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Determination of Lanthanide Metals in Digested Rock Samples by Chelation Ion Chromatography

INTRODUCTION

The naturally occurring high concentrations of certain metals such as iron, aluminum, transition metals, alkali metals, and alkaline earth elements in geological materials usually interfere with the determination of the trace lanthanide metals in these samples. The predominant analytical techniques that have been used to determine lanthanide metals in the geological materials include neutron activation (NAA), isotope dilution mass spectrometry (IDMS), spark-source mass spectrometry (SSMS), inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence (XRF), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and DC-plasma emission spectroscopy. In addition to the high cost of instrumentation and the need for highly skilled operators, these analytical techniques suffer from matrix interference problems. All these techniques require that the sample be taken into solution and the matrix removed prior to the analytical measurement. The removal of sample matrix by opened-column chromatography is a complex process that can take several hours per sample. If the matrix removal method is not employed, several common methods are used to minimize the sample matrix interferences. These include spectral background corrections, standard additions, sample dilution, and matrix matching. These methods help to minimize matrix interferences; however, these methods often result in degraded detection limits and accuracy.

A new technique called *chelation ion chromatography* (chelation IC) has been developed for the determination of transition and lanthanide metals in complex matrices. The sample pretreatment system (chelation concentration) coupled directly to the ion chromatograph (IC) offers the analyst a solution to the detection limit and interference problems commonly experienced when analyzing complex matrices. Chelation IC combines a selective concentration and matrix elimination with analytical separations and specific detection for lanthanide metals. Selective ion exchange materials such as chelating resins can concentrate transition and lanthanide metals while eliminating alkali and alkaline earth elements. Then the selective elimination process removes most of the iron, aluminum, and transition metals from the sample matrix. By using a matrix selective complexing agent, 90 to 99% of the iron, aluminum, and transition metals are removed while all of the lanthanides are quantitatively retained. Finally, the concentrated lanthanide metals are separated by high performance ion chromatography with specific detection. The overall analysis time after sample dissolution is approximately one hour.

INSTRUMENT REQUIREMENTS

This Technical Note gives detailed descriptions of the system components, installations, and operation of the chelation ion chromatographic system. Consult this information carefully before operating the chelation IC

system. It is important to understand each step of the sample pretreatment process to maintain the best performance of the chelation IC system. This chelation IC technique was designed to operate on a Dionex Series 4000i, 4500i, or DX-300 IC system. The recommended system configuration is shown in Figure 1.

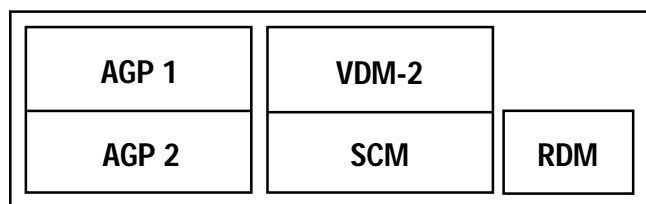


Figure 1. Chelation ion chromatography system.

A gradient pump, designated AGP1, performs the steps of chelation concentration and controls valves. Another gradient pump, designated AGP2, is used as the analytical pump for analytical separation. A DQP pump (labeled Sample Pump) in the Sample Concentration Module (SCM) is used for loading the sample from the sample loop onto the MetPac™ CC-1 chelating column. Another DQP pump (eluent pump, labeled Carrier Pump) with a pulse damper is used as an accessory pump if required. Five 4-way slider valves are located in the front section of the SCM.

To improve the detection limits of the chelation IC system, a membrane reactor is recommended in place of the mixing tee. The membrane reactor lowers detection limits for metals fivefold compared to adding reagent using the mixing tee. The membrane reactor should be used if lanthanide metals are being determined below 0.5 ppb. A beaded reaction coil (P/N 036036) or a knitted reaction coil (P/N 039349) should always be used with the membrane reactor.

The chelation ion chromatography system comprises a Dionex chromatographic system with the following components:

- Advanced Gradient Pump (AGP; two required)
- Sample Concentration Module
- Reagent Delivery Module (RDM)
- Variable Wavelength Detector Module (VDM-2)
- Eluent Degas Module (EDM-2)
- Eluent Container Set, glass (P/N 038752)
- High Pressure 4-Way Valve (BF-2), 1/4-28 fittings (P/N 038598)

- IonPac® Membrane Reactor (P/N 035354, optional)
- Knitted reaction coil (P/N 039349)
- MetPac CC-1 Column (P/N 042156)
- TMC-1 Concentrator Column (P/N 042155)
- IonPac NG1 Guard Column (P/N 039567)
- HPIC CG2 Guard Column (P/N 035370)
- IonPac CG5 Guard Column (P/N 037029)
- ACI/AI-450 data acquisition and handling system

SYSTEM CONFIGURATION

Sample Concentration Module

The block schematic of the chelation IC system is shown in Figure 1. The SCM contains two single-piston Dionex QIC Pumps (DQP), 2000 psi (13.8 MPa); inert double stack 4-way pneumatically controlled slider valves; and a pulse damper. One of the DQPs is used to pump sample into the MetPac CC-1 column; the other pump is used as an accessory pump. All of these components are housed in a single enclosure. The rear panel of the SCM contains bulkhead fittings for connecting waste lines and eluent lines.

Figure 2 shows a detailed pneumatic and hydraulic schematic of the SCM system. From the factory, the SCM is configured to be used for sample pretreatment with an external detector (ICP). For chelation IC applications, configure and plumb the SCM as shown in Figure 2.

Advanced Gradient Pump

The AGP is a microprocessor-controlled, high performance quaternary gradient IC pump. It is chemically inert and has a metal-free flow path. The AGP permits the time-dependent selection of up to four different eluents, flow rate, and the control of two sets of air solenoids for external valve control. Controls 5 and 6 of the pump (referred to as V5 and V6, respectively) are used to control the five valves in the SCM. Valve control is programmable from the front panel and can store up to 10 different programs. Refer to the *AGP Operator's Manual* for information on operation and maintenance.

