



Anion-exchange separation of interfering iron from liquid samples for accurate determination of uranium by spectrophotometric method

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ABSTRACT

The spectrophotometric determination of uranium by Arsenazo III (Ar-III) method in the presence of milligrams of iron is not possible due to the interference caused by iron. To overcome this problem an anion-exchange method for liquid samples (environment, process stream, tailings, wastewater etc.) has been developed for the separation of milligram concentration of iron from dilute solutions of microgram concentration of uranium prior to the spectrophotometric determination. Dowex 1X8 resin was utilized for the separation of iron and uranium in 0.1 M sulfate media. The elution of loaded uranium on the resin column was done with 4% (v/v) nitric acid. Excellent separation was achieved with 97%–101% recovery of uranium. Afterward, the samples were analyzed by Ar-III method; the results were found in good agreement with the already established dibenzoylmethane and fluorimetric methods of uranium analysis.

Keywords: Arsenazo-III; Ion exchange; Iron separation; Uranium

1. Introduction

Uranium determination is of much interest for many decades due to its use as fuel in power generation [1], defense and environmental concerns because of its radioactivity and toxicity effects [2,3]. Many procedures were developed for the measurement of uranium in liquid samples [4–9]. Out of these methods, more emphasis was given to the spectrophotometric determination due to its low cost, simple instrumentation and rapidness [6,7,10–14]. However, the major disadvantage of spectrophotometric determinations over the other methods is that it is prone to interferences by many metal ions [4,6,7,14]. Different researchers used various approaches like precipitation, solvent extraction, preconcentration, the use of masking agents, ion-exchange separation and so on [3,6,7,14–24] to cope with these interferences.

Precipitation separation has its own disadvantage of co-precipitation of uranium [25,26]. The ion-exchange methods have been identified as most suitable for removal of many elements, including iron [18,19,27–31]. For ion-exchange separation, a number of resins had been investigated [17,19,32–36].

There are many reagents used for the determination [5,23,24,37] of uranium, but Arsenazo III (Ar-III) is extensively used. Besides uranium, other metals like Fe, Ca, Th and Zr also form colored complexes with Ar-III [5,38,39], making the usefulness of this reagent limited for spectrophotometric determination of uranium. This problem was tried to overcome by different workers. One group utilized diethylenetriaminepentaacetic acid (DTPA) as masking agent, which masked iron up to 100 µg/mL [14]. The other researchers used ion-exchange preconcentration method and reported the tolerance level of iron impurity up to 100 µg/mL [6,7].

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Above cited references depict that the samples having iron concentration more than 100 $\mu\text{g/mL}$ cannot be analyzed by Ar-III (DTPA) method. The only options remained to analyze the uranium in iron containing liquid samples are the dibenzoylmethane (DBM) spectrophotometric method and fluorimetric technique [18,40] after the removal of impurities by solvent extraction. But the problem is that these extraction and separation procedures are hazardous, expensive, waste generating, laborious and time consuming as well.

To the best of our knowledge till date, no direct spectrophotometric method is available for the determination of uranium in liquid samples having iron matrix interference more than 100 $\mu\text{g/mL}$.

In the present study, an anion-exchange method using dilute sulfate media, simple glass column, and single step uptake/elution of uranium has been developed for the separation of uranium from iron matrix before performing its spectrophotometric determination with Ar-III method. The objective was to establish an easy and reliable method for the determination of uranium in the iron matrix to indulging its interfering effects by coupling with ion-exchange separation.

2. Materials and methods

2.1. Apparatus

A spectrophotometer 6305 by Jenway (Staffordshire) was used for the determination of uranium by Ar-III method (2 mL 0.125% Ar-III, 5 mL 0.5 M HCl, total volume 50 mL) at 648 nm. Iron determination was carried out by using a PerkinElmer AAnalyst 700 atomic absorption spectrophotometer (AAS) by following [41] method. The pH measurements were made using Jenway 3305 pH meter.

2.2. Chemicals/reagents

All reagents (usually 0.125% Ar-III, HCl 0.5 M, nitric acid 0.6 M, ammonium sulfate 0.1 M, dilute sulfuric acid, dilute ammonia) used during the entire experimental work were of analytical grade. Uranium standard was prepared from specpure U_3O_8 (purchased from JMC, UK) and iron standard of 1,000 $\mu\text{g/g}$ from analytical reagent (AR) grade salt of ferric chloride. 100 mL sample aliquots were used to carry out all the experiments.

