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Decay-Associated Fluorescence for Boron Determination in Uranium-Based Nuclear Fuels

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Cite This: *ACS Omega* 2023, 8, 47271−47276

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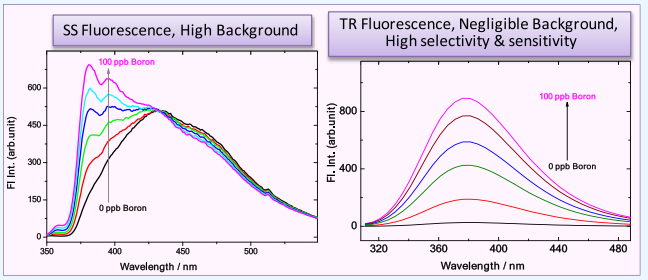
ABSTRACT: Herein is reported a novel as well as simple, sensitive, and cost-effective method for determination of boron by time-resolved fluorescence spectrometry in uranium-based nuclear fuels. Boron is complexed with fluorescent ligand chromotropic acid, and the complex formed is a measure of boron. Since the steady-state fluorescence spectra of excess ligand and complex are overlapping, the developed method emphasizes the power of time resolution. The signatory fluorescence decay times of ligand and complex are employed to derive their decay-associated spectra (DAS) and, thereby, spectroscopically eliminate the high background of ligand fluorescence. The calibration plot has a wide linear dynamic range of 5−100 ppb with r^2 better than 0.998. Precision is better than 5% at the 10 ppb level and 4% at the 50 ppb level (n = 9). The detection limit is 1.5 ppb, and recovery of spiked boron (25 ppb) from the uranium samples was better than 94%. The developed method was validated by analyzing U_3O_8-based ILCE Standards and applied to enriched uranium fuel samples. The main advantage of the developed method is a reduction in sample size requirement due to better sensitivity and selectivity. This in turn reduces the load of uranium recovery from analytical waste, especially in the case of enriched uranium samples. Additionally, it eliminates the need of organic solvents/medium.



1. INTRODUCTION

Chemical quality assurance (CQA) is a crucial step in nuclear material fabrication because impurities present above the specification limit affect the optimum performance and life of a nuclear reactor. The impurities present in the nuclear materials either come directly from the ore or are picked up during the processing/fabrication step of the nuclear material.

Boron present in nuclear materials is a neutron poison due to its high neutron absorption cross section. Natural boron has about 20% ^{10}B, which has a thermal neutron absorption cross section (σ) of 3846 barns. ^{10}B undergoes nuclear reaction $^{10}B(n, \alpha)^7Li$ and forms gaseous product helium in the nuclear reactor. This reaction reduces the neutron economy of the reactor and may induce structural changes in the reactor materials. Thus, boron is a critical impurity in nuclear materials and the maximum limit allowed in nuclear fuels of thermal reactors is very stringent (1 $\mu g\ g^{-1}$).[1,2] Hence, boron determination at trace levels with good accuracy and precision is an essential requirement in the nuclear field.

Boron determination is quite challenging especially at trace levels due to probability of cross- contamination from glassware (borosilicate glass), chemicals, personnel, laboratory apparatus, and environment.[3] There are many methods to determine trace amounts of boron in various matrices.[4,5] Methodologies generally used in characterization of nuclear fuels including boron are inductively coupled plasma atomic emission spectroscopy (ICP-AES),[6−9] carrier distillation DC arc atomic emission spectroscopy (DC arc-AES),[10] and curcumin-based spectrophotometry.[11,12] However, these techniques, except curcumin-based spectrophotometry, require sophisticated instrumentation and high operation cost. Curcumin-based spectrophotometry is the most widely used method for boron analysis. However, this is tedious and time-consuming. Moreover, it needs sulfuric acid and organic *N*,*N*-dimethylformamide in color development step for deprotonation of protonated curcumin. Fluorimetric methods have greater sensitivity, and many fluorogenic reagents are reported.[13−17]

