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SEPARATION AND DETERMINATION OF THORIUM IN URANIUM MINERALIZATIONS USING A MIXED ION EXCHANGE COLUMN BY ION CHROMATOGRAPHY

SHERIEN H. AHMED

Nuclear Materials Authority, P.O. Box 530 El Maadi, Cairo, Egypt

ABSTRACT

An ion chromatographic method for the separation and determination of thorium in uranium mineralizations has been developed using a mixed ion-exchange column; IonPac CSSA containing both cation and anion exchange sites. Selective separation of U(VI) and Th(IV) was performed by on-line gradient elution using two mobile phases of composition 0.1 M $(\text{NH}_4)_2\text{SO}_4$ / 0.1M HCl and 0.2 M $(\text{NH}_4)_2\text{SO}_4$ / 0.1 M HCl, respectively. Post-column spectrophotometric detection with 3 mM arsenazo III was then coupled at 655 nm. The separation factors between U and Th ions were found to be dependent on $(\text{NH}_4)_2\text{SO}_4$ and HCl concentrations of the eluent constituents and to a much more extent on its flow rate. The optimized developed method has been validated by its application for the analysis of both uranium and thorium in a sample from Abu Rusheid mineralization that is considered as a reference material and has then been used for the analysis of a mineralized sample from Abu Zeneima area.

INTRODUCTION

Thorium is a trace impurity associated with all uranium-based fuel materials (Mukherjee, 2003) which on irradiation with a neutron produces the useful fissile isotope (^{233}U). Small amounts of ^{232}U isotope are also produced along with ^{233}U (IAEA-TECDOC-1450, 2005). Determination of trace Th in uranium is indispensable in the chemical quality control of fast reactor fuels. Although different analytical techniques are available for the determination of Th at its trace levels (Joannon et al., 1997; Adriaens et al., 1992; Borai and Mady, 2002), they require its quantitative separation from the uranium matrix which is a prerequisite for analytical determination. Techniques such as radiochemistry (Clesceri et al., 1989), atomic absorption spectroscopy (Clesceri et al., 1989), neutron activation analysis (Honda

et al., 1990), inductively coupled plasma mass spectrometry (ICP-MS) (Igarashi et al., 1990; Deb et al., 2008), isotope dilution mass spectrometry (Adriaens et al., 1992) and X-ray fluorescence (XRF) (Robinson et al., 1986) were earlier reported for the determination of Th in uranium matrix. However, these techniques are often not suited to routine analysis, due to interferences from other metals present in the matrix, cost of operation or poor detection limits (Harrold et al., 1992; Cassidy, 1998). Ion chromatography (IC) and high performance liquid chromatography (HPLC) are promising techniques for the separation of polyvalent metal cations by adding suitable complexing agents in the mobile phase (Hao et al., 1996; Hao et al., 1996; Jackson et al., 1996; Vaibhavi Raut et al., 2013).

Many chromatographic studies have been

reported on the selective separation of Th and U in a variety of samples using reversed phase surfaces with weak organic acids as chelating agents (Sutton et al., 1998; Cassidy and Fraser, 1984). In these separations, the extent of separation depends on the nature of the metal complexes formed and their conditional stability constants (Jones and Nesterenko, 1997). Interestingly, it is reported that the elution order of U and Th on a reversed phase surface could be altered by selecting a suitable complexing agent. For example, an elution order of Th followed by U was observed in a RP surface when α -hydroxyisobutyric acid (α -HIBA) was used as a complexing agent (Raju et al., 2007; Akhila Maheswari et al., 2007). However, this elution order got reversed when mandelic acid (MA) was used in place of α -HIBA (Hao et al., 1996). The change in elution order may be explained on the basis of differences in the complexing abilities of the ligands with respect to individual metal cation, effective charge, thermodynamic and kinetic stabilities and hydrophobicities of the metal complexes formed. Although α -HIBA and MA are widely used as complexing agents in the separation of U and Th, 2,6-pyridine dicarboxylic acid (PDCA), a non-hydroxydicarboxylic acid, has been identified as a promising ligand for the separation of heavy metal ions (Vaibhavi Raut et al., 2013; Shaw et al., 1999; Jones, 2000; Shaw et al., 2000; Jeyakumar et al., 2011).

The separation of uranium and thorium by cation-exchange chromatography is complicated by the large differences in distribution coefficients of the two analytes. Uranium is generally present as a divalent cation (UO_2^{2+}) while thorium exists as the tetravalent Th^{4+} species and therefore considerable differences are observed in their relative affinity for a cation-exchange resin. With both HCl and HNO_3 eluents, a relatively low acid concentration will elute UO_2^{2+} as an anionic complex, but a much higher concentration of acid (>3 M) is required to elute thorium. Although an acid gradient can be used for the separation, this approach will cause difficulties in detec-

tion (Harrold et al., 1992; Dionex Application Note, 1998; Al-Shawi and Dahl, 1995).

