Designation: D 5381 – 93 (Reapproved I998)

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Guide for X-Ray Fluorescence (XRF) Spectroscopy of Pigments and Extenders[1]

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1. Scope

1.1 This guide covers the general considerations for proper use of X-ray fluorescence (XRF) spectroscopy. Because many differences exist between XRF instruments, no detailed operating instructions are provided. The analyst should follow the instructions provided by the manufacturer for his instrument.

1.2 The analyst is encouraged to consult the chemical literature, various trade journals, pigment supplier publications, etc., as well as the instrument manuals from the manufacturer.

1.3 XRF is commonly employed to determine the elements present in inorganic pigments and extenders, often in concert with other analysis techniques. Organic pigments cannot normally be identified solely by XRF. On occasion, organic pigments contain heavier elements that can distinguish between major classes of these pigments or may serve to distinguish one of the two distinct pigments. However, the analyst should be wary of a qualitative pigment identification solely by XRF technique.

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.* For specific hazard information see Section 3 on Radiation Concerns.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings[2]

3. Radiation Concerns

3.1 Modern XRF instrumentation has been designed to minimize exposure of laboratory personnel to X-ray radiation during instrument use. However, most laboratories use dosimetry to monitor personnel who are normally present around the XRF instrument while it is in operation. Such dosimetry devices are normally read on a monthly basis.

3.2 After XRF instrument maintenance (especially where the X-ray tube, detector, or shielding has been moved or replaced), an X-ray survey of all areas around the instrument (while in operation) is recommended. The results of such a survey should be documented and stored for future reference.

3.3 It is recommended that the laboratory check its compliance with all applicable local, state, and federal requirements. Many companies also have policies concerning use of X-ray equipment in their laboratories.

3.4 It is common laboratory practice to post placards on all entrances to the laboratories containing X-ray equipment that indicate its presence.

4. Summary of the Guide

4.1 A general guide for qualitative elemental analysis of paint and paint components is provided. Knowledge of the elements present in a sample can be used to infer the identity of pigments and extenders that may be present. The absence of specific pigments and extenders can be proven by the absence of their constituent elements. The presence or absence of toxic elements can be demonstrated. Analysis consists of irradiating the test specimen with monochromatic X-rays and determining the energy or wavelength of the fluorescent X-ray emitted by the specimen. Since different elements emit X-rays with different energy and wavelength under these conditions, the element content of the specimen can be determined by examination of the X-ray spectrum. The spectrum is recorded either on chart paper or magnetic media. Identification of the constituent elements is accomplished by comparing the peaks in the spectrum with known tabulated data, using either manual or computer-assisted procedures.

5. Significance and Use

5.1 The identification of pigments in a sample of liquid paint or paint film is often important for regulatory purposes. Many inorganic pigments or extenders utilized in past paint formulation are now regulated by federal, state, or municipal health authorities. XRF is one of the more common and convenient methods employed to characterize the pigment composition of a paint formulation.

5.2 XRF techniques, in general, do not provide the ability to identify the chemical nature of organic pigments. There are instances where XRF techniques, used in tandem with other analytical methods, such as solid state Carbon 13 Nuclear Magnetic Resonance (C-13 NMR), can identify the organic

[1] This guide is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

Current edition approved April 15, 1993. Published June 1993.

[2] *Annual Book of ASTM Standards*, Vol 06.01.

pigments utilized in coatings. However, XRF provides only an elemental sketch of the inorganic pigmentation. The chemical composition of the pigments is inferred by the analyst from the samples, color, elemental information, and common sense. Small impurities are often found in pigments, so the relative XRF intensities also serve to guide the analyst in proposing the probable pigment present.

6. Apparatus

6.1 *XRF Spectrometer*—Either an energy dispersive or wavelength dispersive X-ray fluorescence spectrometer is required. The instrument should be able to operate with the analysis chamber either evacuated or purged with helium. The instrument should be able to detect all elements with atomic number 11 (sodium) or higher. Extention of the atomic number range below 11 may be desirable for some users, an option available at higher cost.

6.2 *Sample Cups*—Suitable sample containers are normally specified in the manufacturer's operating manuals. Sample containers are after polyethylene cups that are sealed with polyester film or polypropylene sheeting.

7. Samples

7.1 Samples may be either a solid or liquid sample of paint or pigment.

7.1.1 Liquid paint samples may be introduced directly into the sample containers and the container sealed to prevent spillage. Normally, the XRF specimen chamber is purged with helium while running liquid samples.

7.1.2 Solid samples may be in powder form, supported tablets (briquettes), or paint chips. If paint chips contain several distinct paint layers, the resulting XRF spectrum will be a compilation of elements detected in all paint layers. If a supported pellet or briquette is made prior to analysis, the analyst should know the binder's elemental composition to avoid misinterpreting the resulting spectrum. Analyze loose powder under helium purge. Firmly briquetted samples may be run under vacuum.

8. Calibration

8.1 Set up the XRF instrument in accordance with the specific manufacturer's instructions.

8.2 Perform calibration of the XRF spectrometer based on the manufacturer's recommendation. Stainless Steel #316 discs are often used to check the operation of the XRF instrument. Because of the wide variety of XRF instruments on the market, no specific calibration instructions will be provided.

9. Interpreting Results

9.1 Computer–based elemental identification routines are often employed for determining the identity of the various X-ray fluorescence lines. Despite the sophistication of these software routines, the analyst must be wary of placing too much reliance on them. It is important that the analyst check the identification of each peak based on the sample's color and the knowledge of the common inorganic pigments used in coatings.

9.2 Some paint formulations employ inorganic driers. The elements contained in these dryers may appear in the XRF spectrum. Normally, these peaks are of lower intensity compared to the intensity of the inorganic pigments.

9.3 The energy dispersive XRF instruments normally produce a less well–resolved X-ray spectrum than wavelength dispersion instruments. It is even of greater importance that the operator use caution with computer-based peak identification routines.

10. Keywords

10.1 briquette; extender; energy dispersive XRF; inorganic drier; pigment; spectroscopy; wavelength dispersive XRF; X-ray fluorescence