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APPLICATION NOTE 75

Determination of trace transition metals in reagent grade acids, bases, salts, and organic solvents using chelation ion chromatography

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Keywords
Ion chromatography, IC, chelation, sample preconcentration, semiconductor, ICS-5000+, iron, copper, nickel, zinc, cobalt, cadmium, manganese

Introduction

The SEMI (Semiconductor Equipment and Materials International) specifications for maximum permitted levels of transition metals in concentrated acids used in fabrication of semiconductor devices is in the range of 0.1 to 1.0 part per billion (ppb). Labor-intensive manual preconcentration methods are usually required prior to analytical measurements. Typical preconcentration procedures involve evaporation of a specific volume of sample for 2.5 to 4 hours on a hot plate before transfer to a volumetric flask and analysis. Also, a class-100 clean room environment is normally required during sample pretreatment. The chelation ion chromatographic technique (chelation IC) provides the sample preconcentration step and direct determination of trace transition metals by ion chromatographic separation and postcolumn derivatization prior to detection. Preconcentration is performed in minutes rather than hours. Sampling, preconcentration, and analyte transfer to the IC system is on-line and automated. The sample is never exposed to the ambient atmosphere

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during preconcentration. Typical recoveries are 95 to 100% in the 2 to 5 ppb concentration range in concentrated acids. Detection limits are in the 0.5 to 5 ppb range for most metals using 5 mL of sample. Methodology for the determination of transition metals in concentrated acids using chelation ion chromatography is applicable to semiconductor grade bases and solvents. Currently, the chelation IC is applicable to iron, copper, nickel, zinc, cobalt, cadmium, and manganese. Typical detection limits for semiconductor solvents and bases using chelation IC are one to two orders of magnitude better than by using direct flame atomic absorption spectroscopy and plasma emission spectroscopy.

This application note describes a method for the determination of trace transition metals in trace metal grade reagents by chelation IC. The detection limits for most elements present in concentrated trace-metal grade reagents are in the sub part-per-billion range.

Experimental

Instrument requirements*

Two chelation IC system configurations can be used for this application. Both systems include a Thermo Scientific™ Dionex™ gradient pump, Sample Concentration Module (SCM), Reagent Delivery Module (RDM), and Variable Wavelength Detector Module (VDM-2). System 1 is configured for manual operation, while system 2 is for automated operation. Refer to Thermo Scientific™ Application Update 168 for complete details on configuring a chelation chromatography system.

* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000⁺ HPIC™ system.

Chelation IC system 1

- Thermo Scientific™ Dionex™ Gradient Pump Module or Advanced Gradient Pump
- Thermo Scientific™ Dionex™ Sample Concentration Module
- Thermo Scientific™ Dionex™ Reagent Delivery Module
- Thermo Scientific™ Dionex™ Variable Wavelength Detector Module
- Thermo Scientific™ Dionex™ Eluent Degas Module
- Thermo Scientific™ Dionex™ IonPac™ Membrane Reactor (optional)
- Thermo Scientific™ Dionex™ Knitted Reaction Coil (P/N 039349)
- Thermo Scientific™ Dionex™ MetPac™ CC-1 Column (P/N 042156)
- Thermo Scientific™ Dionex™ TMC-1 Column (P/N 049000)
- Thermo Scientific™ Dionex™ IonPac™ CG5 (P/N 37029)

Chelation IC system 2

- Dionex Gradient Pump Module or Advanced Gradient Pump
- Dionex Sample Concentration Module
- Dionex Reagent Delivery Module
- Dionex Variable Wavelength Detector Module
- Dionex Eluent Degas Module
- Dionex Valve, 4-Way Slider Double Stack (3), 2000 psi (P/N 35914)
- Dionex IonPac Membrane Reactor (optional)
- Dionex Knitted Reaction Coil (P/N 039349)
- Dionex MetPac CC-1 Column (P/N 042156)
- Dionex TMC-1 Column (P/N 049000)
- Dionex IonPac CG2 (2, P/N 035370)
- Dionex IonPac CG5 (P/N 37029)

