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Standard Test Method for Determination of Metallic Constituents of Tungsten Alloys and Tungsten Hardmetals by X-Ray Fluorescence Spectrometry¹

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1. Scope

1.1 This test method describes a procedure for the determination of the concentration, generally reported as mass percent, of the metallic constituents of tungsten-based alloys and hardmetals utilizing wavelength dispersive X-ray fluorescence spectrometry (XRF). This test method incorporates the preparation of standards using reagent grade metallic oxides, lithium-borate compounds, and fusion techniques. This test method details techniques for preparing representative specimens of both powder and sintered tungsten-based material. This test method is accurate for a wide range of compositions, and can be used for acceptance of material to grade specifications.

1.2 This test method is applicable to mixtures of tungsten or tungsten carbide with additions of refractory metal carbides and binder metals. Table 1 lists the most common elemental constituents and their concentration range. Note that many of these occur as metallic carbides.

1.3 *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 1361 Guide for Correction of Inter-element Effects in X-Ray Spectrometric Analysis³

2.2 ISO Standard:

ISO-4503(E) Hardmetal—Determination of contents of metallic elements by X-ray fluorescence - Fusion method⁴

2.3 *Handbook of Chemistry and Physics*,⁵ 67th ed

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E 135.

4. Summary of Test Method

4.1 A suite of standards which closely match the chemical content of the material to be analyzed are prepared using reagent grade metallic oxides. Test samples are oxidized in a high-temperature furnace open to air. Fused glass specimens are prepared for these standards and for the test samples to be analyzed. These specimens of oxidized tungsten or tungsten carbide alloys are irradiated with an energetic primary X-ray beam. The intensity of the resultant secondary X-rays, characteristic in energy, for each elemental constituent is measured by means of a suitable detector or combination of detectors after diffraction by a Bragg spectrometer. The concentration of each constituent element is calculated by comparison with standard samples which closely match the chemical content of the analyzed material. The calculation may be manual, incorporate a calibration curve, or be

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

³ *Annual Book of ASTM Standards*, Vol 03.06.

⁴ Available from American National Standards Institute, 11 West 42nd St., 13th Floor, New York, NY 10036.

⁵ CRC Press, Boca Raton, FL, 1987.

TABLE 1 Elemental Constituents and Concentration Range

Element	Concentration, Mass % (minimum - maximum)
Chromium (Cr)	0.05 - 5.0
Cobalt (Co)	0.05 - 40
Hafnium (Hf)	0.05 - 2.0
Iron (Fe)	0.05 - 2.0
Molybdenum (Fe)	0.05 - 5.0
Molybdenum (Mo)	0.05 - 5.0
Nickel (Ni)	0.05 - 30
Niobium (Nb)	0.05 - 15
Tantalum (Ta)	0.05 - 30
Titanium (Ti)	0.05 - 30
Vanadium (V)	0.05 - 2.0

performed by a computer program which incorporates correction routines for X-ray absorption and enhancement effects (see Guide E 1361).

5. Significance and Use

5.1 This test method allows the determination of the chemical composition of powdered and sintered tungsten-based hardmetals. This test method is not applicable to material which will not oxidize readily at high temperatures in air, such as tungsten/copper or tungsten/silver alloys.

5.2 This test method specified lithium-borate compounds for the glass fusion material. However, numerous other choices are available. These include other lithium-borate compounds, sodium carbonate and borate mixtures, and others. The methodology specified here is still applicable as long as the same fusion mixture is used for both standards and specimens.

6. Interferences

6.1 Errors in XRF-determined compositional values may be encountered due to X-ray enhancement and absorption effects dependent on the elements present and the X-ray line being measured for a specific element. This effect can be reduced by determination of correction factors using appropriate standards and interelement correction routines, manual or computerized.

6.2 Accuracy and precision of the analytical results obtained from molybdenum-containing samples may be rendered unreliable due to the sublimation and evaporation of molybdenum from the material during the oxidation step in specimen preparation.

6.3 Incorporation of the fusion method of specimen preparation will:

6.3.1 Reduce the deleterious influence of particle size effects experienced when analyzing powder materials by varying particle size.

