platinize, immerse the electrodes in the above solution and pass a current from a 1.5-volt dry battery through the cell. The current should be such that only a small quantity of gas is evolved, and the direction of current flow should be reversed occasionally.

Reagents

A. Standard potassium chloride solution, 0.01 N. Dissolve 0.7456 gm. of potassium chloride in distilled water and make to 1 liter at 25° C. This is the standard reference solution and at 25° C. has an electrical conductivity of 1411.8×10^{-6} (0.0014118) mhos/cm.

Procedure

Place 4 tubes of reagent A in a water bath. (For subsequent sets of determinations, discard the first tube of potassium chloride solution, shift the others one place, and insert a tube of fresh solution.) Place 2 tubes of each sample in the bath, adjust the temperature to approximately 25° C., and hold at this temperature for 20 to 30 min. If the room temperature is not close to 25° C., it is better to adjust the temperature of the bath to approximately that of the room and hold it at that temperature until equilibrium is attained. The bath temperature is here represented by t. Rinse the electrode in three of the tubes of potassium chloride solution, transfer to the fourth, and measure the cell resistance (R'_t). Rinse the electrode several times in one tube of the water sample, transfer to the other tube, and read the resistance (R_t). The electrical conductivity (EC at 25° C.) of the sample is calculated from the equation:

$$EC = \frac{0.0014118 \times R'_t}{R_t}$$

This is multiplied by 1,000,000 (10^6) and reported as $EC \times 10^6$ at 25° C., or as EC, micromhos/cm. at 25°.

The expression "electrical conductivity" is synonymous with "specific electrical conductance." The standard unit for conductivity is the mho/cm. It is so large that most natural waters have a value of much less than 1 unit. For purposes of convenience in recording or expressing such results, the value in mhos/cm. is multiplied by 10^6 (decimal point moved 6 places to the right) and reported as $EC \times 10^6$ at 25° C. The several methods of reporting conductivity are shown below, using as an example a western surface water with a conductivity of 0.00117 mho/cm.:

$$\begin{aligned} EC &= 0.00117 \text{ mho/cm.} \\ EC \times 10^3 &= 1.17 \text{ mmhos/cm.} \\ EC \times 10^5 &= 117 \ (= K \times 10^5) \\ EC \times 10^6 &= 1{,}170 \text{ micromhos/cm.} \end{aligned}$$

References

Wilcox (1950), National Research Council, International Critical Tables (1929, *v. 6, p. 234*).

(73) Boron

(73a) Boron, Electrometric Titration

Remarks

The addition of mannitol to a neutral, unbuffered solution of mixed salts containing boron causes the solution to become acid. The quantity of standard alkali required to titrate the solution back to the initial pH is an accurate measure of the boron present. Electrometric or direct methods of titration may be used.

The choice of apparatus for the electrometric titration of boron should be determined by the instruments available, the number of analyses to be made, and the frequency of use. Three sets of apparatus are described below, any one of which will give satisfactory results. The first requires a minimum of equipment. The operation depends on the fact that a 0.7 N calomel electrode and a quinhydrone electrode come to a null point (reversal of polarity) at approximately pH 7.0.

Apparatus

Galvanometer. An enclosed lamp and scale type sensitive to 0.025 microampere per scale division.

Quinhydrone electrode. A piece of platinum wire 7.5 cm. (3 in.) in length, with suitable contact above the surface of the solution. This type is preferable to an electrode of platinum sealed through glass and connected with mercury, as minute cracks develop in the glass and cause erratic results.

Calomel electrode, 0.7 N with respect to potassium chloride. A silver-silver chloride electrode can be used in place of the 0.7 N calomel electrode. For details see Wilcox (1932).

Motor-driven stirrer.

Switch, single-pole single-throw.

The electrodes are connected through the switch to the galvanometer. A shunt to protect the galvanometer is desirable but not essential.

The second apparatus is a simple potentiometer (fig. 33). In addition to the parts listed above, the following are required: resistance wire, 1,500 ohms tapped at 60 ohms; and a 1.5-volt dry cell. A calomel electrode, 0.1 N with respect to potassium chloride, is substituted for the 0.7 N electrode described above.

