

**SEMATECH Provisional Test Method  
for Determining Leachable Trace  
Inorganics in UPW Distribution  
System Components**

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# SEMATECH Provisional Test Method for Determining Leachable Trace Inorganics in UPW Distribution System Components

Technology Transfer # 92010936B-STD

**SEMATECH**

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**Abstract:** This test method provides a procedure for the determination of trace inorganic impurities that leach from a water distribution system component into ultrapure water. Samples are analyzed for trace metals by inductively coupled plasma-mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectroscopy (GFAAS); for cations and anions by ion chromatography (IC); and for silica by colorimetry. It is intended for UPW components including tubing, piping, fittings, valves, regulators, filter housings, filter cartridges, o-rings, gaskets, and ion-exchange resins. This document is in development as an industry standard by Semiconductor Equipment and Materials International (SEMI). When available, adherence to the SEMI standard is recommended.

**Keywords:** Ultrapure Water Distribution Systems, Testing, Tubing, Fittings, Valves, Piping, Filters, Pressure Regulators, O-Rings, Leaching, Trace Inorganic Contaminants

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## SEMASPEC #92010936B–STD

### SEMATECH Provisional Test Method for Determining Leachable Trace Inorganics in UPW Distribution System Components

#### 1. Introduction

- 1.1 *Purpose*—This method provides a procedure for the determination of the trace inorganic impurities that leach from a water distribution system component into ultrapure water (UPW). Trace inorganic impurities can be quantified by inductively coupled plasma-mass spectrometry (ICP-MS), graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), ion chromatography (IC), and colorimetry.
- 1.2 *Scope*—Samples previously prepared according to SEMASPEC #92010934B–STD are analyzed for trace metals by ICP-MS and GFAAS, for cations and anions by IC, and for silica by colorimetry. Water components for analysis include tubing, piping, fittings, valves, regulators, filter housings, filter cartridges, O-rings, gaskets, and ion-exchange resins.
- 1.3 *Limitations*
- 1.3.1 The accuracy of the method is limited by the detection limits of the instruments and by the sample preparation procedures.
- 1.3.2 This test method discusses IC analysis for cations only. Anion analysis is discussed in ASTM D4327.
- 1.3.3 Only reactive silicas are analyzed by the colorimetric method, not total silicon. Nonreactive contaminants such as silicones, colloidal silica, and mold release compounds may not be detected. Total leachable silicon may be analyzed by ICP-MS, ICP-AES, and GFAAS at a better detection limit.

#### 2. Referenced Documents

##### 2.1 *ASTM Standards*<sup>1</sup>

ASTM D859	Standard Test Method for Silica in Water
ASTM D1068	Standard Test Methods for Iron in Water
ASTM D1129	Standard Definitions of Terms Relating to Water
ASTM D3859	Standard Test Methods for Selenium in Water
ASTM D3919	Standard Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
ASTM D4327	Standard Test Methods for Anions in Water by Ion Chromatography
ASTM D4375	Standard Practice for Basic Definitions, Notation and Symbolology for Statistics in Committee D19 on Water

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<sup>1</sup>American Society for Testing and Materials. 1916 Race St. Philadelphia, PA 19103.

ASTM E200 Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis, Practice for

## 2.2 *SEMATECH<sup>2</sup>*

SEMASPEC SEMATECH Guide to Test Methods for UPW Distribution #92010933B–STD System Components

SEMASPEC SEMATECH Provisional Test Method for Sample Preparation for #92010934B–STD Chemical Testing of UPW Distribution System Components

## 3. **Terminology**

### 3.1 *Acronyms and Abbreviations*

3.1.1 *ICP-MS*—inductively coupled plasma-mass spectrometry

3.1.2 *ICP-AES*—inductively coupled plasma-atomic emission spectroscopy

3.1.3 *GFAAS*—graphite furnace atomic absorption spectroscopy

3.1.4 *IC*—ion chromatography

3.1.5 *UPW*—ultrapure water (see Section 7.1)

3.1.6 *ppbw*—parts per billion by weight, ng/g (equivalent to ng/ml for H<sub>2</sub>O at ambient temperature)

## 4. **Summary of Test Method**

Samples previously prepared using SEMASPEC #92010934B–STD are analyzed to determine the leachable inorganic contribution of the component using ICP-MS, GFAAS, IC, and colorimetry methods. Data from different tests can be compared to determine the inorganic contamination contribution from different components and from different manufacturers of the same type of component.

