

Sampling and Analysis of Boron Trifluoride

CARL F. SWINEHART, AUGUST R. BUMBLIS, AND HARRY F. FLISIK

The Harshaw Chemical Company, Cleveland, Ohio

An accurate and safe procedure for weighing samples of boron trifluoride from cylinders, accurate methods for determining common impurities, and a reasonably accurate method for total acidity are described.

OVER a period of several years methods for sampling and analysis of boron trifluoride have been developed in the laboratories of the Harshaw Chemical Company. The usual method of separating boron and fluorine by distillation of methyl borate from calcium fluoride as given by Treadwell and Hall (10) is not suitable for process or quality control.

The complex nature of water solutions of boron trifluoride, boric acid, and hydrofluoric acid has been described by Mellor (7), Gasselin (5), Travers and Malaprade (9), and others without reaching definite conclusions as to their composition. Variable and ambiguous titrations are obtained unless steps are taken to promote the completion of the hydrolysis when titrating total acidity or to convert the boron trifluoride to a stable salt when titrating fluosilicate. Methods are here presented for dealing with boron trifluoride, so that regular volumetric procedures can be employed.

PROPERTIES AND HANDLING TECHNIQUE

Boron trifluoride is a colorless gas at atmospheric pressure and temperature. It condenses to a liquid which freezes at -128°C ., boils at -99.9°C ., and has a density of 3.065 grams per liter at 0°C . and 760 mm. (4). Its critical temperature is -12.25°C . at 49.2 atmosphere (1). The gas is shipped in high-pressure steel cylinders of two sizes: H-size cylinders of 43,262-ml. (2640 cubic inch) capacity hold 27.2 kg. (60 pounds) of gas at 105.5 to 126.5 kg. per square cm. (1500 to 1800 pounds per square inch) while E cylinders hold 2.7 kg. (6 pounds) of gas at the same pressures. There is no liquid phase in these cylinders at ordinary temperatures and therefore no segregation of gaseous impurities. Boron trifluoride is an "oil-pumped" gas; therefore it, or equipment for it, must not be used with high-pressure oxygen without taking suitable precautions. It can be diluted without reaction with nitrogen, dry air, carbon dioxide, sulfur dioxide, hydrochloric acid, chlorine, and hydrogen.

The gas is very soluble in water, alcohol, ether, amines, etc.; when it is to be introduced into liquids of this type suck-back is a hazard that must be prevented by a vacuum breaker or other features of apparatus design. Mercury, white mineral oil, mineral spirits, and carbon tetrachloride are typical liquids in which the gas has a low solubility and are suitable for use in displacement bottles, manometers, and vacuum breakers.

For the construction of equipment to hold dry boron trifluoride steel tubing or pipe, forged steel fittings, steel-to-steel ground unions, and bar stock valves give the best service. For temporary low-pressure lines malleable iron fittings can be used. Moisture causes the gas to attack steel. Litharge and white mineral oil make a good dope for pipe threads. Copper tubing and brass fittings are satisfactory for low-pressure lines carrying either dry or moist gas. Pyrex, Saran, hard rubber, paraffin wax, polyethylene,

and Vistanex are resistant to both the dry gas and its water solutions. Rubber tubing can be used for temporary connections. Booth and Willson (2) have described the handling of boron trifluoride in glass laboratory apparatus.

Standard regulators are not suitably constructed for reducing the pressure from cylinders. A bar stock needle valve, 2, attached to the cylinder valve, 1, as shown in Figure 1 can serve this purpose. The cylinder valve should never be used to regulate flow, since there is a danger of cutting the seat and losing the contents. These valves are flat seated and not intended for regulation of flow.

GENERAL PLAN OF ANALYSIS

Separate samples are taken for water-insoluble and water-soluble gases and the results are combined and calculated to weight per cents in the original gas. For estimating the insoluble gas, principally air, a known volume is absorbed in sodium chloride solution and the undissolved gas measured. For the soluble gases (boron trifluoride, sulfur dioxide, silicon tetrafluoride, etc.) a sample of about 20 grams is absorbed by reaction with chopped ice. After the ice melts, weighed aliquots of the solution are taken for the individual determinations.

