Plastics — Plastics identification using Raman spectrometric methods

Plastiques — Identification des plastiques par spectrométrie Raman

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This document was prepared by Technical Committee ISO/TC 61, *Plastic technical committeePlastics*, Subcommittee SC 5, *Physical-chemical properties*.

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Introduction

Plastic is an essential component used in making many types of products. Plastic formulations consist of polymeric or resin material and additives for affecting specific functions, such as plasticizers, foaming agents for low density parts, UV absorbers or colorants.

As a result, plastic and polymer identification and characterization is increasingly becoming more important in several distinct areas including, but not limited to, identification of unknown substances, product development, multi-layer materials, microplastics and environmental impact, including the ability to recycle and to allow informed decisions to be made.

Raman spectroscopy is an inelastic light scattering analysis technique, and is used to provide a structural fingerprint, by which materials can be identified. Monochromatic light, typically from a laser source, interacts with molecular vibrations, resulting in an energy shift. This energy shift is displayed as a spectrum. Raman spectra provide information about the vibrational modes in the sample, allowing materials to be identified. For example, different types of plastics have unique Raman spectral fingerprint. According to this principle, it is possible to identify unknown plastics by comparing them to known materials. The role of Raman spectroscopy is to identify the chemical composition of unknown plastics.

Plastics — Plastics identification using Raman spectrometric methods

1 Scope

This document is applicable to the qualitative analysis of plastic materials in their original form by Raman spectroscopy. It describes procedures to determine the composition of unknown general plastics and multi-layer film plastics.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 472, Plastics — Vocabulary

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 and the following apply.

ISO and IEC maintain ~~terminological~~terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at ~~https://www.iso.org/obp~~https://www.iso.org/obp

— IEC Electropedia: available at ~~https://www.electropedia.org/~~https://www.electropedia.org/

3.1
general plastics
wide range of synthetic or semi-synthetic materials that use polymers as a main ingredient, which may also have a colourant added

3.2
multi-layer film plastic
material having two or more thermoplastic polymer layers

3.3
Z stack
set of confocal images taken from the sample so that the image area along the x- and y-axes remains the same but the distance from the objective z-axis is different for each image

3.4
pseudo-colour
colour added during the processing of spectra acquired through mapping to aid interpretation of the spectrum in pictorial form

4 Principle

In order to identify unknown plastics the sample is subjected to monochromatic light, such as laser light, which upon interaction with molecular vibrations or other excitations results in a shift of photons creating a characteristic fingerprint, the Raman spectrum. This fingerprint can be matched to reference spectra allowing for rapid identification of the unknown plastic. The method is non-destructive and does not require sample preparation for most materials, allowing for use of the plastic directly after identification.

5 Apparatus

5.1 Raman spectrometer, of at least one highly stable monochromatic laser source used to excite the sample.

5.1.1 Several ~~Laser~~laser **wavelength**s are suitable for plastics identification such as 532 nm, 638 nm, 785 nm and 1 064 nm. Infrared excitation is recommended to reduce unwanted background fluorescence signal that can obscure the Raman spectrum.

5.1.2 Optical **power attenuation** of the laser is required to prevent photodamage to the sample, this can be controlled via adjustment of laser current or with neutral density filters.

5.1.3 The excitation light should be focussed on to the sample using high quality optical components such as **objective lenses** and **fibre probes**. The working distance, numerical aperture and magnification of the optics can vary between instrument types, with some systems allowing these components to be exchangeable by the user.

5.1.4 The scattered light shall then be collected by the same optics and filtered using an **edge** or **notch filter** to block the Rayleigh scattered light at the laser wavelength, this allows the weaker Raman scattered light to be detected and analysed.

5.1.5 A high throughput spectrometer with **spectral resolution** of at least 2 cm^{-1} is required to analyse the scattered light to be able to resolve and distinguish fine detail in the Raman spectrum to allow accurate identification. Spectral resolution is defined as the full width half maximum (FWHM) of the line width of a gas emission line measured on the spectrograph with the highest groove density grating. Typically, the pixel resolution should be at least 0,8 cm^{-1}/pixel. The spectral resolution will depend on the focal length of the spectrograph, the entrance slit width, the detector pixel size and the groove density of the diffraction grating. The Raman spectrometer should at least have a spectral range of 500 cm^{-1} to 1 800 cm^{-1} however a wider spectral range of 100 cm^{-1} to 3 500 cm^{-1} is recommended to ensure that the material will be correctly identified.

5.1.6 The **detector**, matching the chosen laser source and with an appropriate spectral response to cover the wavelength range required.

Several types of detectors are suitable for these measurements such as:

5.1.6.1 **front or back illuminated charge coupled detectors (CCD)**,

5.1.6.2 **electron multiplied charge coupled detectors (EM-CCD)**, and

5.1.6.3 **InGaAs arrays for infra-red detection**.