## 5. **Significance and Use**

The degree of leaching from a component is an important criterion in determining the suitability of that component. Contaminants in UPW may adversely affect microelectronic processing.

## 6. **Apparatus**

6.1 *ICP-MS*, capable of scanning the mass range of 1 to 300 amu with a resolution capability of 1-amu peak width at 10% peak height.

6.2 *Fume Hood*.

6.3 *Metric Ruler*.

6.4 *Caliper*.

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<sup>2</sup>SEMATECH. 2706 Montopolis Dr. Austin, TX 78741.

6.5 *Oven*, with temperature control range to a minimum of 100°C, with air exhaust if analysis is performed using hot UPW and laminar flow if used for preconcentration.

6.6 *GFAAS*.

6.7 *IC* (for cation analysis).

6.8 *ICP-AES*.

## 7. **Materials**

7.1 *Test Fluid*. For purposes of this test, references to water shall be understood to mean ultrapure water as defined by maximum individual metal and anion impurity levels of 0.1 ppbw or less, total organic carbon (TOC) levels of 10 ppbw or less, nonvolatile residue levels of 0.1 ppmw or less, resistivity of 18 megohm-cm or greater, and reactive silica impurity of less than 1.0 ppb.

7.2 *Ultrapure Nitric Acid*, less than 10 ppbw for each trace metal.

7.3 *Ultrapure Hydrochloric Acid*, less than 10 ppbw for each trace metal.

7.4 *Ultrapure Isopropyl Alcohol*, less than 50 ppbw for each trace metal.

7.5 *Argon Gas*, 99.99% pure or better.

7.6 *Trace Metallic Standards*, NIST<sup>3</sup> or NIST traceable (including SRM-series standards).

7.7 *Multi-Element Working Standard*. This can be prepared by pipeting appropriate volumes of the trace metal standards and diluting to the desired concentrations. (Prepare these working standards using the same amount of acid used in the sample.)

## 8. **Precautions**

8.1 *Safety Precautions*

8.1.1 This test method may involve hazardous materials, operations, and equipment. This test method does not purport to address the safety considerations associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations before using this method.

8.1.2 Care must be taken in the handling and use of the acids to avoid acid burns or contamination of the acid. Acid should be neutralized before disposal.

8.2 *Technical Precautions*

8.2.1 The reagent blank must have low levels of metallic contamination; otherwise, the results will not be valid or the detection level will not be low enough. A blank value of 10% of the sample concentration or less is recommended, except when the analyte of interest is close to the detection limit.

8.2.2 Sample preparation should be performed in a clean environment and under a fume hood to minimize contamination.

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<sup>3</sup>National Institute of Standards & Technology, Semiconductor Electronics Division, Building 225, Gaithersburg, MD 20899.

8.2.3 If high nickel, copper, or platinum concentrations are found in the blank, check to determine if the cone is causing the contamination. If so, ensure that the cone is cooled properly.

### 8.3 *Interferences*

8.3.1 If chloride is found in the sample, the concentrations of arsenic (As) and vanadium (V) as determined by ICP-MS may not be accurate without chloride correction.

8.3.2 Phosphorus requires pre-concentration in the ICP-MS method due to interference from the oxygen peak, which degrades the detection limit of phosphorus. See Section 13.6.

8.3.3 Additional spectrometer interferences may occur with some of the test methods. Refer to the documents cited in *Additional References* for further information.

## 9. **Sampling, Test Specimens, and Test Units**

### 9.1 *Sampling of Test Specimens*

9.1.1 Test specimens must be representative of the component being tested and must be free of embedded particles and grease.

9.1.2 Test samples shall be prepared according to SEMASPEC #92010934B-STD.

## 10. **Preparation of Apparatus**

### 10.1 *ICP-MS*

10.1.1 Warm up the ICP-MS instrument for a minimum of 30 minutes and optimize it following the manufacturer's recommended procedure.

10.1.2 Install a mass flow controller at the nebulizer flow to improve precision of signal intensity. A peristaltic pump is required to ensure constant delivery of sample solution. Use argon gas with a purity rating of 99.99% or better.

