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Standard Guide for
Spectrometric Analysis of Reactive and Refractory Metals[1]

This standard is issued under the fixed designation E2626; 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.

ε^1 NOTE—Editorial corrections were made throughout in October 2009.

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 Analysis of Titanium Alloys by X-Ray Fluorescence Spectrometry

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

E1097 Guide for Determination of Various Elements by Direct Current Plasma Atomic Emission Spectrometry

E1184 Practice for Determination of Elements by Graphite Furnace Atomic Absorption Spectrometry

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.

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[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.

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 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 out-perform 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 Technology[4] 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.

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

TABLE 1 Potential Wavelengths (nm)

	Element/Matrix							
	Hf	Mo	Nb	Ta	Ti	V	W	Zr
Al	167.078					396.152	308.216	167.079
Al	349.403							308.215
Al			394.403	394.403	394.403			309.271
Al		394.403					394.403	394.403
B	182.460				249.678	136.246		182.589
B	182.640					249.773		
Bi						190.241		
Ca	422.673	396.847		422.673			396.847	422.673
Cd	214.438							214.438
Cd	226.502							226.502
Cd								228.802
Co	194.128			345.350				194.128
Co	228.615							238.892
Co	350.228					230.786		
Cr	267.716	284.325	359.349	357.869	267.716	205.552	284.325	267.716
Cr	359.349						282.237	285.568
Cr	425.435							359.349
Cu	324.754			324.754		219.226	324.754	324.754
Cu	327.396	327.396			327.396	224.700		327.396
Fe	259.940		259.940	258.588	259.940			259.940
Fe		302.107				238.204	299.443	261.187
Hf			277.34	264.141		232.247		273.876
Hf								277.336
Mg	279.553	280.270	279.553	279.553			277.983	279.553
Mn	257.610		259.370		257.610		257.610	257.610
Mn	403.076	280.106		403.076				
Mo	202.030		379.83	386.411	202.030	204.598		202.030
Mo	379.825					379.825	313.259	
Nb	309.418		269.89	309.418	321.604	319.498		
Nb	316.340					322.548		316.340
Ni	231.604	300.249	341.476	341.476		231.604	300.363	231.604
Ni	352.454	336.957				227.021	310.547	352.454
P	178.290		213.620	213.620		177.495		
P	213.620					178.287		
Pb	220.353							168.215
Pb	405.783	283.306						
Pd					360.955			
Ru					240.272			
Sn	189.989	283.999			175.790	181.134	286.333	283.999
Sn	251.611				242.949	189.991		317.502
Sn	283.999			283.999		242.949		
Si	251.612	251.612	251.612	251.612		251.612	251.612	251.612
Si	288.158				288.160		298.765	
Ta	240.063		240.063			223.948		240.063
Ta	269.452					240.063		
Ti	323.452		252.56	323.452		324.199		323.452
Ti	334.941		323.452			334.941		334.941
V	309.311		309.311	309.311	292.402			
V	311.838							311.838
V	437.924							
W	400.875	400.875	207.91	400.875		239.709		207.916
Y					360.073			377.433
Zn	213.856			213.856				213.856
Zr	339.198		339.198	339.198	343.823	339.198		
Zr	436.081					343.823		

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 material. Single element spectrometric CRMs are available from NIST and several commercial suppliers.

10. Test Sample Preparation (Liquids)

10.1 The instructions below have been found to be sufficient to prepare a 100 mL test solution of the metals indicated for techniques utilizing a liquid sample. This 100 mL is an arbitrary amount, but should be adequate for most instrumentation requiring a solution. Changes to these relative amounts may be adjusted to yield the desired final volume of solution. Other concentrations may be used as long as test samples and reference materials are prepared in the same manner. Since all of these preparations involve the use of hafnium, all vessels used for dissolution and dilution should be resistant to hafnium. The examples below are written for mass-volume dilutions because that is the common manner in which most laboratories dissolve metal samples. It should be pointed out that mass-mass dilution is recommended by metrological agencies.

10.2 *Hafnium (Hf) Matrix*—1.000 g Hf turnings or chips + depending on the thickness of the turnings, add 25 mL to 50 mL Type II water. Add 2 mL concentrated nitric acid (HNO_3) + 3 mL 48 % HF. Cap loosely and heat gently until dissolution is complete. Dilute the solution to 100 mL with Type II water and mix well.

10.3 *Molybdenum (Mo) Matrix*—1.000 g Mo chips or turnings + 15 mL Type II water + 5 mL concentrated HNO_3. Cap loosely until dissolution slows. Add 5 mL concentrated HNO_3 + 3 mL 48 % HF. Cap loosely until dissolution is complete. Add 5 mL concentrated HCl. Dilute to 100 mL with Type II water and mix well.

