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Determination of Trace Metals in Water Miscible Organic Solvents by Ion Chromatography/Inductively Coupled Argon Plasma Spectroscopy (IC/ICAP)

INTRODUCTION

The direct analysis of organic solvents such as low molecular weight alcohols and acetonitrile by inductively coupled argon plasma spectroscopy (ICAP) requires significant changes in the operating parameters of ICAP. In addition, calibration standards made in the same base solvent are required. Due to the high solvent loading of the plasma, high power levels are often required to maintain a stable plasma. Analytical results tend to drift over time because of the varying vapor pressure as a function of ambient temperature. Cooled spray chambers are often employed to minimize this effect.

A method for determining trace metals in water miscible organic solvents has been developed. The method uses a solvent compatible MetPac™ CC-1 chelating column to extract the metals of interest from the organic solvent. The MetPac CC-1 selectively retains the transition metals and allows the solvent matrix to go to waste. The concentrated metals are eluted with a nitric acid eluent and delivered to the plasma. As a result, this technique normalizes the matrix from the organic solvent to that of normal dilute acid solutions in water. Normally, calibration standards are made up in the solvent (matrix matching) before analytical measurements of the unknown samples. The IC system eliminates the solvent matrix and the trace metals are extracted into an aqueous environment. As a result, IC eliminates the need to change the operating parameters of

**Table 1 SEMI Standard
for Water Miscible Organic Solvents**

Element	Methanol	Acetone	Propanol
Copper	0.1 ppm max.	0.1 ppm max.	0.1 ppm max.
Iron	0.1	0.1	0.1
Lead	0.1	0.1	0.1
Manganese	0.1	0.1	0.1
Nickel	0.1	0.1	0.1
Zinc	0.1	0.1	0.1

Source: SEMI BOSS 1990

the ICAP when changing from aqueous to organic samples.

This method can also be applied to determining selected transition elements in organic solvents used in semiconductor fabrication. The SEMI (Semiconductor Equipment and Materials International) guidelines for maximum allowable concentrations of selected transition metals in several water miscible solvents are listed in Table 1.

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*.

SAMPLE PREPARATION

Since trace metal grade organic solvents contain very low concentrations of metal contaminants, dilution of the sample must be minimized. Undiluted samples can be introduced directly into the IC without sample modification. If sample modification (e.g., dilution, buffering) is required, the sample must be prepared in clean polyethylene containers. Avoid using pipets and glassware that may contaminate the samples. It is strongly recommended to acidify the organic solvent sample to stabilize the trace metals.

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 or stock solution of the standard and prepare the high standard by dilution of the stock solution.

SYSTEM PREPARATION

Modification of the standard SCM (P/N 42134) is required for this application. The 1-mL sample loop that normally provides a portion of the raw or unprocessed sample to the nebulizer is replaced with a 10-μL loop (P/N 42949).

For complete details in system preparation and setup, operation, and automation, refer to Dionex Technical Note No. 28: “IC/ICAP: A New Technique for Trace Metal Determinations”.

DISCUSSION OF THE METHOD

The method described here has been applied to 100% denatured ethanol, 100-proof distilled spirits, methanol, and acetonitrile. The organic solvent samples containing 1%

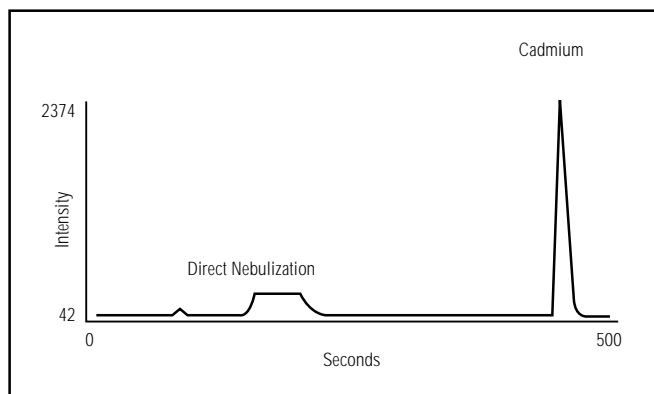


Figure 1 A typical time scan of trace metal analysis of cadmium by IC/ICAP

nitric acid to stabilize the trace metals are automatically buffered with 2.0 M ammonium acetate prior to the loading onto the column. The trace metals are desorbed from the column by 1.5 M nitric acid. The output of the SCM is connected directly to the nebulizer.

The gradient program described in Technical Note 28 for the standard configuration may be used for this application. If desired, the amount of time allocated for loading the sample may be shortened since the 1-mL loop for the direct nebulization run is not required. Also, the amount of time used to wash the column with the ammonium acetate buffer to eliminate alkaline earth elements may be shortened if these elements are not at high concentrations in the solvent.