### 10.2 *ICP-AES, IC, GFAAS*

10.2.1 See the specific test methods referenced in Section 2.1 for instructions on set-up of these instruments.

## 11. **Calibration and Reference Standards**

### 11.1 *Optimization and Calibration of Instruments*

11.1.1 Before using an instrument for analysis, optimize it each day by following the manufacturer's recommended procedure. Check calibration throughout the day to ensure that the instrument does not drift.

### 11.2 *ICP-MS or ICP-AES*

11.2.1 A two-point calibration using peak area and consisting of a blank and a high concentration level standard (higher than expected sample concentration) may be used because of the wide linear dynamic concentration range of ICP-MS and ICP-AES.

11.2.2 It is recommended that the linear range for each element of interest be established for a particular instrument by running multiple standards.

11.2.3 Quantitative calibrations must be performed. (Semi-quantitative calibrations are only permitted to screen samples to determine appropriate analysis concentrations.)

11.3 *GFAAS and IC*

11.3.1 A three-point calibration consisting of a blank and two standards is recommended. The sample concentration must be below the concentration of the highest standard.

## 12. **Conditioning**

Refer to SEMASPEC #92010934B–STD.

## 13. **Test Procedure**

If the sample must be concentrated to obtain a low detection limit, refer to Section 13.6 for concentration procedure.

13.1 *ICP-MS*

13.1.1 Typical operating parameters are as follows. These parameters may be varied to optimize the signal-to-noise ratio:

Radio frequency (RF) plasma power :	1.2 kW
Plasma flow rate :	11 l/min
Auxiliary flow rate :	1.0 l/min
Nebulizer flow rate :	0.5 to 0.9 l/min
Sample uptake rate :	1.0 ml/min

13.1.2 Operate the instrument as recommended by the manufacturer; the operator should have a minimum of six months' experience on the instrument or demonstrated skill.

13.1.3 This method is used to determine the concentrations of Al, Sb, As, Ba, Be, Bi, B, Cd, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ga, Ge, Au, Hf, Ho, In, Ir, La, Pb, Li, Lu, Mg, Mn, Hg, Mo, Nd, Ni, Nb, Os, Pd, P, Pt, Pr, Re, Rh, Rb, Ru, Sm, Sc, Se, Ag, Sr, Ta, Te, Tb, Ti, Th, Tm, Sn, W, U, V, Yb, Y, Zn, and Zr.

Fe, K, Si, Na, and Ca may be analyzed by ICP-MS. However, the detection limit may be higher and will depend on the instrument. For a more sensitive analysis, use GFAAS, IC, or the colorimetry method.

13.1.4 Analyze the concentrated sample obtained from SEMASPEC #92010934B–STD by ICP-MS or ICP-AES. Expected detection limit by this technique for phosphorus at 10 times concentration is approximately five ppb.

13.2 *GFAAS*

13.2.1 This method is used to analyze for iron in concentration ranges of 1 ppb or less in the sample solution. Refer to the manufacturer's instructions for operating procedure and refer to ASTM D3919 and D3859 for analysis procedure.

### 13.3 *Ion Chromatography*<sup>4</sup>

13.3.1 This method is used to determine calcium ion, potassium ion, sodium ion, and ammonium ion concentrations in UPW in ranges of 0.1 ppb or greater.

### 13.4 *Colorimetry Method*

13.4.1 For silica concentration in the leachate, analyze the concentrated sample obtained from SEMASPEC #92010934B-STD by following ASTM D859. By following this technique, the expected detection limit for silica at 20 times concentration is one ppb.

### 13.5 *ICP-AES*

If the concentrations of trace metals in the sample solution are greater than the detection limit of ICP-AES, then ICP-AES can be used to analyze for the trace metals of interest. For operation of the instrument, refer to the manufacturer's instructions.

13.5.1 Typical operating parameters are as follows (These parameters may be varied to optimize the signal-to-noise ratio):

Incident Power	1.25 kW
Reflected Power	< 5 watts
Plasma Gas Flow Rate	15 l/min
Auxiliary Gas Flow Rate	0.2 l/min
Nebulizer Gas Flow Rate	1.0 l/min
Viewing Height	15 mm above load coil
Sample Uptake Rate	1.3 ml/min

13.5.2 Operate the instrument as recommended by the manufacturer; the operator should have a minimum of six months' experience on the instrument or demonstrated skill.

