



# A novel luminescence method for the estimation of uranyl ions using trimesic acid-cadmium complex

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## ABSTRACT

Cadmium ion (Cd<sup>2+</sup>) with trimesic acid forms water insoluble complex. When uranyl ion (UO<sub>2</sub><sup>2+</sup>) is present with Cd<sup>2+</sup>, the complex shows intense luminescence of UO<sub>2</sub><sup>2+</sup> and it is used for the trace level determination of UO<sub>2</sub><sup>2+</sup> ions. A linear response of luminescence intensity of UO<sub>2</sub><sup>2+</sup> ions was obtained over a concentration range of 1–75 ng mL<sup>-1</sup>. Analytical data showed that the detection limit of 0.2 ng mL<sup>-1</sup> (7.4 × 10<sup>-10</sup> M) of UO<sub>2</sub><sup>2+</sup> ion is achieved with a relative standard deviation (RSD) 8.5% (n = 5). The proposed method was successfully applied for quantification of UO<sub>2</sub><sup>2+</sup> ions in natural water and waste water from nuclear fuel processing plant. Furthermore, the estimation of UO<sub>2</sub><sup>2+</sup> ions in cadmium matrix also has been carried out. This study provides a very simple, promising and a novel alternative method for the detection of UO<sub>2</sub><sup>2+</sup> ions in environment.

## 1. Introduction

Uranium being a naturally occurring radionuclide is found to be present at low levels in different environmental samples like soil, rock and water. It is commercially used for nuclear power generation as well as for the production of nuclear weapons. Unfortunately, a significant amount of radioactive waste containing uranium is generated during various steps like mining, purification, nuclear fuel fabrication, waste reprocessing etc. This can lead to widespread contamination of soil, sediments and water if it is not handled carefully [1,2]. Uranium is known to be a carcinogenic element and has toxicological effects to human beings. Large intake of uranium can lead to damage of vital organs like lung, kidney and urinary system [3,4]. World Health Organization (WHO) and Environmental Protection Agency (EPA) have fixed the permissible limit of uranium in drinking water to be 30 ng mL<sup>-1</sup> [5]. In India, Atomic Energy Regulatory Board (AERB) has set the limit of 60 ng mL<sup>-1</sup> of uranium in drinking water [6]. Hence, detection and determination of uranium is utmost important particularly in waste, ground and drinking water.

A number of methods based on different instrumental techniques are reported in literature to determine UO<sub>2</sub><sup>2+</sup> ions, such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [7,8], X-ray Fluorescence Spectrometry (XFS) [9], Atomic Absorption Spectrometry (AAS) [10,11], Fluorimetry [12], Spectrophotometry [13,14] and Surface Enhanced Raman Spectroscopy (SERS) [15–17]. Most of these methods require expensive and sophisticated instruments. To avoid these

limitations researchers have developed sensors for the detection of UO<sub>2</sub><sup>2+</sup> ions [18–22]. One of the drawbacks of these sensors is complexity in the preparation. Therefore, there is a constant demand for the development of a simple, sensitive and selective method for UO<sub>2</sub><sup>2+</sup> ion detection.

Fluorescence spectroscopy is an excellent analytical method for the low level detection of UO<sub>2</sub><sup>2+</sup> ions. As the luminescence of UO<sub>2</sub><sup>2+</sup> ions is weak in aqueous medium due to quenching by water molecules, luminescence enhancing reagents such as H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub> and fluran are being used [23–26] to detect low levels of UO<sub>2</sub><sup>2+</sup> ions. Other popular techniques such as ligand sensitized luminescence and co-luminescence, known for enhancement of lanthanide luminescence by overcoming the low molar absorptivities and non-radiative deactivation pathways [27–29], are also reported for the enhancement of UO<sub>2</sub><sup>2+</sup> ion luminescence [30–32].

In literature, heterometallic hybrid materials synthesized out of UO<sub>2</sub><sup>2+</sup> ions and transition metals/lanthanides with organic acids have been reported [33–43]. Some of these are on co-ordination polymer materials that incorporate both UO<sub>2</sub><sup>2+</sup> and cadmium ions [40,41]. In these reports, the structure of the compounds is demonstrated by single crystal XRD methods. To the best of our knowledge, no such compounds are used for analytical purpose even though some of them are reported as luminescent [33–35,41,43].