The AGP can be controlled by an integrator or the AI-450 Chromatography Workstation. For automation of the system, the Dionex Automated Sampler Module (ASM) for 1- to 3-mL sample preconcentration can also be used and controlled by the AI-450.

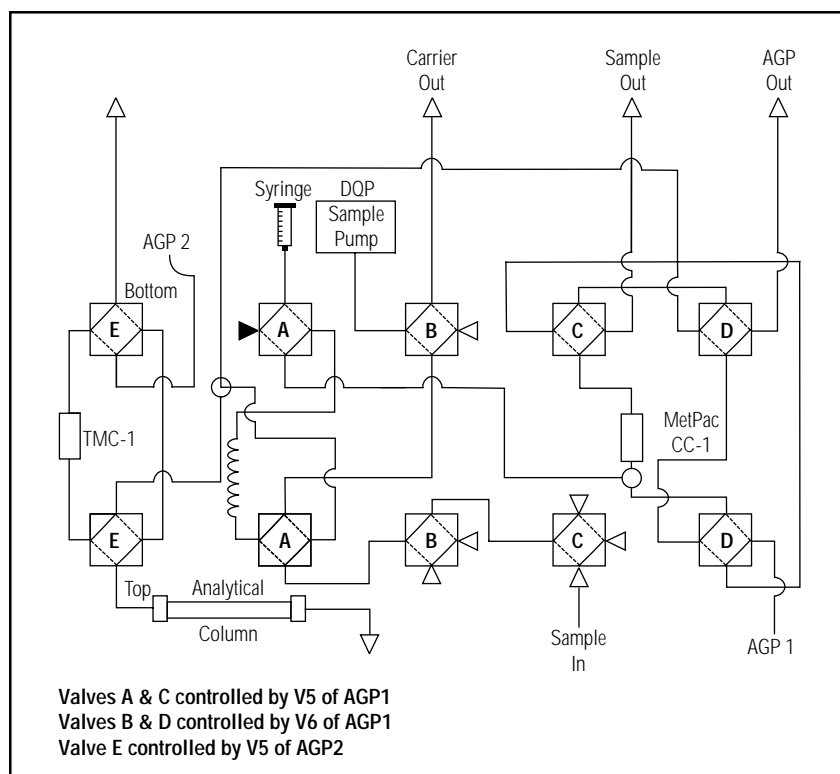


Figure 2. Schematic of chelation ion chromatography system.

Pneumatic Connections

Disconnect all the air tubings in the SCM and reconnect as indicated in Figure 2. This system configuration contains two AGPs. The first AGP, designated AGP1, performs the chelation concentration steps. The second AGP, designated AGP2, is the analytical pump used for the chromatography. Be sure that valves A and C are controlled by V5 and that valves B and D are controlled by V6 of AGP1. Valve E is controlled by V5 of AGP2. Connect the air tubing between the two AGPs and the SCM. Confirm that the air tubings are connected to the proper valves (A, B, C, D, and E) as shown in Figure 2. Also confirm that the orange tubing is connected to the tops of valves A and C and the green tubing to the tops of valves B and D. Connect the yellow tubing to the bottom of valves A and C and the blue tubing to the bottom of valves B and C. From AGP2, connect the orange tubing to the top of valve E and the yellow tubing to the bottom of the same valve. Next, connect about 2 ft (65 cm) of air tubing (P/N 030091) to the small barbed fitting on the back of the two AGPs. Insert a barbed tee (P/N 030538) into the end of this tubing. One arm of the tee will go to the nitrogen or argon source (regulator) and the other arm to the eluent regulator or EDM (optional).

Next, using a barged tee, connect the air tubing from the nitrogen or argon source (eluent regulator, or EDM) to the inlet of the eluent bottle regulator (P/N 038201). Using the required lengths of the tubing, connect the tee to the gas source and to the eluent pressure regulator. Using the 1/4-in. x 10/32 brass reducer (P/N 030087) and the 1/16-in. x 10/32 barbed fitting (P/N 030017), connect the air tubing to the gas source regulator. This completes the pneumatic set-up.

Hydraulic Connections

Refer to the *AGP Operator's Manual* and the *SCM Operator's Manual* for details on the installation and operation of the different modules. Begin the hydraulic connections by connecting the four eluent lines from the four eluent container caps

to the front panel eluent port of the pump. Notice that the eluent lines are labeled 1, 2, 3, and 4. Be sure that the eluent lines are connected to the appropriate eluent port of the pump.

Connect the eluent line from the 4-L plastic eluent container (P/N 039164) to the SAMPLE IN port of the SCM rear panel. This port is connected to the check-valve inlet of the sample pump located on the right side of the SCM. Next, connect the three blue waste lines (P/N 039341) to the ports of the SCM rear panel labeled CARRIER OUT, AGP OUT, AND SAMPLE OUT, and place them in a waste container. Also, another waste line from valve E can be placed in the waste container. This completes the hydraulic connections.

Electrical Connections

Verify that the front PUMP 1 and PUMP 2 power switches of the SCM are off. Using the power cords provided (P/N 096078), connect the AC receptacles on the rear panel of the SCM to the SWITCHED AC on the rear panel of the ACI. Connect the AC receptacles on the rear panels of the AGP and VDM-2 to the white outlets of the power strip located on the rear upper section of the system enclosure. Next, connect the AC receptacles of the power strip enclosure and of the ACI to AC (110 V) power outlets.

Connect the ACI cables (ribbon cables) to the appropriate components as configured in system configuration in AI-450. Also assign AC1 in the system configuration as SP (sample pump), relay 1 as AGP2, and relay 2 as ASM (autosampler module).

Connect two relay TTL cables (P/N 042599) from the rear panels of the ACI to AGP2 and the autosampler. Consult the appropriate manuals for proper installation.

Chemicals, Reagents, and Standards

Appendix A shows a complete list of reagents and instructions for reagent preparation. The reagents used for chelation concentration — 2.0 M ammonium acetate, pH 5.5, 2.0 M nitric acid, and 0.1 M ammonium nitrate, pH 3.5 — are available from Dionex. In addition, high purity water containing less than 500 ppt of common transition metals (iron, zinc, copper, etc.) is required.

