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An American National Standard

Standard Guide for Using Micro X-Ray Fluorescence (µ-XRF) in Forensic Polymer Examinations[1]

This standard is issued under the fixed designation E3295; 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.

INTRODUCTION

Micro X-ray fluorescence spectrometry (µ-XRF) is one technique in an analytical scheme that can provide information regarding potential relationships between the sources of polymeric materials.

1. Scope

1.1 This guide covers recommended techniques and procedures intended for use by forensic laboratory personnel that perform µ-XRF analysis of polymer samples.

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1.2 This guide describes various techniques and procedures used in the µ-XRF analysis of polymers that include sample handling and preparation, instrument operating conditions, and spectral data collection, evaluation and interpretation.

1.3 This guide describes the application of µ-XRF systems equipped with either mono- or poly- capillary optics and an energy dispersive X-ray detector (EDS).

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1.4 This guide is intended to be applied within the scope of a broader analytical scheme (for example, Guide E1610, Guide E3260) for the forensic analysis of a polymer sample (**1-6**).[2] A µ-XRF analysis can provide additional information regarding the potential relationships between the sources of polymeric materials.

1.5 The fundamental aspects of the composition and manufacture of polymeric materials or theory of X-ray fluorescence can be found in various texts (**7-18**).

1.6 This standard is intended for use by competent forensic science practitioners with the requisite formal education, discipline-specific training (see Practices E2917, E3233, E3234), and demonstrated proficiency to perform forensic casework.

1.7 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

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1.9 *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:*[3]

E620 Practice for Reporting Opinions of Scientific or Technical Experts
E1492 Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory
E1610 Guide for Forensic Paint Analysis and Comparison
E1732 Terminology Relating to Forensic Science
E2917 Practice for Forensic Science Practitioner Training, Continuing Education, and Professional Development Programs
E2926 Test Method for Forensic Comparison of Glass Using Micro X-ray Fluorescence (μ-XRF) Spectrometry
E3233 Practice for Forensic Tape Analysis Training Program
E3234 Practice for Forensic Paint Analysis Training Program
E3260 Guide for Forensic Examination and Comparison of Pressure Sensitive Tapes

2.2 *SWGMAT Documents:*[4]

SWGMAT Trace Evidence Recovery Guidelines
SWGMAT Trace Evidence Quality Assurance Guidelines

2.3 *ISO Standard:*[5]

ISO/IEC 17025 Laboratory Competence

3. Terminology

3.1 *Definitions*—The terms defined relate specifically to μ-XRF as described in this document. For additional terms commonly employed for general forensic examinations, see Terminology E1732.

3.2 *Definitions:*

3.2.1 *background radiation, n*—X-rays resulting from scattered Bremsstrahlung and coherently and incoherently scattered tube target peaks.

3.2.2 *characteristic X-ray, n*—X-ray emission resulting from de-excitation of an atom following inner shell ionization.

3.2.2.1 *Discussion*—
The energy of a characteristic X-ray is related to the atomic number of the atom, providing the basis for energy dispersive X-ray spectroscopy.

3.2.3 *coherent (Rayleigh) scatter peaks, n*—spectral artifacts that result from elastic scattering of the tube target characteristic X-rays by the sample.

3.2.3.1 *Discussion*—
Because no energy is lost in elastic scattering, coherent scatter peaks occur at the same energies as the tube target characteristic X-rays.

3.2.4 *dead time, n*—the time (expressed as a percentage of real time) during which the energy dispersive X-ray spectrometer is not able to process X-rays.

3.2.5 *diffraction peaks, n*—spectral artifacts that result from preferential diffraction of tube X-rays into the detector as a result of striking a crystalline sample.

3.2.5.1 *Discussion*—
Diffraction peaks vary in energy and intensity depending on orientation of the crystalline planes with respect to the beam angle.

3.2.6 *escape peak, n*—a spectral artifact resulting from incomplete deposition of the energy of an X-ray entering the energy dispersive X-ray spectrometer detector.

