Determination of Uranium and Thorium in Complex Matrices Using Chelation Ion Chromatography

**INTRODUCTION**

A recently developed technique called chelation ion chromatography has been applied successfully to a number of transition and post-transition metals. This application note describes the use of the chelation ion chromatography for the analytical determination of uranium and thorium in complex matrices.

Uranium and thorium are naturally occurring elements found at trace levels in the environment. The determination of these two metals is often made complicated and tedious because of their very low concentrations and the interferences present in the sample matrix. Solvent extraction and sample preconcentration/pretreatment methods traditionally used prior to sample analysis are usually time-consuming and complicated.

Chelation ion chromatography combines selective chelation concentration with analytical separation and specific detection. Chelation concentration preconcentrates uranium and thorium, eliminating alkali and alkaline earth metals from the sample matrix. Uranium and thorium are then separated from high concentrations of iron, aluminum, actinides, lanthanides, hafnium, and zirconium (1:1,000 to 1:10,000 concentration ratio of uranium and interfering species) by cation exchange and detected using specific and sensitive postcolumn derivitization. In some instances, uranium and thorium in a relatively clean matrix can also be determined by direct injection of the sample.

**EQUIPMENT**

Any Dionex chromatography system comprising:
- Advanced Gradient Pump (AGP), 2 required
- Reagent Delivery Module (RDM)
- Variable Wavelength Detector Module (VDM-2)
- Slider valve, 4-way, 4000 psi/27.4 MPa (P/N 38598), 2 required
- AI-450 Chromatography Workstation or data integrator

**REAGENTS AND STANDARDS**

Concentrated hydrochloric acid (trace metal grade)
- Glacial acetic acid (trace metal grade)
- Concentrated ammonium hydroxide (trace metal grade)
- Ultrapure 2.0 M ammonium acetate, pH 5.5 (P/N 33440)
- Arsenazo III
- Triton X-100
- Uranium 1000-ppm atomic absorption standard
- Thorium 1000-ppm atomic absorption standard

**CONDITIONS**

Columns: MetPac™ CC-1 concentrator
- IonPac® CS2 analytical
- Deionized water
- 2.0 M Hydrochloric acid
- 1.0 M Sodium sulfate
- 2.0 M Ammonium acetate (ultrapure)
Rinsing Solution: 0.1 M Acetic acid (trace metal grade)
Postcolumn Reagent: 0.3 mM Arsenazo III*
  0.5 M Acetic acid (trace metal grade)
  0.1% Triton X-100
Postcolumn Flow Rate: 0.5 mL/min
Postcolumn Mixing: Membrane Reactor (P/N 35354)

**WARNING:** Handle arsenazo III with extreme caution. Prepare the reagent under a fume hood, and be sure to wear protective clothing and gloves.

**PREPARATION OF SOLUTIONS AND REAGENTS**

**2.0 M HCl**
Add 165 mL (196.8 g) of concentrated HCl to 500 mL deionized water. Mix and dilute to 1.0 L.

**1.0 M Sodium Sulfate**
Dissolve 142 g of sodium sulfate (anhydrous) in 800 mL deionized water. Dilute to 1.0 L with deionized water.

**0.1 M Acetic Acid**
Add 6.0 g (5.75 mL) of glacial acetic acid to 500 mL deionized water. Dilute to 1.0 L with deionized water.

**Arsenazo III Postcolumn Reagent**
Prepare the postcolumn reagent in the RDM reagent container to minimize contamination. Add 28.5 mL of glacial acetic acid to 500 mL of deionized water. Dissolve 0.24 g of arsenazo III in the solution. After complete dissolution of arsenazo III, add 1.0 mL of Triton X-100 and dilute to 1.0 L with deionized water.

**STANDARD AND SAMPLE PREPARATIONS**
All samples and standards must be buffered to pH 5.5 prior to analysis. This is most easily done by adding an aliquot of ultrapure 2.0 M ammonium acetate to all samples and standards. The volume of ammonium acetate that must be added to buffer a particular sample will depend on the pH of the sample. Samples of moderate pH 2-10 will usually require only 20% buffer added to adjust the pH to 5.5. Strongly acidic samples may require as much as 50% 2.0 M ammonium acetate to adjust pH to 5.5, and in some cases, a dilution may be required prior to buffering the sample. Always add the same amount of buffer to the standards and blanks as is added to the sample. This will result in a consistent background, or blank.