Other Supplies

In addition to the items listed above you will also need:

- Electrical power
- Compressed nitrogen (80-120 psi; 55-83 kPa)
- Standard analytical laboratory equipment such as a balance, pH meter, etc.

DISCUSSION OF THE METHOD

The method described in this Note was developed for determining trace lanthanide metals in complex matrices containing high levels of alkali metals, alkaline earth elements, iron, aluminum, and transition metals. The elimination of alkali and alkaline earth metals is based on the nonselective property of the MetPac CC-1 chelating resin for these elements. The weakly retained alkali and alkaline earth metal ions are separated from other elements using ammonium acetate. The selective removal of iron, aluminum, and transition metals is based upon the metal chloride formation induced by a water-miscible organic eluent, for example, a hydrochloric acid/ethanol mixture. This eluent not only promotes the formation of metal chloride complexes, it also decreases the distribution coefficient of the metal complexes on the cation exchange resin. Thus, the relatively stable metal chloride complexes of iron, aluminum, and most transition metals are selectively removed from the TMC-1 cation exchange column using hydrochloric acid/ethanol eluent. On the other hand, the lanthanide metals form less stable metal

chloride complexes and are retained quantitatively on the TMC-1 column. Therefore, by using the optimal concentration of hydrochloric acid/ethanol eluent, lanthanide metals are selectively concentrated on the cation exchange column, while the majority of iron, aluminum, and transition metals is eliminated. Then, the TMC-1 column is converted from hydrogen to ammonium form with ammonium nitrate. Finally, the concentrated lanthanide metals are eluted with the PDCA eluent to the IonPac CS5 column, where they are resolved chromatographically.

Note: Metal chloride complexes are formed by the hydration reduction of the cationic species by the organic solvents. Generally, the effects of increasing amounts of the organic solvent are a reduction of the water molecules around the metals, a decrease in the forces binding the coordinated hydration shell, and a decrease in the size of the outer hydration cloud. Consequently, the metal chloride complexes formed in the organic solvent are relatively stable.

Chelation Concentration and Matrix Elimination

The chelating concentrator column, the MetPac CC-1, is used to selectively concentrate lanthanide metals from the aqueous sample. Alkali and alkaline earth metals are selectively eluted to waste using 2.0 M ammonium acetate, pH 5.5. Transition metals, which are concentrated along with the lanthanide metals, are removed in a tight band to the high capacity cation exchange column (TMC-1), where further separation takes place. Next, the transition metals are eluted to waste using 1.5 M hydrochloric acid/75% ethanol, while the lanthanide metals are retained in the TMC-1 column. The experimental results suggest that at least 17 mL of the hydrochloric acid/ethanol eluent can be used without eluting lanthanide metals from the TMC-1 column.

Summary of Method

In summary, chelation concentration comprises five major processes:

1. The digested sample is loaded into the sample loop. Then, the valve diverts the sample loop in-line with the MetPac CC-1. The sample loop is flushed by water from the sample pump, and the sample stream is buffered with 2.0 M ammonium acetate (pH 5.5) and passes through the MetPac CC-1 column and out to waste. Most polyvalent cations

are quantitatively concentrated from the sample while anions and alkali metals pass through the column essentially unretained.

- Weakly bound alkaline earth metals such as calcium and magnesium are selectively eluted. This is accomplished by using 2.0 M ammonium acetate eluent (pH 5.5).
- Concentrated transition and lanthanide metals are eluted in a 100 to 200- μ L volume using 1.0 M nitric acid. The acid effluent from the MetPac CC-1 column is diluted on-line with deionized water from the sample pump before entering the TMC-1 column. The purpose of on-line dilution is to maximize the metal retention on the TMC-1 column.
- Next, the transition metals are selectively eliminated from the TMC-1 column using a mixture of 1.5 M hydrochloric acid/75% ethanol solution. The lanthanide metals are quantitatively retained on the TMC-1, while the transition metals are eluted to waste.
- The MetPac CC-1 is converted back to the ammonium form using 2.0 M ammonium acetate.

Before the TMC-1 can be injected into the analytical stream, it must be converted from the acid (H^+) form to ammonium (NH_4^+) form by using 0.1 M ammonium nitrate (pH 3.5). Converting the column from the acid form to the ammonium form prevents a pH disturbance of the weak acid eluents, which causes analytical problems.

The separation of lanthanide metals is accomplished by anion exchange of lanthanide-chelator complexes. By using PDCA as an eluent chelator, the concentrated transition and lanthanide metals are eluted from the TMC-1, as metal-PDCA complexes, to the IonPac CS5 column. Transition metals form stable monovalent or divalent anionic complexes with PDCA, while lanthanide metals form stable trivalent anionic complexes with PDCA. The resulting ionic charge differences between the lanthanide and transition metals permit separation of the transition metals while the lanthanides are retained in the CS5 column. After the transition metals are separated and completely eluted from the analytical column, the lanthanide metals are separated and eluted using the oxalate and diglycolate eluent.

Separations of lanthanide metals in digested rock samples are shown in Figures 3 through 5 on page 7. This method has been applied to the United States

Geological Survey (USGS) Basalt (BHVO-1), Andesite (AGV-1), and Peridotite (PCC-1) Geochemical Standard Reference Materials. Table 1 shows the matrix compositions of those samples. The results of the spike/recovery experiment and the USGS Geochemical Standard Reference Materials are shown in Tables 2 and 3.