Solutions and reagents

- Thermo Scientific™ Dionex™ ultrapure 2.0 M ammonium acetate, pH 5.4 ± 0.1 (1 L, P/N 033440; 6 L, P/N 033441)
- Thermo Scientific™ Dionex™ ultrapure 2.0 M nitric acid (1 L, P/N 033442; 6 L, P/N 033443)
- Thermo Scientific™ Dionex™ ultrapure 0.1 M ammonium nitrate, pH 3.5 ± 0.3 (1L, P/N 033444) 20%
- Ultrapure ammonium hydroxide, JT Baker (Fisher Scientific P/N 14-650-228, 490 mL)
- Ultrapure glacial acetic acid, JT Baker (Fisher Scientific P/N 14-650-230, 500 mL)
- 0.006 M pyridine-2,6-dicarboxylic acid (PDCA)
- 0.040 M sodium hydroxide
- 0.090 M acetic acid
- 0.5 mM 4-(2-pyridylazo) resorcinol (PAR)
- 1.0 M 2-dimethylaminoethanol
- 0.5 M ammonium hydroxide
- 0.3 M sodium bicarbonate

The first three reagents used for chelation concentration are available from Thermo Fisher Scientific in a ready-to-use form. If you wish to prepare your own reagent solutions, please refer to “Preparation of Solutions and Reagents”.

Conditions

The conditions for chelation concentration and analytical chromatography are presented in Table 1.

Table 1A. Chelation concentration operation conditions.

Chelation concentration–transition metals	
Columns:	Dionex MetPac CC-1, Dionex TMC-1
Eluents:	E1: H_20 E2: 2.0 M ammonium acetate, pH 5.4 ± 0.1 E3: 2.0 M nitric acid E4: 0.10 M ammonium nitrate, pH 3.5 ± 0.3

Gradient program, system 1

t (min)	*%E1*	*%E2*	*%E3*	*E4*	*V5*	*V6*	*Flow (mL/min)*
0.0	0	100	0	0	1	0	3.0
0.1	0	100	0	0	1	1	3.0
2.5	0	100	0	0	1	1	3.0
2.6	72	0	28	0	0	1	3.0
5.0	72	0	28	0	0	1	1.0
5.1	0	0	0	100	0	0	3.0
6.6	0	0	0	100	1	0	1.0
6.7	0	0	100	0	1	1	3.0
7.7	0	0	100	0	1	1	3.0
7.8	0	100	0	0	1	1	3.0
9.3	0	100	0	0	1	1	3.0
9.4	100	0	0	0	1	1	0.0

Gradient program, system 2

t (min)	*%E1*	*%E2*	*%E3*	*E4*	*V5*	*V6*	*Flow (mL/min)*
0.0	0	100	0	0	1	0	3.0
2.0	0	100	0	0	0	1	2.0
5.0	0	100	0	0	1	0	3.0
7.0	0	100	0	0	1	0	1.2
7.1	50	0	50	0	1	1	1.2
12.0	50	0	50	0	1	1	1.2
12.1	0	0	0	100	1	1	2.0
13.0	0	0	0	100	0	0	3.0
15.0	0	0	0	100	0	0	3.0
15.1*	0	0	100	0	1	0	4.0
16.0	0	0	100	0	1	0	4.0
17.0	0	0	100	0	1	0	4.0
18.0	0	100	0	0	1	0	0.0

*Begin sample analysis

Table 1B. Analytical chromatography conditions.

