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APPLICATION NOTE 131

Determination of transition metals at ppt levels in high-purity water and SC2 (D-clean) baths

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Introduction

Metal atoms and conductive particle contaminants are undesirable and potentially damaging in semiconductor manufacturing processes. Oxidative cleaning baths and large volumes of ultrapure rinse water are used to remove metallic contamination from wafer surfaces.[1] For optimal cleaning efficiency, the concentrations of iron and other metals in cleaning solutions should be minimized.[2] To monitor metals in cleaning baths and rinse water, improved analytical methods are needed.

This Application Note describes a method for determining low ng/L amounts of transition metals in high purity water and semiconductor bath solutions. The Thermo Scientific™ Dionex™ IonPac™ CS5A column is used for the separation of transition metals. This column has a unique bilayer latex structure consisting of both anion- and cation-exchange retention mechanisms. Transition metals can be separated using either anion or cation exchange chromatography, depending on the choice of the complexing agent used in the eluent. Pyridine-2,6-dicarboxylic acid (PDCA) is a very strong complexing agent that forms stable, anionic metal complexes. This results in very efficient chromatography. Another commonly used complexing agent is oxalic acid, a moderate chelating agent. Because the complexation is weaker, metals are separated either as free metal cations (Pb, Mn, Cd), as anionic

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complexes (Cu), or as a combination of the two (Co, Zn, Ni). Transition metals are detected using postcolumn derivitization with 4-(2-pyridilazo)resorcinol (PAR) with absorbance detection at 520–530 nm. The PAR displaces the PDCA and forms highly absorbing metal complexes. PAR exhibits broad selectivity for transition metals and provides a very sensitive detection method with low background.

Experimental

Equipment

- Thermo Scientific™ Dionex™ DX-500 Ion Chromatography system* consisting of:
  - GP40 Gradient Pump (microbore configuration)
  - AD20 UV/Vis detector with 10 mm path length cell
  - LC30 Chromatography Enclosure with rear-loading Rheodyne® injection valve
  - Concentrator Pump, DQP
  - RP-1 Postcolumn reagent pump with pulse damper (2' of 0.020" i.d. tubing after the RP-1)
  - Postcolumn reagent bottle (P/N 044411 with its O-ring replaced by a Teflon® encapsulated O-ring (P/N 043523))
  - Knitted Reaction Coil (P/N 053640)
  - Pressurizable Reservoir Chamber

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

- Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstation

Reagents and standards

- Deionized water (DI H_2O), Type 1 reagent grade, 18 MΩ·cm resistance or better
- PDCA Eluent: 7.0 mM Pyridine-2,6-dicarboxylic acid (PDCA), 66 mM KOH, 5.6 mM K_2SO_4, 74 mM Formic acid (Thermo Scientific™ Dionex™ MetPac™ PDCA Eluent Concentrate P/N 046088).
- Postcolumn reagent: 0.06 g of PAR (P/N 039672) in 1 L Dionex MetPac PAR postcolumn reagent diluent (P/N 046094). The formulation of the diluent is 1.0 M 2-dimethylaminoethanol + 0.50 M ammonium hydroxide + 0.30 M Sodium bicarbonate.
- Hydrochloric acid, ultrapure reagent. ULTREX® II (J.T. Baker® or equivalent)
- Hydrogen peroxide, semiconductor grade (Aldrich, 99.999% solution in water)
- 1 g/L individual transition metal standards (VWR, atomic absorption grade)

Conditions	
Columns:	Dionex IonPac CS5A Analytical, 2 × 250 mm (P/N 052576) Dionex IonPac CG5A Guard, 2 × 50 mm (P/N 052836) Thermo Scientific™ Dionex™ IonPac™ TCC-2 Concentrator, 3 × 35 mm (P/N 043103)
Eluent:	PDCA
Eluent Flow Rate:	0.3 mL/min
LC-30 Temperature:	30.0 °C
Postcolumn Reagent:	0.06 g of PAR in 1 L Dionex MetPac PAR Postcolumn Diluent
Postcolumn Flow Rate:	0.15 mL/min
Concentrator Pump Flow Rate:	2.0 mL/min
Run Time:	15 min
Detection:	Visible, High setting, 530 nm
System Backpressure:	1700–2000 psi

Preparation of solution and reagents

Transition metals standards

Appropriate concentrations of standards are prepared from 1 g/L stock standards solutions. All standards were prepared in 2 mM HCl to ensure their stability and prevent the formation of insoluble oxides and hydroxides.