A good separation of lanthanides, Th and U at relatively large concentrations was reported (Raju et al., 2007) where the C-18 RP column was coated with bis-2-ethylhexyl succinamic acid (BEHSA). However, the same study showed that it could not separate Th from U when the uranium concentration in the sample was more than 5 mg ml^{-1} . Mandelic acid, another complexing agent frequently used in the separation of U and Th, could not be used as it brings reversed order of elution i.e. U followed by Th and both uranium and thorium mandelate complexes interact hydrophobically with the reversed phase surface and exhibit significant retentions. A similar elution order was reported in the case of cation exchange chromatography as uranium forms weaker cationic species with the frequently used eluents like hydrochloric and nitric acids (Nelson et al., 1964). Nowadays, stationary phases having both cation and anion exchange capacities are found to be more useful in separating heavy and transition metal ions (Hojabri et al., 1987) because the separation is controlled by the concentrations of free metal ions and the various insitu metal complexes formed, which are in an equilibrium with each other (Park et al., 1993). One such mixed ion exchanger namely IonPac CS5A has been widely used for the separation of lanthanides and transition metal cations in several matrices (Cardellicchio et al., 1997; Borai et al., 2002; Perna et al., 2002).

In the present investigation, it was decided to examine IonPac CS5A mixed ion exchanger column for the separation of traces of Th from a bulk of U. For this purpose, ammonium sulphate has been chosen as a complexing agent as it has a high affinity for complex formation with polyvalent metal cations. The aim of this investigation was to develop a rapid and reliable method for the separation and determination of a trace level of thorium in uranium mineralizations using a mixed ion exchanger column.

EXPERIMENTAL

Instrumentation

Ion chromatographic separation was performed on Dionex DX-500 ion chromatograph system (Sunnyvale, CA, USA) consisting of gradient pump (GP40), UV-VIS detector (AD20) and rear-loading Rheodyne six port injection valve. Separator ion-exchange columns; Dionex IonPac CG5A guard column (4.6x50mm) and IonPac CS5A analytical column (4.6x250mm), containing mixed anion and cation beds with sulfonic acid and alkanol quaternary ammonium functional groups, were used in this work. A pneumatic post-column reagent addition facility consisting of a 1000 ml reservoir bottle, gas pressure gauge to control the flow rate of the gas, a T-junction and a 375 μ L capacity reaction coil was placed between the separator column and the detector. The samples were injected through a 50 μ L loop fitted to a Rheodyne six port injector. The pH measurements were made on a digital Jenway pH meter (UK).

Reagents

All reagents were of analytical grade (AR). Two appropriate mobile phases consisting of a mixture of ammonium sulphate and HCl were prepared and operated at a flow rate of 1.0 ml min^{-1} . The post-column reagent solution contained 3 mM Arsenazo III (BDH, UK), Triton X-100 (Sigma Aldrich, Germany) and glacial acetic acid (Panreac Quimica, SP) and was delivered through a "T" piece at a flow-rate of 0.5 ml min^{-1} for the detection of the separated metal ions at 655nm. All eluents and post-column reagent were degassed with a nitrogen gas. Thorium and uranium standards were prepared from 1000 ppm standard stock solutions (Merck, USA). All solutions were prepared using nanopure water (18.2 M Ω) obtained from a Thermo Scientific "Barnstead" lab water system (Thermo Fisher Scientific Inc., USA).

Characterization of the Uranium Mineralizations

Two uranium mineralization samples were collected from two different locations in Egypt; one of which is from Abu Rusheid area, Southeastern Desert, Egypt while the other is from Abu Zeniema area, Southwestern, Egypt. Abu Rusheid area is located at 50 km southwest of Marsa Alam on the Red Sea coast between long. 34° 46' and 34° 46'35" E and lat. 24° 37' 16" and 24° 38' N. The main rock units of Abu Rusheid area from the point of view of mineralization are the cataclastic group and the lamprophyre dykes cutting through it (Ibrahim et al., 2004).

The mineralized Um Bogma Formation of Abu Zeniema area is located between long. 33° 18' and 33° 27'E and lat. 28° 55' and 29° 04' N. Um Bogma Formation was assigned to the middle carbonate series of the Paleozoic sequence in south west Sinai, Egypt (Kora, 1984; El Aassy et al., 1986). The collected sample therefore represents one of the uranium occurrences related to the dolostone of Um Bogma Formation. The main mineral constituents of the dolostone facies are calcite, ankerite, kaolinite, limonite, goethite besides arsenopyrite, chalcopyrite and framboidal pyrite.

Preparation of Uranium Solutions

To 1 g sample of Abu Rusheid ore, a mixture of acid solutions (Hf, HNO₃ and H₂SO₄) was added in a Teflon beaker and heated till dryness. A 0.1 M HCl solution was then added to dissolve the residue under heating condition. Once a clear solution was obtained, it was kept to cool and finally completed to 100 ml volume. On the other hand, a sulphate leach liquor of Abu Zeniema ore sample was prepared by stirring 50 ml of 15% H₂SO₄ solution with 50 g of the ore sample in a glass beaker for about 4 hours at room temperature. The mixture was then filtered and the filtrate (sulphate leach liquor) pH was adjusted using Na₂CO₃ powder (Merck, Germany).