Analytical chromatography–transition metals	
Column:	Dionex IonPac CS5
Eluent:	0.0060 M pyridine-2,6-dicarboxylic acid, 0.090 M acetic acid, 0.040 M sodium hydroxide or 0.050 M oxalic acid, 0.095 M lithium hydroxide
Eluent Flow Rate: 1.0 mL/min	
Postcolumn derivatization	
Reagent:	4×10^{-4} M 4-(2-pyridylazo) resorcinol 1.0 M 2-dimethylaminoethanol 0.50 M ammonium hydroxide 0.30 M sodium bicarbonate
Reagent Addition:	Membrane reactor or mixing tee
Reagent Flow Rate:	0.5 mL/min
Reactor:	Packed or knitted reaction coil
Detection	
Detector:	Visible absorbance, VDM or UDM
Wavelength:	520 or 530 nm
Time Constant:	1 s

Preparations 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 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 5.4 ± 0.1 (eluent 2)

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 5.5, add 5 g of acetic acid. Adjust the pH of the ammonium acetate to 5.4 ± 0.1 using acetic acid if the pH is greater than 5.5, or ammonium hydroxide if the pH is less than 5.3. Once the pH is 5.5 ± 0.1, bring to a volume of 1 L.

2.0 M nitric acid (eluent 3)

Place 200 mL of deionized or high purity water into 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 ammonium nitrate, pH 3.5 ± 0.3 (eluent 4)

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 water deionized water to give a final volume of 1 L and mix thoroughly. Calibrate pH meter to pH 4.0. Take a 10 mL aliquot of the solution and measure the pH. Add either 0.10 M ammonium hydroxide or 0.10 M nitric acid in 3 to 5 mL aliquots to the bulk solution to adjust the pH. Continue taking aliquots and adjusting the pH to 3.4 ± 0.3.

PDCA stock solution

- 0.060 M PDCA
- 0.40 M Sodium Hydroxide

Place 200 mL of deionized water into a clean 1 L polyethylene bottle. Add 32 g (21 mL) of 50% sodium hydroxide and stir with a stir bar. While stirring, add 10.0 g of pyridine-2,6-dicarboxylic acid. Continue to stir for about 10 min or until all the PDCA has dissolved. Dilute to 1 L and stir thoroughly. Label the solution “0.060 M PDCA, 0.40 M NaOH”.

Acetic scid stock solution

- 0.90 M Acetic Acid

Place 200 mL of deionized water into a clean 1 L polyethylene bottle. Add 54 g (52 mL) of trace metal grade acetic acid and dilute to 1 L. Label the solution “0.90 M Acetic Acid”.

PDCA eluent

- 0.0060 M PDCA
- 0.040 M Sodium Hydroxide
- 0.090 M Acetic Acid

Add 100 g (100 mL) of the PDCA and acetic acid solutions to a 1 L glass eluent container. Dilute to 1 L with deionized water. Label the container "0.0060 M PDCA, 0.040 M NaOH, 0.090 M Acetic Acid". The eluent should have a final pH of 4.6.

PAR postcolumn reagent

- 0.5 mM 4-(2-Pyridylazo)resorcinol
- 1.0 M 2-Dimethylaminoethanol
- 0.5 M Ammonium Hydroxide
- 0.3 M Sodium Bicarbonate

Prepare PAR directly in 1 L plastic reagent reservoir container (P/N 37054). To 200 g (200mL) of deionized water, add 31 g (35 mL) trace-metal grade ammonium hydroxide. Next, add 0.12 g of 4-(2-pyridylazo) resorcinol, monosodium, monohydrate, and ultra-sonicate for 5 min. Stir solution for several minutes with a stir bar to ensure that PAR has completely dissolved. Add 500 g (500 mL) of deionized water and then 89 g of 2-dimethylaminoethanol (DMAEOH). The solution should turn from red to orange yellow. Add 25.4 g of sodium bicarbonate and stir thoroughly until dissolved. Fill the reagent container with deionized water up to the threads on the neck, and stir. The color of the final solution should be yellow to yellow orange. Place the reagent container in the reagent reservoir.

Standard preparation

Standards should be prepared daily. Maintain the sample pH between pH 1–2. The standards listed below are intended for the determination of metals in the low ppb (ng/mL) range. If quantitation at higher levels is required, standards can be prepared at concentrations five times greater than those listed. If Chelation IC System 1 is used, the pH of the standard solution must be adjusted to 5.5 with ammonium acetate prior to sample introduction.

