Designation: F2405 – 04 (Reapproved 2011)

Standard Test Method for
Trace Metallic Impurities in High Purity Copper by High-Mass-Resolution Glow Discharge Mass Spectrometer[1]

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 (ε) 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:*[2]

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E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)[3]

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

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E876 Practice for Use of Statistics in the Evaluation of Spectrometric Data (Withdrawn 2003)[3]

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

---

[1] This test method is under the jurisdiction of ASTM Committee F01 on Electronics and is the direct responsibility of Subcommittee F01.17 on Sputter Metallization.

Current edition approved June 1, 2011. Published June 2011. Originally approved in 2004. Last previous edition approved in 2004 as F2405–04. DOI: 10.1520/F2405-04R11.

[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.

[3] The last approved version of this historical standard is referenced on 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_3, 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.

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

NOTE 1—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			

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

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.

8.2.3 Prepare etching solutions in a clean container insoluble in the contained solution.

8.2.3.1 *Etching*—Perform etching by immersing the specimen in a suitable acid mixture solution (4:1:1 H_2O:HF:HNO_3 and 1:1 H_2O:HNO_3 were found applicable). Etch the specimen until smooth, clean metal is exposed over the entire surface.

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

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

8.4.1 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 7.4.5).

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

9. Preparation of the GDMS Apparatus

9.1 See Test Method F1593, Section 9 on Preparation of the GDMS Apparatus.

10. Instrument Quality Control

10.1 See Test Method F1593, Section 10 on Instrument Quality Control, using a copper reference standard in place of an aluminum standard.

11. Standardization

11.1 The GDMS instrument should be standardized using international recognized reference materials, preferably copper, to the extent such reference samples are available.

11.1.1 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.

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

TABLE 2 Isotope Selection[A]

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

Element		Isotope
Aluminum	Al	27
Antimony	Sb	121
Arsenic	As	75
Beryllium	Be	9
Bismuth	Bi	209
Boron	B	11
Calcium	Ca	44
Carbon	C	12
Chromium	Cr	52
Cobalt	Co	59
Germanium	Ge	70
Gold	Au	197
Iron	Fe	56
Lead	Pb	208
Lithium	Li	7
Magnesium	Mg	24
Manganese	Mn	55
Molybdenum	Mo	98
Nickel	Ni	58
Niobium	Nb	93
Nitrogen	N	14
Oxygen	O	16
Phosphorous	P	31
Potassium	K	39
Selenium	Se	82
Silicon	Si	28
Silver	Ag	109
Sodium	Na	23
Sulfur	S	32
Tellurium	Te	125
Thorium	Th	232
Tin	Sn	124
Titanium	Ti	48
Uranium	U	238
Vanadium	V	51
Zinc	Zn	68
Zirconium	Zr	90

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

TABLE 3 Required Relative Standard Deviation (RSD) for RSF Determinations, Pre-Sputtering Period, and Plasma Stability Tests (between the last two measurements)

Analyte Content Range	Concentration Difference, %
Major (>100 ppm)	5
Minor (100 ppm > × >1 ppm)	10
Trace (1 ppm > × >100 ppb)	20

12. Analysis Procedure

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

12.1.1 The protocol must include, but is not limited to, the measurement of elements tabulated in Table 1 and isotopes tabulated in Table 2. Annex A1 lists significant spectral interference in this testing.

12.1.2 Instrumental parameters selected for isotope measurements must be appropriate for the analysis requirements: *(1)* ion current integration times to achieve desired precision and detection limits; and *(2)* mass ranges about the analyte mass peak over which measurements are acquired to clarify mass interference.

TABLE 4 Summary of Copper Round Robin Test Results Providing Precision and Bias on Interlaboratory GDMS Analysis of High Purity Copper[A]