Table 1 Sample Matrix Composition of USGS Geological Samples

Element	Basalt (BHVO-1)	Andesite (AGV-1)	Peridotite (PCC-1)
SiO ₂ *	49.94%	58.79%	41.67%
Al ₂ O ₃	13.80%	17.14%	0.67%
Fe ₂ O ₃	12.23%	6.76%	8.25%
MnO	0.168%	0.092%	0.119%
MgO	7.23%	1.53%	43.43%
CaO	11.40%	4.94%	0.52%
Cu	136 ppm	60 ppm	10 ppm
Ni	121 ppm	16 ppm	2360 ppm
Zn	105 ppm	88 ppm	42 ppm

*SiO₂ must be removed from the sample matrix during sample digestion with concentrated hydrofluoric acid

Table 2 Low Spike/Recovery of Trace Lanthanide in PCC-1 Matrix

Element	Spike (ppm)	Found (ppm)
La	0.07	0.088 \pm 0.002
Ce	0.133	0.127 \pm 0.087
Pr	0.033	0.035 \pm 0.005
Nd	0.067	0.079 \pm 0.003
Sm	0.017	0.018 \pm 0.000
Eu	0.0067	0.007 \pm 0.000
Gd	0.0167	0.017 \pm 0.000
Tb	0.0033	0.004 \pm 0.000
Dy	0.0167	0.020 \pm 0.000
Ho	0.0033	0.004 \pm 0.000
Er	0.0067	0.008 \pm 0.000
Tm	0.0033	0.004 \pm 0.000
Yb	0.0067	0.009 \pm 0.000

Sample dilution is 1:150 and 3 mL is concentrated. All values are blank corrected.

Table 3 Analysis of Lanthanide Metals in the USGS Geochemical Standard Reference Materials Using Chelation Ion Chromatography

Element	AGV-1 (ppm) Sugg. Value	AGV-1 (ppm) Chelation IC	BHVO-1 (ppm) Sugg. Value	BHVO 1 (ppm) Chelation IC
La	38	43 ± 1	15.8	12.3 ± 0.3
Ce	67	75.83 ± 0.05	39	33.4 ± 0.4
Pr	7.6	9.2 ± 0.2	5.7	4.66 ± 0.02
Nd	33	33.26 ± 0.02	25.2	23.8 ± 0.6
Sm	5.9	5.99 ± 0.07	6.2	6.3 ± 0.1
Eu	1.64	1.5 ± 0.1	2.06	2.40 ± 0.046
Gd	5	4.58 ± 0.09	6.4	6.69 ± 0.07
Tb	0.7	0.66 ± 0.02	0.96	1.14 ± 0.01
Dy	3.6	3.556 ± 0.001	5.2	5.45 ± 0.02
Ho	0.67	NA	0.99	NA
Er	1.7	1.75 ± 0.01	2.4	2.42 ± 0.06
Tm	0.34	0.246 ± 0.003	0.33	0.485 ± 0.004
Yb	1.72	1.727 ± 0.006	2.02	1.98 ± 0.004
Lu	0.27	NA	0.291	NA

*Sample dilution is 1:150 and 3.0 mL of diluted sample is concentrated. The lanthanide concentrations are averaged from three runs.

SYSTEM PREPARATION, SET-UP, AND TEST

- Confirm that the SCM is configured as shown in Figure 2. Be sure that an NG1 column is installed between AGP1 and valve D of the SCM. Also, confirm that the HPIC-CG2 column is installed between the sample pump and valve B. Install a MetPac CC-1, TMC-1, and IonPac CG5 and CS5 columns as indicated in Figure 2.
- Remove the GM-2 mixer from the low pressure side of AGP1. This mixer is located between the valve manifold and the eluent priming block of the AGP. Connect the two lines using a coupler (P/N 039056). Do not install a mixer on the high pressure side of the pump (i.e., between the pump and valve D). Refer to the *AGP Operator's Manual* for details.
- Prepare 1 L of 0.2 M oxalic acid by dissolving 25.2 g of reagent grade oxalic acid dihydrate in 1 L of deionized water. This solution will be used to clean the eluent flow path.
- Connect the 0.2 M oxalic acid to E1 of the AGP. Pump the oxalic acid through the pump and to waste at 2.0 mL/min for 10 min. Repeat this procedure for ports 2, 3, and 4 to remove all trace metals from the flow path.
- Place the sample inlet tube into the 0.2 M oxalic acid solution. Fill each of the four 1-L eluent bottles and the 4-L plastic eluent bottle with 500 mL of 0.2 M oxalic acid. Enter the following program for system preparation from the front panel of the AGP. Refer to the *AGP Operator's Manual* for details on programming.

Time	E1	E2	E3	E4	V5	V6	Flow Rate
0.0	100	-	-	-	1	0	2.0
5.0	-	100	-	-	1	1	2.0
10.0	-	-	100	-	0	1	2.0
15.0	-	-	-	100	0	0	2.0
20.0	100	-	-	-	0	0	0.0

- Replace the 0.2 M oxalic acid in the 4-L plastic bottle with deionized water. Be sure that the cap has an o-ring for proper sealing.
- Clean five 1-L glass eluent bottles by filling them with 0.2 M oxalic acid. Allow the acid to remain in the eluent bottle for at least 4 hours. Prepare eluents as described in Appendix A. Use caution in preparing and transferring these reagents to minimize contamination. Connect the filled eluent bottles to the appropriate eluent caps connected to the pump. Be sure that the eluents are plumbed to the proper ports. Adjust the eluent bottle regulator to 4 to 6 psi and check for gas leaks.
- Prime the AGP with each eluent using the following procedure: Enter the previous program into the AGP. Set the flow rate to 3.0 mL/min and select 100% of E1. Start the AGP, hold the program, and loosen the needle valve located on the pressure transducer housing. This will flush any air out of the eluent lines and the pump compartments, thus priming the pump. Repeat this procedure for E2, E3, and E4 by selecting the next sequence of the gradient program. Be sure to hand-tighten the needle valve when priming is complete.

