

FLAME PHOTOMETRIC MICRODETERMINATION OF BORON IN ORGANO-BORON COMPOUNDS, USING ION-EXCHANGE RESIN

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Boron is determined in organic compounds by fusion with sodium in a nickel capsule in a sealed glass tube. The fused mass is passed through a cation-exchange resin when boric acid is obtained which is estimated by a flame photometer. The accuracy of the method is $\pm 0.3\%$.

Introduction

The organically bound boron is usually determined by applying flame photometric, colorimetric and boron-mannitol complex methods. Brunisholz and Bonnet¹ used ion-exchange resin IR-120(H) for converting boron compounds to boric acid and to remove all metallic ions. The eluate was titrated with carbonate and boron free sodium hydroxide using bromocresyl purple as indicator, mannitol was then added and titrated till a pink colour was obtained. The sodium hydroxide, used between the bromocresyl purple and phenol-phthalein indicator changes, is equivalent to boric acid present. Dean and Thompson² investigated the effect of a number of cations and anions on the emission of boron. It was found that hydrogen ion concentration above 0.5M caused a marked depression in the flame emission of boron. It was observed that the emission increased with the increasing concentration of methyl alcohol. Muto³ determined boron in the range of 127-20 mg. by passing acid samples containing boron through a cation exchange resin IR-120(H) and then through an ion exchange resin IRA-400(CI). Boron was then determined in the column effluent by either titration or colorimetric procedures. Kubota⁴ titrated the borate complex with mannitol. The pH of the solution was adjusted between 3-4. Nitrogen gas was bubbled through the solution prior to the start of the titration to prevent the carbonate interference, the free acid end point was determined by titration with 0.01M sodium hydroxide. A drop of 0.05M hydrochloric acid was added and the solution was titrated to the end point corresponding to the neutralization of free acid. Bovalini, Pucini and Lo Moro⁵ dissolved a precipitate of $Ba_3B_2C_{16}H_8O_2$ in hydrochloric acid and barium was estimated by flame photometry at 873m μ . Wickbold and Angel⁶ dissolved the boron compounds in a combustible solvent. A hydrogen-oxygen flame was used. The combustion gases were passed through sodium hydroxide and the boron was determined by titration. Strahm and Hawthorne⁷ converted the boron

compounds to boric acid with trifluoroperoxy acetic acid and the resulting boric acid was titrated with sodium hydroxide using a fixed pH method. Shoniger combustion method has been used by Corner⁸ for the determination of boron etc. In order to prevent the formation of boron nitride the sample was mixed with potassium hydroxide before combustion. The decomposition products together with the residue of potassium hydroxide were dissolved in distilled water at pH 3 and carbon dioxide was blown out by bubbling oxygen through the solution. The pH was raised to 5.5 with sodium hydroxide, mannitol was added and the solution titrated to pH 8.

In the present work the organo-boron compound is decomposed with sodium metal in a sealed tube in a nickel capsule so as to avoid contamination from the glass tube during fusion. There is therefore no danger of loss of the compound through volatilization or incomplete digestion. The fused mass after the destruction of excess of sodium is then passed through the ion-exchange column when free boric acid is obtained thus avoiding all interference during the flame photometric measurement from the presence of other cations and anions. Interference due to nitrogen in the organo-boron compound has been studied by mixing boric acid with melamine and m-dinitro benzene and then fusing the mixture with sodium.

Experimental

Fusion Tubes.—(10×100 mm.) pyrex thick walled test tubes.

*Heating Block.*⁹—An electrically heated Dural block thermostatically controlled ($\pm 5^\circ C.$) with eight holes to accommodate fusion tubes.

Nickel Capsules.—Nickel capsules are made of pure nickel metal, internal diameter 0.8 cm. and length 2.5 cm.

Cation Exchange Resin.—Cation exchange resin

Amberlite IR-120(H) (Rohm & Hass Co., Philadelphia USA).

Ion-Exchange Column.—A glass column with a 18 cm. bed of cationic exchange resin IR-(120-H) in hydrogen form.

Boric Acid.—E. Merck guaranteed analytical grade reagent.

Flame Spectrophotometer.—Unicam SP 900 flame spectrophotometer.

