National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 457

Unalloyed Copper – Cu IV

This Standard Reference Material (SRM) is intended for use in the validation of chemical and instrumental methods of analysis for trace elemental analysis of copper materials. SRM 457 is designed for use with all techniques applicable to elemental analysis of unalloyed copper, and it is particularly well suited for optical emission spectrometric methods of analysis. A unit of SRM 457 consists of a single rod 6.6 mm diameter and 103 mm long.

Certified Mass Fraction Values: Certified mass fraction values are provided in Table 1 [1]. Value assignment categories are based on the definitions of terms and modes used at NIST for certification of chemical reference materials [2]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy, in that all known or suspected sources of bias have been investigated or taken into account. A certified value is the present best estimate of the true value based on the results of analyses performed at NIST and collaborating laboratories.

Reference Mass Fraction Values: Reference mass fraction values are provided in Table 2. Reference values are non-certified values that are the present best estimates of the true values; however, the values do not meet the NIST criteria for certification [2] and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient agreement among multiple analytical methods.

Information Mass Fraction Values: Information values are provided in Table 3. An information value is considered to be a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2].

Expiration of Certification: The certification of **SRM 457** is valid indefinitely, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Use"). Accordingly, periodic recalibration or recertification of this SRM is not required. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this material over the period of its certification. If substantive technical changes occur that affect the certification, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Coordination of technical measurements for the original certification of this SRM was performed by I.L. Barnes of the NIST Chemical Sciences Division. Review and revision of value assignments were performed by J.R. Sieber of the NIST Chemical Sciences Division.

Measurements for value assignment of SRM 457 were performed by I.L. Barnes, R.W. Burke, B.I. Diamondstone, M.G. Diaz, E.L. Garner, L.A. Geldner, J.W. Gramlich, G.J. Lutz, L.A. Machlan, T.J. Murphy, P.J. Paulsen, L.J. Powell, and P.A. Sleeth of the NIST Chemical Sciences Division. Additional measurements were performed by collaborating laboratories: R.K. Bell of ASTM International, Gaithersburg, MD; P.F. Stryker and A.J. Simon, Anaconda Co., Perth Amboy, NJ; A.P. Langheinrich, T.N. Andersen, and N.N. Linde, Kennecott Copper Corp., Magna and Salt Lake City, UT; A.A. DiLeonardi, Kennecott Refining Corp., Baltimore, MD; T.L. Young, S.K. Young, Magma Copper Co., San Manuel, AZ; A.L. Cardinal, Phelps Dodge Refining Corp., El Paso, TX and R. Murray-Smith, Anglo American Corp. of South Africa, Ltd., Johannesburg, South Africa.

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Statistical consultation for this SRM was provided by D.D. Leber of the NIST Statistical Engineering Division.

Coordination of the preparation and fabrication of SRM 457 was performed by J.G. Hust, NIST, Boulder, CO.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

INSTRUCTIONS FOR USE

Prior to using this rod SRM and after any machining, cutting, or drilling operations, the specimen should be etched to remove any contaminated material. Etching may be done by placing the rod in a solution of concentrated nitric acid and water in a 1:1 ratio by volume, and then placing in a solution of concentrated hydrochloric acid and water in a 1:1 ratio by volume. The rod is then rinsed with distilled H_2O, and air-dried on filter paper.

PREPARATION AND ANALYSIS[(1)]

This material is one in a series of 12 different composition copper "Benchmark" materials, Cu "0" through Cu XI, prepared in a cooperative industry, ASTM International and NIST program. The material was supplied by Magma Copper Co. Copper cathodes were melted and continuously cast into a rod of 7.92 mm diameter that was coiled (approximately 320 kg). To form SRM 457, the continuous cast material was machine shaved through silicon carbide dies at the Kagen-Dixon Wire Corp. (Osceola, AK).

Specimens for homogeneity testing of SRM 457 were obtained to be representative of the leading, middle, and trailing sections of the rod stock. These specimens were end-milled to chips and blended. Homogeneity studies were made at NIST using residual resistivity ratio measurements and chemical analysis methods and at Kennecott Refining Corp using optical emission spectrometry. The results indicated the maximum gross material variability to be less than 5 %. Quantitative determinations were performed at NIST and at collaborating laboratories using the test methods listed in Table 4.

Certified Mass Fraction Values: The values for antimony, lead, selenium, silver, and tellurium are the weighted means of the individual sets of measurements made by NIST and collaborating laboratories estimated using a Gaussian random effects model [3] and the DerSimonian-Laird procedure [4,5]. The associated measurement uncertainty was evaluated by the application of the parametric statistical bootstrap, consistent with the ISO Guide and its Supplement 1 [6–9]. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c represents, at the level of one standard deviation, the combined effects of between-laboratory, within-laboratory, and inhomogeneity components of uncertainty. The coverage factor, k, corresponds to an approximately 95 % confidence level.