All entries are wt. ppm

Material	CuA (6N + 10)					CuB (6N + 1)					CuC (6N)				
Element	Avg	Sr	SR	r	R	Avg	Sr	SR	r	R	Avg	Sr	SR	r	R
Li	0.007	0.003	0.012	0.433	1.746	0.010	0.011	0.017	1.119	1.693	0.001	0.001	0.003	1.000	3.000
Be	7.86	0.94	2.82	0.12	0.36	0.73	0.08	0.25	0.11	0.35	0.010	0.003	0.004	0.300	0.400
B	10.12	1.02	2.86	0.10	0.28	1.16	0.09	0.36	0.07	0.31	0.278	1.215	1.286	4.371	4.626
C	4.40	7.35	10.58	1.67	2.40	3.00	2.72	5.75	0.91	1.92	2.602	1.898	6.185	0.729	2.377
Na	0.08	0.05	0.16	0.67	1.96	0.12	0.17	0.24	1.43	2.07	0.020	0.034	0.060	1.714	2.995
Mg	11.87	0.81	2.79	0.07	0.23	1.13	0.06	0.35	0.06	0.31	0.022	0.007	0.011	0.318	0.500
Al	13.32	1.06	3.74	0.08	0.28	1.68	0.41	0.65	0.25	0.39	0.120	0.251	0.358	2.092	2.983
Si	14.21	1.39	3.32	0.10	0.23	1.41	0.58	0.68	0.41	0.48	0.137	0.175	0.194	1.277	1.416
P	14.95	1.76	5.52	0.12	0.37	1.82	0.19	0.73	0.10	0.40	0.029	0.005	0.012	0.166	0.414
S	18.77	1.14	4.60	0.06	0.25	2.21	0.24	0.49	0.11	0.22	0.121	0.013	0.047	0.107	0.388
K	0.10	0.09	0.18	0.95	1.84	0.10	0.13	0.17	1.31	1.76	0.009	0.019	0.029	2.111	3.222
Ca	0.08	0.09	0.17	1.09	1.98	0.11	0.11	0.20	0.98	1.84	0.026	0.067	0.091	2.577	3.500
Ti	5.77	0.54	1.04	0.09	0.18	1.70	0.08	0.36	0.05	0.21	0.008	0.015	0.017	1.875	2.125
V	1.00	0.10	0.31	0.10	0.31	0.03	0.00	0.01	0.17	0.27	0.001	0.000	0.001	0.000	1.000
Cr	18.99	1.72	5.19	0.09	0.27	1.79	0.14	0.49	0.08	0.28	0.021	0.004	0.008	0.190	0.381
Mn	3.30	0.23	0.97	0.07	0.29	0.98	0.06	0.27	0.06	0.28	0.004	0.004	0.004	1.000	1.000
Fe	9.44	0.75	1.97	0.08	0.21	1.73	2.10	2.10	1.21	1.21	0.125	0.019	0.034	0.152	0.272
Co	15.42	0.67	11.26	0.04	0.73	1.51	1.55	1.69	1.03	1.12	0.005	0.003	0.005	0.600	1.000
Ni	9.60	1.18	2.03	0.12	0.21	1.00	0.13	0.20	0.12	0.20	0.032	0.026	0.027	0.813	0.844
Zn	8.47	0.58	1.96	0.07	0.23	1.33	1.38	1.38	1.04	1.04	0.056	0.049	0.064	0.875	1.143
Ge	16.97	1.15	5.27	0.07	0.31	2.19	0.23	0.59	0.11	0.27	0.002	0.000	0.002	0.000	1.000
As	14.04	0.68	1.77	0.05	0.13	1.46	0.11	0.22	0.07	0.15	0.028	0.002	0.025	0.071	0.893
Se	11.99	0.65	2.70	0.05	0.23	1.46	0.14	0.35	0.10	0.24	0.031	0.076	0.080	2.452	2.581
Zr	6.42	0.48	1.87	0.08	0.29	0.93	0.12	0.28	0.13	0.30	0.003	0.001	0.005	0.333	1.667
Nb	0.02	0.01	0.01	0.56	0.56	0.00	0.00	0.00	0.50	1.00	0.000	0.000	0.000	0.000	0.000
Mo	4.27	10.32	10.55	2.42	2.47	0.43	0.95	0.95	2.18	2.18	0.004	0.001	0.005	0.250	1.250
Ag	10.55	0.43	2.18	0.04	0.21	0.99	0.07	0.19	0.07	0.19	0.061	0.021	0.023	0.344	0.377
Sn	16.79	0.87	10.23	0.05	0.61	1.93	0.30	1.05	0.16	0.54	0.007	0.008	0.014	1.143	2.000
Sb	11.71	0.56	3.35	0.05	0.29	1.17	0.14	0.36	0.12	0.31	0.010	0.002	0.009	0.200	0.900
Te	20.43	1.29	4.90	0.06	0.24	2.05	0.28	0.52	0.14	0.25	0.023	0.024	0.042	1.043	1.826
Au	9.65	0.54	5.34	0.06	0.55	1.39	0.33	0.99	0.24	0.71	0.085	0.138	0.240	1.624	2.824
Pb	11.37	1.13	2.15	0.10	0.19	1.36	0.15	0.28	0.11	0.21	0.012	0.004	0.005	0.333	0.417
Bi	13.28	0.77	5.26	0.06	0.40	1.30	0.11	0.47	0.08	0.36	0.005	0.000	0.003	0.000	0.600
Th	0.005	0.0003	0.0006	0.600	1.200	0.0004	0.0005	0.0005	1.250	1.250	0.0002	0.0003	0.0004	1.500	2.000
U	0.0008	0.0002	0.0007	0.250	0.875	0.0001	0.0000	0.0001	0.000	1.000	0.0000	0.0000	0.0000	0.000	0.000
Total	306					36					4				

[A] Summary of F0-1.17 Cu Round Robin Statistics, per Practice E691, B. Gehman, January 7, 2003.

12.2 Insert the prepared specimen into the GDMS ion source, allow the specimen to cool to source temperature, and initiate the glow discharge at pre-analysis sputtering conditions.

12.3 After at least 5 min of pre-analysis sputtering, adjust the glow discharge ion source sputtering conditions to the conditions required for analysis, ensuring that the gas pressure required to do so is within normal range.

12.4 Analyze the specimen using the DAP protocol, and accept as final the concentration values determined only as detection limits.