Sample preparation

Since the trace-metal grade samples contain a very low level of metal contaminants, dilution of the concen-trated sample must be minimized. One important step in sample preparation is to adjust the concentrated acid samples to pH 1–2, which requires a great deal of precaution. Several guidelines will be discussed that are applicable to most of the concentrated acid samples.

The sample should be prepared in clean polyethylene containers. Avoid using pipets and glassware, which can contaminate the samples. For the concentrated acid sample, it is advisable to keep the acid sample in a cooling bath during neutralization with ammonium hydroxide and ammonium acetate.

For inorganic salts (e.g., ammonium chloride, ammonium nitrate) and organic solvents, the sample solution must be acidified to pH 1–2 with ultrapure nitric acid. For concentrated acid, the sample must be neutralized and buffered with ultrapure concentrated ammonium hydroxide/ammonium acetate solution. For example, calculate 0.5 mole equivalent of concentrated acid (g/L) and weigh it in a clean 100 mL volumetric polyethylene container (e.g., 44.5 g of HNO^3 or 49 g of HC1). Place the sample container in the ice bath and slowly add 10 g of ultrapure 6.0 M ammonium acetate buffer (pH 5.5) to the sample. In a separate container, weigh 30 g of saturated ammonium hydroxide (20%). Slowly add ammonium hydroxide (drop-wise) to the sample with constant swirling. *Warning*: The sample will become very HOT. Allow the sample to cool to room temperature and dilute sample to volume with deionized water. Check that the final pH is 1–2. Note the amount of 6.0 M ammonium acetate added to the sample.

Prepare the blank solution by using the exact amount of saturated ammonium hydroxide and 6.0 M ammonium acetate. For concentrated bases, neutralize the sample with ultrapure concentrated nitric acid and ammonium acetate. For organic solvents, it is strongly recommended that the samples be acidified to stabilize the trace metals. If Chelation IC System 1 is used, the sample pH must be adjusted to 5.5 with ammonium acetate prior to sample introduction.

For complete details on system preparation and setup, operation, and automation, refer to Application Update 168.

Discussion of the method

The method described in this application note was developed for a high ionic strength matrix of acid, base, and salt samples. In general, the high ionic strength matrices usually interfere with the chromatographic separations and degrade the detection limits for many transition metals. Chelation IC not only offers a sample concentration capability to enhance the detection limits, it also standardizes or matches the sample matrix to the standard matrix without an off-line sample pretreatment step. For discussion of the chelation IC method, refer to Application Update 168 for complete details. The chelation IC method has been applied to the analysis of trace transition metals in magnesium chloride, sodium hydroxide, hydrochloric acid, and acetonitrile matrices as shown in Figures 1 through 4. The detection limits for most metals are in the sub-part-per-billion to low-part-per-billion range. Spike recoveries in these matrices are listed in Table 2.

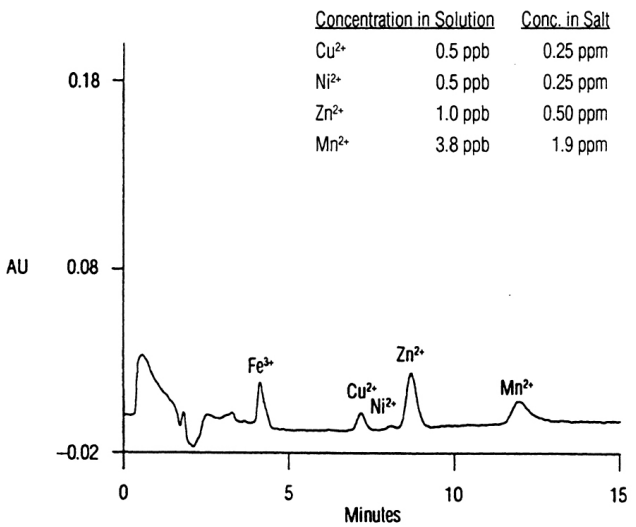

Figure 1. Transition metals in reagent grade magnesium chloride.

