

# Determination of ultratrace boron concentrations in uranium oxide by isotope dilution-thermal ionization mass spectrometry using a simplified separation procedure

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**Abstract** Boron was determined at sub-ppm levels in uranium oxide by ID-TIMS. Following nitric acid dissolution, a solvent extraction method was adapted for extraction of boron by 5% 2-ethylhexane-1,3-diol in chloroform followed by evaporation of the extractant in presence of sodium carbonate and mannitol. This procedure allowed TIMS analysis of boron by monitoring the  $\text{Na}_2\text{BO}_2^+$  ions formed from the sodium borate salt in the ion source. Reproducibility of about 1% was obtained for boron determination in the three different uranium oxide samples containing sub-ppm amounts of boron.

**Keywords** Boron · Isotope dilution mass spectrometry (IDMS) · Positive-thermal ionization mass spectrometry (P-TIMS) · Uranium oxide · Solvent extraction

## Introduction

In view of the stringent specification limits of boron in nuclear materials, its precise and accurate determination at submicrogram levels is important. Certification of reference materials for their impurities also requires accurate determination of the trace constituents present. The most common methods for the determination of boron (B) are spectrophotometry, emission spectrometry and plasma-source spectrometric methods. Spectrophotometric methods suffer from numerous interferences and have poor precision. Spectroscopic methods also have limited applications due to

interferences when sub-ppm amounts of boron need be determined. Though ICP-AES is a multielement analysis technique, it is prone to spectral interference due to spectral overlap of analyte emission line by emission lines of other elements e.g. iron or the matrix [1]. High background and low signal to noise ratio limit the sensitivity of optical emission spectroscopic methods. Spectrophotometric methods in general suffer from interferences due to absorption by the interfering element or compound at the same wavelength as that of the boron colored complex, necessitating a separation step (e.g. boron curcumin complex absorbs at the same wavelength as the reagent curcumin) [2, 3].

Exhaustive reviews on analytical methodologies and mass spectrometric instrumentation for the determination of boron in different matrices such as biological tissues, geological samples and steel are available [1, 4, 5]. It is an established fact that Isotope Dilution Mass Spectrometry (IDMS) is a precise and accurate method for quantitative determination of most of the elements present at trace to ultra-trace levels [6–8]. Since IDMS uses an isotope of the analyte as reference, separation does not have to be quantitative, if addition of spike is carried out prior to separation of the analyte and isotopic equilibration is ensured. Since the determination is dependent on measuring change in isotopic ratio, this methodology offers the potential to provide accurate and precise data. Different mass spectrometric techniques have been compared in the past with respect to the sensitivity and precision [4, 5, 9, 10]. In the recent years, inductively coupled plasma mass spectrometry (ICP-MS) has found wide spread use due to its high sensitivity for determination of boron and elimination of sample purification from certain matrices [9]. Though spectral interference from  $^{12}\text{C}^+$  peak at  $^{11}\text{B}$  peak (observed in old quadrupole based instruments) is not a problem in the presently available state of art magnetic

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sector instruments, non-spectral matrix interferences as well as memory effect can influence the accuracy and sensitivity [11–14]. It has been observed that presence of matrix ions or high salt concentrations in the sample suppresses the signal of low *Z* elements like boron and also effects the isotope ratio. This makes separation and purification of boron mandatory from these samples even when using HR-ICPMS [11]. One of the major problems for isotopic analysis of boron even in purified solutions by ICP-MS is the error on the measurement due to memory effect when samples of different isotopic compositions are analyzed [1, 11]. Electrothermal vaporization (ETV) for sample introduction in ICP has been found to be a useful technique for ultra-trace and microlitre scale analyses with possibility to separate the analyte of interest from matrix [15, 16]. In presence of halogenating agents or mannitol which is useful in preventing the formation of carbides, the method was found to enhance sensitivity for boron and reduce memory effects. Though TIMS methods are tedious as high purity of analyte is required for reliable determinations, it is still a reference technique due to the high precision and accuracy obtainable for boron isotopic ratios [17]. This makes ID-TIMS an ideal technique for certification of boron content in reference materials [18]. Though N-TIMS using  $\text{BO}_2^-$  ion is at least two orders more sensitive than PTIMS using  $\text{Na}_2\text{BO}_2^+$  for boron, large ion source isotope fractionation and spectral interferences from  $\text{CNO}^-$  at *m/z* 42 ( $^{10}\text{B}^{16}\text{O}_2^-$ ) are the two sources of uncertainties in the isotopic ratio measurement by N-TIMS [5]. The chemical treatment and methodology followed can also affect the precision and accuracy in boron determination due to loss of boron and isotope fractionation during the chemical treatment step. Blank contribution from reagents and environmental contamination are other major sources of error in boron determination. The objective of chemical treatment should be to minimize these sources of error in the measurement of isotopic ratio. In addition, a simple and rapid method to convert boron to a suitable chemical form for analysis by TIMS would be beneficial. In this study, three in-house reference uranium oxide samples with sub-ppm concentrations of impurities prepared and characterized in our laboratory previously, served as working standards [19]. The various methods used such as spectrophotometric and spectroscopic methods by the various participating laboratories had resulted in a large spread in the values for the impurity concentrations. The characterization methods did not include isotope dilution mass spectrometric technique. Uncertainty of more than 30% was obtained for boron concentration in the three uranium oxide reference materials.

