Designation: D 5839 – 96

Standard Test Method for
Trace Element Analysis of Hazardous Waste Fuel by Energy-Dispersive X-Ray Fluorescence Spectrometry[1]

1. Scope

1.1 This test method applies to the determination of trace element concentrations by energy-dispersive X-ray fluorescence (EDXRF) spectrometry in typical liquid hazardous waste fuels (LHWF) used by industrial furnaces.

1.2 This test method has been used successfully on numerous samples of LHWF that are mixtures of solvents, oils, paints, and pigments for the determination of the following elements: Ag, As, Ba, Cd, Cr, Hg, Ni, Pb, Sb, Se, and Tl.

1.3 This test method also may be applicable to elements not listed above and to the analysis of trace metals in organic liquids other than those used as LHWF.

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:*

C 982 Guide for Selecting Components for Energy-Dispersive X-Ray Fluorescence (XRF) Systems[2]

3. Summary of Test Method

3.1 A weighed portion of the sample is transferred to a porcelain evaporating dish and placed on a hot plate. The sample is heated for 15 to 30 min at a temperature not exceeding 105°C to evaporate highly volatile components. The dish is removed from the hot plate and allowed to cool. Graphite powder is blended with the evaporated sample until a homogeneous paste is produced and the sample weight is recorded. The blended sample is inserted in a disposable sample cup and placed in the X-ray spectrometer for analysis.

3.2 The K Spectral X-ray emission lines are used for Ag, As, Ba, Cd, Cr, Ni, Sb, and Se.

3.3 The L spectral X-ray emission lines are used for Hg, Pb, and Tl.

4. Significance and Use

4.1 The analysis of trace elements is often a regulatory and process specific requirement for facilities utilizing LHWF. With proper instrument standardization, set-up, and quality control, this test method provides the user an accurate, rapid, nondestructive method for trace element determinations.

5. Interferences

5.1 *Spectral Overlaps*:

5.1.1 Samples containing a mixture of elements often exhibit X-ray emission line overlap. Modern Si (Li) detectors generally provide adequate resolution to minimize the effects of spectrum overlaps on the analytical results of the LHWF. In those cases where direct emission line overlap exists, spectral deconvolution methods extract corrected analyte emission line intensities. Table 1 lists the significant line overlaps observed for the elements analyzed in LHWF. Follow the EDXRF manufacturer's recommendations concerning spectral deconvolution of the emission lines.

NOTE 1—Not all possible interferences are listed in Table 1. The LHWF samples to be analyzed may have other emission line interferences not mentioned. Consult the manufacturer's recommendations for optimum deconvolution methods.

5.2 *Matrix Interferences*:

5.2.1 Large concentration variations of metal or matrix components, or both, in LHWF samples can result in nonlinear metal X-ray intensity response at increasing metal concentrations. Untreated matrix interactions may have a deleterious effect on metal determination accuracy. Matrix interactions, if exhibited by the LHWF samples, must be accounted for by method calibration.

6. Apparatus

6.1 *Energy Dispersive X-Ray Spectrometer*, capable of measuring the wavelengths listed in Table 1. Refer to C 982 for system specifications.

6.2 *Hot Plate*, with temperature control to 105°C.

6.3 *Analytical Balance*, capable of weighing to 0.001 g.

6.4 *Porcelain Evaporating Dishes*, 70 to 150 mL capacity.

7. Reagents and Materials

7.1 *Purity of Reagents*—Use reagent grade chemicals in all tests. Unless otherwise indicated, all reagents will conform to

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[1] This guide is under the jurisdiction of ASTM Committee D-34 on Waste Management and is the direct responsibility of Subcommittee D34.02 on Physical and Chemical Characterization.

Current edition approved Jan. 10, 1996. Published March 1996.

[2] *Annual Book of ASTM Standards*, Vol 12.01.

