Designation: F 1593 – 97

Standard Test Method for
Trace Metallic Impurities in Electronic Grade Aluminum by High Mass-Resolution Glow-Discharge Mass Spectrometer[1]

This standard is issued under the fixed designation F 1593; 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 test method covers measuring the concentrations of trace metallic impurities in high purity aluminum.

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

1.3 The aluminum matrix must be 99.9 weight % (3N-grade) pure, or purer, with respect to metallic impurities. There must be no major alloy constituent, for example, silicon or copper, greater than 1000 weight ppm in concentration.

1.4 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 sensitivity limits, etc.) known by the responsible technical committee to affect the reliability of high purity aluminum analyses.

2. Referenced Documents

2.1 *ASTM Standards:*
E 135 Terminology Relating to Analytical Atomic Spectroscopy[2]
E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]
E 1257 Guide for Evaluating Grinding Materials Used for Surface Preparation in Spectrochemical Analysis[4]

3. Terminology

3.1 Terminology in this test method is consistent with Terminology E 135. Required terminology specific to this test method and not covered in Terminology E 135 is indicated below.

3.2 *campaign*—a series of analyses of similar specimens performed in the same manner in one working session, using one GDMS setup. As a practical matter, cleaning of the ion source specimen cell is often the boundary event separating one analysis campaign from the next.

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

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

3.5 *test sample*— material (aluminum) to be analyzed for trace metallic impurities by this GDMS test method. 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 the Test Method

4.1 A specimen is mounted as the cathode 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, that is, the ion current, is collected as magnetic field, or acceleration voltage is scanned, or both.

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 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*. RSFs are determined in a separate analysis

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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 *RSFs*. $I(X_i)$ and $I(Y_j)$ refer to the measured ion current from isotopes X_i and Y_j, respectively, of atomic species X and Y.

$$(X)/(Y) = RSF(X/M)/RSF(Y/M) \times A(Y_j)/A(X_i) \times I(X_i)/I(Y_i) \quad (1)$$

where $(X)/(Y)$ is the concentration ratio of atomic species X to species Y. If species Y is taken to be the aluminum 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 by 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 pure aluminum. 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 weight 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 aluminum materials.

6. Apparatus

6.1 *Glow Discharge Mass Spectrometer*, with mass resolution greater than 3500, and associated equipment and supplies. The GDMS must be fitted with a liquid nitrogen cooled ion source specimen cell.

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

6.3 *Electropolishing Apparatus*, capable of removing the contaminants from the surfaces of specimens.

7. Reagents and Materials

7.1 *Reagent and High Purity Grade Reagents*, as required (MeOH, HNO_3, HCl).

7.2 *Demineralized Water*.

7.3 *Tantalum Reference Sample*.

7.4 *Aluminum Reference Sample*.

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

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

7.4.3 Reference materials should be homogeneous and free of cracks or porosity.

7.4.4 At least two reference materials are required to establish the relative sensitivity factors, including one nominally 99.9999 % pure (6N-grade) aluminum metal to establish the background contribution in analyses.

7.4.5 The concentration of each analyte for relative sensitivity factor determination should be a factor of 100 greater than the detection limit determined using a nominally 99.9999 % pure (6N-grade) aluminum specimen, but less than 100 ppmw.

7.4.6 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 specimen 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 electropolishing or 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 analysis 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.

8.2.3 Prepare and use electropolishing or etching solutions in a clean container insoluble in the contained solution.

8.2.4 *Electropolishing*— perform electropolishing in a solution of methanol and HNO_3 mixed in the ratio 7:5 by volume. Apply 5–15 volts (dc) across the cell, with the specimen as anode. Electropolish for up to 4 min, as sufficient to expose smooth, clean metal over the entire polished surface.

8.2.5 *Etching*—perform etching by immersing the specimen in aqua regia (HNO_3 and HF, mixed in the ratio 3:1 by

TABLE 1 Suite of Impurity Elements to Be Analyzed [A]

NOTE 1—Establish RSFs for the following suite of elements.

silver	arsenic	gold	boron	beryllium	calcium	cerium	chromium	cesium	copper	iron
potassium	lithium	magnesium	manganese	sodium	nickel	phosphorus	antimony	silicon	tin	thorium
titanium	uranium	vanadium	zinc	zirconium						

[A] Additional species may be determined and reported, as agreed upon between all parties concerned with the analyses.

volume). Etch for several minutes, until smooth, clean metal is exposed over the entire surface.

8.2.6 Immediately after cleaning, wash the specimen with several rinses of high purity methanol or other high purity reagent to remove water from the specimen surface, and dry the specimen in the laboratory environment.

8.3 Immediately mount and insert the specimen into the glow discharge ion source, minimizing exposure of the cleaned, rinsed specimen surface to the laboratory environment.

