

**SEMATECH Provisional Test Method
for Determining Bulk Trace Metals in
Polymer Materials of UPW
Distribution System Components**

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SEMATECH Provisional Test Method for Determining Bulk Trace Metals in Polymer Materials of UPW Distribution System Components

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Abstract: This test method provides a procedure for determining the nonvolatile trace inorganic impurities in bulk polymeric material used for components of UPW distribution systems. It can be used with inductively coupled plasma-mass spectrometry (recommended), graphite furnace atomic absorption spectroscopy, or inductively coupled plasma atomic emission spectroscopy. It is intended for UPW components including tubing, piping, fittings, valves, regulators, filter housings and 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, Materials Testings, Trace Inorganic Contaminants, Polymers, ICP-MS, Bulk Analysis

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SEMASPEC #92010938B–STD

SEMATECH Provisional Test Method for Determining Bulk Trace Metals in Polymer Materials of UPW Distribution System Components

1. Introduction

1.1 *Purpose*—This method provides a procedure for determining the nonvolatile trace inorganic impurities in the bulk of a polymeric material used in ultrapure water (UPW) components. Trace inorganic impurities can be quantified by inductively coupled plasma-mass spectrometry (ICP–MS), graphite furnace atomic absorption spectroscopy (GFAAS), and inductively coupled plasma-atomic emission spectroscopy (ICP–AES).

1.2 *Scope*

1.2.1 In this method, samples previously prepared according to SEMASPEC #92010934B–STD are analyzed for trace inorganics by ICP–MS, GFAAS, and ICP–AES. Components for analysis include tubing, piping, fittings, valves, regulators, filter housings, filter cartridges, O–rings, gaskets, and ion-exchange resins used in UPW distribution systems.

1.2.2 This is a bulk analysis technique, not a surface analysis technique. For surface analysis, refer to SEMASPEC #92010956B–STD.

1.2.3 ICP–MS, GFAAS, and ICP–AES are all appropriate methods for bulk inorganic analysis. ICP–MS is the preferred method because it is more sensitive and efficient.

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 procedure.

1.3.2 This procedure anticipates analysis levels in the ppmw range. Impurities less than 0.1 ppm may not be detected by this method.

1.3.3 Recovery rates of less than 60% are often found for volatile elements such as boron (B), arsenic (As), antimony (Sb), mercury (Hg), gold (Au), and tungsten (W) because of the relatively high temperature sample preparation method and poor stability of some elements in aqueous solution.

2. Referenced Documents

2.1 *ASTM Standards*¹

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

¹American Society for Testing and Materials. 1916 Race St. Philadelphia, PA 19103.

ASTM D4375 Standard Practice for Basic Definitions, Notation, and Symbology for Statistics in Committee D19 on Water

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

2.2 SEMATECH²

SEMASPEC SEMATECH Provisional Test Method for Analyzing the Plastic #92010956B–STD Surface Composition and Chemical Bonding of Components of UPW Distribution Systems (ESCA Method)

SEMASPEC SEMATECH Provisional Test Method for the Determination of #92010936B–STD Leachable Trace Inorganics from UPW Distribution System Components

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

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

3. Terminology

3.1 Acronyms and Abbreviations

3.1.1 AAS/GFAAS—atomic absorption spectroscopy/graphite furnace atomic absorption spectroscopy

3.1.2 *amu*—atomic mass unit

3.1.3 GFAAS—graphite furnace atomic absorption spectroscopy

3.1.4 ICP–MS—inductively coupled plasma–mass spectrometry

3.1.5 ICP–AES—inductively coupled plasma–atomic emission spectroscopy

3.1.6 *ppbw*—parts per billion by weight (ng/g)

3.1.7 *ppmw*—parts per million by weight (μg/g)

3.1.8 UPW—ultrapure water (see Section 7.7)

3.2 Definitions

3.2.1 *ash* *v.*—to apply heat to a material until the material has been reduced to a mineral residue.

4. Summary of Test Method

4.1 Samples previously prepared using SEMASPEC #92010934B–STD are ashed, and trace inorganics in the ash are dissolved into acid and UPW. The sample is then analyzed by ICP–MS, GFAAS, or ICP–AES to determine the bulk inorganic content of the material. This method applies only to nonvolatile metals (i.e., alkali metals, alkaline earths, and

²SEMATECH. 2706 Montopolis Dr. Austin, TX 78741.

transition metals). Other methods such as neutron activation may be used but are not discussed in this method.

- 4.2 Data from different tests can be compared to determine the bulk inorganic content in different materials and in the same material from different manufacturers.

5. Significance and Use

- 5.1 Metallic contamination concentration in the bulk of a component used in UPW distribution systems is an important criterion for determining the suitability of a component. Ultrapure water contaminated by distribution system components may adversely affect microelectronic and other processes.
- 5.2 This method measures the total amount of impurities in the bulk of the material. These impurities will not necessarily leach into an UPW stream. Use SEMASPEC #92010936B-STD to quantify the leachate concentration of each component.