All detectors shall have high sensitivity and low noise to be able to detect the Raman signal. Detectors should be cooled to manufacturers recommendations, most require air cooling down to -60 °C, but some detectors require further cooling with water or liquid nitrogen. The system should have comprehensive software to allow hardware control and acquisition of spectra along with file export options compatible with the spectral library.

5.1.7 Use of a **microscope**-based system is recommended due to the versatility it offers when studying plastic materials that come in many formats, shapes and sizes. Portable devices can successfully be used to acquire spectra from bulk materials but have limited use determine composition of micrometre thick layers in the case of multilayer plastics. ~~Further,~~

5.1.8 A truly **confocal Raman system** with the ability to change pinhole size to allow accurate analysis of multi-layers of plastic material is also applicable and recommended. Additionally, it is recommended that the

confocal Raman system has a motorised microscope stage, so that multi-layer plastics can be analysed by regularly taking measurements at set distances, through appropriate software, allowing the layer thickness to be determined. Multiple excitation wavelengths are recommended as plastics can give different background effects with different sources, and these can obscure relevant peaks. It is recommended to start analysis of unknown materials with 785 nm excitation as this usually gives a good balance between Raman signal strength and low background fluorescence.

6 Specimen

This method is suitable for general plastics including bulk plastics, particles, liquids, coloured plastics, single layer and multilayer films. Both transparent and opaque samples can be identified.

Generally, the sample does not need to be pre-processed, it can be directly presented to the Raman apparatus for identification. Depending on the requirements of the apparatus, the sample may need to be placed in a sample holder or on to a microscope stage for testing. The maximum size and thickness of the sample suitable for testing will be specified by the manufacturer of the apparatus, for very large samples a specimen may need to be prepared by cutting the sample to suitable dimensions. For powdered samples, a vessel to contain the sample will be required, such as a microscope slide, vial or dish. If the powder can contain a mixture of materials microscopy investigation is recommended. Other plastics, especially reinforced materials and multilayer film materials can be sliced and then their cross-sections can be tested. Microscopy is more appropriate for identification of specimens containing micrometre thick layers.

7 Testing procedure

7.1 Calibration and parameter settings

The Raman spectrometer should have, at a minimum, two forms of calibration: an underlying wavelength calibration that do not need to be repeated by the user and a Raman wavenumber calibration reference that shall be run daily when the system in use, as well as after any apparatus change such as change of laser source or grating.

The wavelength calibration of the spectrometer is performed by the manufacturer using atomic emission lines from a mercury, argon or neon discharge lamp. The wavelength of emission lines are known to a high accuracy and precision. Measuring the position of these emission lines on the detector for each grating and grating angle available on the spectrometer, allows for the detector pixels to be calibrated to the correct wavelength. This is required to acquire accurate spectra that can be compared to other systems as well as cross referenced to spectral databases. The calibration record for the system can be requested from the instrument manufacturer. The Raman wavenumber calibration uses a suitable reference material such as Silicon which has a known peak at approximately 520,7 cm^{-1} to offset the wavelength calibration of the system. This reference will take in to account any environmental changes that can cause small drifts in the calibration of the system. This reference material is generally provided by the manufacturer inside the apparatus, it can also be presented to the apparatus externally by the user. The silicon peak position can vary with stress in the material and, therefore, each manufacturer recommends the exact peak position to use for the wavenumber calibration.

7.2 Measurement of Raman spectrum

7.2.1 Method 1 — General method

The test steps for analysing general use plastics on a Raman spectrometer are as follows.

a) Choose the appropriate excitation wavelength. If available, it is recommended that 785 nm is chosen as the starting wavelength for any sample. If the instrument contains fully integrated lasers and is completely software controlled, go to step c).

b) ~~b)~~ If the Raman instrument has external lasers or manually exchangeable optical components, follow the set-up procedure given by the manufacturer for the chosen laser wavelength. This alignment and calibration shall be checked before sample analysis can begin.

c) ~~c)~~ Turn on the Raman spectrometer and selected laser. Allow the system to warm up for 30 minutes until the system is stable.

d) ~~d)~~ Place the sample on a stage or sample holder as directed by the manufacturer. If not using a microscope go to step f). If using a microscope select a suitable magnification objective, such as x10, x20, or x50.

e) ~~e)~~ Switch on the microscope lamp to illuminate the sample. Focus on the sample using the microscope camera or eyepieces. Use the fine focus knob to precisely focus on the surface of the material.

f) ~~f)~~ It is important to adjust the laser power density on the sample, starting at a lower power and then increasing generally starting from $1\,\text{mW/μm}^2$. The approximate area of the excitation spot can be calculated using ~~Formula (1):~~ Formula (1):

$$A = \pi \frac{\left(\frac{0,61\lambda}{N.A}\right)^2}{\left(\frac{0,61\lambda}{N.A}\right)^2} \tag{1}$$

where

A ~~A~~ is the area;

λ ~~λ~~ is the wavelength;

N.A ~~N.A~~ is the numerical aperture.