Sodium Metal.—Purified sodium metal in wire form. The sodium metal was purified by Burger's¹⁰ procedure. It is heated with petroleum ether (100-120°C.) and 2 percent amyl alcohol. The outer carbonate layer is removed and clear molten sodium settles down at the bottom of the flask. The carbonate layers are decanted from the surface and fresh amount of petroleum ether and amyl alcohol are added. The clear metal is cooled and drawn in the form of wire.

Procedure

Weigh 5-10 mg. of the organic compound in a weighing stick and transfer it to the nickel capsule. Clean a piece of sodium wire 3-4 cm. long of 0.1 mm. diameter between the folds of a filter paper and place it in the capsule. Seal the capsule in a glass tube at a point 2.0-2.5 cm. from the top. Heat the sealed tube, in the heating block for $\frac{1}{2}$ hr. at 400°C. Open the cooled tube by making a scratch with a glass knife at a point 2.0 cm., from the point of sealing and touch the moistened end with a red hot soft glass rod. Destroy the excess of sodium left after fusion by moistening the tip of the transference pipette and let the metal react slowly with the small amount of water. When the excess of sodium has reacted, add 0.5 ml. of deionized water to completely dissolve the fused mass. Wash the ion-exchange column with 100 ml. of water before passing the fused mass through it.

Determine blank on 100 ml. of deionized water for the freshly washed column. Dilute the fused mass to 5 ml. and transfer it on to the ion-exchange column with six portions of 2 ml. deionized water. Wash the smaller part of the digestion tube with five 0.5 ml. portions of deionized water. Wash the column with 75 ml. of deionized water to elute the boric acid completely. Make the volume of the solution to 100 ml. Adjust the galvanometer of SP 900 at wave length 518 to give a deflection of 100 divisions

with boric acid solution of 10 p.p.m. Read the concentration of boric acid from the calibration curve corresponding to the galvanometer reading and the percentage of boron is calculated.

$$\text{Boron Percentage} = \frac{10 \times \text{p.p.m.}}{\text{Wt. in mg.}}$$

Instrument Setting.—The setting of the SP 900 flame spectrophotometer were as follows:

Air pressure 28 psi.
Gas pressure (acetylene) 13 cm.
Slit width 0.08 mm.
Shutter filter 3.

Discussion

B_xO_y molecule in oxyacetylene flame emits a band spectra and the radiation are spread over a portion of the spectrum rather than a straight line. Most of the boron band systems overlap each other. The more intense flame emissions occurs around 492, 518 and 546 $m\mu$. In this work a wave length of 518 $m\mu$ has been used. The boron emission depends upon the species of atoms attached to boron atom in solution,¹¹ in this method all the interferences are eliminated because only boric acid is present in solution. Fusion with sodium metal in a nickel capsule eliminates any chance of contamination from glass and also the uncertainties associated with the usual methods of decomposition of the organo-boron compounds. The method is, therefore, universal in application and all types of boron compounds can be handled with ease. It has also been observed that the intensity of boron emission increases with the addition of methanol and other alcohols probably due to the lowering of surface tension of solution whereby larger amounts of sample are injected in the solution. No solvents like methanol or naphtha has been used to increase the emission of boron because it has been observed that rapid depression of emission may occur during the period of measurement due to solvent evaporation. The ambiguities and uncertainties of titrimetric methods are eliminated. Since boric acid alone is obtained after passage through the ion-exchange column there is no need to calibrate or apply corrections due to the interference of other elements. The method is simple and universal in application. No interference is obtained from organo-boron compounds containing nitrogen. Since the hydrogen ion concentration is less than 0.5M no correction is applied to

TABLE I.

S. No.	Compound	% Boron found SP 900 method	Mannitol complex method	% of Boron present	Average theory
1.	Boric acid ..	17.45 17.44	17.36 17.48	17.49	-0.04 -0.05
2.	Na ₂ B ₄ O ₇ ·10H ₂ O ..	2.74 2.80	2.72 2.78	2.81	-0.07 -0.01
3.	Sodium tetraphenyl boron ..	3.08 3.20	3.10 3.24	3.16 —	-0.08 +0.04
4.	Glucose boron complex A ₁ ..	8.09	8.20	—	
5.	„ A ₂ ..	15.4	15.35	—	
6.	„ A ₃ ..	6.01	6.10	—	
7.	„ A ₄ ..	7.03	7.08	—	

compensate for the depression produced by higher concentration of the acid used for elution from the ion-exchange resin.

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