

Note

Determination of boron in zirconium-niobium alloys by spectrophotometry

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Boron doped zirconium-niobium alloy rods are used as neutron reactivity control rods in advanced nuclear reactors. Accurate knowledge about the boron content in this alloy is an essential requirement prior to its usage in nuclear reactors. In view of the refractory nature of the alloy, boron determination in these type of matrices is a challenging task. Also due to non-availability of matrix matched reference materials, direct solid analysis cannot be resorted to. Quantitative dissolution of the matrix without losing any boron followed by its determination is the only alternative. In the present work, Zr-Nb sample was dissolved in $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 taking care to prevent the loss of boron. Boron was selectively separated employing batch extraction with 10% 2-ethyl hexane 1,3 diol in chloroform and determined spectrophotometrically as B-Curcumin complex. Absorbance was measured at 550 nm. The precision and accuracy of the method is 3%. The absolute detection limit of the method is 12 ng. The method has been evaluated by standard addition method and validated by ICP-AES technique.

Keywords: Zr-Nb alloy, Boron, Spectrophotometry, Curcumin

Boron doped zirconium-niobium alloy rods are used as neutron reactivity control rods in advanced nuclear reactors. In addition to the boron content, information about its distribution over the entire length of the rod is also essential for neutron reactivity calculations. Among the different methodologies available, spectrophotometry^{1,2} is preferable due to its simplicity, desired sensitivity and more importantly non-requirement of matrix matched standards.

Efforts to dissolve zirconium-niobium sample in bromine water and methanol mixture¹ were futile, which may be due to presence of niobium. Hayes and Metcalfe² dissolved the sample in concentrated H_2SO_4 and $\text{NH}_4(\text{SO}_4)_2$ mixture. Absorbance of boron-curcumin complex was measured at 550 nm. About 20% deviation in the results was reported. Furthermore, tin, an alloying element in zircaloy, was reported to interfere in this methodology. To avoid interference from tin, these authors employed

elaborate and tedious column separations before absorbance measurement.

Present investigations are aimed at adopting the H_2SO_4 and $\text{NH}_4(\text{SO}_4)_2$ dissolution method to dissolve Zr-Nb alloy for determining boron. With a view to improving the accuracy in measurements, a separation step for boron from the solution was introduced. This paper describes the standardization and validation of methodology.

Experimental Procedure

All the reagents used were of A.R. grade. Milli-Q grade water was used for all the dilutions/preparations of samples. Standard boric acid stock solution of $974.75 \mu\text{g g}^{-1}$ was prepared by weight method in polypropylene volumetric flask. The final working standard solution of boron was made by diluting this stock solution appropriately.

About 50 mg of zirconium-niobium, 1.0 g of ammonium sulphate and 5.0 mL of concentrated sulphuric acid were taken in a 100 mL quartz round bottom flask which was connected to a water condenser. The outlet end of condenser was dipped in de-ionized water to trap the gaseous products. The flask was heated with the help of heating mantle until clear solution was formed. After cooling the solution to room temperature, the solution in the flask and the condensate were transferred quantitatively to a pre-weighed polypropylene 100 mL flask with de-ionised water. A reagent blank solution was also prepared in the same way by adding all the reagents excepting sample.

A weighed aliquot of the sample solution (about 0.5 g) was taken in a 10 mL quartz beaker and to it 3.0 mL de-ionised water was added. 1.0 mL of 10% 2-ethyl hexane 1,3 diol (EHD) in CHCl_3 was added to the above solution. The mixture was stirred for 3 min using a magnetic stirrer to facilitate the extraction of boron into the organic phase. The two phases were allowed to settle and the organic phase was separated by suction using a polypropylene weight burette. This extraction process was repeated four times (four batch extractions) for quantitative separation of boron. The organic phase separated in each extraction was collected and pooled in another quartz beaker.

Chloroform was evaporated gently from the entire organic phase. 1.0 mL of 0.375% curcumin in CH_3COOH and 0.5 mL of concentrated H_2SO_4 were then added to the residue left subsequent to evaporation of CHCl_3 . After about 50 min, this mixture was quantitatively transferred into a 10 mL standard quartz volumetric flask and diluted with *N,N*-dimethyl formamide (DMF), for deprotonation of protonated curcumin³. The absorbance of the coloured complex with reference to blank solution was measured at 550 nm by using quartz cell having 1 cm path length. Calibration plot, between absorbance and total amount of boron present in aliquot solution was constructed using standard boric acid aliquots.