The third apparatus makes use of either a potentiometer or a pH meter as the indicating system. The

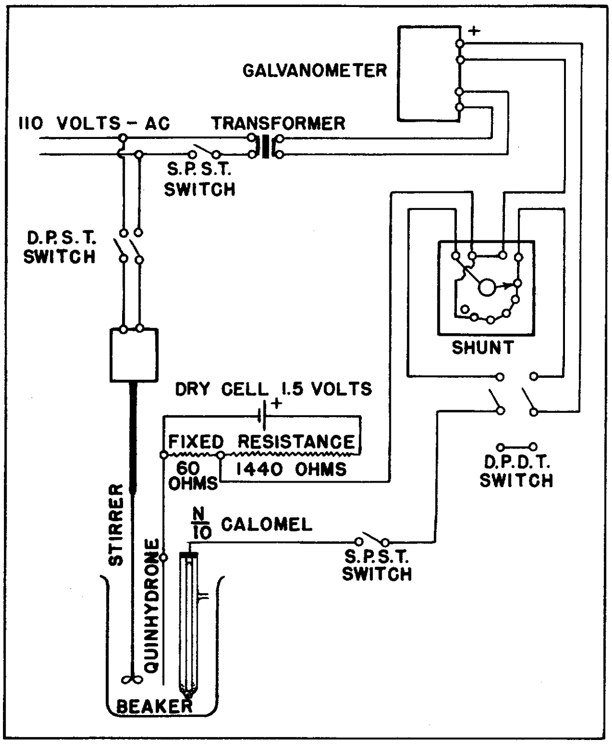

FIGURE 33.—Diagram of electrometric titration apparatus, showing electrical circuit. The 6 volt a. c. line from the transformer supplies the light in the reflecting galvanometer.

instrument is set so that, at balance, the solution under test will have a pH reading of 7.1. The following electrode pairs have been found satisfactory: quinhydrone and 0.1 N calomel; quinhydrone and saturated calomel; glass and saturated calomel.

Reagents

A. Quinhydrone, reagent quality, free from heavy metals.

B. Bromthymol blue indicator solution, 1 percent. Methyl red may be substituted.

C. Sulfuric acid. Approximately 1 N.

D. Sulfuric acid. Approximately 0.02 N.

E. Sodium hydroxide. Approximately 0.5 N, carbonate-free.

F. Sodium hydroxide. Standard 0.0231 N, carbonate-free (1 ml. is equivalent to 0.25 mg. boron).

G. Boric acid solution. Dissolve 0.5716 gm. dry H_3BO_3 in distilled water and dilute to 1 liter. The H_3BO_3 may be dried in a desiccator with calcium chloride. One ml. contains 0.1 mg. boron. This solution is used in standardizing reagent F.

H. Mannitol, neutral. Synthetic mannitol is preferable to the natural product. The "blank" titration for 5 gm. of mannitol should not exceed 0.1 ml. of reagent F.

Procedure

Transfer an aliquot of the sample, containing not more than 1 mg. boron, to a 400-ml. beaker and dilute, if necessary, to 250 ml. Add a few drops of reagent B and acidify with C, adding 0.5 to 1 ml. in excess. Bring to boil, stir, cautiously at first, then vigorously, to expel carbon dioxide. Cool to room temperature, preferably in a water bath. With the S. P. S. T. switch open and the shunt, if used, set at 0.1, introduce the electrodes and stirrer into the solution. Start the stirrer and add E to approximate neutrality as shown by B. Add about 0.2 gm. of A and close the switch in the electrode circuit. The galvanometer should indicate approximate balance. If it swings to the right, excess alkali is indicated, and if to the left, excess acid. Adjust with either F or D until the galvanometer shows no deflection.

If a shunt is used, reverse the switch, thus eliminating it from the circuit and permitting the galvanometer to function at its greatest sensitivity. Again adjust to balance with either dilute acid or alkali. The galvanometer should be steady, showing at most only a slow drift. This is the initial point of the titration. Bring the shunt into the circuit by reversing the D. P. D. T. switch or open the S. P. S. T. switch, if the shunt is omitted. Add 5 ± 0.1 gm. of mannitol. If boron is present, the indicator will change to the acid color and the galvanometer will swing to the left. Add reagent F until approximate balance is again attained; eliminate the shunt, if used, and complete the titration, bringing the galvanometer back to the original null point. This is the end point.

