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Short communication

Optimization of the arsenazo-III method for the determination of uranium in water and plant samples

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ABSTRACT

This work reports a reliable, fast and optimized photometric technique based on the specific chemical complexation of uranyl ion with arsenazo-III. In the case of solid samples (plant samples), for which mineralization under acidic and oxidative conditions was used, addition of ascorbic acid led to stabilization of the arsenazo–uranyl complex over time. The results, in total agreement with data obtained from α and γ spectrometries, demonstrate that the present technique is able to precisely quantify uranium in water as well as in plant samples, within the μg/L and mg/g ranges respectively.

1. Introduction

Uranium mining is a worldwide business. Until 2001, date at which it finally stopped operating on its territory, France was one of the world's largest producers of uranium ore. Although uranium is a slightly radioactive element in its natural state, it is nonetheless toxic, and that is why it is one of the elements for which the WHO recommendations are the most stringent (30 μg/L in drinking water) [1]. Nowadays post-mining wastelands continue to leach significant amounts of uranium that enter ecosystems and more particularly ground waters and streams. This environmental risk demands remediation programs and scheduled monitoring that originate thousands of tests on a yearly basis. Not only can the current techniques not afford the total demand but, owing to their use of complex physical tools and to their cumbersome implementation they can barely deliver data in less than a full week. The only standardized technology capable of providing a result within 24 h shows quantification limits around three times higher than the WHO recommendations (fluorimetry: 100 μg/L). That is why, since the beginning of the uranium mining, researchers have been working on the design of chemical systems which is simpler and faster to implement. Among the chromogenic reagents studied, we can cite solaphens, [2–6] salens [7–9] and azo pigments [10–12]. In the latter family, arsenazo-III under certain operating conditions, allows an accurate and specific quantitation of uranium (Fig. 1) [13–17].

This colorimetric method is fast, economical and easy to implement. However, the quantitation thresholds do not go below the ppm level (1 mg/L). In addition, the acidic conditions required for mineralization of the samples require that UV–vis absorbance be measured immediately after reagent mixing due to instability of the arsenazo–uranyl complex over time. In this paper, through a program aimed at decontaminating a former AREVA mining site located at Bessines-sur-Gartempe (Haute-Vienne, France) in partnership with the Pe@rL company (accredited by COFRAC), we propose an optimized quantitation technique of uranium based on the arsenazo-III technique. We present how to quantify low concentration samples (ppb) and how the use of ascorbic acid stabilizes the arsenazo-III–uranyl complex over time. Results will be discussed and compared with standard techniques commonly used for the measurement of uranium, such as α and γ spectrometries.

2. Material and methods

2.1. Measurement of uranium by the arsenazo-III method

Determination of uranium in solution was adapted from the arsezano-III method proposed by Khan et al. [18]. Reagent was prepared by dissolving 70 mg of the disodium salt of 2,7-bis

Abbreviations: arsenazo-III, 2,7-bis(2-arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid disodium salt; COFRAC, French accreditation committee; ppb, part per billion; ppm, part per million; TTA, toluene-saturated 2-thenoyltrifluoroacetone

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(2-arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (also called arsenazo-III) into 1 l of 3 M $HClO_4$. One milliliter of raw or diluted extract was mixed with 4 mL of reagent. Absorbance was measured at 651 nm with a UV-1700 Shimadzu spectrophotometer. Concentrations of uranium were deduced by comparison with a scale of uranyl nitrate accounting for 1–15 mg L^{-1} (Fig. 2).

2.2. Natural sample preparation for measuring of uranium concentration by the arsenazo-III method

2.2.1. Liquid samples

All liquid samples were collected from a former uranium mine (Margnac, Haute-Vienne, France). 500 mL of the liquid sample were concentrated to dryness using a rotary evaporator and taken up in 1 mL of HNO_3 and brought to a final volume of 10 mL with distilled water. Uranium determination was performed with arsenazo-III on the concentrated sample as described above.

2.2.2. Solid samples

Solid samples (Douglas fir bark from Egletons—France) have been pre-treated with 0.1 M HNO_3 in order to eliminate natural contaminants as described previously [19]. They were mineralized in a Perkin-Elmer Multiwave 3000 system. To each 1 g sample in a PTFE-TFM® tube 5 mL of concentrated HNO_3 and 2 mL of concentrated HCl were added; the tubes were sealed and then subjected to a four phase microwave heating program: 200 W for 1 min; 200–500 W in 15 min; from 500 W to 850 W in 10 min, then 15 min of landing; and 0 W for 15 min (cooling).