Among the fluorogenic reagents, chromotropic acid (1,8-dihydroxy-3,6-naphthalenedisulfonic acid) is desirable as it forms a complex with boron under milder experimental conditions and gives good sensitivity and detection limits. The complexation behavior of chromotropic acid with boron has been well studied and reported.[18−21] The additional advantages of using chromotropic acid reagent are that it forms a complex

Received: September 29, 2023
Revised: November 1, 2023
Accepted: November 15, 2023
Published: November 28, 2023

with boron in a wide pH range and the complex formed is stable. The photophysical properties of chromotropic acid have been reported.[22] Chromotropic acid is used as a photometric[23−28] as well as fluorimetric[16,29−32] reagent, and the concentration of boron is determined by measuring the absorbance/fluorescence of the the boron−chromotrope complex. However, the fluorescence spectrum of excess ligand present in the solution overlaps with that of the complex (cf. Figure 1). Measuring the

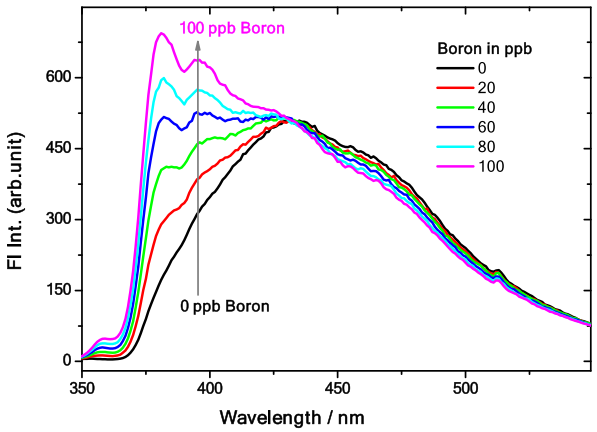


Figure 1. Steady-state emission spectra of the chromotropic acid and boron−chromotropic acid complex with each boron addition. [chromotropic acid)] = 1×10^{-3} M, λ_{ex} = 339 nm, and λ_{em} = 378 nm.

signal of the boron−chromotropic acid complex (species of interest) over a high background increases the uncertainty of the signal to be measured, and thus, it is desirable to either separate excess ligand from the complex formed or quench the background fluorescence. Physical separation of excess ligand from the solution is done either by chromatographic techniques[21,25−29,32] or by solvent extraction.[24] Background fluorescence of free ligand acid can be quenched after boron−chromotrope complex formation by making the medium alkaline.[30,31] However, these methods of decreasing the background signal need the use of additional chemicals/solvents, which may introduce impurities in the solution and increase the error/uncertainty in the results. A better option to overcome this situation is to spectroscopically separate the background/overlapping species. One approach is by the synchronous spectrofluorimetric method in which both the excitation and emission wavelengths are scanned simultaneously with fixed wavelength difference ($\Delta\lambda$, generally Stokes shift of analyte) between the two monochromators throughout the measurement.[15,17,33−37] Synchronous scanning reduces bandwidth and thus offers better resolution from other fluorescent species.

A novel approach for spectroscopic resolution/elimination of overlapping ligand fluorescence is by harnessing the power of the time-resolved fluorescence technique. The present work discusses spectroscopic resolution of the fluorescent species (chromotropic acid ligand and boron−chromotropic acid complex) through their fluorescence decay lifetimes. As ligand fluorescence is separated spectroscopically, a completely resolved spectrum of the analyte is obtained.

2. EXPERIMENTAL SECTION

2.1. Reagents/Chemicals/Materials. Chromotropic acid and surfactant (tetrahexylammonium chloride) were purchased from Sigma-Aldrich. Hydrochloric acid was of suprapure grade and was purchased from E-Merck. 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 subsequent dilution. The reagent solution containing 0.001 M chromotropic acid, 0.5 M sodium acetate buffer (pH 5), and 0.02 M tetrahexyl ammonium chloride was prepared daily and covered with aluminum foil during storage as chromotropic acid is sensitive to light. All solutions were made and stored in polypropylene flasks/polyethylene bottles, and experiments were done in a quartz apparatus. High-purity deionized water of resistivity 18 MΩ cm was used throughout the experiment. Three in-house working reference materials of U_3O_8 (ILCE 3, ILCE 4, and ILCE 5) were used for validating the developed methodology. These working reference materials were prepared in Bhabha Atomic Research Centre, India, via nine interlaboratory comparison experiments. The cation exchange cartridge used for matrix separation is of Dionex make (OnGuard II H) and contains styrene-based strong acid resin in the H^+ form.[38,39]

