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METHODS OF ANALYSIS OF ANISOLE-BF_3 SOLUTIONS

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INTRODUCTION

The methods of analysis given in this report are those which were used in the Analytical Chemistry Division of the Oak Ridge National Laboratory for analyzing samples which were derived from the experimental work on the separation of the isotopes of boron by chemical exchange.

The samples consisted principally of boron trifluoride solutions in anisole (methyl phenyl ether, $CH_3OC_6H_5$). The boron concentration ranged from a few parts per million to 5 or 6 per cent. Boron was determined on all samples. During the early stages of the project, iron and copper were occasionally determined, while a limited number of aqueous solutions and water extracts of anisole solutions of BF_3 were analyzed for fluoboric and hydroxyfluoboric acids, boric acid, total boron, and total fluoride.

Boron was determined by the use of either a spectrophotometric or volumetric method, depending on the amount available. Initially, if the amount of sample and boron concentration were such as to provide a total of at least 2 to 4 mg of boron, the volumetric method was utilized and found to be satisfactory. For smaller amounts, the spectrophotometric method was used. Later, because of its greater speed and simplicity, the spectrophotometric method was used for samples in the intermediate range of 4 to 20 mg of boron in preference to the volumetric method. The latter method includes a step which requires four hours for hydrolyzing fluoboric acid completely to boric acid. This time-consuming step is avoided by the use of the spectrophotometric method.

Iron and copper were determined by spectrophotometric methods. Orthophenanthroline was used as the chromogenic reagent in the determination of iron, whereas sodium diethyldithiocarbamate was used for determining copper.

A special technique, developed by Wamser[1], was used, with some modifications, for the determination of fluoboric and hydroxyfluoboric acids, boric acid, and fluoride in a few samples.

The methods which are compiled in this report are as follows:

Boron, Spectrophotometric Carminic Acid Method
Boron, Volumetric Method
Iron, Orthophenanthroline Spectrophotometric Method
Copper, Sodium Diethyldithiocarbamate Spectrophotometric Method
Determination of Total Fluoride, Total Boron and Products of Hydrolysis of BF_3 in Aqueous Solutions

(1) Wamser, Christian, A. J., Am. Chem. Soc., 73, 409 (1951)

BORON, SPECTROPHOTOMETRIC CARMINIC ACID METHOD

I. SCOPE

This method is suitable for the determination of boron in microgram quantities in aqueous solutions or in organic solutions from which the boron can be extracted by water.

II. PRINCIPLE

Carminic acid or carmine reacts with boron in solutions of concentrated sulfuric acid to produce an intense color, which is suitable for use in the spectrophotometric determination of boron. The color change is from a bright red in the absence of boron, to a bluish red or blue in the presence of boron[2]. The absorbance obeys Beer's law over the range of 0 to 30 μg of boron in a final volume of 22 ml.

III. STATUS

Hatcher and Wilcox[2] first used the color produced by the reaction of boron with carmine No. 40 N. F. for the quantitative determination of boron in water, soil extracts and plant tissues. They noted that carminic acid can also be used for this purpose. In the application of this method to the determination of boron in biological materials, Smith et al.[3] found that, when carminic acid was used as the chromogenic reagent, the color developed and reached maximum intensity within five minutes after the addition of the reagent, and that the color was stable for at least 70 minutes. On the other hand, when carmine No. 40 N. F. was used, 35 minutes was required for the color to reach maximum intensity.

The intensity of the color is affected by the concentration of the sulfuric acid in the solution in which it is developed. Consequently, the ratio of the test portion of the aqueous sample solution to sulfuric acid must closely approximate the ratio used in the preparation of the calibration graphs. To maintain this ratio, a 2-ml test portion is used in all cases. Samples which are too dilute or too concentrated with respect to boron may be concentrated by evaporation or diluted until the total boron concentration falls within the desired range when 2-ml portions are used for analysis.

This method has proved particularly useful for the determination of boron when present as BF_3 in anisole. In water extracts from anisole, the boron is present as fluoboric acid or hydrolytic products thereof, including some boric acid. In the volumetric method for macro amounts of boron, it is necessary to reflux the solution of fluoborate with calcium chloride for a long period of time in order to hydrolyze all of the fluoborates to boric acid. Mannitol is then added and the boric acid is titrated with standard sodium hydroxide. This method is not only time-consuming but it is unsuited for microgram amounts of boron. The spectrophotometric method is much more rapid than the volumetric method, and it is applicable for samples that contain only a few micrograms of boron.

Fluoride, in the concentrations found in the aqueous fluoborate extracts of anisole solutions of BF_3, does not interfere with the spectrophotometric determination of boron to a significant extent. Hatcher and Wilcox[2] eliminated the interference of nitrate and nitrite by the addition of hydrochloric acid. Several workers[2,3] reported that no other inorganic substances commonly found in waters, soils, plants and biological materials appeared to interfere.

Smith et al.[3], using a Beckman Model DU spectrophotometer and developing the color in a final volume of 11 ml, found that the standard deviation for 2 to 15 μg of total boron is of the order of 2 μg.

References

1. R. Q. Brewster, Organic Chemistry, pp. 743 and 744, Prentice-Hall (1948).
2. J. T. Hatcher and L. V. Wilcox, Anal. Chem., 22, 597 (1950).
3. W. C. Smith, Jr., A. J. Goudie, and J. N. Siverston, Anal. Chem. 27, 295 (1955).

IV. APPARATUS

1. Flasks, volumetric, DRY, 25-ml.
2. No other special apparatus is required for aqueous solutions.

Samples containing BF_3, in anisole are commonly delivered in volumetric flasks or in bulbs closed by a stopcock. Provide connecting tubes with the appropriate ground glass joints as needed to transfer the samples from sample bulbs to separatory funnels. Fabricate these connecting tubes, as required, to fit the particular type of sample bulb that is encountered.