TABLE 1 Common Emission Line Spectral Interferences for LHWF Analysis

Element	Lines Determined	Spectral Interferences
As	Kα, Kβ	Pb Lα, Hg Lβ, Tl Lα Lβ
Cr	Kα, Kβ	V Kβ, Mn Kα
Hg	Lα, Lβ	As Kβ, Se Kα, Pb Lβ, Tl Lα, Br Kα
Ni	Kα, Kβ	Cu Kβ, Cu Kα
Pb	Lα, Lβ	As Kα, Se Kβ Hg Lβ Tl Lα, Tl Lβ, Br Kα, Br Kβ
Se	Kα, Kβ	Pb Lβ, Hg Lβ, Tl Lβ
Tl	Lα, Lβ	As Kα, As Kβ, Se Kβ, Pb Lα, Br Kα, Hg Lα, Hg Lβ

the specifications 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 sufficient high purity to permit its use without lessening the accuracy of the determination.

7.2 Use graphite powder, mixing grade, 44 µm, 325 mesh.[4]

7.3 Use oil-based Ag, As, Ba, Cd, Cr, Hg, Ni, Pb, Sb and Se standards, 10 to 10 000 mg/kg depending on the user's analytical requirements. If the results of this test method are to be used for compliance purposes, standards or a commercial source must be traceable to NIST or other certifying body. Quality control samples for analyses done for compliance purposes may need to be prepared with standards from a different vendor or lot number.

7.4 Use oil or solvent-based Tl standard, 10 to 1000 mg/kg depending on the user's analytical requirements. If the results of this test method are to be used for compliance purposes, standards or a commercial source must be traceable to NIST or other certifying body.[5]

7.5 Use paraffinic base oil.

7.6 Use sample cups, vented or unvented.

7.7 Use thin-film sample support.

NOTE 2—The user should select a thin-film support that provides for maximum transmittance and is resistant to typical components in LHWF. The thin-film supports used in the development of this test method were 4 µm Prolene.

8. Sampling

8.1 Because stratification or layering of liquid samples is possible, the laboratory sample should be thoroughly mixed by shaking prior to withdrawing a portion for testing, or use a sampling method that assures all portions of the sample are represented.

9. Preparation of Apparatus

9.1 Follow the manufacturer's instructions for set-up, conditioning, preparation, and maintenance of the XRF spectrometer.

9.2 Obtain reference spectra from pure element standards for all analytes and interelement correction metals.

9.3 Address spectral interferences, as listed in 5.1.1, in accordance with manufacturer's recommendations.

10. Calibration and Standardization

10.1 Calibrate the spectrometer to an appropriate reference element at the minimum frequency specified by the manufacturer.

10.2 Analytical standards should be gravimetrically prepared by blending the elemental standards and graphite listed in Section 7. These preparations can contain single or multiple elements and should be prepared at combinations and ratios to meet the user's individual needs. For example, a Pb and Cd standard at 125 ppm each could be prepared by gravimetrically combining 2 g oil-based Pb standard (500 ppm), 2 g oil-based Cd standard (500 ppm) and 4 g graphite and blending to a homogeneous mixture. For this example, the Pb concentration is calculated as follows:

$$\text{Pb Standard Concentration} = 500\text{ ppm} \times \frac{\text{Pb Std. (g)}}{\text{graphite (g)} + \text{Cd Std. (g)} + \text{Pb Std. (g)}} \quad (1)$$

10.3 The metals standard/graphite paste is placed in an XRF sample cup and affixed with a thin-film support. The sample cup is inverted and lightly tapped on a level surface until the blended paste makes full contact (no air spaces) with the thin-film support.

10.3.1 The standard blends in the sample cups are placed into the spectrometer's designated sample holder. Avoid touching the thin-film, as this can further reduce transmittance. Initiate data acquisition for the desired elements according to the manufacturer's instructions.

