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Standard Guide for Spectrometric Analysis of Reactive and Refractory Metals¹

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1. Scope

1.1 This guide covers a variety of analytical techniques that have proven to be acceptable for the analysis of the reactive and refractory metals titanium, zirconium, niobium, hafnium, tantalum, molybdenum, tungsten, and vanadium.

1.2 The principles and techniques in this guide can be used by ISO 17025 compliant laboratories that need to implement other performance-based test methods or need to document and validate extensions of standard test methods, or non-standard test methods.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

D1193 Specification for Reagent Water

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

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

E539 Test Method for X-Ray Fluorescence Spectrometric Analysis of 6Al-4V Titanium Alloy

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1097 Guide for Direct Current Plasma-Atomic Emission Spectrometry Analysis

E1184 Practice for Electrothermal (Graphite Furnace) Atomic Absorption Analysis

E1479 Practice for Describing and Specifying Inductively-Coupled Plasma Atomic Emission Spectrometers

E1552 Test Method for Determining Hafnium in Zirconium and Zirconium Alloys By Direct Current Plasma—Atomic Emission Spectrometry

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1621 Guide for X-Ray Emission Spectrometric Analysis

E1770 Practice for Optimization of Electrothermal Atomic Absorption Spectrometric Equipment

E2371 Test Method for Analysis of Titanium and Titanium Alloys by Atomic Emission Plasma Spectrometry

E2437 Practice for Designing and Validating Performance-Based Test Methods for the Analysis of Metals, Ores, and Related Materials

E2438 Practice for Implementing Standard Performance Based Test Methods for the Analysis of Metals, Ores, and Related Materials

2.2 ISO Standards:³

ISO 17025 General Requirements for the Competence of Testing and Calibration Laboratories

ISO Guide 32 Calibration in Analytical Chemistry and Use of Certified Reference Materials

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, refer to Terminology E135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *reactive metal, n*—a metal, such as titanium or zirconium, that readily reacts with the environment. It has a strong affinity for oxygen and nitrogen and forms very stable compounds that passivate in thin layers. When the reactive coating is damaged, it self heals by reaction with the atmosphere.

3.2.2 *refractory metal, n*—a metal, such as hafnium, molybdenum, niobium, tantalum, vanadium, or tungsten, characterized by very high melting points, above about 1900 °C, that oxidizes at temperatures far below its melting point.

4. Significance and Use

4.1 Test methods for chemical analysis of reactive and refractory metals are primarily intended to test such materials

¹ This guide is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.06 on Ti, Zr, W, Mo, Ta, Nb, Hf, Re.

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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.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

for compliance with compositional specifications. It is assumed that all who use this guide will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory under appropriate quality control practices such as those described in Guide E882 and Practice E2437, as well as in ISO 17025 and ISO Guide 32.

4.2 This guide is intended to aid analytical chemistry laboratories in the analysis of reactive and refractory metals and their alloys when no specific standard test methods are available. The principles incorporated in this practice can also be applied in laboratories that wish to validate and document non-standard test methods.

4.3 The analysis of reactive and refractory materials is typically performed by only a small number of laboratories. Few of these laboratories have analytical instrumentation in common for use in interlaboratory proficiency testing programs. This requires the use of within-laboratory developed test methods that vary between laboratories. It is intended that this practice will give general guidance to experienced personnel that will assist them in the development of a procedure that will meet their analytical objectives.

4.4 Practice E2438 provides guidance for the development and documentation of an In-House Standard Operating Procedure (SOP).

5. Hazards

5.1 The dissolution of these metals usually requires the use of hydrofluoric acid. Read and follow label precautions and mandatory safety data sheet (MSDS) information, and refer to Practices E50.

5.2 Fine turnings, chips, or powder require more water to moderate the reaction rate. If the metal is solid chunks rather than finely divided, the dissolution will be much slower and require less water. It will also require additional acid to complete the dissolution. See Specification D1193 for reagent water specifications.

