

Determination of uranium in seawater, biological samples and sediments using laser induced fluorescence spectrometry

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Received: 28 March 2015 / Published online: 21 June 2015
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Abstract Uranium has been determined in seawater, biological samples and sediments using laser induced fluorescence spectrometry (LIFS). The biological samples and sediments are digested with a mixture of HNO₃, HClO₄ and HF. The conductivity of the seawater should be below 5.0 mS and the pH of the sample should be in the range 6.5–9.0. The volume of the reagent used to enhance the fluorescence intensity was 0.5 ml. Comparison with other methods was favorable, LIFS being rapid, simple and sensitive, and well suited to environmental monitoring.

Keywords Uranium · Laser induced fluorescence spectrometry · Seawater · Biological samples · Sediments

Introduction

Uranium was the first radioactive element to be discovered and is one of the most important natural nuclides in biogeochemical studies and environment monitoring [1]. The U-series nuclides have been widely used to evaluate biogeochemical processes, including dynamic processes involving sediments, vertical and horizontal diffusion processes and submarine groundwater discharges [2, 3]. The uranium concentration in the oceans is fairly constant at about 3.3 mg/kg [4–6] and the average concentration of uranium in river waters is about 1.3 nmol/kg based on data for some 250 rivers [7].

Uranium can be determined by different analytical methods, including laser induced fluorescence spectrometry (LIFS), resonance light scattering, spectrophotometry, differential pulse adsorptive stripping voltammetry (DPASV), alpha spectroscopy, gamma spectrometry, atomic absorption spectrometry, ICP emission and mass spectrometry and thermal ionization mass spectrometry [5, 6, 8–15].

Laser induced fluorescence spectrometry has been used for uranium determination in environmental samples including seawater since the 1970s [10, 16, 17]. During analysis, several factors may affect results, including the amount of fluorescence intensifier agent added, the pH of the sample and the salinity of the sample [17, 18]. In recent decades, the laser micro-uranium analyzer has been developed. In this study, the ultraviolet pulsed molecular nitrogen laser has been substituted with an ultraviolet laser light source and accuracy has increased. However, whether the operating conditions developed for the previous instrumentation are appropriate for a new instrument is unclear.

With regard to sample preparation, the methods adopted are dependent on the nature of the sample. In recent decades, the measurement of uranium concentrations in biological samples has become important because of the close associations between anthropogenic activities and human health. Previous studies reported that biological samples may be solubilized using sodium persulfate or hydrogen peroxide [19, 20]. However, in in-house experiments it was found that because of the complexity of diverse biological samples, previous methodology was not suitable for all biological sample types. Besides biological samples, marine sediments are also an important sample for environmental monitoring and current sample preparation methods for solid samples have only been tested for rocks, soils and

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minerals [21]. In this research, therefore, we have developed a method that is suitable for the preparation and determination of uranium in biological and sediment samples. We also used a new fluorescence instrument and examined the effects of fluorescence intensifier agent, pH and salinity on system performance.

Experimental

Sample preparation

Seawater

The seawater sample was diluted to appropriate concentration (1–30 times) and analyzed directly.

Biological samples

The sample was first dried at 100 °C for 72 h and completely carbonized. Next, the sample was dry-ashed in a muffle furnace at 500 °C until white ash was generated. Approximately 100 mg of ash was digested with 5 ml HNO₃, 3 ml HClO₄ and 2 ml HF for 2 h. The solution was then diluted to 25 ml with Milli-Q water. For comparison purposes, samples were also prepared using published methods, including a NaS₂O₈ method and a HNO₃ + H₂O₂ method, respectively [19, 20].

Sediments

The sediment was oven dried at 100 °C. Approximately 100 mg of sample was then digested with 5 ml HNO₃, 3 ml HClO₄ and 2 ml HF for 2 h [21, 22]. The solution was then diluted to 25 ml with Milli-Q water. A standard reference sediment sample (GBW08034a, National Institute of Metrology, China) was also analyzed to assess accuracy and precision.

