An alternative method for the purity determination of boron by flame atomic absorption spectrometer (FAAS) using acid dissolution method

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ABSTRACT

Increasing use of boron in High Energy Materials (HEMs) and allied compositions has drawn attention for the frequent analysis of boron for quality assurance. The analysis of boron is faced with two difficulties of the sample preparation of boron powder and estimation in HEMs compositions. Conventionally boron is analysed by alkaline carbonate fusion at very high temperatures followed by tedious double titration involving various additives such as acid-base indicators and complexing agent. The major limitation is that overall analysis involves several hours and is limited to the determination of purity of boron powder and cannot be used for estimation in HEMs compositions owing to their explosive nature. This paper describes a rapid and accurate method with better precision for boron purity determination. Boron dissolution in fuming nitric acid is carried out in reflux condenser on hot plate. The solutions of acid dissolution and fusion methods were analysed by Flame Atomic Absorption Spectrometry (FAAS). The accuracy of the obtained results was checked by comparison of the results with those obtained by titration of samples digested through alkaline carbonate fusion. The purpose of this paper is to demonstrate the acceptable accuracy with better precision obtained from developed alternative rapid method.   © 2011 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Boron is among several readily oxidized non-metallic elements that have found widespread use in the field of pyrotechnics as fuel as it surpasses in heat output every element except hydrogen and beryllium[1,2]. Upon burning, it forms acidic oxide (boric anhydride, B_2O_3) which appears as borates in the secondary exothermic reactions in the "ash"[2]. Boron with low melting oxidizers such as potassium nitrate ignites more readily yielding high heat flux and hence it is widely used

fuel in igniter and delay compositions for military and aerospace applications[3]. A few solid propellant compositions containing nano-sized boron particles as fuel or as a portion of metal fuel component and mixed with an oxidizing agent along with a binder are reported in the literature[4]. Due to its high heat of combustion, boron has been used as a high energy fuel for ram rocket development programs in many fuel rich propellant studies[5-7]. Boron, also called amorphous boron, is a very fine (about 1 μ average particle size) somewhat difficult to disperse dark brown powder and the commercial

product generally contains 84-96% boron, the main impurity being oxygen in the form of oxides (B_2O_3) and suboxides (B_4O etc.) in addition to other impurities of Mg and MgO[2]. Being the most expensive of all regular pyrotechnic ingredients boron is only used in small, accessory items such as first fires, rocket igniters, or delay compositions. Its costliness is somewhat lessened because of a very low equivalent weight, so that it is contained in suitable compositions at as little as 3% up to a maximum of 25%. The great value of such compositions are good stability, ease of initiation, persistence of burning even at greatly diminished atmospheric pressure, and excellent fire transfer properties[2].

Owing to its high cost and increasing use in high energy material compositions, there has been a great concern for the analysis of boron for its purity and its accurate ingredient percentage in the compositions. The determination of purity of boron powder has a main difficulty which is the dissolution of the sample. Until now, the sample dissolution was based on the fusion with alkaline carbonates in a platinum crucible at 800-900 °C for 30 minutes. This conventional method of determination of boron purity is based upon by the titration of boric acid (aqueous solution of fused mass) with sodium hydroxide. Although well established, this two step method is very tedious and time consuming. First step of fusion not only takes a longer time and high temperature of the order of 1000 °C to digest the boron in alkaline carbonate but also sometimes encounters losses due to spattering while expelling CO_2. The second step of titrating the boric acid with NaOH requires neutralization at several stages and employs indicators of two different pH ranges (first methyl red for slightly acidic and then phenolphthalein in moderately basic medium). In addition to this, the process requires addition of poly hydroxy compounds such as glycerol; mannitol etc. at an intermediate stage to keep a check on hydrolysis of alkali salt which interferes with the appearance of sharp end point which adds to the complexity of the procedure and therefore, extreme care has to be taken in determining the end point for reliable results[8]. Sikder and co-workers developed instrumental methods of Ion Chromatography (IC) and Atomic Absorption Spectrophotometer (AAS) for the analysis of solutions eliminating the step of tiresome double titration. However, no attempts were made to eliminate or improve the time consuming fusion method for sample

preparation[9]. In order to overcome these shortcomings, a need for rapid analytical technique involving simpler sample dissolution methods followed by instrumental analysis was felt and the same has been attempted successfully in this work.