PROBABLE IMPURITIES

Judging from the raw materials used and processes employed in the manufacture, the principal gaseous impurities would be air, sulfur dioxide, and silicon tetrafluoride with possibly trace amounts of hydrogen, sulfur trioxide, water, and hydrofluoric acid. Hydrogen would appear with the insoluble gas and be counted as air.

The combined amounts of water (or rather boron trifluoride

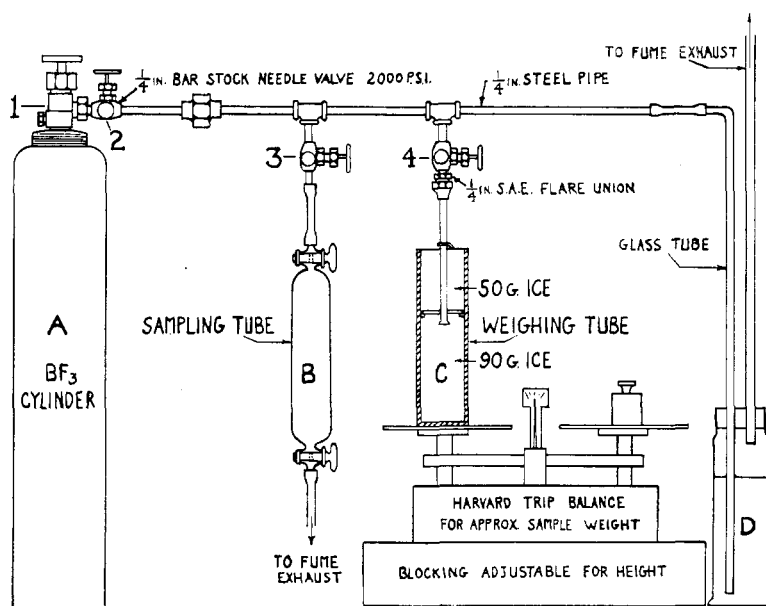


Figure 1. Apparatus for Sampling Boron Trifluoride

Table I. Duplicate Analyses of Some Cylinders of Boron Trifluoride^a

Sample Cylinders Constituent	Sample A		Sample B		Sample C		Sample D		Sample E	
	Found	Mean	Found	Mean	Found	Mean	Found	Mean	Found	Mean
Total acidity as BF ₃	99.9	100.0	98.7	98.9	98.2	99.0	99.5	99.5	99.0	99.1
BF ₃	99.4	99.4	96.5	96.6	96.2	96.7	99.0	99.0	97.8	97.8
SiF ₄	0.50	0.48	2.32	2.34	2.39	2.38	0.37	0.37	1.38	1.37
SO ₂	0.46	0.17	0.39	0.40	0.24	0.24	0.20	0.20	0.27	0.28
Air	0.17	0.03	0.40	0.42	0.23	0.25	0.19	0.12	0.28	0.11
	0.03	0.03	0.42	0.42	0.26	0.26	0.11	0.12	0.13	0.12
Total	100.1		99.7		99.6		99.7		99.6	

^a Produced by Harshaw Chemical Co., each sample representing a different batch. Samples B and C were made from raw materials unusually high in silica, selected to show applicability of method.

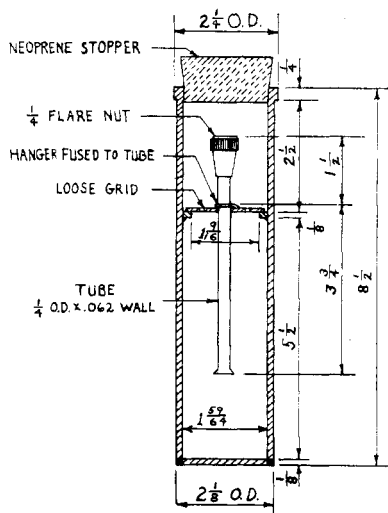


Figure 2. Sample Weighing Tube

Maximum weight of complete assembly 300 grams. Saran construction throughout. All dimensions in inches.

monohydrate), hydrogen fluoride, and sulfur trioxide must be very small, since the dew point of the gas as shipped in cylinders is generally below -40°C . A procedure for estimating sulfur trioxide from the water-soluble gas sample is included, though it is seldom found. Table I shows the distribution of impurities in some samples. The variation in silicon tetrafluoride corresponds to fluosilicate in the raw materials, while sulfur dioxide is formed from sulfuric acid in the process of generation.

