National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 277

Tungsten Concentrate

This Standard Reference Material (SRM) is a tungsten concentrate primarily derived from wolframite ores through commercial refining processes. SRM 277 is intended for use in the validation of chemical and instrumental methods of analysis. A unit of SRM 277 consists of a bottle containing approximately 100 g of powder, of which 100 % passes a sieve size of 0.15 mm.

Certified Mass Fraction Value: A certified value for tungsten expressed as WO_3 on a dry-mass basis in SRM 277 is provided in Table 1 [1]. 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 [2]. 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 values for constituents expressed on a dry-mass basis are provided in Table 2. Reference values are noncertified values that represent the best estimate of the true values based on available data; 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 statistical agreement among multiple analytical methods.

Information Mass Fraction Values: Information values for constituents expressed on a dry-mass basis 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 277** is valid indefinitely, within the measurement uncertainty specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Use"). 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 certification of this SRM was performed by J.I. Shultz of ASTM International. Review and revision of value assignments were performed by J.R. Sieber of the NIST Chemical Sciences Division.

Measurements for value assignment of SRM 277 were performed by E.R. Deardorff and R.E. Michaelis of NIST; J.F.L. Knight, A.H. Knight International, Ltd., Cheshire, UK; R. Peck, Benedict Kitto and Sons, London, UK; J. Rynasiewicz, J.W. Fulton, General Electric Co., Cleveland, OH, US; R. Dyck, J.F. Cosgrove, GTE Sylvania, Towanda, PA and Waltham, MA, US; O. Hilmer, H.C. Starck, Berlin, Germany; S. Kallman, Ledoux & Company, Teaneck, NJ, US; K. Kåårik, Sandvik AB, Stockholm, Sweden; N.R. Sanjana, Sandvik Asia, Ltd.; E.W. Hobart, Spectro Chem Labs, Inc., Franklin Lakes, NJ, US; Z. Otto, Treibacher Chemische Werke, Treibach, Austria; P.J. Walitsky, Westinghouse Electric Co., Bloomfield, NJ, US; E.C. Gibbs, K.M. Wilder, P. Greenberg, Union Carbide Corp., Bishop, CA, US and Niagara Falls, NY, US; and A.J. Leeb, VEW, Ternitz, Austria.

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

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Certificate Revision History on Last Page

Robert L. Watters, Jr., Director
Office of Reference Materials

INSTRUCTIONS FOR USE

The results are based on samples dried for 1 hour at 110 °C. The material should be stored in its tightly capped, original container in a desiccator over desiccant in a cool location. Based on homogeneity testing at NIST, it is recommended to use a minimum of 1 g of material for determinations of WO_3.

NOTICE: The material for this SRM was primarily derived from wolframite ores. It is a mixture of concentrates from China, Thailand, and the USA that contain Nb, Sn, Ta, and Ti in amounts not normally encountered in most wolframite concentrates. These constituents may interfere in classical chemical methods and may necessitate appropriate changes in methodology. X-ray fluorescence methods of analysis that use SRM 277 to make relative measurements of "pure" wolframite (or scheelite) concentrates may exhibit systematic errors as a result of the unusual constituents of this concentrate.

SOURCE, PREPARATION, AND ANALYSIS[(1)]

The material for SRM 277 was provided to NIST by J. Demangone, GTE Sylvania, Towanda, PA, US. At GTE Sylvania, the material was crushed and ground to a fine powder. At NIST, the material was sieved to pass a 0.15 mm sieve opening and thoroughly blended. Homogeneity testing of selected samples representative of the lot of SRM 277 was performed at NIST using X-ray fluorescence spectrometry. Quantitative determinations were performed at NIST and at collaborating laboratories using the test methods listed in Table 4.

Certified Mass Fraction Value: The value for WO_3 in Table 1 was derived from the combination of results provided by NIST and collaborating laboratories. The value is the weighted mean 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 [6,7]. The uncertainty is expressed as an expanded uncertainty, U, represented as $U = ku_c$, where u_c is intended to represent, 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.