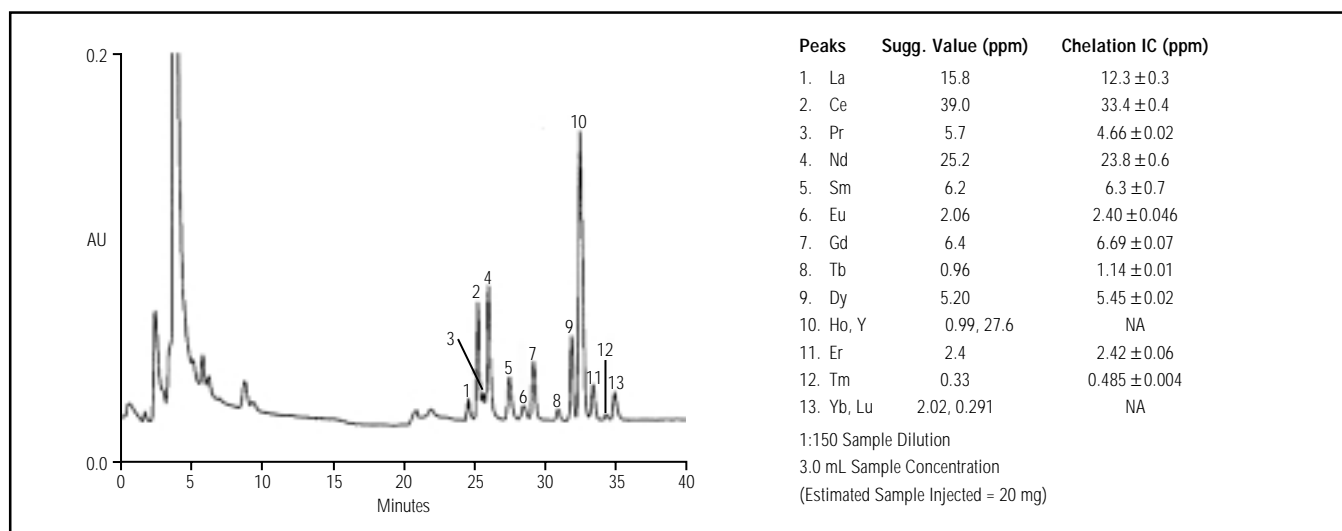


Figure 3. Determination of lanthanide metals in USGS basalt (BHVO-1).

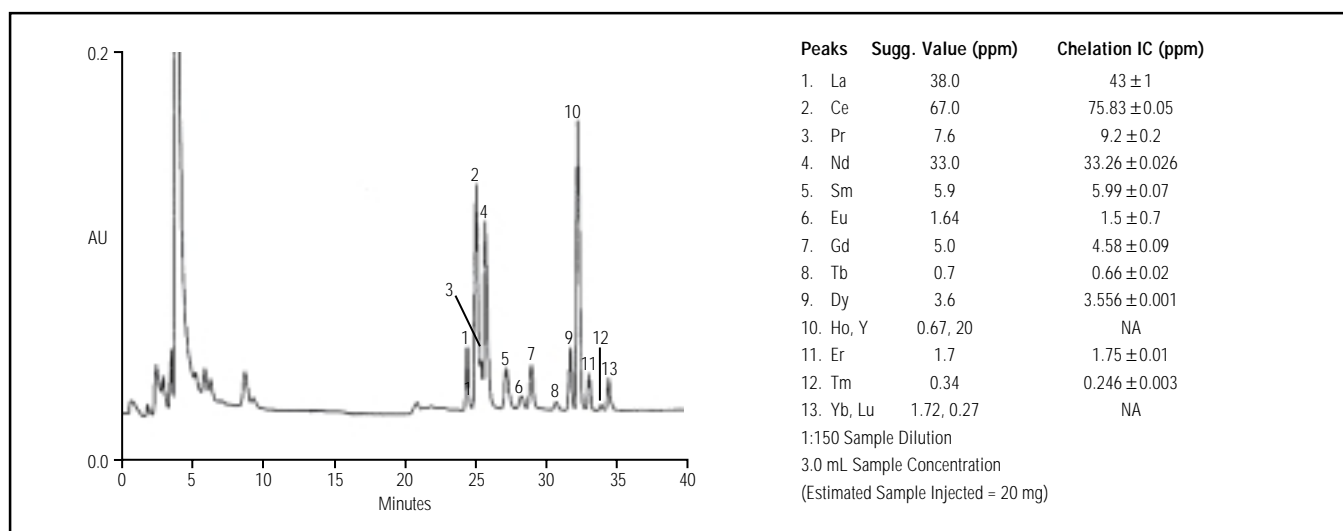


Figure 4. Determination of lanthanide metals in USGS andesite (AGV-1).

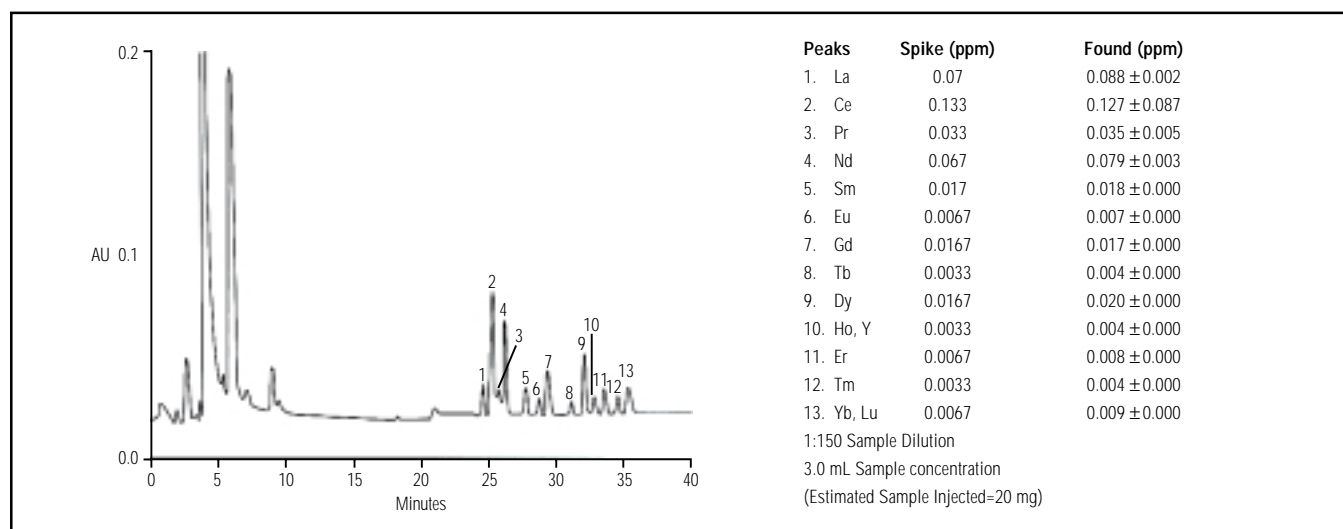


Figure 5. Spike/recovery of lanthanide metals in USGS peridotite (PCC-1) matrix.