The value for copper is the mean of the means of the individual sets of measurements made by NIST and one collaborating laboratory. The expanded uncertainty, U, is calculated as $U = ku_c$, where k is the coverage factor and u_c is the combined standard uncertainty, at the level of one standard deviation. The value of u_c is calculated as the standard deviation of the mean for the two mean values. The coverage factor k is Student's t-value corresponding to a 95 % confidence level and one degree of freedom.

Table 1. Certified Mass Fraction Values for SRM 457 Unalloyed Copper – Cu IV

Element	Mass Fraction (mg/kg)	Coverage Factor, k
Antimony (Sb)	0.214 ± 0.059	1.98
Lead (Pb)	0.512 ± 0.058	2.01
Selenium (Se)	4.05 ± 0.15	1.99
Silver (Ag)	8.086 ± 0.037	2.02
Tellurium (Te)	0.296 ± 0.028	2.30

Element	Mass Fraction (%)	Coverage Factor, k
Copper (Cu)	99.97 ± 0.18	12.7

[(1)] Certain commercial equipment, instrumentation, or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Reference Mass Fraction Values: The values in Table 2 were derived from the combination of results provided by NIST and collaborating laboratories. The values for bismuth, iron, oxygen, and sulfur are the weighted means of the individual sets of measurements made by NIST and collaborating laboratories estimated using a Gaussian random effects model [3] and the DerSimonian-Laird procedure [4,5]. Each associated measurement uncertainty was evaluated by the application of the parametric statistical bootstrap, consistent with the ISO Guide and its Supplement 1 [6–9]. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c represents, at the level of one standard deviation, the combined effect of between-laboratory, within-laboratory, and inhomogeneity components of uncertainty. The coverage factor, k, corresponds to an approximately 95 % confidence level for each analyte.

The values for cobalt and nickel are the means of results from a single NIST method. The expanded uncertainty, U, is calculated as $U = ku_c$, where k is the coverage factor and u_c is the combined standard uncertainty, at the level of one standard deviation. The value of u_c is calculated as the standard deviation of the mean of the multiple observations, n (n = 20 for cobalt, n = 6 for nickel). For nickel, the value of u_c is calculated to also account for the combined effects of method blank and method calibration uncertainty. For each analyte, the coverage factor k is Student's t-value corresponding to a 95 % confidence level and $n - 1$ degrees of freedom.

Table 2. Reference Mass Fraction Values for SRM 457 Unalloyed Copper – Cu IV

Element	Mass Fraction (mg/kg)	Coverage Factor, k
Bismuth (Bi)	0.22 ± 0.04	2.01
Cobalt (Co)	0.227 ± 0.008	2.09
Iron (Fe)	2.4 ± 0.4	1.98
Nickel (Ni)	0.67 ± 0.08	2.57
Oxygen (O)	367 ± 29	1.97
Sulfur (S)	4 ± 1	2.03

Information Mass Fraction Values: In Table 3, the values for the listed constituents are for elements present in the material, but at amounts lower than the test methods were able to quantify.

Table 3. Information Mass Fraction Values for SRM 457 Unalloyed Copper – Cu IV

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Arsenic (As)	<2	Silicon (Si)	<1
Cadmium (Cd)	<1	Tin (Sn)	<0.1
Chromium (Cr)	<2	Titanium (Ti)	<1
Gold (Au)	<0.05	Zinc (Zn)	<3
Manganese (Mn)	<0.1		

Table 4. Methods Used for Analysis of SRM 457 Unalloyed Copper – Cu IV

Method	Elements
Isotope dilution thermal ionization mass spectrometry	Ag, Ni, Pb
Instrumental neutron activation analysis	Ag, Co, Sb, Se, Te
Optical emission spectrometry (spark or arc)	As, Au, Bi, Cd, Cr, Fe, Si, Ti
Ultraviolet absorbance spectrometry	As
Spark source mass spectrometry	As, Sn
Graphite furnace atomic absorption spectrometry	Bi, Pb
Flame atomic absorption spectrometry	Cr, Fe, Mn, Sb, Zn
Electrogravimetry	Cu
Combustion	O, S
Isotope dilution spark source mass spectrometry	Se, Te

REFERENCES

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Certificate Revision History: 20 February 2013 (Revised assignments and values for all constituents based on re-evaluation of the original analytical results; editorial changes); 10 April 1986 (Revision of values and uncertainties for selenium and tellurium; editorial changes); 20 January 1978 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730, email srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.