Application Note 73

Determination of Trace Transition Metals in Reagent Grade Acids, Bases, and Salts Using Ion Chromatography/Inductively Coupled Argon Plasma Spectroscopy (IC/ICAP)

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 before analytical measurement by flame atomic absorption spectroscopy. Typically, evaporation of a specific volume of sample for 2.5 to 4 hours on a hot plate is required before analysis. Also, a Class 100 clean-room environment is normally required during sample pretreatment.

Automated chelation concentration ion chromatography automates the sample preconcentration step before determination by plasma emission spectroscopy. Preconcentration is performed in minutes rather than hours. Sampling, preconcentration, and delivery to the plasma are automated. The sample is never exposed to the ambient atmosphere during preconcentration.* Typical recoveries are 95% to 100% in the 1 ppb concentration range in concentrated acids. Detection limits are in the 0.2 to 2 ppb range for most metals using 5 mL of sample.

Methodology for the determination of transition metals in concentrated acids using coupled IC/ICAP is applicable to semiconductor grade bases and solvents. Typical detection limits for semiconductor solvents and bases using IC/ICAP are one to two orders of magnitude better than by using flame atomic absorption spectroscopy or plasma emission spectroscopy directly.

This application note describes a method for the determination of trace transition metals in trace metal grade reagents by IC/ICAP. The detection limits for most elements present in concentrated trace metal grade reagents are below 1 ppb.

EQUIPMENT

Dionex Advanced Gradient Pump (AGP)

Dionex Sample Concentration Module (SCM)

Thermo Jarrell Ash simultaneous ICAP spectrometer

IBM® or 100% compatible computer with TJA ThermoSpec™software

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)

20% Ultrapure ammonium hydroxide

Ultrapure glacial acetic acid

Ultrapure concentrated nitric 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, information for ordering ultrapure acids and ammonium hydroxide are given below in *Preparation of Solutions and Reagents*.

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*Note: The chelation concentration methods discussed in this application note can also be used for “off-line” preconcentration in conjunction with atomic absorption spectroscopy.

SAMPLE PREPARATION

Since trace metal grade samples contain very low concentrations of metal contaminants, dilution of the concentrated 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 apply to most of the concentrated acid samples.

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

For inorganic salts (e.g., ammonium chloride, ammonium nitrate), 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, weigh 0.5 mole equivalent of concentrated acid in a clean 100-mL volumetric polyethylene container (e.g., 44.5 g HNO_3 or 49 g HCl). Place the sample container in an ice bath and slowly add 10 g 6.0 M ammonium acetate buffer (pH 5.5) to the sample. In a separate container, weigh 30 g concentrated ammonium hydroxide. Slowly add ammonium hydroxide (dropwise) to the sample with constant swirling. WARNING: The sample will become very HOT. Allow the sample to cool and dilute the sample to volume (100 mL) with deionized water. Check that the final pH is 1–2. Note the amount of6.0 M ammonium acetate added to the sample. Prepare the blank solution using the same 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.

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 determination above 1 ppb, high quality trace metal grade reagents can be used. Any metal impurity in these reagents will be concentrated with the sample, constituting a system blank.

2.0 M Ammonium Acetate pH 5.5 ± 0.1

If Dionex ultrapure 2.0 M ammonium acetate is used, no further preparation is required. Otherwise, place 600 mL of deionized or high purity (18 MΩ) water into a clean 1-L glass eluent container. 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. Adjust the pH of the ammonium acetate to 5.5 ± 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 ± 0.1, bring to a volume of 1 L.

2.0 M Nitric Acid

If Dionex ultrapure 2.0 M nitric acid is used, no further preparation is required. Otherwise, place 200 mL of deionized or high purity (18 MΩ) 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.

0.1 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; then, add deionized water to bring the final volume to 4 L and mix thoroughly.

The ultrapure reagents are manufactured by Seastar Chemical and Ultrex Reagents. Seastar reagents are available internationally from Fisher Scientific, who sells these reagents under the OPTIMA® label. Ultrex reagents are available internationally through J.T. Baker.

