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GKI CHLORIDE IN WATER, ANALYSIS METHOD
GKI BORON IN WATER, ANALYSIS METHOD

MASTER

By

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May 1979

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

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KAMP KEROGEN LABORATORY

Water Analysis
Method

CHLORIDE

Mercuric Nitrate Method

Outline:

Chloride can be titrated with mercuric nitrate because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbozone indicate the endpoint of this titration by formation of a purple complex with mercuric ions.

Interferences:

Bromide and iodide are titrated with mercuric nitrate in the same manner as chloride. Chromate, ferric, and sulfite ions interfere when present in excess of 10 mg/l.

Organic anions as found in oil shale process and ground water must be oxidized to eliminate interferences during titration. The procedure is briefly given below.

Procedure to eliminate organic interference:

1. Acidify sample by adding approximately 10% sample volume of concentrated nitric acid.

2. Gently boil in a beaker with watch glass cover until volume is reduced by approximately 15% to 20%.

3. Cool, add sufficient water to reconstitute to original volume. Follow normal procedure for analysis of chloride.

Apparatus;

1. 10 ml microburet capable of being read to 0.01 ml.

2. 150 ml beakers.

3. Magnetic stirrer and stirring bars.

4. General volumetric glassware.

Reagents:

1. Standard sodium chloride 0.0141 N: Dissolve 0.8241 gm NaCl (dried at 140°C) in chloride free water and dilute to 1000 ml; 1.00 ml = 500 μg Cl.

2. Nitric acid, HNO_3, 0.1 N.

3. Sodium Hydroxide, NaOH, 0.1N.

4. Reagents for low-chloride titrations (100 mg/l):

   a. Indicator-acidifier reagent: the nitric acid concentration of this reagent is an important factor in the success of the determination and can be varied as indicated in 1) or 2) to suit the alkalinity range of the sample being titrated.. Reagent 1) contains sufficient nitric acid to neutralize a total alkalinity of 150 mg/l as $CaCO_3$ to the proper pH in a 100 ml sample.

1. Dissolve in the order named, 250 mg S- Diphenylcarbazone, 4.0 ml concentrated HNO_3, and 30 mg Xylene cyanol FF in 100 ml of 95% ethyl alcohol or isopropyl alcohol. Store in a dark bottle in a refrigerator. This reagent is not stable indefinitely and should be discarded when a slow endpoint and high results occur.

2. Because pH control is critical in this method, adjust the pH of highly alkaline or acid samples to 2.5 ± 0.1 with 0.1 N HNO_3 or NaOH, not with Na_2CO_3. Use a pH meter with a non-chloride type reference electrode for the pH adjustment. If only the usual chloride-type reference electrode is available for pH adjustment, determine the amount of acid or alkali required to achieve a pH of 2.5 ± 0.1 and discard this sample portion. Treat a separate sample portion with the determined amount of acid or alkali and continue the analysis to the prescribed end. Under these circumstances, omit the nitric acid from the indicator reagent to maintain the proper sample pH. Alternatively, vary the nitric acid concentration of the indicator-acidifier reagent to accommodate conditions wherein water samples of very high or very low alkalinity are being analyzed.

   b. Standard mercuric nitrate titrant, 0.0141 N: Dissolve 2.3 gm $Hg(NO_3)_2$ or 2.5 gm $Hg(NO_3)_2\text{-}H_2O$ in 100 ml distilled water containing 0.25 ml concentrated HNO_3. Dilute to just under one l. Standardize according to Procedure 1, then adjust to exactly 0.0141 N. Make a final standardization. Store in a dark bottle. Standard titrant of 0.0141 N is equivalent to 500 ug Cl/1.00 ml.

5. <u>Reagents for high-chloride titrations (100 mg/l)</u>:

   a. Mixed indicator reagent: dissolve 5 gm diphenylcarbazone powder and 0.5 gm bromophenol blue powder in 750 ml 95% ethyl or isopropal alcohol and dilute to one l with ethyl or isopropyl alcohol..

   b. Strong standard mercuric nitrate titrant, 0.141 N: Dissolve 25gms Hg $(NO_3)_2\text{-}H_2O$ in900 ml. distilled water containing 5.0 ml concentrated HNO_3. Dilute to just under one l, and perform a preliminary standardization by following Procedure 2. Use replicates containing 25.00 ml standard NaCl solution and 25 ml distilled water. Adjust the titrant to 0.141 N and make a final standardization. The chloride equivalence of the titrant is 5.00 mg/1.00 ml.