9. Prepare PAR reagent as directed in Appendix A. Place PAR reagent into the RDM reagent reservoir and close the reservoir after the eluent is flowing. Turn the RDM reagent 1 switch on and immediately adjust the regulator to 60 psi. Turn the RDM reagent 1 switch off.

Caution: Be sure that PDCA is being pumped through the columns when the RDM is switched on; failure to do so may cause the PAR reagent to back up through the IonPac CS5 column.

10. Enter the AGP1 program for chelation concentration as shown in Table 4 (page 10). This program can be entered from the front panel of the AGP or from the AI-450's Method Editor.

In fully automated system operation, a relay TTL cable (P/N 042599) is used to reset/start the AGP2 pump after the chelation concentration step is completed. Consult the *AI-450 Operator's Manual* or the *Integrator Operator's Manual* for details on installation and operation.

System Test

The purpose of this system test is to ensure that all chromatographic and chemical components of the system are operating properly. The system schematic is shown in Figure 3. Be sure to check all fittings for leaks during the system test.

1. Enter the program for chelation concentration (Table 4) from the front panel of the AGP. Refer to the *AGP Operator's Manual* for details on programming. Check the program carefully for accuracy by listing the program.

The system test will begin with a test of the hydraulic system. If the system fails the hydraulic test at any point, determine the source of the plumbing error. Begin by using the program given above. With the AGP in the STOP-HOLD position, press RESET. This will set the program to time 0.0.

2. Press START. Eluent (E1) should begin to flow to valve D and out to the AGP OUT at the SCM rear panel. Check AGP OUT to confirm that the eluent is flowing to the SCM.
3. Next, prime the sample pump by loosening the tubing fitting that is screwed into the outlet check

valve. Since the eluent reservoir is pressurized (5 psi), the deionized water should begin to flow out of the check valve. As the eluent begins to flow, turn on the carrier pump by pressing the PUMP 2 POWER switch on the SCM front panel. After about 5 seconds, replace the outlet check valve tubing fitting. Generally, this fitting requires only finger-tightening; if the fitting leaks, tighten it another one-eighth of a turn using a 5/16-in. open-end wrench.

4. Set the stroke dial of the carrier pump to about 5.00 (refer to the *SCM Operator's Manual* for details on adjusting the flow rate). Calibrate the sample pump flow rate by mass or volume to 2.0 mL/min. Be sure that the eluent reservoir is pressurized to 5 psi. Turn off the sample pump (PUMP 2).
5. Place the sample inlet tube in a container of deionized water and draw the deionized water through the sample loop using a syringe. Confirm that the solution is flowing through the sample loop.
6. List the AGP program to the next sequence (2.0 min) and press RUN and HOLD. This will forward the program to 2.0 min. Check to see that the eluent is flowing out of the SAMPLE OUT tubing at the SCM rear panel. Stop the pump and confirm that the eluent flow stops. Turn on the sample pump (PUMP 2). Check to confirm that the deionized water is flowing out of the same port at the SCM rear panel. Start the AGP, wait 30 seconds, and then measure the flow rate. The combined flow rate from the sample pump and the AGP must be 4 mL/min. Adjust the sample pump flow rate if necessary. Turn off the sample pump (PUMP 2) and the AGP. If the sample pump loses prime, prime the pump by loosening the tubing fitting on the outlet check-valve. If there is no liquid in the check valve, use a squirt bottle to squirt some deionized water into the check-valve. This will aid in priming the pump. Replace the check valve tube fitting. This completes the hydraulic test.
7. Reset the AGP1 to time 0.0 min. Start the AGP2. Forward the AGP2 program (see Table 4) to time 0.1 min. This should place the TMC-1 column in-line with the AGP2 eluent flow. Disconnect the TMC-1 column and confirm that eluent is flowing through the column. Stop the AGP2.

8. Reset the AGP2 program. Connect the postcolumn system to the CS5 separator column. Start the AGP2 pump. Immediately turn on the RDM reagent 1 valve to pressurize the postcolumn reagent reservoir and start the reagent flow. After 1 min, check to see that the PAR postcolumn reagent is flowing to the VDM-2. Measure the flow rate from the waste line. The flow rate should be 1.4 to 1.6 mL/min. Adjust the RDM regulator to achieve the recommended flow rate. This completes the system test.

SYSTEM OPERATION

The sequencing and operation of the system components are described below. The operating conditions are summarized in Table 4. The chelation ion chromatography system configuration has been designed for use in the fully automated mode, except for the sample introduction step. If the required sample volume is less than 3 mL, the Dionex ASM autosampler is applicable. Unless an autosampler capable of delivering more than 5 mL of sample is used, sample introduction must be performed using a syringe for larger samples.

