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Selective ion exchange separation of uranium from concomitant impurities in uranium materials and subsequent determination of the impurities by ICP-OES

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Abstract An ion exchange method has been developed for the separation of uranium from trace level metallic impurities prior to their determination by inductively coupled plasma optical emission spectrometry (ICP-OES) in uranium materials. Selective separation of uranium from trace level metallic impurities consisting Cr, Co, Cu, Fe, Mn, Cd, Gd, Dy, Ni, and Ca was achieved on anion exchange resin Dowex 1 × 8 in sulphate medium. The resin (100–200 mesh, in chloride form) was packed in a small Teflon column (7.8 cm × 0.8 cm I.D.) and brought into sulphate form by passing 0.2 N ammonium sulphate solution. Optimum experimental conditions including pH and concentration of sulphate in the liquid phase were investigated for the effective uptake of uranium by the column. Uranium was selectively retained on the column as anionic complex with sulphate, while impurities were passed through the column. Post column solution was collected and analyzed by ICP-OES for the determination of metallic impurities. Up to 2,500 µg/mL of uranium was retained with >99% efficiency after passing 25 mL sample through the column at pH 3. Percentage recoveries obtained for most of the metallic impurities were >95% with relative standard deviations <5%. The method established was applied for the determination of gadolinium in urania–gadolinia (UO_2–Gd_2O_3) ceramic nuclear fuel and excellent results were achieved. Solvent extraction method using tributylphosphate (TBP) as extractant was also applied for the separation of uranium in urania–gadolinia nuclear fuel samples prior to the determination of gadolinium by ICP-OES. The results obtained with the present method were found very comparable with those of the solvent extraction method.

Keywords Uranium · Ion exchange · Ceramic nuclear fuel · ICP-OES

Introduction

Nuclear technology is being utilized for significant benefits in number of fields including power sector, defense, agriculture and medicine while many other areas are being explored. A lot of efforts are being made to develop the processes for obtaining the useable grade of uranium for nuclear power plants. Uranium is produced according to required standards of applications and with quality assurance procedures stretched to the highest purity limits. The concentration of metallic impurities in nuclear fuel has to be maintained at certain specified limits to obtain the required density for pellets and also to reduce the loss of neutrons by the elements having high neutron absorption cross section [1, 2]. Determination of metallic impurities in uranium at various stages of nuclear fuel cycle plays significant role in the quality control and achievement of chemical and metallurgical requirement. Hence it is absolutely essential to quantify these impurities in uranium materials prior to its use as nuclear fuel [3, 4]. The chemical characterization of uranium materials at sub parts per million levels has been possible, due to advanced instrumentation. A number of analytical techniques have been used for the determination of trace level metallic impurities in uranium matrices. These techniques include ICP-MS [5–7], AAS [8], GFAAS [9], and HPLC-ICP-MS [10]. Since last 20 years nuclear

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industry has greatly benefited from the analytical power of ICP-OES. A number of studies have been reported for the determination of trace level metallic impurities in nuclear materials using ICP-OES [11–15]. However the direct determination of impurities in uranium matrix by ICP-OES is not successful due to spectral interference caused by the line rich emission spectrum of uranium [16–18]. Contamination of equipment due to direct injection of uranium into ICP is another restriction. Hence an efficient method for the separation of uranium from impurities is essentially required prior to their determination. Various separation methods including extraction chromatography [3], selective precipitation [12], solvent extraction [14], ion exchange [19] and combination of these [4, 13] have been employed by various researchers for the separation of uranium from impurities prior to their determination by ICP-OES.

Solvent extraction method provides satisfactory results but the process is tedious, involves use of hazardous organic solvents and generates a large amount of nuclear waste. Chromatographic separation procedures are lengthy, complicated and are not considered feasible in combination with ICP-OES. The Ion exchange methods have been identified as one of the most appropriate and suitable for the removal of the majority of metals including uranium [20–24]. Ion exchange methods involve compact equipment, simple operating procedures and minimum analyte losses. Moreover these methods are suitable for online combination with ICP-OES and ICP-MS.

