

High-performance ion chromatographic separation of uranium and thorium in natural waters and geological materials

Michael P. Harrold*, Archava Siriraks and John Riviello

Dionex Corporation, 1128 Titan Way, Sunnyvale, CA 94086 (USA)

ABSTRACT

An ion chromatographic separation of uranium and thorium is described. The method uses a cation-exchange resin for the separation of uranium and thorium from other common metal interferences. Detection of uranium and thorium is accomplished using post-column derivatization with arsenazo III followed by spectrophotometric detection. In addition to direct injection of sample, a method for concentrating uranium and thorium from complex matrices will be presented. Using direct injection, detection limits for uranium and thorium in simple matrices is 20 $\mu\text{g/l}$ for uranium and 60 $\mu\text{g/l}$ for thorium using a 50- μl sample loop. The use of a chelating resin for selective sample concentration lowers the detection limit to 1.0 $\mu\text{g/l}$ for uranium and 3.0 $\mu\text{g/l}$ for thorium when concentrating 5.0 ml of sample. Sample concentration on a selective chelating resin also extends the applicability of the method for the analysis of complex matrices.

INTRODUCTION

Uranium and thorium are naturally occurring elements found at trace levels in the environment. The routine determination of trace amounts of uranium and thorium is challenging due in part to the lack of a simple and specific colorimetric test which is not prone to interferences by other metal ions. The natural radioactivity of uranium and thorium is the basis of some common methods of analysis. The determination of uranium in aqueous samples is often done using a radiochemical method [1]. In this method, the uranium is co-precipitated from solution with ferric hydroxide, separated from iron by open column anion exchange using a hydrochloric acid eluent, evaporated and converted to a nitrate salt and finally the alpha activity is measured. Thorium may be analyzed in clean matrices using flame atomic absorption [2]. The flame atomic absorption method requires the use of a nitrous oxide-acetylene flame for analysis. Other accurate means for uranium analysis include neutron activation analysis [3], and inductively coupled plasma mass spectrometry (ICP-MS) [4]; however

these techniques are not well suited to routine analysis, and may suffer interferences from other metals present in the matrix.

The use of ion chromatography for the separation of metals is well documented. Early work focussed on open column separations of metals by both anion and cation exchange using acid eluents [5,6]. These open column ion-exchange separations used detection based on fraction collection and off-line derivatization and detection. The development of on-line detection schemes led to the first modern high-performance ion chromatograph with continuous detection for metal separations [7]. High-performance separations on low-capacity cation-exchange resins and anion-exchange separations of metal complexes have allowed the rapid and accurate determination of many transition metals and lanthanide metals [8]. Separations of a wide variety of metal ions in addition to uranium and thorium have also been determined using reversed-phase columns in the ion-pairing mode [9,10]. More recently, highly selective chelating resins have been used for on-line concentration of metal ions combined with selective elution of potentially interfering matrix components

[11]. The coupling of selective sample concentration with high-performance ion chromatographic separations has increased the scope of sample types that can be analyzed for trace metals using ion chromatography. This paper will describe the development of a high-performance ion chromatographic separation based on cation exchange. The discussion will cover the separation mechanism, detection scheme and use of chelating resins for selective sample preconcentration.

THEORETICAL

Separation

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 (Tables I–III). 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 detection as will be described in the *Detection* section.

The distribution coefficient for thorium in a sulfuric acid eluent is much lower than for a comparable concentration of hydrochloric or nitric acid, presumably due to the formation of a thorium-sulfate (ThSO_4^{2+}) complex which reduces the affini-

TABLE I

WEIGHT DISTRIBUTION COEFFICIENTS AT DIFFERENT CONCENTRATIONS OF HCl ON CATION-EXCHANGE RESIN

From ref. 5.

Cation	HCl concentration (<i>M</i>)				
	0.2	0.5	1.0	2.0	3.0
UO_2^{2+}	860	102	19.2	7.3	4.9
Th^{4+}	$>10^5$	10^5	2049	239	114
Fe^{3+}	3400	225	35.4	5.2	3.6

TABLE II

WEIGHT DISTRIBUTION COEFFICIENTS AT DIFFERENT CONCENTRATIONS OF HNO_3 ON CATION-EXCHANGE RESIN

From ref. 6.