Procedure:

1. Titration of low-chloride concentrations:

    a. Use a 100 ml sample or smaller portion diluted to 100ml so that the chloride content is less than 10 mg.

    b. Add 1.0 ml of indicator-acidifier to the sample. (The color of the solution should be green-blue at this point. A light green indicates a pH of less than 2.0; a pure blue indicates a pH of more than 3.8.)

    c. Titrate the treated sample with 0.0141 N mercuric nitrate titrant to a definite purple end point. The solution will turn from green-blue to blue a few drops from the end point.

    d. Determine the blank by titrating 100 ml distilled water containing 10 mg $NaHCO_3$.

2. Titration of high-chloride concentrations:

    a. Place 50.0 ml sample in a 150 ml beaker (5ml of sample may be used when more than 5 ml titrant are needed).

    b. Add approximately 0.5 ml mixed indicator reagent and mix well. The color should be purple.

    c. Add 0.1 N NHO_3 dropwise until the color just turns yellow.

    d. Titrate with 0.141 N mercuric nitrate to the first permanent dark purple.

    e. Titrate a distilled water blank using the same procedure.

Calculation:

$$\text{mg/l Cl} = \frac{(A-B) \times N \times 35450}{\text{ml sample}}$$

where A= ml titration for sample,
B= ml titration for blank, and
N= normality of $Hg\ (NO_3)_2$.

Precision and Accuracy:

A sample containing chloride in the 250 mg/l range was analyzed by 10 laboratories with a standard deviation of 3.3 % and a relative error of 2.9%.

References:

1. Standard Methods for the Examination of Water and Wastewater, 14 th Edition, pp 306-308, Method 408 (Chloride) (1975).

GEOKINETICS INC.

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WATER ANALYSIS

Method
Boron

Principle:

When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red colored product called rosocyanine is formed. The rosocyanine is taken up in a suitable solvent and the red color is compared with standards visually or photometrically.

Interference:

Nitrate nitrogen concentration above 20 mg/l interfere.

High results are given when the total of calcium and magnesium hardness exceeds 100 mg/l. Passing the sample through a strong acid cation exchange column will remove the interfering cations.

Minimum detectable quantity:

0.2 micrograms B.

Apporatus:

1. Spectrophotometer, for use at 540 nanometer with a light path of 2 cm.
2. Evaporating dishes, 100 to 150 ml. capacity made from teflon or vycor.
3. Water Bath, set at 55°C.± 2°C.
4. Glass-stoppered volumetric flasks, 50, 100,200, and 250 ml capacity.
5. Ion-exchange column, made from a 100 ml. buret.

Reagents:

1. Stock boron solution: Dissolve 571.6 mg. anhydrous boric acid, $H_3 Bo_3$, in distilled water and dilute to 1000 ml. 1.00 ml=100 micrograms B. (Do not dry the boric acid but use ACS grade anhydrous boric acid and keep reagent tightly stoppered to prevent absorption of atmospheric moisture.

2. Standard boron solution: Dilute 10.00 ml. stock boron solution to 1000 ml. with distilled water; 1.00 ml.=1.00 micrograms Boron.

3. Curcumin reagent; Dissolve 100 mg. finely ground curcumin and 12.5 gm. oxalic acid in approximately 100 ml. of 95% ethyl alcohol. Add 10.5 conc. HCl and make the solution up to 250 ml. with ethyl alcohol in a 250 ml. volumetric flask. This reagent will be stable for several days if stored in a refrigerator.

4. Ethyl or isopropyl alcohol: 95%

5. Strongly acidic cation exchange resin; such as Rexyn 101 (from Fisher Scientific Co.)

6. Hydrochloric Acid; HCl, 1+5.

7. Sodium Peroxide; Na_2O_2, to be used in the event of high concentrations of organics that foul the ion-exchange resin.