1. Confirm that the system is configured as given in Figure 2. Check to see that the system has an 80 to 120 psi inert gas supply.
2. Turn on the absorbance detector. If a variable wavelength detector is used, set the wavelength to 530 nm. If a filter-based detector is used, be sure the filter is 520 or 530 nm. Turn on the visible lamp and set the sensitivity to 0.2 AUFS. Be sure that the detector output is connected to a data collection system (integrator or ACI/AI-450).
3. Enter the program listed in Table 4 (page 10). Check the program carefully by listing each step of the program.
4. Reset the AGP2 program at time 0.0 min. Start the AGP2 and the RDM. Confirm that the PAR reagent is flowing through the detector.
5. Turn on the integrator or monitor and begin to monitor the baseline. At 0.1 AUFS, an essentially noise-free and drift-free baseline should be observed.
6. Once the baseline is stable, start the AGP1 and press RUN.
7. Step 1 of program: Confirm that valve 5 is ON and valve 6 is OFF. The sample or the standard can be loaded via the autosampler. If the autosampler is not used, load the sample by drawing the sample through the sample inlet with a syringe. The sample pH should be 1–2. While the sample introduction step is in progress, the AGP1 is pumping 2.0 M ammonium acetate to regenerate/equilibrate the MetPac CC-1 column. Note that the next step (flushing the sample loop to the MetPac CC-1 and on-line buffering) occurs at 2.0 min. If the sample introduction takes more than 2.0 min, adjust the AGP1 program accordingly.
8. Step 2: Valve 5 is OFF and valve 6 is ON. The sample pump is pumping deionized water through the sample loop that was previously loaded with sample. The sample stream is now mixing with the 2.0 M ammonium acetate from the AGP1 and the buffered sample passes through the MetPac CC-1 column.
9. Step 3: Valve 5 is ON and valve 6 is OFF. The AGP1 is pumping 2.0 M ammonium acetate to remove the alkali and alkaline earth metals from the MetPac CC-1 column to waste.
10. Step 4: Valve 5 is ON and valve 6 is ON. The AGP1 is pumping 1.0 M nitric acid to the MetPac CC-1 column. The concentrated metal ions are eluted from the column and the 1.0 M acid stream is diluted on-line to approximately 0.37 M with deionized water from the sample pump and passes through the TMC-1 column. This step maximizes the removal of concentrated metal ions from the MetPac CC-1 and places them on the TMC-1 column in a tight band.
11. Step 5: Valve 5 is OFF and valve 6 is OFF. The AGP1 is pumping 1.5 M hydrochloric acid/75% ethanol to the TMC-1. The step performs the selective elimination of transition metals from the TMC-1 to waste. Note that the backpressure of the TMC-1 increases due to the organic eluent. The backpressure at 1.5 mL/min should not exceed 2500 psi (17 MPa).
12. Step 6: Valve 5 is OFF and valve 6 is OFF. The AGP1 is pumping 0.1 M ammonium nitrate to the TMC-1. This step is required to convert the TMC-1 from acid form to ammonium form.

Table 4 Chelation Concentration Operating Conditions

AGP1 Chelation Concentration System								AGP2 Chromatography System							
Columns: MetPac CC-1, TMC-1								Eluents: E1: Deionized water							
Eluents: E1: 1.5 M Hydrochloric acid, 75% ethanol								E2: 0.006 M Pyridine-2,6-dicarboxylic acid, 0.040 M lithium hydroxide, 0.19 M acetic acid							
E2: 2.0 M Ammonium acetate, pH 5.5 ±0.1								E3: 0.1M Oxalic acid, 0.19 M lithium hydroxide							
E3: 1.0 M Nitric acid								E4: 0.1 M Diglycolic acid, 0.19 M lithium hydroxide							
E4: 0.1 M Ammonium nitrate, pH 3.5 ±0.3								AGP2 program entered at AGP2 front panel.							
AGP1 program for >3 mL loop (AGP1) — downloaded by the ACI								(Reset/start control via ACI's relay TTL cable)							
t (min)	E1	E2	E3	E4	V5	V6	Flow (mL/min)	t (min)	E1	E2	E3	E4	V5	V6	Flow (mL/min)
0.0	0	100	0	0	1	0	3.0	0.0	0	100	0	0	0	0	1.0
2.5	0	100	0	0	0	1	2.0	0.1	0	100	0	0	1	0	1.0
5.0	0	100	0	0	1	0	3.0	12.0	0	100	0	0	1	0	1.0
7.0	0	100	0	0	1	0	1.2	12.1	100	0	0	0	1	0	1.0
7.1	0	0	100	0	1	1	1.2	17.0	100	0	0	0	1	0	1.0
12.0	0	0	100	0	1	1	1.2	17.1	20	0	80	0	1	0	1.0
12.1	100	0	0	0	1	0	4.0	20.0	20	0	80	0	1	0	1.0
12.5	100	0	0	0	0	0	1.5	20.1	20	0	75	5	1	0	1.0
16.0	100	0	0	0	0	0	1.5	30.0	50	0	25	25	1	0	1.0
16.1	0	0	0	100	0	0	1.5	40.0	50	0	25	25	1	0	1.0
18.0	0	0	0	100	0	0	2.0	40.4	0	100	0	0	0	0	1.0
19.0	0	0	0	100	0	0	3.0								
20.0*	0	0	0	100	0	0	1.0								
20.1	0	0	100	0	1	0	3.0								
22.0	0	0	100	0	1	0	3.0								
22.1	0	100	0	0	1	0	3.0								
24.0	0	100	0	0	1	0	0.0								
*Begin sample analysis (start/run AGP2)															
Timed Events Program															
t (min)	ACI SP ¹	ACI ASM ²	ACI AGP2 ³	ACI Begin Sampling	AGP Start	AGP Run	VDM Offset								
Init	off	off	off	off	on	off	off								
0.0	on	on	off	off	on	on	off								
13.0	off	on	off	off	on	on	off								
20.0	off	on	on	on	on	on	on								
¹ AC															
² relay 1															
³ relay 2															

13. Step 7: START/RUN the AGP2 pump program.

This step can also be initialized by the integrator or the ACI/AI-450. At time 0.1 min, the AGP2 valve 5 is ON. Valve E in the SCM is now switched to the INJECT position where the TMC-1 column is placed in-line with the CS5 column. The AGP1 is pumping 1.0 M nitric acid to the MetPac CC-1 for 2 min (3.0 mL/min), followed by 2.0 M ammonium acetate for 2.0 min (3.0 mL/min) before the end of the chelation concentration process.

At this point, the system is ready for calibration and sample analysis.

Analytical Chromatography

Column:	IonPac CS5
Eluents:	E1: Deionized water E2: 0.0060 M Pyridine-2,6-dicarboxylic acid, 0.090 M acetic acid, 0.040 M lithium hydroxide E3: 0.1 M Oxalic acid, 0.19 M lithium hydroxide E4: 0.1 M Diglycolic acid, 0.19 M lithium hydroxide
Eluent Flow Rate:	1.0 mL/min
Postcolumn	
Derivatization	
Reagent:	0.0004 M 4-(2-Pyridylazo)-resorcinol, 3.0 M ammonium hydroxide, 1.0 M acetic acid
Reagent Addition:	Membrane reactor or mixing tee
Reagent Flow Rate:	0.5 mL/min
Reactor:	Packed or knitted reaction coil
Detection:	VDM-2 or UDM, 520 or 530 nm

Sample Preparation

It is beyond the scope of this text to describe in detail the techniques of sample preparation in terms of sample collection, storage, and handling. Several points will be discussed that are applicable to sample preparation before analyzing samples by the method described in this Technical Note.