STANDARD PREPARATION

Since the analytes of interest must be concentrated, the concentration of the "high" standard should not exceed 1 ppm. Typically, a working "high" standard in the range of 5 to 100 ppb is used for ultratrace analysis work. It is convenient to prepare a 10X concentrate of stock solution of the standard and prepare the high standard by dilution of the stock solution.

SYSTEM OPERATION

In Dionex Technical Note 28, "IC/ICAP: A New Technique for Trace Metal Determinations", the gradient program described for the standard configuration may be used for the method described below. To eliminate alkaline earth elements in the sample, the amount of time to wash the column with the ammonium acetate buffer may be shortened if these elements are not at high concentrations. For complete details in system preparation and setup, operation, and automation, refer to Technical Note 28.

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 many instances, a high salt matrix (>6.0 M) precipitates in the sample flow path and in the nebulizer, causing mechanical problems in ICAP instruments. On the other hand, IC not only offers a sample concentration capability to enhance the ICAP detection limits, it also standardizes or matches the sample matrix to the standard matrix, without the need for an off-line matrix matching step.

The MetPac™ CC-1 chelating resin has very high affinity for transition metals compared to the alkali and alkaline earth metals. The resin does not concentrate anions such as the halides, nitrate, sulfate, phosphate, or organic anions. Thus, transition metals can be quantitatively concentrated from high concentrations of anions, alkali, and alkaline earth elements. The chelation concentration process consists of four steps. A known volume of the sample is buffered to pH 1–2 with ammonium hydroxide and ammonium acetate and concentrated on the MetPac CC-1. Most polyvalent cations are quantitatively concentrated, while anions pass through the column. Weakly bound alkaline earth metal ions such as magnesium and calcium are selectively eliminated using a 2.0 M ammonium acetate eluent (pH 5.5). Next, the concentrated transition metals are eluted in a 100 to 200-µL volume to the ICAP. Finally, the MetPac CC-1 is converted to the ammonium form with 2.0 M ammonium acetate eluent. Figure 1 shows a typical time scan of trace metal analysis of cadmium by IC/ICAP.

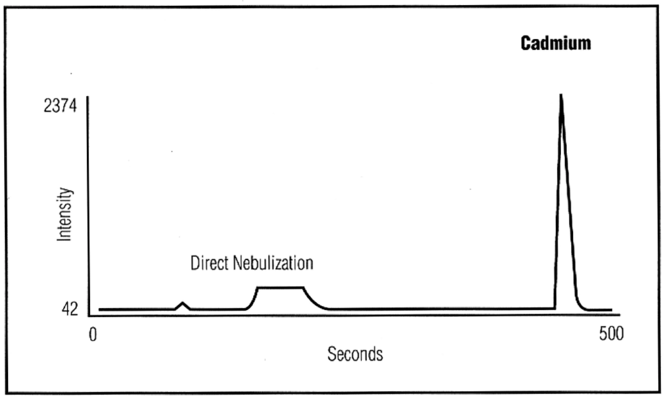

Figure 1 A typical scan of trace metal analysis by IC/ICAP

Tables 1 and 2 show the results of typical trace metals and concentrations found in trace metal grade concentrated nitric acid and hydrochloric acid. These samples were buffered with saturated ammonium hydroxide/6.0 M ammonium acetate. The results of the analysis of buffered blank solutions were used to correct the amount of trace metals in acid samples.

Spike/recovery of trace metals in the ppb range in acid matrix was evaluated. Tables 3 and 4 list the percent recoveries of trace metals in concentrated nitric acid and phosphoric acid.

Table 5 gives the trace metal detection limits attained by IC/ICAP with 5-mL sample concentrations.