Procedure;

1. Precautions. The accuracy and repeatability of this method depends very strongly on the skill and care of the analyst. Close control of all variables such as volume and concentrations of reagents, as well as time and temperature is essential.

2. Preporation of calibration curve.

a. Pipet 0(blank) 0.20, 0.40, 0.60,0.80, and 1.00 micrograms boron into evaporating dishes of the same type, size and shape.

b. Add distilled water to each standard to bring the total volume to 1.0 ml.

c. Add 4.0 ml. curcumin reagent to each and swirl each dish gently to mix contents thoroughly.

d. Float the dishes on a water bath set at 55°C. Make sure the temperature does not vary by more than ± 2°C from 55°C.

e. Time the evaporation for exactly 80 minutes.

f. Remove from bath and let dishes cool to room temp. (3 to 5 Min.)

g. Add 10.0 ml. of 95% ethyl or isopropyl alcohol to each dish. Stir gently with a teflon rod to insure complete dissolution of the red-colored product.

h. Wash the contents of each dish into a 50 ml. volumetric flask. Be sure to remove all colored material Dilute to the mark with 95% ethyl or isopropyl alcohol. Mix thoroughly by inverting.

i. Read the absorbance at 540 nm. in 2 cm. test tubes within 1 hour of drying the samples. The calibration curve is linear from 0 to 1.00 mg. boron, but deviates rapidly from linearity beyond 1.00 micrograms.

3. Sample treatment.

a. Samples that are moderate to highly colored must be digested with, Na_2O_2, sodium peroxide to destroy the organics that foul the ion-exchange column.

1. Evaporate 10.0 ml of sample in a zirconium crucible in a drying oven at 100°C.

2. Add approx. 1-2 grams Na_2O_2 (enough to cover the dried residue to a depth of 1-2 mm.)

3. Gently heat the open crucible over a flame on a wire tripod until the mixture becomes fluid. Heat with gentle swirling for 2-3 min.

4. Cautiously immerse the crucible about 2/3 in a beaker or dish of cool water to solidify the cake and dislodge it from the crucible. (Caution: make sure there is a sizzling sound when the crucible is immersed.)

5. When crucible bottom is only warm to the touch, add 5 to 10 ml. distilled water, cover and let set until all of the solid has dissolved. Proceed to step(b) for ion-exchange treatment.

b. Pour sample (usually 10 ml. for produced water or ground water) through activated exchange column at the rate of about 0.2 ml/ml. resin in column per minute. Wash it through with distilled water.

1. Add a small plug of glass wool to a 100 ml. buret to retain resin.

2. Add strong acid cation exchange resin (sulfonic, acid type) through water to about the 50 ml. mark of the buret.

3. Pass 50 ml. 1+5 HCl through the column at rate given above. Wash resin free of acid with distilled water. The column is now activated.

c. Make an appropiate dilution of sample to contain not more than 1.00 micrograms boron. (a 10.0 ml. aliquot of the 200 ml. of sample from the ion exchange column, diluted to 100 ml. is usually satisfactory as a working solution. 0.1 ml. to 1.0 ml. of this 100 ml. aliquot should be in the proper range. This corresponds to a range of 4 mg/l boron to 2000 mg/l boron.

d. Put 0.1 ml. to 1.0 ml. of aliquot in the evaporating dish. If amount of aliquot used is less than 1.0 ml. add sufficient distilled water (by pipet) to make 1.0 ml., in evaporating dish.

e. Add 4.0 ml. curcumin reagent and proceed as with standards for calibration.

f. A blank (reagent) and a standard must also be carried through the procedures as outlined above every time a sample is run.

Calculation:

Compare absorbance from blank and standard with calibration curve, if acceptable, read micrograms Boron from calibration curve or adjusted curve.

$$\frac{\text{Micrograms Boron,}}{S} = \text{micrograms/ ml. Boron in sample}$$

S = actual mls. of samples contained in aliquot used.

Reference:

Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp. 574-581, Methods 405 A (boron) (1975).