2.2. Apparatus. A JASCO Japan-make double-beam UV−visible−NIR spectrophotometer of model no. V-670 was used to measure absorbance. An F-4700 fluorescence spectrometer was used for steady-state fluorescence measurements. A 150 W xenon arc lamp was used as source. Excitation and emission slit widths were kept at 2.5 and 5 nm, respectively, and a scan speed of 240 nm/min was used. Fluorescence measurements were done in a 1 cm path cell (quartz, four sides polished, Helma make) at room temperature. FL Solutions 2.0 software was used for data procurement and processing. Time-resolved (TR) fluorescence measurements in the nanosecond time domain were carried out using a time-correlated single photon counting (TCSPC)[40,41] spectrometer from HORIBA Jobin Yvon IBH, UK, where samples were excited with a 339 nm diode LED and fluorescence decays were collected at the right angle to the excitation pulses using an MCP PMT detector (IBH, Scotland, UK). All the measurements were carried out with emission polarization set at a magic angle with respect to the vertically polarized excitation light beam to eliminate the effect of rotational reorientation of the dyes on the observed fluorescence decays.

2.3. Procedure. About 40 mg of uranium-based sample was dissolved in 5 mL of 6 M HCl and 0.5 mL of H_2O_2 by heating under an infrared lamp. Subsequent to sample dissolution, cations (including matrix uranyl cations and other minor trace cations) were separated from the solution by employing a cation exchange resin cartridge. The cartridge was first flushed with 15 mL of deionized water and then conditioned with 15 mL of 0.5 M HCl acid. Sample solution diluted to 10 mL with deionized water was passed at the rate of about 1 mL min^{-1} through the cartridge. Washing with 15 mL of 0.2 M HCl acid was done. The separation procedure was repeated twice to ensure complete removal of matrix uranyl cations. The total solution collected was made slightly alkaline with 0.1 M NaOH and then heated to evaporate off the acid medium anions. The final solution was made to 5 mL with deionized water.

One milliliter of chromotropic acid reagent solution was added to the sample solution and made up to 5 mL with deionized water. Steady-state fluorescence intensity and fluorescence decay lifetimes were measured at 378 nm with 339 nm excitation.

3. RESULTS AND DISCUSSION

Prior to boron determination, separation of matrix was done by methods like solvent extraction,[11] pyrohydrolysis,[42] distilla-

https://doi.org/10.1021/acsomega.3c07535
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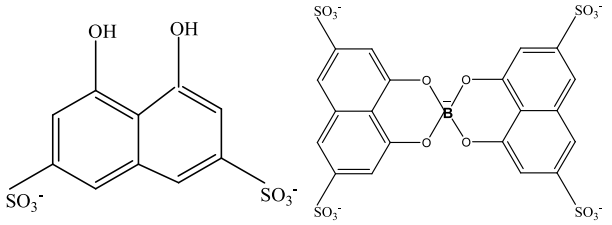
tion,[43] and ion exchange.[44] In the present work, matrix separation was achieved employing a cation exchange resin cartridge, as mentioned in Section 2. Separation with cation exchange resin cartridge is simple, fast, and less tedious.

Subsequent to sample dissolution and matrix separation, boron is complexed with chromotropic acid (1,8-dihydroxy-3,6-naphthalenedisulfonic acid) and the boron−chromotropic acid complex is formed.[18−21] Boron complexes with chromotropic acid in a wide pH range and forms 1:1 and/or 1:2 complexes under different experimental conditions. Among the two types of complexes formed, the 1:2 complex provides larger sensitivity.[24,25,27,30] Thus, experimental conditions (pH 5 by sodium acetate buffer and large excess of ligand) were tuned to form the 1:2 complex exclusively. Formation of the 1:2 complex under these conditions has been experimentally corroborated by job plots, pH, and ESI-Q-TOF MS experiments and has been reported.[45] The structures of the chromotropic acid and 1:2 complex are given in Chart 1.

