

Raman Analysis of Paints, Tapes, and Polymers

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1 INTRODUCTION

This procedure describes the sample preparation and instrumental parameters for the Raman analysis of paints and other polymeric materials, to include certain types of pressure sensitive tapes.

2 SCOPE

This document applies to Chemistry Unit caseworking personnel who analyze paints and polymers via Raman spectroscopy.

3 EQUIPMENT

- Thermo DXR3 Dispersive Raman Spectrometer System with microscope accessory with Omnic Software (or equivalent)
- Lasers: 785 nm; others if applicable
- Microscope slide(s) (e.g., aluminum, gold, quartz)
- General Laboratory Supplies
- Polystyrene film

4 STANDARDS AND CONTROLS

- A. Manufacturer-supplied and commercially available paints, pigments, tapes, and other polymers are maintained within the FBI Laboratory. These materials are used in casework in accordance with CHEM-100.
- B. Refer to IOSS-753 for details on the performance checks and necessary supplies to conduct these checks and operate the instrument. Note that the laser power for collection of the polystyrene performance check is generally set to between 9.0-12.0 mW.

5 SAMPLING

Refer to the current version of PP-800 for guidance as to how samples are selected for analysis and comparison. Record the sample(s) selected for analysis in the case notes.

6 PROCEDURE

- A. From the Experimental Set-up menu, turn on the laser from the "Bench" tab and allow to warm up for approximately 5 minutes prior to use.
- B. Laser alignment should be performed within a week of use to maximize signal. Select the "Alignment" tab from the Experimental Set-up menu and follow the software instructions with the alignment tool on the stage. Ensure alignment tool cord is facing the back of the instrument while in use on the microscope stage.
- C. The grating can then be calibrated if prompted by the software.
- D. Perform the daily performance monitoring procedure according to IOSS-753 using the polystyrene card stored with the instrument.

- E. 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.
- F. Analyze samples directly or use a preparation method to obtain a sample suitable for analysis.
1. Paints/Polymers:
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.
 2. Tapes:
Adhesives can be smeared onto the analysis substrate as a thin film.
- G. Place the sample onto an aluminum microscope slide or other appropriate substrate holder and place the holder onto the microscope stage. Adjust the compensator to focus the sample using the microscope oculars and lightbox to the right of the instrument. Shut the light off before collecting a spectrum.
- H. Collect a spectrum using instrumental conditions that provide suitable signal-to-noise ratio for a given sample. Consider the opacity of the sample and size when optimizing the signal. Repeat the measurement using a different area of the sample, or after changing instrumental conditions under the Experiment Set-up tab (e.g., laser type, laser power) as needed to achieve a reproducible signal response with good signal:noise. Generally, changes in the instrumental conditions are required under the following circumstances:
1. Bleaching time can be increased to mitigate any observed fluorescence.
 2. The number of acquisitions or collection time can be increased to reduce noise.
 3. Change the spectral range from the default 3300-200 cm^{-1} default to 3300-100 cm^{-1} in order to capture peaks from inorganic materials that are present in this region.
- I. The laser power can be increased if intensity is weak (e.g., below 800 counts/s). Laser power can vary between 0.1 to 25 mW depending upon the concentration of analyte in the polymer matrix.
- J. If the intensity is too high (e.g., sample burning, increased fluorescence), the laser power can be reduced, the laser can be changed, or the slit or hole can be decreased.
- K. If a suitable spectrum is unable to be obtained, record that in the case notes.
- L. Save the spectrum.
- M. As appropriate, use spectral search software (e.g., Omnic) to compare the paint, polymer, or tape components against reference samples maintained within the available databases.

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

7 ACCEPTANCE CRITERIA

7.1 Characterization

Characterization of a sample 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 using available library reference spectra or those found in the relevant literature where samples have been collected under comparable instrumental conditions.

7.2 Spectral comparison

- A. Spectral comparisons should be conducted with spectra collected using similar sample preparations, similar sample characteristics (e.g., thickness, topography), and similar instrumental parameters, as appropriate.
- B. Spectra are compared and interpreted based on the observation of any spectral differences, or lack thereof, between sets of data.
- C. Cease comparison examinations whenever a test reveals an exclusionary difference between the samples being compared. Record any factors limiting the analysis (e.g., sample size, condition) in the case notes.
 - 1. Spectral overlay is a recognized approach 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.
 - 2. When assessing differences between spectra, consider sample limitations (e.g., dirty samples, sample smears that eliminate layer structure) and instrumentation limitations (e.g., sampling size, limits of detection).
- D. Possible reasons for spectral differences include dissimilar sample conditions (e.g., size, thickness, surface topography), lack of representativeness of the specimen or source material, contribution from extraneous materials, or origination from different source materials. Additional samples can provide supplemental data to assist in assessing such differences.
- E. If suitable spectra are produced, comparisons can provide information regarding the potential relationship of the sources of the samples.
 - 1. Distinguishable sources: When exclusionary differences are observed between compared spectral features, the sources of the samples are considered distinguishable by Raman spectroscopy. Exclusionary differences in spectral comparisons 1) are outside the variability of spectra originating from the same source; and 2) cannot be explained by considerations such as sample heterogeneity, contamination, different sample conditions, or different sample histories.
 - 2. Indistinguishable sources: When no exclusionary differences are observed between compared spectral features, the sources of the samples are considered indistinguishable by Raman spectroscopy. Differences that are

not considered exclusionary 1) are within the variability of spectra originating from the same source; or 2) can be explained by considerations such as sample heterogeneity, contamination, different sample conditions, or different sample histories. If no exclusionary differences are observed in a Raman comparison, samples can be analyzed by other analytical techniques to provide additional information about the potential relationship between the sources of the samples.

- F. Spectral comparison is one part of a multi-analytical comparative approach. Spectral data alone can be used to distinguish the sources of compared samples but is otherwise not used independent of data obtained from other analytical techniques to reach an overall opinion regarding the potential relationship between the sources of the samples.

8 LIMITATIONS

- A. Fluorescence effects cannot always be controlled to the extent necessary for adequate spectral interpretation and comparison.
- B. Some components of interest are not Raman active.
- C. The spectrum of a mixture can be difficult to interpret due to spectral overlap. Proper sample area selection is critical for adequate sample characterization. The following are some common sample selection problems encountered in analysis.
 1. 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.
 2. 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.
 3. 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 different wavelength laser.

9 SAFETY

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

10 REVISION HISTORY

Revision	Issued	Changes
02	03/01/2024	Reformatted to conform with LAB-100 revisions. Minor grammatical changes throughout. Updated equipment information to account for different instrument. Moved references to training manual.