Cation	HNO_3 Concentration (<i>M</i>)				
	0.2	0.5	1.0	2.0	3.0
UO_2^{2+}	262	69	24.4	10.7	7.4
Th^{4+}	$>10^4$	$>10^4$	1180	123	43
Fe^{3+}	4100	362	74	14.3	6.2

ty of thorium for the ion exchanger. To resolve uranium and thorium without the use of an acid gradient, a sulfate gradient can be used to elute thorium from the resin following the elution of uranium with HCl. A sodium sulfate gradient maintaining a constant concentration of HCl (0.6 *M*), will resolve uranium and thorium from the potential interferences Fe^{3+} , Ca^{2+} , Hf^{4+} , ZrO^{3+} and the lanthanide metals. The separation takes place at constant pH which is necessary in order to maintain baseline stability throughout the separation. Note also that Fe^{3+} and thorium have similar distribution coefficients in sulfuric acid. The use of HCl eluent followed by a sodium sulfate gradient separates ferric ion from thorium by exploiting the differences in selectivity with the HCl eluent.

Detection

The detection of uranium and thorium is accomplished by postcolumn addition of a color-forming

TABLE III

WEIGHT DISTRIBUTION COEFFICIENTS AT DIFFERENT CONCENTRATIONS OF H_2SO_4 ON CATION-EXCHANGE RESIN

From ref. 6.

Cation	H_2SO_4 concentration (<i>M</i>)				
	0.1	0.25	0.5	1.0	1.5
UO_2^{2+}	118	29.2	9.6	3.2	2.3
Th^{4+}	3900	264	52	9.0	3.0
Fe^{3+}	2050	255	58	13.5	4.6

complexing agent followed by spectrophotometric measurement of the metal complex. The postcolumn reagent used is arsenazo III (Fluka, Ronkonkoma, NY, USA) which has been described in many reports as a colorimetric reagent for uranium and thorium [12–14]. The greatest impediment to the use of arsenazo III has been its lack of selectivity for uranium and thorium. Arsenazo III will form colored complexes with many metals including iron, calcium, zirconium, hafnium and the lanthanide series [12]. The use of an ion chromatographic separation prior to detection with arsenazo III eliminates many of the interferences that prevent direct use of arsenazo III as a colorimetric reagent for uranium and thorium. Additionally, the selectivity of arsenazo III increases with decreasing pH. Although many metals will react with arsenazo III at moderate pH, in an acidic environment the number of metals which form stable complexes with arsenazo III is much more limited [12]. Therefore, metals such as iron and calcium which are often present in high levels relative to uranium and thorium, pose a less severe interference due to their diminished response with arsenazo III at low pH. The complex of arsenazo III with a metal ion absorbs strongly at 660 nm while the free arsenazo III absorbs rather weakly at that wavelength. The background absorbance of free arsenazo III observed at 660 nm is pH dependent, with the absorbance decreasing as the pH is lowered [15]. This requires the use of a constant pH separation to prevent a downward sloping baseline that would accompany an acid gradient. The constant pH separation was discussed in the preceding section on separation. In addition to arsenazo III, the post-column reagent contains acetic acid and Triton X-100, a nonionic surfactant. Both components are added to stabilize the solution and prevent the adsorption of arsenazo III and arsenazo–metal complexes on the polymeric membrane reactor and mixing coil.