RESULTS AND DISCUSSION

Preliminary Testing

In a previous paper, a method was developed to investigate the retention behavior of thorium (IV) and uranium (VI) complexes of ammonium sulphate on a CS10 cationic exchange column (Nelson et al., 1964). Based on this study, the present work started with using a gradient program consisting of two eluents composed of 0.1 M $(\text{NH}_4)_2\text{SO}_4$ / 0.4 M HCl and 1 M $(\text{NH}_4)_2\text{SO}_4$ / 0.4 M HCl with a mixed ion exchanger column viz. Ionpac CS5A at eluent flow rate of 1 ml min^{-1} . Detection was done with 3 mM Arsenazo III in 0.5 M glacial acetic acid at a flow-rate of 0.5 ml min^{-1} .

Interestingly, unlike the modified RP column, the mixed ion exchange column exhibited a strong retention for Th(IV) whereas U(VI) got eluted immediately after the solvent front. Hence, the elution order observed in the present case is U(VI) followed by Th(IV); a matter which is similar to that of the elution order obtained with strong cation exchange stationary phase (Harrold et al., 1992; Jeyakumar et al., 2011; Al-Shawi and Dahl, 1995). The separation method thus depends on the difference in the distribution coefficient values of U and Th between the mixed ion exchange resin and the eluent containing a strong mineral acid such as HCl.

Several series of experiments were then conducted to optimize the different variables such as the concentrations of $(\text{NH}_4)_2\text{SO}_4$ and HCl in the mobile phase, the eluent flow rate, the effect of presence of other metal ions in solution and the effect of concentration of U (matrix) on the separation of Th which affect the retention and hence the separation efficiency.

Optimization of the Separation Factors

Effect of $(\text{NH}_4)_2\text{SO}_4$ concentration

In order to understand the effect of $(\text{NH}_4)_2\text{SO}_4$ concentration on the retention of

both U(VI) and Th(IV), two series of experiments were performed where the concentration of $(\text{NH}_4)_2\text{SO}_4$ in the two mobile phases was varied separately from 0.1 to 1.2 M while keeping the concentration of the other component namely; HCl (0.4 M) constant.

The variation in pH of the eluent was insignificant while varying the $(\text{NH}_4)_2\text{SO}_4$ concentration due to the large concentration of HCl. The obtained retention trend with varying $(\text{NH}_4)_2\text{SO}_4$ concentration is shown on Fig.(1). Increasing the latter in the mobile phase had virtually decreased the retention of U(VI) whereas the retention of Th(IV) was drastically reduced and in turn gradually decreased the resolution factor $[R(\text{U}/\text{Th})]$.

The observed retention behavior of U(VI) shows that it has the lower retention on the column and this can occur only when it forms a stable neutral complex with $(\text{NH}_4)_2\text{SO}_4$. Theoretically, though a neutral complex in equilibrium with either its pure metal ions or other kind of complex cations can have feeble interaction on the cation exchange sites provided the complex formed is kinetically labile. In the present case, the complex formed has no interaction with both anion and cation exchangers and this may be due to the high stability of the U- $(\text{NH}_4)_2\text{SO}_4$ neutral complex formed.

In the case of Th(IV), it was found to exhibit a significant retention on the mixed ion

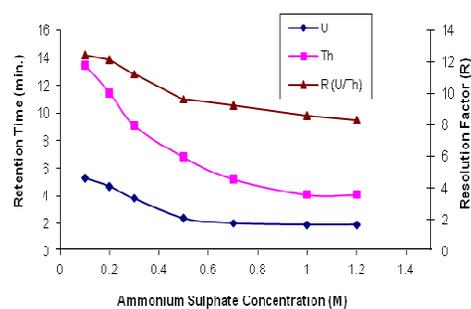


Fig.1: Effect of ammonium sulphate concentration on retention time

exchanger column. Elution with increasing $(\text{NH}_4)_2\text{SO}_4$ concentration in the mobile phase decreased the retention of Th(IV). The cation exchange models proposed in literature (Haddad and Foley, 1990) report that increasing the concentration of complexing agent decreases the retention time of metal ions due to the formation of neutral or weak anionic complexes. Whereas in anion exchange model, it is reported that only strong anion metal-ligand complexes can interact with the anion exchange sites and hence, increasing the concentration of complexing agent in the eluent would increase the retention time.

Therefore, it is seen from the experiments carried out that eluents with $(\text{NH}_4)_2\text{SO}_4$ concentration above 0.2 M are not suitable for separating trace Th and therefore, the $(\text{NH}_4)_2\text{SO}_4$ concentration has been fixed at 0.2 M for the second eluent in the gradient program when using mixed ion exchange column. On the other hand, it has been observed that eluents with $(\text{NH}_4)_2\text{SO}_4$ concentration above 0.1 M are not suitable for separation of large excess of U and that this concentration would reduce the interactions between the UO_2^{2+} - $(\text{NH}_4)_2\text{SO}_4$ complex and the stationary phase, which is desirable to realize the elution of U peak after the excluded peak.

Effect of HCl concentration

Addition of HCl and its concentration play an important role in controlling the effective ligand concentration in the mobile phase which would decide the nature of the metal-complex. In addition, HCl prevents the hydrolysis of metal cations since such heavy metal ions belong to acid hydrolysable group. Moreover, the H^+ ions from the hydrochloric acid also act as competing ion during the elution of metal cations or cation complexes. To investigate the influence of HCl concentration on the elution, a set of experiments was conducted where HCl concentration was varied over a range between 0.1 and 1.0 M. In this regard, it was expected that increasing the acid concentration would

reduce the effective concentration of ligand, which would affect the complexation of U(VI) leaving more metal cations and in such case, the retention times for both Th(IV) and U(VI) are expected to be increased. However, there was no appreciable change in the retention times observed for uranium as it forms weak cationic species than thorium with hydrochloric acid in the form of UO_2Cl^+ . Also as shown on Figure 2, the resolution factor $[\text{R}(\text{U}/\text{Th})]$ decreases slightly.