One of the techniques employed for the treatment of heavy metals is co-precipitation to pre-concentrate the trace metals from matrixes [44–46]. In the co-precipitation method, the metals are extracted and

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separated from the high content matrix elements, prior to their determination by flame atomic absorption spectrometry or ICP-MS. In the present work, trimesic acid (TMA)- $\text{Cd}^{2+}$  system is used to co-precipitate  $\text{UO}_2^{2+}$  ions prior to its determination by luminescence spectroscopy. By employing this method not only  $\text{UO}_2^{2+}$  ions are pre-concentrated but also helps in detecting low concentrations of  $\text{UO}_2^{2+}$  ions as the luminescence of  $\text{UO}_2^{2+}$  is enhanced in TMA- $\text{Cd}^{2+}$  system. The current method is simple, sensitive and at the same time cost saving. Validation of the method is done by analyzing different sources of water samples like ground, tap and waste water collected locally and by comparing the results with ICP-MS analysis. Furthermore, amount of  $\text{UO}_2^{2+}$  ions in the uranium-cadmium sample collected from pyro-processing laboratory where cadmium is equilibrated with uranium is also estimated. This is the first report where TMA- $\text{Cd}^{2+}$  system is used for quantitative estimation of  $\text{UO}_2^{2+}$  ions.

## 2. Experimental

### 2.1. Instrumentation

All luminescence spectra were recorded using Edinburgh spectrofluorimeter, model FLS920, with a 60 W  $\mu\text{-Xe}$  flash lamp as the excitation source with a repetition rate of 100 Hz. To reduce the interference from scattered light, the spectra were acquired in time gated mode with trigger delay and gate width of 20 and 1000  $\mu\text{s}$ , respectively. Fused silica plate was used as a sample holder for recording the luminescence spectra with front face excitation. The luminescence was collected at  $45^\circ$  angle to excitation. A band pass of 2 nm was set for both the excitation and emission monochromators. A long-wavelength pass filter, (UV - 39, Shimadzu) with a maximum and uniform transmittance ( $> 85\%$ ) above 400 nm, was placed in front of the emission monochromator, to reduce the scatter of the incident beam into the emission monochromator. All spectra were blank subtracted; a blank spectrum was recorded using identical experimental conditions without the  $\text{UO}_2^{2+}$  ion in the solution.

Time resolved spectra were recorded without gating. Luminescence decay times were determined by fitting the observed time resolved luminescence signals to an exponential decay function. A single exponential fit was found to be adequate for the decay processes observed in this study. The  $\chi^2$  values of all the fits ranged between 0.8 and 1.1. The lifetimes were extracted through a tail-fit, where the data points in the decay profile extending to long temporal regions were used for the fitting. The relative standard deviation of the lifetime values was  $< 8\%$ .

UV-Vis absorption spectra were recorded using Avantes fiber optic spectrophotometer, model AvaSpec-3648-USB2 with 300 lines per mm grating. Spectrum was recorded using diffuse reflection probe. Infrared spectra were recorded in the range 4000 to 400  $\text{cm}^{-1}$  using a Bruker vertex 70 FTIR spectrometer operated at a resolution of 0.5  $\text{cm}^{-1}$ . Few milligrams of sample were mixed with KBr powder and pellets were made to record the FTIR spectra. The powder X-ray diffraction (XRD) patterns were recorded using PANalytical X'Pert Pro MPD system with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature. The morphology of the product was studied with Philips XL-30, scanning electron microscopy (SEM), coupled with energy dispersive analysis of X-rays (EDAX). For SEM analysis, pellets prepared out of sample were metallized with thin gold coating.

### 2.2. Reagents

#### 2.2.1. Caution

Uranyl nitrate hexahydrate (AR grade) used in this study contains U, hence standard precautions for handling radioactive and toxic substances were followed.