V. REAGENTS

1. Boron solution, stock, 500 μg B per ml, for preparation of standard solutions. Dissolve 2.86 g of boric acid, H_3BO_3, in one liter of water. Dilute aliquots of the stock solution, as required, to prepare solutions for use in the determination of a calibration factor (NOTE b).
2. Carminic acid, 0.05 wt per cent. Dissolve 0.364 g of carminic acid in 400 ml of concentrated sulfuric acid (reagent grade, 95 to 96 per cent H_2SO_4).
3. Diethyl ether.
4. Sulfuric acid, concentrated.

VI. SAFETY

Wear rubber gloves when transferring solutions of concentrated sulfuric acid to small containers, including the absorption cells.

VII. SAMPLING

Transfer all of the sample of BF_3 in anisole to the separatory funnel. Keep the time of exposure of the sample to the atmosphere to a minimum during the transfer, since samples rich in BF_3 in anisole have an appreciable vapor pressure, even at room temperature. See Appendix for a method for accomplishing this transfer.

VIII. PROCEDURE

A. Preparation of a Calibration Graph

1. Prepare boric acid solutions containing 2, 4, 6, 8 and 10 μg of boron per ml. Process 2-ml portions of each of these solutions through Steps 10 thru 16, Part B. (Only one reagent blank solution is required.)

2. Construct a calibration graph by plotting absorbancy as ordinate versus concentration (μg B per ml of **final** test solutions) as abscissa on rectilinear graph paper, or,

3. Calculate a calibration factor as follows: Divide the concentration of boron, μg per ml, by the corresponding absorbancy for each standard solution used. Average the results and take the average as the calibration factor.

B. Boron in a Solution of Boron Trifluoride in Anisole

1. Weigh the sample and container to $\pm$ 0.1 g.

2. Add a suitable volume of water from a measuring cylinder to a 125-ml separatory funnel (NOTE a).

3. Transfer the sample to the 125-ml separatory funnel (see Apx.). Stopper the funnel immediately.

4. Wash the sample container with three portions of ethyl ether, each portion having a volume approximately one-third that of the sample solution. Add the washings to the separatory funnel. Keep the funnel stoppered except when adding solutions.

5. Dry the sample container and weigh it to 0.1 g. Deduct this weight from the weight of the flask and sample (Step 1) to obtain the sample weight. This step may be delayed until later.

6. Shake the separatory funnel for 15 seconds. Let it stand until the two phases are completely separated.

7. Drain off the lower aqueous phase into a 50 or 100-ml volumetric flask (NOTE a).

8. Twice repeat Steps 6 and 7, adding the aqueous phases to the initial extract in the volumetric flask.

9. Dilute the combined aqueous extract to volume (NOTE c). Mix well.

10. Pipet a 2-ml aliquot of the diluted extract into a dry, 25-ml volumetric flask (NOTE d). Also, pipet 2 ml of water into a second 25-ml volumetric flask (for reagent blank) (NOTE e).

11. Pipet 10 ml of concentrated sulfuric acid into each of the flasks and then stopper the flasks.

12. Place the flasks in an ice bath and let the solution cool to room temperature. Mix the solutions by swirling the flasks. Cool the solutions again until they are at approximately room temperature (NOTE e).

13. Pipet 10 ml of the carminic acid reagent into the flasks.

14. Stopper the flasks immediately and mix the contents thoroughly. Let the solutions stand for 10 minutes.

15. Fill one cell from a set of matched cells of 1-cm light path with the sample solution and the other cell with the reagent blank solution (NOTE f).

16. Measure the absorbancy of the sample solution against the reagent blank by means of a Beckman, Model DU or Model B, spectrophotometer at a wavelength of 585 mμ.

C. Boron in Water Solutions

1. Measure the volume of the sample, or dilute or concentrate it to a specific volume (NOTES d and g), and follow the procedure of Part B, Steps 10 through 16.

Calculations

A. Boron in Solution of BF_3 in Anisole

Let W = sample weight, g,

V_1 = volume to which aqueous extract was diluted, ml,

Z = dilution factor = 11 (for volumes specified)

A = absorbancy

F = calibration factor = μg of B per ml in final test solution per unit absorbancy

C = μg of B per ml (from calibration graph) in final test solution

When calibration factor, F, is used,

Boron in sample, $\mu g = AFZV_1$

$$ppm = \frac{AFZV_1}{W}$$

$$\text{per cent} = \frac{10^{-4}AFZV_1}{W}$$

When C is determined from a calibration graph,

$$\text{Boron in sample, } \mu g = CZV_1$$

$$\text{ppm} = \frac{CZV_1}{W}$$

$$\text{per cent} = \frac{10^{-4}CZV_1}{W}$$

B. For Boron in aqueous Solution, where no extraction was necessary,

Let V_1 = volume of sample or volume to which sample was diluted (or concentrated), ml

Use the equations given above for making calculations.

Notes

a. If the total amount of boron in the samples is anticipated to be less then 500 μg, use 10 to 12-ml portions of water for extractions (Steps 2 and 8) and dilute the water extract to 50 ml (Step 9); if more than 500 μg is anticipated, use 20 to 25 ml portions of water for each extraction and dilute the water extract to 100 ml.

b. Smith et al.[3] prepared a stock solution of boron (100 μg B per ml) by dissolving 0.2203 g of National Bureau of Standard sodium tetraborate decahydrate in distilled water and diluting to 250 ml.

c. If the aqueous extract is to be reserved or if the analysis is to be interrupted at this point, store the aqueous extract in a polyethylene bottle that is equipped with a tightly fitting stopper.

d. A 2-ml sample is used in all cases because the intensity of the color is a function of the concentration of the sulfuric acid in the solution in which it is developed. If the absorbancy is found to be too large to measure satisfactorily, dilute an aliquot of the diluted extract (Step 9) to a suitable concentration, that is, one that will yield an absorbancy reading of approximately 0.1 to 0.5.