Note the number of milliliters of reagent F required after adding the mannitol at the initial point of the titration. From this, subtract a blank determined by substituting distilled water for the sample and proceed as indicated above. The net volume of F multiplied by the equivalency (mg. boron per ml. NaOH) gives milligrams of boron in the aliquot titrated. Report as parts per million boron. The equivalency of F is established by titrating an aliquot of G. The buret used should be of such accuracy that the volume of F can be read to 0.01 ml. Borosilicate glassware (Pyrex) can be used for this determination. New beakers should be cleaned by filling with acid and heating on the steam bath before use. If the concentration of phosphate exceeds 10 p. p. m., it should be precipitated with lead nitrate and the excess lead removed with sodium bicarbonate.

Calculations

Parts per million B = (ml. NaOH − blank) × mg. B equivalent to 1 ml. NaOH × 1,000/ml. in aliquot.

References

American Public Health Association and American Water Works Association (1946, *p. 87–90*), Association of Official Agricultural Chemists (1950, *31.52, p. 547*), Wilcox (1932).

(73b) Boron, Colorimetric, Using Carmine

Apparatus

A spectrophotometer with matched square cuvettes.[18]

Centrifuge tubes, flasks, beakers, pipets, and burets (boron-free glass). Alkali-resistant (boron-free) glassware, porcelainware, platinum, or fused quartz dishes are satisfactory. The use of borosilicate glassware is to be avoided. Convenient sizes are centrifuge tubes, 15-ml.; flasks, 125-ml.; beakers, 100-ml.; pipets, 2-ml.; burets, 10-ml. automatic.

Reagents

A. Sodium hydroxide, approximately 0.1 N, boron-free.

B. Hydrochloric acid, conc.

C. Hydrochloric acid, dilute (5 ml. conc.+95 ml. water).

D. Sulfuric acid, conc.

E. Carmine solution. A 0.05 percent solution by weight of carmine in conc. sulfuric acid (0.920 gm./l.). Shake until completely dissolved.

F. Standard boric acid solution. Stock solution. Dissolve 0.5716 gm. of recrystallized H_3BO_3 in distilled water and dilute to 1 liter. One ml. of this solution contains 0.100 mg. of boron.

Preparation of the Standard Curve

Dilute portions of reagent F to obtain standards over the range of 0 to 10 p. p. m. boron. Treat 2 ml. of each solution as described under *Procedure* and determine percent transmittance. For a reference, 2 ml. of distilled water is carried through the entire procedure and set at 100 percent transmittance.

Procedure

Pipet 2 ml. of the sample which should contain not more than 0.02 mg. boron into an Erlenmeyer flask. Add 2 drops of reagent B. Add 10 ml. of D. Mix and cool. Add 10 ml. of E, mix, and allow to stand at least 45 min. for color development. Determine the percent transmittance at 585 mμ against a reference solution of 2 ml. of distilled water carried through the entire procedure. For colored samples such as certain soil extracts, follow the procedure under paragraph headed "Boron Concentration Too Low," except ignite gently after evaporating the sample to dryness.

Calculations

Read the boron concentration from the concentration-transmittance calibration graph. Where the boron concentration is such that the measured transmittance value falls outside the recommended portion of the transmittance range (this method suggests 20 to 95 percent), the sample is either diluted or concentrated to meet these conditions.

Boron Concentration Too Great.—Dilute the sample with distilled water to a known volume, mix, pipet 2 ml. into an Erlenmeyer flask, and proceed as directed above.

Boron Concentration Too Low.—Pipet a suitable aliquot of the sample into a beaker, a platinum dish, or other suitable vessel. Make alkaline with reagent A and add a slight excess. (The same amount should be added to all samples, including a reference.) Evaporate to dryness on a steam bath or in an oven at 95° C. Cool, add 5 ml. of C, and triturate with a rubber policeman. Pour the solution into a conical centrifuge tube and centrifuge at $RCF=1{,}000$ to 1,500. Pipet 2 ml. of the clear solution into an Erlenmeyer flask and follow the procedure shown above, correcting the reading from the standard curve to conform with the aliquot taken.

Reference

Hatcher and Wilcox (1950).

[18] A Coleman Model 14 Universal spectrophotometer with 13 by 13 by 105 mm. matched square cuvettes and filter PC–4 is quite satisfactory. Any good photoelectric colorimeter should be adequate, although perhaps somewhat less accurate.

(74) Dissolved Solids

Procedure

Filter the sample to obtain a perfectly clear liquid. Evaporate a suitable aliquot containing not more than 1.0 gm. of residue to dryness in a weighed platinum dish. Dry to constant weight at 105° C. Cool in a desiccator and weigh. Reserve for the determination of silica under Method 76.