### 13.6 *Concentration Procedure*

13.6.1 Evaporate a known volume of UPW leachate fluid in a clean platinum crucible by placing the dish in an oven at 80–90°C. Alternative heating methods can be used (such as heating with a hot plate), but the temperature should not exceed 80–90°C. Record the weight of the empty crucibles ( $W_C$ ) and the weight of the crucibles containing the UPW leachate fluid ( $W_{C+F}$ ). Clean the platinum crucibles and covers. One method of cleaning

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<sup>4</sup> For purposes of developing this method, a Dionex® Ion Chromatograph was used with the following parameters for cation analysis:

Eluant :	0.005 Molar ultrapure HCl
Flow range :	2.3 ml/min
Concentrator column :	Dionex HPIC-CG1 or equivalent
Separator column :	Dionex HPIC CS-10 or equivalent
Suppressor column :	Dionex CFS - fiber suppressor or equivalent
Conductivity meter setting:	Variable
Sample volume :	20 ml–50 ml, depending on detection limit required

the platinum crucibles and covers is to flame them with a propane torch or other appropriate heating source until they are red hot, rinse in dilute ultrapure nitric acid, and then rinse in ultrapure water.

- 13.6.2 Evaporation must be performed in a laminar flow hood or in a clean environment such as a nitrogen-purged chamber. It is recommended that each UPW leachate fluid sample be evaporated in duplicate.
- 13.6.3 Duplicate blank crucibles containing no UPW leachate fluid should undergo exactly the same procedures as the crucibles containing UPW leachate fluid.
- 13.6.4 Remove UPW leachate samples and blank crucibles from the heat source and reweigh ( $W_A$ ) to determine the concentration factor (F) of the UPW leachate fluid using the following equation:

$$F = \frac{W_{C+F} - W_C}{W_A - W_C}$$

## 14. Data Analysis

### 14.1 Calculations

#### 14.1.1 Concentrated Solution

- 14.1.1.1 If a concentrated solution was prepared according to SEMASPEC #92010934B–STD to analyze for a specific element (such as phosphorus or silica), the calculations in Sections 14.1.2 to 14.1.4 must be divided by the concentration factor (F), as calculated in Section 13.6.4.

#### 14.1.2 Ion-Exchange Resins

$$\frac{\mu\text{g}}{\text{g}} \text{ of resin} = \frac{\text{solution concentration(ppb)} \times \text{solution volume(l)}}{\text{weight of the resin (g)}}$$

#### 14.1.3 Valves, Fittings, Regulators, Filter Housings, Filter Cartridges, O-rings, and Gaskets

$$\frac{\mu\text{g}}{\text{component}} = \frac{\text{solution concentration(ppb)} \times \text{solution volume(l)}}{\text{number / fraction of components per extraction sample}}$$

For example, if two valves were used to obtain the 50 ml required for a test, and the result were five ppb, the calculation is:

$$\frac{5 \text{ ppb } (0.05 \text{ l})}{2 \text{ valves}} = 0.125 \frac{\mu\text{g}}{\text{valve}}$$

## 14.1.4 Piping and Tubing

$$\frac{\mu\text{g}}{m} = \frac{\text{solution concentration(ppb)} \times \text{solution volume(l)}}{\text{component length(m)}}$$

**15. Data Presentation**

- 15.1 Report data on all elements detected in samples as well as the detection limits for all elements. For this document, the detection limit is defined as the concentration equivalent to three standard deviations above the background signal.
- 15.2 Provide information for both components and blank samples.
- 15.3 If multiple samples of the same component are evaluated, an average and standard deviation must be reported.

**16. Precision and Bias**

- 16.1 Expected variation in the blank is 10–20% and is due to environmental and instrumental variation. Actual variation will be determined during validation.
- 16.2 Expected variation in the samples is 20–30% and is due to environmental, instrumental, and procedural variations. Actual variation will be determined during validation.
- 16.3 This test does not give an indication of the variations found in the component.
- 16.3.1 Analyze multiple samples of the same component to determine the component variation.
- 16.3.2 Refer to ASTM D4375 for information regarding sample populations to determine differences between components.

**Additional References***References Pertaining to Spectral Interferences in ICP-MS:*

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