



# Standard Test Method for Trace Metallic Impurities in High Purity Copper by High-Mass-Resolution Glow Discharge Mass Spectrometer<sup>1</sup>

This standard is issued under the fixed designation F2405; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the concentrations of trace metallic impurities in high purity (99.95 wt. % pure, or purer, with respect to metallic trace impurities) electronic grade copper.

1.2 This test method pertains to analysis by magnetic-sector glow discharge mass spectrometer (GDMS).

1.3 This test method does not include all the information needed to complete GDMS analyses. Sophisticated computer-controlled laboratory equipment, skillfully used by an experienced operator, is required to achieve the required sensitivity. This test method does cover the particular factors (for example, specimen preparation, setting of relative sensitivity factors, determination of detection limits, and the like) known by the responsible technical committee to effect the reliability of high purity copper analyses.

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:<sup>2</sup>

[E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials](#)

[E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals<sup>3</sup>](#)

[E180 Practice for Determining the Precision of ASTM](#)

[Methods for Analysis and Testing of Industrial and Specialty Chemicals<sup>3</sup>](#)

[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

[E876 Practice for Use of Statistics in the Evaluation of Spectrometric Data<sup>3</sup>](#)

[F1593 Test Method for Trace Metallic Impurities in Electronic Grade Aluminum by High Mass-Resolution Glow-Discharge Mass Spectrometer](#)

## 3. Terminology

3.1 Terminology in this test method is consistent with Terminology [E135](#). Required terminology specific to this test method, not covered in Terminology [E135](#), is indicated in [3.2](#).

### 3.2 Definitions:

3.2.1 *campaign*—a test procedure to determine the accuracy of the instrument, which was normally performed at the beginning of the day or after the instrument modification, or both.

3.2.2 *reference sample*—material accepted as suitable for use as a calibration/sensitivity reference standard by all parties concerned with the analyses.

3.2.3 *specimen*—a suitably sized piece cut from a reference or test sample, prepared for installation in the GDMS ion source, and analyzed.

3.2.4 *test sample*—material (copper) to be analyzed for trace metallic impurities by this GDMS method.

3.2.4.1 *Discussion*—Generally the test sample is extracted from a larger batch (lot, casting) of product and is intended to be representative of the batch.

## 4. Summary of Test Method

4.1 A specimen is mounted in a plasma discharge cell. Atoms subsequently sputtered from the specimen surface are ionized, and then focused as an ion beam through a double-focusing magnetic-sector mass separation apparatus. The mass spectrum (the ion current) is collected as magnetic field or acceleration voltage, or both, and is scanned.

4.2 The ion current of an isotope at mass  $M_i$  is the total measured current, less contributions from all other interfering sources. Portions of the measured current may originate from

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

<sup>3</sup> Withdrawn. The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

the ion detector alone (detector noise). Portions may be due to incompletely mass resolved ions of an isotope or molecule with mass close to, but not identical with  $M_i$ . In all such instances the interfering contributions must be estimated and subtracted from the measured signal.

4.2.1 If the source of interfering contributions to the measured ion current at  $M_i$  cannot be determined unambiguously, the measured current less the interfering contributions from identified sources constitutes an upper bound of the detection limit for the current due to the isotope.

4.3 The composition of the test specimen is calculated from the mass spectrum by applying a relative sensitivity factor ( $RSF(X/M)$ ) for each contaminant element,  $X$ , compared to the matrix element,  $M$ . RSF's are determined in a separate analysis of a reference material performed under the same analytical conditions, source configuration, and operating protocol as for the test specimen.

4.4 The relative concentrations of elements  $X$  and  $Y$  are calculated from the relative isotopic ion currents  $I(X_i)$  and  $I(Y_j)$  in the mass spectrum, adjusted for the appropriate isotopic abundance factors ( $A(X_i)$ ,  $A(Y_j)$ ) and RSF's.  $I(X_i)$  and  $I(Y_j)$  refer to the measured ion current from isotopes  $X_i$  and  $Y_j$ , respectively, of atomic species  $X$  and  $Y$  as follows:

$$\frac{(X)}{(Y)} = \frac{RSF(X/M)}{RSF(Y/M)} \times \frac{A(Y_j)}{A(X_i)} \times \frac{I(X_i)}{I(Y_j)}$$

where  $(X)/(Y)$  is the concentration ratio of atomic species  $X$  to species  $Y$ . If species  $Y$  is taken to be the copper matrix ( $RSF(M/M) = 1.0$ ),  $(X)$  is (with only very small error for pure metal matrices) the absolute impurity concentration of  $X$ .