Calculations

Parts per million $DS=$gm. residue$\times$1,000,000/ml. in aliquot.

Reference

Association of Official Agricultural Chemists (1950, *31.3, p. 535*).

(75) pH of Waters

Procedure

See Method 21c.

(76) Silica

(76a) Silica, Gravimetric

Procedure

Acidify the sample or the residue from Method 74 with hydrochloric acid and evaporate to dryness on a steam bath in a platinum dish. Continue the drying for about an hour. Thoroughly moisten the residue with 5 to 10 ml. hydrochloric acid. Allow to stand 10 to 15 min. and add sufficient water to bring the soluble salts into solution. Heat on a steam bath until solution of salts is effected. Filter to remove most of the silica and wash thoroughly with hot water. Evaporate the filtrate to dryness and treat the residue with 5 ml. hydrochloric acid and sufficient water to effect solution of soluble salts, as before. Heat, filter, and wash with hot water. Transfer the 2 residues to a platinum crucible, ignite in a muffle furnace, cool, and weigh. Moisten the contents of the crucible with a few drops of water. Add a few drops of sulfuric acid and a few milliliters of hydrofluoric acid and evaporate on a steam bath under a hood. Repeat the treatment if all the silica is not volatilized. Dry carefully on a hot plate, ignite, cool, and weigh. The difference between the two weights is the weight of silica.

Calculations

Parts per million SiO_2 = gm. $SiO_2 \times 1{,}000{,}000$/ml. in aliquot.

Reference

Association of Official Agricultural Chemists (1950, *31.19, p. 539*).

(76b) Silica, Colorimetric[19]

Apparatus

Spectrophotometer or photoelectric colorimeter.

Reagents

A. Ammonium molybdate solution, 20 percent, stock solution. Dissolve 50 gm. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 200 ml. water (do not heat), make to 250 ml. and filter.

B. Sulfuric acid, 10 N. Add 70.2 ml. conc. sulfuric acid with stirring to 185 to 190 ml. water, cool, transfer to 250-ml. volumetric flask, and dilute to the mark. Solutions A and B may be stored in glass because of the small amount used per determination.

C. Ammonium molybdate, sulfuric acid mixture. Add 1 ml. of reagent B and 2 ml. of A to 200 ml. of water. Use 10 ml. for each determination. A fresh lot of this reagent should be prepared for each set of samples.

D. Standard silica solution, 50 p. p. m. SiO_2. To prepare, dissolve more than the calculated amount of crystalline $Na_2SiO_3\cdot 9H_2O$ in water, filter, and analyze gravimetrically, as described under Method 76a. Add the calculated amount of water necessary to dilute the solution to exactly 50 p. p. m. SiO_2. Store in a polyethylene bottle, not in glass.

[19] This method was adapted for use with a spectrophotometer from a method proposed by Scripps Institution of Oceanography at La Jolla, California.

Preparation of the Standard Curve

Dilute portions of reagent D to obtain standards over the range of 0 to 50 p. p. m. SiO_2. Treat 1 ml. of each solution as described under "Procedure" and determine percent transmittance.

Procedure

To 1 ml. of the sample add 10 ml. of reagent C and mix thoroughly. Determine the percent transmittance after standing 10 min., but not more than 45 min., at 350 mμ against a reference solution of 1 ml. of distilled water carried through the entire procedure. Read the silica concentration from the standard curve and report as p. p. m. SiO_2.

(77) Calcium

Reagents

A. Bromcresol green (sodium salt), 0.1 percent in water.

B. Hydrochloric acid, 6 N.

C. Oxalic acid solution, 1 N. Dissolve 63 gm. $(COOH)_2\cdot 2H_2O$ in 1 liter of water.

D. Ammonium hydroxide solution (1+1).

E. Sulfuric acid, dilute solution (45 ml. water plus 5 ml. conc. sulfuric acid).

F. Standard potassium permanganate, 0.05 N.

Procedure

Take an aliquot of the sample containing between 0.20 and 2.0 meq. of calcium and concentrate, if necessary, to a volume of approximately 200 ml. Add 2 to 3 drops of reagent A, acidify with B, and then add 0.5 ml. of B and 0.5 ml. of C for each 100 ml. of solution. Heat to boiling and neutralize with D. An excess of C is added gradually (5 ml. for each 100 ml. of solution) with constant stirring; the hot solution is made slightly alkaline with D and allowed to boil gently for several minutes. Cool and let stand until the precipitate of calcium oxalate settles. During the cooling, further additions of D may be necessary, in order to keep the solution faintly alkaline.