**SYSTEM PREPARATION AND SET-UP**
The valve diagram (Fig. 1) shows the components of the chelation ion chromatography system. Two gradient pumps are required to perform chelation ion chromatography. One gradient pump is used to perform the steps in chelation concentration; the other gradient pump is used to pump the analytical eluent to the analytical column. Two valves (four-way, double-stack) are required for the chelation ion chromatography system. These two valves are installed in the RDM as shown in Figure 1.

Details for operation of individual system components can be found in the appropriate Operator's Manuals.

1. Refer to Figure 1 for set-up and plumbing of the chelation ion chromatography system.
2. Locate four bulkheads on the front panel of the RDM. Connect the lines from the two gradient pumps to the front of the RDM. The line from the gradient pump used for chelation concentration is connected to valve 5. Another line from the second gradient pump is connected to valve 6 as shown in Figure 1.
3. Use 0.020-in. I.D. tubing to connect the membrane reactor (no reaction coil or knitted coil is required) through the front panel bulkhead of the RDM to the VDM-2. Connect a line from the VDM to waste.
the MetPac CC-1 column is being buffered with the 2.0 M ammonium acetate solution. Another gradient pump delivers eluent (2.0 M HCl) to the analytical system.

2. Valve 5 is ON and valve 6 is OFF. Sample that has been previously loaded to the sample loop is being pumped to the the MetPac CC-1 column with 2.0 M ammonium acetate. An additional 2 to 3 minutes is required to ensure the complete removal of alkali and alkaline earth metals from the column.

3. The gradient pump starts pumping 0.1 M acetic acid to convert the MetPac CC-1 column from the ammonium form to the hydrogen form.

4. Valve 5 is ON and valve 6 is ON. The MetPac CC-1 is now switched in-line with the analytical system.

**DISCUSSION**

The method described in this application note is intended for the determination of uranium and thorium in complex matrices. The term complex matrix refers to any matrix containing constituents that may interfere with the analytical measurement. The detection limit for many analytes may be severely compromised using conventional analytical techniques for complex matrices. For example, large quantities of alkali and alkaline earth metals can interfere with the determination of uranium by ion chromatography or atomic spectroscopy. By using selective ion exchange materials such as chelating resin, uranium, thorium, and other transition and post-transition metals can be selectively preconcentrated, while alkali and alkaline earth metals are eluted to waste.

Selective preconcentration of uranium and thorium takes place on a MetPac CC-1 column (iminodiacetate chelating resin) at pH 5.5. At this pH, the resin is highly selective for uranium and thorium relative to alkali and alkaline earth metals. Although alkaline earth metals are concentrated, they are subsequently eluted to waste using 2.0 M ammonium acetate. Then, the concentrated metals are eluted with analytical eluent (HCl) to the analytical column (IonPac CS2) where the metals are separated. The separation of uranium, thorium and other common interferences is accomplished with a hydrochloric acid/sodium sulfate gradient.

### Table 1 Gradient programs for chelation IC

<table>
<thead>
<tr>
<th>Chelation Concentration</th>
<th>Time (min)</th>
<th>E1 (%)</th>
<th>E2 (%)</th>
<th>V5</th>
<th>V6</th>
<th>Flow (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1: 2.0 M ammonium acetate, pH 5.5</td>
<td>0.0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.0</td>
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<tr>
<td></td>
<td>2.5</td>
<td>100</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2.0</td>
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<tr>
<td></td>
<td>7.5</td>
<td>100</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>7.6</td>
<td>0</td>
<td>100</td>
<td>1</td>
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<td>3.0</td>
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<tr>
<td></td>
<td>10.0*</td>
<td>0</td>
<td>100</td>
<td>1</td>
<td>1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Inject concentrated metals to analytical system

<table>
<thead>
<tr>
<th>Analytical System</th>
<th>Time (min)</th>
<th>E1 (%)</th>
<th>E2 (%)</th>
<th>E3 (%)</th>
<th>Flow (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1: deionized water</td>
<td>0.0</td>
<td>70</td>
<td>30</td>
<td>0</td>
<td>1.0</td>
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<tr>
<td></td>
<td>10.0</td>
<td>70</td>
<td>30</td>
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<td>1.0</td>
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<tr>
<td></td>
<td>15.0</td>
<td>0</td>
<td>50</td>
<td>50</td>
<td>1.0</td>
</tr>
</tbody>
</table>

4. Connect the luer lock fitting (P/N 24305) to the bulkhead of the RDM front panel and connect a line to valve 5. This is used as the injector port.