If the absorbancy is too low to be measured satisfactorily, the entire remaining water extract (Step 9) or an aliquot thereof may be concentrated as follows: Transfer the solution to a beaker of boron-free glass or to a platinum or Vycor dish. At the same time, transfer an equal amount of water to a similar container (for the reagent blank). Add one ml of 0.1 M NaOH to each container and evaporate the solutions to dryness. Add to each 3 ml of water and dissolve all of the residues. Pipet 2 ml of each solution into 25-ml volumetric flasks and follow the procedure through Steps 10 to 16, inclusive. Measure the absorbancy of the sample solution against the reagent blank solution processed in the same manner as the sample solutions.

e. In order to determine when the solutions are cooled sufficiently, check the temperature (Step 12), by reference to a thermometer in an additional 25-ml flask that also contains 2 ml of water and 10 ml of concentrated sulfuric acid, which were mixed and placed in the cooling bath at the same time as the samples.

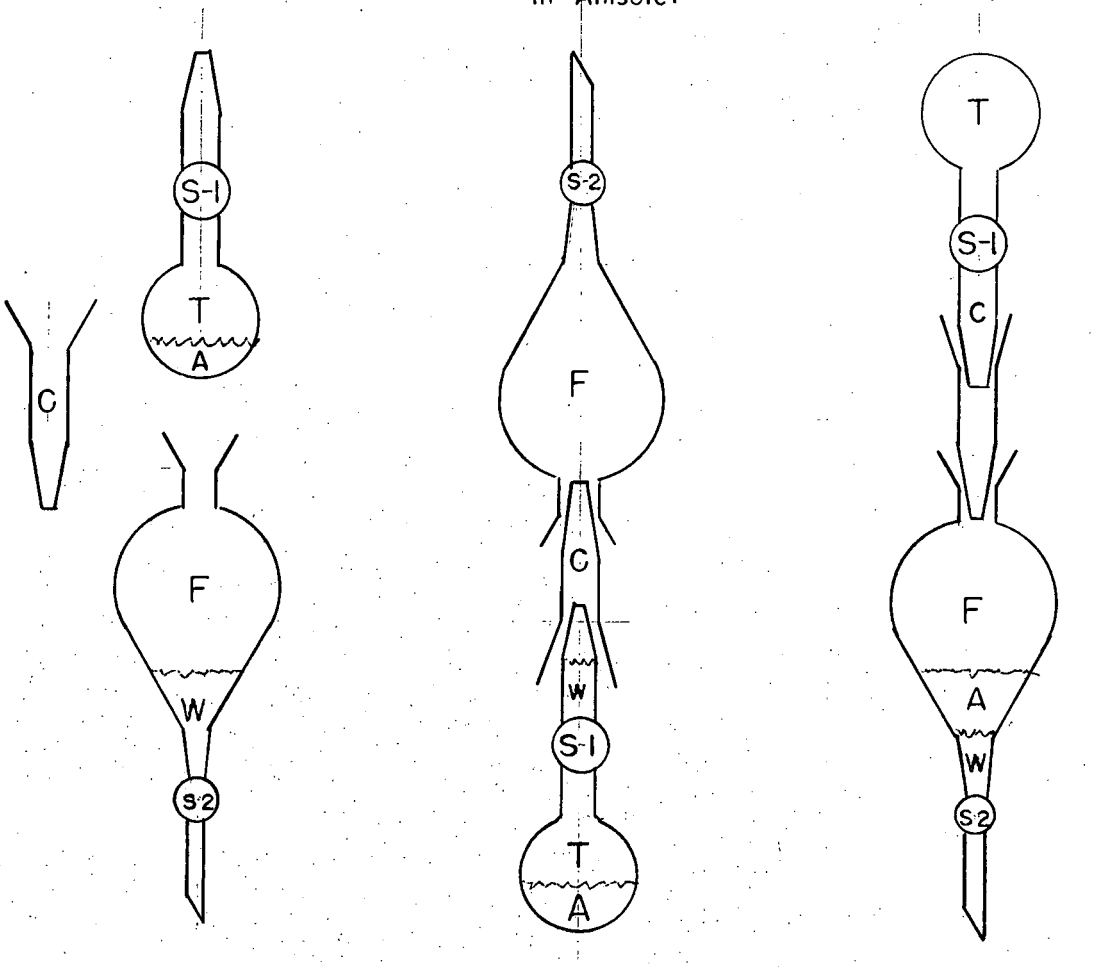
f. Stopper the cell that contains the reagent blank solution. This is especially necessary if it is to be used as a reference solution for measuring a series of samples. Experience in this laboratory and elsewhere[3] indicates that, especially in humid weather, the concentrated sulfuric acid will rather rapidly absorb sufficient water to dilute the sample enough to change the intensity of the color to a measurable degree.

The act of emptying the absorption cell without smearing concentrated sulfuric acid on the optical face of the cell, is one of the most troublesome steps in this procedure. In order to accomplish this transfer, it is convenient to place a damp cloth in a shallow tray. Empty the cell by inverting it over a beaker and, after the solution has drained out and, while the cell is still inverted, touch the open end of the cell to the damp cloth. The cell can now be turned open end up and is ready to be filled again. Smearing of sulfuric acid is further controlled by wiping the face of the cell with a damp cloth from bottom to top before wiping it with lense tissue.

g. If boron concentration, μg per ml, only is required, it is unnecessary to measure the volume of the sample or to dilute it to a known volume.

IX. APPENDICES

Figure A. Schematic Arrangement of Apparatus for Transferring Samples of BF_3 in Anisole.