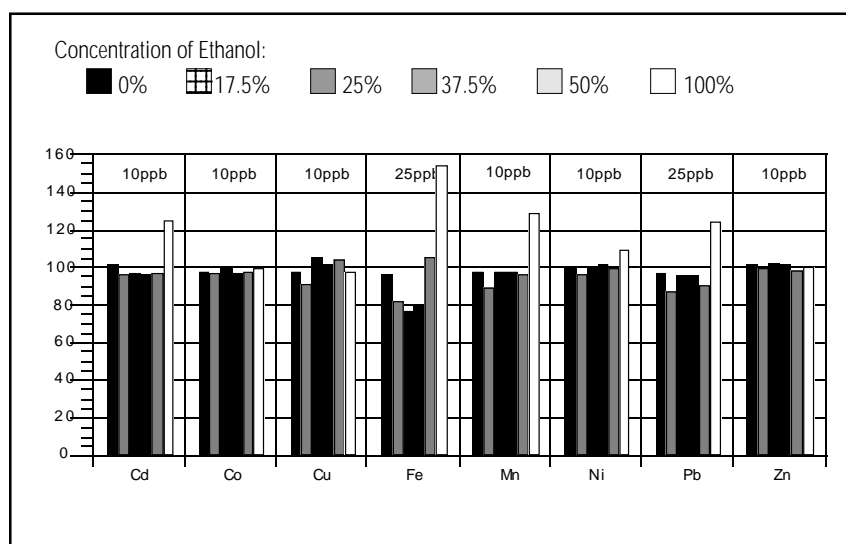


Figure 2 Graphic plot of recovery versus varying concentration of ethanol

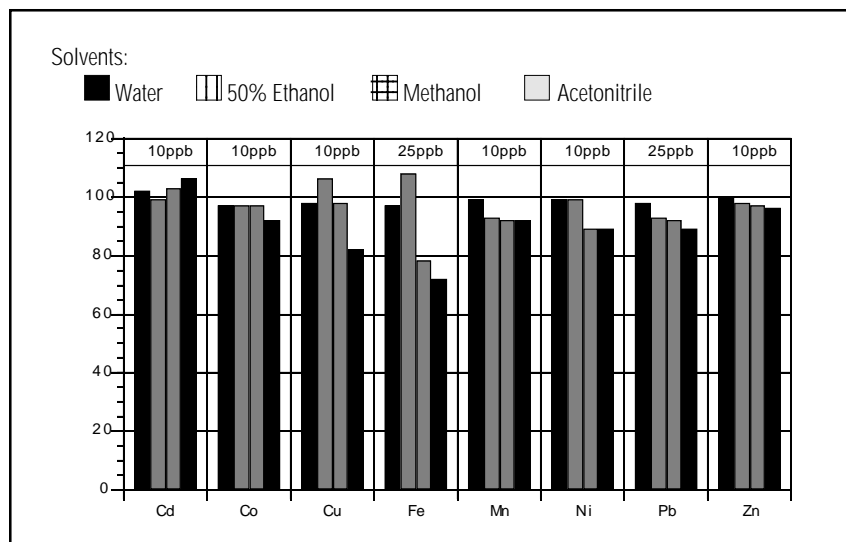


Figure 3 Sample spiking levels as in Figure 2 for different solvents

Chelation Concentration

A 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 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- μ L 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.

All analytical results presented in this application note are based upon aqueous calibration standards. All data relating to recovery reflect this fact. Figure 2 shows a graphic plot of recovery versus varying concentrations of ethanol. The concentrations of ethanol varied from 0% on the left to 100% on the right side of the block for each ele-

Table 2 Analysis of 100-proof ethanol

Element	Average	Std. Dev.
Cadmium	0.0002	0.0001
Cobalt	0.0003	0.0002
Copper	0.0017	0.0002
Manganese	0.0005	0.0005
Nickel	0.0002	0.0003
Lead	0.0009	0.0008
Zinc	0.0005	0.0005

All units in ppm/4 replicates

ment. All compositions below 100% were prepared from the distilled spirits. The 100% composition was obtained from denatured ethanol reagent. The result shows that the 100% ethanol peaks are higher than the others, indicating potential contamination effects from the ethanol reagent. Also, since the reagent contained a denaturing agent that is not totally water soluble, residual organic may be present in the portion being eluted to the plasma. Spike recoveries for all the solutions prepared from the ethanol spirits were close to 100%. This indicates that the MetPac CC-1 chelating column was efficient in retaining the transition metals. The only element that appeared to exhibit poor recovery was iron. The spike concentration was 0.010 ppm for all elements except lead and iron, which were spiked at levels of 0.025 ppm.

Figure 3 shows the sample spiking levels as in Figure 2 for different solvents. The results indicate that the chelation concentration is effective in extracting the transition metals from these common matrices. Iron, however, exhibits erratic behavior as in Figure 2.

Note that the spiking levels of these elements are very close to the detection limits obtained from normal sample introduction with a pneumatic nebulizer. The spiking level for lead at 0.025 ppm was at the detection limit. The use of the chelation concentration sample pretreatment not only eliminates the sample matrix but retains all the benefits of preconcentration. To estimate the limits of detection that may be obtained, Tables 2–4 show data for the analyses of the original solvents without any spikes. The standard deviations obtained may be scaled to a specific definition of detection limit.

Table 3 Analysis of methanol solvent

Element	Average	Std. Dev.
Cadmium	0.0002	0.0002
Cobalt	0.0003	0.0001
Copper	0.0014	0.0002
Manganese	0.0005	0.0004
Nickel	0.0002	0.0003
Lead	0.0007	0.0006
Zinc	0.0004	0.0001

All units in ppm/4 replicates

Table 4 Analysis of acetonitrile

Element	Average	Std. Dev.
Cadmium	0.0003	0.0002
Cobalt	0.0001	0.0001
Copper	0.0010	0.0004
Manganese	0.0008	0.0004
Nickel	0.0001	0.0002
Lead	0.0004	0.0009
Zinc	0.0002	0.0001

All units in ppm/4 replicates

Table 5 Low level spike recovery in 50% ethanol

Element	Average	Std. Dev.
Cadmium	0.0011	0.0001
Cobalt	0.0003	0.0002
Copper	0.0014	0.0006
Iron	0.0026	0.0008
Manganese	0.0005	0.0006
Nickel	0.0002	0.0003
Lead	0.0007	0.0011
Zinc	0.0004	0.0001
Vanadium	0.0008	0.0001

All units in ppm/4 replicates

All elements at 0.001 except Fe and Pb which are 0.0025

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