Filter through a good grade filter paper designed for fine precipitates, receiving the filtrate in a 400-ml. beaker. Reserve the filtrate for the determination of magnesium. Transfer the precipitate to the filter paper and wash both beaker and precipitate with water until free from soluble oxalates. Remove the beaker containing the filtrate and substitute the original beaker. Puncture the tip of the filter paper and wash the precipitate down into the beaker. Pour 50 ml. of reagent E through the funnel and rinse with water. The beaker is heated nearly to boiling and the liberated oxalic acid titrated with F until faintly pink. Add the filter paper and continue the titration until a very slight permanent pink color appears.

Calculations

Milliequivalents per liter of Ca=1,000×normality of $KMnO_4$×(ml. $KMnO_4$−blank)/ml. in aliquot.

Reference

Blasdale (1909).

(78) Magnesium

Reagents

A. Hydrochloric acid (1+1).

B. Diammonium-hydrogen phosphate solution. Make up a 20 percent solution of diammonium-hydrogen phosphate in water. Filter before use. A fresh lot of this reagent should be prepared for each set of samples.

C. Ammonium hydroxide solution (1+1).

D. Ammonium hydroxide, conc.

Procedure

Acidify the filtrate from the calcium determination (Method 77) with reagent A then add 2 ml. in excess. Evaporate on a hot plate. If the weight of pyrophosphate is expected to be 0.0500 gm. or more, reduce the volume to 100 ml.; otherwise, evaporate to 50 ml. and allow to cool. Add 5 ml. of B for each 50 ml. volume, then C drop by drop with stirring, until the solution is strongly alkaline. After a few minutes add 10 ml. of D for each 100 ml. final volume. On the following day, filter on ashless paper and wash with dilute ammonium hydroxide (5+95). Transfer the paper with the precipitate to a weighed silica or porcelain crucible, dry, and ignite to whiteness in a muffle. Cool in a desiccator and weigh.

Calculations

Milliequivalents per liter of Mg=gm. $Mg_2P_2O_7$× 17,969/ml. in aliquot.

Reference

Association of Official Agricultural Chemists (1950, *31.26, p. 541*).

(79) Calcium and Magnesium by the Versenate Method

Procedure

See Method 7.

(80) Sodium

(80a) Sodium by Uranyl Zinc Acetate, Gravimetric

The method of Barber and Kolthoff is the basis for the one here described. It has been modified in only minor details.

Reagents

A. Uranyl zinc acetate:

Uranyl acetate, dihydrate	300 gm.
Zinc acetate, dihydrate	900 gm.
Acetic acid, 30 percent	270 ml.
Distilled water	2,430 ml.

Weigh the salts and transfer to a large flask; add acetic acid and water; shake or stir occasionally until the salts are dissolved. This may take several days. Filter before use.

B. Ethyl alcohol, saturated with *sodium*-uranyl-zinc-acetate precipitate. Filter before use.

C. Ether, anhydrous.

Procedure

Evaporate an aliquot of water sufficient to give 50 to 200 mg. of the triple salt (usually 10 to 20 ml.) in a Pyrex beaker to a volume of 1 to 2 ml. Cool. Add 20 ml. of the filtered reagent A. Stir the solution and allow to stand for 1 hr. Filter through a porous-bottomed porcelain filtering crucible, taking care to transfer all the triple salt onto the filter by means of a small wash bottle filled with A. Wash the beaker 5 times with 2-ml. portions of A and pass the washings through the filter. Allow the crucible to drain completely, because it is important to have the filter and the precipitate free from the reagent before washing with the alcohol. Wash the crucible 5 times with 2-ml. portions of B and, after removing all the alcohol by suction, wash once or twice with C. The suction is continued until the precipitate is dry. Allow the crucible to stand in a desiccator 2 hr. and weigh.

Return the crucible to a suction apparatus and wash with small portions of water until all the soluble material is dissolved and passes through the crucible. Wash with alcohol and ether as above. Dry and weigh. The difference between the first and last weight represents the weight of sodium precipitate. The precipitate is assumed to have the composition $(UO_2)_3NaZn(CH_3COO)_9{\cdot}6H_2O$; molecular weight, 1538.079; percent sodium, 1.4952.