1. Apparatus

2. Arrangement of apparatus connected to evacuate (F)

3. Arrangement of apparatus for transfer of anisole

LEGEND:

T. Sample tube
F. Separatory funnel
A. Anisole
C. Connecting tube
S—1 and S—2. Stopcocks
W. Water

Method of Transfer

Refer to Figure A 1

1. Close stopcock S-2 and add a suitable quantity of water (Step 2 of the Procedure) to the separatory funnel (F).
2. Connect the sample tube (T) to the separatory funnel (F) by means of the connecting tube (C).

Refer to Figure A 2

1. Invert the assembled apparatus and open stopcock S-2.
2. Connect the end of the separatory funnel to a source of vacuum and evacuate the separatory funnel (F).
3. Close stopcock S-2 and then disconnect the funnel from the vacuum source.

Refer to Figure A 3

1. Invert the assembly and open stopcock S-1.
2. Transfer the anisole solution from the sample tube (T) to the separatory funnel (F) by gently shaking the assembled apparatus.
3. Remove, as a unit, the connecting tube (C) and the sample tube (T), then immediately stopper the separatory funnel.
4. To wash the sample tube (T) (Step 4 of the Procedure), first evacuate it and then connect it to the connecting tube (C).
5. Pour the predetermined quantity of ether (Step 4 of the Procedure) into the connecting tube (C).
6. Gradually open stopcock S-1 to permit the ether to run into the sample tube; then quickly close the stopcock when the ether level reaches the top of the stopcock.
7. Shake the sample tube to dissolve any anisole that remains in the tube.
8. Assemble the apparatus, as shown in Fig. 1c, and transfer the ether to the separatory funnel by gently shaking the assembled apparatus.
9. Twice repeat the above Steps 3 to 8, inclusive.

IX APPENDICES (Continued)

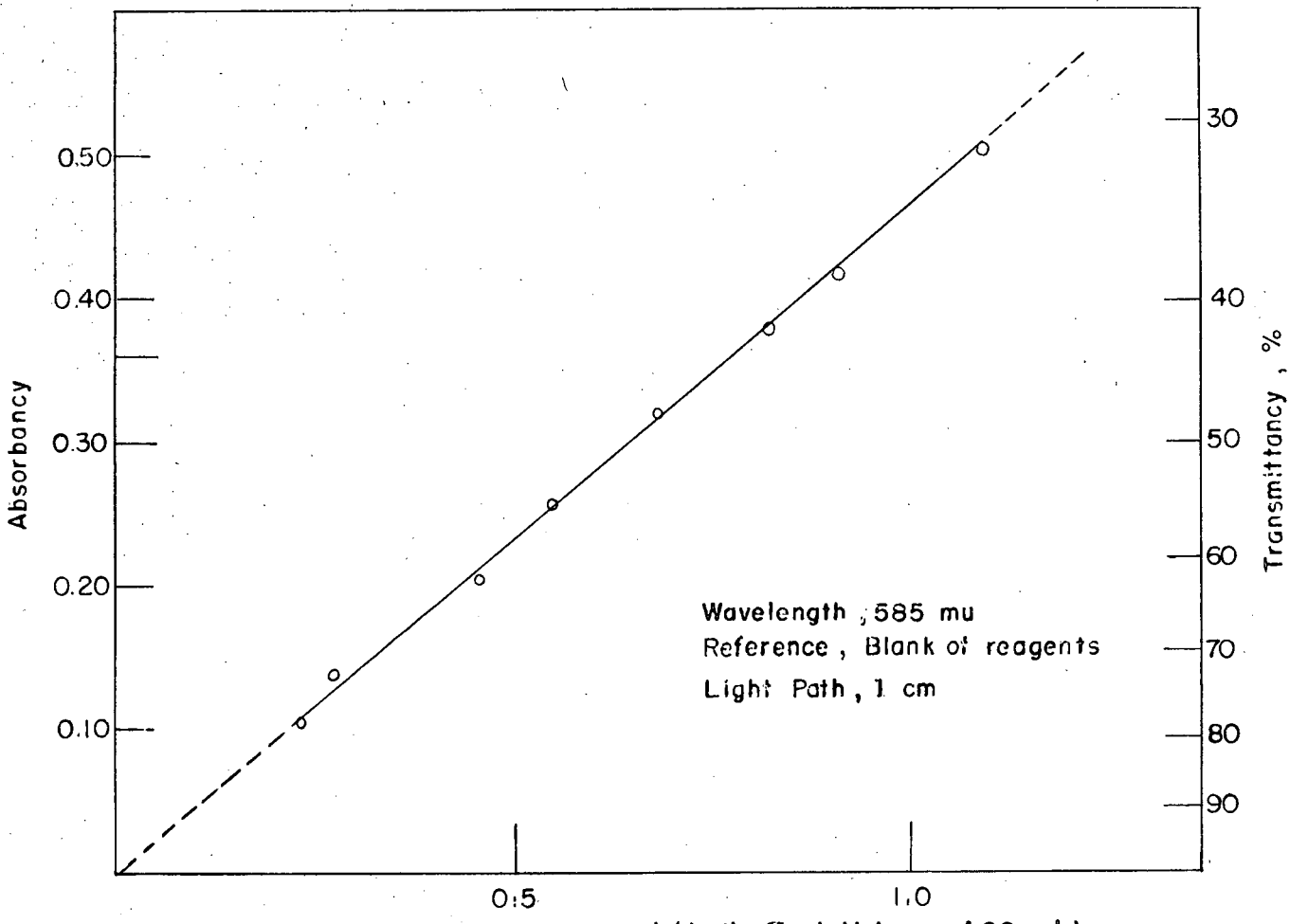


Figure B. Calibration Curve for Boron by the Spectrophotometric Carminic Acid Method (Not for Reuse)

BORON, VOLUMETRIC METHOD

I. SCOPE

This method is suitable for the determination of boron in macro amounts as boric acid in aqueous solutions or in organic solutions from which the boron can be extracted and converted to boric acid.

