X-Ray Diffraction Analysis of Tapes

1 Scope

This procedure applies to Chemistry Unit caseworking personnel who analyze paints and polymers via X-ray diffractometry (XRD). This document describes the sample preparation and suggested instrumental parameters for the XRD analysis of pressure sensitive adhesive tapes.

2 Equipment/Materials/Reagents

a. X-ray Diffractometer system (e.g., Malvern Panalytical Empyrean, Rigaku MiniFlex, or equivalent) and accompanying software

b. Sample holder equipped with low background substrate

c. Stereo microscope (~6X to ~50X) with appropriate lighting

d. Scalpel handle with blades

e. Glass microscope slides

f. Tweezers

g. Disposable wipes

h. Cotton-tipped applicators

i. Acetone

j. Chloroform

k. Hexane

l. Methanol

3 Standards and Controls

3.1 Standards

Manufacturer-supplied and commercially available tapes, polymers, and adhesives are maintained in reference collections within the FBI Laboratory. These materials are used in

casework in accordance with the Chemistry Unit's *Procedures for the Use of Reference Materials and Known Materials.*

3.2 Performance Checks

Performance checks for the Trace Evidence Unit (TEU) XRD instrument are conducted by personnel in the Mineralogy Subgroup. Refer to both the instrument logbook as well as the *X-ray Powder Diffractometry Using the Empyrean X-ray Diffractometer* SOP (TEU XRD SOP) to determine if this check is current.

The performance check for the Rigaku Miniflex XRD instruments is conducted on the day of analysis according to the guidance set forth in the *Performance Monitoring Protocol (QA/QC) for the Rigaku MiniFlex X-Ray Diffractometer (XRD)* SOP (CU XRD SOP).

4 Sampling

Refer to the current version of *General Approach for Tape Casework* (PPSU 102) for guidance on sample(s) selection. Record the samples selected for analysis in the case notes.

5 Procedure

1. Sample preparation will depend on sample type, size, and condition. If the sample is contaminated or too limited in size, record as such in the case notes. All tapes are generally analyzed intact. Additionally, the film backing can be analyzed separately.

    a. Prior to analysis, clean the tape backings using a cotton swab or disposable wipe and as necessary, an appropriate solvent (e.g., methanol, acetone).

    b. To analyze an intact specimen, obtain a sample area large enough to fill the sample holder. Using the sample holder as a template, cut a sample of the specimen with a scalpel blade. If the specimen is a partial roll of tape, the roll should be unwound approximately three to four inches before sampling in order to eliminate stretching or distorting the film.

    c. The same sample preparation should be used for the analysis of the tape backing. The adhesive and scrim fabric, if present, is removed using a suitable solvent (e.g., hexane or chloroform for rubber-based adhesives, acetone for acrylic-based adhesives).

    d. Place the specimens on the sample holder in a manner that results in a flat, uniform surface for X-ray beam interaction. Specimens containing adhesive can be affixed directly onto the XRD sample holder. When only the film backing is analyzed, a

small amount of adhesive can be applied to affix the sample to the sample holder outside the sampling area where the X-ray beam impinges.

2. Ensure that the quality assurance procedures to include performance checks have been conducted. Refer to the instrument logbook for this information.

3. Analyze the sample(s) by XRD. Note: depending upon the instrument used, manually adjust operating conditions if they are not automatically set when selecting an analysis method.

4. If the compositions of two specimens are to be compared, analyze them both under the same instrumental conditions.

5. Ensure the instrument identification and the operating parameters are recorded on the printed spectra or elsewhere in the case notes.

6. If phase identification in the resulting diffraction pattern is necessary, use the Powder Diffraction File, or analyze an appropriate reference material under the same operating conditions as the unknown sample.

7. Upon completion of the analysis, remove all samples from the sample chamber and, if necessary, return the instrument to standby conditions.

6 Instrumental Conditions

6.1 Suggested operating conditions for the Malvern-Panalytical Empyrean XRD are listed in the TEU XRD SOP. The following instrumental conditions serve as a guide for analysis of tape and adhesive standards and samples described in this SOP:

<u>Generator Settings:</u>

Standby:	30 kV 10 mA
Analysis:	45 kV 40 mA
Anode material:	Copper (Cu)
Filter type:	Nickel (Ni)

<u>Incident Beam Path:</u>

Soller slits incident beam:	0.03 rad.
Soller slits diffracted beam:	0.04 rad.
Fixed divergence slit:	¼°
Fixed anti-scatter slit:	¼°
Fixed beam mask:	14 mm

Scan range:	8 – 80 ° 2Θ
Step size:	0.0131 ° 2Θ (~5 mins/sample)
Scan type:	Continuous

6.2 Suggested operating conditions for the Rigaku MiniFlex XRD are listed in the CU XRD SOP. The following instrumental conditions serve as a guide for analysis of tape and adhesive standards and samples described in this SOP:

Anode material: Copper (Cu)
Scan range: 5 – 75 ° 2Θ
Scan width: 0.0200 ° 2Θ
Scan speed: 2.000 degrees/min (slow scan, ~ 15mins/sample)
Scan type: Continuous

7 Decision Criteria

a. If exclusionary differences are observed between the diffraction patterns of two (or more) samples being compared, then it is concluded that the specimens differ from one another.

b. If no differences are observed between the diffraction patterns of two (or more) samples being compared, then it is concluded that they are indistinguishable from one another.

c. If XRD is being used to characterize a component of the tape(e.g., polyethylene, calcite), the diffraction pattern of that material should compare favorably to a corresponding reference powder diffraction file or known duct tape analyzed in-house.

d. Proper sample preparation is critical for XRD analysis. The following are some common sample preparation problems encountered in XRD analysis:

   i. The displacement of the surface of the specimen away from the diffraction axis is the primary source of error in the measurement of diffraction peak positions. The sample must be spread flat on the specimen holder without extending above or below the instrument's diffraction axis.

   ii. Any sample preparation technique should minimize introducing stress and orientation effects ("preferred" orientation).