Chart 1. Structure of Chromotropic Acid and 1:2 Boron−Chromotropic Acid Complex



3.1. Steady-State Fluorescence and Time-Resolved Fluorescence Studies. The fluorescence spectra of chromotropic acid and its boron complex are shown in Figure 1. The λ_{max} of chromotropic acid in fluorescence emission is 430 nm, whereas that for the boron−chromotropic acid complex λ_{max} is 378 nm. It is evident from Figure 1 that the fluorescence spectrum of the chromotropic acid overlaps with that of the boron−chromotropic acid complex. The analyte peak of the boron−chromotropic acid complex emerges over the high background of excess chromotropic acid present in the solution, which is undesirable in an analytical methodology as it introduces uncertainty error of the high background and thereby reduces the sensitivity and selectivity of the determination.

One of the advantages of fluorescence spectroscopy is that the fluorescence of emitting species is characterized not only by unique excitation and emission spectra but also by signatory fluorescence decay times. The fluorescence decay lifetimes of chromotropic acid and complex were measured and found to be 1.92 and 7.13 ns, respectively, as shown in Figure 2. Thus, resolution through fluorescence lifetimes was employed to overcome the challenge of overlapping steady-state fluorescence spectra and high fluorescence background by the TR fluorescence technique.

The fluorescence lifetime of chromotropic acid is about 1.92 ns by excitation at 339 nm and monitoring emission at 378 nm. Boron is gradually added to a chromotropic acid solution, and the fluorescence lifetime was measured for the entire spectral range at each boron addition. Each fluorescence lifetime was measured for a fixed time of 200 s. As observed in Figure 2, fluorescence decays changed from monoexponential to biexponential with boron addition, exhibiting two components, shorter (1.92 ns) for chromotropic acid and longer (7.13 ns) for

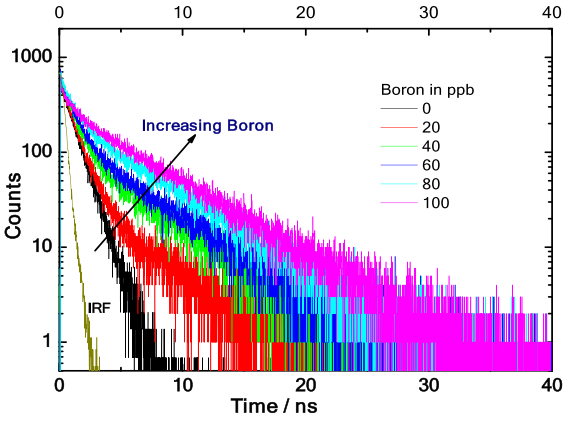


Figure 2. Decays of chromotropic acid and the boron−chromotropic acid complex with each boron addition. Decays normalized to peak count. [chromotropic acid)] = 1×10^{-3} M, λ_{ex} = 339 nm, and λ_{em} = 378 nm.

the boron−chromotropic acid complex. It is evident from Figure 2 that the pre-exponential amplitude of each decay component changed with boron addition. The pre-exponential amplitude of the longer decay component (boron−chromotropic acid complex) increased, while that of the shorter decay component decreased with increase in boron addition to the solution. The TR fluorescence decay data obtained was used to derive the decay-associated fluorescence spectra (DAS).