During the digestion, pressure and temperature reached maximal values of 6×10^6 Pa and 260 °C. After reaction and without filtration, the digests were transferred into vials and volumes were brought to 25 mL with ultrapure water, then the amount of uranium present in solution was measured in 1 mL aliquots by the arsenazo-III method.

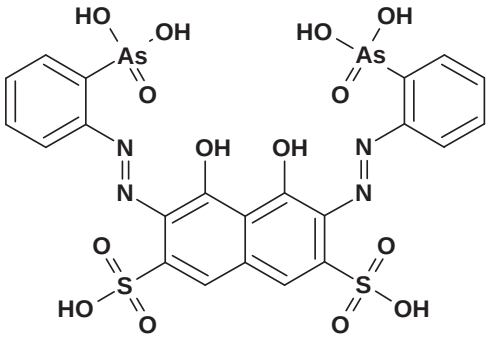

Fig. 1. Structural formula of arsenazo-III.

2.3. Measurement of uranium by α spectrometry

Samples of water were first acidified to pH 1 and then treated according to the NF M60-805-5 standard. A known amount of a solution of uranium 232 with known activity (tracer) was added at the beginning of the chemical treatment. Pre-concentration of uranium from the acidified aqueous samples was performed by co-precipitation with $Fe(OH)_3$ which was done by raising pH to 9 with NH_4OH and further addition of a 10% $FeCl_3$ solution. The precipitate containing the actinides was separated from the sample by centrifugation, and then dissolved in 6 M HCl. Iron was extracted with di-isopropylether using a separating funnel. Separation of uranium from the other actinides was effected by ion exchange chromatography in a glass column (∅ 15 mm) filled with 10 mL of Dowex 1 × 8 (100–200 mesh) equilibrated with 8 M HCl. Uranium-containing solutions were dried, re-dissolved in 50 mL of 8 M HCl and passed through the column. The uranium fraction was eluted with an equal volume of 0.1 M HCl. Purified uranium was extracted from this fraction with toluene-saturated 2-thenoyltrifluoroacetone (TTA). Extracts were deposited by evaporation on small aluminum dishes and dried before counting. The deposit has to be as thin as possible (around 0.1 mm) in order to limit self-absorption and to reduce counting time. Samples were counted for alphas (Canberra Alpha Quarto) using detectors lodged in vacuum chambers. Detectors were coupled to low-noise pre-amplifiers, amplifiers and a multichannel analyzer. Spectra were collected after at least 1000 counts in the channels corresponding to ^{232}U which were sufficient to obtain good statistics. Activities of ^{238}U and ^{234}U were deduced from the ^{232}U activity. Then, uranium concentration was calculated by using the appropriate conversion factors.

2.4. Measurement of uranium by γ spectrometry

Natural isotopes of uranium are not easily measured by means of γ spectrometry. Regarding ^{238}U, an indirect method consists in measuring the activity of its descendant, ^{234}Th. Since the period of the latter is 24.1 days, repeated measurements spaced out at several-week intervals are required to extrapolate thorium re-growth curve at time zero and to calculate initial uranium concentration with maximum precision. 1 g-samples were crushed down to particle size smaller than 200 μm and were placed in a hermetically sealed tube fit to the detector (Canberra Eurisys gamma spectrometer).

3. Results and discussion

3.1. Analysis of natural water samples: comparison of the arsenazo-III method and α spectrometry

Five water samples from the uranium mining site of Bessines-sur-Gartempe (Haute-Vienne, France) have been assayed by the