This paper describes the development of acid dissolution method for determining the purity of boron powder samples and then employing flame atomic absorption spectrometry (FAAS) for estimating boron. Though few references are available in the literature for the boron dissolution in acids (nitric acid and sulphuric acid) but these methods remained confined to the trace analysis rather than determining the purity of boron[10,11]. Stotesbury et al. carried out trace analysis of boron using 50% nitric acid[10] where as Al-Ammar and co-workers employed conc. nitric acid and sulphuric acid for determining boron in biological samples[11]. In the present study, a simpler acid dissolution method has been developed for boron which can be carried out at around 60-70 °C in simple laboratory glass wares and does not involve expensive platinum crucible. It has greater efficiency than fusion with alkaline carbonates thereby avoiding losses which are otherwise caused by spattering. Three acids conc. nitric acid (70%), conc. sulphuric acid (98%) and fuming nitric acid (95-96%) were tried for dissolution. Sulphuric acid required very high temperature ($\approx$300 °C) under reflux (1 hr) for complete dissolution where as nitric acid failed to dissolve boron completely. Fuming nitric acid was found to dissolve the boron completely upon heating at around 70 °C. The boric acid solutions obtained by fuming nitric acid as well as standard fusion method were analyzed by AAS for boron content and the results have been compared. As the presence of large amount of sodium often lowers the sensitivity of FAAS for boron, the analysis of solution of fused samples were carried out using standards having equal amount of alkali. These results were also compared with those obtained by titration of solution of fusion method with sodium hydroxide. Boron received from three different sources, one imported (New Metals Pvt. Ltd., U.K) and two grades indigenously produced at Chemical Engineering Pilot Plant (CEPP) of High Energy Materials Research Laboratory (H.E.M.R.L) were analysed and the results have been compiled with a view to assess the reliability and repeatability of the results.

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EXPERIMENTAL

Reagent and apparatus

All chemicals and solvents were of analytical grade as mentioned below were used. Deionised water was obtained from the MILLIPORE water system (Elix-10 followed by Milli-Q 185 Plus and 0.22 μm filter unit).

Reagents/Chemicals	Source/Grade
Boron (1000 ppm standard solution)	Merck
Anhydrous Sodium Carbonate	Qualigen
Hydrochloric Acid	Merck
Sodium Hydroxide	Merck
Mannitol	Merck
Methyl red & Phenolphthalein (Indicators)	Merck
Fuming Nitric Acid (95-96%)	HMX Plant, CEPP (HEMRL)

Preparation of standard solution

Standard solution of boron of 1000mg/l (1000ppm) of Merck grade has been used for analysis. The standard solutions in the range of 50 to 400 ppm concentration were freshly prepared by diluting boron standard of 1000 ppm by deionised water before each analysis and these solutions were kept in polyethylene flasks.

Analytical procedure

Fusion method

Dried boron powder (0.1 g) was taken in platinum crucible containing sodium carbonate (5.0 g). The whole mass was further covered with a layer of Na_2CO_3 (6.0g) and kept in a muffle furnace at 900 °C for about 30 minutes for fusion. After cooling to room temperature, the crucible along with the fused mass was taken in a 250 ml beaker and treated with 150ml of 6N hydrochloric acid (HCl) to digest the fused mass. The solution was further heated at 80-90°C for 30 minutes without allowing it to boil in order to avoid the vaporization of borontrichloride formed in the solution. The solution mainly contained HCl and boric acid (H_3BO_3). This solution was stored in polyethylene flask and analysed by titration as well as AAS for boron content.

