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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.

1.6.1 *Exception*—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.*

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[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.

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.

1.8 *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]

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

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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] 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 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
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 μ 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 is to recalibrate or adjust calibrations using monitors each time a new batch of film is used.

5.1.3.2 Film types are composed of different polymer materials. Those containing oxygen or nitrogen will absorb lighter elements more than those that do not. Examples of oxygen and nitrogen containing polymers are polyester and polyamide. For the determination of elements lighter than sulfur, these films should be avoided in favor of polymers containing only carbon and hydrogen, provided that the film is not attacked by the sample.

5.1.3.3 Chemical resistance is often a compromise with film type. Often, the best resistance is offered by polymers containing oxygen or nitrogen. Physical aspects such as temperature will also be an issue especially if hot liquids are to be measured. Most film types will withstand temperatures up to 80 °C, but relaxation of the polymer, especially in wide cups, will affect accuracy and precision.

5.1.3.4 All films contain element contaminants. Before using any film, blanks should be run to ensure that the backgrounds are not elevated by the existence of a contaminant element present in the film. These contaminant elements will affect detection limits if they correspond to, or interfere with, the analyte element(s).

5.1.3.5 It is necessary to verify that the sample does not dissolve the film or permeate through it. This is especially important for gasoline-range samples, when a new product is to be analyzed, or when a new kind of film is used for a sample type. This verification can be done as follows:

(1) Prepare a specimen cup and fill it with a typical specimen.

(2) Place the cell on a clean tissue and wait for 30 min to 60 min.

(3) Remove the cell, and inspect the tissue and the underside of the film. Both should be dry.

(4) This test does not need to be repeated for every measurement when the analyst is certain that the film and the material to be analyzed are compatible.

5.1.3.6 *Use of Multiple Films*—A common method of ensuring that spectrometers are not contaminated by leaking films is to use a second film in the sample cup holder of the instrument. This provides a high level of security, and for many systems is essential to avoiding costly down times if a sample should leak. The use of this second film will increase both the detection limits as well as the errors of measurement. Some petroleum products can permeate through polymer films and, while this may not be a problem for any single analysis, the buildup on a second protective film in some cases may cause drift of analysis results. When trace level determinations are required and the optimum performance in both precision and detection limit are required, the use of secondary films should be given careful consideration. If they are considered essential, they should be inspected or replaced for every analysis as part of standard operating procedures.

6. Sample Stability

6.1 Sample stability during measurement is essential for accurate determinations. Pay particular care, since a sample can undergo physical change during analysis. An example of this is catalyst residues in fuel oils that can settle during measurement. When this type of situation can occur or is suspected, maintaining constant masses, heating times (in the case of fuel oils), mixing times, transfer time from preparation to measurement, and the determination of low atomic number elements first in a sequential analysis scheme should be used.

6.2 This procedure will not eliminate the particulate settling problem; filtering of such samples may be needed before analysis.

7. Instrument Set-Up Specific to Technique

7.1 *Wavelength Dispersive X-Ray Fluorescence (WDXRF):*

7.1.1 Before using any WDXRF spectrometer, it is essential that the instrument is performing to the manufacturer's specifications. Consult with the manufacturer on how to perform spectrometer quality control checks.

7.1.2 Pay particular attention to the goniometer settings for sequential instruments, and ensure the goniometer positions are set correctly. Before performing a calibration of the goniometer angles, it is highly recommended that pulse height discriminator settings (PHDs) be carried out for each element and background being used.

7.1.3 Account for observation of known instrument interferences. These include crystal fluorescence, tube line overlaps, and any element spectral contamination from the metals within the instrument construction. A number of these interferences can be avoided by careful selection of window settings during PHD set-up. For element interference, the selection of an alternative line or minimizing overlap using higher resolution collimators and crystals with higher resolving power (or smaller 2d spacing) can be used.

7.1.4 When carrying out analysis for trace elements, it is important to monitor the bias in the measurement using a blank specimen. Improved consistency in analysis can be achieved by subtracting the measured concentration of the analyte in the blank from the determined concentration of the analyte in the recently measured samples.

7.1.5 Even though minimizing the background using a fine collimator will improve the theoretical detection limit, it does so only by increasing the analysis time. Many types of samples do not remain stable during exposure to X-ray radiation. Therefore the analyst is responsible for establishing the benefits of lower detection limits at the expense of increasing the time the sample is exposed to X-ray radiation. Generally, the selection of a mid-range collimator balances a quality detection limit with an effective analysis time. However, contact the manufacturer for the best settings to achieve this for each element of interest or determine the settings experimentally.

7.2 *Energy Dispersive X-Ray Fluorescence, EDXRF:*

7.2.1 Before using any EDXRF spectrometer, it is essential that the instrument is operating at the manufacturer's specifications. Consult with the manufacturer on how to perform spectrometer quality control checks.

