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Standard Test Method for Determination of Metallic Constituents of Tungsten Alloys and Tungsten Hardmetals by X-Ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation B890; 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 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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis

~~2.2 *Handbook of Chemistry and Physics,*[3] 67th ed~~

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E135.

[1] This test method is under the jurisdiction of ASTM Committee B09 on Metal Powders and Metal Powder Products and is the direct responsibility of Subcommittee B09.06 on Cemented Carbides.

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[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.

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 (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

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 performed by a computer program which incorporates correction routines for X-ray absorption and enhancement effects (see Guide E1361).

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~~tungsten/copper, tungsten/silver alloys, or tungsten/cobalt-ruthenium 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 inhomogenieties within a sample.

6.3.3 Improve penetration of X rays.

6.3.4 Reduce interelement ~~interferences by tungsten on all other elements.~~interferences.

7. Apparatus

7.1 *X-Ray Fluorescence Wavelength Dispersive ~~Spectrometer~~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~~preferred.

7.3 *Analytical Balance,* readability of ~~0.00001 g~~0.0001 g.

7.4 *Toploading Balance,* readability of 0.001 ~~g~~g.

7.5 *Ordinary Laboratory ~~Apparatus .~~Apparatus.*

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

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

7.8 *Platinum Tipped ~~Tongs~~Tongs.*

7.9 *Weighing ~~Paper~~Paper.*

7.10 *Chemical Spoon and ~~Scoopula~~Scoopula.*

7.11 *Ceramic or Quartz Combustion ~~Boat~~Boat.*

7.12 *High Temperature Tube or Muffle Furnace,* open to the ~~atmosphere~~atmosphere.

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

~~7.14 *High-Temperature marking pen*~~

7.14 *Ceramic Mortar and ~~Pestle~~Pestle.*

7.15 *Tungsten Carbide Mortar and ~~Pestle~~Pestle.*

7.16 *Miniature Mixer,* ~~optional~~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.[3] 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* ($Li_2B_4O_7$):*Lithiummetaborate* ($LiBO_2$), 66 + ~~34.~~34 by mass percentage.

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

[3] *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 Formulatory*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockvale, MD.

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 *Citric Acid* (HO·C(COOH)(CH_2·COOH)$_2$~~.~~, used for cleaning purposes only.

~~8.6 *Silicic Acid* (SiO_2·x$H_2$0).~~

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. To crush or pulverize a sample, a tungsten carbide mortar and pestle should be used to reduce the incidence of contamination.

9.3 Oxidize the specimen in the heat zone of a high-temperature tube or muffle furnace open to the atmosphere at 825 ± ~~25°C.~~25 °C. All specimens must be fully 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~~sample is 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 dilithium tetraborate: lithiummetaborate mixture, 1.5 ± 0.001 g of the silicic acid, 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.~~Prepare a fusion mixture to be used with the oxidized samples. For example, a mixture of dilithium tetraborate: lithium metaborate with a 0.2 g addition of lithium bromide can be used. The mixture should be used the day it is made. Unused portions can be stored in an air tight container or dessicator.

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~~0.0005 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, or the amount of the total mixture is too large for the casting dish, 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 ± 100°C~~ the lowest temperature required for dissolution of the sample by the fusion mixture used 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 absorb 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.~~cool.

9.12 Place the crucible in a ~~1000-mL~~1000 mL beaker which has a 2-volume percent solution of citric 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 (cooling slowly) or fractures ~~on cooling,~~(cooling fast), 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 2-volume percent citric acid 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~~ typically used 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~~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 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.

TABLE 2 Analytical X-ray Lines

Element Symbol	Shell Series	Reflection Order	Bragg Angle 2Θ	Wavelength, A	Crystal
Co	Kα	1	52.788	1.7906	LiF100
Cr	Kα	1	69.368	2.2913	LiF100
Fe	Kα	1	57.526	1.9376	LiF100
Hf	Lα	1	45.880	1.5690	LiF100
Mo	Kα	1	20.276	0.7092	LiF100
Nb	Kα	1	21.340	0.7461	LiF100
Ni	Kα	1	48.632	1.6594	LiF100
Ta	Lα	1	64.640	1.5222	LiF110
Ti	Kα	1	86.186	2.7502	LiF100
V	Kα	1	123.172	2.5054	LiF110