Preconcentration

The determination of uranium and thorium in a simple, low-ionic-strength matrix can be accomplished by direct injection of the sample. In many cases however, the levels of uranium and thorium may be very low (less than 50 $\mu\text{g/l}$) or may be present in a high ionic strength matrix. A high ionic

strength matrix may compromise the analysis by overloading the separator column with high levels of alkali and alkaline earth metals. Additionally, these same interferences may saturate a conventional ion-exchange concentration column resulting in poor concentration efficiency from a high ionic strength matrix. The use of chelating resins as selective preconcentrators has been previously described for the selective preconcentration of transition metals from high ionic strength matrices [11]. Uranium and thorium can be selectively preconcentrated on an iminodiacetate chelating resin at pH 5.5. At this pH, the chelating resin is highly selective for transition and post-transition metals relative to alkali and alkaline earth metals. Alkaline earth metals which are weakly retained by the chelating resin are subsequently eluted to waste by an ammonium acetate wash of the resin. The ammonium acetate wash is performed at pH 5.5 where the selectivity of the resin for uranium and thorium relative to alkaline earth metals is optimum. The chelating resin, containing a weak acid functional group, has very low selectivity for most metals at low pH. Therefore, the concentrated uranium and thorium, as well as other concentrated transition and post-transition metals, can be efficiently eluted from the concentrator column with the acid eluent used for the analytical separation. The use of chelating resins for sample pretreatment not only selectively concentrates uranium and thorium from high ionic strength matrices, but also eliminates alkali metals, alkaline earth metals and anions which were present in the original matrix.

EXPERIMENTAL

Experiment

All chromatography was performed on a Dionex (Sunnyvale, CA, USA) 4500i ion chromatograph equipped with two quaternary gradient pumps (GPM-II), a reagent delivery module (RDM), and a variable wavelength UV–VIS detector (VDM-II). The entire flow path of the ion chromatograph was metal free, permitting the use of acid eluents. A Dionex IonPac CS-2 (250 \times 4 mm) cation analytical column was used for the chromatography. The concentrator was a Dionex MetPac CC-1 (50 \times 4 mm) containing an iminodiacetate-functionalized chelating resin. Postcolumn reagent addition and

mixing was done using a Dionex membrane reactor followed by a short delay coil to allow for complete reaction of the postcolumn reagent with the analytes. Data was collected and processed using Dionex AI-450 software.

The separation was accomplished on a Dionex CS2 column using a 15 minute linear gradient from 0.6 M HCl to 0.6 M HCl-0.5 M Na₂SO₄. The gradient was generated by proportioning with a gradient pump from reservoirs containing (1) 2.0 M HCl, (2) 1.0 M sodium sulfate and (3) deionized water. The eluent flow-rate was 1.0 ml/min. The postcolumn reagent consisted of 0.3 mM arsenazo III, 0.5 M acetic acid and 0.1% Triton X-100. The postcolumn flow rate was 0.5 ml/min and the reagent was added pneumatically using a Dionex membrane reactor with a mixing coil. Detection was by absorbance in the visible region at 660 nm.

Chemicals

Concentrated hydrochloric acid used to prepare the HCl eluent and glacial acetic acid for the postcolumn reagent were trace-metal grade from Fisher Scientific (Pittsburgh, PA, USA). Sodium sulfate eluent was prepared from anhydrous sodium sulfate (Fisher Scientific). Arsenazo III and Triton X-100 used for the postcolumn reagent were from Fluka (Ronkonkoma, NY, USA). Ultrapure 2.0 M ammonium acetate, pH 5.5 (for elution of alkaline earth metals from the concentrator column) was from Dionex. Deionized water (18 MΩ) was used to prepare all reagents and standards. 1000 ppm uranium and thorium atomic absorption standards were used as primary standards (Aldrich, Milwaukee, WI, USA).

RESULTS AND DISCUSSION

Direct injection

The chromatography of uranium and thorium is illustrated in Fig. 1. The separation was accomplished using a 15 minute linear gradient from 0.6 M HCl to 0.6 M HCl-0.5 M Na₂SO₄. These were the conditions for all chromatograms run by both direct injection and with preconcentration. The separation was run at 1.0 ml/min for the eluent, and the postcolumn reagent was mixed in at 0.5 ml/min. The stability of the baseline is due to the pH remaining constant throughout the sodium sulfate gradient.