Variety of ion exchange resins such as IRA 910 U and Dowex – A [25, 26], Dowex 1 × 8, 19 [27], Bio-Rad AG 1 × 8 and MP-1 [28] and AR-01 [29] using different media i.e. carbonate, nitrate, chloride, and sulphate have been investigated for the separation of uranium. Certain limitations have been observed in most of the studies such as the use of highly concentrated acids for the elution of impurities, use of several eluents for the selective elution of different components of the samples from the column and poor recoveries of impurities. Due to these limitations the ion exchange methods reported previously are cumbersome and are relatively less feasible compared to the solvent extraction methods.

In the present study an ion exchange method, using dilute media, small column and utilizing single step uptake/elution of uranium, has been developed for the separation of uranium from trace level metallic impurities prior to their determination by ICP-OES. An anion exchange resin Dowex 1 × 8 was used to separate uranium from concomitant metallic impurities including calcium (Ca), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), dysprosium (Dy), iron(Fe), gadolinium (Gd), manganese (Mn), and nickel (Ni). The aim was to develop a reliable analytical method for the determination of trace level metallic impurities in uranium materials by ICP-OES.

Experimental

Apparatus

An iCAP 6500 ICP-OES from Thermo Fisher Scientific UK, with ITEVA (version 8) operating software for full control of all instrument functions and data handling, was used for the measurement of metals. This instrument is equipped with high performance solid state CID camera system having RACID 86 detector containing a 512 × 512 array of charge injection devices (CID). The high precision peristaltic pump of the instrument having 12 rollers, 4 channels with adjustable speed (0–125 rpm) was used for sample introduction into the plasma. The operating conditions of ICP-OES were: viewing height 15 mm radial, nebulizer gas flow 0.7 L/min, flush pump rate 100 rpm, analysis pump rate 50 rpm, pump stabilization time 5 s, auxiliary gas flow 0.5 L/min, coolant gas flow 12 L/min. Wave lengths (nm) used for measurement of metals were: Cr 205.55, Co 228.62, Cu 324.75, Cd 214.44, Mn 257.61, Fe 259.94, Gd 335.05, Dy 353.17, Ca 393.366, Ni 231.60 and U 409.01.

The pH measurements were made on pH meter 780 of Metrohm Herison Switzerland. Ion exchange separation system consisted of Teflon column packed with the Dowex 1 × 8 resin. DESAGA PLG peristaltic pump from Desaga Germany was used for passing the sample through the column.

Reagents/chemicals

Stock solution of 10 mg/mL uranium was prepared from the spec pure grade U_3O_8 purchased from JMC, UK. Stock solutions of Ca, Cd, Cr, Co, Cu, Dy, Fe, Gd, Mn and Ni, 1,000 µg/mL each, were obtained from JFS Chemical Inc. USA. Standard solutions of different concentration used for optimization study were prepared by appropriate dilution of the stock solutions.

Ammonium sulphate stock solution (1 M) was prepared from analytical grade ammonium sulphate obtained from E. Merck Germany. Sulphuric acid and ammonium hydroxide used for pH adjustment were also of analytical grade from E. Merck Germany. De-ionized distilled water (DDW) was used for making solutions.

Preparation of ion exchange column

The resin Dowex 1 × 8 (100–200 mesh, chloride form), was slurry packed in a Teflon column (7.8 cm × 0.8 cm I.D.). Glass wool buds were placed at both ends of the column before closing the tapered screwed caps of the column. The tapered ends of the screwed caps were connected to tygon tubing for fitting in the peristaltic pump.

Conditioning of the column was carried out by passing 0.6 M HNO_3 (equivalent to 4% (v/v) HNO_3) to convert the resin into nitrate form. A 20 mL volume of 0.6 M HNO_3 was found adequate for the complete removal of chloride from the column. Finally 20 mL of 0.1 M ammonium sulphate solution was passed through the column to bring the resin in sulphate form.

Ion exchange separation procedure

The aqueous samples containing uranium were pretreated, before passing through the column, so that they contain 0.1 M sulphate and their pH was adjusted to 3. The column was conditioned by passing 15 mL of 0.1 M ammonium sulphate solution having pH 3. A 25 mL portion of each pretreated sample was then passed through the column at flow rate 6 mL/min. Uranium was retained at the column and the concomitant impurities in the post column solution were collected and analyzed by ICP-OES.

Results and discussion

Optimization of conditions for the separation of uranium

Maximum retention of uranium on the resin and achievement of high recoveries of impurities were kept as leading criteria for the optimization study using ion exchange separation procedure. For the purpose, various parameters including concentration of sulphate, pH, and column efficiency for % retention of uranium were optimized.