Eluent solution

PDCA eluent

Add 200 mL of Dionex MetPac PDCA Eluent Concentrate to 800.0 mL of degassed water for a total volume of 1000.0 mL or 204.0 g of Dionex MetPac PDCA Eluent Concentrate to 800.0 g of degassed water for a total weight of 1004.0 g.

Postcolumn reagent

Dissolve 0.06 g of PAR in 1.0 L Dionex MetPac PAR postcolumn diluent.

Stock solution for sample and pH adjustment

1 M Hydrochloric acid

Weigh 909.70 g of deionized water (Type I reagent grade, 18 MΩ·cm resistance or better) into an eluent bottle. Tare the bottle and carefully add 90.3 mL of ultrapure reagent grade hydrochloric acid directly to the bottle.

Standard and sample preparation

Add 1.0 mL of 1 M hydrochloric acid to 499 g of sample or standard solution. The final concentration of hydrochloric acid is 2 mM.

Glassware cleanings

Prior to use, high density polyethylene (HDPE) containers used for samples and standards preparation were rinsed with DI water and an aliquot of the sample to reduce the amount of leachable transition metals from the bottle. To avoid contamination and pH errors when formulating the eluent and the PAR reagent, use the high purity reagents offered by Thermo Fisher Scientific.

System operation

System configuration and operation parameters for this application are outlined in a previously published document.[3]

To ensure efficient 2 mm column operation, 0.125 mm (0.005 in.) tubing must be used. Lengths of connecting tubing should be kept as short as possible to minimize system void volume. Carefully use a razor blade or plastic tubing cutter so that the ends of the tubing cuts are straight and smooth. Irregularity on the surface of a tubing end can result in unwanted dead volume.

Sample preconcentration is used to improve sensitivity and lower the detection limits. Samples with transition metal concentrations below 2 µg/L must be preconcentrated for accurate quantification. The sample is loaded onto the Dionex IonPac TCC-2 (Trace Cation Concentrator) with a pressurized reservoir or Dionex DQP concentrator pump. The Dionex IonPac TCC-2 column stationary phase is surface-functionalized sulfonated resin. We used a flow rate of 2 mL/min and times of 5 and 15 minutes to concentrate 10 and 30 mL of sample. A Dionex RP-1 pump was used to deliver postcolumn reagent (PAR). Pneumatic delivery is also acceptable and either of these techniques can be used successfully in this method. Figure 1 shows the system configuration.

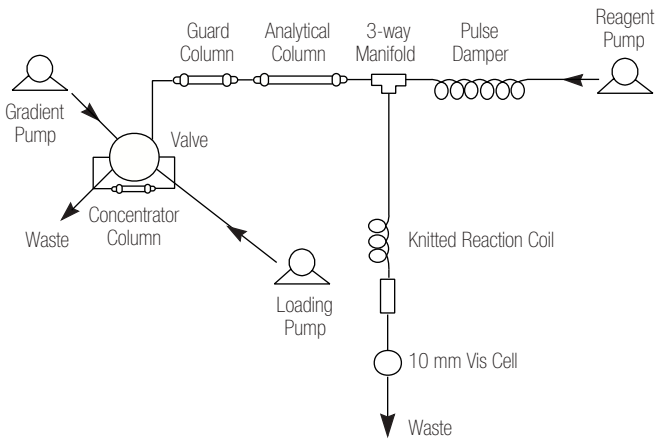

Figure 1. System configuration for detection of transition metals.

Results and discussion

Trace level analysis of transition metals is limited by the purity of water and the reagents. PEEK™, metal-free flow paths are a very important factor in the integrity of the analytical system. Precautions must be taken at every step of sample and standard preparation to minimize contamination. All plastic containers and pipettes must be cleaned with highest purity reagents (soak in 10 mM HCl overnight and rinse thoroughly with water). Information about the content of leachable transition metals in these containers should be obtained from the supplier. The analytical system flow path, including tubing, pumps, postcolumn reagent, and sample must be thoroughly cleaned with 50% IPA/H_2O at start-up.