Table 1. Certified Mass Fraction Value (Dry-Mass Basis) for SRM 277

Constituent	Mass Fraction (%)	Coverage Factor, k
WO_3	67.50 ± 0.13	2.00

Reference Mass Fraction Values: The values in Table 2 were derived from the combination of results provided by NIST and collaborating laboratories. Except for Ca, Fe, and Mn, the values 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 [6,7]. The uncertainty is expressed as an expanded uncertainty, U, represented as $U = ku_c$, where u_c is intended to represent, 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 Ca, Fe, and Mn are the mean of the mean values from multiple collaborating lab/method combinations. The associated uncertainty is expressed as an expanded uncertainty, U, 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 sample standard deviation of the multiple mean values divided by the square root of the number of lab/method combinations, n (in these cases $n = 2$). The value of k controls the level of confidence associated with U, which, for this SRM, is approximately 95 %. The value of k is $t_{0.975,n-1}$, the $1 - \alpha / 2 = 0.975$ quantile value of the Student's t-distribution with $\nu = n - 1$ degrees of freedom, and is indicated in the table.

[(1)]Certain commercial equipment, instruments 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.

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) for SRM 277

Constituent	Mass Fraction (%)	Coverage Factor, k
As	0.0120 ± 0.0076	2.01
Ca	0.38 ± 0.22	12.7
Fe	7.47 ± 0.92	12.7
Mn	10.2 ± 1.7	12.7
Mo	0.0598 ± 0.043	1.98
Nb	1.018 ± 0.078	2.40
O	22.0 ± 1.3	1.99
P	0.034 ± 0.018	1.98
Pb	0.0676 ± 0.0086	2.37
S	0.2668 ± 0.0092	1.87
Si	0.842 ± 0.032	2.00
Sn	0.53 ± 0.14	2.00
Ti	2.20 ± 0.38	2.01

Information Mass Fraction Values: In Table 3, the values for Bi, Cu, and Ta are the weighted means of the individual sets of measurements made by collaborating laboratories estimated using a Gaussian random effects model [3] and the DerSimonian-Laird procedure [4,5]. Because the biases among laboratories and methods are high, the estimated uncertainties were too great to be useful and are not reported. Values for antimony and zirconium are intended to indicate that the two elements are present in the material, but at amounts lower than the test methods were able to quantify.

Table 3. Information Mass Fraction Values (Dry-Mass Basis) for SRM 277

Constituent	Mass Fraction (%)	Constituent	Mass Fraction (%)
Bi	0.05	Cu	0.014
Sb	< 0.01	Ta	0.14
Zr	< 0.8		

Table 4. Methods Used for Analysis of SRM 277

Element	Methods[(a)]	Element	Methods[(a)]
As	1, 2	Pb	1, 3
Bi	1, 3	S	12
Ca	1, 3	Sb	1, 2
Cu	1, 3	Si	1, 9
Fe	4, 5	Sn	1, 5
Mn	6	Ta	5, 14
Mo	1, 3, 5, 7	Ti	1, 15
Nb	5, 8, 9	WO_3	5, 16, 17, 18, 19
O	10, 11	Zr	1
P	2		

[(a)]Key to Methods in Table 4:

1. Optical emission spectrometry
2. Molybdenum blue photometric method
3. Flame atomic absorption spectrometry
4. Reduction and CrO_4^- titration
5. X-ray fluorescence spectrometry
6. Reduction and titration
7. Na_2O_2 fusion, thiocyanate complexation, and photometric measurement
8. Photometric method with hydroquinone
9. Gravimetric method
10. Inert gas fusion and chromatographic measurement of CO_2
11. Neutron activation analysis
12. Combustion and iodometric titration
13. Spark source mass spectrometry
14. Photometric method with benzene-1,2,3-triol (pyrogallol)
15. Photometric method with H_2O_2
16. $HgWO_3$ gravimetric method
17. Gravimetric method using cinchonine
18. Gravimetric method using *pp*-tetramethyl-diamoni-diphenyl methane
19. Gravimetric method using nemadine

REFERENCES

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[7] JCGM 101:2008; *Evaluation of Measurement Data – Supplement 1 to the "Guide to the Expression of Uncertainty in Measurement" - Propagation of Distributions Using a Monte Carlo Method*; JCGM (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed Jan 2013).

Certificate Revision History: 18 January 2013 (Updated assignments and mass fraction values for all listed constituents; editorial changes); 24 October 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; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.