10.4 Two alternative standards calibration methods may be used:

10.4.1 *Test Method A (Empirical Calibration Method)*—Organic-based metals standards containing the metals of interest are prepared as described in 10.2. The standard metal concentrations must bracket the unknown LHWF concentration levels. If the standard concentrations are less than 0.1 % by weight, a linear calibration method may be used to plot metal emission intensity response against metal concentration.

10.4.1.1 If metal concentration exceeds 0.1 % by weight, then a matrix correction technique is employed. Standard mixtures of varying metal composition must be prepared that bracket the LWHF unknown concentrations. Eq A is solved for the slope, intercept and all alpha terms:

$$C_i = B_i + K_i I_i\,(1 + \Sigma\alpha_{ij} C_j) \quad (2)$$

where:

C_i = concentration of analyte element i,
B_i = intercept term,
K_i = slope term,
I_i = X-ray intensity of element, i,
α_{ij} = alpha coefficient describing the matrix interaction of element j on analyte i, and
C_j = concentration of matrix element j.

10.4.2 *Test Method B (Fundamental Parameters Method)*—

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[3] *Reagent Chemicals, American Chemical Society Specifications*, 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), Rockville, MD.

[4] This reagent, or its equivalent, is available from Chemplex Industries, Inc., 160 Marbledale Road, Tuckahoe, NY 10707.

[5] This reagent, or its equivalent, is available from Alfa Aesar, Johnson Matthey Inc., 30 Bond Street, Ward Hill, MA 01835.

Some instrument vendors provide software capable of estimating matrix interferences with a minimum number of standards. A high and low standard concentration mixture or a mid-range concentration mixture gives the fundamental parameters method an initial emission response determination. Using this information and calculations using the principles of X-ray absorption and emission, a data matrix is created sufficient to solve equations of the form in Eq 2 for all sample matrix interactions.

10.4.2.1 Follow the software manufacturer's fundamental parameters set-up recommendations on the number of standard mixtures and the nature of the matrix balance estimate (usually a stoichiometric combination of carbon, hydrogen, and oxygen) for LWHF.

10.4.3 Calibration should be repeated at least every two weeks or whenever quality control results as specified in Section 13 are outside data quality objectives as determined by the user.

11. Procedure

11.1 Mix the LHWF sample thoroughly, see 8.1.

11.1.1 To a clean, dry, and tared evaporating dish, add 10 g of the LHWF sample and weigh to the nearest 0.001 g. Record the mass.

11.1.2 Place the dish on a hot plate at a temperature such that the sample material does not exceed 105°C. Samples containing significant levels of very volatile components may need to be heated initially at a lower temperature. If spattering of the sample is observed, the sample should be removed from the hot plate and allowed to cool slightly. Adjust the hot plate to a lower temperature and replace evaporating dish and sample on the hot plate and continue heating. The heating of the sample is a concentration step, so the heating time is not a critical factor. Generally, the time required to evaporate the volatile fraction from most LHWF is approximately 15 to 30 min.

11.1.3 Remove the dish from the hot plate and allow to cool to the touch.

11.1.4 If the evaporated sample appears to contain large or variable sized solid material, it may be necessary to grind the sample in a mortar and pestle or other suitable device.

11.1.5 Mix graphite into the evaporated sample with a lab spatula or equivalent device until a homogeneous paste results that has no clumping, and when allowed to stand briefly, exhibits no visible liquid phase separation. An approximate amount of 4 to 6 g of graphite is normally sufficient. Weigh the graphite/sample mixture and record.

11.1.6 Mount the graphite/sample preparation in an XRF sample cup as described in 10.3.

11.1.7 Place the mounted sample preparation into the spectrometer's designated sample holder. Avoid touching the thin-film, as this can reduce transmittance. Initiate data acquisition for the desired elements according to the manufacturer's instructions.