To perform analysis of trace levels less than 2 µg/L, samples must be preconcentrated rather than directly injected. Figure 2 shows the analysis of 30 mL of a 1 µg/L transition metals standard. All peaks are well separated from the void volume and from each other and are therefore easily quantified. Figures 3 and 4 show the analyses of 10 and 30 mL of high quality deionized water. These samples were concentrated at 2 mL/min for 5 and 15 min respectively. Iron, copper, and zinc are major contaminants. Trace analysis of real samples containing these analytes will depend on the levels of transition metals present in the water blank. The iron concentration in 30 mL of water is estimated to be 45 ng/L (ppt) based on the iron area count in the standard (30 mL of 1 µg/L (ppb) of each transition metal).

Analytical Columns:	Dionex IonPac CS5A, CG5A (2 mm)	Concentration Time:	15 min		
Eluent:	PDCA	Sample Volume:	30 mL		
Eluent Flow Rate:	0.3 mL/min	Total Run Time:	30 min		
Post Column Reagent:	PAR	Detection:	Vis, 530 nm		
Post Column Reagent:	0.15 mL/min	Peaks:	1. Iron	1 µg/L	
Concentrator Column:	Dionex IonPac TCC-2		2. Copper	1	
Concentrator Pump:	DQP		3. Nickel	1	
Concentrator Pump Flow:	2 mL/min		4. Zinc	1	
			5. Cobalt	1	
			6. Cadmium	1	
			7. Manganese	1	

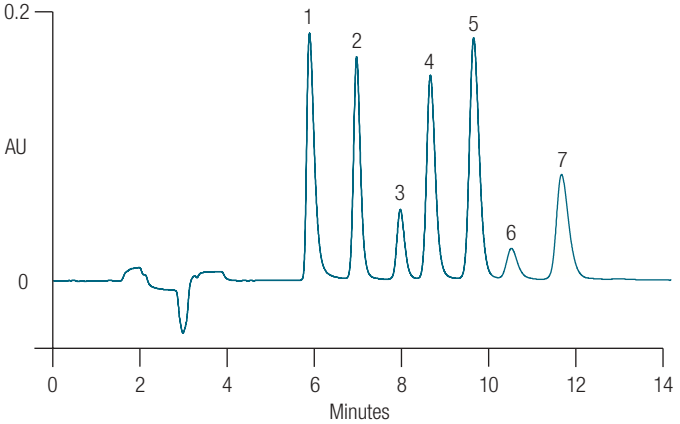

Figure 2. 1 µg/L (ppb) transition metals standard (30 mL concentrated).

Analytical Columns:	Dionex IonPac CS5A, CG5A (2 mm)	Sample Volume:	10 mL
Eluent:	PDCA	Total Run Time:	20 min
Eluent Flow Rate:	0.3 mL/min	Detection:	VIS, 530 nm
Post Column Reagent:	PAR	Peaks:	1. Iron
Post Column Reagent:	0.15 mL/min		2. Copper
Concentrator Column:	Dionex IonPac TCC-2		3. Nickel
Concentrator Pump:	DQP		4. Zinc
Concentrator Pump Flow:	2 mL/min		
Concentration Time:	5 min		

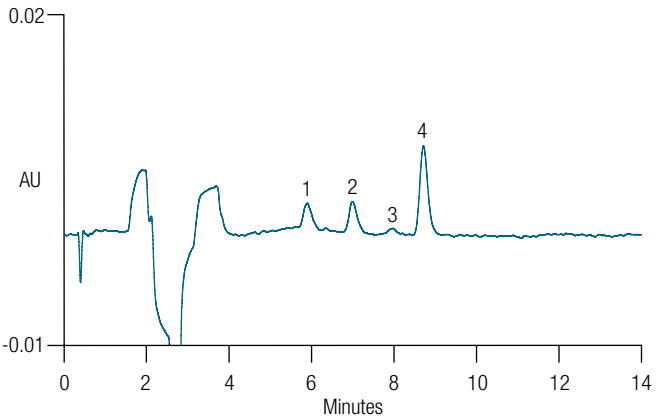

Figure 3. Water blank (10 mL concentrated).