2.3. Ion-exchange column

The resin Dowex 1X8 (5 mL soaked) having 100–200 mesh size in chloride form was packed in a glass column having inner diameter 1.8 cm with 30 cm height. The flow rate was kept at 2 mL/min for loading and elution. Conditioning of the column was carried out by passing 40 mL of 0.6 M HNO_3 to convert the resin into nitrate form, which was found adequate to make resin column chloride free. At the end, 40 mL of 0.1 M sulfate (from ammonium sulfate) solution was passed to bring the resin column in the sulfate form.

2.4. Separation procedure

The synthetic solutions containing iron and uranium were conditioned before passing through a resin column so

that they contain 0.1 M sulfate and the pH was adjusted to 3. The column was conditioned by passing 20 mL of 0.1 M sulfate solution to bring it in sulfate form and at pH 3. A 100-ml pretreated sample was then passed through the resin column at a flow rate of 2 mL/min. Uranium was retained on the column, and iron was passed through as such and analyzed by AAS. Uranium was eluted by 40 mL of 0.6 N HNO_3 in two batches, and concentrated uranium was analyzed by Ar-III method as stated above.

3. Results and discussion

3.1. Optimization of sulfate concentration

This method provides a simple one-step procedure with better efficiency for the removal of interfering iron from aqueous solutions containing uranium. Since uranium forms negatively charged complex $[\text{UO}_2(\text{SO}_4)]^{-2}$ with sulfate ions; therefore, it was retained on column resin by replacing sulfate ions [17]. Originally, the resin was in chloride form since the distribution coefficients of chloride and sulfate anions are different with anion-exchange resin, and our whole work was done in sulfate-nitrate media. Therefore, it was brought into sulfate form during the preconditioning step. The preconditioning was performed with 20 mL of ammonium sulfate solution in which the sulfate concentration was maintained at 0.1 M, and complete removal of chloride with sulfate was checked by silver nitrate solution as silver formed white precipitates with chloride. In the last few drops, there was no formation of white precipitates with silver nitrate indicating the complete replacement of chlorides into sulfates. To achieve the best separation between uranium and iron first of all, sulfate concentration was optimized, and this was done by applying different concentrations of sulfate ranging from 0.05 to 0.3 M in fixed concentration of uranium 10 $\mu\text{g/mL}$. The results obtained from this experiment were plotted as sulfate concentration vs. uranium retention percentage as shown in Fig. 1. From Fig. 1, it is very clear that the maximum retention of uranium was achieved at 0.1 M sulfate solution. Therefore, this sulfate concentration was chosen for the maximum uranium retention.

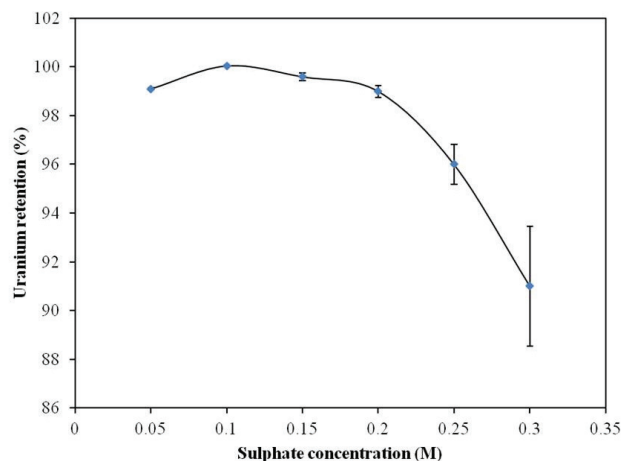


Fig. 1. Uranium retention at various concentrations of sulfate.

To proceed further, sulfate concentration was also optimized for maximum recovery of iron because for maximum separation it was needed that at a single concentration of sulfate media maximum uranium retention and maximum iron recovery should be obtained. Therefore, in the next experiment, 10 $\mu\text{g}/\text{mL}$ of iron made in the range of 0.05–0.3 M; sulfate medium was passed through the column; and a graph plotted between sulfate concentrations and iron recovery in percentage as shown in Fig. 2. The figure depicts that maximum iron recovery was also obtained at 0.1 M sulfate concentration which is the same concentration at which maximum uranium was retained. Hence, 0.1 M sulfate concentration was optimized for maximum separation between uranium and iron metals.