Calculations

Milliequivalents per liter of Na=gm. sodium-uranyl-zinc-acetate precipitate×650.16/ml. in aliquot.

Reference

Barber and Kolthoff (1928).

(80b) Sodium by Flame Photometer

Procedure

See Method 10a.

(81) Potassium

(81a) Potassium by Cobaltinitrite, Gravimetric

Reagents

A. Nitric acid, 1 N.
B. Trisodium cobaltinitrite solution. Prepare an aqueous solution containing 1 gm. of the salt of reagent quality in each 5 ml., allowing 5 ml. for each determination. Filter before use. The solution is stable for some time, but it is preferable to make up a fresh lot before each set of determinations.
C. Nitric acid, 0.01 N.
D. Ethyl alcohol, 95 percent.

Procedure

The aliquot for analysis should contain between 2 and 15 mg. of potassium in a neutral aqueous solution of 10-ml. volume. (Ammonia interferes and if present must be removed by evaporation with sodium hydroxide.) Add 1 ml. of reagent A and 5 ml. of B, mix, and allow to stand for 2 hr. at 15° to 20° C. Filter in a porous-bottomed porcelain filtering crucible, the tare weight of which is known, using C in a wash bottle to make the transfer. Wash 10 times with C and 5 times with 2-ml. portions of D. Aspirate until quite dry. Wipe the outside with a cloth, dry for 1 hr. at 105° C., cool in a desiccator, and weigh.

Modified Procedure

For very small quantities of potassium (0.2 meq./l. or less). Evaporate 200 ml. of the sample in a platinum dish and remove silica as under Method 76a. This aliquot may be used for the determination of dissolved solids as under Method 74 and silica as under Method 76a. After removal of silica, evaporate the filtrate to dryness to remove hydrochloric acid, add 10 ml. of water, 1 ml. of reagent A, and 5 ml. of B, and put the sample in the refrigerator at 5° to 15° C. overnight. When gypsum is high, add more of the reagents (10 ml. of water, 1 ml. of A, and 5 ml. of B for each 5 meq./l. of gypsum present). The following morning, remove the samples from the refrigerator, filter through a porous-bottomed porcelain crucible, and proceed as directed above.

If the sample is high in organic matter, such as a sewage effluent, evaporate the filtrate to dryness, take up in aqua regia (3 parts conc. hydrochloric acid + 1 part conc. nitric acid), and evaporate again before potassium is precipitated.

The composition of the precipitate can be represented by the formula $K_2NaCo(NO_2)_6{\cdot}H_2O$. K = 17.216 percent.

Calculations

Milliequivalents per liter of K = gm. di-potassium sodium cobaltinitrite precipitate × 4,403.4/ml. in aliquot.

Reference

Wilcox (1937).

(81b) Potassium by Cobaltinitrite, Volumetric

Reagents

In addition to the reagents listed under the gravimetric procedure, except 95 percent ethyl alcohol, the following are required:
A. Sodium hydroxide, approximately 0.5 N.
B. Sulfuric acid, conc.
C. Potassium permanganate solution, standard 0.05 N.
D. Sodium oxalate solution, standard 0.05 N.

Procedure

Follow the gravimetric procedure of Method 81a through the precipitation and washing with nitric acid. Omit washing with alcohol. Wash the precipitate into a 250-ml. beaker, place the crucible in the beaker, and make to about 100 ml. with water. Add 20 ml. of reagent A and boil for 3 min. Withdraw into another beaker a slight excess of C, make to 50 ml. with water, and add 5 ml. of B. Pour the hot potassium cobaltinitrite solution into the cold potassium permanganate solution, transfer the crucible, and wash the beaker with a small quantity of water. Add an excess of D, heat to boiling, and complete the titration with potassium permanganate.

Calculations

Milliequivalents per liter of K = normality of $KMnO_4$ × (ml. $KMnO_4$ − blank) × 181.81/ml. in aliquot.

Reference

Wilcox (1937).

(81c) Potassium by Flame Photometer

Procedure

See Method 11a.

(82) Carbonate and Bicarbonate

Reagents

A. Phenolphthalein, 0.25 percent solution in 50 percent alcohol.
B. Sulfuric acid, standard 0.050 N.
C. Methyl orange, 0.1 percent in water.