6. Apparatus

- 6.1 *Muffle Furnace*, with temperature control ranging up to 700°C and equipped with a means to regulate air circulation.
- 6.2 *Crucibles*, made of platinum and with a 30 mL capacity.
- 6.3 *ICP-MS*, capable of scanning the mass range of 1 to 300 amu with resolution capability of one atomic mass unit (amu) peak width at 10% peak height.
- 6.4 *GFAAS*.
- 6.5 *ICP-AES*, either simultaneous or sequential reading type.
- 6.6 *Variable Temperature Hot Plate*.
- 6.7 *Chemical Fume Hood*.
- 6.8 *Propane Torch or Appropriate Heating Source*, with a minimum temperature of 600°C.
- 6.9 *Analytical Balance*, capable of weighing at least 0.1 mg.

7. Materials

- 7.1 *Argon Gas*, 99.99% pure or better.
- 7.2 *Multi-Element Working Standard*. This standard must be prepared daily by pipeting the appropriate volumes of the trace metal standards and diluting to the desired concentrations. (Prepare these working standards using the same amount of acid as used for the sample.)
- 7.3 *Trace Metallic Standards*, NIST³ or NIST-traceable.
- 7.4 *Ultrapure Hydrochloric Acid*, less than 10 ppb for each trace metal.
- 7.5 *Ultrapure Isopropyl Alcohol*, less than 50 ppb for each trace metal.

³National Institute of Standards and Technology. Semiconductor Electronics Division. Gaithersburg, MD 20899.

7.6 *Ultrapure Nitric Acid*, less than 10 ppb for each trace metal.

7.7 *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.

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.

8.1.3 Care must be taken when using the propane torch to avoid burns. The torch should not be used near flammable materials or solvents.

8.1.4 Care must be taken when using the muffle furnace to avoid burns.

8.1.5 When ashing fluoropolymeric materials, the ashing must be performed in a fume hood. When heated, fluoropolymer materials outgas hydrofluoric acid fumes and may also emit fluoropolymeric particles which, if inhaled, can cause a condition known as "polymer fume fever." If hot fluoropolymer fumes are inhaled, remove the individual to a well-ventilated area. The flu-like symptoms of polymer fume fever will last approximately one day.

8.2 *Technical Precautions*

8.2.1 Flaming and ashing temperatures must be controlled so that they do not exceed 600°C to minimize metal loss due to volatilization. If the platinum crucible becomes red hot for longer than about one minute during flaming, it may have overheated. When testing the method for recovery rates, it will become apparent that the sample has been overheated from the low recovery of metals.

8.2.2 When ashing a sample, take care that all of the ash residue remains in the platinum crucible.

8.2.3 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 value or less is recommended, except when the analyte of interest is close to the detection limit.

8.2.4 Perform sample preparation in a clean environment and under a fume hood to minimize contamination.

8.2.5 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 Trace metallic levels of reagent blanks must be significantly lower than those in the sample in order to obtain accurate results for the analyte of interest.
- 8.3.2 Perform sample preparation in a clean environment and under a fume hood to minimize contamination.
- 8.3.3 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.
- 8.3.4 Spectrometer interferences may occur with some of the test methods. Refer to documents cited in "Additional References" at the end of this document for further information.

9. **Sampling**

9.1 *Sampling of Test Specimens*

- 9.1.1 Test specimens shall be representative of the component being tested and shall be free of embedded particles and grease when visually inspected.
- 9.1.2 Two samples of each material shall be prepared per SEMASPEC #92010934B–STD. This test is performed in duplicate. More samples may be analyzed if desired.

[Note: The samples are weighed and cleaned according to SEMASPEC #92010934B–STD. This sample preparation begins with the ashing of the component material.]

9.2 *Sample Preparation*

- 9.2.1 Clean the platinum crucibles and covers. One method of cleaning 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.
- 9.2.2 Place the sample in a cleaned platinum crucible.
- 9.2.3 Use a propane torch or other appropriate heating source to carefully flame the outside of the platinum crucible until the polymer inside the crucible is completely charred. Do not flame exceedingly, i.e., do not allow the platinum crucible to become red hot, as excessive heat will allow some metals to volatilize.
- 9.2.4 Prepare two test blanks by flaming two empty crucibles using the method discussed in Section 9.2.3. The results from these blanks will be used to determine the metallic contribution from the crucibles themselves and from the test procedure. Crucibles should be rotated in and out of service so that the same two crucibles are not always used for blanks.
- 9.2.5 Place the charred sample crucibles and blank crucibles in a muffle furnace, cover the crucibles with the cleaned platinum covers, and continue to char at 600°C until all the carbon is removed (usually over a period of 6–10 hrs). The removal of all carbon is indicated by the absence of black material in the sample.