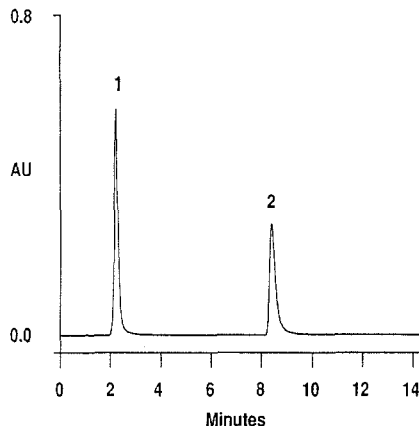


Fig. 1. Cation-exchange separation of uranium and thorium in reagent water. Direct injection (50 μ l) of (1) 40 ppm uranium (as UO₂²⁺) and (2) 20 ppm thorium. Dionex CS2 column, 15-min gradient from 0.6 M HCl to 0.6 M HCl-0.5 M Na₂SO₄. Eluent flow-rate 1.0 ml/min. Postcolumn reagent: 0.3 mM arsenazo III, 0.5 M acetic acid, 0.1% Triton X-100. Postcolumn flow-rate 0.5 ml/min. Visible detection at 660 nm.

Fig. 2 shows the analysis of an acid digested phosphate rock sample by direct injection. Although the sample contained percent levels of calcium, aluminum and iron, uranium was resolved from the major metal interferences. The sample was diluted 500 \times and a 50- μ l sample loop was injected. The

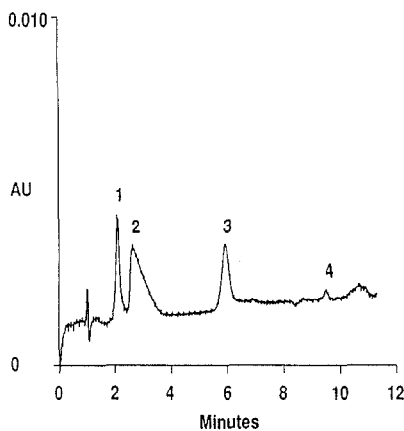


Fig. 2. Direct injection of acid digested phosphate rock sample, National Institute of Standards and Technology (NIST) Standard Reference Material (SRM 120c). Dilution of 500 \times . Conditions as in Fig. 1. Peaks: 1 = uranium; 2 = calcium (48.02% in rock as CaO); 3 = iron(III) (1.02% in rock as Fe₂O₃); 4 = thorium. Uranium: ion chromatography 108 \pm 3 μ g/g; certified value, 114.48 \pm 1.7 μ g/g ($n = 4$).

value determined from this direct injection was close to the certified value of uranium in SRM 120c. A small thorium peak was detected, but no value for thorium was specified for SRM 120c. The determination of thorium may be problematic in the presence of several common inorganic ions. Fluoride, iodate, oxalate and phosphate all form insoluble precipitates with thorium even in strongly acidic (6 M) solutions [16]. This raises serious concerns that thorium analysis in many matrices which contain the previously mentioned ions may not be quantitative. Note that despite the high levels of calcium and iron in the rock sample, uranium was still resolved from both elements. Fig. 2 illustrates the need for concentration in uranium and thorium analysis. While the peaks are resolved from other metals in the sample, the calcium is very near the uranium peak. Additionally, the level of uranium (220 µg/l) is approaching the minimum detection limit for direct injection with a 50-µl sample loop. The low level of uranium as well as the calcium interference can be addressing by selective pre-concentration on a chelating resin.

Fig. 3 illustrates the valving required to concentrate uranium and thorium on a chelating resin and selectively elute alkaline earth metals (chelation concentration). All aspects of the concentration step were controlled by a microprocessor-based gradient pump (chelation concentration pump). This pump was used to load sample onto a concentrator column as well as to control the valves in the system. A 5 ml sample loop was loaded with the raw sample buffered to pH 5.5 with an aliquot of 2.0 M ammonium acetate (ultrapure). The contents of the sample loop was loaded onto the chelation concentrator column (MetPac CC-1) by the chelation concentration pump. Loading the sample in this manner serves two functions. First, the pump loads the buffered sample onto the column where the uranium and thorium are retained. Second, because the chelation concentration pump is pumping 2.0 M ammonium acetate (pH 5.5), it selectively elutes the alkaline earth metals to waste while leaving the concentrated uranium and thorium on the concentrator column. Following the elution of the alkaline earth metals to waste a valve was actuated which places the chelation concentra-