II. PRINCIPLE

In applying this method to the determination of boron as boron trifluoride in anisole, the boron is first extracted into water. In the hydrolysis of boron trifluoride, fluoboric acid and hydrolytic products of fluoboric acid, including some boric acid, are formed. Before a titration can be made, the hydrolysis to boric acid must be complete. This is accomplished by refluxing the aqueous extract with calcium chloride for four hours. The fluoride released is precipitated as calcium fluoride and the boron salts are completely hydrolyzed. The boric acid, which is released, is too weak an acid to be titrated; however, it forms a much stronger monobasic acid with certain organic compounds containing hydroxy groups, such as mannitol. The acidity of the boric acid solution is first adjusted until it is neutral to methyl red. Mannitol is then added, forming a complex acid with the boric acid which titrates as a fairly strong monobasic acid. The solution is then titrated with standard sodium hydroxide, phenolphthalein being used as the indicator.

III. REAGENTS

1. Standard Sodium Hydroxide, 0.1 N.
2. Standard Hydrochloric Acid, 0.1 N.
3. Methyl Red Indicator, 0.1 per cent. Dissolve 0.1 g of methyl red in 100 ml of ethyl alcohol.
4. Calcium Chloride Solution, 20 per cent. Dissolve 20 g of calcium chloride (anhydrous) in 100 ml of water.
5. Phenolphthalein Indicator, 0.1 per cent. Dissolve 0.1 g of phenolphthalein in 100 ml of ethyl alcohol.

IV. PROCEDURE

1. Weigh the sample and container to $\pm$ 0.1 g.
2. Add 25 ml of water from a measuring cylinder to a 125-ml separatory funnel.
3. Transfer the sample to the 125-ml separatory funnel. Stopper the funnel immediately.
4. Wash the sample container with three portions of ethyl ether, each portion having a volume approximately one-third that of the sample solution. Add the washings to the separatory funnel. Keep the funnel stoppered except when adding solutions.

5. Dry the sample container and weigh it to 0.1 g. Deduct this weight from the weight of the flask and sample (Step 1) to obtain the sample weight. This step may be delayed until later.

6. Shake the separatory funnel for 15 seconds. Let it stand until the two phases are completely separated.

7. Drain off the lower aqueous phase into a 100-ml volumetric flask.

8. Twice repeat Steps 6 and 7, adding the aqueous phases to the initial extract in the volumetric flask.

9. Dilute the combined aqueous extract to volume. Mix well.

10. Add a test portion from the solution prepared in Step 9, containing 10 to 30 mg of B, to a 250-ml glass-stoppered erlenmeyer flask.

11. Add 25 ml of the calcium chloride solution (20%).

12. Add 3 drops of methyl red indicator and titrate with 0.1 N NaOH until neutral to methyl red.

13. Attach a 16-in. water-cooled reflux condenser to the flask. Reflux for 4 hours, keeping the solution neutral to methyl red by the addition of 0.1 N NaOH through the condenser as required.

14. Cool the solution and adjust carefully with 0.1 N NaOH or 0.1 N HCl until the solution is neutral to methyl red.

15. Add approximately 3 g of mannitol to the solution. (Add 1.1 g of mannitol for each millimole of boric acid.)

16. Add 5 drops of phenolphthalein indicator and titrate to a phenolphthalein end point with standard 0.1 N NaOH.

17. Add approximately 0.5 g of mannitol and again titrate to the phenolphthalein end point with 0.1 N NaOH. Repeat the addition of mannitol and titration until the end point does not change with the addition of mannitol.

Calculations

Let N = normality of sodium hydroxide solution,

T = volume of sodium hydroxide from Steps 14 and 15, ml

W = weight of the sample, g

V = volume to which aqueous extracts are diluted, ml

A = test portion taken in Step 10, ml

Then total boron, per cent = $\frac{T \times N \times V \times 1.082}{W \times A}$

IRON, ORTHOPHENANTHROLINE, SPECTROPHOTOMETRIC METHOD

I. PRINCIPLE

This method is based on the absorbancy of an orange-red complex, $(C_{12}H_8N_2)_3\ Fe^{++}$ which is formed by the reaction of orthophenanthroline and ferrous iron. Hydroquinone is used to reduce the iron to the ferrous condition before the addition of the orthophenanthroline. The absorbancy is measured at a wavelength of 515 mμ. Copper, in concentrations up to twice that of the iron and chromium (CrIII) and nickel up to 64 and 0.8 times the iron, respectively, do not cause interference.

References

1. F. D. Snell and C. T. Snell, Colorimetric Methods of Analysis, Vol. II, Nostrand Co., New York, N. Y., 1949.

2. E. B. Sandell, Colorimetric Determination of Traces of Metals, 2nd Ed., Interscience Publishers, Inc., New York, 1950.

3. L. G. Soywell and B. B. Cunningham, "Determination of Iron," Ind. Eng. Chem., Anal., Ed. 9, 67 (1937).

4. C. J. Rodden, Analytical Chemistry of the Manhattan Project, p. 422, McGraw-Hill Co., New York, 1950.

II. REAGENTS

1. Ammonium Acetate Buffer Solution. To prepare this solution, dissolve 200 g of ammonium acetate in 800 ml of water. Then add 380 ml of glacial acetic acid and 115 ml of concentrated hydrochloric acid. Adjust the pH of the solution to 3.5 by the dropwise addition of concentrated hydrochloric acid or ammonium hydroxide.

2. Hydroquinone Solution, 1.0 w/v per cent. To prepare this solution, dissolve 1 g of hydroquinone in 100 ml of water. Store this solution in an amber-colored bottle.

