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Standard Guide for Ion-Chromatographic Analysis of Anions in Grab Samples of Ultrapure Water (UPW) in the Semiconductor Industry[1]

This standard is issued under the fixed designation D7980; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide applies to ultrapure water that is thought to contain low ppt (parts-per-trillion, weight/weight) levels of anionic contaminants (for example, bromide, chloride, fluoride, nitrate, nitrite, phosphate, and sulfate). To minimize carry-over problems between analyses, it is best to limit the concentration of any one contaminant to approximately 200 ppt (although this limit is only an approximation and may vary, depending on the user's application).

1.2 This guide is intended to help analysts avoid contamination of ultrapure-water samples, since contamination control is the primary challenge when quantifying ppt-level anions in grab samples.

1.3 This guide does not include recommendations for collecting samples from the water source.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

D5127 Guide for Ultra-Pure Water Used in the Electronics and Semiconductor Industries

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Acronyms:*

3.2.1 *HDPE, n*—high-density polyethylene

3.2.2 *IC, n*—ion chromatograph

3.2.3 *PEEK, n*—polyether ether ketone

3.2.4 *ppb, n*—parts-per-billion (weight/weight)

3.2.5 *ppt, n*—parts-per-trillion (weight/weight)

3.2.6 *UPW, n*—ultrapure water

4. Significance and Use

4.1 This guide is intended to help analysts in the semiconductor industry. Examples of the usefulness of anion monitoring include: (*1*) determining when ion-exchange resin beds (in water-purification systems) need to be regenerated, and (*2*) ensuring that anion levels are low enough to allow the water to be used for the manufacture of semiconductor devices.

4.2 To ensure that the anions are indeed at low-ppt levels, it is recommended to check the conductivity of a subsample before proceeding with Section 5 of this guide. This check does not need to be exact; its purpose is simply to let the analyst know if the conductivity is higher than that of the highest-level standard solution being tested. Any high reading signifies that the sample, if analyzed, might contaminate the instrument.

5. Guidelines

5.1 *General Considerations:*

5.1.1 In working with grab samples of ultrapure water, concentrate on controlling contamination, which is the overriding challenge when analyzing for anions in UPW. Precautions must be taken, including the following. Wear gloves (for example, nitrile) that do not shed anions. Do not touch anything that might contact the samples. Minimize anionic contamination in the laboratory air; for example, do not work in the same lab where concentrated mineral acids are being used or where acid fumes might be brought in by means of the ventilation system.

5.1.2 Use only fresh, running-from-the-tap UPW whenever water is needed. For guidelines regarding maximum contamination levels allowed in this water, consult Guide D5127; recommendations are based on the type of semiconductor device that ultimately is involved. To ensure highest purity and

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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minimize the build-up of contamination, keep the water stream flowing at all times (a slow rate is acceptable when the water stream is not in use).

5.2 *Ion Chromatograph (IC):*

5.2.1 Use caution in selecting the IC that will be used for these analyses. While an entirely new instrument is not mandatory, a unit that has been used for, for example, parts-per-million-level samples often needs extensive clean-up before the anion levels are acceptably low. When utilizing such "used" chromatographs, replace all tubing with new lengths and clean the Load/Inject valve thoroughly with fresh, running-from-the-tap UPW; in some cases, the internal parts of this valve will need to be replaced with new ones.

5.2.2 Use new PEEK (polyether ether ketone) tubing to plumb the instrument.

5.2.3 Use a low-back-pressure concentrator column for sample loading; install the device such that the sample will be loaded onto the bottom of the concentrator.

5.2.4 Use columns with the smallest internal diameter possible, thereby lowering the amount of sample that must be loaded to achieve a given level of sensitivity. Install new (from the manufacturer) columns to avoid carryover from previous applications.

5.2.5 Keep tubing lengths at a minimum, to decrease dead-volume.

5.2.6 Use columns that will give adequate separation of all ions of interest and that will provide adequate sensitivity.

5.3 *Containers for Standards and Samples:*

5.3.1 Use new, UPW-soaked plastic [for example, polystyrene, high-density polyethylene (HDPE)] that will bleed down to acceptably low background levels.

5.3.2 Use ONLY fresh, running-from-the-tap UPW for rinsing and soaking; never use soap or acid to clean containers, as they will introduce high levels of anionic contamination and make background reduction extremely difficult (if not impossible).

5.3.3 Analyze the soaking water from UPW-soaked new bottles to determine if the anion levels are acceptably low. (Not all brands and formulations of a given plastic type are equally clean. For example, polystyrene tissue-culture flasks are typically clean enough, but the background levels depend on the manufacturer. Other types of polystyrene containers, such as coffee cups, are not acceptable).

5.3.4 Dedicate standards bottles to specific concentrations. Also, dedicate a bottle to UPW, for use in making dilutions.

5.3.5 When not in use, keep bottles filled (**completely**) with UPW that has been obtained fresh and running from the tap.

5.3.6 After each use, immediately rinse bottles with UPW by emptying and then refilling at least 3–4 times. Once the cycles have been completed, fill the bottle to the brim with UPW and cap for storage. Rinse the cap, too; while rinsing the bottle, leave the cap filled with UPW. Before capping the bottle for storage, rinse the cap once more with UPW. In all of these rinsing procedures, use only UPW that has been obtained fresh and running from the tap.

NOTE 1—Early-eluting organic acids (for example, acetate, formate) will be the most difficult species to eliminate from the background.

5.4 *Preparation of Standards:*

5.4.1 Follow the guidelines in 5.3 when selecting, preparing, and storing containers for standards.

5.4.2 Prepare all standards by weight, not by volume.

5.4.3 Prepare all low-level standards [that is, approximately 1 ppb (parts-per-billion, weight/weight) and lower] by pouring, since transfer pipets will contaminate.

5.4.4 Remake low-level standards (that is, approximately 1 ppb and lower) daily.

5.4.5 Prepare and analyze the following types of blanks: (*1*) a sample of the UPW that has been obtained fresh and running from the tap (to test the purity of the UPW used for dilutions), and (*2*) a standard-preparation blank. (The second type of blank is a water sample that has been through all the preparation steps needed to prepare any given working standard; the only difference is that an aliquot of UPW is added instead of the usual stock standard.) When calibrating the IC, use the second type of blank to obtain data points for inclusion in the calibration curve.

5.5 *Loading the Concentrator Column:*

5.5.1 Use loading procedures that minimize contact with potential sources of contamination. The best choices involve only a single piece of tubing that runs from the sample bottle to the Load/Inject valve of the IC.

5.5.2 Do not "store" the aliquot (to be loaded) in a portion of tubing or other device at any time during the process.

5.5.3 If the back pressure is low enough, pull the sample through the concentrator column; otherwise, push the aliquot through by means of a pressurizable container and inert, ultrapure gas.

5.5.4 Follow manufacturer's instructions for determining the concentrator column's break-through volume (that is, the volume beyond which further concentrating will result in the elution of some of the already trapped anions).

NOTE 2—Sensitivity of the analysis can be increased by concentrating a larger mass of water sample, as long as the break-through volume of the concentrator column has not been exceeded.

NOTE 3—Automated liquid-handling devices for delivering precise volume for pre-concentration technique are acceptable, if such devices have been proven not to contaminate the sample.

6. Keywords

6.1 anions; contamination control; high purity; ion chromatography; trace analysis; ultrapure water

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