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Standard Practice for Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants[1]

This standard is issued under the fixed designation D7343; 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 practice covers information relating to sampling, calibration and validation of X-ray fluorescence instruments for elemental analysis, including all kinds of wavelength dispersive (WDXRF) and energy dispersive (EDXRF) techniques. This practice includes sampling issues such as the selection of storage vessels, transportation, and sub-sampling. Treatment, assembly, and handling of technique-specific sample holders and cups are also included. Technique-specific requirements during analytical measurement and validation of measurement for the determination of trace elements in samples of petroleum and petroleum products are described. For sample mixing, refer to Practice D5854. Petroleum products covered in this practice are considered to be a single phase and exhibit Newtonian characteristics at the point of sampling.

1.2 *Applicable Test Methods*—This practice is applicable to the XRF methods under the jurisdiction of ASTM Subcommittee D02.03 on Elemental Analysis, and those under the jurisdiction of the Energy Institute's Test Method Standardization Committee (Table 1). Some of these methods are technically equivalent though they may differ in details (Table 2).

1.3 *Applicable Fluids*—This practice is applicable to petroleum and petroleum products with vapor pressures at sampling and storage temperatures less than or equal to 101 kPa (14.7 psi). Use Practice D4057 or IP 475 to sample these materials. Refer to Practice D5842 when sampling materials that also require Reid vapor pressure (RVP) determination.

1.4 *Non-applicable Fluids*—Petroleum products whose vapor pressure at sampling and sample storage conditions are above 101 kPa (14.7 psi) and liquefied gases (that is, LNG, LPG, etc.) are not covered by this practice.

1.5 *Sampling Methods*—The physical sampling and methods of sampling from a primary source are not covered by this guide. It is assumed that samples covered by this practice are a representative sample of the primary source liquid. Refer to Practice D4057 or IP 475 for detailed sampling procedures.

1.6 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.7 *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.*

[1] This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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This practice was jointly prepared by ASTM International and the Energy Institute.

*A Summary of Changes section appears at the end of this standard

TABLE 1 XRF Standard Test Methods for Analysis of Petroleum Products and Lubricants

Technique	Analysis	ASTM	EI
WD-XRF	Sulfur in Petroleum Products	D2622	
	Additive Elements in Lubricating Oils and Additives	D4927	IP 407
	Lead in Gasoline	D5059	IP 228
	Lead in Gasoline		IP 489
	Sulfur in Gasoline	D6334	
	Additive Elements in Lube Oils and Additives	D6443	
	Vanadium and Nickel		IP 433
	Sulfur		IP 447
	Sulfur in Automotive Fuels		IP 497
	Chlorine and Bromine		IP 503
	Sulfur in Ethanol as Blending Agent		IP 553
	Si, Cr, Ni, Fe, and Cu in Used Greases		IP 560
	Several Metals in Burner Fuels Derived from Waste Mineral Oils		IP 593
MWD-XRF	Sulfur in Gasoline and Diesel	D7039	
	Silicon in Gasoline and Naphtha	D7757	
ED-XRF	Sulfur in Petroleum Products	D4294	IP 336
	Sulfur in Gasoline	D6445	
	Additive Elements in Lubricating Oils	D6481	
	Sulfur in Automotive Fuels	D7212	IP 531
	Sulfur in Automotive Fuels	D7220	IP 532
	Additive Elements in Lubricating Oils	D7751	
	Lead in Gasoline		IP 352
	Sulfur in Automotive Fuels		IP 496
	Low Sulfur in Automotive Fuels		IP 600

TABLE 2 Technically Equivalent XRF Test Methods for Petroleum Products and Lubricants[A]

Analysis	ASTM	EI	Other
Sulfur by WD-XRF	D2622		DIN 51400T6; JIS K3541
Additive Elements by WE-XRF	D4927	IP 407	DIN 51391T2
Lead in Gasoline	D5059	IP 228	
Sulfur by ED-XRF	D4294	IP 336	ISO 8754
Sulfur in Automotive Fuels	D7212	IP 531	
Sulfur in Automotive Fuels	D7220	IP 532	

[A] Nadkarni, R. A., *Guide to ASTM Test Methods for the Analysis of Petroleum Products and Lubricants*, 2nd edition, ASTM International, West Conshohocken, PA, 2007.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry

D4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy

D5059 Test Methods for Lead in Gasoline by X-Ray Spectroscopy

D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6334 Test Method for Sulfur in Gasoline by Wavelength Dispersive X-Ray Fluorescence

D6443 Test Method for Determination of Calcium, Chlorine, Copper, Magnesium, Phosphorus, Sulfur, and Zinc in Unused Lubricating Oils and Additives by Wavelength Dispersive X-ray Fluorescence Spectrometry (Mathematical Correction Procedure)

D6445 Test Method for Sulfur in Gasoline by Energy-Dispersive X-ray Fluorescence Spectrometry (Withdrawn 2009)[3]

D6481 Test Method for Determination of Phosphorus, Sulfur, Calcium, and Zinc in Lubrication Oils by Energy Dispersive X-ray Fluorescence Spectroscopy

D7039 Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry

D7212 Test Method for Low Sulfur in Automotive Fuels by Energy-Dispersive X-ray Fluorescence Spectrometry Using a Low-Background Proportional Counter

D7220 Test Method for Sulfur in Automotive, Heating, and Jet Fuels by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry

D7751 Test Method for Determination of Additive Elements in Lubricating Oils by EDXRF Analysis

D7757 Test Method for Silicon in Gasoline and Related Products by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry

2.2 *Energy Institute Standards:*[4]

IP 228 Determination of lead content of gasoline – X-ray spectrometric method

IP 336 Determination of sulfur content – Energy-dispersive X-ray fluorescence method

IP 352 Determination of lead content of automotive gasoline- Energy-dispersive X-ray fluorescence spectrometry method

IP 407 Determination of barium, calcium, phosphorus, sulfur and zinc by wavelength dispersive X-ray fluorescence spectrometry

IP 433 Determination of vanadium and nickel content – Wavelength dispersive X-ray fluorescence spectrometry

IP 447 Determination of sulfur content - Wavelength dispersive X-ray fluorescence spectrometry

[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] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.uk.