3. Orthophenanthroline Solution, 0.25 w/v per cent. To prepare this solution, dissolve 0.25 g of 1,10-orthophenanthroline in 100 ml of water. Heat the solution to dissolve the solid reagent. Store the solution in an amber-colored bottle.

4. Standard Iron Solution, 10 micrograms per ml. This solution is prepared by pipeting 25 ml of a stock solution which contains 200 micrograms of iron per ml, into a 500-ml volumetric flask and diluting to volume with water. To prepare the stock solution, weigh 200 mg of standard iron wire (99.9% Fe) to the nearest mg and transfer it to a 300-ml Erlenmeyer flask. Add 30 ml of 1 to 1 HCl and heat the solution on a steam bath until the wire dissolves completely. Cool this solution and transfer it to a 1-liter volumetric flask; then dilute to the mark with water.

III. SAMPLING

The sample consists of boron trifluoride dissolved in anisole (methoxybenzene). Take a portion of the sample and evaporate it to dryness on the hot plate. Destroy any organic matter that may be present by boiling with 5 ml of concentrated nitric, 2 ml of 70-per cent perchloric, and 2 ml of concentrated sulfuric acid. Boil the solution until white fumes of sulfur trioxide appear. Cool and then dilute the aqueous solution to a specific volume. Shake it thoroughly, and take an appropriate aliquot for analysis.

IV. PROCEDURE

1. Process a test portion of the sample, V, as outlined in Section III, Sampling, diluting the water solution to volume, V_1. Pipet an aliquot, a_1, of the aqueous solution which is estimated to contain 10 to 60 micrograms of iron, into a 50-ml beaker.

2. Dilute the solution to approximately 10 ml with water. Then, after adding 5 ml of buffer solution, adjust the pH to 3.5 $\pm$ 0.2 by the addition of 1 to 1 NH_4OH. Measure the pH with a pH meter.

3. By means of a pipet, add 1 ml of hydroquinone solution.

4. Transfer the solution to a 25-ml volumetric flask; then add 2 ml of orthophenanthroline and dilute it to volume with water. Mix the reagents by shaking the flask.

5. After 30 minutes, measure the absorbancy of the sample against a reference solution of the reagents at a wavelength of 515 mμ with a Beckman, Model DU or B, spectrophotometer. Use absorption cells of 1-cm light path.

6. Determine the calibration factor (F) by pipeting 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquots of the standard iron solution into 50-ml beakers and analyzing them by the procedure outlined in Steps 1 through 5. For each of the five test results, calculate the calibration factor from the following equation,

$$F_1 = \frac{\text{Fe, micrograms per ml in the final solution}}{\text{Absorbancy}}$$

Take the average of the five values as the calibration factor, F.

7. After the calibration factor has been determined, analyze at least one standard sample as a control with each series of samples tested.

Calculations

Let A = absorbancy of the final solutions, (Step 5).

F = calibration factor (determined in Step 6).

V = volume of test portion of sample, ml and

V_1 = volume to which the test portion was diluted, ml

a_1 = aliquot, ml

V_f = final volume = 25 ml

W = weight of test portion of sample, g,

$Z = \frac{V_1 \times V_f}{a_1}$ = dilution factor

Then Iron in sample, mg/ml = $\frac{A \times Z \times F}{V \times 1000}$, or

Iron in sample, per cent = $\frac{A \times Z \times F}{W \times 10,000}$

COPPER, SODIUM DIETHYLDITHIOCARBAMATE, SPECTROPHOTOMETRIC, METHOD

I. PRINCIPLE

An aqueous solution of sodium diethyldithiocarbamate, when added to a solution of cupric salt, produces a colloidal suspension or, in more concentrated solutions, a copper carbamate precipitate which is soluble in organic solvents such as amyl alcohol and carbon tetrachloride. In this method, carbon tetrachloride is used to extract the copper carbamate which imparts a yellowish-brown color to the solution. The intensity of the color is proportional to the amount of copper present. The copper is, therefore, determined by measuring the absorbancy of the carbon tetrachloride solution at a wavelength of 440 mμ against a reagent blank as reference solution.

II. STATUS

Titanium and the rare earths do not form colored compounds with diethyldithiocarbamate. Iron(III) forms a brown-black precipitate in acid or neutral solution but it does not react in ammonical citrate solution if the pH is 9 or above, provided the amount is not too large. The chief interfering metals in the determination of copper are nickel, cobalt, and bismuth. The interference of nickel can be prevented by adding 1 ml of 0.5 per cent dimethylglyoxime and separating the nickel precipitate by centrifugation. Cobalt imparts an orange color to the aqueous solution, but it is not extracted by the carbon tetrachloride. Small amounts of platinum do not interfere.

References

1. C. J. Rodden, Analytical Chemistry of the Manhattan Project, pp. 408-409, McGraw-Hill, New York, Edition, 1950.

2. E. B. Sandell, Colorimetric Determination of Trace Metals, pp. 304-309, Interscience, New York, Second Edition, 1950.

III. APPARATUS

Spectrophotometer, Model DU or B, with absorption cells of 1-cm light path.

IV. REAGENTS

1. Sodium Diethyldithiocarbamate, 0.1 per cent solution. Prepare by dissolving 100 mg of sodium diethyldithiocarbamate in water and diluting the solution to 100 ml. Preserve the solution in a brown bottle.

2. Ammonium Citrate Solution, approximately 10 w/v per cent. Prepare by dissolving 25 g of $(NH_4)_3C_6H_5O_7$ in water and diluting the solution to 250 ml. Filter the solution if it is not clear.

3. Copper Stock Solution, 0.5 mg Cu per ml. Prepare by dissolving 250 mg $\pm$ 1 mg of copper metal in 15 ml of 1 to 1 HNO_3. Add 10 ml of H_2SO_4 and evaporate until SO_3 fumes appear. Cool and dilute the solution to 500 ml with water.