Results and Discussion

Sample dissolution

The open beaker dissolution resulted in significant loss of boron (40-50%). Closed loop dissolution step incorporating condenser was necessary to prevent not only loss of boron during dissolution but also avoid rigorous bumping of solution. Within five minutes the sample was dissolved and a clear solution was obtained.

Preliminary studies on standard boric acid aliquot solutions showed that three batch extractions with 10% EHD in CHCl_3 were adequate for quantitative recovery of boron. Hence, in all further experiments, extraction was carried out four times. It was found that 40 min was required for quantitative complex formation between curcumin and boron in EHD. Detailed investigations carried out earlier⁴ indicated no interference from ions, Al, Cr, Mg, Ca, Fe, Mn, Mo, F⁻, W even at presence of 1000 times to the amount of boron present in aliquot. Interference from tin could be eliminated by selectively separating boron.

Calibration plot, Precision and detection limit of the method

A linear regression was carried out on the calibration plot. Absorbance and the amount of boron present in the sample are related by the equation

$$A = 1.3879 \times w \quad \dots (1)$$

where A = Absorbance and w = Amount of boron present aliquot in μg .

The linear correlation coefficient is 0.9994 over the linear range of 0.1-0.8 μg with eight data pair points.

Relative standard deviation (RSD) and mean recovery of boron in ten independent standard boric acid aliquots were 3.0% (precision at 1σ level) and

98% respectively. The calibration plot was checked for its reproducibility by analyzing standard boric acid aliquots at different time intervals over a three month period and there was no deviation in the statistics. From a given sample, four independent solid aliquots were taken, dissolved and boron was determined in each of the dissolved solid aliquots in duplicate (total 8 determinations.) A relative standard deviation of 3.33% was attained. This is in contrast to about 14% reported by Hayes and Metcalfe². The improvement, both in terms of RSD and recovery obtained in the present work is possibly due to prevention of loss of boron during dissolution of sample and also quantitative and selective separation of boron with EHD prior to its complexation with curcumin. In order to determine the limit of detection, ten independent blank solutions were prepared and absorbance was measured with respect to water. The standard deviation (σ) in absorbance measurement was 0.00556. The absolute limit of detection of this method has been evaluated employing the relation $3\sigma/\text{slope}$ of calibration plot and found to be 0.012 μg (0.048 wt% for an aliquot of 0.5 mL from 100 mL solution at sample size of 50 mg).

Evaluation of the method

The method has been evaluated by standard addition method. Standard boric acid aliquot was added (B_{added}) to the solid sample aliquot and then total boron (B_{total}) was determined as described in experimental section. Boron in the sample was calculated as

$$B_{\text{sample}} = B_{\text{total}} - B_{\text{added}} \quad \dots (2)$$

Results obtained by both the methods i.e. direct and standard addition methods, agreed well within $\pm 4\%$.

Validation of the method

The method has been validated by an independent method, wherein sample was dissolved in a mixture of HNO_3 and HF in the presence of mannitol and boron was determined by inductively coupled plasma atomic emission spectroscopy, ICP-AES. It was observed that, by applying statistical treatment to the data (t - test), there is no significant difference (at 95% confidence interval) between the two methods.

Application to real samples

After establishing the methodology, the present method is being employed to determine boron content in several zirconium-niobium alloy samples, on routine basis. A few results are given Table 1.

Table 1—Typical results of analysis for boron in Zr- Nb alloy samples

Sample Id	Amount of sample (g)	Amount of boron obtained (μg)	Conc. of boron (wt%)
Zr- 01	0.0359	66.11	0.218
Zr - 02	0.0396	79.40	0.200
Zr - 03	0.0360	123.80	0.343
Zr - 04	0.0357	143.40	0.402
Zr - 05	0.0592	94.13	0.159
Zr - 06	0.0571	246.12	0.431

Calculation of combined and expanded uncertainty in measurement

The combined and expanded uncertainty in the measurements was calculated following the procedure as given in earlier paper⁵. The combined uncertainty (relative), calculated employing error propagation formula is found to be 4.387%. The expanded uncertainty at 95% confidence level is 8.774% (coverage factor 2).

Conclusion

Zirconium-niobium samples were dissolved with ammonium sulphate and sulphuric acid without loss of boron by incorporating water cooled condenser in the system. Boron has been determined in these

samples with a precision and accuracy of 3%. The present method has been evaluated with standard addition method and validated by an independent method based on Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The present investigation is a significant improvement over the existing methodologies.

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