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# Elimination of Iron and Aluminum Interferences in Sample Matrices by Ion Chromatography/Inductively Coupled Argon Plasma Emission Spectroscopy (IC/ICAP)

## **INTRODUCTION**

The naturally occurring high concentrations of certain metals such as iron, aluminum, alkali metals, and alkaline earth elements in sample matrices usually interfere with the determination of the trace transition metals in these samples. Common methods for minimizing sample matrix interferences include spectral background corrections, standard additions, sample dilution, and matrix matching. These methods help minimize matrix interferences; however, these methods often result in degraded detection limits and accuracy.

The chelation concentration technique offers the analyst a solution to the detection limit and interference problems commonly experienced when analyzing complex matrices. Selective ion exchange materials such as chelating resins can concentrate transition metals while eliminating alkali and alkaline earth elements. The selective elimination process has been extended to the elements iron and aluminum. By using a matrix selective complexing agent, 95% to 99% of the iron and aluminum is removed, while the other transition metals are quantitatively retained.

In this application note, the determination of trace transition metals in samples that contain high levels of iron and aluminum will be discussed.

## **EQUIPMENT**

Dionex Gradient Pump Module (GPM-2) or Advanced Gradient Pump (AGP)

Dionex Sample Concentration Module (SCM)

Thermo Jarrell Ash Simultaneous ICAP Spectrometer

IBM®-compatible personal computer with TJA ThermoSpec software

MetPac™ CC-1 Column (P/N 42156)

## **SOLUTIONS AND REAGENTS**

Ultrapure 2.0 M ammonium acetate, pH 5.5  
(1 L, P/N 33440; 6 L, P/N 33441)

Ultrapure 2.0 M nitric acid  
(1 L, P/N 33442; 6 L, P/N 33443)

0.020 M Pyrophosphoric acid / 2.0 M ammonium acetate

Ultrapure 20% ammonium hydroxide

Ultrapure glacial acetic acid

Chelex-100™, 50-100 mesh (BioRad Laboratories)

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 "Preparation of Solutions and Reagents". The other ultrapure reagents are manufactured by Seastar Chemical and Ultrex Reagents. Seastar reagents are available internationally through Fisher Scientific; in North America, Fisher Scientific sells these reagents under the OPTIMA® label. Ultrex reagents are available internationally through J.T. Baker. Chelex-100 is used for eluent purification.

## CONDITIONS

The AGP program for chelation concentration is shown in Table 1.

**Table 1 AGP Program for Chelation Concentration**

t	%E1	%E2	%E3	%E4	V5	V6	Flow Rate (mL/min)
0.0	100	0	0	0	1	0	2.0
1.5	100	0	0	0	1	0	2.0
1.6	0	0	0	100	1	0	2.0
2.0	0	0	0	100	0	1	2.0
6.0	0	0	0	100	0	1	2.0
6.1	100	0	0	0	0	0	4.0
7.2	100	0	0	0	0	0	4.0
7.3	0	75	25	0	0	0	4.0
7.7	0	75	25	0	0	0	2.0
7.9	0	75	25	0	1	1	2.0
9.3	0	75	25	0	1	1	2.0
9.4	100	0	0	0	0	0	0.0

E1: 2 M Ammonium acetate, pH 5.5

E2: 2 M Nitric acid

E3: Deionized water

E4: 20 mM Pyrophosphate/2.0 M ammonium acetate

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  $5.5 \pm 0.1$  using acetic acid if the pH is greater than 5.5, or ammonium hydroxide if the pH is less than 5.5. Once the pH is  $5.5 \pm 0.1$ , bring to a volume of 1 L.

### 2.0 M Nitric Acid

Place 200 mL of deionized or high purity water in a clean 1-L glass eluent container. Add 179 g (126 mL) of ultrapure nitric acid. Add deionized water to bring the final volume to 1 L and mix thoroughly.

### 0.10 M Nitric Acid (Carrier Solution)

Place about 1000 mL of deionized water into the 4-L plastic eluent container. Add 89 g (63 mL) of concentrated nitric acid and an additional 2740 mL of deionized water.

### Preparation of Chelex-100 for Eluent Purification

Suspend approximately 30 g of Chelex-100 (50–100 mesh) resin in 300 mL of 2.0 M nitric acid (trace–metal grade) in a 1-L polyethylene bottle. Using a stir bar, stir the solution for approximately 10 min. Decant the nitric acid and the fine resin particles. Repeat the acid cleaning step twice before rinsing the resin with 500 mL of deionized water. Store the cleaned resin in 200 mL of 2.0 M ammonium acetate, pH 5.5, until use.