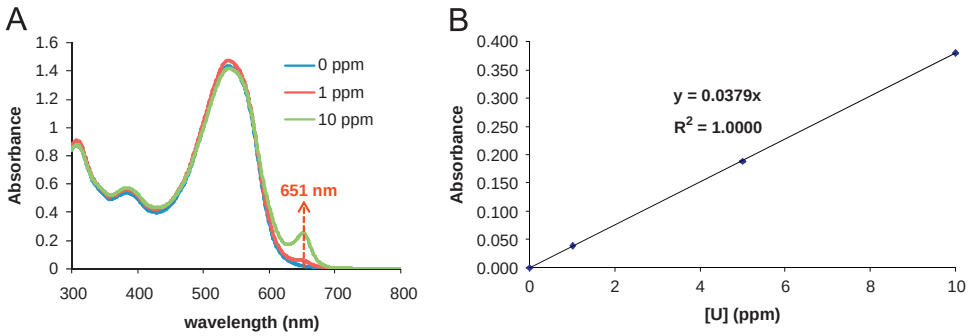

Fig. 2. UV spectra of assay mixture in presence of different uranium concentrations (0, 1 and 10 ppm) (A). Correlation curve between uranium concentration (ppm) and absorbance at 651 nm (B).

techniques of arsenazo-III and α spectrometry. The results obtained by these two methods are compared in Fig. 3.

We could observe a strong correlation of results between the two methods. Samples 1 and 2, representative of highly concentrated samples (350–400 μg/L) gave similar results obtained respectively with arsenazo-III and α spectrometry. So sample 1 gave respectively: 363 μg/L (arsenazo-III) and 347 μg/L (α spectrometry) of uranium. Similarly, concentrations found in sample 2 were 359 and 381 μg/L respectively. For samples 3, 4 and 5 representing the lowest concentrated samples (35–50 μg/L), we obtained by the two methods uranium concentrations respectively 50 and 43, 49 and 46, 38 and 45 μg/L. We also noted that the arsenazo-III experimental errors (average of 6.6%) were smaller than those occurring with α spectrometry (average 12%). Moreover, the arsenazo-III method was quickly completed (1 h for sample preparation and 15 min for the assay), although α counting required 3 days for preparation followed by a 1-day counting time.

3.2. *Analysis of Douglas fir bark samples: comparison between the arsenazo-III method with γ spectrometry*

The first step was to assess the feasibility and the stability of the dosage with arsenazo-III on solid samples which requires a step of mineralization. To do this, we first performed a stability study of the dosage over time according to the same protocol as for liquid samples. We found that the protocol for liquid samples cannot be applied to solid samples since absorbance drops to 15% of its initial value within 10 min following mixing of sample with arsenazo-III (Fig. 4: blue curve). Thinking that this instability was due to the oxidizing character of the mineralization medium which can lead to the formation of free radicals and further arsenazo-III degradation, 0.5 mL of a 100 g/L ascorbic acid solution was added to each assay (Fig. 4: red curve). In this manner, 93% of the assay sensitivity was retained up with the use of the anti-oxidant. Therefore, we conducted a study which also included five solid samples from the same sampling site (Douglas fir bark) from a previously reported uranium decontamination process [17]. All these samples have been assayed by the arsenazo-III method and γ spectrometry. The results obtained by these two methods are shown in Fig. 5.

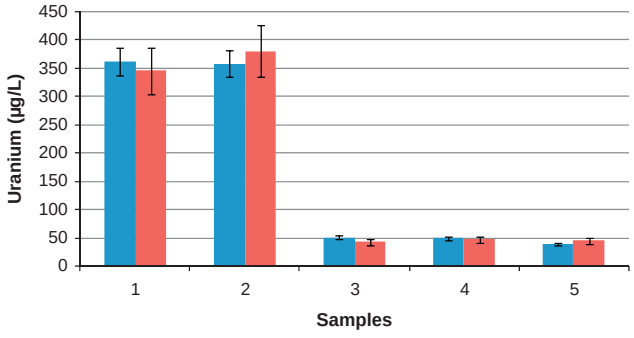

Fig. 3. Uranium concentrations of water samples: the arsenazo-III method (blue bars) and α spectrometry (red bars). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