SAMPLING

The arrangement of apparatus shown in Figure 1 has been found satisfactory for obtaining a laboratory sample of boron trifluoride from cylinders and storage tanks.

Apparatus. A is the container for the original boron trifluoride gas sample. In order to obtain a representative sample of a plant batch, 16 additions of quantities of the gas corresponding to pressure increments of 0.35 kg. per square cm. (5 pounds per square inch) each are run into an E-type cylinder, A, from the production system. It is then attached to the manifold as shown in Figure 1. A may also be a shipping cylinder in which case the pressure would probably be about 126.5 kg. per square cm. (1800 pounds per square inch). In any case there is no liquid phase to cause segregation in cylinders or storage tanks at ordinary temperatures.

B is a 250-ml. Pyrex sampling tube in which a separate sample is taken for the determination of water-insoluble gas (oxygen, nitrogen, hydrogen, etc.).

C is the Saran sample weighing tube detailed in Figure 2, in which the laboratory sample is weighed for determining water-soluble gases. (Saran weighing tubes can be obtained from The Harshaw Scientific Division, Harshaw Chemical Company.)

This is of the same design as the wax-lined hard rubber tube (7) for sampling anhydrous hydrofluoric acid.

D is a trap for limiting the pressure in the manifold. The receptacle is a glass bottle containing carbon tetrachloride, into which dips a glass tube attached to the end of the manifold. The outlet tube serves for guiding vented fumes into a hood.

Procedure. Before taking samples for either water-insoluble or water-soluble gases, flush the entire manifold system for at least 5 minutes with the boron trifluoride to be sampled; then just before attaching B, or

the Saran delivery tube of C, flush out valve 3 or 4 for 15 seconds.

Water-Insoluble Gases. Determine the capacity of the glass sampling tube, B, if not already calibrated. After cleaning, dry by sweeping with dry air or preferably by alternately evacuating and admitting dry air ten times—then at atmospheric pressure close both stopcocks.

After sweeping the manifold with the boron trifluoride to be sampled, open valve 3 (Figure 1) for a few seconds, then immediately attach one end of B to the rubber tube on valve 3 and to the other end attach a rubber tube for guiding the fumes into a hood. Open in the following order: valve 3, the upper stopcock, and then the lower stopcock. Allow the boron trifluoride to pass through B at least 15 minutes. Close the upper stopcock, then the lower stopcock, and then valve 3. Note the temperature of the air around B. Disconnect and proceed with the determination of water-insoluble gases as described below.

Water-Soluble Gases. Before taking this sample, set up the Harvard trip balance with C as shown in Figure 1. Add enough weights to hold C at its highest position on the balance. Loosely couple the Saran delivery tube assembly of C to valve 4 adapter, then raise or lower the balance so that the hanger on the delivery tube is in line with the top of the weighing tube. Caution: This adjustment is necessary to prevent suck-back of liquid into valve 4 when the ice melts. Disconnect the Saran delivery tube assembly and dry it by blowing with dry air or by a combination of warming in an oven at 105°C . for a few minutes and blowing with dry air. Dry the neoprene stopper by blotting with a clean cloth. The weighing tube is most conveniently dried by rinsing in alcohol and blowing with air until the odor of alcohol is gone.

Weigh the entire dried weighing tube (Saran delivery tube assembly and stopper) on a torsion balance having a sensitivity of 15 mg. and capacity of 500 grams, using rough weights or an approximate tare weight, and balance exactly. Test the accuracy of this torsion balance for such factors as equality of arms and positioning of weights, and make suitable corrections if the errors are in excess of 20 mg. After thus establishing the weight of the entire weighing tube, do not disturb the tare weights, for succeeding weighings must be made by adding only analytical quality weights. From this point on complete the sampling as quickly as possible.

Place about 90 grams of chopped ice in the bottom part of the weighing tube. Properly insert the Saran delivery tube, so that the perforated disk rests flat on the narrow ledge and the hanger rests over the rim of the weighing tube. Add about 50 grams more of chopped ice to the top part of the weighing tube above the perforated disk. Wipe off any droplets of water on the outside of the weighing tube or on the coupling of the delivery tube. Weigh exactly on the torsion balance, adding only analytical weights. Check this weight immediately after wiping off water condensed on the outside of the weighing tube. Record the weight of ice.