7.2.2 Pay particular attention to detector resolution. The manufacturer will provide the detector specifications that need to be met for different detector types.

7.2.3 Account for observation of known instrument interferences. These include the normal artifacts seen in EDXRF: escape peaks, pile-up or summation peaks, tube line overlaps, diffraction peaks, and any element spectral contamination from the metals within the instrument construction. A number of these interferences can be avoided by careful selection of voltage, primary beam filter, choice of secondary target (if provided in the instrument), and pulse processor settings. For element interference, consider selecting an alternative line or minimizing overlap using optimal settings for a particular element.

7.2.4 Accurate deconvolution of elements in EDXRF is very important in providing the most precise intensities for any analysis. Minimizing the number of deconvolution components overlapping for any analyte element will provide the most reliable data. The use of regions of interest (ROI), where appropriate, will produce data with the minimum of statistical error.

7.2.5 When carrying out analysis for trace elements, it is important to minimize background while still obtaining the maximum sensitivity possible. Generally, the selection of the highest resolution settings with narrow excitation conditions will achieve the best limits of detection. Contact the manufacturer for the best settings to achieve this for each element of interest or determine the settings experimentally.

8. Procedure

8.1 *Cup Preparation and Measurement (Open Cell):*

8.1.1 Prepare the cups in strict accordance with the manufacturer's recommendations. When attaching the support film ensure that the film is not torn or left with any creases. (**Warning—**Do not touch the analytical surface of the film. This includes both sides of the film area that are subject to excitation and detection (the bigger of these two areas if they are not equal).)

8.1.2 Place the prepared cup film face down on a clean, lint-free, tissue-covered surface, ready for use, or on a sample tray specifically designed to hold cups during the sample preparation process.

8.1.3 Pour either a sample or standard into the prepared sample cup so that it is level to any recommended mark on the cup. If there is no mark, then fill the cups about two–thirds full. It is important that all samples and standards used for a particular application contain approximately the same quantity of sample.

8.1.4 Verify that the prepared cup does not leak as in 5.1.3.5 for the first time a new sample type is analyzed. After that, look at each prepared cup for any signs of a leak. If a leak is detected, prepare another cup, fill it, and check again for leaks.

8.1.5 Use instrument autosamplers only if repeatability data demonstrates that the sample and sample cup (including film) integrity do not change during the waiting time on the autosampler and during the analysis time.

8.1.6 When the measurement is complete, remove the sample/standard, and check for leaks that may have occurred during the measurement. If the sample shows signs of leakage, repeat the measurement with a new cup, and discard the leaking sample's measurement.

8.2 *Cup Preparation and Measurement (Closed Cell):*

8.2.1 Place a new sample cell on a supporting surface, and pour the liquid to be analyzed into the cell to the recommended level or two-thirds full. It is important that all samples and standards used for a particular application contain approximately the same quantity of sample.

8.2.2 Seal the film over the open end of the cell using the provided sleeve or snap-on ring. (**Warning—**Take care not to touch the film to avoid contamination. Take care to avoid wrinkles in the film.) Ideally the film surface will be taut and flat.

8.2.3 Avoid puncturing the film during the sealing process. Check the completed cell for leaks. This can be done immediately after attaching the film by inverting the cell and reinverting. If a leak is present, a liquid front can be seen migrating from the leak across the outside film surface. This can also be done by placing the cell on a clean tissue, film side down, and observing the appearance of liquid on the tissue. Use extreme care with the tissue method to avoid contamination.

8.2.4 Immediately after the cell is sealed and it has been determined that it does not leak, pierce the top of the plastic cup for a vent to avoid pressure buildup and bulging of the film. This can be accomplished by placing the cell into the sample holder and using a push pin or other such tool to puncture the plastic.

8.2.5 Place the cup in the analysis position of the instrument, and measure it promptly. Use instrument autosamplers only if repeatability data demonstrates that the sample and sample cup (including film) integrity do not change during the waiting time on the autosampler and during the analysis time.

8.2.6 When the measurement is complete, remove the sample/standard, and check for leaks that may have occurred during the measurement. If the sample shows signs of leakage, repeat the measurement with a new cup, and discard the leaking sample's measurement.

8.3 *Sealed Sample Holders (Closed Cells)*—There are special sealed cups available to analyze high vapor pressure liquids. These cups are necessary when the liquid could contaminate the optical path of the spectrometer and are useful when analyzing so called winter gas. They are also necessary when using a spectrometer with tube above optics. They function by displacing the air bubble from the cell. Without any head space for vapors to expand into, the sample may be analyzed without undue fear of rupture.

9. Measurement of Standard/Sample

9.1 Ensure all support gases are turned on, for example, helium or nitrogen if this is required, or the supply gas for the flow counter. Check that gas pressure is set to the appropriate level for the instrument. Also, check the cooling medium for the detectors (if required), and verify the temperature stability of the instrument.