Fuming nitric acid method

Dried boron powder (0.1g) was taken in 250 ml round bottom flask and to it was added 15-20ml of fuming nitric acid. Then reaction mixture was heated to about 70°C until the appearance of clear solution. The solution mainly contained the boric acid. The reaction was carried out in a reflux condenser so as to achieve two purposes. Firstly, NO_2 gas released during the reaction condenses and further reacts with water to regenerate nitric acid which reacts with boron. Secondly it prevents the boric acid loss from its solution which may occur otherwise occur at a higher temperature (≈ 100°C). After cooling, the solution was transferred to 500 ml volumetric flask and the volume was made up with deionised water. The solution was stored in polyethylene flasks for analysis by AAS.

$$B + HNO_3 \longrightarrow H_3BO_3 + NO_2$$
$$NO_2 + H_2O \longrightarrow HNO_3$$
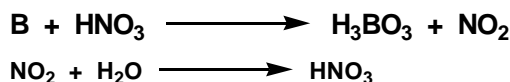
ANALYSIS

Analyses were carried out with AA800 atomic absorption spectrometer (Perkin Elmer) equipped with Deuterium as well as Zeeman background correction.

All absorption measurements were made with Hollow Cathode Lamp (HCL) for boron at 30 mA current as light source at 249.7 nm wavelength with 0.7 nm slit width and 0.1 nm spectral bandwidth. To achieve the best sensitivity the 5 cm burner head was fixed at height of 175.13 mm. Nitrous oxide-acetylene flame having 16.0 l/min oxidant flow and 7.9 l/min C_2H_2 flow was used.

The standard and sample solutions were aspirated through the flame and absorbances were measured and using a calibration equation, the concentrations of boron present in the sample solutions were calculated. To check the linearity, standard solution of boron (50 ppm
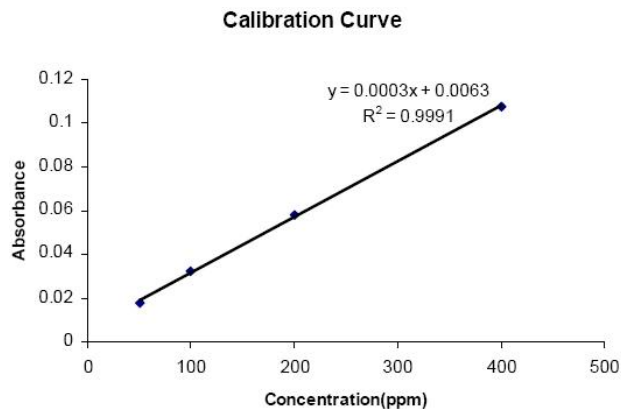
Figure 1 : Calibration curve for the standard solutions of boron by FAAS

to 400 ppm) were analysed and the graph was plotted between concentration and absorbance. The correlation coefficient is found to be 0.9991 (Figure 1).

RESULTS AND DISCUSSION

The boron content of solution through fusion method was estimated by titration with 0.5N NaOH as well as FAAS. The boron content in the solutions

prepared by fuming nitric acid method was determined by FAAS. The results are tabulated in TABLE 1. To check the repeatability, number of sets of measurements was made by testing both the method several times and the relative standard deviations (%RSD) were found to be less than 1% for each method. The mean value obtained from FAAS measurements were also found to be well in agreement with those obtained from titration method.

TABLE 1 : Purity of boron (U.K.) determined by titration & FAAS

Sample (Specified Limit)	% Boron		
	Standard Method (Fusion + Titration)	Fusion Method (I) (Fusion + FAAS)	Fuming Nitric Acid (II) (Acid + FAAS)
U.K. (97-98%)	96.6, 97.4, 97.2, 96.8, 97.2	97.5, 97.0, 97.1, 96.9, 97.4, 97.2, 97.1, 97.0, 97.1, 97.0, 96.6, 97.2, 97.4, 97.0, 97.1	97.2, 96.8, 97.1, 97.3, 96.9, 97.2, 97.1, 97.0, 97.2, 97.1, 97.4, 97.0, 96.9, 97.2, 97.1
Mean	97.04	97.12	97.10
Standard Deviation (S.D.)	0.3286	0.2153	0.1603
Relative SD (R.S.D, %)	0.338	0.221	0.165

The results show that boron purity percentage as obtained by both the methods are comparable and are in the specified limit. Analytical measurements for new method of acid dissolution for sample preparation were subjected to F-test to ascertain whether there is any significant difference between the new method and the fusion method of sample preparation. F-test was carried out by comparing the variance .i.e., the square of the standard deviations of the fusion method and acid dissolution method at 95% confidence level.