Optimization of sulphate concentration

Uranium forms negatively charged complex $[UO_2(SO_4)]^{-2}$ with sulphate [30] which is retained on the resin in the column. Optimization of sulphate concentration is therefore an essential parameter to achieve the best separation of uranium. For this optimization study, a series of solutions having 0.05, 0.1, 0.15 and 0.20 M ammonium sulphate were prepared. Each solution also had 2,000 μg/mL uranium and 1 μg/mL each of the concomitant impurities mentioned in the introduction section. These solutions were passed through the column one by one using the optimum procedure given above. Percentage retention of U and % recoveries of the impurities at different concentrations of sulphate was reflected in Table 1 and Fig. 1, respectively.

From the results it can be concluded that at 0.1 M ammonium sulphate concentration, uranium retention was maximum and percent recoveries of the added impurities were also reasonable. Lower retention of uranium at 0.05 M sulphate could be due to insufficient concentration of sulphate required to complex all the uranium. Therefore 0.1 M sulphate concentration was established as optimum for the most efficient separation of uranium as well as optimal recoveries for all the impurities.

Table 1 Recoveries (%) of metallic impurities obtained at various concentrations of sulphate

Elements	Recoveries (%) at different sulphate concentration (mol/L)			
	0.05 M	0.1 M	0.15 M	0.2 M
Cr	89.1	97.7	70.2	72.1
Co	91.3	98.8	89.4	90.3
Cd	92.5	97.6	81.3	80.1
Cu	90.4	100.1	62.5	65.2
Fe	87.1	99.3	35.8	48.1
Mn	92.7	100.7	62.2	62.7
Gd	89.2	98.1	82.7	84.5
Dy	91.4	100.4	68.9	70.2
Ca	88.2	89.1	83.2	82.6
Ni	85.3	99.3	80.1	80.8

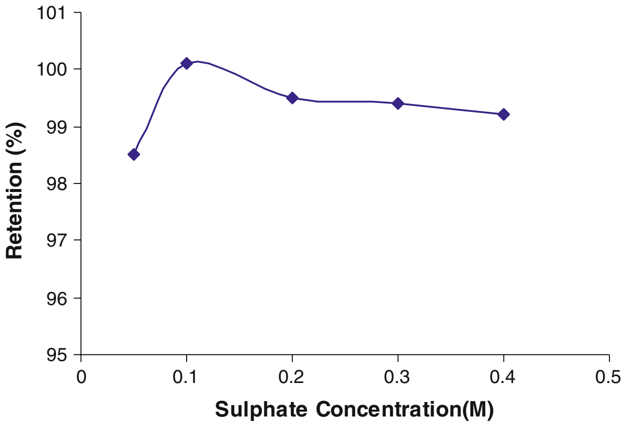

Fig. 1 Retention (%) of uranium on the column at different concentrations of sulphate

pH Optimization

Percent uranium retention and recoveries of impurities were studied in the pH range 1–6. A series of solutions were prepared, each having 2,000 μg/mL of uranium, 0.1 M sulphate and 1 μg/mL of each impurity. Each solution was adjusted to desired pH before passing through the column according to the optimum procedure. The data obtained for % retention of uranium and percent recoveries of metallic impurities is given in Table 2 and Fig. 2, respectively. From Table 2 it can be observed that the optimum pH for best retention of U on the column is 3. The lower retention of uranium at pH 1 and 2 may be due to the weak complexation behaviour of sulphate with uranium at these acidic pH values. The results shown in Table 2 reflect