8 Calculations

Not applicable.

9 Measurement Uncertainty

Not applicable.

10 Limitations

a. On average, the lower limit of detection of a component in a mixture is approximately 1%. This limit will vary depending on composition, degree of crystallinity, and crystallite size.

b. Limited sample size can preclude analysis by this technique.

c. Contamination of the adhesive is not always readily visible under macroscopical or microscopical examination, yet can affect a comparative analysis with a pristine sample.

d. Accurate or reproducible results can be affected when one or more of the following circumstances occur:

   i. The specimen is not homogeneous.

   ii. Crystallites are not randomly oriented; “preferred” orientation or stress exists within the specimen.

   iii. The specimen is amorphous.

11 Precautionary Statements

a. As with any procedure involving trace evidence, ensure actions minimize the potential for loss or contamination of the sample.

b. If two (or more) components in a sample yield a similar diffraction pattern, the peaks can overlap one another; therefore, comparing the composite pattern with known powder diffraction patterns of individual compounds can be difficult.

c. The elasticity inherent in some polymers can cause the flattened backing sample to curl up if insufficient mounting media is used to hold the sample flat and stationary.

12 Safety

Take standard precautions for the handling of potentially biohazardous materials, chemicals, or sharps. Refer to the *FBI Laboratory Safety Manual* and appropriate Safety Data Sheet(s) for further details. Personal radiation monitors (dosimeters) are administered by the Health and Safety group to monitor exposure to ionizing radiation. Operators should familiarize themselves with the specific User’s Guide safety section of the instrument prior to use.

13 References

Buhrke, V.E., et. al, editors. *A Practical Guide for the Preparation of Specimens for X-Ray Fluorescence and X-Ray Diffraction Analysis*, Wiley-VCH, New York, 1998.

Cullity, B.D. *Elements of X-Ray Diffraction*, 2d ed., Addison-Wesley, Reading, MA, 1978.

Procedures for the Use of Reference Materials and Known Materials, FBI Laboratory, Chemistry Unit Quality Assurance Manual

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General Approach for Tape Casework, FBI Laboratory, Chemistry Unit – Paints and Polymers SOP Manual

Jenkins, R., and de Vries, J.L. *An Introduction to X-ray Powder Diffractometry*. N.V. Philips Gloeilampenfabrieken, Eindhoven, Holland, pp.1-40.

Johnston, J. *Pressure Sensitive Adhesive Tapes: A Guide to Their Function, Design, Manufacture, and Use*; Pressure Sensitive Tape Council, Northbrook, IL, 2000.

Manufacturer's Instrument Manuals for the specific models and accessories used.

Mehltretter, A.H., Bradley, M.J. Forensic analysis and discrimination of duct tapes, *Journal of the American Society of Trace Evidence Examiners*, 2012, 3(1): 2-20.

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Sata, D., ed. *Handbook of Pressure Sensitive Adhesive Technology*, 2d ed., NY: Van Nostrand Reinhold, 1989.

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Wright, D.M. and Mehltretter, A.H. Forensic duct tape sourcing examinations: Developing investigative leads using multiple resources, *Journal of the American Society of Trace Evidence Examiners*, 2013, 4(1): 13-28.

X-Ray Powder Diffractometry Using the Empyrean X-ray Diffractometer; FBI Laboratory – Trace Evidence Unit SOP Manual

Rev. #	Issue Date	History
0	05/05/06	New document that replaces previous document also titled *XRD Analysis of Tapes.*
1	09/30/09	Updated sampling section and references.
2	03/14/12	Corrected chemical name of corundum in section 4d. Changed "sampling" plan to "sample selection" plan in section 7. Removed reference to contacting TEU's Mineralogy Subgroup in section 8, part 3. Updated decision criteria in sections 10a and 10b. Changed macroscopic/microscopic to macroscopical/microscopical as well as clarified sample condition in section 13c. Updated references in section 16.
3	02/11/13	Updated section 3. Added more detail to section 8, step 4 to clarify that operating conditions are not automatically set with the analytical method selected.
4	02/03/14	Made minor changes to equipment list to make item descriptions less specific; minor change to specify that performance check monitoring is evaluated within QA review prior to analysis, and updated references.
5	09/18/18	Modified scope to align with LOM revisions; deleted equipment or performance monitoring already contained in instrumental QA/QC SOPs; added flexibility to accommodate broader instrument use; minor grammatical changes throughout; aligned safety section with other P&P SOPs.
6	10/28/20	Updated to reflect newest TEU instrument and SOP throughout. Removed grade of reagents used in equipment list. Minor edits as needed to conform to LOM changes. Minor grammatical edits. Removed need to refer to instrument manuals in Section 5. Edited Section 7 for clarity. Edited Section 10 to remove limitation previously covered in 10iv.

Approval

Redacted - Signatures on File

Paints and Polymers
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