IP 475 Methods of test for petroleum and its products

IP 489 Determination of low lead contents in gasolines - Wavelength dispersive X-ray fluorescence spectrometry

IP 496 Determination of sulfur content of automotive fuels – Energy-dispersive X-ray fluorescence spectrometry

IP 497 Determination of sulfur content of automotive fuels - Wavelength dispersive X-ray fluorescence spectrometry

IP 503 Determination of chlorine and bromine content - Wavelength dispersive X-ray fluorescence spectrometry

IP 531 Determination of sulfur content of automotive fuels – Low-background proportional counter energy-dispersive X-ray fluorescence spectrometry method

IP 532 Determination of the sulfur content of automotive fuels – Polarized X-ray fluorescence spectrometry

IP 553 Ethanol as a Blending Component for Petrol — Determination of Sulfur Content — WDXRF Method

IP 560 Determination of Silicon, Chromium, nickel, Iron, and Copper in Used Greases — WDXRF Method

IP 593 Determination of Pb, Ni, Cr, Cu, Zn, As, Cd, Tl, Sb, Co, Mn, and V in Burner Fuels derived from Waste Mineral Oils — WDXRF Method

IP 600 Petroleum Products — Determination of Low Sulfur Content of Automotive Fuels — EDXRF Spectrometry

3. Significance and Use

3.1 Accurate elemental analyses of samples of petroleum and petroleum products are required for the determination of chemical properties, which are in turn used to establish compliance with commercial and regulatory specifications.

4. Sample Handling

4.1 It is necessary to use precautions to minimize the possibility of contamination of trace elemental analysis samples. Good laboratory practices in this area include:

4.1.1 Samples received by the laboratory and required for trace element analysis should be stored in a designated specific location for storage while awaiting analysis. This area, whenever possible, should not contain samples that could contaminate those requiring trace element analysis.

4.1.2 All laboratory equipment used specifically for trace element analysis should be free of any source of contamination. This may require that specific equipment be used only for trace element analysis.

4.1.3 Analyses of blank samples are highly recommended.

4.1.4 Sample preparation should be carried out in a clean area. This area should use surfaces that can be decontaminated easily if a spillage occurs.

4.1.5 Operators should wear clean, fresh, protective gloves for sample preparation for trace element analysis. Tests should be run to confirm that the gloves do not contain interfering elements or elements of interest, since they may cause contamination. The development of clean area sample handling protocols is encouraged.

5. Sample Preparation

5.1 *Choice of Sample Carrier*—XRF testing requires a sample cell and a support film to hold the liquid sample in place during analysis. The choice of the sample cell or cup, the material in which it is held, and the type of support film used can all influence the result.

5.1.1 *Sample Cell*—The most common cell is a plastic cup, of which various designs are available. These designs allow for a variety of sample types to be measured either in a liquid or powder form. It is important to check that the cup type used is best suited for the compositions of samples to be analyzed. Liquid sample cups usually have a seal that ensures the film is sealed to a level above that of the liquid in the cell and that the film is taut with no wrinkles.

5.1.1.1 Within XRF spectrometers heat is produced, both from the spectrometer components themselves and from the interaction of X-rays with the sample. Petroleum products that are not stable due to volatility should only be placed into vented sample cups or special sealed sample cups specifically designed for volatile samples (see 8.3).

5.1.1.2 The cup size may be important. Depending on the film type used to support the liquid, different films will sag due to the weight of sample and relax due to chemical interaction, or heat, or both. To reduce this sagging effect, the smallest diameter sample cups should be used. Cups with diameters well in excess of the area detected by the spectrometer are likely to increase errors due to sagging.

5.1.1.3 A number of petroleum products require heating to ensure homogenization prior to analysis or to enable transfer to the sample cell; examples include fuel oils and wax products. The sample cup should be able to withstand the temperature used in this process. In general, most plastic sample cells should withstand temperatures up to 70°C.

5.1.2 *Sample Cell Holder*—Many manufacturers recommend metal holders to hold sample cups while they are transferred into the XRF instrument. These holders can be made from aluminum, stainless steel, or other materials. It is important to recognize that these represent a potential spectral contamination to the analysis either if the spectrometer is to determine an analyte that the holder is made from or if the material from the holder causes an interference with the analyte. Generally, this is not a problem for elements with atomic number <30. For elements with atomic number >30 it is advisable to check the potential contamination from the sample cup holder using a blank.

5.1.3 *Sample Support Films*—Many support films are available from both XRF instrument manufacturers and accessory suppliers. It is important to examine the film types specified in any method being used. There are four criteria that should be considered when selecting a X-ray transmission sample support film:

(1) Thickness of film,

(2) Composition of film,

(3) Chemical and physical resistance of film to the liquid intend for analysis, and

(4) Element contaminants contained within the film.

5.1.3.1 Film thickness typically ranges from 2 to 6 µ for most applications. Consideration should be given to the variations in thickness from batch to batch of films. For thinner films, the relative variance in film thickness is often higher than that of the thicker films, thus precision of analysis can be affected more if thinner films are used. One way to avoid this