Recently we developed an HPLC method for determination of boron based on separation of the boron curcumin complex from excess reagent with a precision of better than 5% [2]. But the values obtained for the three uranium

samples showed 30 to 100% negative bias from the mean values calculated by different methods that had been used for characterization. Very few IDMS methods are reported for determination of boron in uranium matrix. A prerequisite for trace analysis by TIMS is the analyte purity. Though a number of methods exist for boron separation such as methyl borate distillation, pyrohydrolysis, ion exchange separation, solvent extraction etc. [1, 5], each method has its advantages and drawbacks. The suitability of the separation approach depends on the matrix and also on the method of analysis. For determination of B in steel by HR-ICPMS [11], the matrix was precipitated at pH 10 and the supernatant was passed through a cation exchanger resulting in recovery of only 37% for B. Amberlite resin IRA-743 was used for the separation of boron from iron matrix after complexing iron with cyclohexane diamine tetra acetic acid (CyDTA) prior to determination of boron by ID-ICPMS [14]. Coedo et al [13] employed a three step solvent extraction method with acetylacetone-chloroform for removing Fe matrix for determination of boron in steel samples. Separation of boron (from uranium in the present case) by distillation as methyl borate ester requires special apparatus. Pyrohydrolysis separation gives low reagent blanks. However, as spike (enriched isotope) is added after extraction when pyrohydrolysis separation is used, quantitative extraction at sub  $\text{mg kg}^{-1}$  levels is required which cannot be guaranteed. Ion exchange methods require uranium to be complexed to prevent its hydrolysis, and this can increase reagent blank values. A fusion method would also lead to increase in reagent blank and contaminate the leachate with large excess of alkali. Extraction with a suitable extractant for boron would be a good alternative provided back extraction procedures are simplified and boron in the final solution is present in a medium suitable for TIMS analysis preferably as an alkali borate.

In the present work, boron was separated using 2-ethyl-1,3-hexane diol (EHD) as an extractant [2, 3] and boron was converted to a state suitable for determination by P-TIMS without using back extraction. This was done by decomposition of the organic extract in the presence of sodium carbonate and mannitol. The alkaline environment helped retain boron without loss or fractionation. The extraction by EHD is fast, quantitative and specific. Determination of  $^{10}\text{B}/^{11}\text{B}$  isotopic ratio employing P-TIMS as alkali borate ( $\text{M}_2\text{BO}_2^+$ ) is influenced by the loading and analysis parameters such as B/alkali mole ratios, acidity of the loading solution etc. [20, 21]. Since the accuracy of IDMS primarily depends on accuracy of the isotopic ratios obtained, initial experiments were carried out with boron isotopic reference material NIST-SRM-951. The isotopic reference materials NIST-SRM-951 was subjected to the separation procedure and was analysed by TIMS to determine  $^{10}\text{B}/^{11}\text{B}$  ratio in the extract. The uranium samples

spiked with enriched boron were also extracted and converted to sodium borate using the developed procedure. Determination of boron by TIMS was carried out by monitoring  $\text{Na}_2\text{BO}_2^+$  ions (at  $m/z$  88 and 89 corresponding to boron isotopes 10 and 11) formed from the sodium borate salt in the ion source. The advantage of determining boron as  $\text{Na}_2\text{BO}_2^+$  is that excess of Na (Na/B mole ratio up to 20) can be tolerated during analysis using the loading conditions described in detail in our previous studies [20, 21].

## Experimental

### Reagents

Freshly deionized water (18.2 M $\Omega$  cm) purified with a Milli Q system (Gradient, Millipore) was used for all the dilutions and dissolutions. All the experiments were carried out using quartz beakers for dissolution and polyethylene weight burettes and pipette tips. High purity acids and EHD (98%) from Merck ([www.merck.de](http://www.merck.de)) were used.