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[3] 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.

[4] Available from https://www.asteetrace.org/subtrace.

[5] Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, https://www.iso.org.

3.2.6.1 *Discussion—*
An escape peak is produced when an incoming X-ray excites a silicon atom within the detector crystal, and the resulting Si Kα fluorescence X-ray exits the detector crystal. It occurs at the energy for the original X-ray minus the energy of the Si Kα fluorescence X-ray (1.74 keV). The escape peak intensity is about 1-2 % of the parent peak.

3.2.7 *exclusionary difference, n*—a difference in ~~a feature or property~~ one or more characteristics between compared items that is ~~substantial enough~~ sufficient to determine that ~~they~~ the compared items did not originate from the same ~~source.~~source, are not the same source, or do not share the same composition or classification.

3.2.8 *incoherent (Compton) scatter peaks, n*—spectral artifacts that result from inelastic scattering of the tube target characteristic X-rays by the sample.

3.2.8.1 *Discussion—*
Because energy is lost in inelastic scattering, incoherent scatter peaks occur at a lower energy than the tube target characteristic X-rays.

3.2.9 *KLM reference lines, n*—the energies associated with the transitions of the K, L, and M shell electrons.

3.2.9.1 *Discussion—*
Each element has characteristic energies of transitions of electrons between shells.

3.2.10 *live time, n*—the time during which an energy dispersive X-ray spectrometer is available to accept and process incoming X-rays.

3.2.10.1 *Discussion—*
Live time is often expressed as a percentage of real time, in seconds.

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3.2.11 *pulse processor time constant, n*—operator-selected value for the time designated to record a response by the detector. A higher value (longer time) results in a more accurate determination of the detector amplifier pulse height (better spectral resolution). A lower value results in a higher count rate but with reduced spectral resolution.

3.2.12 *spectral artifacts, n*—spectral peaks other than characteristic peaks from the sample, produced during the energy dispersive detection process. Examples include escape peaks, sum peaks, tube target coherent and incoherent scatter peaks, system peaks, and diffraction peaks.

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3.2.13 *spectral resolution, n*—measure of the ability to distinguish between adjacent peaks in a spectrum; it is usually determined by measuring peak width at half the maximum value of the peak height or full-width half-maximum (FWHM).

3.2.13.1 *Discussion—*
This value is usually quoted for the FWHM of Mn Kα.

3.2.14 *sum peak, n*—a spectral artifact that results from the simultaneous detection of two X-rays, manifested as a peak at the combined energy of the detected X-rays.

3.2.15 *system peaks, n*—spectral artifacts that result from the production of characteristic X-rays from structural components of the XRF instrument.

4. Significance and Use

4.1 µ-XRF is a nondestructive qualitative elemental analysis technique used for polymers. It involves excitation of a sample by an X-ray source resulting in the emission of characteristic X-rays detected using an energy dispersive X-ray detector. Results are displayed simultaneously as a spectrum of intensity as a function of energy for elements of atomic number 11 or greater.

4.2 µ-XRF enables the determination of the elemental composition of a specimen and can be utilized for comparisons of components of polymeric materials (for example, tape backings, tape adhesives, paint layers).

4.3 Comparisons of X-ray spectra acquired from polymer samples are conducted for source discrimination or potential association.

4.4 Quantitative processes for μ-XRF analysis are available but are not used for polymer analyses because of the lack of prepared polymer standard reference samples.

4.5 In general, information available from a heterogeneous specimen diminishes as its size is reduced or its condition degrades, which lessens its likelihood of being representative of the source material.

4.6 μ-XRF data collected from polymers is limited to specific information (for example, elements detected, relative elemental abundance); additional analytical procedures are required to further characterize and identify the chemical composition of the polymer sample.

4.7 Limitations of μ-XRF include the inability to detect some elements in trace concentrations, the inability to analyze individual particles, the potential interference related to the penetration depth of the beam relative to the sample thickness, the inability to resolve the peaks of some elements (for example, Ba Lα / Ti Kα), and the potential for discoloration of some materials due to exposure to radiation.