5.3 Fine turnings or powder of hafnium, titanium, and zirconium are pyrophoric. Observe the proper precautions.

6. Test Methods

6.1 *Atomic Absorption Spectrometry (AAS)*—This technique is applicable to elements that can be dissolved and placed in the vapor state (flame or flameless) as ground state atoms. Radiation from a hollow cathode light source emits the spectrum of the element to be analyzed, which is then passed through vapor containing the element to be analyzed, and into a monochromator set for radiation characteristic of the element. The degree of absorption is measured, and is proportional to the amount of the particular element present. Analysis is made by comparison to reference materials. Lists of elements that can be determined, sensitivities, wavelengths, and operating parameters are provided by the instrument manufacturers. Due to the requirements of the materials specifications, the AAS detection limits for many elements will not be low enough for the use of this technique. AAS has been utilized for the analysis of iron, chromium, nickel, and tin in zirconium alloys and for the determination of iron and zirconium in hafnium. Practices E1184 and E1770 provide further details.

6.2 *Atomic Emission Spectrometry (AES)*—This technique has historically been the main means of analysis for these metals. Analysis by the techniques described in this section is based upon the fact that each vaporized element, when suitably excited by an arc, spark, plasma, or other means, is made to emit its characteristic spectrum. The radiation thus emitted passes into a spectrometer where it is resolved into its component wavelengths and recorded by various means as a definite pattern. The position of the spectral information indicates QUALITATIVELY which elements are present. The intensity determines QUANTITATIVELY the amount of each element in the sample when compared to intensities obtained by using calibration materials. Calibration materials can be reference materials or industry acceptable analyzed specimens.

6.2.1 *Arc/Spark Spectrometry (AS-AES)*—Instruments utilizing photographic film or plates were the mainstay for many years until parts and supplies became very difficult, if not impossible, to obtain. Electronic read-out arc/spark instruments are still used by a number of laboratories. The primary problem with arc/spark is the unavailability of solid reference materials for calibration. Metallurgical history and surface grain size effects can become an issue. However, if proper calibration materials were available, the majority of the necessary elements in a typical material specification could be analyzed.

6.2.2 *Direct Current Plasma Atomic Emission Spectrometry (DCP-AES)*—Since DCP-AES analysis, like atomic absorption, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (see 6.2.3), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (see 6.2.4), relies on sample dissolution, the major difficulties with reference materials for calibration with can be overcome by the techniques discussed in 9.4. One of the main positive attributes of this technique is the high resolution available due to the Echelle grating. The highly complex spectra of reactive and refractory metals require an instrument with good spectral resolving power in order to find interference-free wavelengths. The DCP-AES has a rugged sample introduction system that lends itself well to the analysis of materials that have been dissolved in acids such as hydrofluoric, nitric, and hydrochloric acids. In most cases, due to the nature of the source design, the DCP-AES does not achieve the detection limits or the precision of an Inductively Coupled Plasma (ICP) source. In some cases, however, its significantly superior resolving power may allow it to outperform an ICP that utilizes a conventional ruled grating. The corrosion resistant nature of the sample introduction system and jet materials on DCP-AES has allowed it to be very capable for the analysis of silicon in a hydrofluoric acid solution. DCP-AES is unable to achieve the necessary detection limits for elements such as boron and cadmium in a zirconium sample at the levels required by most specifications. Test Method E1552 gives details for the analysis of hafnium in zirconium and zirconium alloys using the DCP-AES technique and Test Method E2371 describes the analysis of titanium and titanium alloys. Guide E1097 discusses the technique in more general terms.

6.2.3 *Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)*—Practice E1479 describes the components of an ICP-AES that are basic to its operation and to the

quality of its performance. ICP-AES and ICP-MS represent the instruments most commonly used for the analysis of reactive and refractory metals. These solution-based techniques complement each other to provide a reliable means of analysis of reactive and refractory metals. Care must always be taken to avoid serious spectral interferences due to the line-rich nature of reactive and refractory metals. The advent of solid-state detectors has provided much flexibility in the selection of wavelengths. Section 8.3 gives guidance in wavelength selection. Test Method E2371 gives details for the analysis of titanium and titanium alloys, while Practice E1479 discusses the techniques in more general terms.

6.2.4 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)—This technique is distinguished from ICP-AES by the detection system used to analyze the species excited by a plasma. A mass spectrometer is utilized in this case. Much of the information in Practice E1479 is applicable to ICP-MS. This technique is capable of analyzing the majority of the metal elements necessary to satisfy the material specifications for reactive and refractory metals. The high sensitivity of ICP-MS may require significant dilution of the sample solution in order to analyze elements at concentrations above 0.1 %, by mass.