Procedure

Take an aliquot of the sample containing not more than 1.0 meq. of carbonate plus bicarbonate and dilute to 50 ml., if less than that volume. Add a few drops of reagent A, and, if a pink color is produced, titrate with B, adding a drop every 2 or 3 seconds until the pink color disappears. To the colorless solution from this titration or to the original solution, if no color is produced with phenolphthalein, add 1 or 2 drops of C, continue the titration (without refilling the buret) to the methyl orange end point, and note the total reading. (Reserve the solution for the determination of chloride.) Blank determinations should be run with the reagents and carbon dioxide-free distilled water and corrections made, if necessary.

Remarks

To facilitate calculations a table similar to that shown in APHA Standard Methods (1946) is included (table 18).

TABLE 18—*The titration of hydroxide, carbonate, and bicarbonate ions in the presence of phenolphthalein and methyl orange indicators.*

Result of titration [1]	Titration value related to each ion—		
	Hydroxide	Carbonate	Bicarbonate
$P=0$	0	0	T
$P<\frac{1}{2}T$	0	$2P$	$T-2P$
$P=\frac{1}{2}T$	0	$2P$	0
$P>\frac{1}{2}T$	$2P-T$	$2(T-P)$	0
$P=T$	T	0	0

[1] P=Titration to the phenolphthalein end point; T=total titration to the methyl end point.

Calculations

Ion sought, milliequivalents per liter of either OH, CO_3, or $HCO_3=1000\times$ normality of the acid $\times$ [titration value (from table 18) in ml. acid − blank]/ml. in aliquot.

References

American Public Health Association and American Water Works Association (1946, *p. 9*), Association of Official Agricultural Chemists (1950, *31.18, p. 539*).

(83) Sulfate

Reagents

A. Hydrochloric acid, conc.

B. Barium chloride solution, 10 percent. Dissolve 100 gm. $BaCl_2 \cdot 2H_2O$ in 1 liter of water and filter.

C. Methyl orange, 0.1 percent in water.

Procedure

Take an aliquot of the sample containing between 0.2 and 5 meq. of sulfate and, if necessary, dilute to a volume of approximately 200 ml. Add a few drops of reagent C and 1 ml. of A. Heat to boiling and add an excess of B drop by drop with constant stirring. Allow to stand on the water bath until the volume is reduced to about 50 ml. After cooling, the precipitate of barium sulfate is filtered through an ashless filter paper and washed with water until free from chloride. The filter paper is then carefully folded, placed in a tared porcelain or silica crucible, ignited in a well-ventilated muffle at low red heat, and weighed.

Calculations

Milliequivalents per liter of SO_4=gm. $BaSO_4\times$ 8568.2/ml. in aliquot.

Reference

Association of Official Agriculture Chemists (1950, *31.27, p. 541*).

(84) Chloride

Reagents

A. Potassium chromate indicator. Dissolve 5 gm. of potassium chromate in water and add a saturated solution of silver nitrate until a slight permanent red precipitate is produced; filter and dilute to 100 ml.

B. Standard silver nitrate solution, 0.05 N. Dissolve 8.4944 gm. silver nitrate in water and dilute to 1 liter. Check by titration against pure sodium chloride or standard potassium chloride (reagent A, Method 72).

Procedure

To the solution from the carbonate and bicarbonate determination (Method 82), add 1 ml. of reagent A and titrate with B. Correct for the quantity of silver nitrate solution necessary to give, in 50 ml. of chloride-free water with 1 ml. potassium chromate indicator, the shade obtained at the end of the titration of the sample.

If the size of aliquot that is suitable for the carbonate-bicarbonate titration is too large for the chloride determination, a smaller aliquot must be taken and neutralized to methyl orange. The aliquot should contain not more than 2 meq. of chloride.

Calculations

Milliequivalents per liter of Cl = $1000\times$ normality of the $AgNO_3\times$ (ml. $AgNO_3$ − blank)/ml. in aliquot.

Reference

Association of Official Agricultural Chemists (1950, *31.10, p. 536*).

(85) Fluoride

Remarks

Method suggested is given in Standard Methods, APHA (1946), substituting sulfuric acid for perchloric acid and silver sulfate for silver perchlorate.