Analytical methods: standard addition method

- (1) 5 ml of sample was dispensed into a cuvette, which was then placed in the cuvette housing of the LIFS. The count rate (f_0) was then recorded using the WGJ-III laser micro-uranium analyzer (Hangzhou Daji Electric Instrument Co., Ltd.)
- (2) Fluorescence intensifier agent (Briug-201, 0.5 ml) was added to the sample solution and the count rate (f_1) was recorded.
- (3) Finally, 5 μ l of uranium standard solution (1 μ g/ml) was added to the above sample solution and the count rate (f_2) was recorded.

- (4) The concentration of uranium in the sample (C_x , μ g/ml) was calculated using Eq. (1):

$$C_x = \frac{f_1 - f_0}{f_2 - f_1} \cdot 10^{-3} \quad (1)$$

Effects of fluorescence intensifier, pH and salinity

- (1) The effect of the volume of fluorescence intensifier agent was tested for a seawater sample. The seawater (1.0 ml) was first diluted to 25 ml with Milli-Q water and then 5.0 ml of diluted seawater were dispensed into the cuvette. Next, increasing volumes of fluorescence intensifier agent, ranging from 0 to 2000 μ l, were added to the cuvette giving, in total, 24 different solutions (Fig. 1). The pH and conductivity of the diluted seawater samples were 8.00 and 2.64 mS, respectively.
- (2) To test the effect of solution pH on fluorescence response, a seawater sample (1.0 ml) was diluted to 25 ml with Milli-Q water. Next diluted samples were adjusted to different pHs using NH₄OH or HNO₃. The fluorescence intensities of the prepared solutions were recorded (Fig. 2). The volume of fluorescence intensifier agent added and the conductivity of the diluted seawater samples were 5 ml and 2.64 mS, respectively.
- (3) To study the effect of salinity on fluorescence response, a seawater sample was diluted with Milli-Q water to give solutions of differing salinity. Eleven samples were prepared (Fig. 3).