6.3 Glow Discharge Spectrometry—The issue mentioned above in securing solid reference materials is a concern that must be addressed with this technique. Glow Discharge instrumentation is normally divided into two types of instrumentation.

6.3.1 Glow Discharge-Mass Spectrometry (GD-MS)—In this technique, the surface of a solid sample is sputtered with argon gas. Ionized species are then subjected to high-resolution mass spectrometric analysis. This results in the high sensitivity analysis of all elements in the periodic table, except hydrogen at the trace level. GD-MS has been used for the multi-element survey analysis for these metals included in the scope of this guide. Care must be taken in the interpretation of the results, however, due to the non-homogeneity of the sample surface. Reactive and refractory metals typically exhibit a relatively large grain size compared to the small area sampled by the conventional “pin” sample used by the GD-MS. It is also possible to sample a flat surface, which may help alleviate the grain size problem. One should keep in mind that only a few hundred micrograms of material are sampled, which underscores the importance of homogeneity. Due to the high cost and complexity of the instrumentation, GD-MS is found in very few captive laboratories. Commercial analysis is available through a limited number of laboratories.

6.3.2 Glow Discharge Atomic Emission Spectrometry (GD-AES)—The glow discharge excitation source is a device that produces luminous plasma. Solid samples are sputtered using the low-pressure argon plasma. The argon ions etch atoms and small atomic clusters from the sample surface making them available for dissociation and excitation in the plasma. Metallurgical history is reduced because sampling and excitation take place in separate locations. Calibration requires the use of reference materials and where available it is possible to determine the alloying and minor constituents simultaneously.

6.4 X-ray Emission Spectrometry (XRF)—See Guide E1621 for details of the instrumentation. Again, the requirement for a

set of homogeneous, solid reference materials limits the use of this technique. The low detection limit requirements for many of the required elements in these materials will not be achieved by this technique. The analysis of iron, chromium, nickel, and tin in zirconium alloys and zirconium in hafnium have been demonstrated to work well by X-ray. Test Method E539 and Guide E1621 give valuable guidance.

7. Calibration

7.1 Set up the instrument for calibration as recommended by the manufacturer. The publications listed in Section 2, as well as in texts, the analytical literature, and other standards organizations, will also provide valuable guidance.

8. Interferences

8.1 Guide E1097, Practice E1184, Practice E1479, Guide E1621, and Practice E1770 describe some of the interferences encountered during analysis. The user is responsible for ensuring the absence of, or compensating for interferences that may bias test results obtained using their standard operating procedures.

8.2 The physical interferences resulting from variations in sample and calibration solution aerosol transport rates may be compensated for by the use of an internal standard in some techniques.

8.3 Table 1 lists wavelengths that have been used to analyze the listed elements in the given metals and are suggested for the user of atomic emission spectrometers. Due to the resolution of individual instruments, confirmation of these suggestions will be required. Depending on the specific spectrometer, other wavelengths will be found to be applicable.

9. Reference Materials

9.1 Standard Reference Material (SRM) Zircaloy-4, SRM 360b, is available from National Institute of Standards and Technology⁴ and other commercial suppliers. Three zirconium materials known as Zr 20, Zr 30, and Zr 40 are available from several commercial suppliers. Due to non-homogeneity, they are recommended for X-ray fluorescence use only. BCR-098 is a Zircaloy-4 alloy that is certified for chromium, hafnium, iron, and tin.

9.2 A number of titanium Certified Reference Materials (CRMs) are available from NIST and other commercial suppliers. These can be used to calibrate any of the techniques mentioned in Section 7.

9.3 No CRMs are available for niobium, hafnium, molybdenum, tantalum, tungsten, or vanadium.

9.4 Since CRMs are not available for hafnium, niobium, molybdenum, tantalum, tungsten, and vanadium and only for a limited range of elements in zirconium, it is necessary to use laboratory-prepared Reference Materials (RMs) to calibrate the instrumentation being utilized. For instruments utilizing a solution form of sample introduction, Test Method E2371 may be used as a model for preparing matrix-matched reference

⁴ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov>.