The 90 grams of ice in the bottom serve to absorb the heat of reaction of boron trifluoride and the 50 grams in the top section serve to trap any cloud formed by boron trifluoride contacting water vapor. The ice must not greatly exceed 140 grams. This amount, when melted with 20 grams of sample, will not bring the liquid level above the outlet of the Saran delivery tube. If the setup is exactly as described above, ample clearance is assured.

Absorbing and Weighing Sample. Immediately after flushing the manifold and valve 4 as described above, couple the Saran delivery tube to the adapter on valve 4 and tighten it with pliers. Balance with rough weights, make certain that the delivery tube does not hinder the balance swing, then add a 20-gram weight to overbalance the tube. Carefully open valve 4 and adjust the flow of boron trifluoride, so that no cloud appears over the top of the ice in the weighing tube. During the flow, watch the top of

the weighing tube for the appearance of a cloud in the ice and as soon as noticed reduce the flow. Keep testing the balance to make certain that its swing is not hindered by shifting ice. After the 20-gram weight is slightly overbalanced, close valve 4, disconnect the Saran delivery tube, and carefully drop it into the weighing tube before removing from balance. Tightly stopper the weighing tube without delay.

Weigh on the torsion balance, adding more analytical weights. Record the additional weight over the ice weight as the water-soluble sample weight. Mix thoroughly by careful inversion until all the ice melts, being certain to keep the tube tightly stoppered, so that none of the liquid is lost before the solution becomes homogeneous. Remove the Saran delivery tube and restopper immediately to avoid loss of sulfur dioxide. The diluted acid clinging to the Saran delivery tube is of no consequence, since aliquot weights of the solution are taken for analysis. Proceed with the determination of water-soluble gases as described below.

ANALYSIS

Air. Connect one end of the sampling tube, *B*, to a 500-ml. leveling bulb containing 400 ml. of sodium chloride solution (300 grams dissolved in 1.0 liter of water) and the other end to a gas buret also filled with the sodium chloride solution. Take care to have no air bubbles in these connections. A trace of a wetting agent such as Ultrawet (Atlantic Refining Co.) in the salt solution assists in freeing small air bubbles from the walls of connecting tubes. Clamp *B* in a vertical position and allow the solution in the leveling bulb to run up into *B*, rapidly at first but slowly at the end, lest the impact of the solution break the glass. After absorption is complete, draw the insoluble gas into the buret and record the volume of air and the buret temperature.

Sulfur Dioxide. This must be the first water-soluble constituent determined, because opening the weighing tube for other aliquot samples may result in loss of sulfur dioxide.

In a 250-ml. beaker place 50 ml. of water and exactly 10 ml. of standard 0.1 *N* iodide-iodate solution and weigh on a torsion balance. Place a 50-gram weight on the balance pan, then add the sample to the beaker until slightly overbalanced. Weigh to the nearest 0.5 gram. Immediately back-titrate the excess liberated iodine with standard 0.1 *N* thiosulfate, using starch solution as indicator.

Standardize the iodide-iodate solution against the standard thiosulfate under like conditions, substituting 50 ml. of water for the sample and making acid with 5 ml. of 1 to 1 sulfuric acid.

Calculate the equivalent thiosulfate for the aliquot to grams of sulfur dioxide in the entire water-soluble weight absorbed in *C* by the following equation, which also applies to the other water-soluble gases.

$$\frac{(\text{Ml. of standard solution}) \times (\text{factor } X) \times (\text{grams of ice} + \text{grams of sample})}{\text{grams of aliquot}} = \text{grams of } X$$

$$\text{Factor } X = (\text{normality of standard solution}) \times (\text{milliequivalent weight of } X)$$

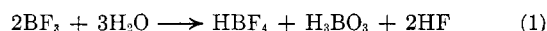
$$1 \text{ ml. of } N \text{ thiosulfate} = 0.032 \text{ gram of } \text{SO}_2$$

The above procedure is satisfactory for the determination of sulfur dioxide in commercial boron trifluoride. It is accurate when the sulfur dioxide content is below 0.2%. Above this amount some may be lost when opening the sampling tube to remove the delivery assembly and weighing the aliquot.