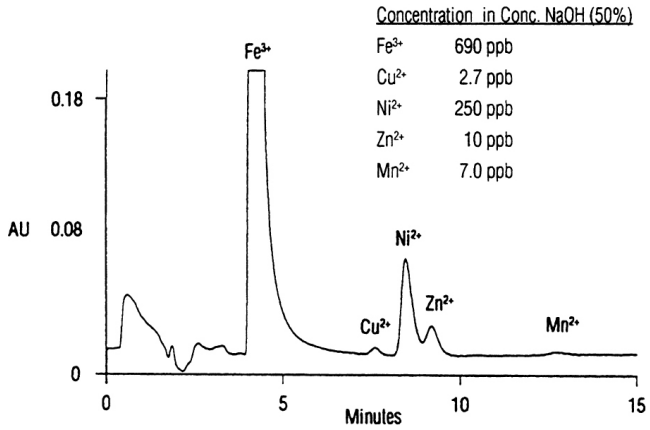

Figure 2. Transition metals in sodium hydroxide.

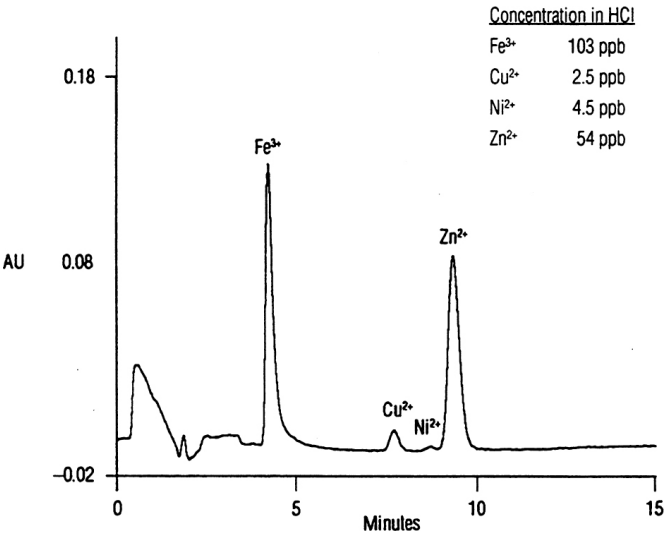

Figure 3. Trace metals in hydrochloric acid.

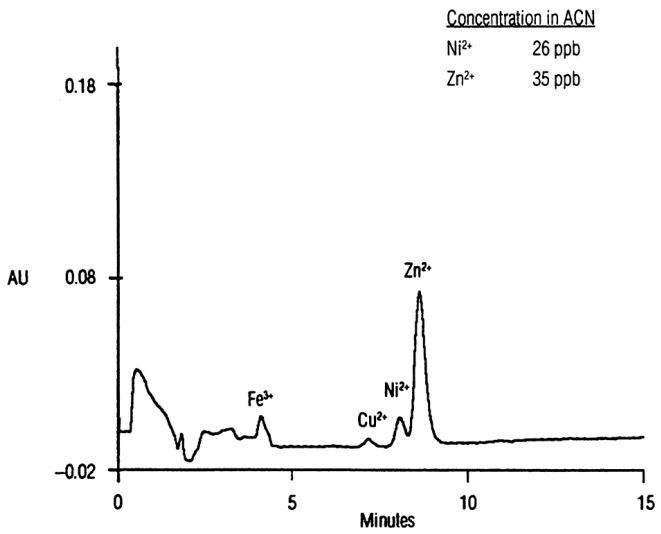

Figure 4. Trace metals in acetonitrile.

Table 2. Spike recoveries in various matrices.

Element	Spike Level (ppb) in Each Sample	Concentration in Matrix (ppb)			Percent Recovery		
		NaOH	HCl	CAN	NaOH	HCl	ACN
Fe^{3+}	20	690	103	–	27	92	40
CU^{2+}	20	2.7	2.5	–	105	103	97
Ni2+	40	250	4.5	–	106	106	100
Zn^{2+}	40	10	54	1.8	96	98	102
Co^{2+}	40	–	–	–	98	103	103
Mn^{2+}	60	7	–	–	91	75	96

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