From this Figure, it was indicated that when the chloride concentration of the eluent increased, the concentration of the cationic species retained on the stationary phase decreases because the solution equilibrium is displaced to higher complex species and the uranium weak cationic species can be eluted easily with low concentration of the mobile phase (Bunus, 1974). Uranium is, in fact, eluted close to solvent front when the concentration of HCl is at 0.1 M in the initial gradient program (first mobile phase).

The combination of high charge and low hydrolysis makes thorium ion particularly retainable on mixed ion-exchange resins from HCl solutions at concentrations below about 1 M. Complexing agents such as citric acid, oxalic acid, hydrofluoric acid, carbonate and sulphate are necessary for its elution from the column (Korkisch and Tera, 1961). This implies that thorium forms weak cationic species

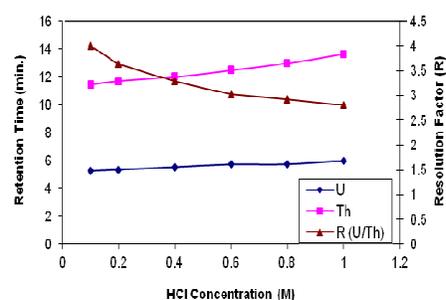


Fig. 2: Effect of hydrochloric acid concentration on retention time

with a sulphate ligand in the form of ThSO_4^{2+} because it has a much lower mass distribution ratio with sulphate (Harrold et al., 1992; Kawabuchi et al., 1969).

In the meantime and as shown in Table 1 (Hao et al., 1996; Strelow, 1960), thorium has a strong affinity for the cationic sulphonated stationary phase when elution is carried out with 0.4 M HCl, while uranium has a much weaker affinity for the same stationary phase. In case of our mixed ion stationary phase (CS5A), 0.1 M HCl concentration is suitable enough for thorium elution and where it would lose this strong affinity when the sulphate ligand was introduced and therefore it was eluted after the uranium ion by the second mobile phase of the gradient program.

Accordingly, it has been indicated that from the analytical point of view and considering separation (resolution) factor and other chromatographic parameters, it is desirable to have low concentration of HCl with the mixed ion exchange resin and which has been fixed at 0.1 M in the two mobile phases of the gradient program.

Effect of eluent flow rate

The effect of the eluent flow rate on the chromatographic separation was carried out at different eluent flow rates ranging from 0.25 to 1.5 ml min^{-1} . As shown on Fig.(3), it is evident that the retention of U and Th on the column increases as the flow rate decreases. For Th, a stronger retention causes greater peak broadening at lower flow rate. Consequently,

Table 1: Distribution ratio of uranium and thorium ions between strong cation-exchange resin polymer and hydrochloric acid (Hao et al., 1996&Strelow, 1960)

Cation	HCl Concentration (M)			
	0.1	0.2	0.5	1.0
UO_2^{2+}	5420	860	102	19.2
Th^{4+}	$>10^5$	$>10^5$	10^5	2049

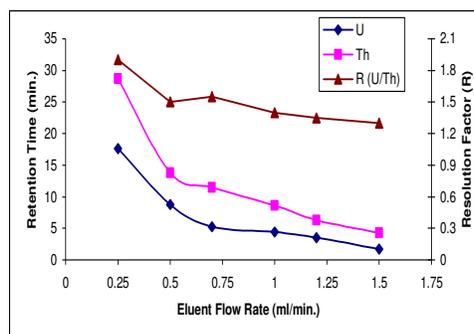


Fig.3: Effect of eluent flow rate on retention time

the resolution $[R(\text{U}/\text{Th})]$ decreases by increasing the flow rate. At a flow rate of 0.7 ml min^{-1} , sufficient separation among U and Th was found as indicated by the R-value of 1.55(U/Th). So, eluent flow rate of 0.7 ml min^{-1} was chosen as an optimum flow rate all over the gradient system for U and Th elution on mixed ion-exchange resin.

Effect of presence of other metal ions

Since the uranium mineralization samples are expected to contain other metallic impurities like Fe, Cd, Cu, Ca, Mg, Ni, Cr, Mn, rare earth elements, etc. (within the specification limits), separations were carried out in the presence of these metal ions to observe the interference effects, if any, during the separation of Th. For this purpose, two synthetic sample solutions were prepared and used. The first solution was a mixture of thorium with transition metals (together with Ca and Mg) and the second one consisted of thorium and mixture of all lanthanides. The individual metal ion to Th concentration ratio was kept ten in both solutions. It has been observed that the first solution did not give any peak whereas the second solution containing the mixture of lanthanides showed a small triplet peak after the thorium peak with very poor detection sensitivity. Therefore, the formulated eluent composition was found to be suitable for the interference free determination of Th.

