

Raman Analysis of Paints and Polymers

1 Scope

This document applies to Chemistry Unit caseworking personnel who analyze paints and polymers via Raman spectroscopy. This document describes the sample preparation and suggested instrumental parameters for the Raman analysis of paints and other polymeric materials.

2 Equipment/Materials/Reagents

- a. Raman spectrometer with microscope attachment (Horiba or other manufacturer)
- b. Lasers installed in spectrophotometer: 785 nm and 532 nm; others if applicable
- c. Objectives for spectrophotometer microscope attachment: 10x, 100x; others as applicable
- d. Spectral search library (e.g., Know-It-All by Bio-Rad or equivalent)
- e. Stereomicroscope (~6X to ~100X) with appropriate lighting (e.g., annular ring light, fiber optic light)
- f. Polystyrene film
- g. Tweezers
- h. Scalpel handle with blades
- i. Microscope slide(s) (e.g., aluminum, gold, quartz)
- j. Disposable paper wipes

3 Standards and Controls

3.1 Standards

Manufacturer-supplied and commercially available paints, pigments, polymers, or tapes are maintained in reference collections within the FBI Laboratory. These materials are used in casework in accordance with the *Procedures for the Use of Reference Materials and Known Materials*.

3.2 Performance Checks

Refer to the *Performance Monitoring Protocol (QA/QC) for the Raman Spectrometers* for details on the performance checks and necessary supplies to conduct these checks and operate the instrument.

Additionally, polystyrene is analyzed prior to sample analysis on a given day using the following parameters: the 532 nm laser with the 1800 lines/mm grating, 100X objective, the number of acquisitions as 10, and a collection time of 10 seconds. The Decision Criteria for acceptable peak positions for polystyrene are also listed in the *Performance Monitoring Protocol (QA/QC) for the Raman Spectrometers* SOP. This spectrum should be printed and placed in the instrument logbook with the option to also print it for the casefile as applicable.

4 Sampling

Refer to the current version of the relevant material's *General Approach* Paints and Polymers Standard Operating Procedures (P&P SOP) (e.g., PPSU 100, PPSU 101, PPSU 102) for guidance on sampling. Record the samples selected for analysis in the case notes.

5 Procedure

Cease comparison examinations whenever a test reveals an exclusionary difference between two (or more) samples being compared. Record any factors limiting the analysis (e.g., sample size, condition) in the case notes.

1. Turn on the laser and allow to warm up for approximately 20 minutes prior to use.
2. Perform the daily performance monitoring procedure. See the Instrument's *Performance Monitoring (QA/QC) Protocol for the Raman Spectrometers* for specific details.
3. Sample preparation will depend on sample type, size, and condition. Where possible take all samples from a clean, core area (e.g., cut into the sample and discard the top portion, or clean the surface). If appropriate, sample dried material (e.g., cured spray paint on the nozzle) from the container of an uncured specimen. Alternatively, mix an uncured sample (glues, two-part adhesive systems, liquid paint), apply an aliquot to a clean microscope slide or other suitable substrate, and permit it to dry/harden according to the manufacturer's recommendations.

Analyze samples directly or use a preparation method to obtain a sample suitable for analysis.

- a. **Paint:**
 Most samples are analyzed as is, but multi-layered specimens can also be prepared as thin peels of individual layers. Thin peels can be achieved by cutting through individual layers with an angled scalpel blade or similar tool. Create cross-sections manually or with a microtome.

4. Place an aluminum microscope slide or other appropriate sample holder containing the sample onto the microscope stage. Adjust the compensator to focus the sample. View the sample of interest through the microscope oculars. When in focus, the sample easily fills the field of view (~10 microns). Using the video option, focus the laser beam onto the sample. Collect a spectrum using the instrumental conditions listed in section 6. Repeat the measurement using a different area of the sample, or after changing instrumental conditions (e.g., laser type, laser power) as needed to achieve the best, reproducible signal.

