

Determination of Aluminum in Complex Matrices Using Chelation Ion Chromatography

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INTRODUCTION

The determination of trace metals in complex matrices has traditionally been a difficult analytical challenge. High levels of interfering species, combined with non-specificity of concentration and detection schemes, have led to severe compromises in the detection limits for many elements. The technique presented below, chelation ion chromatography, has been applied successfully to a number of transition and post-transition metals.¹ This application note describes the extension of that technique for the analytical determination of aluminum in complex matrices.

Chelation ion chromatography is a technique that combines selective chelation concentration with analytical separation and selective detection. Chelation ion chromatography allows aluminum to be preconcentrated from matrices high in salts, acids, or bases. Following selective concentration, aluminum is eluted to a conventional cation exchange column for separation from other transition metals. Selective detection is accomplished using post-column derivitization with Tiron and subsequent UV detection at 310 nm.

APPLICATION AREAS

Waste water
Tissue/biological samples
Soils
Ground/surface water
Seawater/brines
High purity acids, bases, and salts

RECOMMENDED EQUIPMENT

Dionex Gradient Pump Module (GPM)
Sample Concentration Module (SCM)
Reagent Delivery Module (RDM)
Variable Wavelength Detector Module (VDM-II)

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 (Dionex P/N 033440)
Tiron (4,5-Dihydroxy-1,3 benzene disulfonic acid, disodium salt monohydrate)
Aluminum 1000-ppm atomic absorption standard

CONDITIONS

Concentrator:	MetPac CC-1 (P/N 042156-2 pack)
Trap Column:	MetPac CC-1
Analytical Column:	IonPac® CS5 (P/N 37028)
Eluent:	0.75 M HCl
Flow Rate:	1.0 mL/min

¹ For a detailed description of chelation ion chromatography of transition metals analysis, refer to Dionex Technical Note #25.

CONDITIONS (CONT'D)

Chelation

Concentration Reagent:	2.0 M ammonium acetate (ultrapure)
Postcolumn Reagent:	0.3 mM Tiron in 3 M ammonium acetate
Postcolumn Flow Rate:	0.5 mL/min
Postcolumn Mixing:	Membrane Reactor (P/N 035354)
Reaction Coil:	Packed (P/N 036036) or Knitted (P/N 039349)
Backpressure Regulator:	100 psi (P/N 039760)

REAGENT PREPARATION

0.75 M HCl

Add 62.0 mL (73.8g) concentrated HCl to 500 mL deionized water. Mix and dilute to 1.0 L. Degas before use.

Tiron Postcolumn Reagent

Prepare the postcolumn reagent in the RDM reagent container to minimize contamination. Work in a fume hood. To prepare 1.0 L of Tiron reagent, add 206-mL (186g) trace-metal grade NH_4OH to 200-mL deionized water. Mix and slowly add 172-mL (180-g) trace-metal grade acetic acid. **WARNING: This solution will become very HOT.** Add 98.0-mg Tiron to the solution and mix to dissolve. Bring the solution to a final volume of 1.0 L with deionized water and degas with ultrasonic agitation. Allow to cool before using.

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 the 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 standards and blanks as is added to the sample. This will result in a consistent background or "blank".

When matrices with high concentrations of salts (particularly with high phosphate concentration) and/or complexing agents are to be analyzed, an aluminum "spike" recovery analysis is advisable. Matrices that show poor recovery of "spiked" aluminum should be diluted and reanalyzed.

As with all trace-level work, great care must be taken to prevent contamination. Aluminum is common in most laboratory environments. Avoid pipettes and other volumetric glassware. Reagent and sample preparation using gravimetric techniques will minimize contamination.