12.5 Generate a MDAP (Modified Data Acquisition Protocol) including only the elements determined to be present in the sample (from results of 12.4).

12.6 Measure the sample at least two additional times (with at least 10-min intervals between the measurements) using the MDAP protocol until the criteria of 12.6.1 are met.

12.6.1 If the concentration differences between the last two measurements are less than 5, 10 or 20 %, depending on concentration (Table 3), the measurements are confirmed and the last two measurements are averaged.

12.6.2 If the concentration differences between the last two measurements are greater than 5, 10 or 20 %, depending on concentration (Table 3), the sample is measured again with at least 10 minutes between measurements. The measurements are repeated until the concentration differences between the last two measurements are less than 5, 10 or 20 %, depending on concentration (Table 3). The last two measurements are then averaged.

12.7 The confirmed values from 12.6 and the detection limits determined from 12.4 are reported together as the result of the analysis.

13. Detection Limit Determination

13.1 See Test Method F1593, Section 13 on Detection Limit Determination.

14. Report

14.1 Provide concentration data for the suite of elements listed in Table 1. Additional elements may be listed as agreed upon between all parties concerned with the analysis.

14.2 Element concentration shall be reported, typically, in units of parts per million by weight.

14.3 Numerical results shall be presented using all certain digits plus the first uncertain digit, consistent with the precision of the determination.

14.4 Non-detected elements shall be reported at the detection limit.

14.5 Unmeasured elements shall be designated with an asterisk (*) or other notation.

15. Precision and Bias

15.1 *Round Robin Test Materials :*

15.1.1 Nine laboratories cooperated in testing three different purities of copper. Material A was 6N pure copper doped with 10 ppm wt of each of the following elements; Be, B, Mg, Al, Si, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ge, As, Se, Zr, Nb, Mo, Ag, Sn, Sb, Te, Au, Pb, and Bi. Material B was doped with 1 ppm wt of each of the same doping elements used for Sample A. Material C was undoped 6N pure copper. Mitsubishi Copper in Japan manufactured the doped and undoped test materials. The cast ingots were drawn into 10-m lengths of 3-mm diameter wire. The 10-m wire samples were divided into three equal lengths; the front length, middle length, and end length. Each wire section was subdivided into 10-cm long samples. A test sample was randomly selected from each group of samples cut from the front, middle and end of the ingot-wires and sent to the testing laboratories. Each laboratory received 9 samples for analysis; three from Material A, B, and C.

15.1.2 The analysis tests on the Mitsubishi Copper manufactured material showed that all the doping elements were homogeneously distributed throughout the ingot except for Mo. The results for Mo should be treated with caution due to the sample segregation.

15.2 *Precision*—The results of the round robin interlaboratory test are provided in Table 4. The testing and statistical analyses were performed according to the provisions of Practice E173. Analyses were performed according to the provisions of Practices E173, E180 and E876.

15.3 *Bias:*

15.3.1 Bias was evaluated according to the provisions of 10.4 of Practice E173 by the regression analysis of the analyzed samples versus the sample's certified value.

15.3.2 Since the 95 % confidence limits for *a* include 0 and the 95 % confidence limits for *b* include 1, there is no evidence of overall bias in this test method over the range of values used.

16. Keywords

16.1 copper; electronics; glow discharge mass spectrometer (GDMS); purity analysis; sputtering target; trace metallic impurities

ANNEX

(Mandatory Information)

A1. MASS SPECTRUM INTERFERENCES

A1.1 Ions of the following atoms and molecular combinations of copper, argon plasma gas isotopes, plasma impurities (carbon, hydrogen, oxygen, chlorine), and tantalum source components can significantly interfere with the determination of the ion current of the selected isotopes at low element concentrations.

$^{38}Ar^{++}$ interferes with $^{19}F^{+}$
$^{12}C^{16}O^{+}$ interferes with $^{28}Si^{+}$
$(^{16}O_2)^{+}$ interferes with $^{32}S^{+}$
$^{38}Ar^{1}H^{+}$ interferes with $^{39}K^{+}$
$^{40}Ar^{+}$ scattered ions interfere with $^{39}K^{+}$
$^{12}C^{16}O_2^{+}$ interferes with $^{44}Ca^{+}$
$^{40}Ar^{12}C^{+}$ interferes with $^{52}Cr^{+}$
$^{40}Ar^{16}O^{+}$ interferes with $^{56}Fe^{+}$
$^{40}Ar^{35}Cl^{+}$ interferes with $^{75}As^{+}$
$^{40}Ar^{36}Ar^{1}H^{+}$ interferes with $^{77}Se^{+}$
$^{40}Ar^{38}Ar^{1}H^{+}$ interferes with $^{79}Br^{+}$
$(^{40}Ar_2)^{+}$ scattered ions interfere with $^{79}Br^{+}$
$^{40}Ar^{36}Ar^{38}Ar^{+}$ interferes with $^{114}Cd^{+}$
$^{181}Ta^{16}O^{+}$ interferes with $^{197}Au^{+}$