6.3.2 Reduce inhomogenities within a sample.

6.3.3 Improve penetration of X rays.

6.3.4 Reduce interelement interferences by tungsten on all other elements.

7. Apparatus

7.1 *X-Ray Fluorescence Wavelength Spectrometer*

7.2 *Fluxer*—An automated high-temperature mixing device capable of melting, mixing, and pouring a molten liquid specimen into a proper casting dish, is highly preferred:

7.3 *Analytical Balance*, readability of 0.00001-g-g

7.4 *Toploading Balance*, readability of 0.001-g-g

7.5 *Ordinary Laboratory Apparatus*.

7.6 *One Pt - 5 % Au Casting Dish* (minimum)

7.7 *One Pt - 5 % Au Crucible* (minimum)

7.8 *Platinum Tipped Tongs*:-

7.9 *Weighing Paper*:-

7.10 *Chemical Spoon and Scoopula*:-

7.11 *Ceramic Combustion Boat*:-

7.12 *High Temperature Tube or Muffle Furnace*, open to the atmosphere:-

7.13 *Self-adhering Stickers*, ¾ by 1 in.

7.14 *High-Temperature marking pen*

7.15 *Ceramic Mortar and Pestle*:-

7.16 *Miniature Mixer*:-, optional:-

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specification of the Committee on Analytical Reagents of the American Chemical Society where such

specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Di-lithiumtetraborate* ($\text{Li}_2\text{B}_4\text{O}_7$):*Lithiummetaborate* (LiBO_2), 66 + 34.

8.3 *Lithium Bromide*(LiBr).

8.4 *Metallic Oxide Powder*, highest oxidation state for elements of interest; that is Co_3O_4 , Cr_2O_3 , Fe_3O_4 , HfO_2 , MoO_3 , Nb_2O_5 , NiO , Ta_2O_5 , TiO_2 , V_2O_5 , and WO_3

Warning—Several of the metallic oxides used in this test method are highly toxic and possibly carcinogenic, such as Cr_2O_3 , NiO , or V_2O_5 . Extreme care should be used at all times when handling this material (especially V_2O_5). All mixing of standards should be performed in a fume hood. All of the lithium compounds are water-soluble and therefore able to be absorbed into the body by inhalation and possibly by absorption through the skin. This material should be weighed in a fume hood.

8.5 *Nitric Acid* (HNO_3).

9. Specimen Preparation

9.1 Prepare specimens of the material to be analyzed by oxidizing, weighing, and fusing starting powders, chips, or crushed sintered hard metal samples.

9.2 Place 3 to 5 g of powdered specimen in a labeled ceramic combustion boat. If a sintered sample is to be analyzed, then the sample must be crushed or pulverized into small pieces or chips must be produced by machining prior to placement in the combustion boat.

9.3 Oxidize the specimen in the heat zone of a high-temperature tube or muffle furnace open to the atmosphere at $825 \pm 25^\circ\text{C}$. All specimens must be oxidized.

9.4 When the specimen has been completely oxidized (4 to 6 h), remove from the furnace and allow to cool.

NOTE 1—Complete oxidation of a sintered magnetic tungsten hard metal sample can be checked by testing the cool oxidized chips with a magnet. If any of the chips are still magnetic, recrush the sample and place back in the furnace for further oxidation.

9.5 Pour the specimen onto a clean sheet of paper or into a clean mortar and gently crush with a pestle.

9.6 Transfer the specimen to a labeled specimen vial.

9.7 In a fume hood, weigh out 15.000 ± 0.001 g of the di-lithium tetraborate: lithiummetaborate mixture and 0.200 ± 0.001 g of LiBr and transfer to a clean sample vial. This mixture will be referred to as the “fusion mixture.” Seal and store until needed.

NOTE 2—Other fusion materials can be used. See 5.2.

9.8 In a fume hood, transfer the fusion mixture to a platinum crucible immediately prior to weighing of the oxidized sample material.

9.9 Weigh out 1.0000 ± 0.00005 g of oxidized specimen and transfer to the platinum crucible. Mix gently with the fusion mixture.

NOTE 3—If there is not enough sample to make a standard fusion, proportionate amounts of oxidized test sample and fusion mixture can be utilized to prepare a specimen recognizing that larger fractional errors may be incurred in the analysis. This should only be used when absolutely necessary.