[Note: Some oxides (such as SnO₂) are black and may confound this determination. If a sample is still black after 10 hours, assume that it is an oxide and continue with the procedure.]

- 9.2.6 Allow the platinum crucibles to cool.
- 9.2.7 Add the appropriate amount (1–2 mL) of concentrated ultrapure hydrochloric acid to each crucible.
- 9.2.8 Evaporate the hydrochloric acid to dryness in the chemical hood on a hot plate at less than 100°C. The presence of chloride in the sample can result in interferences for the determination of arsenic and vanadium.
- 9.2.9 Add 0.5 mL concentrated nitric acid to each crucible and dilute with ultrapure water to the required volume (usually 20 mL). The samples are now ready for analysis.

10. Preparation of Apparatus

10.1 *ICP–MS*

10.1.1 Allow the ICP–MS instrument to warm up for a minimum of 30 minutes and then optimize the instrument by 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 of at least 99.99%.

10.2 See the specific test methods for instructions on preparing the other 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. Calibration should be checked throughout the day to ensure that the instrument does not drift.

11.1.2 ICP–MS and ICP–AES

11.1.2.1 A two-point calibration 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.

11.1.2.2 It is recommended that the linear range for each element of interest be established for a particular instrument first by analyzing multiple samples. Quantitative calibrations must be performed. Semi-quantitative calibrations are only permitted to screen samples for appropriate analysis concentrations.

11.1.3 GFAAS

11.1.3.1 A three-point calibration (using peak area) consisting of a blank and two standards is recommended. The sample concentration must be below the concentration of the highest standard.

11.2 *Recovery Percentage Determination*—Metal recovery percentage must be determined for all instruments by the individual laboratory by spiking the crucible containing a

polymer sample with a known concentration of metals and determining the percentage of each metal recovered after the ashing and acid digestion. The following provides the recommended method for spiking:

- 11.2.1 Add a known volume of a standard to the crucible containing the polymer sample.
- 11.2.2 Gently evaporate the standard solution to dryness.
- 11.2.3 Char the dried standard and dried polymer using the procedure described in Section 9.2. Typical recovery rates are 70–100% for the alkali, alkaline earths, and transition metals.

12. Conditioning

Refer to SEMASPEC #92010934B–STD.

13. Test 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 flowrate:	11 l/min.
Auxiliary flowrate:	1.0 l/min.
Nebulizer flowrate:	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 Aspirate the samples prepared from Section 9.2 into the ICP–MS and analyze them.

13.2 ICP–AES

- 13.2.1 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 and to the reference documents cited in Section 2 of this document.

13.3 GFAAS

- 13.3.1 This method can also be used to analyze for trace metals in the sample solutions. Refer to the manufacturer's instructions for the operating procedure and to ASTM D3919 and D3859.

14. Data Analysis

14.1 Calculations

- 14.1.1 The concentration of trace metals in the solution must be calculated to determine the concentration in $\mu\text{g/g}$ (ppmw) of the polymeric material using the following equation:

$$\text{polymer concentration}\left(\frac{\mu\text{g}}{\text{g}}\right) = \frac{\text{solution concentration}\left(\frac{\text{mg}}{\text{ml}}\right) \times \text{solution volume}(\text{ml})}{\text{weight of the polymer}(\text{g})}$$

15. Data Presentation

- 15.1 *Data On All Elements Detected in Samples*—Report this information along with detection limits and recovery rates 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 due to environmental and instrument variation.
- 16.2 Expected variation in the samples is 20–30% and is due to environmental, instrumental, and ashing variations.
- 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*

- Horlick, G., S.H. Tan, M.A. Vaughan, and C.A. Rose. "The Effect of Plasma Operating Parameters on Analyte Signals in Inductively Coupled Plasma Mass Spectrometry." *Spectrochimica Acta* 40B (1985):1555.
- Shao, Y. and G. Horlick. "Recognition of Mass Spectral Interferences in Inductively Coupled Plasma–Mass Spectrometry." *Applied Spectroscopy* 45 (1991):143.
- Tan, S.H. and G. Horlick. "Background Spectral Features in ICP–MS." *Applied Spectroscopy* 40 (1986):445.
- Vaughan, M.A. and G. Horlick. "Oxide, Hydroxide, and Doubly Charged Analyte Species in Inductively Coupled Mass Spectrometry." *Applied Spectroscopy* 40 (1986): 434.

References Pertaining to ICP–AES

- Garbarino, J.R., B.E. Jones, G.P. Stein, W.T. Belser, and H.E. Taylor. "Statistical Evaluation of an ICP–AES Method for Routine Water Quality Testing." *Applied Spectroscopy* 39 (1985):535.
- Winge, R.K., V.S.Fassel, R.N. Kniseley, E. De Kalb, and W.J. Haas Jr. "ICP as an Analytical Source." *Spectrochimica Acta* 32B (1977):327.

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