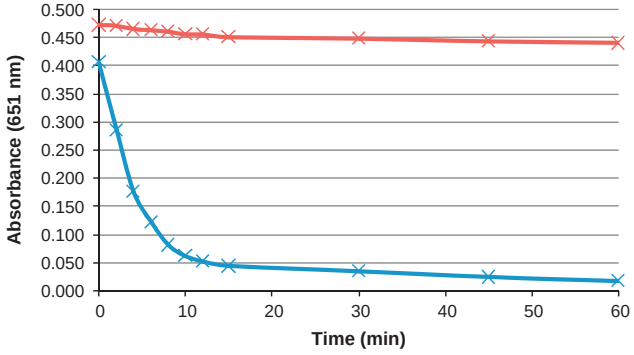

Fig. 4. Absorbance stability of assay mixtures obtained with solid samples after mineralization, without (blue curve) or with (red curve) ascorbic acid. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For solid samples, we also observed a very good correlation of results between the two methods. Samples 1 and 2, representative of samples with large amounts of adsorbed uranium (25–50 mg/g) gave similar results obtained respectively with arsenazo-III and γ spectrometry, hence, 48.2 and 48.0 mg/g (sample 1) and 28.6 and 28.9 mg/g (sample 2) respectively. For samples 3, 4 and 5 which represent smaller amounts adsorbed onto bark (2–15 mg/g), we obtained with the two methods respective uranium concentrations of 12.8 and 12.6 (sample 3), 5.3 and 5.8 (sample 4), and 2.5 and 2.8 mg/g (sample 5). We could also notice that experimental errors were smaller with arsenazo-III assays (average 6.6%), than with γ spectrometry (average 25%). Moreover, for each sample, the first method which required 2 h of sample preparation and 20 min of assays, was found actually much more rapid than γ spectrometry that demanded a 3-month delay in order to achieve equilibrium with ^{234}Th and 2 h of γ counting.

3.3. *Influence of Fe(III) on the assay*

To ensure the specificity of the test with arsenazo-III for uranium, we conducted a study of the influence of Fe(III). Indeed, this metal ion is cited in the literature as one of the most commonly found in nature that can interfere with uranyl ion for the formation of multidentate complexes [19–23]. We added known amounts of $FeCl_3$ in a natural water sample, before uranium determination with the arsenazo-III method (Fig. 6).

We found that Fe(III) had little influence on the assay with the proposed method. At least, 1 g/L of $FeCl_3$ has been added in order to notice a significant impact on the assay. However, this ion is almost never present at these concentrations in natural waters. Iron concentrations in natural waters usually lie around a few tens of μg/L [24].

4. Conclusions

Although the proposed technique is and remains a laboratory technique, we have clearly demonstrated that it is possible to use the arsenazo-III method as a rapid and specific determination of uranium

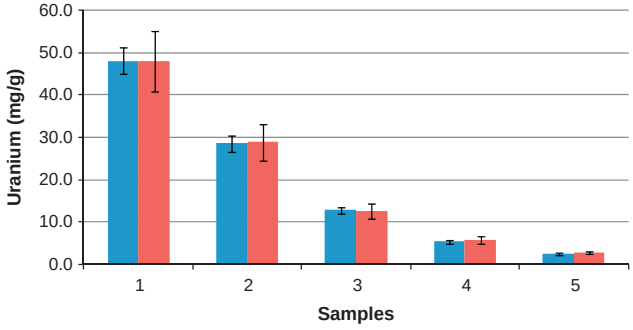

Fig. 5. Uranium concentrations of bark samples deduced from the arsenazo-III method (blue bars) or the γ spectrometry method (red bars). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

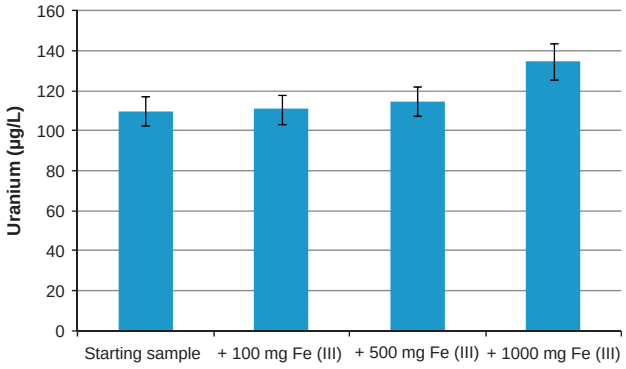

Fig. 6. Influence of Fe(III) on uranium determination with the arsenazo-III method.

in natural complex systems. We have also shown that it is possible by optimizing the operating conditions, to lower the limit of quantification and to stabilize the assay over time. In this way, we propose a protocol used on natural samples that overcomes operator-dependent factors. This method could be used by many research teams or workers in uranium analysis and/or decontamination, who need repeatable and usable analytical methods.

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