9.10 Using the fluxer, melt the specimen at $1300 \pm 100^\circ\text{C}$ and cast into a heated platinum casting dish.

9.10.1 Warning—The process of making glass fusions exposes personnel to high-temperature liquids. Extreme care should be exercised while preparing these samples. These high temperatures also cause some volatilization of the lithium compounds. The fluxer should have an exhaust hood to remove these gases from the facility. The lithium compounds used in this procedure are hygroscopic. Material open to the atmosphere for an extended period of time will pick up moisture. Exposure of this material to subsequent high heat will cause rapid formation of steam and may cause spattering of the molten glass onto the instrument and possibly the operator.

9.11 While the fused specimen is cooling, remove the crucible from the instrument with the platinum-tipped tongs and cool under a stream of water.

9.12 Place the crucible in a 1000-mL beaker which has a 10-volume percent solution of nitric acid. Put the beaker on a hot plate and warm the solution. The crucible should be clean in approximately 30 min. Remove the crucible from the acid bath with tongs and rinse with water. Dry the crucible and store.

9.13 When the fused specimen is cool, remove from the casting dish by gripping the dish firmly with tongs, turning the dish over, and gently tapping against a clean paper. The dish and fused specimen should cleanly separate. Label the fused specimen with a self-adhering tag.

NOTE 4—Any evidence of wetting between the specimen and the platinum crucible or casting dish is an indication that the specimen has reacted with these vessels and is not a valid representative sample.

9.14 If the fusion crystallizes or fractures on cooling, crush the fusion and recast. If the fused specimen cannot be removed from the platinum casting dish with very light tapping, dissolve the specimen from the dish using a warm 10-volume percent nitric acid

⁶ *Reagent Chemicals, American Chemical Society Specification*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockvale, MD.

solution. Prepare a new specimen in accordance with 9.7-9.10.

Caution—Excessive prying or tapping of the crystallized specimen while it is in the dish will damage the platinum ware.

10. Standardization of Spectrometer and Analysis

10.1 Based on the X-ray spectrometer configuration and instrument manufacturer's operating instructions, determine the instrument operating parameters to provide optimum spectral analysis for each element being analyzed in a given matrix. Table 2 provides the approximate X-ray peak positions (Bragg angle - 2Θ) and crystals recommended for each of the elements of interest.

10.2 If required, normalize the X-ray spectrometer operating parameters to obtain the appropriate secondary x-ray intensities from the reference standards utilized.

10.3 Measure X-ray intensities on a sufficient number of fused standards to establish a calibration curve (intensity versus concentration of analyte) for each element of interest.

NOTE 5—The number of standards sufficient to establish a calibration curve is dependent on the range of concentrations to be analyzed for each element. In all cases, a minimum of ~~three~~ six standards is required.

10.4 Calibration curves may be established manually, or corrections for interelement effects may be calculated using XRF vendor-supplied computer software.

NOTE 6—Accuracy of a given interelement correction routine can be verified by including one or more reference standards as "blind" unknowns as part of an analysis.

11. Procedure

11.1 Obtain X-ray intensity data from the fused test specimens.

11.2 Calculate relative concentrations utilizing appropriate calibration curves and absorption and enhancement correction routines, if available.

12. Report

12.1 Report the results of the analysis as mass percent of the metallic or carbide constituent. Report average values of replicate determinations, either measurements or samples, if performed, along with the concentration range. The correction routine employed to determine final concentration values should also be specified by the party completing the analysis, if required.

12.2 The parties involved may require reporting of the actual X-ray spectrometer operating parameters employed for each element of interest. These typically include:

- 12.2.1 Specimen form,
- 12.2.2 X-ray source type,
- 12.2.3 X-ray tube operating conditions, kV and mA,
- 12.2.4 X-ray line analyzed,
- 12.2.5 Diffracting crystal,
- 12.2.6 Type of detector, and
- 12.2.7 X-ray path whether vacuum, air, or inert gas.

13. Precision and Bias

13.1 *Precision*—The repeatability standard deviation of major constituents has been determined to be <0.25 % of the relative concentration of the analyte. The repeatability standard deviation for minor constituents has been determined to be ≤ 3.35 % of the relative concentration of the analyte. The 95 % repeatability limits for major constituents is 0.7 % of the relative concentration of the analyte. The 95 % repeatability limits for minor constituents is 9.4 % of the relative concentration of the analyte. The reproducibility is being determined.