A weighed quantity of  $\text{UO}_2(\text{NO}_3)_2$  was dissolved in dilute nitric acid to have a  $10 \text{ mg L}^{-1}$  solution. This was used as stock solution and the requisite working standard solutions were prepared by appropriate

dilution. The trimesic acid was from Merck ( $> 98\%$ ) and used as received. Stock solution ( $2 \times 10^{-1} \text{ M}$ ) of TMA was prepared in water and for complete dissolution of TMA, required amounts of sodium hydroxide was added. The nitrate or chloride salts of the cations used (from Merck or Aldrich) were of the highest grade available and used without further purification. All other chemicals were of analytical reagent grade unless stated otherwise. De-ionized water with resistivity of  $18 \text{ M}\Omega \text{ cm}^{-1}$  obtained from Milli-Q (Millipore) system was used for preparing the solutions.

### 2.3. Procedures

The pH of TMA stock solution ( $2 \times 10^{-1} \text{ M}$ ) was adjusted to 5.6 by adding perchloric acid. Into a 50 mL flask, 50–150  $\mu\text{L}$  of  $\text{Cd}^{2+}$  (from 2 M stock prepared from  $\text{CdCl}_2$ ), 0.25–1.0 mL of TMA solution and a known amount of  $\text{UO}_2^{2+}$  solution was added and then diluted up to the mark. The pH of the final solution was found to be about 5.5. The solution was placed in a beaker and mixed at  $\sim 400$  RPM stirring for  $\sim 2$  min. Substantial precipitation was formed and it was allowed to settle for  $\sim 5$  min. A filtration was then performed using Whatman 540 filter paper and the filtrate was used as such for luminescence studies. For FTIR, XRD and SEM studies the filtrate was dried under IR lamp. The pH of water samples collected from different sources was adjusted to 5.5 prior to analysis. Cadmium sample (0.315 g) collected from pyro-processing laboratory was taken in a 100 mL flask and then dissolved in dilute nitric acid before analyzing.

## 3. Results and discussions

### 3.1. Characterization

FTIR spectrum of TMA and the complex formed with cadmium is shown in Fig. 1a and b, respectively. The concentration of  $\text{UO}_2^{2+}$ ,  $\text{Cd}^{2+}$  and TMA in the complexes was  $100 \text{ ng mL}^{-1}$ ,  $5 \times 10^{-3} \text{ M}$  and  $2 \times 10^{-3} \text{ M}$ , respectively. The broad band observed at  $3100\text{--}2550 \text{ cm}^{-1}$  (Fig. 1a) is due to the O–H stretching vibration ( $\nu_{\text{O-H}}$ ) of TMA. The strong peak observed at  $1715 \text{ cm}^{-1}$  is due to the

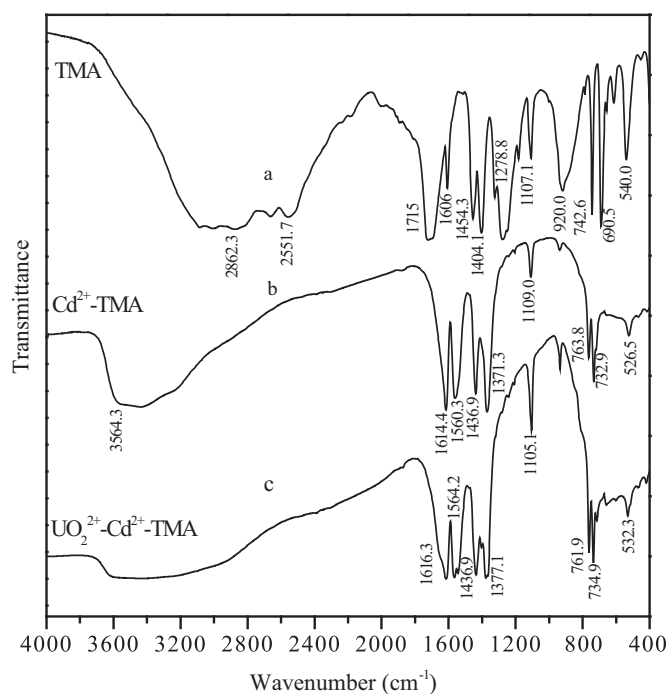


Fig. 1. FTIR spectra of (a) Trimesic acid (TMA), (b)  $\text{Cd}^{2+}$ -TMA complex and (c)  $\text{UO}_2^{2+}$ - $\text{Cd}^{2+}$ -TMA complex.

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