9.2 Handling of samples once prepared for measurement requires consideration prior to the establishment of an analytical method. Some petroleum products are unstable at room temperature and pressure. Samples can lose analytes preferentially giving rise to erroneous results.

9.2.1 When measuring volatile samples, a measurement protocol should be developed to ensure that sample loss will not affect a result. Suggested procedures to consider are as follows:

9.2.1.1 Only prepare a sample just prior to analysis. All standards and samples should follow a strict time-based preparation procedure. If a sample is prepared outside this time base or a measurement is delayed for any reason, then a new sample should be prepared. This should include the preparation of a new sample cup and film.

9.2.1.2 Design a measurement strategy to monitor the effect of sample loss during analysis. The most common method for this is the measurement of a matrix sensitive portion of the spectrum such as the Compton peak. The ratio of this peak to the analyte peak can correct for changes in samples, however constant mass or volume should be used if this method is to provide accurate correction for physical changes in a sample during measurement.

9.2.1.3 Use of an automated sample handling system should be avoided if a sample undergoes any changes during the time from preparation to completion of analysis, or if sample loss is expected. Common matrix types that this would apply to are gasoline, diesel, and sample types that cause any change to the sample support film, like relaxation or permeation. This is because samples will be stored in the sample handler for varying times giving rise to drift or bias in results.

10. Calibration of Acquired Data (Regression)

10.1 Once intensity data has been generated using either a WDXRF or EDXRF spectrometer, the treatment of the data is essentially the same. Within regression, a number of corrections can be made for background, line overlap, and matrix. For each correction made, there is an associated error. It is important to minimize the number of corrections to minimize the overall error on any element analysis.

10.1.1 Background corrections can be carried out in many ways. WDXRF makes discrete measurements of background around and near the element peak of interest, determines the amount of background existing beneath a peak, and removes it. EDXRF deconvolutes a spectrum and uses various mathematical background fitting models to remove background from a result. Background can also be removed by measuring a region of background close to the peak of interest, which does not contain any element, and establishing a relationship between this background region and the background that exists beneath the peak of interest. This latter technique is referred to as measured background subtraction. For trace element analysis where very small peak intensities often exist on relatively high backgrounds, the method used to measure and remove background is critical. A careful assessment of the most appropriate method should be undertaken by looking at the associated errors involved and whether background removal is needed at all. In petroleum products, backgrounds are often considerable.

10.1.2 Line overlaps of any type require the measurement of a component of an overlapping line that is related directly to the overlap of the element of interest. The overlapping line is then subtracted from the element of interest by the measurement of the related component and applying an overlap factor to remove the overlap. This is often achieved via the measurement of a K series line where the L series overlap. It is important that the statistical counting error of the overlap function does not add significantly to the error of the overall analysis. The coefficient of variation for each overlapping line should be at least equal to that of the analyte line of interest.

10.1.3 Various matrix correction models are available to spectroscopists for XRF. The two most common are the application of theoretical concentration alphas and ratio to Compton or Compton Correction. Theoretical alphas have the advantage of not adding additional error via the correction itself but are restricted in that all major constituents need to have a concentration associated with them and it is not advisable to apply them over very wide concentration ranges. Compton correction requires the measurement of the X-ray tube most sensitive α Compton line. This is often the Kα line. For low atomic number tube types, this line is often not available for measurement. Statistical counting errors should be carefully assessed if this method is used. For elements with lines lower in energy and greater in wavelength than the first major element in a sample, this method should not be used.

10.1.4 Infinite thickness is an important factor for the determination of high atomic number elements in petroleum products. To use matrix correction methods and to correctly assess and remove backgrounds and overlaps, samples should be infinitely thick with respect to all elements measured. Where this is not the case, using a fixed mass standard/sample should be employed.

11. Validating an Analysis

11.1 Once a standard or sample has been measured, a procedure should be carried out to validate that measurement. This requires the operator to check for obvious signs of damage to the sample such as leaking sample cells, crinkled sample cell window (especially important for low atomic number elements atomic number <13) and inspection of any secondary film.

11.2 If a measured result is considered to be outside the range of expected results, the sample should be prepared again and reanalyzed.

11.3 Regular checks should be carried out to ensure that purging gas performance is within the instrument manufacturer's specification.

11.4 Quality control standards/monitors should be run on a regular basis. The tolerance levels of the checks made using these monitors should be such that a protocol of either drift correction or total recalibration is carried out if the results fall outside these levels. All measurements between the last accepted monitor result and the point of non-compliance should be repeated, if a current monitor measurement proves to be outside acceptable levels.

11.4.1 Selection of calibration samples and elemental interferences are addressed in the test methods listed in the Referenced Documents (2).

11.4.2 The use of correct statistical quality control (SQC) techniques with all XRF methods is highly encouraged. It is recommended that at least one type of quality control sample be analyzed that is representative of typical laboratory samples as defined in Practice D6299.

12. Keywords

12.1 calibration; EDXRF; regression; validation; WDXRF

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