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Synchronous derivative fluorimetric determination of boron in Uranium fuel samples

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ABSTRACT

We report a sensitive and selective method for determination of boron in uranium samples by spectrofluorimetry in synchronous derivative mode. This method is based on the complexation of non-fluorescent boron with fluorescent chromotropic acid to form fluorescent boron–chromotrope complex. The spectrum of native fluorescence of chromotropic acid seriously overlaps with that of the complex and hence, synchronous derivative mode was employed in which physical separation of excess ligand and complex is not necessary. With the optimized experimental and instrumental conditions, limit of detection obtained is 2 ng mL^{-1} . The linear concentration range is $5\text{--}100 \text{ ng mL}^{-1}$ with regression coefficient better than 0.997. The precision is better than 5% at 10 ng mL^{-1} level and 3% at 50 ng mL^{-1} level ($n=9$). Fluorescence quenching by residual matrix elements in the final sample solution is corrected by slope-ratio method. The method is validated with reference materials and successfully applied to the uranium nuclear fuels with the accuracy of $\pm 10\%$. The proposed method reduces sample size requirement; thereby reducing load of uranium recovery from analytical waste in case of enriched uranium based samples.

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1. Introduction

Boron plays a crucial role in the nuclear power industry because of its high neutron absorption cross-section. Natural boron contains about 20% of ^{10}B which has a thermal neutron absorption cross-section (σ) equal to 3846 barns and undergoes nuclear reaction $^{10}\text{B}(n,\alpha)^7\text{Li}$. Due to this reaction; (1) gaseous (helium) product released may lead to structural changes/damages to reactor materials and (2) neutron economy is affected [1]. Hence, the specification for boron in nuclear fuels of thermal reactors is very stringent ($1 \mu\text{g g}^{-1}$) and its determination at ng mL^{-1} levels is an important requirement in nuclear technology.

Saha and Brown have reviewed analytical methods for the determination of boron [2]. Among the atomic spectroscopic methods, inductively coupled plasma atomic emission spectrometry (ICP-AES) and electro-thermal atomic absorption spectrometry (ETAAS) are used most frequently, although they suffer from interferences, memory effects and insufficient sensitivity for the determination of low levels of boron [3,4]. Inductively coupled plasma mass spectrometry (ICP-MS) offers higher sensitivity and lower detection limits [2,5,6], but it suffers from poor precision of lighter mass elements in presence of heavy mass matrix elements

remaining after matrix separation even in $\mu\text{g mL}^{-1}$ level. Ion Chromatography is a multi-elemental technique but does not offer desired detection limit and sensitivity required for enriched nuclear fuel samples [7,8]. Non-destructive methods [1,9,10] suffer from insufficient sensitivity.

Spectrophotometry with reagents such as curcumin [11], carminic acid [12], 1,1-dianthrimide [13], crystal violet [14] and methylene blue [15] have the disadvantage of time consuming procedures and possible interferences especially when boron is present at ultratrace levels. Moreover, the complex formation needs sulfuric acid medium, that may create problems during recovery of the actinide elements in the analytical waste generated. Azomethine-H and its derivatives [16,17] as well as H-resorcinol [18] have been used for photometric determination of boron. However, fluorimetric methods show greater sensitivity and literature with reagents, such as, morin, benzoin, chinizarin, quinizarin-2-sulphonic acid [19], carminic acid [20], alizarin red S [21] and chromotropic acid [22] have been reported. Among these reagents, chromotropic acid (1,8-dihydroxy-3,6-naphthalenedisulphonic acid) requires milder experimental conditions for complexation with additional advantage of (1) wide pH range for complex formation, (2) the complex formed is very stable (3) the reaction time for complex formation is short. Its complexation behavior with boron is well studied and reported [23–25]. The only limitation is that the native spectrum of chromotropic acid seriously overlaps with that of the boron–chromotrope complex

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and it is desirable to either quench the excess ligand fluorescence [26] or physically separate excess ligand from the complex by solvent extraction [27] and more commonly by chromatographic techniques [28–30]. In fluorimetry, this could also be achieved spectrally by scanning the spectra in synchronous mode without resorting to physical separation between different emitting species [31,32]. This eliminates the use of excess chemicals that may increase the chance of introduction of contaminants/error.

In synchronous fluorimetric mode, both excitation and emission wavelengths are scanned simultaneously with fixed wavelength difference ($\Delta\lambda$) between the two monochromators throughout the measurement. Its main attribute is to get sharper spectra and better resolution from other emitting species. Further, on taking the derivative, broad bands are suppressed relative to the sharper bands. The synchronous band narrowing effect with greater discrimination of derivative spectroscopy increases the selectivity and sensitivity of the narrower boron-complex peak with respect to the broader chromotropic acid peak. In addition, due to low photon noise from other emissions/blank there is an increase in the signal to noise ratio leading to lower detection limit. Moreover, this technique requires simple instrumentation with just an additional interlocking capability of the two monochromators.