Effect of uranium concentration (matrix)

Several synthetic samples in duplicates having U/Th ratios 1, 2, 20, 100 and 200 were prepared and injected for Th separation. The observed recoveries for Th listed in Table 2 were found to exceed 95%; a matter which showed that the method has a high tolerance for uranium and hence, the direct separation of trace Th from bulk uranium solution samples would be feasible.

From the above mentioned results, the studied optimum conditions that have been developed for the gradient program are summarized in Table (3). A typical chromatogram obtained for such gradient program using a standard solution containing U and Th is shown on Fig. (4).

Calibration Plots and Performance of the Developed Method

Calibration of the used ion chromatographic system was carried out using different standard solutions assaying 25 to 200 ppm for each of U and Th species. Two calibration plots shown on Figs. 5 & 6 were constructed between the peak areas and their respective U and Th concentrations. Linear relations with regression coefficients of 0.9953 and 0.9976 for U and Th respectively have thus been reported.

Performance of the developed method was done by calculating the relative standard deviation with multiple injections ($n = 10$) and was found to be 1% for uranium and 0.5% for tho-

Table 3: Gradient program of the developed optimized method

Run time (min.)	Eluent (conc.)	
	0.1 M (NH ₄) ₂ SO ₄ / 0.1M HCl	0.2 M (NH ₄) ₂ SO ₄ / 0.1M HCl
Int.	Flow rate 0.7 ml/min	
Int.	100%	-
0.00	100%	-
8.00	100%	-
8.10	-	100%
19.90	-	100%
20.00	100%	-

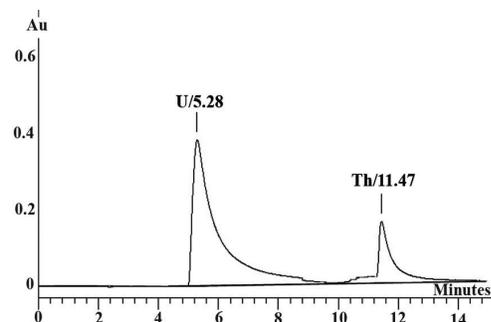


Fig. 4: Typical chromatogram obtained for a standard solution of U(VI) and Th(IV) using mixed ion-exchanger column. Peaks: U(VI) 50 ppm and Th(IV) 50 ppm. Column: IonPac CS5A (4.6 × 250 mm). Eluents: 0.1 M (NH₄)₂SO₄ / 0.1M HCl and 0.2 M (NH₄)₂SO₄ / 0.1M HCl; Flow rate: 0.7 ml/min. Detection: Post-column addition of 3mM arsenazo III and detection at 655 nm.

Table 2: Effect of concentration of U (matrix) on the separation of Th

Sample No.	U(VI) mg/l	Th(IV) mg/l	U/Th Ratio	Measured Th	Recovery Th %
S1	5	5	1	4.99	99.8
S2	10	5	2	4.98	99.6
S3	100	5	20	4.87	97.4
S4	500	5	100	4.81	96.2
S5	1000	5	200	4.78	95.6

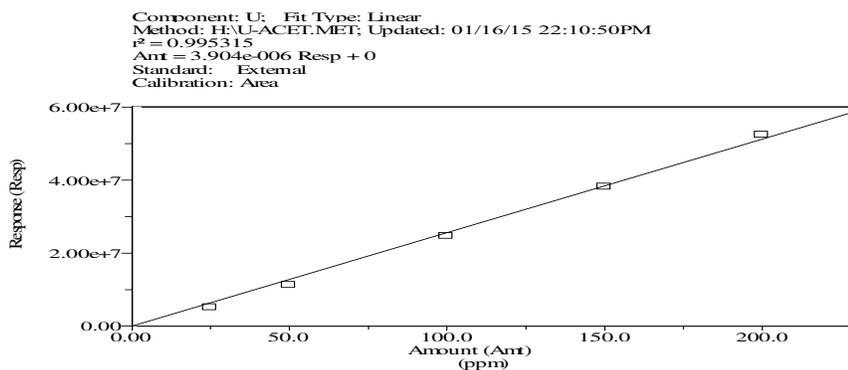


Fig. 5: Calibration plot obtained for U over a concentration range of 25 - 200 ppm

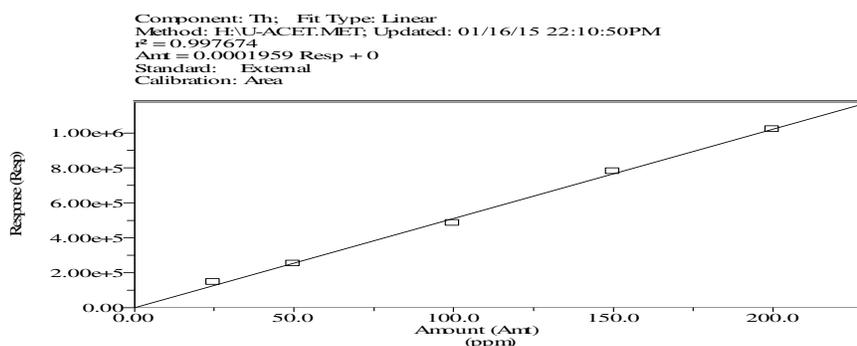


Fig. 6: Calibration plot obtained for Th over a concentration range of 25 - 200 ppm

rium. These repeatability experiments were conducted on standard solutions with uranium and thorium concentrations of about twenty times the detection limits. Detection limits for a 0.05 ml injection volume were 0.02 mg L⁻¹ for uranium and 0.01 mg L⁻¹ for thorium.