5. Calibration and Standardization

5.1 *Performance Checks*—The instrument is optimized in accordance with manufacturer's instruction.

5.1.1 Prior to sample analysis, operating tolerances for each of the following parameters and the minimum frequency at which they are monitored are established and recorded:

5.1.1.1 *Energy Calibration*—The X-ray energy scale is calibrated to characteristic X-ray emission lines by either measuring the centroid energy of a low- (<2 keV) and high- (>6 keV) energy peak or by using software provided by the instrument manufacturer. For example, the aluminum (1.486 keV) and copper (8.040 keV) Kα -X-ray energy lines can be used.

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5.1.1.2 *Stage Calibration*—For automated or multiple point analysis, the stage position is initialized to ensure that the stage coordinates accurately reflect the stage position.

5.1.1.3 *Optical Alignment*—X-ray optics are aligned to obtain the maximum count rate. Align visualization optics to ensure that the visual target area coincides with the X-ray beam position.

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5.1.1.4 *Reference Standard*—A reference sample (for example, NIST SRM 1831, Mn, and Zr) is analyzed to verify calibration of X-ray energy lines for elements present and determine if the instrument response is within acceptable limits.

5.1.1.5 *Blanks*—A spectrum is collected of a sample devoid of elements having an atomic number of 11 or greater, such as the plastic stage plate or an area of the support material having no sample present. System peaks present are recorded for future reference.

6. Specimen and Sample Handling

6.1 Practice E1492 and relevant portions of the SWGMAT Trace Evidence Quality Assurance Guidelines and Trace Evidence Recovery Guidelines are followed for the collection, handling, and tracking of samples and specimens.

6.2 In developing an analytical scheme, consider the following:

6.2.1 Presence of extraneous materials and a strategy for removal,

6.2.2 Means of attachment to an inert XRF mount,

6.2.3 Procedure(s) for producing a uniform geometry, and

6.2.4 Determination of the presence of surface features of analytical interest.

6.3 *Sample Preparation:*

6.3.1 The specimen is examined to determine an appropriate sample preparation approach. The choice for sample preparation depends on the size, nature, and condition of the specimen, as well as the analytical objective. Multiple preparation procedures are described below for use as necessary.

6.3.2 Samples for comparison are prepared under the same conditions whenever possible. The preparation approach, any details required to reproduce the preparation process, and differences between sample preparations are recorded.

6.3.3 Samples for μ-XRF analysis are prepared in a manner that permits resolution and analysis of individual layers, using one or more of the following:

6.3.3.1 A portion or all of the specimen is cleaned to remove any contamination or extraneous materials that might interfere with the analysis. This can be accomplished using physical means (for example, particle picking with a probe, exposing underlying polymer with a scalpel) or chemical means (for example, washing in a solvent).

6.3.3.2 Cross-sections of multiple layers or thin sections within a single layer are removed using a scalpel, microtome, or other separation technique.

6.3.4 The sample mounting technique depends on the sample size and shape, beam size, X-ray fluorescence spectrometer chamber design, and purpose of the examination.

6.3.5 Samples are elevated off the surface of the analysis stage using an X-ray transparent sample holder or supportive X-ray film, or both. This sample mounting improves the spectrum signal-to-noise ratio by reducing X-ray scatter from the surface of the stage. Because analysis is performed under vacuum, samples are secured with adhesive to retain their position on the sample holder. Several different thin polymer support films are commercially available (for example, mylar, polypropylene, ~~polycarbonate, Kapton).~~ polycarbonate). These films vary in their X-ray transmission characteristics and therefore should be evaluated and selected based upon their transmission characteristics.

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6.3.6 The penetration depth of the X-ray beam in a polymer sample is difficult to predict since it is dependent on the elemental composition of the sample and, hence, the absorption characteristics of that sample. Because beam penetration can reach several millimeters below the top surface, X-ray emissions from underlying layers, substrate, or both can be detected. In addition, the intensity of the X-ray emissions from an element in the uppermost layers can be enhanced. These effects will generally be confined to the higher energy X-rays in each layer and will be affected by the total elemental composition of each layer.