13.2 *Bias*—No information can be presented on the bias in this test method because no material having an accepted reference value is available.

TABLE 2 Analytical X-ray Lines

Element Symbol	Shell Series	Reflection Order	Bragg Angle 2Θ	Wavelength, A	Crystal
Co	K α	1	52.788	1.7906	LiF100
Cr	K α	1	69.368	2.2913	LiF100
Fe	K α	1	57.526	1.9376	LiF100
Hf	K α	1	45.880	1.5690	LiF100
Mo	K α	1	20.276	0.7092	LiF100
Nb	K α	1	21.340	0.7461	LiF100
Ni	K α	1	48.632	1.6594	LiF100
Ta	K α	1	44.384	1.5222	LiF100
Ti	K α	1	86.186	2.7502	LiF100
V	K α	1	123.172	2.5054	LiF110

14. Keywords

14.1 absorption and enhancement effects; fusion; interelement effects; tungsten alloys; tungsten carbides; tungsten hardmetals; X-ray fluorescence spectrometry

ANNEX

(Mandatory Information)

A1. PREPARATION OF FUSED MATCHED STANDARDS

A1.1 Determine the composition of the reference standard required for calibration of the spectrometer. Using the conversion factors listed in Table A1.1, convert the mass percent of metallic carbides or elements to their oxide mass percent for each of the reference standards. A minimum of six standards with matrices which cover the concentration range of the material to be measured is required for accurate determination of constituents. A reference standard may also be required for periodic monitoring of the X-ray spectrometer to correct for instrument drift. This test method should contain all elements of interest.

A1.2 Using an analytical balance, weigh out each of the required metallic oxides to ± 0.00005 g and combine into one container.

A1.3 Mix this material using a miniature laboratory mixer or a mortar and pestle to obtain a homogeneous mixture of components.

A1.4 Make three fusion specimens of each standard in accordance with 9.7-9.10.

A1.5 Crush all three specimens of each standard and blend together to form a homogenous mixture.

A1.6 Weigh out approximately 16 g of this mixture and recast.

TABLE A1.1 Conversion Factors for Carbides, Oxides, and Elements

Material	Density ^A	Molecular Mass ^A	Conversion Carbide→ Element	Conversion Element→ Oxide
W	19.35	183.85		
WC	15.63	195.86	WC%·(0.938676)	
WO ₃	7.16	231.85		W%·(1.261073)
Co	8.85	58.93		
Co ₃ O ₄	6.07	240.80		Co%·(1.361990)
Ti	4.50	47.90		
TiC	4.93	59.89	TiC%·(0.799519)	
TiO ₂	4.26	79.88		Ti%·(1.667641)
Ta	16.60	180.95		
TaC	14.53	192.96	TaC%·(0.937754)	
Ta ₂ O ₅	8.20	441.89		Ta%·(1.221042)
Nb	8.57	92.91		
NbC	7.85	104.92	NbC%·(0.885520)	
Nb ₂ O ₅	4.47	265.81		Nb%·(1.430526)
Ni	8.90	58.69		
NiO	6.67	74.69		Ni%·(1.272402)
Fe	7.86	55.85		
Fe ₃ O ₄	5.18	231.54		Fe%·(1.381990)
Cr	7.19	52.00		
Cr ₃ C ₂	6.68	180.01	Cr ₃ C ₂ %·(0.866552)	
Cr ₂ O ₃	5.21	151.99		Cr%·(1.460000)
Hf	13.31	178.49		
HfC	12.20	190.50	HfC%·(0.936951)	
HfO ₂	9.68	210.49		Hf%·(1.179282)
V	5.96	50.94		
VC	5.77	62.95	VC%·(0.809205)	
V ₂ O ₅	3.36	181.88		V%·(1.785190)
Mo	10.20	95.94		
Mo ₂ C	8.90	203.89	Mo ₂ C%·(0.941091)	
MoC	8.20	107.95	MoC% (0.888740)	
MoO ₃	4.69	143.94		Mo%·(1.500300)

^AHandbook of Chemistry and Physics, 67th ed, CRC Press, Boca Raton, FL, 1987.

A1.7 Label each fusion sample with a suitable sticker.

NOTE A1.1—Maintain standards in a desiccator while not in use. If devitrification of the fusion occurs, crush and recast in accordance with 9.10.

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