Validation and Application of the Developed Method

The studied method was validated by its application for the analysis of uranium and thorium in a sample from Abu Rusheid mineralization and which is considered as a reference material after having been analyzed by the ACME Analytical Labs. Ltd., Vancouver,

Canada by ICP-MS technique. For this purpose, 50 μL of the sample solution was injected into IC for separation and the values obtained for U and Th ions are listed in Table 4 and are actually in a good agreement with the mean value reported by the ACME Lab. using ICP-MS method.

On the other hand, a proper leach liquor of a sample from Abu Zeneima mineralization has been prepared and 50 μL of the sample solution was subjected to the developed IC procedure that has been optimized in the present work. Two mobile phases of composition 0.1 M (NH₄)₂SO₄ / 0.1 M HCl and 0.2 M (NH₄)₂SO₄ / 0.1 M HCl in a gradient system were used

by a mixed ion exchange resin (CS5A) at a flow rate of 0.7 ml min⁻¹ for separation. The separated fraction of metals are detected and measured by post column addition of 3 mM arsenazo III at a flow rate of 0.5 ml min⁻¹. The results obtained for typical sample are listed in Table 5.

Table 4: Results obtained for Abu Rusheid reference sample

Elements	Abu Rusheid Sample	
	IC Procedure (ppm)	ACME Lab. ICP-MS (ppm)
U	510.3	514.7
Th	14.7	15.20

Table 5: Results obtained for Abu Zeniema mineralized sample

Elements	IC Reading / ppm
U	1035
Th	51.15

CONCLUSION

An ion chromatographic method had been developed for online separation of trace levels of Th in uranium matrix without employing prior separation from the matrix. The method is simple, rapid and accurate and allows their analysis in about 15 minutes. For this purpose, a mixed ion exchange column; IonPac CS5A (4.6x250mm) containing both anion and cation sites has been used. The selective separation of U and Th was achieved by gradient elution using 0.1 M (NH₄)₂SO₄ / 0.1M HCl and 0.2 M (NH₄)₂SO₄ / 0.1 M HCl respectively. The developed method is actually considered promising for its adaptation in the routine quality control analysis of thorium in uranium mineralizations.

REFERENCES

- Adriaens, A.G.; Fassett, J.D.; Kelly, W.R.; Simons, D.S., and Adams, F.C., 1992. Determination of Uranium and Thorium Concentrations in Soils; Comparison of Isotope Dilution-Secondary Ion Mass Spectrometry and Isotope Dilution-Thermal Ionization Mass Spectrometry. *Analytical Chemistry*, 64(23), 2945-2950.
- Akhila Maheswari, M.; Prabhakaran, D.; Subramanian, M.S.; Sivaraman, N.; Srinivasan, T.G., and Vasudeva Rao, P.R., 2007. High Performance Liquid Chromatographic Studies on Lanthanides, Uranium and Thorium on Amide Modified Reversed Phase Supports. *Talanta*, 72(2), 730-740.
- Al-Shawi, A.W., and Dahl, R., 1995. Determination of Thorium and Uranium in Nitrophosphate Fertilizer Solution by Ion Chromatography. *J. Chromatography A*, 706(1-2), 175-181.
- Borai, E.H.; Eid, M.A., and Aly, H.F., 2002. Determination of REEs Distribution in Monazite and Xenotime Minerals by Ion Chromatography and ICP-AES. *Analytical and Bioanalytical Chemistry*, 372(4), 537-541.
- Borai, E.H., and Mady, A.S., 2002. Separation and Quantification of ²³⁸U, ²³²Th and Rare Earths in Monazite Samples by Ion Chromatography Coupled with On-Line Flow Scintillation Detector. *Applied Radiation and Isotopes*, 57(4), 463-469.
- Bunus, F.T., 1974. An ion exchange study of uranium (U4+ and UO2++) complex species with Cl- as ligand. *J. Inorg. Nucl. Chem.*, 36, 917.
- Cardellicchio, N.; Ragone, P.; Cavalli, S., and Rivello, J., 1997. Use of Ion Chromatography for the Determination of Transition Metals in the Control of Sewage-Treatment-Plant and Related Waters. *J. Chromatography A*, 770(1-2), 185-193.
- Cassidy, R.M., 1998. Determination of Rare-Earth Elements in Rocks by Liquid Chromatography. *Chemical Geology*, 67(3-4), 185-195.