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6.3.7 Samples removed from individual layers of multi-layered items (for example, paint layers, tape backing and adhesive) should be mounted separately.

6.3.8 The geometry of compared samples, including flatness, thickness, and take-off angle, should be similar.

6.3.9 A small amount of the mounting adhesive and mounting film is also analyzed to determine the presence of any elements in the sample X-ray spectrum that can be attributed to these materials.

7. Instrument Operating Conditions

7.1 The following are recommended operating parameters that can be altered to optimize conditions for various analytical needs. As the analyst determines specific analytical needs, actual operating conditions can vary.

7.1.1 Samples being compared are analyzed using the same operating conditions.

7.1.2 Instrumental configurations can impact operating conditions.

7.1.3 *Vacuum Mode*—Samples are analyzed under vacuum.

7.1.4 *Tube Voltage*—A tube voltage of at least 30 kV allows for sufficient over-voltage necessary for efficient X-ray excitation. Typical X-ray emissions from polymers can be displayed with an energy range of 0 to 20 keV.

7.1.4.1 Tube voltage is increased when higher energy line excitation is desired.

7.1.5 *Tube Current*—The tube current is adjusted to yield an adequate X-ray detector count rate (counts per second) that does not exceed the dead time threshold recommended for a particular instrument. Increase tube current when the X-ray count rate is too low. Tube current is decreased when the X-ray count rate is too high.

7.1.6 *Pulse Processor Time Constant*—The detector shall be configured to produce a resolution of better (less) than 150 eV during analysis, measured or extrapolated as the full width at half maximum height of the Mn Ka peak. The time constant can be set to allow the maximum rate at the poorest acceptable resolution (150 eV) from the detector and electronics. The time constant is used to balance the tradeoff between speed of analysis, X-Ray resolution, and spectral artifacts (sum peaks). An example of need for better resolution would be for peak overlaps.

7.1.7 *Collection Time*—Select a live time that provides a sufficient signal-to-noise ratio to meet the analytical needs.

7.1.7.1 A longer X-ray acquisition time is used for samples that contain elements with concentrations near the detection limits.

8. Spectral Data and Interpretation

8.1 *Spectral Collection:*

8.1.1 Replicate spectra are collected to be representative of each comparison specimen.

8.1.1.1 The sampled area and number of replicate spectra necessary to be representative of the specimen depend on the characteristics of the material, instrument configuration, and procedure parameters.

8.1.1.2 Spectra representing larger areas can be collected using optics that allow for a larger sampled area or can be produced by summing spectra from multiple areas.

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8.2 *Spectral Evaluation:*

8.2.1 A typical XRF sample spectrum consists of characteristic X-rays from elements within the sample, background radiation, and spectral artifacts. Spectral evaluation includes assessment of the heterogeneity of the material and determination of its elemental composition.

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8.2.2 *Heterogeneity:*

8.2.2.1 When no apparent spectral variations are evident among replicate spectra of multiple samples from a specimen, the specimen is considered homogeneous in the elemental composition as observed by micro-XRF.

8.2.2.2 When spectral variations exist among replicate spectra of one or more samples from a specimen, the specimen is considered heterogeneous.

8.2.3 *Peak Detection*—A peak is generally considered to be detected when the signal is greater than three times the noise, where noise is the square root of the background (**19, 20**).

8.2.4 *Peak Assignment*—Assign peaks to elements or spectral artifacts.

8.2.4.1 *Element Assignment*—As possible, identify all elements in a spectrum using X-ray peak centroid energy values/markers for K, L, or M α X-rays; the presence of their associated β X-ray peak centroid energies; and the possible presence of L γ X-ray peaks in a spectrum (**21**). Typically, software packages can detect peaks above background, locate their centroid energies, compare those energies with established tables of K, L and M X-ray energies, and automatically identify those elements by placing element symbols on those peaks. It is the analyst's responsibility to manually confirm that each automatically identified element is present in the spectrum by inspecting each assigned element's peak to ensure that the peak centroid is located at its characteristic energy. In addition, determine that the intensities of each element's characteristic α, β, and γ X-ray peaks, or a combination thereof, are in the proper ratios. Only then can the analyst conclude that a particular element is within a sample spectrum.