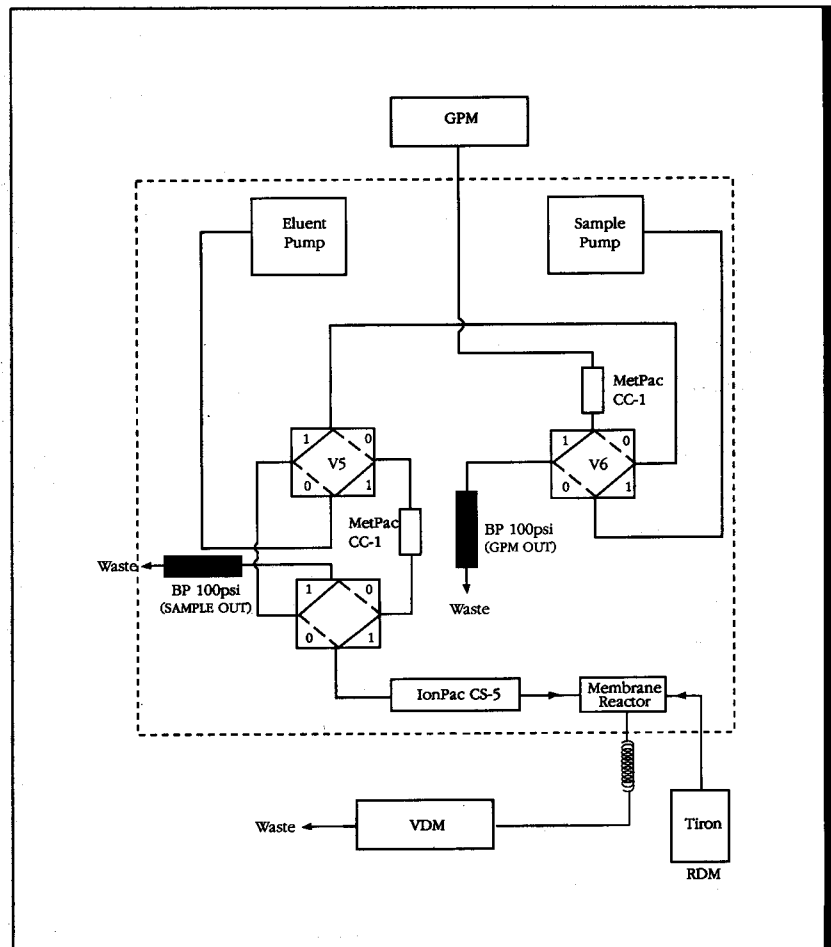


FIGURE 1. ALUMINUM BY CHELATION ION CHROMATOGRAPHY VALVE DIAGRAM

SYSTEM PREPARATION AND SET-UP

The valve diagram (Fig. 1) shows the components of the chelation ion chromatography system. Three pumps are required to perform chelation ion chromatography. A gradient pump (GPM) is used to manage the chelation concentration eluents and perform timing and valve switching functions. A pulse-dampened Dionex QIC Pump (DQP) is used to pump the analytical eluent (0.75 M HCl), and a second DQP is used for sample loading. Two valves (four-way, double-stack) are required for running the chelation ion chromatography system. The Sample Concentration Module (SCM) consists of two DQPs, a pulse damper, and valves required for chelation ion chromatography. A “gradient” chelation ion chromatography system consisting of two GPMs, a DQP, and two valves may also be used to perform this analysis.

The SCM is configured in the factory for use as an IC/ICP interface. The SCM manual contains a procedure for converting the SCM for use as a chelation ion chromatography system. The following procedure is similar to that described in the SCM manual, but with some plumbing changes unique to the aluminum chelation ion chromatography application.

1. To begin the conversion to a chelation IC system, remove all of the liquid lines from the valves in the SCM. Keep these lines in a safe place, as they will be used to re-plumb the instrument. Do not alter the pneumatic connections in the SCM.
2. Locate the DQP with a pulse damper in the left rear corner of the SCM. This DQP will be used to pump 0.75 M HCl as the analytical eluent and is henceforth referred to as the “eluent pump”. The second DQP located in the right rear of the SCM is the sample loading pump. Locate these pumps in the SCM and in the plumbing diagram (Fig. 1).
3. Four valves are located across the front of the SCM. The first three valves from the left are controlled by the V5 (or load/inject) actuator on the GPM (for information on air connections between the GPM and SCM, see the SCM manual). The valve on the far right is designated as valve 6 and is controlled by the V6 actuator on the GPM. Only the valves on the far left and far right of the SCM will be used for this application. The two middle valves, although controlled by the V5 actuator, will not be used in this application. The far left valve is thus designated valve 5, and the far right valve is designated valve 6.
4. Using Figure 1 as a guide, replumb the SCM with the tubing removed in step 1. Only two lines should enter the SCM through the front panel, the GPM IN line and the line out to the VDM. All other connections should be made through the labeled bulkheads on the rear panel.
5. Connect a line from the GPM through the front panel of the SCM. This should run to a MetPac CC-1 in the SCM and then to the proper port of valve 6 as shown in Figure 1. Note that there are two MetPac CC-1 columns used in this method. The MetPac CC-1 connected to the line from the GPM to the SCM serves as a trap column. Its function is to trap residual metals from the ultrapure ammonium acetate. The trap column should be cleaned after approximately 20 L of 2.0 M ammonium acetate is used. (To clean the MetPac CC-1 trap column, elute with 2.0 M HNO₃ at 1.0 mL/min for 10 min. Regenerate the trap column with 20 mL of 2.0 M ammonium acetate).
6. Connect a line from the reaction coil through the front panel of the SCM and into the VDM. Connect a line from the VDM to waste. Do NOT attach any back-pressure device to this line.
7. Two waste lines must be connected to the bulkheads on the rear panel of the SCM. One waste line from each of the two valves (see Fig. 1) connects to the waste bulkheads. A 100-psi back-pressure regulator (P/N 039760) should be attached to each of these two waste lines. Connect the waste line from valve 6 (far right) to the “GPM OUT” bulkhead on the rear panel. The other waste line (from valve 5) is connected to the bulkhead labeled “SAMPLE OUT”. The back-pressure regulators may be installed either inside the SCM before the bulkhead, or at the terminus of the waste line.
8. The feed line to the eluent pump should be connected to the bulkhead labeled “WATER IN”. Make this connection with 1/8-in. ID Teflon® tubing. A line from the eluent bottle is connected to the SCM through the same bulkhead. A pressure of 5 to 7 psi must be maintained on the eluent bottle.