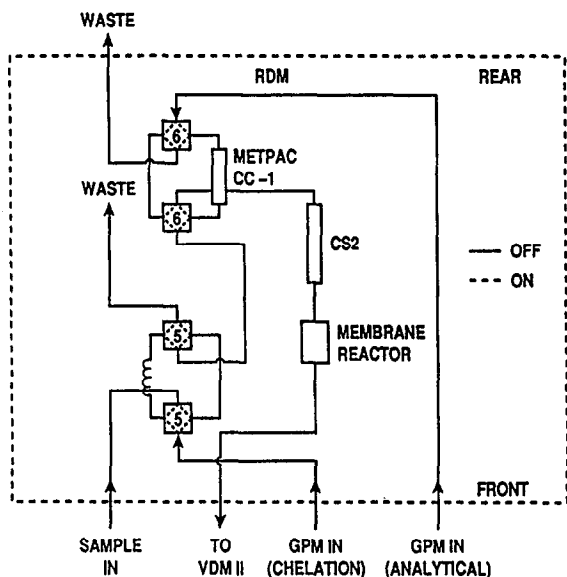


Fig. 3. Schematic diagram of system used for separation of uranium and thorium with on-line pre-concentration using chelating resin. The valving is contained within the reagent delivery module. Two pumps are used, one to perform the analytical separation and one to perform the concentration and matrix elimination steps. The valves are controlled by the chelation concentration pump microprocessor.

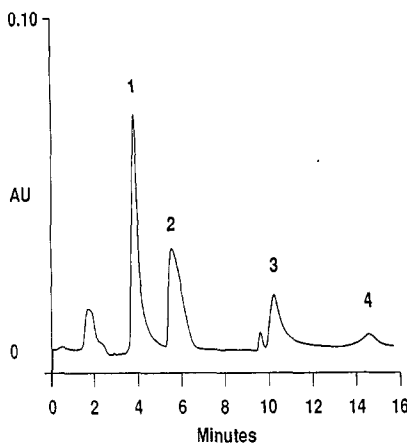


Fig. 4. Acid-digested phosphate rock sample using pre-concentration on chelating resin. NIST Standard Reference Material (SRM 120c). Dilution of 500 ×. A 5.0-ml volume of buffered sample concentrated on MetPac CC-1 concentrator. Concentrator column washed with 6 ml of 2.0 M ammonium acetate prior to injection. Chromatographic conditions as in Fig. 1. Peaks: 1 = uranium (111.2 ppm in rock); 2 = iron(III) (1.02% in rock as Fe₂O₃); 3 = zirconium, hafnium and lanthanide metals; 4 = thorium (7.3 ppm in rock). Uranium: chelation ion chromatography, 111.2 ± 2.2 µg/g; certified value, 114.48 ± 1.7 µg/g. Thorium: chelating ion chromatography, 7.3 ± 0.6 µg/g; no certified value (n = 4).

tion column in line with the analytical pump flow path. The uranium and thorium were eluted to the CS2 column where the previously described separation takes place.

Fig. 4 is an example of a chromatogram generated using preconcentration of uranium and thorium on a chelating resin. The sample, NIST SRM 120c, is the same sample shown by direct injection in Fig. 2. In Fig. 4, the sample was run by buffering the digested rock to pH 5.5 using ultrapure 2.0 M ammonium acetate and concentrating 5.0 ml of buffered sample on a chelating resin. Following sample loading, the chelating column was washed with ultrapure 2.0 M ammonium acetate to elute the alkaline earth metals to waste. Unlike Fig. 2 where a high level of calcium was observed near the uranium peak, using selective preconcentration of uranium and thorium followed by selective elution of the matrix, calcium was eliminated. Some metals present in the sample at low concentrations are concentrated with uranium and thorium. Among these metals which are concentrated and also detected by arsenazo III are iron, zirconium, hafnium and the lanthanides. None of these components interfere with the separation of uranium and thorium. The increase in retention time for uranium and thorium using the concentration method (Fig. 4) relative to direct injection (Figs. 1 and 2) is a result of the added capacity in the system due to the presence of the concentrator column. Note that relative to direct injection (Fig. 2), using preconcentration (Fig. 4)

results in a greatly enhanced signal to noise ratio for uranium as well as higher accuracy when compared using the NIST certified value.