4. Copper Standard Solution, 5 micrograms per ml. Prepare by diluting 10 ml of the stock solution (0.5 mg Cu/ml) to one liter with water.

5. Ammonium Hydroxide, approximately 1 to 1. Prepare by diluting 50 ml of concentrated ammonium hydroxide to 100 ml with water.

6. Thymol Blue Solution, approximately 0.1 per cent. Prepare by dissolving 100 mg of thymol blue (thymolsulfonphthalein) in 20 ml of hot ethanol and diluting to 100 ml with ethanol.

7. Carbon Tetrachloride, Reagent Grade.

V. SAFETY

Carbon tetrachloride vapors are known to be toxic; therefore, exposure to this reagent should be avoided by carrying out the extraction in a well-ventilated fume hood.

VI. SAMPLING

The sample consists of boron trifluoride dissolved in anisole (methoxybenzene). Take a portion of the sample and evaporate it to dryness on the hot plate. Destroy any organic matter that may be present by boiling with 5 ml of concentrated nitric, 2 ml of 70-per cent perchloric, and 2 ml of concentrated sulfuric acid. Boil the solution until white fumes of sulfur trioxide appear. Cool and then dilute the aqueous solution to a specific volume. Shake it thoroughly, and take an appropriate aliquot for analysis.

VII. PROCEDURE

A. Preparation of Calibration Curve

1. Pipet 2-, 3-, 5- and 10-ml portions of the standard solution containing 5 micrograms of copper per ml, into 60-ml separatory funnels.

2. Dilute the solution in each separatory funnel to approximately 15 ml with water. Also, add 15 ml of water to a 60-ml separatory funnel and process it in the same manner as the test portions (for use as reagent blank reference solution).

3. Add 5 ml of ammonium citrate solution and 3 drops of thymol blue indicator solution.

4. Swirl the solution to mix the reagents; then add 1 to 1 NH_4OH dropwise until the color of the solution changes from yellow to purple.

5. Add 1 ml of sodium diethyldithiocarbamate solution and mix by swirling the solution. Then, let the solution stand for approximately two minutes.

6. Add 10 ml of carbon tetrachloride and shake the funnel vigorously for one minute.

7. After the water and organic phases have separated, drain the carbon tetrachloride (lower phase) into a 25-ml volumetric flask.

8. Add 5 ml of carbon tetrachloride to the aqueous phase and shake the funnel for one minute. Allow the phases to separate and add the organic phase to the organic extract withdrawn in Step 7.

9. Repeat Step 8; then discard the aqueous phase.

10. Dilute the combined organic extracts from Step 7, 8, and 9 to 25 ml with carbon tetrachloride.

11. By means of a Beckman (Model DU or B) spectrophotometer, measure the absorbancy of the standards against the reagent blank reference solution at a wavelength of 440 mμ.

12. Prepare a calibration curve by plotting the absorbancy as ordinate versus micrograms of copper per ml of the final solution as abscissa on rectilinear graph paper.

B. Analysis of the Sample

1. Process a test portion of the sample, V, as outlined in Section III, Sampling, diluting the water solution to volume, V_1. Pipet an aliquot, a_1, of the aqueous solution which is estimated to contain from 10 to 60 micrograms of copper, into a 60-ml separatory funnel and follow Steps 2 through 11 of Section A of this Procedure.

2. From the calibration curve, determine the micrograms of copper per ml of CCl_4 solution that correspond to the absorbancy of the sample.

Calculations

Let C = copper, micrograms per ml in CCl_4 extract (from calibration graph).

V = test portion, ml

V_1 = volume to which aqueous solution of residue from test portion was diluted, ml

a_1 = aliquot, ml

V_f = final volume of CCl_4 extract, ml

W = weight of test portion, g

$$Z = \text{dilution factor} = \frac{V_1 \times V_f}{a_1}$$

Then, copper, mg per ml $= \dfrac{C \times Z}{V \times 1000}$

and, copper, per cent $= \dfrac{C \times Z}{W \times 10{,}000}$

DETERMINATION OF TOTAL FLUORIDE, TOTAL BORON AND PRODUCTS OF HYDROLYSIS OF BF_3 IN AQUEOUS SOLUTIONS

I. PRINCIPLE

In aqueous solutions which contain boric acid and fluoride ions a complex equilibrium exists between the following complex acids, HBF_4, $HBF_3(OH)$, $HBF_2(OH)_2$, $HBF(OH)_3$, and $B(OH)_3$, and HF. The equilibria which exist in such solutions have been studied in detail by Wamser[1]. The fluoborate ion is relatively stable at room temperature while the hydroxy fluoboric acids are readily hydrolyzable and, therefore, cannot be distinguished from one another by analytical methods. By first hydrolyzing the hydroxy fluoboric acid and then the fluoboric acid by reacting their solutions with calcium chloride and titrating the resulting acid, the concentration of HBF_3 can be determined and the molar concentration of hydroxy fluoboric acid group can be calculated. By making the assumption that no acidic constituents are present, other than those which result from the interaction of HF and $B(OH)_3$ the total fluoride concentration can also be calculated. After the addition of mannitol to the hydrolyzed solutions, the uncomplexed boric acid can be titrated.

The method can also be applied to solutions of the complex acids in organic solvents such as anisole, by extracting the acids into an aqueous phase, in accordance with the procedure outlined in, "Boron, Spectrophotometric Carminic Acid Method," Section VIII, Part B, Steps 1 through 9, p. 8.