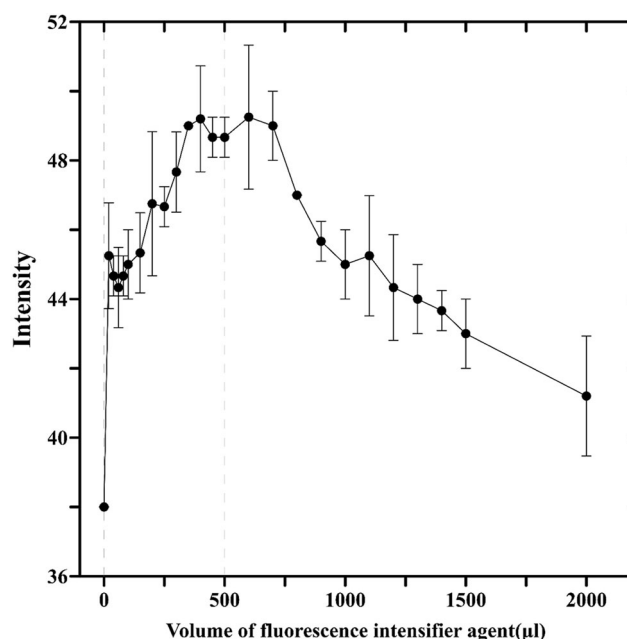


Fig. 1 Effect of fluorescence intensifier agents for uranium determination

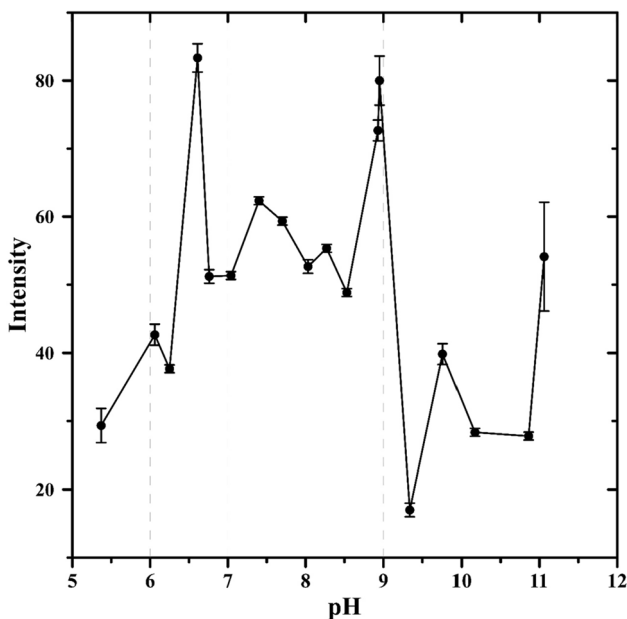


Fig. 2 Effect of pH for uranium determination

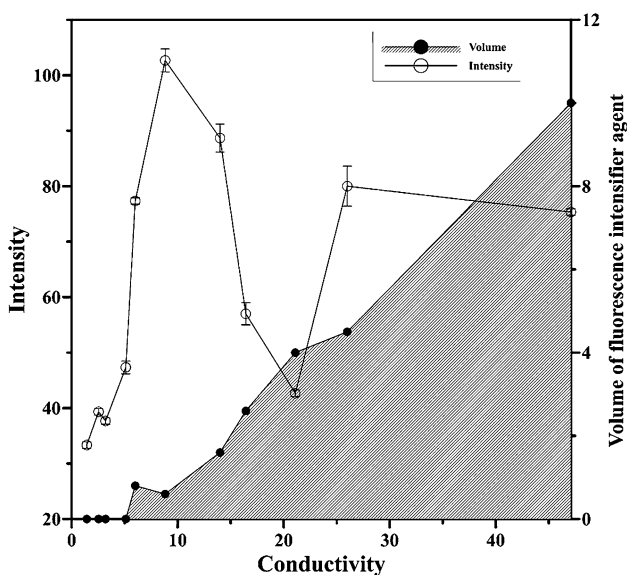


Fig. 3 Effect of salinity for uranium determination

Results and discussion

Sample preparation

Sediments

The LIFS has been widely used for uranium determination in rocks, minerals and soils [16, 21]. Normally, a mixture of HNO₃, HClO₄ and HF is used for sample dissolution. For the present study, a typical recovery value for determination of uranium in sediments by this digestion method was 95.0 ± 8.3 %. This recovery value is comparable with

that reported for dissolution of rocks by accepted methods [21], thus indicating that the proposed digestion procedure was suitable for sediment samples.

Biological samples

Prawn and porphyra samples from the Taishan and Ningde coast of east China were collected for analyses. These samples were considered to be representative of crustacean and alga, respectively and are typical biological specimens used in environmental monitoring programs. As shown in Table 1, methods based on Na₂S₂O₈ or HNO₃ + H₂O₂ were unsuitable for this sample digestion, whereas the three-acid mixture, as used for sediment analysis, was very effective, achieving complete sample dissolution.

Effect of fluorescence intensifier agent

The complex reactions between the uranyl ion in the sample and the fluorescence intensifier agent can enhance the fluorescence intensity [18]. The effect of the fluorescence intensifier agent on the count rate for uranium is shown in Fig. 1. As the figure shows, the intensity increased as the volume of the agent increased from 0 to 0.35 ml. However, signal intensity decreased when the volume added was greater than 0.70 ml. On this basis, a volume for the enhancer of 0.50 ml was used in subsequent experiments.

Effect of pH

The pH of the sample can also influence fluorescence intensity [17]. The relationship between fluorescence intensity and pH is shown in Fig. 2. The fluorescence intensity was relatively constant when the pH of the solution was between 6.5 and 9.0. However, the intensity was reduced when the pH was lower than 6.5 or higher than 9.0. This finding was consistent with a previous study, which used an older generation fluorescence spectrometer [17].