3.2. Optimization of pH

The separation of uranium from iron impurity was studied at pH values ranging from 1–7. A number of samples were prepared, each having 10 $\mu\text{g}/\text{mL}$ of uranium, 0.1 M sulfate and 10 $\mu\text{g}/\text{mL}$ of iron. Before passing through the column, each sample solution was adjusted (by using dilute sulfuric acid and ammonia) to the desired pH from 1 to 7. The results obtained for percent retention of uranium and percent recovery of iron impurity are given

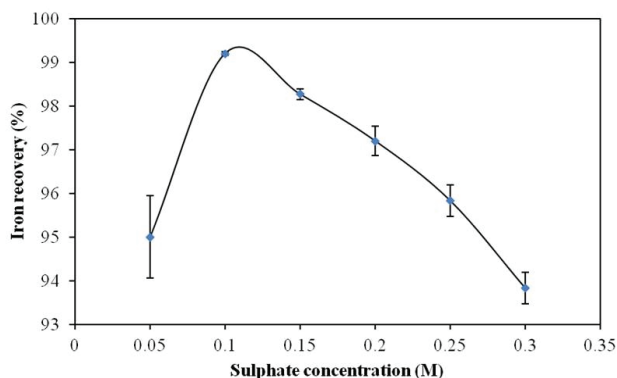


Fig. 2. The recovery of iron matrix at different concentrations of sulfate.

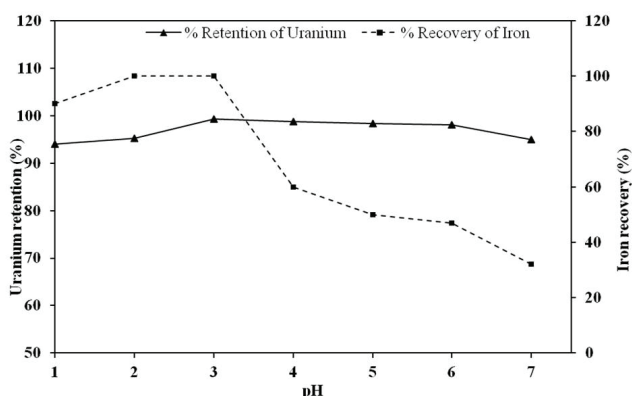


Fig. 3. The recovery of iron and retention of uranium at different pH values.

in Fig. 3. It can be seen that the maximum retention of uranium on the column was obtained at pH 3. The reason for low retention of uranium on the resin column at pH 1 and 2 may be the weak complexing behavior of sulfate ions with uranium at these highly acidic pH values, while somewhat decreasing trend of uranium retention at higher pH may be due to more solvation of sulfate ions and less stability of uranyl sulfate. The results shown in Fig. 3 also reflected that the removal of iron does not show any significant change up to pH 3. But the recovery of iron got more inadequate at pH 4 and 5, perhaps due the formation of a stronger complex of sulfate with iron [18,35] which was further alleviated at higher pH values. At this stage, two important parameters were optimized for the effective separations which are 0.1 M sulfate and pH 3.

3.3. Elution and analysis of uranium by Ar-III

The resin column loaded with uranium was eluted with nitric acid and 25 mL of 0.6 M nitric acid was found to be sufficient to completely elute the loaded uranium from the column according to the procedure mentioned in the reference [17]. After elution, the eluate was analyzed by the standard procedure of uranium analysis with Ar-III method in which there was no more interference of iron, as the whole of the iron was removed in the first step of separation of uranium and iron. Table 1 shows the results of uranium spiked in the iron matrix of varying concentrations. The samples were analyzed by Ar-III method as published in the references [5,12]. In this case, no separation was done; and the results behavior was similar to already reported results [14] that uranium was suppressed by interfering metallic iron as shown in Table 1. The iron in uranium matrix is tolerated to a maximum of 100 $\mu\text{g}/\text{mL}$ as impurity followed by the determination with Ar-III method without separation.