Fig. 5 shows the analysis of seawater for uranium. The sample was a seawater standard reference material from the Canadian Marine Analytical Chemistry Standards Program (National Research Council of Canada). The sample, NASS-2 (open ocean seawater) has certified values for trace elements including uranium. The certified value for uranium in NASS-2 is 3.00 $\mu\text{g/l}$. The sample was run using 5.0-ml, 10.0-ml and 20.0-ml sample loops for concentration. The results of the analysis agreed with certified values for uranium in all cases (Fig. 5). The reproducibility of the method, as evidenced by the standard deviation, was good, particularly when larger quantities of sample were concentrated.

CONCLUSIONS

A cation-exchange separation of uranium and thorium has been developed. The separation uses a hydrochloric acid eluent with a sodium sulfate gradient to efficiently separate uranium and thorium as well as several interfering metals. Detection based on postcolumn addition of acidic arsenazo III provides a sensitive and specific detection scheme for uranium and thorium. The detection limit by direct injection is 20 $\mu\text{g/l}$ for uranium and 60 $\mu\text{g/l}$ for thorium using a 50- μl sample loop. The use of chelating stationary phases for sample preconcentration

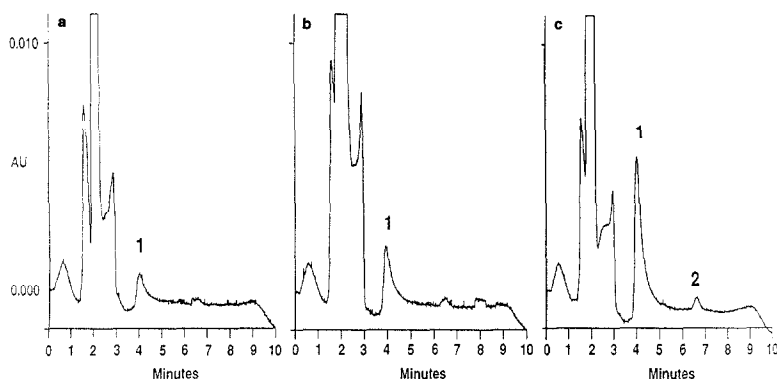


Fig. 5. Seawater sample using preconcentration on chelating resin. Canadian Marine Analytical Chemistry Standards Program (National Research Council of Canada) seawater sample NASS-2. Dilution 2 \times with ammonium acetate buffer. Concentration on MetPac CC-1 concentrator of (a) 5.0, (b) 10.0 and (c) 20.0 ml of sample. Concentrator column washed with 6 ml of 2.0 M ammonium acetate prior to injection. Chromatographic conditions as in Fig. 1. Peaks: 1 = uranium (certified value 3.00 $\mu\text{g/l}$); 2 = iron(III). Uranium values from ion chromatography: (a) $3.14 \pm 0.25 \mu\text{g/l}$; (b) $3.12 \pm 0.18 \mu\text{g/l}$; (c) $3.02 \pm 0.04 \mu\text{g/l}$ ($n = 4$).

tration has led to an enhancement of detection limits for uranium and thorium as well as elimination of potential interferences. Using a chelating resin and concentrating 5.0 ml of sample, the detection limit has been extended to 1.0 $\mu\text{g/l}$ for uranium and 3.0 $\mu\text{g/l}$ for thorium. Additionally, the use of chelating resins for concentration has greatly increased the scope of matrices which may be analyzed for uranium and thorium without significant interference from the matrix.

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