10.4 *Niobium (Nb) Matrix*—1.000 g Nb metal turnings or chips + 13 mL Type II water + 4 mL concentrated HNO_3 + 8 mL 48 % HF. Cap loosely and heat gently until dissolution is complete. Dilute the solution to 100 mL with Type II water and mix well.

10.5 *Vanadium (V) Matrix*—1.000 g V metal turnings or chips + 20 mL to 30 mL Type II water + 10 mL concentrated HNO_3. Add 10 mL concentrated hydrochloric acid (HCl) + 3 mL 48 % HF and mix well. Cap loosely until dissolution is complete. Dilute the solution to 100 mL with Type II water and mix well.

10.6 *Tantalum (Ta) Matrix*—1.000 g Ta metal turnings or chips + 10 mL Type II water + 10 mL concentrated HNO_3 and 10 mL 48 % HF. Cap loosely until dissolution is complete. Heat gently if needed. Dilute the solution to 100 mL with Type II water and mix well.

10.7 *Titanium (Ti) or Zirconium (Zr) Matrix*—1.000 g Ti or Zr metal turnings or chips + depending on the thickness of the turnings, 25 mL to 50 mL Type II water + 2.5 mL concentrated HNO_3 + 5 mL 48 % HF. Cap loosely until dissolution is complete. Heat gently if needed. Dilute the solution to 100 mL with Type II water and mix well.

10.8 *Tungsten (W) Matrix*—1.000 g W metal turnings or chips + 10 mL Type II water + 15 mL concentrated HNO_3 + 20 mL 48 % HF. Cap loosely and heat gently until dissolution is complete. Dilute the solution to 100 mL with Type II water and mix well.

11. Keywords

11.1 AA; AAS; AES; alloys; arc; AS-AES; atomic absorption; atomic emission; DCP-AES; direct current plasma; FAAS; GD-AES; GD-MS; glow discharge; hafnium; ICP; ICP-MS; inductively coupled plasma; inductively coupled plasma-mass spectrometry; mass spectrometry; molybdenum; niobium; reactive metals; refractory metals; spark; spectrometry; tantalum; tungsten; vanadium; x-ray emission; XRF; zirconium

APPENDIX

(Nonmandatory Information)

X1. ZIRCONIUM ROUND ROBIN RESULTS

X1.1 During the time period of 2005–2006, an international Round Robin was carried out on three specimens of zirconium material. Samples were submitted to laboratories that routinely analyzed zirconium alloys. Each laboratory was asked to test the samples using the analytical techniques that they normally used on a day-to-day basis, and the calibration materials they normally would use. Table X1.1 shows an example of one of these materials tested in that study. It is presented here to illustrate the range of test results that can be expected when laboratories use their in-house procedures and do not have the availability of internationally recognized CRMs that can be used for all elements.

TABLE X1.1 Statistical Information for Zirconium Metal

Element	Number of Laboratories	Mean ($\bar{x}$, E1601)	Minimum SD[A] (S_M, E1601)	Reproducibility SD[A] (S_R, E1601)	Reproducibility Index (R, E1601)	R_{rel}, %
Al	5	65 µg/g	4.1	5.3	14.8	22.8
B	4	0.35 µg/g	0.038	0.106	0.297	85.2
Co	5	15.4 µg/g	0.77	2.09	5.85	38.0
Cr	5	0.061 µg/g	11.7	28.6	80.0	7.6
Cu	5	37 µg/g	2.2	6.8	19.1	52.2
Fe	5	2316 µg/g	16.6	78.3	219.1	9.5
Hf	5	78 µg/g	1.9	5.8	16.2	20.8
Mn	5	52 µg/g	3.1	3.6	10.1	19.5
Mo	4	52 µg/g	1.2	2.4	6.8	13.1
Nb	5	303 µg/g	18.9	19.5	54.7	18.0
Ni	5	66 µg/g	2.6	5.7	16.1	24.3
Pb	5	45 µg/g	4.1	7.8	21.9	48.5
Sn	5	1.63 wt %	0.011	0.029	0.081	4.97
Si	5	80 µg/g	4.3	13.0	36.3	45.3
Ta	4	389 µg/g	17.7	18.6	52.0	13.4
Ti	5	46 µg/g	3.0	5.6	15.3	34.1
V	5	47 µg/g	1.5	6.2	17.4	37.3
W	5	42 µg/g	4.1	10.5	29.3	69.5

[A] SD = Standard Deviation

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