When the sulfur dioxide content is much above 0.2% a more accurate procedure is to take a separate sample from the cylinder and with the ice add a measured excess of iodide-iodate solution and 5 grams of potassium iodide, then back-titrate the excess liberated iodine as above. By this more accurate procedure an increase of 0.05% over the recommended procedure may be expected when the content is around 0.75%.

Silicon Tetrafluoride. Weigh into a 75-ml. platinum dish 1 gram of reagent sodium fluoride and 5.0 grams of the sample. Add 5 ml. of 0.5 *N* hydrochloric acid and 5 ml. of water. Place the dish on a steam bath and stir with a plastic or platinum rod until the sodium fluoride dissolves. Evaporate to dryness, remove the dish from the steam bath, and add 20 ml. of ethyl alcohol and 10 ml. of carbon dioxide-free water.

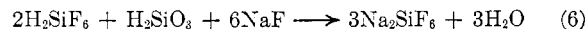
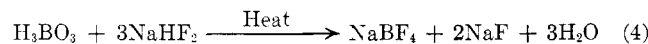
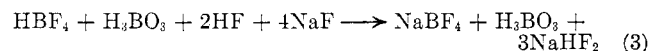
The products formed when boron trifluoride is absorbed in ice are complex in behavior and not clearly understood. Gasselin (5) writes the equation as follows to account for the alkali consumed before and after the addition of glycerol or mannitol:



This reaction is an oversimplification, since the fluoride ions of hydrofluoric acid are not found in this solution. It acts as if something like an easily hydrolyzed form of fluoboric acid (5) were present. In any case, hydrolysis and the buffered behavior seriously interfere with a direct titration of silicon tetrafluoride, the solution of which in water may be represented as follows:



Evaporation of the solution with sodium fluoride containing some hydrochloric acid forms a mixture of salts consisting of sodium fluoborate, sodium fluosilicate, sodium acid fluoride, sodium fluoride, and sodium chloride. Assuming Equation 1 for the solution of boron trifluoride, the conversion upon evaporation would be as follows:



An excess of sodium fluoride is desirable to allow for variations in original boron trifluoride sample weights. The 1 gram called for in the method is a 33% excess for the 5-gram aliquot of a 20-gram sample in 140 grams of ice. The addition of hydrochloric acid is a convenient way of forming sodium acid fluoride (Equation 5), which aids the completion of the reaction shown in Equation 4. Alcohol is added to prevent partial hydrolysis of sodium fluoborate; sodium fluosilicate does not dissolve in 50% or stronger alcohol. Ethyl alcohol was used in this work. Methyl or isopropyl alcohols are fair substitutes.

Stir and break up the lumps until the salts become disintegrated. Add 5 drops of phenolphthalein indicator and titrate with 0.5 *N* sodium hydroxide to a pink color that remains permanent during 30 seconds of continuous stirring. (Sodium hydroxide should always be used for this titration; if potassium hydroxide is used potassium fluoborate precipitates and occludes some sodium acid fluoride which cannot be conveniently leached out. The sodium hydroxide should be silica-free. It should be stored in a wax-lined bottle or steel drum and not allowed to stand in a glass buret longer than necessary.) Disregard this titration (3.5 to 4.5 ml.) because the acidity is due to acid fluoride with which we have no concern except to neutralize it exactly.

Pour the contents of the dish into a 250-ml. beaker. Nearly fill the dish with carbon dioxide-free water (at 25° C.), stir somewhat to aid solution of the insoluble residue, and pour into the beaker. Rinse the dish twice in this manner to dissolve and completely transfer contents to beaker. To the beaker add 10 more drops of phenolphthalein indicator and without delay titrate with standard 0.1 *N* alkali to a faint pink color remaining permanent 15 seconds. (Sodium fluoborate hydrolyzes in aqueous solution to a small extent. No serious error results if a 15-second end point is accepted.) This titration is equivalent to the four fluorine atoms in silicon tetrafluoride plus the reagent blank. Run the blank according to this procedure, substituting 5 ml. of water for the sample.