Table 1 Typical trace transition metals and concentrations found in trace metal grade nitric acid

Element	Buffer Blank (ppm)	Buffered HNO_3 (ppm)	Blank Corrected (ppm)
Lead	0.0013 ± 0.001	0.0056 ± 0.0016	0.0043
Cadmium	0.0028 ± 0.0007	0.0034 ± 0.0002	0.0006
Copper	0.0001 ± 0.0003	0.0032 ± 0.0002	0.0031
Cobalt	–0.0001 ± 0.0000	0.0004 ± 0.0002	0.0004
Zinc	0.0001 ± 0.0000	0.0012 ± 0.0002	0.0011
Nickel	0.0006 ± 0.0002	0.0024 ± 0.0002	0.0018
Manganese	–0.0009 ± 0.0001	0.0006 ± 0.0004	0.0006
Iron	–0.0065 ± 0.0006	–0.0026 ± 0.0010	ND
Aluminum	–0.0167 ±0.0005	0.0082 ± 0.0010	0.0082

Table 2 Typical trace transition metals and concentrations found in trace metal grade hydrochloric acid

Element	Buffer Blank (ppm)	Buffered HCl (ppm)	Blank Corrected (ppm)
Lead	0.0013 ± 0.0001	0.0075 ± 0.0005	0.0062
Cadmium	0.0028 ± 0.0007	0.0047 ± 0.0002	0.0019
Copper	0.0001 ± 0.0003	0.0024 ± 0.0008	0.0023
Cobalt	–0.0001 ± 0.0000	0.0008 ± 0.0002	0.0008
Zinc	0.0001 ± 0.0000	0.0133 ± 0.0006	0.0132
Nickel	0.0006 ± 0.0002	0.0127 ± 0.0004	0.0121
Manganese	–0.0009 ± 0.0001	0.0039 ± 0.0006	0.0039
Iron	–0.0065 ± 0.0006	0.0562 ± 0.0091	0.0562
Aluminum	–0.0167 ± 0.0005	0.0543 ± 0.0096	0.0543

Table 3 % Recovery of trace transition metals in 30% nitric acid

Element	Conc. (ppm)	Spike	Found (ppm)	% Recovery
Lead	0.0010 ± 0.0010	0.0500	0.0510 ± 0.0018	100
Cadmium	0.0009 ± 0.0002	0.0200	0.0194 ± 0.0004	93
Copper	0.0009 ± 0.0002	0.0200	0.0212 ± 0.0002	101
Cobalt	0.0006 ± 0.0002	0.0200	0.0207 ± 0.0002	100
Zinc	0.0013 ± 0.0002	0.0200	0.0214 ± 0.0003	101
Nickel	0.0000 ± 0.0001	0.0200	0.0208 ± 0.0001	104
Manganese	0.0012 ± 0.0002	0.0200	0.0206 ± 0.0003	97
Iron	0.0035 ± 0.0006	0.0500	0.0473 ± 0.0034	88
Aluminum	0.0074 ± 0.0011	0.0500	0.0579 ± 0.0022	101

Table 4 % Recovery of transition metals in 30% phosphoric acid

Element	Conc. (ppm)	Spike	Found (ppm)	% Recovery
Lead	0.0043 ± 0.0020	0.0500	0.0534 ± 0.0017	98
Cadmium	0.0214 ± 0.0002	0.0200	0.0412 ± 0.0005	100
Copper	0.0011 ± 0.0001	0.0200	0.0210 ± 0.0001	100
Cobalt	0.0007 ± 0.0002	0.0200	0.0207 ± 0.0002	100
Zinc	0.0961 ± 0.0006	0.0200	0.1146 ± 0.0006	99
Nickel	0.0130 ± 0.0006	0.0200	0.0327 ± 0.0006	99
Manganese	0.0023 ± 0.0004	0.0200	0.0215 ± 0.0003	96
Iron	0.0810 ± 0.0006	0.0500	0.0193 ± 0.0005*	15*
Aluminum	ND*	0.0500	ND*	ND*

*Fe and Al are poorly retained on the MetPac CC-1 in samples containing a high concentration of phosphate.

Table 5 Detection limits by IC/ICAP with 5-mL sample concentration

Element	Conc. (ppb)*
Lead	2.0
Cadmium	0.2
Copper	0.2
Cobalt	0.2
Zinc	0.2
Nickel	0.2
Manganese	0.4
Iron	0.8
Aluminum	0.8

*Estimate based on 2 x standard deviation.

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