The numerical aperture, N.A, of the objective lens or fibre probe should be provided by the manufacturer. The integration time generally should be set to less than 60 s to avoid the sample being heated and damaged by the laser.

g) ~~g)~~ Set the spectral range from 100 cm^{-1} to 3 500 cm^{-1}. The full extended range is recommended, however if not possible on the apparatus, record the spectral range at least from 500 cm^{-1} to 1 800 cm^{-1}.

h) ~~h)~~ It is recommended to select at least 3 points on the sample for testing to ensure uniformity across the sample surface. The focal spot size will vary depending on the apparatus used. Line illumination can also be used, which will sample from a larger region of the sample than a gaussian focussed laser spot.

i) ~~i)~~ Raman peaks should be clearly observed to allow appropriate analysis of the sample to take place. If fluorescence background prevents good quality spectra being acquired, try steps j) to n).

j) ~~j)~~ If available, close the confocal pinhole to reject the out of focus background signal from contributing to the measurement. This often will require increasing the exposure time to maintain good signal to noise.

k) ~~k)~~ If the fluorescence background is still too high and reducing the quality of the Raman spectrum, then bleach the fluorescence signal by illuminating the sample with the laser for a set time before taking another measurement. The time required will depend on the sample ranging from 60 s to 60 min. Increasing the power density on the sample can improve the effectiveness of photobleaching.

l) ~~l)~~ Check that the sample has not been burned by the laser during this time, by checking the microscope image of the sample after each measurement. If burning has been observed, move to a new location on the sample, reduce laser power and repeat sample bleaching step.

m) ~~m)~~ If previous steps do not achieve a suitable Raman spectrum, changing the laser excitation to a longer wavelength source and repeating the procedure can improve results.

n) ~~n)~~ If the previous steps do not completely remove background, then post process the data to remove the background signal.

7.2.2 Method 2 — Test method for multi-layer film plastics

7.2.2.1 General

It is advisable to use a microscope-based Raman system with a motorised stage, controllable through software to analyse multi-layer film plastics. For thick multilayer films, manual analysis of a cross section using method 2.2 (see 7.2.2.3) without a microscope is possible when the probe excitation spot is smaller than the layer thickness and can be positioned accurately to measure each layer distinctly. ~~Annex E~~ Annex E provides further information on the identification of multilayer plastics. The test steps for analysing these materials are as follows.

7.2.2.2 Method 2.1 ~~—~~ Setup protocol

a) ~~a)~~ Follow steps a-c of method 1 to set up the instrument.

b) ~~b)~~ Depending on the thickness and transparency of the sample, additional sample preparation steps may need to be taken before placing the sample on the microscope.

c) ~~c)~~ If non-destructive sample preparation is required go to method 2.3 (~~7.2.2.4~~see 7.2.2.4) If destructive sample preparation is required continue to method 2.2 (~~7.2.2.3~~see 7.2.2.3).

7.2.2.3 Method 2.2 — For multilayer films with very thin layers or for thick partially opaque films

a) ~~a)~~ If layers thinner than 3 μm are expected to be in the sample, then it is recommended to start with cross sectioning the film. This will allow for inspection of individual layer thickness before spectroscopy investigation. If layers are more than ~~1mm~~1 mm then a non-microscope-based system could be used if the excitation spot is smaller than the layer thickness.

b) ~~b)~~ Place the specimen on the stage of the Raman spectrometer. To analyse thin layers select a high numerical aperture objective, such as x50/0,8 N.A. or x100/ 0,9 N.A. this will give suitable spatial resolution to identify layers thinner than 3 μm.

c) ~~c)~~ If available, switch on the microscope lamp to illuminate the specimen. Focus using camera or eyepieces or by eye until the objective or fibre is in the correct position for analysis. Use the fine focus control to precisely focus on the surface of the specimen. In the case of a portable or probe system position, the probe such that only one layer is investigated at a time.

d) ~~d)~~ It should be possible to see boundaries between layers in the film. If the specimen can be visualised on a camera, use the digital image and scale bar to measure the thickness of each layer. If no camera is available, then view the specimen with the eyepieces. A graticule eyepiece can be used to estimate the layer thickness.

e) ~~e)~~ If the layers are thicker than 3 μm then continue analysis with 785 nm laser.

f) ~~f)~~ If layers thinner than 3 μm are observed it is recommended to use a shorter wavelength excitation source, as this will improve the spatial resolution of the system ensuring very thin layers will not be missed during analysis. If the specimen has high fluorescence, then this may prevent analysis with shorter excitation.