### Extraction procedure

Boron was extracted from 10 mL of 1 M nitric acid solution in a quartz separating funnel with 2 mL of 5% EHD in chloroform. The extraction was carried out in two batches using equilibration time of 3 min each. The organic layer containing boron was transferred into a 10 mL quartz beaker. The solution was washed with 2 mL milliQ water, twice, to remove traces of dissolved acid. The chloroform was then evaporated and sodium carbonate and mannitol were added in small volume of about 0.5 mL so as to wet the organic surface and make the medium alkaline. Sodium carbonate was added so that the B/Na mole ratio was in the range 0.5 to 0.05 and mannitol added was about 40 times the boron amount. The solution in the quartz beaker was further heated on a hot plate (adjusted at its lowest heating rate) for 10–15 min. This step vaporized/decomposed EHD leaving the borate residue which was dissolved in 20  $\mu\text{L}$  of water for P-TIMS analysis.

The extraction procedure for isotopic analysis by TIMS was initially developed using isotopic reference NIST SRM-951. A solution of SRM-951 containing about 10  $\mu\text{g}$  boron was subjected to the extraction procedure described above, and the purified solution was analysed for isotopic ratio by TIMS. Boron in the three different in-house uranium oxide standards served as working standards for the determination of boron by ID-TIMS. The expected boron content in all these samples was less than 1 mg  $\text{kg}^{-1}$ . Triplicate IDMS experiments involving three separate dissolutions of 1 to 2 g uranium oxide in  $\text{HNO}_3$  were carried out for each of the three samples. Utmost care was taken to keep the environment free from boron to avoid contamination of the samples.

The uranium oxide samples were first dissolved in 10 mL of 3 M  $\text{HNO}_3$  in quartz beakers and  $^{10}\text{B}$  enriched spike SRM-952 solution containing about 4  $\mu\text{g}$  boron was added to the sample solution. Though boron in the sample was expected to be of natural origin, an additional experiment was carried to determine the isotopic composition of boron in the uranium oxide sample using about 3 gm of the sample. The reagent blank was determined using the same procedure as for the sample. The samples treated according to the above mentioned procedure for separation and conversion to inorganic borates were analysed by P-TIMS for determination of isotopic ratio.

### Instrumentation

A single focusing TIMS (Isoprobe-T, Micromass U.K now known as IsotopX, U.K) with 9 Faraday cups for multi-collection was employed in the present work. High purity tantalum single filament assemblies with dimensions (10 mm $\times$ 1 mm $\times$ 0.04 mm) were used for loading the samples. For TIMS analysis, the sample was loaded onto a single Ta filament, using precoated graphite to enhance the  $\text{Na}_2\text{BO}_2^+$  signals. About 0.5 to 1  $\mu\text{g}$  boron was loaded onto the filament. The acquisition was carried out in 5 blocks, each block consisting of 12 scans.

## Results and Discussion

During the initial stages of experiments for separation of boron from the uranium samples, using Amberlite IRA 743 it was observed that the eluent contained some of the matrix (uranium) in spite of several washings. This was attributed to precipitation of uranium on the resin during loading, which was carried out under alkaline conditions. Complexing uranium with EDTA or citric acid was attempted but this did not prevent adsorption of uranium on the non-polar resin. This resulted in poor intensity of  $\text{Na}_2\text{BO}_2^+$  ions during TIMS analysis. Solvent extraction from an acidic solution using EHD for extracting boron into chloroform is quantitative, fast and clean as the extracting agent is specific for boron. However, for P-TIMS analysis, boron should be in the form of inorganic alkali borate. Conventional back extraction into aqueous medium can be brought about only in an alkaline aqueous medium containing large excess of sodium. This would have necessitated the removal of excess of sodium by passage of the solution through ion exchange column or passage through boron specific resin. It is well known that long separation procedures are not only time consuming but also include the risk of increase in reagent blank.