DAS is the derived spectra of the individual fluorescent species, which contribute to the total fluorescence.[46−51] Construction of the DAS with global analysis (global analysis is the simultaneous analysis of all measurements) is done according to eqs 1 and 2:

$$F(\lambda, t) = \sum_i a_i(\lambda) a^{-t/\tau_i} \quad (1)$$

$$\mathrm{DAS}(\lambda, t) = \frac{a_i(\lambda)\tau_i F^{SS}(\lambda)}{\sum_i a_i(\lambda)\tau_i} \quad (2)$$

where i = 1 denotes component 1 (τ_1 = 1.92 ns) is the free ligand (free chromotropic acid), i = 2 denotes component 2 (τ_2 = 7.13 ns) is attributed to the boron−chromotropic acid complex, and FSS (λ) is the measured steady-state fluorescence spectrum. In global analysis, the decay times of the species are fixed while the pre-exponential factors are varied in iterations until convergence is reached. DAS of boron−chromotropic acid is shown in Figure 3 and represents the boron concentration.

3.2. Interference Studies. Nuclear grade uranium-based nuclear fuels may contain metallic and nonmetallic impurities, which either come directly from the ore or get picked up during the processing/fabrication step of the nuclear material. These impurities may interfere with the determination of boron and may affect the accuracy and precision of the analytical methodology. Thus, investigations were done with impurities mentioned in Table 1. The impurities added were 10 times their specification limit for enriched uranium metal in accordance to ASTM C1462[52] along with the maximum permissible boron of 1 μg g^{-1} of uranium. 250 mg of uranium sample would give maximum 50 ng mL^{-1} of boron in 5 mL of solution. Therefore, impurities mentioned in Table 1 were added to a 50 ng mL^{-1} standard solution of boron and then boron was determined. Table 1 shows that the presence of these impurities has no significant effect on the determination of boron by the

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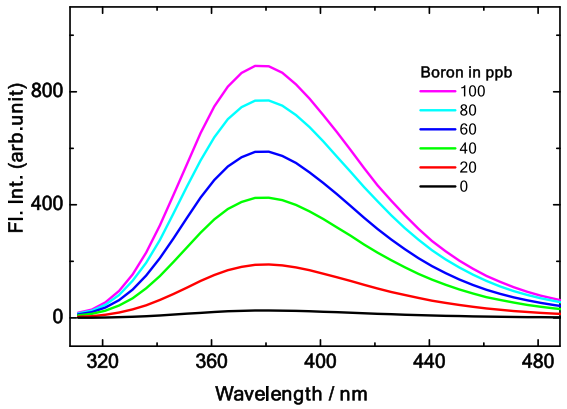

Figure 3. Decay-associated spectra of the boron−chromotropic acid complex.

Table 1. Interference Studies in Solution with 50 ppb of Boron

element	ASTM C1462 specification limit (μg g^{-1} of U)	max. conc. of impurity for 250 mg of sample in 5 mL solution, μg mL^{-1}	impurity added, μg mL^{-1}	recovery of boron[a]
Al	150	7.5	75	96.4 ± 2.9
Ca	100	5	50	101.2 ± 3.5
Cr	50	2.5	25	102.2 ± 1.7
Cu	50	2.5	25	97.5 ± 2.2
Fe	250	12.5	125	96.2 ± 3.1
Pb	10	0.5	5	99.3 ± 3.0
Li	10	0.5	5	100.4 ± 2.4
Mg	50	2.5	25	98.9 ± 3.2
Mn	50	2.5	25	97.4 ± 3.2
Mo	100	5	50	96.1 ± 2.8
Ni	100	5	50	98.4 ± 3.3
Na	25	1.25	12.5	96.8 ± 2.4
Sn	100	5	50	99.3 ± 3.1
W	100	5	50	96.5 ± 2.3
Zr	250	12.5	125	98.0 ± 3.2
Sm, Eu, Gd, Dy	3	0.15	1.5	101.1 ± 1.9

[a]Mean of three determinations.

developed analytical method at 95% confidence interval (t test). Furthermore, as boron is determined in the uranium matrix and it is reported that uranium affects boron determination with chromotropic acid,[17] the dissolved uranium sample was passed twice through the cation exchange cartridge to ensure quantitative matrix separation. Furthermore, the final sample solution was analyzed for uranium by the spectrofluorimetric method having a detection limit of 10 ppb.[53] The result of the uranium analysis was below the detection limit and thus will have no significant interference in the boron analysis at 95% confidence interval (t test).