Calculate to grams of silicon tetrafluoride in the entire water-soluble sample weight absorbed in *C*, using the general equation given above under sulfur dioxide,

$$1 \text{ ml. of } N \text{ alkali} = 0.02600 \text{ gram of } \text{SiF}_4$$

EXPERIMENTAL

Because of the difficulty of preparing boron trifluoride free from silicon tetrafluoride, synthetic preparations of standards were made up from reagent hydrofluoric acid and boric acid corresponding to 20 grams of boron trifluoride in 140 grams of water. The proportions used were based on Equation 1. The boric acid used showed no silica when the ammonium molybdate colorimetric method (3) was used. The hydrofluoric acid used showed 0.003% of silicon tetrafluoride by the fixation method (8), which corresponds to 0.006% based on the 20-gram boron trifluoride preparation.

The calculated amounts of hydrofluoric acid, boric acid, and water were weighed into 500-ml. polyethylene bottles. Five

Table II. Determination of Silicon Tetrafluoride in Synthetic Standards

SiF ₄ Present %	SiF ₄ Found %	Deviation ^a %
0.006	0.02	0.03
0.006	0.02	0.01
0.006	0.02	0.01
0.11	0.11	0.00
0.21	0.10	0.01
0.21	0.22	0.01
0.51	0.49	0.02
0.51	0.50	0.01
1.01	1.05	0.04
1.01	1.10	0.09

^a Most of these deviations are within the variations of the reagent blank which is =0.02 from the average deducted.

standards were thus prepared (Table II). To four of these was added reagent sodium fluosilicate to make standards containing the equivalent of 0.10, 0.20, 0.50, and 1.00% silicon tetrafluoride based on 20 grams of boron trifluoride in addition to the amount introduced through the hydrofluoric acid. The reagent blank for the determinations of these synthetic standards averaged 0.35 ml. of 0.1 N alkali. Individual values of the blank titration were 0.28, 0.32, 0.40, and 0.40, which indicates that a variation of =0.02% silicon tetrafluoride might be expected.

Sulfur Trioxide. Sulfur trioxide is not likely to be present. If present, it will be very little and may be disregarded in the final calculation.

On a torsion balance weigh 50 grams of the sample into a 400-ml. beaker and dilute to about 100 ml. Add a drop of methyl orange indicator and make slightly ammoniacal. Digest hot several minutes to hydrolyze fluosilicate, filter, and wash moderately with water. To the filtrate add 4 ml. of 1 to 1 hydrochloric acid, precipitate with barium chloride, and determine the sulfate in the usual manner.

Boron Trifluoride. Weigh a glass or platinum weighing bottle half-filled with water on the analytical balance. Add as quickly as possible 50 to 60 drops (3 to 4 grams) of the solution of the sample by means of a dropping pipet, cover the bottle promptly, and reweigh. Carefully wash the sample into a 300-ml. Erlenmeyer flask containing 5 grams of neutral calcium chloride dissolved in 25 ml. of water, add one drop of methyl orange indicator, and titrate with standard 0.5 N alkali to a yellow color. Record this titration and all succeeding titrations. Heat to a gentle boil and digest at about 90° C. for 10 minutes. Titrate the hot solution to an approximate end point. If the sulfur dioxide content is above 0.2% the methyl orange indicator may be destroyed. In such cases the solution should be cooled somewhat and another drop of indicator added before titration.

Repeat the boiling and digestion, until only 1 ml. or less of alkali is required to reach an approximate end point. Boil and digest at 90° C. for 30 minutes. Cool to room temperature and titrate to an exact end point. Repeat the boiling, 30-minute digestion, and cooling until no more acidity develops. The total amount of alkali required is equivalent to sulfur dioxide, silicon tetrafluoride, and boron trifluoride. Calculate to grams of boron trifluoride in the total water sample weight, using the general equation given under sulfur dioxide, and from this value deduct the sum of: grams of sulfur dioxide × 0.706, and grams of silicon tetrafluoride × 0.869 to obtain grams of boron trifluoride,

$$1 \text{ ml. of } N \text{ alkali} = 0.02260 \text{ gram of } \text{BF}_3$$

Calculations. The above determinations on the water-soluble gas give the grams of each constituent in the sample. In order to calculate weight percentage of each, a calculated weight of the air (the insoluble gas) must be added to obtain the true sample weight.