- Cassidy, R.M., and Fraser, M., 1984. Equilibria Effects in the Dynamic Ion-Exchange Separation of Metal Ions. *Chromatographia*, 18(7), 369-373.
- Clesceri, L.S.; Greenberg, A.E., and Trussell, R.R. (Eds.), 1989. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC, 17th Ed.
- Deb, S.B.; Saxena, M.K.; Nagar B.K., and Ramakumar, K.L., 2008. Determination of Trace Amounts of Thorium in a Uranium Matrix by Inductively Coupled Plasma Mass Spectrometry and Validation of the Separation Procedure by Standard Addition and Tracer Techniques. *Atomic Spectroscopy*, 29(2), 39-44.
- Dionex Application Note, 1998. Determination of Uranium and Thorium in Complex Matrices Using Chelation Ion Chromatography. Dionex Application Note, No. 79, LPN 034670-01.
- El Aassy, I.E.; Botros, N.H.; Abdel Razik, A.; Sherief, H.; El Shamy, A.; Attia, K.; Ibrahim, S.K., and Moufei, A.A., 1986. Report on the prospection and proving of some radioactive occurrences in West Central Sinai, Egypt. Inter. Report, NMA, Cairo, 12p.
- Haddad, P.R., and Foley, R.C., 1990. Modelling of Cation Retention in Ion Chromatography Using Fixed-Site and Dynamically Coated Ion-Exchange Columns. *J. Chromatography A*, 500, 301-312.
- Hao, F.; Paull, B., and Haddad, P.R., 1996. Determination of Thorium and Uranyl in Nitrophosphate Solution by On-Line Matrix-Elimination Reversed-Phase Chromatography. *Chromatographia*, 42(11-12), 690-696.
- Hao, F.; Paull, B., and Haddad, P.R., 1996. Determination of Trace Levels of Thorium (IV) and Uranyl by Reversed-Phase Chromatography with On-Line Preconcentration and Ligand Exchange. *J. Chromatography A*, 749(1-2), 103-113.
- Hao, F.; Paull, B., and Haddad, P.R., 1996. Retention Behaviour of Thorium (IV) and Uranyl on a Reversed-Phase Column with Glycolate and Mandelate as Eluents. *J. Chromatography A*, 739(1-2), 151-161.
- Harrold, M.P.; Siriraks, A., and Riviello, J., 1992. High-Performance Ion Chromatographic Separation of Uranium and Thorium in Natural Waters and Geological Materials. *J. Chromatography A*, 602(1-2), 119-125.
- Hojabri, H.; Lavin, A.G.; Wallace, G.G., and Riviello, J.M., 1987. Determination of Metal Ions Using Ion Chromatography and Indirect Amperometric Detection. *Analytical Chemistry*, 59(1), 54-57.
- Honda, T.; Oi, T.; Ossaka, T.; Nozaki T., and Kaki-hana, H., 1990. Determination of thorium and uranium in hot spring and crater lake waters by neutron activation analysis. *J. Radioanal. Nucl. Chem.*, 139, 65p.
- IAEA-TECDOC-1450, 2005. *Thorium Fuel Cycle- Potential Benefits and Challenges*. IAEA, Austria, 68- 69.
- Ibrahim, I.; Saleh, G.M.; Amer, T.; Mahmoud, F.; Abu El Hassan, A.; Ali, M.; Azab, M.S.; Rashed, M.; Khaleal, F., and Mahmoud, M., 2004. Uranium and associated rare metals potentialities of Abu Rusheid brecciated shear zone II, South Eastern Desert, Egypt. Inter. Report, NMA, Cairo, Egypt.
- Igarashi, Y.; Kim, C.K.; Takatu, Y.; Shiraishi, K.; Yamamoto, M., and Ikeda, N., 1990. Application of Inductively Coupled Plasma Mass Spectrometry to the Measurement of Long-Lived Radionuclides in Environmental Samples. *Anal. Sci.*, 6, 157p.
- Jackson, P.E.; Carnevale, J.; Fuping, H., and Haddad, P.R., 1996. Determination of Thorium and Uranium in Mineral Sands by Ion Chromatography. *J. Chromatography A*, 671(1-2), 181-191.
- Jeyakumar, S.; Mishra, V.G.; Das, M.K.; Raut, V.V.; Sawant, R.M., and Ramakumar, K.L., 2011. Separation Behavior of U(VI) and Th(IV) on a