8.2.4.2 An element is considered to be present if a distinctive set of lines is produced or when a single peak occurs at an energy which cannot be mistaken for another element or spectral artifact. Identification of an element is not always possible, such as when an element is present at low levels or the lines required for confirmation are overlapped with the lines of other elements.

8.2.4.3 *Overlap Assignment*—The K, L, or M X-ray peak energies for specific elements can overlap. The interpretation of overlapping peaks can be aided by spectral simulation and automated spectral deconvolution tools present in most EDS data collection software. The deconvolution of interferences depends on the detector resolution, time constant, excitation voltage, and concentration of overlapping elements. In addition, the collection of additional data under different conditions (for example, the use of higher voltage to examine higher energy X-ray emission lines, the use of slower time constants to obtain better peak resolution) can help to confirm the presence of certain elements or resolve element peak overlaps. Common overlapping element X-rays include:

- Ti Kβ / V Kα
- V Kβ / Cr Kα
- Cr Kβ / Mn Kα
- Mn Kβ / Fe Kα
- Fe Kβ / Co Kα
- Pb Mα / S Kα / Mo Lα
- Ba Lα / Ti Kα
- K Kβ / Ca Kα
- Zn Lα / Na Kα
- P Kα / Zr Lα
- Al Kα / Br Lα

8.2.4.4 *Spectral Artifact Assignment*—Spectral artifacts result from detector processes (escape peaks, sum peaks), beam-sample interactions (coherent and incoherent scatter peaks, diffraction peaks), or non-sample sources (system peaks). Possible approaches to identifying spectral artifacts include the collection of a spectrum under different conditions (for example, vary the time constant, beam current, or sample tilt or height), the collection of a reference sample (for example, pure acrylic block), or the use of software tools. Some software tools can filter out some spectral artifacts.

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8.2.5 *Peak Labeling*—Each identified peak is labeled with the corresponding elemental symbol. Denote if the identification is tentative.

8.2.6 *Documentation*—Each spectrum is annotated with assigned peaks to permit a future review of peak assignments. It is recommended that additional views of a spectrum, with expanded axes, are also recorded to illustrate the presence of minor peaks.

8.3 *XRF Spectral Comparison:*

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8.3.1 XRF spectral comparisons should be conducted between spectra collected using similar sample preparations, similar sample characteristics (for example, thickness, topography), and similar instrumental parameters, as appropriate.

8.3.2 XRF spectra are compared and interpreted based on the observation of any spectral differences, or lack thereof, between the sets of XRF data. Such comparisons can be conducted using statistical analyses in concert with expert judgment, as appropriate, or through expert judgment alone if the data sets do not provide a basis for the use of statistical methods.

8.3.2.1 Spectral overlay can be used for comparing data where the presence or absence of peaks, peak shapes, and relative intensities are all considered in the evaluation as to whether exclusionary differences exist between compared samples (Test Method E2926) (**20, 22-28**).

8.3.2.2 When assessing differences between spectra, consider sample limitations (for example, small samples, thin layers, dirty samples, sample smears that eliminate layer structure) and instrumental limitations (for example, sampling size, limits of detection).

8.3.3 Possible reasons for spectral differences include dissimilar sample characteristics (for example, size, thickness, surface topography), heterogeneity, contribution from extraneous materials, or origination from different source materials. Additional samples can provide supplemental data to assist in assessing such differences.

8.3.4 If suitable XRF spectra are produced, comparisons can provide information regarding the potential relationship between the sources of the samples.

8.3.4.1 When exclusionary differences are observed between compared spectral features, the sources of the samples are considered