## 5. Significance and Use

5.1 This test method is intended for application in the semiconductor industry for evaluating the purity of materials (for example, sputtering targets, evaporation sources) used in thin film metallization processes. This test method may be useful in additional applications, not envisioned by the responsible technical committee, as agreed upon between the parties concerned.

5.2 This test method is intended for use by GDMS analysts in various laboratories for unifying the protocol and parameters for determining trace impurities in copper. The objective is to improve laboratory-to-laboratory agreement of analysis data. This test method is also directed to the users of GDMS analyses as an aid to understanding the determination method, and the significance and reliability of reported GDMS data.

5.3 For most metallic species, the detection limit for routine analysis is on the order of 0.01 wt. ppm. With special precautions, detection limits to sub-ppb levels are possible.

5.4 This test method may be used as a referee method for producers and users of electronic-grade copper materials.

## 6. Apparatus

6.1 *Glow Discharge Mass Spectrometer*, with mass resolution greater than 3500, and associated equipment and supplies.

6.2 *Machining Apparatus*, capable of preparing specimens and reference samples in the desired geometry and with smooth surfaces.

## 7. Reagents and Materials

7.1 *Reagents*—Reagent and high purity grade reagents as required (MeOH, HNO<sub>3</sub>, and HF).

7.2 *Demineralized Water*.

7.3 *Tantalum Reference Sample*.

7.4 *Copper Reference Sample*:

7.4.1 To the extent available, copper reference materials shall be used to produce the GDMS relative sensitivity factors for the various elements being determined (see **Table 1**).

7.4.1.1 As necessary, non-copper reference materials may be used to produce the GDMS relative sensitivity factors for the various elements being determined.

7.4.2 Reference materials should be homogeneous (see **11.1**) and free of cracks or porosity.

7.4.3 At least two reference materials are required to establish the relative sensitivity factors, including a 99.9999 % pure copper metal to establish the background contribution in analyses.

7.4.4 The concentration of each analyte for relative sensitivity factor determination should be at a factor of 100 greater than the detection limit determined using a 99.9999 % pure copper specimen, but less than 100 ppmw.

7.4.5 To meet expected analysis precision, it is necessary that specimens of reference and test material present the same size and configuration (shape and exposed length) in the glow discharge ion source, with a tolerance of 0.2 mm in diameter and 0.5 mm in the distance of sample to cell ion exit slit.

## 8. Preparation of Reference Standards and Test Specimens

8.1 The surface of the parent material must not be included in the specimen.

8.2 The machined surface of the specimen must be cleaned by etching immediately prior to mounting the specimen and inserting it into the glow discharge ion source.

8.2.1 In order to obtain a representative bulk composition in a reasonable analytical time, surface cleaning must remove all contaminants without altering the composition of the specimen surface.

8.2.2 To minimize the possibility of contamination, clean each specimen separately, immediately prior to mounting in the glow discharge ion source.

**TABLE 1 Suite of Impurity Elements to Be Analyzed<sup>A</sup>**

NOTE—Establish RSFs for the following suite of elements:

Aluminum	Antimony	Arsenic	Beryllium	Bismuth	Boron	Calcium	Carbon
Chromium	Cobalt	Germanium	Gold	Iron	Lead	Lithium	Magnesium
Manganese	Molybdenum	Nickel	Niobium	Nitrogen	Oxygen	Phosphorous	Potassium
Selenium	Silicon	Silver	Sodium	Sulfur	Tellurium	Thorium	Tin
Titanium	Uranium	Vanadium	Zinc	Zirconium			

<sup>A</sup> Additional species may be determined and reported, as agreed upon between all parties concerned with the analyses.