3.3. Analytical Figures of Merit, Method Validation, and Application to Uranium Metal/Alloy Samples. The calibration plot obtained with DAS of boron−chromotropic acid was linear between 5 and 100 ng mL^{-1} with r^2 better than 0.998. The precision is better than 5% at the 10 ppb level and 4% at the 50 ppb level (n = 9). The limit of detection (LOD) and limit of quantification (LOQ) were calculated using the formulas LOD = 3.3S/b and LOQ = 10S/b (where S is the standard deviation and b is the slope of the calibration plot). LOD and LOQ of boron by the developed method are 1.5 and 4.5 ppb, respectively. The recovery of spiked boron (25 ppb) from the uranium samples was found to be better than 94%. The developed method was validated by analyzing the three U3O8-based certified reference materials (ILCE III, ILCE IV, and ILCE V) prepared by the Department of Atomic Energy (DAE), India. The results obtained for boron analysis in ILCE standards is shown in Table 2 and found to be within the 95% confidence level of their certified values.

Table 2. Method Validation ILCE Boron standards in U_3O_8

standard	certified value (μg g^{-1})	value from the developed method (μg g^{-1})[a]
ILCE III	0.22 ± 0.08	0.23 ± 0.04
ILCE IV	1.10 ± 0.24	1.07 ± 0.05
ILCE V	0.77 ± 0.08	0.81 ± 0.05

[a]Mean of three determinations.

The developed TR fluorimetric method was applied for the analysis of uranium-based nuclear fuel samples. Uranium metal samples were analyzed by the developed method as well as with a curcumin-based spectrophotometric method. The results of boron analysis by both the methods are shown in Table 3. The results were found to be within 95% confidence interval and hence further authenticate the developed method.

Table 3. Results of Uranium Metal Samples Analyzed by the Developed Time-Resolved Fluorescence Method and by the Curcumin-Based Spectrophotometric Method

sample no.	by the present method, μg g^{-1}[a]	by the curcumin-based photometric method, μg g^{-1}[a]
U-metal 1	1.10 ± 0.06	1.00 ± 0.10
U-metal 2	0.82 ± 0.05	0.74 ± 0.07
U-metal 3	1.17 ± 0.07	1.21 ± 0.12
U-metal 4	0.80 ± 0.04	0.84 ± 0.08
U-alloy 1	4.89 ± 0.09	5.00 ± 0.50

[a]Mean of three determinations.

4. CONCLUSIONS

The developed time-resolved fluorescence method focuses on the spectroscopic separation of excess ligand because its fluorescence spectrum overlaps with that of the boron−chromotropic acid complex. Time-resolved fluorescence decay data were used to derive DAS of fluorescent species in the sample solution. DAS of the boron−chromtropic acid complex (measure of boron) is a completely resolved spectrum and contains fluorescence of the boron complex exclusively. Thus, this method allowed the measurement of the analyte peak over negligible background, thereby reducing the uncertainty from the background.

To sum up, the developed method has better sensitivity and selectivity, small sample size requirement, no requirement of organic solvents/medium, reduction in waste generation, and reduced load of uranium recovery from analytical waste, specifically in the case of enriched uranium-based samples. To the best of our knowledge, this is the first report on the application of time-resolved fluorescence as an analytical methodology in the CQA of nuclear fuels.

https://doi.org/10.1021/acsomega.3c07535
ACS Omega 2023, 8, 47271−47276

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Notes

The author declares no competing financial interest.

ACKNOWLEDGMENTS

The author is thankful to Dr. P.S. Ramanjenyulu and Ms. Kanaklata Pandey for boron analysis by the curcumin-based photometric method; to Dr. Bhasikuttan A. C. and Dr. Dutta Choudhury S. for providing the TCSPC setup for doing time-resolved measurements; and to Dr. S. Jeyakumar, RACD, Shri M. K. Saxena, Head, RACD, and Dr. P. K. Mohapatra, Associate Director RC & IG, BARC, for their constant encouragement.

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https://doi.org/10.1021/acsomega.3c07535
ACS Omega 2023, 8, 47271−47276