The pH of seawater used in this study was about 8.1 [23] and the pH of most environmental samples ranges typically from 2.0 to 12.5. As the fluorescence intensifier agent also functions as a buffer, the pH value of samples can be adjusted within the range 7.4–8.8 [24]. The results of the present study suggest that most environmental and biological samples that do not require acid solubilization can be analyzed directly without adjustment of the pH.

Effect of salinity

The conductivity of pure seawater is about 47.1 mS at 30.8 %. When the conductivity was higher than 5.1, there was precipitation when the fluorescence intensifier agent

Table 1 The uranium concentration ($\mu\text{g/g}$) of the biological samples using different preparation methods

Sample	$\text{Na}_2\text{S}_2\text{O}_8$	$\text{HNO}_3 + \text{H}_2\text{O}_2$	$\text{HNO}_3 + \text{HClO}_4 + \text{HF}$
Prawn	–	–	0.30 ± 0.09
Porphyra-1 (Taishan)	–	–	0.67 ± 0.06
Porphyra-2 (Ningde)	–	–	0.37 ± 0.01

Table 2 Comparison of uranium analyses methods in seawater

Methods	Volume of sample	Operation	Analyses time	Detection limit (ppb)	Accuracy (%)	Reference
Laser induced fluorescence spectrometry	5 ml	No need	Minutes	0.01–0.04	<15	This study, [17, 26]
Solid fluorescence	100 ml	Extraction	Hours	0.05	<20	[26]
Spectrophotometric	100 ml	Extraction or coprecipitation	Hours	1–2	<10	[27, 28]
Alpha spectroscopy	20 l	Coprecipitation and ion exchange	2–3 days	–	–	[29]
ICP-MS	10 ml	Ion exchange	Hours	<0.01	<5	[6, 30, 31]

was added (Fig. 3). As more intensifier was added, precipitation was not observed. As depicted in Fig. 3, the shaded part of the graph represents the boundary conditions for precipitation. The volume of fluorescence intensifier agent causes the precipitate to form or re-dissolve in accord with the salinity of the different seawater samples. Clearly then, seawater samples must be diluted to the appropriate salinity level to avoid precipitation. Given that the salinity of seawater samples will be different, depending on location, dilution factors for sample preparation would not remain the same for the different samples. On this basis, the optimum conductivity value for seawater samples is less than 5.0 mS.

Determination of uranium in seawater by LIFS and comparison with other methods

Fluorescence and spectrophotometric methods were the main methods for determination of uranium in environmental samples before the 1980s [25]. Laser induced fluorescence spectrometry, which offers high sensitivity and rapid analysis, has been in widespread use since the 1980s. Thereafter, with technological developments, alpha spectroscopy and mass spectrometry have been widely used for elemental and isotopic measurement of uranium.

Comparative data for uranium in environmental samples by LIFS and alternative methods are shown in Table 2. The ICP-MS technique afforded the lowest detection limit and the highest accuracy. This technique together with alpha spectroscopy also permitted measurement of uranium isotopes. In comparison with other methods, LIFS required minimal sampling, and analysis time (several minutes) was also short as the method does not require complex sample

treatment steps. Furthermore, LIFS is also well suited to monitoring uranium in the marine environment.

Conclusions

Based on results for uranium determination in seawater, biological samples and sediments by LIFS, it is concluded that:

1. The biological samples should be dissolved using a mixed acid solution of HNO_3 , HClO_4 and HF.
2. Seawater samples should be diluted, sample salinity adjusted (conductivity <5.0 mS) and fluorescence intensifier agent added (0.35–0.70 ml) to ensure an optimum fluorescence response. The pH of the sample should be within the range 6.5–9.0 (normally for environmental waters, no adjustment of sample pH would be required).
3. The analytical procedure is simple and requires only a small sample size (<5 ml for seawater or 100 mg for biological and sediment samples). Accordingly, LIFS is well suited to environmental monitoring.

Acknowledgments This research was supported by the Scientific Research Foundation of Third Institute of Oceanography, SOA (NO. 2013011), the Public science and technology research funds projects of ocean (201505005-1), the Natural Science Foundation of China (41306073) and the foundation of State Oceanic Administration.

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