## 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 determinations (sub-ppb), the reagents must be ultrapure grade. For determinations above 5 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 $5.5 \pm 0.1$

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

### 20 mM Pyrophosphoric Acid/2.0 M Ammonium Acetate, pH 5.5

Dissolve 3.7 g of pyrophosphoric acid (97%, Aldrich Chemical Co., Inc.) in 1 L of 2.0 M ammonium acetate, pH 5.5. Since pyrophosphoric acid is not available in ultrapure grade reagent, the trace transition metal contaminants in this solution can be removed by using Chelex-100 resin. Place the cleaned Chelex-100 resin into the pyrophosphoric acid / ammonium acetate solution and stir using a stir bar. After stirring the solution for 1 hr, decant the pyrophosphoric acid / ammonium acetate solution into the glass eluent container.

### 20 mM Pyrophosphoric Acid/2.0 M Ammonium Acetate, pH 8.5

Dissolve 3.7 g of pyrophosphoric acid in 200 mL of 2.0 M ammonium acetate (pH 5.5). Add 500 mL of ammonium acetate to this solution. Then, add 60 g (65 mL) of ultrapure

20% ammonium hydroxide. 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), and measure the pH. If the pH is below 8.5, add about 5 mL of ammonium hydroxide to the buffer solution. If the pH is above 8.5, add 5 g of acetic acid. Adjust the pH of the ammonium acetate to  $8.5 \pm 0.1$  using ammonium hydroxide. Once the pH is  $8.5 \pm 0.1$ , bring to a volume of 1 L. Place the cleaned Chelex-100 resin into the pyrophosphoric acid / ammonium acetate solution and stir using a stir bar. After stirring the solution for 1 hr, decant the pyrophosphoric acid / ammonium acetate solution into the glass eluent container.

### STANDARD PREPARATION

Since the analytes of interest are concentrated, the concentration of the "high" standard should not exceed 1 ppm. Typically, a working "high" standard in the range of 0.005 to 0.1 ppm is used for ultratrace analysis work. It is convenient to prepare a 10X concentrate or stock solution of the standard and prepare the high standard by dilution of the stock solution.

For complete details in system preparation and setup, operation, and automation, refer to Dionex Technical Note 28.

### SAMPLE PREPARATION

To avoid hydrolysis of transition metals during long storage, it is recommended that the pH of the sample be maintained at 1–2. If the sample has been acid digested, it must be neutralized with ammonium hydroxide to pH 1–2 prior to analysis. Avoid using pipets and glassware, which usually contaminate the samples.

If the sample contains more than 400-ppm iron or more than 600-ppm aluminum in the final dilution, the sample should be further diluted. Note that the mass ratio of iron to aluminum and transition metals should not exceed 20,000 to 1, otherwise background correction must be incorporated in the analysis. For example, if the sample contains 2% iron and 1 ppm copper, the sample must be diluted at least 50-fold to give less than 400-ppm iron and 2.5-ppb copper.

### DISCUSSION OF THE METHOD

The method described in this application note was developed for determining trace transition metals in complex matrices containing high levels of alkali metals, alkaline earth

elements, iron, and aluminum. The removal of iron and aluminum is based upon the electroselectivity difference between iron and aluminum with pyrophosphate eluate and iron and aluminum with iminodiacetate functionality on the stationary phase (MetPac CC-1). The other transition metals are not eluted by pyrophosphate and are quantitatively retained by the MetPac CC-1 chelating resin. The alkali and alkaline earth metals in the MetPac CC-1 column are removed with ammonium acetate eluent.

The selective elimination of iron and aluminum using chelation sample pretreatment is possible only with on-line buffering. Off-line buffering of the samples that contain the high levels of iron and aluminum (>10 ppm) would result in precipitation of iron and aluminum. The Sample Concentration Module (SCM) is equipped with a high-pressure valve system that allows the acidified sample to be neutralized on-line with a known quantity of buffer solution. The neutralization by on-line buffering is instantaneous and the sample preconcentration processes occur in a few seconds. As a result, hydrolysis of aquated metal ions and adsorption of metal-hydroxide complexes on the surface of inert polymeric tubing is prevented.