- The feed line to the sample pump should be connected with 0.037-in. ID tubing (pink) to the "SAMPLE IN" bulkhead on the rear panel of the SCM. The sampling line should also be 0.037-in. ID tubing and run from the "SAMPLE IN" bulkhead to the sample container.

PROCEDURE: RUNNING THE CHELATION IC SYSTEM

The chelation ion chromatography system for aluminum is a semi-automated system for concentrating and analyzing aluminum in a variety of matrices. The samples and standards must be buffered before concentration. See the STANDARD AND SAMPLE PREPARATION section of this application note for information on sample preparation. Running the chelation ion chromatography system consists of the following steps:

- Start the eluent pump (0.75 M HCl) and confirm that the flow rate is 1.0 mL/min out of the waste line from the VDM. Turn on the pressure to the post-column reagent delivery system, and increase the pressure to approximately 50 psi. Check the flow rate from waste line 3 and adjust the pressure on the RDM until the flow is a total of 1.5 mL/min—1.0 mL/min from the HCl eluent and 0.5 mL/min from the Tiron post-column reagent. It is advisable to confirm the flow rate of 1.5 mL/min at the beginning of each day and make any necessary adjustments in the RDM pressure. *Note:* Always have the eluent flowing before you turn on the post-column system pressure. Likewise, at shut down, turn off the post-column pressure before turning off the eluent pump. Allow the eluent to purge all of the post-column reagent from the lines before shut down.
- Allow the system to equilibrate for at least 20 min. At the beginning of this equilibration, actuate both valves two or three times and then leave them in the position specified in the first step of the GPM program (see step 6 below).
- Enter the GPM program listed below, and start the GPM pump. The GPM program is designed to pump deionized water to waste at a flow rate of 0.5 mL/min while the sample is being loaded. This is considered the standby position for the system.
- Prime the sample loading pump with sample or standard. With the valves in the V5=1(or inject), V6=0 position, the sample pump will purge the lines of the SCM, but not

concentrate the sample. Check the flow rate at the "GPM OUT" waste line, and adjust the flow rate of the sample loading pump to approximately 3–4 mL/min. At GPM time=2.2 min, the valves will switch to the V5=0, V6=1 position, and the sample will concentrate on the CC-1 column. The GPM program below will concentrate sample for 3 min, but this time may be increased or decreased depending on the needs of analysis. Following sample loading, GPM program time=5.3 min, the sample pump may be turned off.

- The sample loading pump should be turned on at the beginning of the analysis. With the valves in the standby position, no sample will concentrate, but the lines will be flushed with sample. Regardless of how long the sample pump is left on, sample will only concentrate when the valves are in the V5=0(load), V6=1 position.
- The "injection" of the concentrated aluminum does not occur until 7.4 min into the analysis. For ease of operation, the data collection system can be started at 0.0 min, although meaningful data does not begin until 7.4 min. Alternatively, if an automated data collection system is used (e.g., the Dionex AI-450), data collection can begin at GPM time=7.4 min. The chromatogram shown in Figure 2 was run with data collection beginning at time=7.4 min. Below is the GPM program:

Eluent 1 = H₂O (deionized, 18 MΩ)