Table 2 Retention (%) of uranium obtained at different pH values

pH	Retention of U (%)
1	94.0
2	95.2
3	99.9
4	98.7
5	98.4
6	98.1

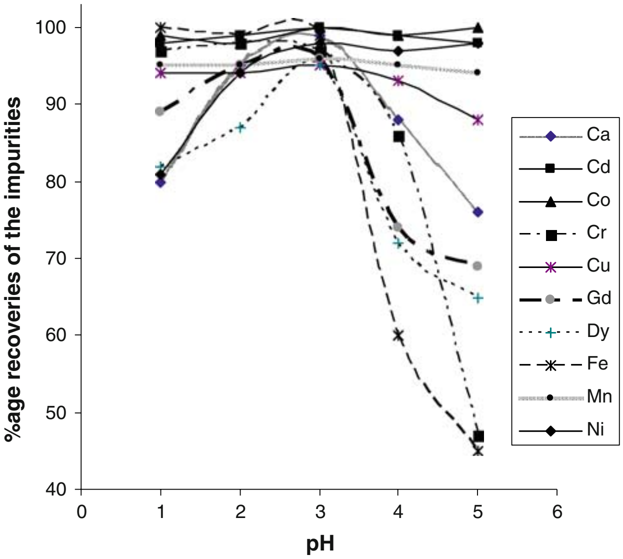

Fig. 2 Recovery (%) of metallic impurities at different pH values

that the recovery of most of the elements does not show any substantial change up to pH 3. However the recoveries of some elements such as Cr, Fe Gd and Dy gets poorer at pH 4 and 5, possibly due the formation of stronger complexes of sulphate with these elements [30] which is further facilitated at high pH value.

Breakthrough limit of uranium uptake

To find out the maximum uranium concentration that can be retained by the resin under optimized conditions, a series of solutions having uranium concentration ranging between 1,500 and 4,000 µg/mL were prepared. Each solution contained 0.1 M ammonium sulphate and pH was adjusted to 3. These solutions were passed through the column according to the optimized procedure. The results are shown in Table 3. From the results it is concluded that ion exchange column is capable of retaining maximum uranium concentration up to 2,500 µg/mL with retention efficiency of >99%. The poor retention at higher concentrations indicates that break through capacity of the column has been exhausted.

Table 3 Column efficiency at different concentrations of uranium

Concentration of U (µg/mL)	Retention of uranium (%)
1,500	100.3
2,000	100.5
2,500	99.8
3,000	82.5
4,000	58.6

Application of developed method for analysis of urania–gadolinia nuclear fuel

The method displayed good recoveries for trace level elemental impurities added to uranium matrix as shown in Tables 1 and 2. Remarkable results were obtained when this method was applied for the analysis of gadolinium in urania–gadolinia mixed nuclear fuel. In this type of fuel gadolinium oxide (Gd_2O_3) is added as burnable poison, to enrich uranium oxide to improve the core physics in light water reactor [31].

Two samples A, B of urania gadolinia mixed fuel, containing 2.5 and 5.0% gadolinium oxide by weight, respectively, were prepared by mixing gadolinium oxide with nuclear grade natural UO_2 using the wet milling method mentioned in the literature [32], acetone was used as wetting medium and mixing was carried out at 55 rpm in planetary ball mill having rubber lined container and uranium balls. 0.125 g of each sample was dissolved in acid mixture (1 mL concentrated nitric acid and few drops of concentrated HCl) followed by addition of 1 mL concentrated sulphuric acid (H_2SO_4). The mixture was heated to fume out nitric acid, then cooled and made up to 25 mL in a volumetric flask. Ten mL of each solution was mixed with 2.5 mL of 1 M $(NH_4)_2SO_4$ solution, pH was adjusted to 3 and final volume made up to 25 mL by adding water. Each sample was prepared in triplicate. These samples were passed through the ion exchange column using the optimized procedure, post column solutions were collected and analyzed for the measurement of gadolinium by ICP-OES. Sample blank and standards were also passed through the ion exchange column under same conditions.

The results obtained were compared with those achieved with the TBP solvent extraction method as shown in Table 4. Both the methods are in good agreement.

Conclusion

The study has concluded that this method could be conveniently applied for the selective separation of uranium from trace level metallic impurities in uranium materials. Excellent results were obtained in the analysis of urania–

Table 4 Comparison of results obtained by ion exchange method with solvent extraction method

Sample name	Ion exchange (Gd_2O_3) (%)	Solvent extraction (Gd_2O_3) (%)	Actual amount of Gd_2O_3 (%)	Recovery ion exchange (%)	Recovery solvent extraction (%)
Sample A	2.52	2.46	2.50	100.1	98.4
Sample B	4.96	4.91	5.00	99.2	98.1

gadolinia nuclear fuel samples. The developed method is efficient and could be applied reliably for the determination of impurities in uranium matrices using ICP-OES. This is the first part of the study; in future we shall apply this method for the determination of other additional impurities in uranium materials.

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