11.1.8 After instrument analysis is completed, process analytical results in accordance with Section 12.

12. Calculation

12.1 The analytical results for each element obtained by either empirical calibration or fundamental parameters models in 11.1.8 should be corrected for the sample preparation dilution as follows:

$$\text{Corrected concentration (mg/kg)} = \text{Analytical Result (mg/kg)} \times \frac{\text{Mass of graphite (g) and sample mix (g)}}{\text{Initial mass of LHWF (g)}} \quad (3)$$

13. Quality Control

13.1 Before using this test method, fully investigate any specific regulatory quality control requirements.

13.2 Process a minimum of one quality control check standard, matrix spike/matrix spike duplicate and one analytical blank consisting of graphite powder/analyte-free paraffinic oil blend with each batch of LHWF samples.

13.3 Evaluate quality control sample with each batch of analyzed samples. These results will verify that user defined data quality objectives have been met.

14. Precision and Bias

14.1 *Precision*—No statement is made about precision at this time. An interlaboratory test study will be conducted in the future.

14.2 *Bias*—No statement is made about bias at this time. An interlaboratory test study will be conducted in the future.

14.3 Appendix X1 contains analytical results following this test method (10.4.2) on typical LHWF, MS/MSD, check standard, and blank. Lower Limits of Detections also are listed.

15. Keywords

15.1 EDXRF; hazardous waste fuel; spectrometry; spectroscopy; trace elements; XRF

APPENDIX

(Nonmandatory Information)

X1. ANALYTICAL AND QUALITY CONTROL RESULTS AND LOWER LIMITS OF DETECTION FOR LHWF

LHWF Sample No. 1	Element															
	V	Cr	Ti	Ni	Cu	Zn	Se	As	Tl	Pb	Hg	Ag	Cd	Sb	Ba	Sn
Blank (ppm)	<13.0	<3.0	<8.0	<6.0	<8.0	<7.0	<3.0	<16.0	<6.0	<4.0	<3.0	<3.0	<2.0	<8.0	<34.0	<4.0
Check standard recovery (%)	102.1	106.1	110.0	94.5	102.8	102.8	115.0	124.8	...	104.6	110.0	100.3	105.8	108.0	130.0	104.8
MS/MSD-RPD[1](%)	2.1	1.2	8.2	9.9	0.2	1.5	25.1	16.4	...	7.2	1.1	4.6	1.3	18.7	15.1	1.2
MS/MSD Recovery[2] (%)	75.7	103.9	102.7	93.0	100.5	102.3	145.7	91.2	...	97.3	123.4	101.9	86.5	70.1	153.2	80.2

[1] Relative Percent Difference $= 1C_1 - C_21 / ((C_1 + C_2) / 2) \times 100.$ (X1.1)

where:

C_1 = concentration result of the matrix spike.

C_2 = concentration result of the matrix spike duplicate.

1 1 = denotes the absolute value of the difference.

$$^2\frac{((\text{MS} - \text{sample result}) + (\text{MSD} - \text{sample result}) / 2}{\text{Matrix Spike (Added)}}(100) = \%\ \text{Recovery} \tag{X1.2}$$

Lower Limits of Detection (LLD)[1]			
Element	LLD (ppm)	Element	LLD (ppm)
V	5.0	Tl	...
Cr	2.0	Pb	4.0
Ti	3.0	Hg	3.0
Ni	10.0	Ag	3.0
Cu	7.0	Cd	3.0
Zn	6.0	Sb	8.0
Se	4.0	Ba	26.0
As	4.0	Sn	3.0

$$^1\text{LLD} = \frac{3\sqrt{\text{Bi}}}{\text{Pi}} \times \frac{1}{\sqrt{\text{T}}} \times \text{conc.} \tag{X1.3}$$

where:

Bi = background intensity (counts/sec) under fitted analyte peak.

Pi = fitted peak intensity (counts/sec) of analyte peak.

T = counting livetime (sec).

conc. = concentration of analyte from metallic oil standard.

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