- Cation Exchange Column Using 2,6-Pyridine Dicarboxylic Acid as a Complexing Agent and Its Application for the Rapid Separation and Determination of U and Th by Ion Chromatography. *J. Separation Science*, 34(6), 609-616.
- Joannon, S.; Telouk, P., and Pin, C., 1997. Determination of U and Th at Ultra-Trace Levels by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry Using a Geysler-Type Ultrasonic Nebulizer: Application to Geological Samples. *Spectrochimica Acta B*, 52(12), 1783-1789.
- Jones, P., 2000. Major Sensitivity Improvements in Ion Chromatography Determinations Involving Post-Column Spectrophotometric Reaction Detectors through Elimination of Pump Noise Using a Dual Wavelength Monitoring Procedure. *Analyst*, 125(5), 803-806.
- Jones, P., and Nesterenko, P.N., 1997. High-Performance Chelation Ion Chromatography a New Dimension in the Separation and Determination of Trace Metals. *J. Chromatography A*, 789(1-2), 413-435.
- Kawabuchi, K.; Ito, T., and Kuroda, R., 1969. Cation exchange behavior of metal ions in ammonium sulfate media. *J. Chromatography A*, 39, 61.
- Kora, M., 1984. The Paleozoic exposures of Um Bogma area, Sinai. Ph.D. Thesis, Mansoura Univ., 280p.
- Korkisch, J., and Tera, F., 1961. Separation of thorium by anion exchange. *Anal. Chem.*, 33, 1264-1266.
- Mukherjee, T.K., 2003. Characterization and Quality Control of Nuclear Fuels (CQCNF-2002), Allied Publishers, New Delhi.
- Nelson, F.; Murase, T., and Kraus, K.A., 1964. Ion Exchange Procedures. I. Cation Exchange in Concentration HCl and HClO₄ Solutions. *J. Chromatography A*, 13, 503-535.
- Park, Y.S.; Han, S.H.; Joe, T.Y.; Eom, K.S., and Lee, G., 1993. Retention Behaviour of Transition Metal Ions with Some Complexing Agents on Cation Exchanger. *Bull. Korean Chemical Society*, 14(6), 692-696.
- Perna, L.; Bocci, F.; Aldave de las Heras, L.; De Pablo, J., and Betti, M., 2002. Studies on Simultaneous Separation and Determination of Lanthanides and Actinides by Ion Chromatography Inductively Coupled Plasma Mass Spectrometry Combined with Isotope Dilution Mass Spectrometry. *J. Analytical Atomic Spectrometry*, 17(9), 1166-1171.
- Raju, Ch.S.K.; Subramanian, M.S.; Sivaraman, N.; Srinivasan, T.G., and Vasudeva Rao, P.R., 2007. Retention Studies on Uranium, Thorium and Lanthanides with Amide Modified Reverse Phase Support and Its Applications. *J. Chromatography A*, 1156(1-2), 340-347.
- Robinson, P.; Higgins, N.C., and Jenner, G.A., 1986. Determination of rare-earth elements, yttrium and scandium in rocks by anion exchange-X-ray fluorescence technique. *Chem. Geol.*, 55, 121.
- Shaw, M.J.; Hill, S.J., and Jones, P., 1999. Chelation Ion Chromatography of Metal Ions Using High Performance Substrates Dynamically Modified with Heterocyclic Carboxylic Acids. *Analytica Chimica Acta*, 401(1-2), 65-71.
- Shaw, M.J.; Hill, S.J.; Jones, P., and Nesterenko, P.N., 2000. Determination of Uranium in Environmental Matrices by Chelation Ion Chromatography Using a High Performance Substrate Dynamically Modified with 2,6-Pyridinedicarboxylic Acid. *Chromatographia*, 51(11-12), 695-700.
- Strelow, F.W.E., 1960. An ion exchange selectivity scale of cations based on equilibrium distribution. *Anal. Chem.*, 32, 1185p.
- Sutton, R.M.C.; Hill, S.J.; Jones, P.; Sanz-Medel, A., and Garcia-Alonso, J.I., 1998. Comparison of the Retention Behaviour of Uranium and Thorium on High-Efficiency Resin Substrates Impregnated or Dynamically Coated with Metal Chelating Compounds. *J. Chromatography A*, 816(2), 286-291.

Vaibhavi Raut, V.; Roy, S.P.; Das, M.K.; Jeyakumar, S., and Ramakumar, K.L., 2013. Separation Behavior of U(VI) and Th(IV) on a Mixed Ion Exchange Column Using 2,6-Pyridine Dicarboxylic Acid as a Complexing Agent

and Determination of Trace Level Thorium in Uranium Matrix Employing High Performance Ion Chromatography. Inter. J. Analytical Mass Spectrometry and Chromatography, 1, 61-71.

فصل وتقدير الثوريوم في تمعدنات اليورانيوم باستخدام عمود فصل ذو تبادل ايونى مختلط بواسطة التحليل الكروماتوجرافى الايونى

شيرين حسين أحمد

تم تطوير طريقة تحليل كروماتوجرافية لفصل وتقدير عنصر الثوريوم في تمعدنات اليورانيوم باستخدام عمود فصل ذو تبادل ايونى مختلط يحتوى على كلا من مواقع التبادل الكاتيونى والانيونى. وقد تمت عملية الفصل الانتقائى لعنصرى اليورانيوم السداسى والثوريوم الرباعى عن طريق الازاحة المتدرجة باستخدام الوسط المتحرك الذى يحتوى على محلولى ازاحة يتكونان من ٠,١ جزيئى كبريتات الامونيوم / ٠,١ جزيئى حمض الهيدروكلوريك و ٠,٢ جزيئى كبريتات الامونيوم / ٠,١ جزيئى حمض الهيدروكلوريك على الترتيب. كما تم تعيين الايونات المفصولة للعنصرين باستخدام التحليل الطيفى اللونى عند الطول الموجى ٦٥٥ ن م بعد خلطه بالمادة الملونة ٣ مللى جزيئى من الارزينازو الثلاثى. وقد اجريت دراسة لعوامل الفصل بين اليورانيوم والثوريوم والتي اثبتت انها تعتمد على تركيز كلا من مكونات الوسط المتحرك وهما كبريتات الامونيوم وحمض الهيدروكلوريك والى مدى اكبر بكثير على معدل سريانه. ولقد تأكدت صلاحية الطريقة التى تم تطويرها عن طريق تطبيقها لتحليل العنصرين (اليورانيوم والثوريوم) فى عينة مرجعية من تمعدن منطقة أبو رشيد وقد تلى ذلك استخدامهما فى تحليل العنصرين فى عينة متمعدنة من منطقة أبو زريمة.