Eluent 2 = 2.0 M ammonium acetate (ultrapure)

GPM Program: Refer to valve diagram (Fig. 1)

Time	Flow	%1	%2	V5	V6	Comments
0.0	0.5	100	0	1	0	standby
0.1	3.0	0	100	0	0	CC-1 to ammonium form
2.1	3.0	0	100	0	0	end conversion
2.2	0.5	100	0	0	1	load sample
5.2	0.5	100	0	0	1	end loading
5.3	3.0	0	100	0	0	wash CC-1
7.3	3.0	0	100	0	0	end CC-1 wash
7.4	0.1	100	0	1	0	INJECT

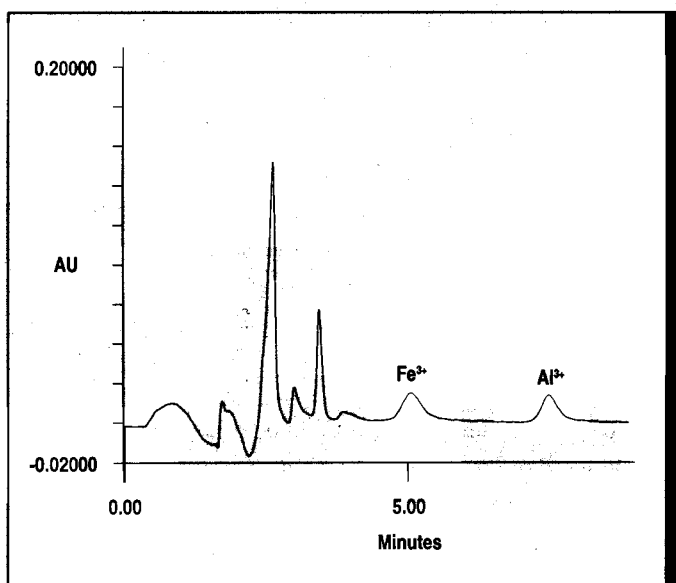


FIGURE 2. ANALYSIS OF RIVER WATER SLRS-1 (CANADIAN STANDARD REFERENCE MATERIAL) 12 ML CONCENTRATED

DISCUSSION

The method described in this application note is intended for the determination of aluminum 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 aluminum by ion chromatography or atomic spectroscopy. By using selective ion exchange materials such as chelating resins, aluminum can be selectively preconcentrated while alkali and alkaline-earth metals are eluted to waste. This form of sample pretreatment is called chelation concentration. Unlike conventional ion exchange concentration methods, which are typically not selective for ions of the same valency, chelation concentration is a selective concentration method.

Selective preconcentration of aluminum takes place on an iminodiacetate chelating resin (MetPac CC-1). At pH 5.5, this resin has high selectivity for aluminum relative to alkali and alkaline-earth metals. While alkaline-earth metals are concentrated, they are subsequently eluted to waste using 2.0 M ammonium acetate. Following concentration of aluminum and selective elution of alkaline-earth metals, the MetPac CC-1 chelating column is switched in line with the

analytical eluent (0.75 M HCl). At the very low pH of the analytical eluent, aluminum is eluted from the MetPac CC-1 and separated from other transition metals on an IonPac CS5 column.

Aluminum is detected using selective post-column chemistry. Reaction of Tiron with aluminum forms a UV absorbing complex that may be detected at 310 nm. The reaction of aluminum with Tiron proceeds only at moderate pH. This requires the use of a buffer in the post-column system to adjust the pH of the eluent. The acid eluent mixes post-column with 3.0 M ammonium acetate to form a 0.50 M acetate buffer. (*Note:* The eluent mixes with post-column reagent in a 2:1 ratio.) The production of the 0.50 M acetate buffer ensures that the pH of the post-column system will remain at approximately 4.8, which is within the optimum range for the reaction of aluminum with Tiron.

PERFORMANCE CHARACTERISTICS

The detection limit of this method is 1 to 5 ppb of aluminum for a 10 to 20-ml sample. In general, the aluminum contamination level in the chelation concentration reagent (2.0 M ammonium acetate) will determine the detection limit of the method. A standard reference material (river water SLRS-1) with 23.5-ppb aluminum was analyzed using this method and accurately determined to within 1% of the known value (see Fig. 2).

The method described above will allow concentration of aluminum from a variety of complex sample matrices. In some cases, however, a small dilution may be required for the analysis of a very complex matrix. In the case of seawater, a 3x dilution resulted in a 98% recovery of aluminum.