5. Save the spectrum.

6. Use spectral search software (e.g., KnowItAll) to compare the paint, polymer, or tape against the reference samples maintained within the databases.

7. Record use in the instrument-specific binder. After last use on a given day, shut off the laser and close out of the software.

6 Instrumental Conditions

The following instrumental conditions are a guide for all standards and samples described in this SOP, and as such, are set within the instrument method and can be adjusted as necessary:

Parameter	785nm laser	532nm laser
Detector:	CCD: Silicon	CCD: Silicon
Laser power:	10%	10%
Grating (g/m):	1800 max	2400 max
Spectral range (cm ⁻¹):	3200 – 200	3200 – 250
Number of acquisitions:	5	5
Collection time:	10 sec	10 sec

Generally, changes in the suggested instrumental conditions, listed above, are required under the following circumstances:

- a. Bleaching time can be increased to mitigate any observed fluorescence.

- b. The number of acquisitions or collection time can be increased to reduce noise.

- c. The laser power can be increased if intensity is weak (e.g., below 800 counts/s).
- d. If the intensity is too high (e.g., sample burning, increased fluorescence), the laser power can be reduced, the laser can be changed (e.g., green to red), or the slit or hole can be decreased.

Conditions for processing of spectra prior to use in the KnowItAll software:

Parameter	Baseline Correction	Smoothing and Filtering
Type:	Line	deNoise
Degree:	20	33
Max Points:	256	
Noise Points:	64	
Size:		8

7 Decision Criteria

In general, characterization should be based on a comparison of the spectral data of the resulting peaks with data from a contemporaneously analyzed reference material. In situations where a reference material is not available for comparison, major components are still able to be determined.

- a. If exclusionary differences are observed between the spectra of two (or more) samples being compared (e.g., the presence or absence of observable components), then the specimens are considered different.
- b. If no exclusionary differences are observed between the spectra of two (or more) samples being compared (e.g. agreement in the presence and relative intensity of observable components), then it is concluded that they are indistinguishable.
- c. If Raman is being used to characterize a material type, the spectrum should compare favorably to a corresponding reference or library spectrum (e.g., in-house library, reference, published in peer-reviewed format).

8 Calculations

Not applicable.

9 Measurement Uncertainty

Not applicable.

10 Limitations

- a. Fluorescence effects cannot always be controlled to the extent necessary for adequate spectral interpretation and comparison.
- b. The spectrum of a mixture can be difficult to interpret due to spectral overlap.
- c. The sub-generic class of polymers cannot always be determined by Raman analysis.
- d. Proper sample area selection is critical for adequate sample characterization. The following are some common sample selection problems encountered in analysis.
 - i. Binder determination can be hindered by focusing on a large pigment particle. Multiple areas of the sample should be analyzed to ensure major components are adequately recorded.
 - ii. Minor pigment constituents or smaller-sized pigments can be masked by larger particle-sized filler pigments. Re-analyze the sample using an area relatively free of larger pigment particles.
 - iii. Fluorescence is often observed in the spectrum of a sample collected using a particular laser or laser power. To reduce this effect, re-analyze the sample at a lower laser power or increase the bleaching time. Alternatively, repeat the analysis using a lower intensity laser.

11 Precautionary Statements

- a. As with any procedure involving trace evidence, ensure actions minimize the potential for loss or contamination of the sample.
- b. The presence of some large particle pigments (e.g., calcium carbonate) within a mixture can cause difficulty with interpretation of the resulting spectrum.

12 Safety

Use 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. Operators should familiarize themselves with the specific User's Guide safety section of the instrument prior to use.

13 References

FBI Laboratory Safety Manual

Performance Monitoring Protocol (QA/QC) for the Raman Spectrometers, FBI Laboratory, Chemistry Unit - Instrument Operation and Systems Support SOP

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

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Rev. #	Issue Date	History
0	01/10/19	Original Issue
1	02/03/20	Removed reference to Instrument manual and made changes to conform to LOM revisions; minor edits throughout.

Approval

Redacted - Signatures on File

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