In the present work, this back extraction to form alkali borate was simplified by wetting the organic extractant with

**Table 1**  $^{10}\text{B}/^{11}\text{B}$  ratio in isotopic reference material NIST SRM-951 employing two different B/Na mole ratios

B/Na mole ratio	$^{10}\text{B}/^{11}\text{B}$ ratio obtained without extraction	$^{10}\text{B}/^{11}\text{B}$ ratio obtained after extraction
0.25	0.24698±0.00005	0.24711±0.00004
0.1	0.24691±0.00004	0.24702±0.00006

Certified isotopic ratio of boron in NIST SRM 951=0.2473±0.0002

mannitol and alkali in the form of sodium carbonate followed by vaporization of the extractant i.e. EHD. Mannitol forms an anionic complex with boron and prevents its vaporization even under acidic conditions [20]. During decomposition of EHD, non-volatile sodium salt of boron-mannitol complex remains in the residue from which  $\text{Na}_2\text{BO}_2^+$  is formed during TIMS analysis. The physical and chemical properties making this procedure viable were (a) instability of boron-EHD complex in basic medium, (b) tolerance to a wide range of B/Na ratio from 5 to 0.05 when graphite with mannitol is used without adversely effecting the results of TIMS analysis [20, 21] (c) lower boiling point of EHD (244°C) compared to the high boiling point of sodium borates which is around 1,500°C, (iv) use of small quantities of extractant (0.1 mL to 0.2 mL). This allows easy vaporization of EHD while the sodium borate substrate is being formed.

Results of the analysis of isotopic reference NIST SRM-951 employing two different B/Na mole ratios are given in Table 1. The  $^{10}\text{B}/^{11}\text{B}$  isotope ratio obtained for the isotope reference material, NIST SRM-951 following extraction procedure is also given. It is seen that the extraction procedure does not alter the ratio and there is no difference in the precision of the  $^{10}\text{B}/^{11}\text{B}$  isotope ratio for the two different B/Na mole ratios studied. These results demonstrate that the developed separation methodology will be useful to determine small changes in  $^{10}\text{B}/^{11}\text{B}$  isotope ratios for isotope hydrology.

Table 2 lists the boron determinations from the three independent IDMS experiments for each of the three uranium oxide samples. Reagent blank was determined to be about 0.05  $\mu\text{g}$  and was subtracted from total boron

determined in the three samples. The mean values obtained employing different methods such as emission spectroscopy with DC arc using photographic detection and electrical detection, spark source mass spectrometry, atomic absorption spectroscopy and spectrophotometry using curcumin are also given in Table 2 [19]. The precision on the mean values is 30 to 40% for the three uranium oxide samples. The Table also gives our previous values obtained using HPLC [2]. As can be seen, a relative precision of about 1% is obtained by ID-TIMS. The agreement of the mean value for boron in the three different uranium oxide samples obtained by ID-TIMS is within 10% with the data reported previously using HPLC. However, both TIMS values as well as HPLC values are 20% to 100% lower than the mean values obtained from various techniques mentioned above. This could be due to interferences in the boron determination and low sensitivity of the methods used during inter-laboratory comparisons in 1982. The isotope ratios obtained for boron during the ID-TIMS experiment have no isobaric interferences and show negligible fractionation which makes the boron concentration determination accurate and reliable. A precision of better than 2% was obtained for boron concentrations at levels less than 1  $\text{mg kg}^{-1}$ . The detection limit of the IDMS method was 0.006  $\text{mg kg}^{-1}$  (3×std. dev. of reagent blank). The results obtained by HPLC previously and by ID-TIMS in the present work suggest that for determination of ultratrace quantities, state of art methods having high sensitivity should be used to establish the true value of the impurity/trace element. In the present case, additional isotope dilution experiments using state of art ICP-MS can be carried out using the boron extraction procedure developed here to further validate these data.

## Conclusion

ID-TIMS was used for determination of boron in uranium oxide at submg  $\text{kg}^{-1}$  levels. A simplified chemical treatment method was used for purification of boron and conversion to borate which is a pre-requisite for P-TIMS. The use of

**Table 2** Boron determined by ID-TIMS in uranium oxide samples

Sample code	Expt. I <sup>a</sup> $\text{mgkg}^{-1}$	Expt. II $\text{mgkg}^{-1}$	Expt. III $\text{mgkg}^{-1}$	Mean.± $\sigma_{\text{obs}}^{\text{b}}$ ( $\text{mgkg}^{-1}$ )	Using HPLC <sup>2</sup>	Expected value <sup>c</sup>
ILCE-1	0.099	0.097	—	0.098±0.001	0.107±0.005	0.21±0.06
ILCE-2	0.206	0.204	0.208	0.206±0.002	0.208±0.005	0.32±0.14
ILCE-3	0.598	0.614	0.606	0.606±0.008	0.56±0.01	0.73±0.23

<sup>a</sup> Values obtained after subtraction of reagent blank which was determined to be 0.056±0.002  $\mu\text{g}$

<sup>b</sup> Gives the reproducibility from the two/three different experiment

<sup>c</sup> From interlaboratory comparison exercise conducted in 1982

The  $^{10}\text{B}/^{11}\text{B}$  isotopic ratio in sample was determined to be 0.2480±0.0002

small amounts of reagents also results in low blank values which is important when sub mg kg<sup>-1</sup> content need be determined. The method is simple and applicable for determination of boron by isotope dilution in any type of matrix. A precision of better than 2% was obtained for boron at concentrations from 0.1 mg kg<sup>-1</sup> to 0.6 mg kg<sup>-1</sup> in uranium oxide samples.

