



Designation: F 1710 – 97

Standard Test Method for Trace Metallic Impurities in Electronic Grade Titanium by High Mass-Resolution Glow Discharge Mass Spectrometer¹

This standard is issued under the fixed designation F 1710; 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 the determination of concentrations of trace metallic impurities in high purity titanium.

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

1.3 The titanium 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, aluminum or iron, 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 effect the reliability of high purity titanium analyses.

1.5 *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:

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals²

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals³

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴

E 1257 Guide for Evaluating Grinding Materials Used for

Surface Preparation in Spectrochemical Analysis⁵

3. Terminology

3.1 Terminology in this test method is consistent with Terminology E 135. Required terminology specific to this test method, not covered in Terminology E 135, is indicated in 3.2.

3.2 Definitions:

3.2.1 *campaign*—a series of analyses of similar specimens performed in the same manner in one working session, using one GDMS setup.

3.2.1.1 *Discussion*—As a practical matter, cleaning of the ion source specimen cell is often the boundary event separating one analysis campaign from the next.

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 titanium 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 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, or both, 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 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.

¹ This test method is under the jurisdiction of ASTM Committee F-1 on Electronics and is the direct responsibility of Subcommittee F01.17 on Sputtered Thin Films.

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² *Annual Book of ASTM Standards*, Vol 03.05.

³ *Annual Book of ASTM Standards*, Vol 15.05.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ *Annual Book of ASTM Standards*, Vol 03.06.

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:

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

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

7. Reagents and Materials

7.1 *Reagent and High Purity Grade Reagents*, as required (MeOH , HNO_3 , HF , H_2O_2).

7.2 *Demineralized Water*.

7.3 *Tantalum Reference Sample*.

7.4 *Titanium Reference Sample*.

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

7.4.2 As necessary, non-titanium 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 99.999 % pure (5N-grade) or better titanium 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 99.999 % pure (5N-grade) or better titanium 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 chemical 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 etching solutions in a clean container insoluble in the contained solution.

8.2.4 Useful etching solutions are $\text{HNO}_3:\text{HF}::3:1$ or $\text{HNO}_3:\text{HF}:\text{H}_2\text{O}_2::1:1:1$ or $\text{H}_2\text{O}:\text{HNO}_3:\text{HF}:\text{H}_2\text{O}_2::20:5:5:4$ (double etched), etching until smooth, clean metal is exposed over the entire surface.

8.2.5 Immediately after cleaning, wash the specimen with high purity rinses and thoroughly dry the specimen in the laboratory environment.

NOTE 1—Examples of acceptable high purity rinses are very large scale integration (VLSI) grade methanol and distilled water.

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 noncontacting 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).

TABLE 1 Suite of Impurity Elements to be Analyzed, with Appropriate Isotope Selection

NOTE 1—Establish RSFs for the following suite of elements, using the indicated isotopes for establishing RSF values and for performing analyses of test specimens.

NOTE 2—This selection of isotopes minimizes significant interferences (see Annex A1.). Additional species may be determined and reported, as agreed upon by all parties concerned with the analyses. Other isotopes can be selected to assist mass spectrum peak identification or for other purposes.

Lithium	⁷ Li
Beryllium	⁹ Be
Boron	¹¹ B
Carbon	¹² C
Nitrogen	¹⁴ N
Oxygen	¹⁶ O
Fluorine	¹⁹ F
Sodium	²³ Na
Magnesium	²⁶ Mg
Aluminum	²⁷ Al
Silicon	²⁸ Si
Phosphorus	³¹ P
Sulfur	³² S
Chlorine	³⁵ Cl
Potassium	³⁹ K
Calcium	⁴² Ca
Scandium	⁴⁵ Sc
Titanium	⁴⁸ Ti
Vanadium	⁵¹ V
Chromium	⁵² Cr
Manganese	⁵⁵ Mn
Iron	⁵⁶ Fe
Cobalt	⁵⁹ Co
Nickel	⁶⁰ Ni
Copper	⁶³ Cu
Zinc	⁶⁶ Zn or ⁶⁸ Zn
Gallium	⁶⁹ Ga or ⁷¹ Ga
Germanium	⁷⁰ Ge or ⁷³ Ge
Arsenic	⁷⁵ As
Selenium	⁷⁷ Se
Bromine	⁷⁹ Br
Rubidium	⁸⁵ Rb
Yttrium	⁸⁹ Y
Zirconium	⁹¹ Zr
Niobium	⁹³ Nb
Molybdenum	¹⁰⁰ Mo
Ruthenium	¹⁰¹ Ru
Rhodium	¹⁰³ Rh
Silver	¹⁰⁷ Ag
Palladium	¹⁰⁶ Pd or ¹⁰⁸ Pd
Cadmium	¹¹⁴ Cd
Indium	¹¹⁵ In
Tin	¹¹⁷ Sn or ¹¹⁹ Sn
Antimony	¹²¹ Sb
Iodine	¹²⁷ I
Tellurium	¹²⁵ Te or ¹³⁰ Te
Cesium	¹³³ Cs
Barium	¹³⁸ Ba
Lanthanum	¹³⁹ La
Cerium	¹⁴⁰ Ce
Neodymium	¹⁴⁶ Nd
Hafnium	¹⁷⁶ Hf or ¹⁷⁸ Hf
Tantalum	¹⁸¹ Ta
Tungsten	¹⁸⁴ W
Rhenium	¹⁸⁷ Re
Osmium	¹⁹⁰ Os or ¹⁹² Os
Iridium	¹⁹¹ Ir
Platinum	¹⁹⁴ Pt or ¹⁹⁶ Pt
Gold	¹⁹⁷ Au
Mercury	²⁰¹ Hg or ²⁰² Hg
Thallium	²⁰⁵ Tl
Lead	²⁰⁸ Pb
Bismuth	²⁰⁹ Bi
Thorium	²³² Th
Uranium	²³⁸ U

8.4 Sputter etch the specimen surface in the glow discharge plasma for a period of time before data acquisition (12.3) to ensure the cleanliness of the surface. Pre-analysis sputtering conditions can be limited by the need to maintain sample integrity. If sputter cleaning and analysis are carried out under different plasma conditions, accuracy should be established for the analytical protocol adopted and elements measured.

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 (¹⁸¹Ta) using the ion current Faraday cup detector, and measure the ion current from the minor isotope (¹⁸⁰Ta) 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 ¹⁸⁰Ta ion current to the ¹⁸¹Ta ion current by the ¹⁸¹Ta/¹⁸⁰Ta 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 titanium 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 nonrandom 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.