Synchronous derivative spectrofluorimetric technique is applied successfully in inorganic analysis including that for boron [21,33]. It has been applied to environmental samples and to the best of our knowledge this technique is not yet applied for determination of boron in uranium based nuclear fuel samples. Therefore, the present paper describes the analytical methodology for determination of boron with chromotropic acid in uranium based nuclear fuel samples by synchronous derivative spectrofluorimetric technique.

2. Experimental

2.1. Reagents

Unless otherwise stated, all reagents used were of analytical grade quality and were used without further purification. Chromotropic acid and surfactants were purchased from Sigma-Aldrich. Hydrochloric acid was of supra pure grade and purchased from E-Merck. EHD was purchased from E-Merck and chloroform from Merck-India. A stock solution of boric acid (1 mg L^{-1}) was prepared by dissolving the appropriate amount of boric acid and working solutions were prepared by dilution subsequently. The reagent solution containing 0.001 M chromotropic acid, 0.05 M EDTA, 0.5 M sodium acetate and 0.02 M Tetrahexyl ammonium chloride was prepared daily and covered with aluminum foil during storage as chromotropic acid is sensitive to light. High purity deionised water of resistivity $18.2 \text{ M}\Omega \text{ cm}$ from Millipore system was used throughout.

All solutions were made and stored in polypropylene flasks/polyethylene bottles and experiments were done in quartz apparatus.

2.2. Apparatus

F-4500 Hitachi fluorescence spectrometer was used for all excitation and fluorescence measurements. 150 W Xenon arc lamp was used as source and R3788 side-on Hamamatsu PMT as detector. Excitation and emission slit widths were kept at 2.5 and 5 nm respectively and a scan speed of 240 nm min^{-1} was used. For synchronous spectrum measurements, excitation and emission monochromators were locked together and scanned simultaneously with a constant wavelength difference $\Delta\lambda = (\lambda_{\text{em}} - \lambda_{\text{ex}})$ of 24 nm. Fluorescence measurements were done in

1 cm path cell at room temperature. FL Solutions 2.0 software was used for data procurement and processing.

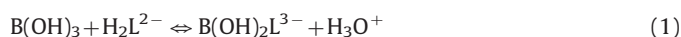
2.3. General procedure

About 50 mg of uranium based sample was taken in a quartz beaker and dissolved in 3 mL of 6 M HCl and 0.5 mL H_2O_2 under infra red lamp. After dissolution of the sample, 3 mL of water was added to the sample solution and boric acid was extracted with 2 mL of 10% EHD in CHCl_3 . The organic extract was scrubbed with 5 mL of 6 M HCl. Boron was back-extracted in 2 mL of 0.3 M NaOH. After neutralizing NaOH with HCl, 1 mL of chromotropic acid reagent solution was added to the sample solution and made up to 5 mL with water. Fluorescence intensity was then measured against reagent blank in synchronous mode and derivative of the synchronous spectrum was plotted. The first derivative value is measured as the vertical distance from peak to trough. A calibration graph was constructed using synthetic standard solutions of boron of known concentration in the range of $5\text{--}100 \text{ ng mL}^{-1}$.

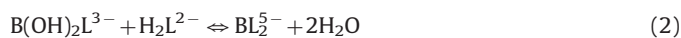
3. Results and discussion

Before boron determination, separation of boron from uranium based matrix was done by solvent extraction using 2-ethyl-1,3-hexane diol (EHD) in chloroform [11]. Boron reacts with EHD to form a weak chelate which is very soluble and extractable in chloroform. Extraction of boron with EHD is quantitative, fast and less cumbersome as compared to other separation methods like pyrohydrolysis [7,34], distillation [35] and ion exchange [8].

For fluorimetric determination of boron, non-fluorescent boric acid is complexed with fluorescent chromotropic acid and fluorescence intensity of boron-chromotrope is a measure of boron concentration in the sample solution. Fluorogenic character of chromotropic acid is reported [36] and its complexation behavior with boric acid is well studied [23–25]. Boric acid complexes with chromotropic acid in the pH range of 2–10 and forms 1:2 complex under reagent excess conditions in the pH range of 2–7 whereas 1:1 complex is formed in extremely dilute solution and at a higher pH. Therefore under present reaction conditions that will be discussed in the later sections, there is a mixture of both types of complexes with 1:2 dominating. The formation of 1:1 and 1:2 complexes can be described as follows:



where L = chromotropic acid



The structure of chromotropic acid and 1:2 complex is given in Chart 1.

3.1. Spectral characteristics of excitation, emission and synchronous spectra

The fluorescence excitation, emission and synchronous spectra of chromotropic acid and its boron complex are shown in Fig. 1 and are represented in blue, red and black color respectively. The emission spectrum was scanned with excitation wavelength of 352 nm while an excitation spectrum was measured at emission wavelength of 378 nm. In Fig. 1, the bold lines represent the spectra of the standard solution containing 50 ng mL^{-1} of boron while dotted lines represent spectra of reagent blank. The conventional luminescence spectra are quite broad and the λ_{max} of chromotropic acid in conventional fluorescence emission is 430 nm whereas for boron-chromotrope complex λ_{max} is 378 nm. It is clear from this figure that the spectrum of the native fluorescence of chromotropic acid

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