The titrations which are carried out and the attendant reactions are described below:

1. An excess of calcium chloride is added to a test portion of the sample and the solution is titrated to a methyl red end point. The hydroxy fluoboric acids are completely hydrolyzed while the fluoboric acid is titrated as a monobasic acid.

$$HBF_4 + NaOH \longrightarrow NaBF_4 + H_2O$$

$$2\ HBF_3OH + 3\ CaCl_2 + 6\ NaOH \longrightarrow 3\ CaF_2 + 6\ NaCl + 2B(OH)_3 + 2\ H_2O$$

$$HBF_2(OH)_2 + CaCl_2 + 2\ NaOH \longrightarrow CaF_2 + 2\ NaCl + B\ (OH)_3 + H_2O$$

$$2\ HBF(OH)_3 + CaCl_2 + 2\ NaOH \longrightarrow 2\ CaF_2 + 2\ NaCl + 2\ B(OH)_3 + 2\ H_2O$$

2. After the addition of an excess of mannitol, the above solution is titrated with standard sodium hydroxide to the phenolphthalein end point. The boric acid is titrated but the fluoboric acid does not react.

3. A second test portion of the sample is treated with an excess of calcium chloride and then heated to completely hydrolyze the fluoboric acid. The solution is titrated to the methyl red end point. The reaction for the complete hydrolysis of the HBF_4 is as follows:

$$HBF_4 + 2\ CaCl_2 + 4\ NaOH \rightarrow 4\ NaCl + 2\ CaF_2 + B(OH)_3 + H_2O$$

Since all of the fluoride is precipitated to liberate an equivalent quantity of strong acid, this titration corresponds to the total equivalent of fluoride in the test portion.

4. An excess of mannitol is added to the above solution and the solution is titrated with standard sodium hydroxide to the phenolphthalein end point. This titration is equivalent to the total boron in the test portion.

II. REAGENTS

1. Standard Sodium Hydroxide Solution, 0.1 N.
2. Standard Hydrochloric Acid Solution, 0.1 N.
3. Methyl Red Indicator, 0.1 per cent. Dissolve 0.1 g of methyl red in 100 ml of ethyl alcohol.
4. Calcium Chloride Solution, 20 per cent. Dissolve 20 g of anhydrous calcium chloride in 100 ml of water. Add 3 drops of the methyl red indicator solution and neutralize the solution to the methyl red end point.
5. Phenolphthalein Indicator, 0.1 per cent. Dissolve 0.1 g of phenolphthalein in 100 ml of ethyl alcohol.

III. PROCEDURE

1. Transfer a test portion of the sample (V) which contains from 10 to 30 mg of B, to a 250-ml Erlenmeyer flask.
2. Add 25 ml of the calcium chloride solution.
3. Add 3 drops of methyl red indicator and titrate to a permanent methyl red end point with 0.1 N NaOH. Record the volume of titrant as V_1.
4. Add approximately 3 g of mannitol to the solution.
5. Add 5 drops of phenolphthalein indicator and titrate to a phenolphthalein end point.
6. Add approximately 0.5 g of mannitol and again titrate to the phenolphthalein end point. Repeat the addition of mannitol and titration until the end point does not fade with the addition of mannitol. Record the volume of mannitol required for the titration from the methyl red to the phenolphthalein end point as V_2.
7. Transfer a second test portion of volume A to a 250-ml glass-stoppered Erlenmeyer flask.
8. Add 25 ml of the calcium chloride solution.
9. Add 3 drops of methyl red indicator and titrate to a permanent methyl red end point.

10. Attach a reflux condenser to the Erlenmeyer flask and heat the solution at reflux temperature while the methyl red end point is maintained by the addition of 0.1 N NaOH solution. Continue the titration until the end point is stable for at least five minutes.

11. Cool the solution to room temperature and, if necessary, adjust it to the methyl red end point by the addition of 0.1 N HCl or 0.1 N NaOH.

12. Correct the total titration of 0.1 N NaOH by subtracting the volume of 0.1 N HCl which was required to readjust the cooled solution to the end point. Record the volume of the net titration as V_3.

13. Add mannitol and phenolphthalein indicator and titrate the solution to a permanent phenolphthalein end point with 0.1 N NaOH as described in Steps 5 and 6. Record the volume of 0.1 N NaOH which was required to titrate the solution from the methyl red to the phenolphthalein end point as V_4.

Calculations

Let V = volume of test portion, ml

D = density of sample, g/ml

N = normality of sodium hydroxide

V_1, V_2, V_3, V_4 = volume of sodium hydroxide for the four titrations in Steps 3, 6, 11, and 13, respectively, ml

$T_1, (T_2 T_3 T_4) = \dfrac{V_1(V_2, V_3, V_4) \times N}{V}$ = base consumption in the above titration, meq/ml

Then HBF_4, millimoles/ml $= \dfrac{T_3 - T_1}{3}$

HBF_4, per cent $= \dfrac{(T_3 - T_1) \times 8.78}{3 \times D}$

*"Fluoride as hydroxy fluoboric acid, meq/ml =

$T_1 - \dfrac{(T_3 - T_1)}{3}$, if $T_2 \gg T_1 - \dfrac{(T_3 - T_1)}{3}$

"Fluoride as hydroxy fluoboric acid, meq/ml = $3T_2$, if

$3T_2 \ll T_1 - \dfrac{(T_3 - T_1)}{3}$

Total fluorine, meq/ml = T_3

Total fluorine, per cent $= \dfrac{T_3 \times 1.9}{D}$

Total Boron, millimoles/ml = T_4

Total Boron, per cent $= \dfrac{T_4 \times 1.082}{D}$

* The three hydroxy fluoboric acids are not distinguishable by analytical methods and therefore are reported as a group. The concentration of the individual complex acids may be calculated from the equilibrium constants of Wamser[1]. The calculation for the total fluoboric acid concentration is based on the assumption that the equilibrium concentration of uncomplexed fluoride is negligible in the presence of excess boric acid and that of $B(OH)_3$ is negligible when fluoride ion is present in large excess.

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(1) Wamser, Christian A., "Equilibria in the System Boron Trifluoride - Water at 25°", J. Am. Chem. Soc., 73, 409 (1951).