It has been found reliable for potable waters of ordinary composition. Up to the following limits expressed as parts per million it is not interfered with by: Chloride ion (Cl)—500 ppm., sulfate ion (SO_4)—200 ppm., alkalinity (expressed as $CaCO_3$)—200 ppm., acidity (expressed as $CaCO_3$)—200 ppm., iron (Fe)—2 ppm., aluminum (Al)—0.5 ppm., phosphate ion (PO_4)—1 ppm., color 25, turbidity 25.

If limits are exceeded, separate fluoride by distillation.

Reagents

A. Acid zirconium alizarin reagent. Dissolve 0.3 gm. zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) in 50 ml. distilled water contained in a 1-liter glass-stoppered flask. Dissolve 0.07 gm. alizarin sodium monosulfonate in 50 ml. distilled water and pour slowly into the zirconium oxychloride solution, while swirling the flask. This solution clears on standing for a few minutes. Prepare a mixed acid solution as follows: Dilute 112 ml. conc. hydrochloric acid to 500 ml. with distilled water. Dilute 37 ml. conc. sulfuric acid to 500 ml. with distilled water. After cooling, mix the two acids. To the zirconium alizarin solution in the 1-liter flask, add the mixed acid solution to the mark and mix. The reagent changes in color from red to yellow within an hour and is then ready for use. If stored in a refrigerator, it may be used for 60 to 90 days.

B. Standard sodium fluoride solution. Dissolve 0.221 gm. sodium fluoride in distilled water and make up to 1 liter. Dilute 100 ml. of the stock sodium fluoride solution to 1 liter with distilled water. One ml. is equivalent to 0.01 mg. of fluoride.

Procedure

To 100 ml. of sample containing not more than 0.14 mg. fluoride and to standards made up to 100 ml. with distilled water, contained in 100-ml. matched Nessler tubes, add 5 ml. of reagent A, accurately measured from a 5-ml. volumetric pipet. Mix and compare sample with standards after standing 1 hr. at room temperature. Recommended standards are 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, 0.10, 0.12, and 0.14 mg. of fluoride. Since the color of the zirconium-alizarin lake varies with temperature, samples and standards should have the same temperature within 1° or 2° C., before adding the reagent.

Calculations

Parts per million F = mg. F × 1,000/ml. in aliquot.

Reference

American Public Health Association and American Water Works Association (1946, *39A–2, p. 76,* and *39B–2, p. 77*).

(86) Nitrate

(86a) Nitrate, Phenoldisulfonic Acid

(For water of low chloride content.)

Procedure

See Method 15.

(86b) Nitrate, Devarda

(For water of high chloride content.)

Apparatus

Nitrogen distilling apparatus with scrubber bulbs.

Reagents

A. Devarda alloy.
B. Sodium hydroxide, saturated solution.
C. Boric acid, 2 percent solution.
D. Standard sulfuric acid, 0.05 N.
E. Bromcresol green-methyl red (BCG–MR) indicator solution.[20] Prepare a 0.1 percent bromcresol green solution, adding 2 ml. 0.1 N sodium hydroxide per 0.1 gm. of indicator. Prepare a 0.1 percent methyl red solution in 95 percent ethyl alcohol, adding 3 ml. 0.1 N sodium hydroxide per 0.1 gm. of indicator. Mix 75 ml. bromcresol green, 25 ml. methyl red, and 100 ml. of 95 percent ethyl alcohol. The indicator should be gray in a solution containing boric acid and ammonium sulfate in concentrations equal to those encountered in the Devarda procedure. It is often necessary to add a little of one or the other of the indicators until the proper shade is obtained. The color change is from green in alkali through gray at the end point to red in acid solution.

Procedure

Place 50 ml. of the sample, or such volume as will contain not less than 0.2 meq. nitrate, in a Kjeldahl flask and add 2 gm. Devarda alloy. Make up to 300 ml. with distilled water, then add 2 ml. of reagent B, allowing it to run down the side of the flask so that it does not mix with the contents at once. Connect with the distilling apparatus and rotate the flask to mix. Heat slowly at first and then at such a rate that the 200 ml. of distillate required will pass over in 1 hr. Collect the distillate in 50 ml. of C. The ammonia is titrated with D, using indicator E.

Calculations

Milliequivalents per liter of $NO_3 = 1{,}000 \times$ normality of acid × (ml. acid − blank)/ml. in aliquot.

Reference

Association of Official Agricultural Chemists (1950, *2.30, p. 14*).

[20] Chapman, H. D. Private communication.