5. A sample loop can be prepared from an appropriate length of 0.032-in. I.D. tubing. Connect the sample loop as indicated in Figure 1.

6. A helium pressure of 5 to 7 psi (34–48 kPa) must be maintained on the eluent bottles.

**SYSTEM OPERATION**

The chelation ion chromatography system for uranium and thorium is a semi-automated system for concentrating and determining uranium in a variety of matrices. The sample and standards must be buffered prior to sample concentration step. Operation of the chelation ion chromatography system consists of the following steps.

1. Enter the program shown in Table 1 to the appropriate gradient pump. Start the two gradient pumps. Start the post-column reagent flow by switching the RDM ON. Adjust the regulator so that the postcolumn flow rate at the detector waste line is approximately 0.5 mL/min. At the beginning of the gradient program, valve 5 is OFF and valve 6 is OFF. The sample can be loaded to the sample loop while the MetPac CC-1 column is being buffered with the 2.0 M ammonium acetate solution. Another gradient pump delivers eluent (2.0 M HCl) to the analytical system.
The selective postcolumn derivitization of uranium and thorium is accomplished by using arsenazo III. The reaction of uranium and thorium with arsenazo III proceeds even at very low pH (>1.0). These metal complexes have a wavelength of maximum absorbance at 660 nm.

**APPLICATIONS**

Uranium and thorium in a relatively clean matrix can easily be determined by direct injection. Table 1 lists a similar gradient separation that can be used to separate of uranium and thorium, as shown in Figure 2. Figure 3 shows the determination of uranium in phosphate rock sample (SRM 120C) using direct injection. The detection limit by direct injection (50-µL loop) is 20 to 35 ppb of uranium and thorium.

For those samples that contain less than 20 ppb of uranium or thorium, these elements can be concentrated from the sample matrix by chelation concentration. Using a 5-mL sample, trace concentrations of uranium and thorium can be determined, as shown in Figure 4. Note that the concentration ratio of uranium and iron (III) is 1:10,000.

This method has been applied to the determination of uranium and thorium in phosphate rock samples. Figure 5 shows the typical chromatogram of uranium and thorium in SRM 120C phosphate rock NIST standard reference material (U.S. National Institute of Standards and Technology) and the analytical data is compared to the certified value. Note that this sample matrix contains 48% CaO and 1.5% Fe₂O₃.

The detection limit of this method is 1 to 5 ppb of uranium and thorium for 5 mL of sample concentrated. Lower detection limits may be accomplished by concentrating a 10 or 20-mL sample, depending on the sample matrix. For example, Figure 6 shows the determination of uranium in seawater (NASS-2). As evidenced by the detection of iron, concentration of a 20-mL sample results in a significantly lower detection limit than obtained by concentrating a 5-mL sample. Typically, a sample with a 1:5000 concentration ratio of uranium or thorium to the interfering species (iron, aluminum, lanthanides, zirconium, and hafnium) can be analyzed by chelation ion chromatography.

![Figure 2](image2.png) Determination of uranium and thorium by ion chromatography using direct injection

![Figure 3](image3.png) Determination of uranium in phosphate rock (SRM 120C) by ion chromatography using direct injection
Chelation IC

Sample: 1. Uranium 0.02 ppm percent by weight
2. Iron (III) 200 ppm
3. Thorium 0.05 ppm

Figure 4  Determination of uranium and thorium by chelation ion chromatography

Figure 5  Determination of uranium and thorium in phosphate rock (SRM 120C) by chelation ion chromatography

Certified Value* = 3.00 ± 0.15 ppb

*Isotope Dilution Solid Source Mass Spectrometry
Immobilized Ligand Separation/Isotope Dilution Inductively Coupled Plasma Mass Spectrometry

Figure 6  Determination of uranium in seawater (NASS-2) by chelation ion chromatography