The geological materials must be carefully digested with proper acids to dissolve the lanthanide metal ions in the solution. If the sample contains a large quantity of

SiO₂, it must be digested with concentrated hydrofluoric acid. Most reagents are available free of lanthanide contamination. If you suspect that those reagents may contain any lanthanide contaminants, it is advisable to prepare and analyze a reagent blank with the samples.

The digested sample should be stored in clean polyethylene containers. Avoid sample dilution if possible. If the sample contains more than 1000 ppm of iron and aluminum and more than 800 ppm of transition metals in the final volume, a further dilution of the sample is strongly recommended. The sample should not contain more than 4% nitric or hydrochloric acid. Samples with more than 4% acid must be neutralized to pH 1–2 prior to the sample loading step.

APPENDIX A

Sample Loop

The 1-mL and 5-mL sample loops are available and supplied with the SCM.

Solutions and Reagents

Ultrapure 2.0 M ammonium acetate, pH 5.5

(1 L, P/N 033440; 6 L, P/N 033441)

Ultrapure 2.0 M nitric acid

(1 L, P/N 033442; 6 L, P/N 033443)

Ultrapure 0.1 M ammonium nitrate

(1 L, P/N 033445)

20% Ultrapure ammonium hydroxide

Ultrapure glacial acetic acid

The first two reagents used for chelation concentration are available from Dionex in a ready-to-use form. If you wish to prepare your own reagent solutions, please refer to the “Preparation of Solutions and Reagents” section below for information on ordering ultrapure acids and ammonium hydroxide.

PREPARATION OF SOLUTIONS AND REAGENTS

Three concentrated reagents are required for eluents in chelation concentration: Nitric acid, acetic acid and ammonium hydroxide. For ultratrace level determination (sub-ppb), the reagents must be ultrapure grade. For determination above 1 ppb, high quality trace-metal grade reagents can be used. Any metal impurity in these reagents will be concentrated with your sample, constituting a system blank.

2.0 M Ammonium Acetate pH 5.5 ± 0.1

Place 600 mL of deionized or high purity water into a clean 1-L glass eluent container. Tare the bottle. Add 121 g (115 mL) of ultrapure glacial acetic acid and mix thoroughly. In a fume hood, slowly add 120 g (130 mL) of 20% ultrapure ammonium hydroxide and mix thoroughly. Agitate the bottle to thoroughly mix the solution. Calibrate a pH meter to pH 7. Pour about 10 mL of the buffer into a small container (e.g., scintillation vial, 10-mL disposable beaker, etc.) and measure the pH. If the pH is below 5.4, add about 5 mL of ammonium hydroxide to the buffer solution. If the pH is above 5.6, add 5 g of acetic acid. Adjust the pH of the ammonium acetate to 5.5 ± 0.1 using acetic acid if the pH is less than 5.5. Once the pH is 5.5 ± 0.1, bring to a volume of 1.0 L with 18-MΩ deionized water.

2.0 M Nitric Acid

Place 200 mL of deionized or highly purity water into a clean 1-L glass eluent container. Add 179 g (126) of ultrapure nitric acid. Dilute to 1.0 L with 18-MΩ deionized water and mix thoroughly.

0.1 M Ammonium Nitrate, pH 3.4 ± 0.3

Place 200 mL of deionized water into a clean 1-L glass eluent container. Add 8.9 g (6.3 mL) of ultrapure nitric acid. Next, add 7.6 g (8.5 mL) of ultrapure 20% ammonium hydroxide. Add sufficient deionized water to give a final volume of 1 L and mix thoroughly. Calibrate the pH meter to pH 4.0. Take a 10-mL aliquot of the solution and measure the pH. Add either 0.1 M ammonium hydroxide or 0.10 M nitric acid in 3- to 5-mL increments to the bulk solution to adjust the pH. Continue taking aliquots and adjusting the pH to 3.4 ± 0.3.

The ultrapure reagents are manufactured by Seastar Chemical and Ultrex Reagents. Seastar reagents are available internationally through Fisher Scientific; in North America, Fisher Scientific sell these reagents under the OPTIMA® label. Ultrex reagents are available internationally through J. T. Baker.

0.0060 M Pyridine-2,6-dicarboxylic Acid (PDCA) Eluent

Prepare by dissolving the following reagents, in the order listed, in 18-MΩ deionized water:

0.040 M (1.7 g) Lithium hydroxide, monohydrate

0.0060 M (1.0 g) PDCA

0.090 M (5.42 g) Glacial acetic acid

Dilute to 1.0 L with 18-MΩ deionized water.

0.10 M Oxalic Acid, 0.19 M Lithium Hydroxide

Prepare by dissolving the following reagents in 18-MΩ deionized water:

0.10 M (13 g) Oxalic acid, dihydrate

0.19 M (8.0 g) Lithium hydroxide, monohydrate

Dilute to 1.0 L with 18-MΩ deionized water.

0.10 M Diglycolic Acid, 0.19 M Lithium Hydroxide

Prepare by dissolving the following reagents in 18-MΩ deionized water:

0.10 M (13 g) Diglycolic acid

0.19 M (8.0 g) Lithium hydroxide, monohydrate

Dilute to 1.0 L with 18-MΩ deionized water.

1.5 M Hydrochloric Acid/75% Ethanol

Prepare by slowly adding 120 mL (150 g) of concentrated HCl (trace metal grade) to 750 mL of 95.5% ethanol (Baker Analyzed, J.T. Baker). Dilute to 1.0 L with 18-MΩ deionized water.

PAR Postcolumn Reagent

Place 400 mL of 18-MΩ deionized water in a 1-L container. Add 200 mL of trace metal grade 30% ammonium hydroxide solution. Add and dissolve 0.10 g of 4-(2-pyridylazo)resorcinol (PAR). Add 57 mL of trace metal grade glacial acetic acid. Dilute to 1.0 L with 18-MΩ deionized water.



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