The insoluble gas is assumed to be air and the volume measured (over salt solution) is corrected for moisture and temperature in order to have it under the same conditions as the gas in sample tube B.

$$\text{Milliliters of air in } B = \text{ml. measured} \left[\frac{P-p}{P} \times \frac{273+t''}{273+t'} \right]$$

t' = temperature of B when sample tube is filled

t'' = temperature of buret when air is measured
 p = vapor pressure of 23 weight % sodium chloride solution (6) at t''
 P = barometric pressure

The barometric pressure has little effect when the percentage is small. Table III gives approximate values for the factor $\left[\frac{P-p}{P} \times \frac{273+t''}{273+t'} \right]$, which are applicable at barometric pressures from 720 to 760 mm.

The ratio of the corrected volume of air in B to the volume of water-soluble gas in B $\left[\frac{\text{ml. of air in } B}{(\text{volume of } B \text{ in ml.}) - (\text{ml. of air in } B)} \right]$ permits the calculation of a weight of air corresponding to the water-soluble sample in C as follows:

$$\text{Grams of air} = L_N(\text{air}) \times \left[\frac{\text{ml. of air in } B}{(\text{volume of } B \text{ in ml.}) - (\text{ml. of air in } B)} \right] \times \left[\frac{\text{grams of } \text{BF}_3}{L_N(\text{BF}_3)} + \frac{\text{grams of } \text{SO}_2}{L_N(\text{SO}_2)} + \frac{\text{grams of } \text{SiF}_4}{L_N(\text{SiF}_4)} \right]$$

$L_N(\quad)$ is the density of the respective gases at 0° C. and 760 mm. Substituting these values, the equation becomes

$$\text{Grams of air} = 1.29 \times \left[\frac{\text{ml. of air in } B}{(\text{ml. of } B) - (\text{ml. of air in } B)} \right] \times [(\text{grams of } \text{BF}_3 \times 0.325) + (\text{grams of } \text{SO}_2 \times 0.34) + (\text{grams of } \text{SiF}_4 \times 0.21)]$$

True sample weight = water-soluble sample weight + grams of air.

$$\% \text{BF}_3 = \frac{\text{grams of } \text{BF}_3 \times 100}{\text{true sample weight}}$$

$$\% \text{SO}_2 = \frac{\text{grams of } \text{SO}_2 \times 100}{\text{true sample weight}}$$

$$\% \text{SiF}_4 = \frac{\text{grams of } \text{SiF}_4 \times 100}{\text{true sample weight}}$$

$$\% \text{Air} = \frac{\text{grams of air} \times 100}{\text{true sample weight}}$$

Table III. Correction Factors for Air Volume

Temperature t' of B When Filled, ° C.	Temperature t'' of Buret			
	19° C.	20° C.	30° C.	40° C.
10	0.99	0.95	0.92	0.85
20	1.02	0.98	0.94	0.88
30	1.06	1.01	0.97	0.91
40	1.10	1.05	1.00	0.94

DISCUSSION OF RESULTS

Table I shows the analysis of some cylinders of boron trifluoride. The variation in silicon tetrafluoride originates in the raw materials, while sulfur dioxide and air result from the process of manufacture.

The sampling procedure developed for anhydrous hydrofluoric acid has been adapted to boron trifluoride.

Procedures for the determination of air and sulfur dioxide are essentially those in common use.

The procedure for silicon tetrafluoride is new, in that after conversion of boron trifluoride to a stable salt the differential hydrolysis of fluosilicate can be titrated. This was found to be reasonably exact, even though a relatively large but constant reagent blank is involved.

Total acidity corrected for sulfur dioxide is essentially a determination of total fluorine which after correction for silicon tetrafluoride is calculated to boron trifluoride. This is permissible, since no appreciable amounts of other acidic gases are to be expected in commercial boron trifluoride. The correction for sulfur dioxide may be uncertain, because of small losses in steps subsequent to the absorption of the sample in ice, especially when the

sulfur dioxide content is in excess of 0.2%. A total boron determination is not usually required for commercial boron trifluoride. However, experiments not reported above have shown that if the heating periods in the presence of calcium chloride solution for total acidity are carried out under a reflux condenser the total boron as boric acid can be titrated as a second step after adding glycerol, invert sugar, or mannitol.