$$F_{cal.(Fusion/Acid)} = \frac{S^2_{fusion(I)}}{S^2_{acid(II,new)}} = \frac{(0.2153)^2}{(0.1603)^2} = 1.80$$

$$F_{critical.(15,15)} = 2.40$$

$$F_{cal.(Standard/Acid)} = \frac{S^2_{Std}}{S^2_{Acid(New)}} = \frac{(0.3286)^2}{(0.1603)^2} = 4.20$$

$$F_{critical.(5,15)} = 2.90$$

Since $F_{cal} < F_{critical}$ (for Fusion/Acid method) at confidence level of 95%, there is no significant difference between the fusion method and the acid method and therefore it can be concluded that the two methods give equivalent precision. However, $F_{cal} > F_{critical}$ (for Standard/Acid method) indicates that new acid method appears to give better precision than the standard method at the 95% confidence level. The same has also been indicated by the plot of frequency distribution curve (poly-

nomial trend line) showing the trends. Thus, in figure 2, that curve for acid method with lesser spread and higher peak is the characteristic of more precise results as compared to curve for standard method (shown dotted) which represents the less precise analytical measurements.
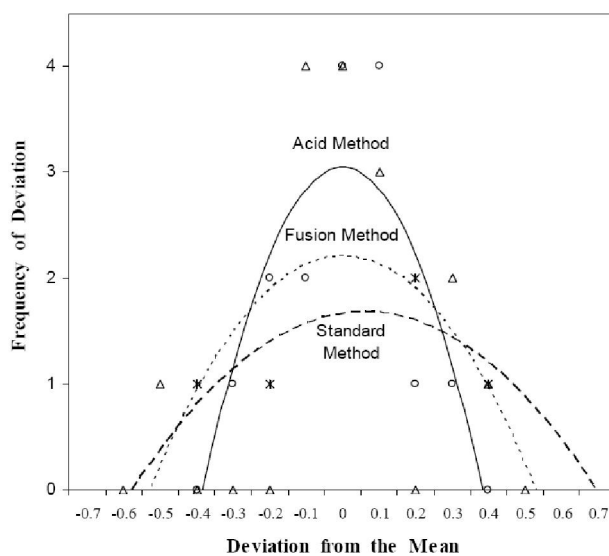

Figure 2 : Frequency distribution curves

The same comparisons for fusion (I) and acid (II) methods were also made by determining purities of the boron from two grades of boron indigenously produced at CEPP, HEMRL. The results are tabulated in TABLE 2. The purities determined from both the methods are in well agreement with almost similar R.S.D.

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TABLE 2 : Purities of boron (CEPP) determined by FAAS

S. No.	Sample (Specified Limits)	% Boron	
		Fusion Method (I) (FAAS)	Fuming Nitric Acid (II) (FAAS)
1	Boron (CEPP, 86-88%)	86.6, 86.2, 85.8	86.1, 86.5, 85.9
	Mean	86.23	86.17
	S.D.	0.4000	0.3055
	R.S.D (%)	0.46	0.35
2.	Enriched Boron (CEPP, = 92%)	92.4, 91.8, 92.3	92.1, 92.3, 91.9
	Mean	92.17	92.10
	S.D.	0.3214	0.2000
	R.S.D (%)	0.35	0.21

CONCLUSION

The purity of boron is determined by two method of sample preparation following analysis by FAAS. The results of both the methods are well in agreement. There is no significant difference between the two methods as established by F-test. The results of the acid dissolution method are accurate, reproducible, and more precise than standard method. It does not involve the time-consuming steps compared to tedious fusion and volumetric analysis. The time taken for sample preparation by fusion method is more (5-6 hrs) and it requires a platinum crucible while fuming nitric acid method is comparatively simple and it requires only 30 min for sample preparation. Though the results of both the methods of sample preparation, fusion as well as the fuming nitric acid method are comparable, it is recommended to use the fuming nitric acid method as it takes lesser time for sample preparation. (approx. 80 % time can be saved using this method). The other major advantage of this method is that it can also be applied successfully for boron based HEMs composition which are otherwise difficult to be analysed by alkaline carbonate fusion owing to their explosive nature.

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