Analytical Columns:	Dionex IonPac CS5A, CG5A (2 mm)	Sample Volume:	30 mL
Eluent:	PDCA	Total Run Time:	30 min
Eluent Flow Rate:	0.3 mL/min	Detection:	VIS, 530 nm
Post Column Reagent:	PAR	Peaks:	1. Iron
Post Column Reagent:	0.15 mL/min		2. Copper
Concentrator Column:	Dionex IonPac TCC-2		3. Nickel
Concentrator Pump:	DQP		4. Zinc
Concentrator Pump Flow:	2 mL/min		
Concentration Time:	15 min		

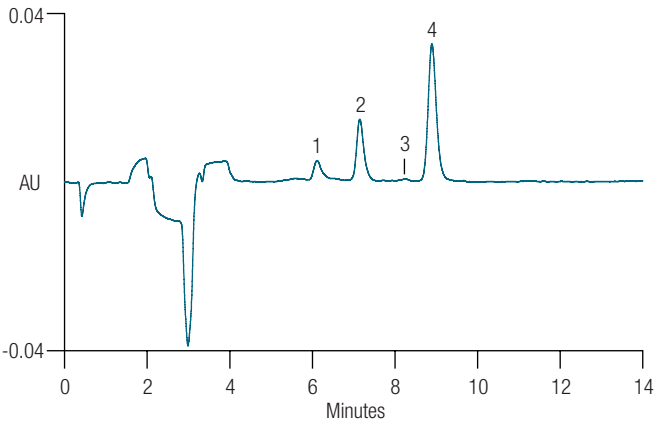

Figure 4. Water blank (30 mL concentrated).

The concentration of Fe^{3+} in 10 mL of water was also approximately 45 ng/L (ppt). Therefore, the concentration of the Fe^{3+} is due to the Fe^{3+} in the water and reagents and not the chromatography system. Because it is possible to quantify the amount of Fe in the 10 mL sample, if that amount was found in a 30 mL sample (less contaminated water), the minimum detection limit would be 15 ppt. Table 1 shows the result of the analysis of 30 mL of high quality deionized water on three consecutive days. The peak area and retention time RSDs were less than 2%.

Table 1. Analysis of iron in 30 mL DI H_2O.

Day #	Concentration ng/L (ppt)	Area count	Retention Time
1	38.1	71,123	6.13
2	37.4	69,786	6.17
3	38.7	72,075	6.10
RSD	1.71	1.62	0.57

Figure 5 shows the chromatogram of an SC2 bath. Concentrations of Fe^{+3}, Cu^{+2}, and Zn^{+2} were 80, 75, and 106 ng/L (ppt), respectively. Recovery of iron from the bath is higher than from water, indicating that chemicals used in bath preparation contain iron.

Analytical Columns:	Dionex IonPac CS5A, CG5A (2 mm)	Concentration Time:	15 min
Eluent:	PDCA	Sample Volume:	30 mL
Eluent Flow Rate:	0.3 mL/min	Total Run Time:	30 min
Post Column Reagent:	PAR	Detection:	VIS, 530 nm
Post Column Reagent:	0.15 mL/min	Peaks:	1. Iron 80 ng/L
Concentrator Column:	Dionex IonPac TCC-2		2. Copper 75
Concentrator Pump:	DQP		3. Nickel -
Concentrator Pump Flow:	2 mL/min		4. Zinc 106

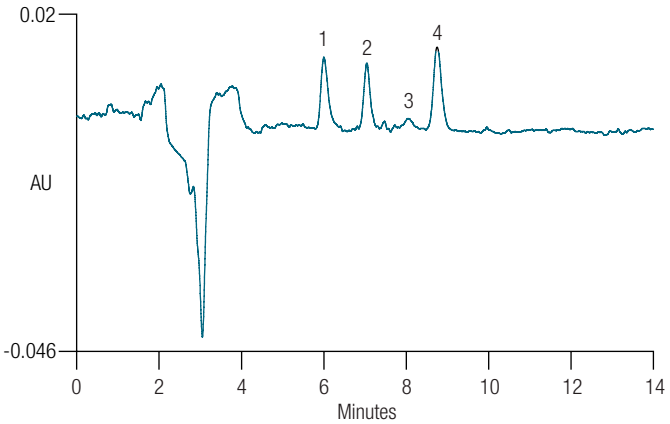

Figure 5. SC2 batch (30 mL concentrated) containing 1 mL HCl / 5 mL H_2O_2 / 494 mL H_2O.

Summary

The method outlined in this Application Note describes the chromatographic analysis of trace levels of transition metals using a preconcentration technique.

References

1. Wayne M. Moreau, *Semiconductor Lithography Principles, Practices, and Materials,* 1988 Plenum Press, New York,1988, 270–280.
2. Suggested Guidelines for Pure Water used in Semi-conductor Processing. Doc 2796. SEMI, 1998, 1–3.
3. Dionex 2-mm Transition Metal System with Postcolumn Delivery Installation and Troubleshooting Manual, P/N 031355

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