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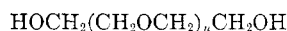
Solid Polyethylene Glycols (Carbowax Compounds)

Quantitative Determination in Biological Materials

C. BOYD SHAFFER AND FRANCES H. CRITCHFIELD, *Mellon Institute, Pittsburgh, Pa.*

Two methods are described for the quantitative determination of the solid polyethylene glycols (Carbowax compounds) in biological materials. These methods, one gravimetric, the other colorimetric, are based upon a reaction of the polyglycols with the heteropoly acids, silicotungstic and phosphomolybdic. Certain features of this reaction are discussed, and evidence is presented to demonstrate its applicability to the estimation of the polyglycols in plasma and urine.

THE polyethylene glycols are compounds of the general formula



The lower members of this series, diethylene glycol and triethylene glycol, have been familiar industrial chemicals for some years. More recently, there has come into production a series of polyethylene glycols of higher molecular weight, not as separate and distinct compounds, but as mixtures of individual polymers. There are now available in this group four liquids and five solids, the solids being sold under the trade-mark name of Carbowax compounds (Carbide and Carbon Chemicals Corporation). Each product represents a band of molecular weights, the average of which (except in the case of Carbowax compound 1500) is employed in characterizing that particular member of the series. The exception noted is a blend of substantially equal weights of polyethylene glycol 300 and Carbowax compound 1540. The liquid compounds are thus known as polyethylene glycols 200, 300, 400, and 600, and the solids as Carbowax compounds 1000, 1500, 1540, 4000, and 6000.

By their combination of unique chemical and physical properties, the solid polyethylene glycols have become well established in a number of major pharmaceutical applications. In consequence of their widespread use and in anticipation of their future possibilities, an extensive study of their pharmacological properties was initiated in this laboratory several years ago. It was early shown (5, 6) that the polyethylene glycols are substances of a very low order of acute toxicity both by mouth and on the skin. Positive information on their absorption, intermediary metabolism, and excretion from the body has been lacking, primarily because no method has been available for their detection and estimation in blood and excreta.

The low order of chemical reactivity of the polyethylene glycols, coupled with the fact that they are actually mixtures, renders the formulation of an analytical method extremely difficult. In the course of a considerable amount of investigation toward this end, the only reaction of any practical analytical significance that they have been observed to undergo is the formation in acid solution of highly insoluble complexes with the heteropoly inor-

ganic acids, such as phosphomolybdic and silicotungstic, in the presence of a heavy metal cation such as barium. No explanation is offered of the mechanism of this reaction, but it has proved useful as a basis for the quantitative determination of the solid polyethylene glycols. Two methods have been devised.

In the gravimetric method, the polyglycol is precipitated in hydrochloric acid solution with silicotungstic acid and barium chloride, and the precipitate is filtered, washed, dried, and ignited at 700° C. in a muffle furnace. The residue, consisting of the mixed oxides of barium, silicon, and tungsten, is weighed. The amount of polyglycol originally present in the sample is calculated from the weight of residue by means of an empirical factor determined from known quantities by this method. This procedure is suitable for quantities of polyglycol of the order of 5 to 100 mg. where an ordinary macroanalytical balance is used.

In the colorimetric modification the polyglycol is precipitated from the sample in a small centrifuge tube by the addition of barium chloride and phosphomolybdic acid. The precipitate is isolated and washed by repeated centrifugation, following which it is digested in concentrated sulfuric acid. The digest is diluted, neutralized, and made up to a definite volume, in an aliquot of which molybdenum is determined. The useful range of this method is of the order of 0.05 to 1.0 mg. of polyglycol at a minimum concentration of 0.01 mg. per ml. Phosphomolybdic is substituted for silicotungstic acid in this case because molybdenum can be determined somewhat more satisfactorily than tungsten.

Owing to the variation in useful range of the two methods, the colorimetric modification has been applied principally to whole blood and plasma, while the gravimetric technique is used almost exclusively for urine.

REAGENTS

Silicotungstic Acid, 10%. Dissolve 10 grams of silicotungstic acid ($4\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 22\text{H}_2\text{O}$) in a small quantity of water and neutralize with 10% sodium hydroxide to a methyl red end point. Dilute to 100 ml.

Hydrochloric Acid, 1 to 4. Dilute 1 volume of concentrated hydrochloric acid to 4 volumes with water.

Barium Chloride, 10%.

Phosphomolybdic Acid, 10%.