8.3.1 As necessary, use a non-contacting gage when mounting specimens in the analysis cell specimen holder to ensure the proper sample configuration in the glow discharge cell (see 7.4.6).

8.4 Sputter etch the specimen surface in the glow discharge plasma for a period of time before data acquisition (see 12.3) to ensure the cleanliness of the surface. Pre-analysis sputtering conditions are limited by the need to maintain sample integrity. Pre-analysis sputtering at twice the power used for the analysis should be adequate for sputter etch cleaning.

9. Preparation of the GDMS Apparatus

9.1 The ultimate background pressure in the ion source chamber should be less than 1×10^{-6} Torr before operation. The background pressure in the mass analyzer should be less than 5×10^{-7} Torr during operation.

9.2 The glow discharge ion source must be cooled to near liquid nitrogen temperature.

9.3 The GDMS instrument must be accurately mass calibrated prior to measurements.

9.4 The GDMS instrument must be adjusted to the appropriate mass peak shape and mass resolving power for the required analysis.

9.5 If the instrument uses different ion collectors to measure ion currents during the same analysis, the measurement efficiency of each detector relative to the others should be determined at least weekly.

9.5.1 If both Faraday cup collector for ion current measurement and ion counting detectors are used during the same analysis, the ion counting efficiency (ICE) must be determined prior to each campaign of specimen analyses using the following or equivalent procedures.

9.5.1.1 Using a specimen of tantalum, measure the ion current from the major isotope (^{181}Ta) using the ion current Faraday cup detector, and measure the ion current from the minor isotope (^{180}Ta) using the ion counting detector, with care to avoid ion counting losses due to ion counting system dead times. The counting loss should be 1 % or less.

9.5.1.2 The ion counting efficiency is calculated by multiplying the ratio of the ^{180}Ta ion current to the ^{181}Ta ion current by the ^{181}Ta/ ^{180}Ta isotopic ratio. The result of this calculation is the ion counting detector efficiency (ICE).

9.5.1.3 Apply the ICE as a correction to all ion current measurements from the ion counting detector obtained in analyses by dividing the ion current by the ICE factor.

10. Instrument Quality Control

10.1 A well-characterized specimen must be run on a regular basis to demonstrate the capability of the GDMS system as a whole for the required analyses.

10.2 A recommended procedure is the measurement of the relative ion currents of selected analytes and the matrix element in aluminum or tantalum reference samples.

10.3 Plot validation analysis data from at least five elements with historic values in statistical process control (SPC) chart format to demonstrate that the analysis process is in statistical control. The equipment is suitable for use if the analysis data group is within the 3-sigma control limits and shows no non-random trends.

10.4 Upper and lower control limits for SPC must be within at least 20 % of the mean of previously determined values of the relative ion currents.

11. Standardization

11.1 The GDMS instrument should be standardized using National Institute of Standards Technology (NIST) traceable reference materials, preferably aluminum, to the extent such reference samples are available.

11.2 Relative sensitivity factor (RSF) values should, in the best case, be determined from the ion beam ratio measurements of four randomly selected specimens from each standard required, with four independent measurements of each pin.

11.3 RSF values must be determined for the suite of impurity elements for which specimens are to be analyzed (see Table 1) using the selected isotopes (see Table 2) for measurement and RSF calculation.

12. Procedure

12.1 Establish a suitable data acquisition protocol (DAP) appropriate for the GDMS instrument used for the analysis.

12.1.1 The DAP must include, but is not limited to, the measurement of elements tabulated in Table 1 and the isotopes tabulated in Table 2.

12.1.2 Instrumental parameters selected for isotope measurements must be appropriate for the analysis requirements:

12.1.2.1 Ion current integration times to achieve desired precision and detection limits; and,

12.1.2.2 Mass ranges about the analyte mass peak over which measurements are acquired to clarify mass interferences.

TABLE 2 Isotope Selection [A]

NOTE 1—Use the following isotopes for establishing RSF values and for performing analyses of test specimens.

^{109}Ag	^{63}Cu/ ^{65}Cu	^{121}Sb
^{75}As	^{56}Fe	^{28}Si
^{197}Au	^{39}K	^{119}Sn
^{11}B	^{7}Li	^{232}Th
^{9}Be	^{24}Mg	^{48}Ti
^{44}Ca	^{55}Mn	^{238}U
^{140}Ce	^{23}Na	^{51}V
^{52}Cr	^{60}Ni	^{64}Zn/ ^{66}Zn
^{133}Cs	^{31}P	^{90}Zr

[A] This selection of isotopes minimizes significant interferences (see Annex A1). Additional species may be determined and reported, as agreed upon between all parties concerned with the analyses.