A series of sample solutions having uranium 10 $\mu\text{g}/\text{mL}$ and iron concentrations between 126 and 1,000 $\mu\text{g}/\text{mL}$ were prepared. This will give the efficiency of uranium retention in high concentration of iron. Each sample solution was conditioned to ensure 0.1 M ammonium sulfate, and the pH was adjusted to 3 which were preoptimized. These sample solutions were passed through the column according to the previously mentioned procedure. The results are shown in Table 1. From the results it can be highlighted that ion-exchange column was capable of retaining added uranium with retention efficiency of greater than 99%. It is also very clear from Table 1 that iron was recovered up to 1,000 $\mu\text{g}/\text{mL}$ with more than 98% recovery. Table 1 provides the results of lab-synthesized samples after applying this developed separation method to encounter the iron interference. The results revealed the good efficacy of the developed method up to mg/mL concentration of iron as an impurity. Each reported result in this paper is the average of three replicas (separation and determination).

3.4. Application of method

The proposed separation method was applied to the process leach solutions obtained from some uranium

Table 1

Results of uranium analysis with Ar-III method [14] before and after applying proposed separation procedure

Sr. No.	Iron matrix ($\mu\text{g/mL}$)	U_3O_8 spiked ($\mu\text{g/mL}$)	Uranium analysis with Ar-III method without separation			Uranium analysis with Ar-III method with proposed separation		
			U_3O_8 ($\mu\text{g/mL}$)	% efficiency	% error	U_3O_8 ($\mu\text{g/mL}$)	% efficiency	% error
1	126	10	9.00	90	10	9.75	97.50	2.50
2	300	10	7.55	75.50	24.50	10	100	0.00
3	680	10	5.35	53.50	46.50	9.92	99.20	0.80
4	1,000	10	5.19	51.90	48.10	9.56	95.60	4.40

Table 2

Comparison of the results by modified method with DBM and fluorimetric methods

Sample ID	Ion exchange U_3O_8 ($\mu\text{g/mL}$) by Ar-III	DBM U_3O_8 ($\mu\text{g/mL}$)	Fluorimetric U_3O_8 ($\mu\text{g/mL}$)
PL-1	8.32	8.9	8.5
PL-2	6.56	6.5	6.5
PL-3	12.15	12.0	12.5
PL-4	60	58	61

reclamation facility. The method displayed excellent results for the separation of iron impurity added to uranium matrix as shown in Table 2. In this type of process, leach solutions iron was already present in varying amounts; therefore, the direct determination of uranium by spectrophotometric methods was not possible, and in routine, solvent extraction was used before the determination of uranium [17,18].

Four samples PL-1, PL-2, PL-3 and PL-4 (collected from reclamation facility) of process leach, having 85, 325, 700 and 1,000 $\mu\text{g/mL}$ of iron impurity, respectively, were collected. 20 mL of each sample solution was conditioned as brought in 0.1 M sulfate (using ammonium sulfate) medium, and pH was adjusted to 3 by sulfuric acid (the pH of 0.1 M sulfate medium was 5.5). All sample solutions were prepared in triplicate. These sample solutions were passed through the anion-exchange column using the optimized procedure; post column solutions were collected and analyzed for the measurement of iron by AAS. While the loaded resin column was eluted with 40 mL of 0.6 M nitric acid and then a measured amount of this eluted sample solution was put into a 50 mL flask and after adding reagents for Ar-III, final volume was kept to 50 mL. Standard and sample blank were also passed through the ion-exchange column under the same conditions. The results obtained were compared with those achieved with DBM [14,18,40] and fluorimetric methods [39], which are used after solvent extraction separation. It was found that the results were in good agreement with DBM and fluorimetric methods. Besides this, the new method showed a high degree of accuracy and reproducibility.

The developed method is very efficient, low cost, environment friendly, quick and waste free, and can be applied reliably for uranium determination in liquid sample having iron contamination ranging from $\mu\text{g/mL}$ to mg/mL levels.

4. Conclusions

Till date, no direct method is available for the determination of uranium in liquid samples having iron interference higher than 100 $\mu\text{g/mL}$. The enrichment of low levels of uranium, followed by determination of uranium with this method in samples containing iron matrix more than 100 $\mu\text{g/mL}$ concentration, was successfully done in the present studies. The proposed ion-exchange method selectively removed iron from aqueous uranium samples which was further analyzed spectrophotometrically by applying Ar-III method. This new analytical procedure produced very accurate results with good reproducibility even to the samples containing up to 1,000 $\mu\text{g/mL}$ of iron.

Abbreviations

- Ar-III — Arsenazo III
- DBM — Dibenzoylmethane
- DTPA — Diethylenetriaminepentaacetic acid
- AAS — Atomic absorption spectrophotometer
- DDW — Double distilled water

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