The chelation concentration with selective elimination of iron and aluminum can be described as shown in Figure 1. A complexing agent is used which will selectively bind iron and aluminum, thus preventing uptake by the chelating resin

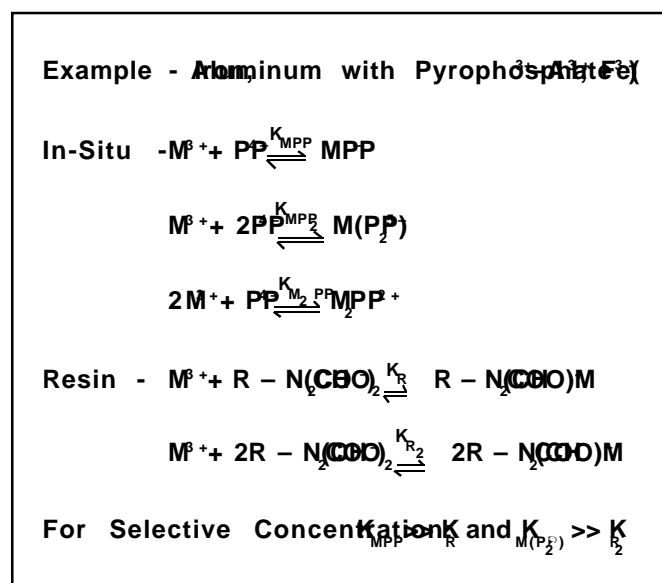


Figure 1 Selective concentration using the MetPac CC-1 with complexing agents

**Table 2 Metal Recovery from High Calcium–Iron–Aluminum Matrix Using MetPac CC-1 with Pyrophosphate for Complexation**

Element	Amount Added (ng/g)	Found (pH 5.5) ng/g (%RSD)*	Found (pH 8.5) ng/g (%RSD)*
Ca	50,000	15	15
Al	50,000	5	5
Fe	100,000	10	10
Pb	100	98.4 (3.08%)	99.3 (0.93%)
Cd	100	98.1 (1.20%)	99.5 (0.61%)
Cu	100	104 (0.80%)	105 (0.31%)
Co	100	100 (0.96%)	102 (0.25%)
Mn	100	70.2 (2.46%)	105 (0.49%)
Ni	100	98.3 (1.09%)	102 (1.07%)
Zn	100	98.2 (1.69%)	106 (1.17%)

\* n = 4

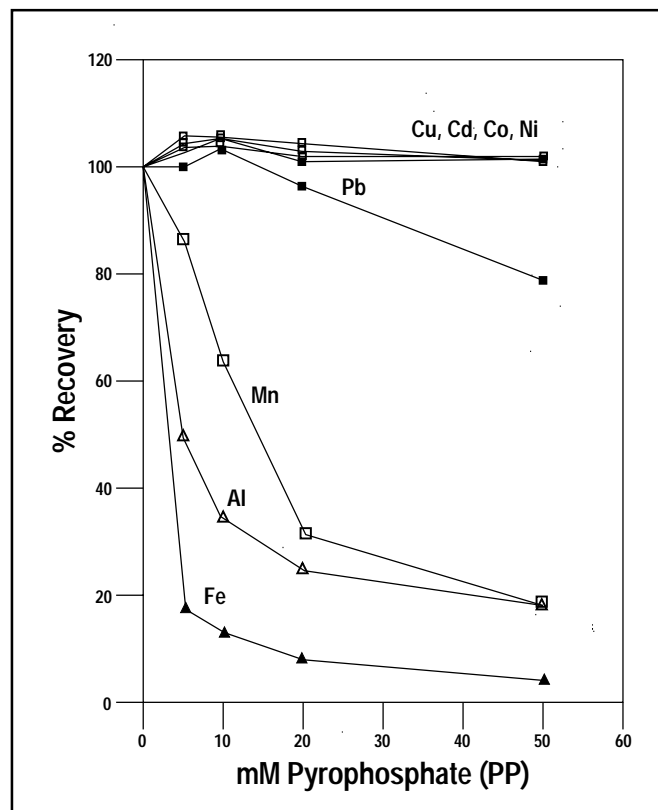


Figure 2 Recoveries of metals using the MetPac at various concentrations of pyrophosphate

during concentration. This approach not only prevents the precipitation of iron and aluminum at high concentrations, it also allows an effective removal of iron and aluminum from the MetPac CC-1 column. The relatively stable metal-pyrophosphate complexes formed during the on-line neutralization step (in-situ) do not interact with iminodiacetate and are not retained in the column. Figure 1 shows the scheme of the selective concentration using MetPac CC-1 with complexing agents.

The high levels of iron, aluminum, and manganese, which are normally found in rock, sediment, and soil samples, can be separated from trace transition metals by using 20 mM pyrophosphate, pH 5.5. Other metals such as lead, copper, cadmium, cobalt, nickel, and zinc are retained by the MetPac CC-1 chelating resin. Figure 2 and Table 2 show the percent recoveries of these metals using the MetPac CC-1 at various concentrations of pyrophosphate. If manganese is one of the analytes of interest, it can be determined by using 20 mM pyrophosphate at pH 8.5, as shown in Table 2.

MetPac is a trademark of Dionex Corporation. Optima is a registered trademark of Fisher Scientific. Chelex-100 is a trademark of BioRad Laboratories. IBM is a registered trademark of International Business Machines Corporation.

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