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## References

1. Sah RN, Brown PH (1997) Boron determination—a review of analytical methods. *Microchem J* 56:285–304
2. Rao RM, Aggarwal SK (2008) Determination of boron at sub-ppm levels in uranium oxide and aluminum by hyphenated system of complex formation reaction and high performance liquid chromatography (HPLC). *Talanta* 75:585–588
3. Donaldson EM (1981) Spectrophotometric determination of boron in iron and steel with curcumin after separation by 2-ethyl-1, 3-Hexanediol-chloroform extraction. *Talanta* 28:825–831
4. Sah RN, Brown PH (1998) Isotope ratio determination in boron analysis. *Biol Trace Elem Res* 66(1–3):39–53
5. Aggarwal JK, Palmer MR (1995) Boron isotope analysis: a review. *Analyst* 120:1301–1307
6. Heumann KG (1987) Mass spectrometric element analysis: advances and new perspectives in a modern analytical method. *Comments on modern chemistry. Part A, Comments Mod Chem* 6:145–173
7. De BP, Savory J, Lamberty A, Savory G (1988) Quality assurance, interlaboratory comparisons: meeting the need for reference measurements. *Fresenius' Z Anal Chem* 332:718–721
8. Heumann KG (1986) High accuracy in the element analysis by mass spectrometry. *Fresenius' Z Anal Chem* 324:601–611
9. Demuth N, Heumann KG (1999) Determination of trace amounts of boron in rainwater by ICP-IDMS and NTI-IDMS and the dependence on meteorological and anthropogenic influences. *J Anal At Spectrom* 14:1449–1453
10. Aggarwal JK, Mezger K, Pernicka E, Meixner A (2004) The effect of instrumental mass bias on  $\delta^{11}\text{B}$  measurements: a comparison between thermal ionization mass spectrometry and multiple-collector ICP-MS. *Int J Mass Spectrom* 232:259–263
11. Chang JP (2002) Determination of boron in steel by isotope-dilution inductively coupled plasma mass spectrometry after matrix separation. *Bull Korean Chem Soc* 23(11):1541–1543
12. Gregoire DC (1990) Determination of boron in fresh and saline waters by inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 5:623–626
13. Coedo AG, Dorado MT, Padilla I, Alguacil FJ (2002) Evaluation of flow injection ICPMS determination of microgram per gram levels of boron in iron and steel after matrix removal. *Anal Chem* 68:991–996
14. Fujimoto K, Shimura M, Satoh S (2002) Determination of trace amounts of antimony and boron in high-purity iron and steel by isotope dilution/inductively coupled plasma mass spectrometry. *Mater Trans (Japan)* 43(2):101–104
15. Wei WC, Chen CJ, Yang MH (1995) Determination of boron using mannitol assisted electrothermal vaporization for sample introduction in inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 10:955–961
16. Huang M, Jiangt Z, Zeng Y (1991) Fluorination and volatilization of refractory elements from a furnace for sample introduction into an inductively coupled plasma using a polytetrafluoroethylene slurry. *J Anal At Spectrom* 6:221–224
17. Platzner IT (1997) *Modern Isotope Ratio Mass Spectrometry*. Wiley, New York
18. Heumann KG (1992) Isotope dilution mass spectrometry (IDMS) of the elements. *Mass Spectrom Rev* 11:41–67
19. B.A.R.C—ILCE—1982 report.
20. Rao RM, Parab AR, Sasibhushan K, Aggarwal SK (2008) Studies on the isotopic analysis of boron by thermal ionization mass spectrometry using NaCl for the formation of Na<sub>2</sub>BO<sub>2</sub><sup>+</sup> species. *Int J Mass Spectrom* 273:105–110
21. Rao RM, Parab AR, Sasibhushan K, Aggarwal SK (2009) A robust methodology for high precision isotopic analysis of boron by thermal ionization mass spectrometry using Na<sub>2</sub>BO<sub>2</sub><sup>+</sup> ion. *Int J Mass Spectrom* 285:120–125