Qualitative Screening Method for Plastic Microbeads in Personal Care and Cosmetics Products

NIEA M907.00B

1. Summary of the Method

This method is applicable to the analysis of plastic microbeads with particle size larger than 0.05 mm but less than 5 mm. Samples is dispersed with warm water, passed through a 5 mm screen and then filtered using a 0.05 mm filter. The microbeads remaining on the filter is dried and subjected to Fourier transform infrared spectrometer (FTIR) or Raman Spectrometer for qualitative analysis.

2. Scope of Application

This method is applicable to the qualitative analysis of plastic microbeads in personal care and cosmetics products that include cosmetics products, personal care products, scrubs, toothpastes, etc. The composition of plastic microbeads can include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polymethylmethacrylate (PMMA), nylon, or polylactide (PLA). The characteristic peaks of the common plastic materials in FTIR and Raman spectrum are shown in Table1 and Table2 respectively.

3. Interferences

3.1. In background measurement using FTIR, a strong absorption at 2250 to 2450 cm^{-1}indicates high concentration of carbon dioxide in the equipment or testing environment. The absorption at 1300 to 1800 cm^{-1} and 3500 to 3800 cm^{-1}, due to water vapor, may seriously affect the detection sensitivity of the instrument.

3.2. Inorganic powder and surfactant added to personal care and cosmetics products may cause absorption interference.

3.3. To subtract background due to water vapor and carbon dioxide, background measurement is needed in FTIR analysis.

3.4. Raman is known to be interfered by fluorescence. If the sample emits fluorescence after the sample pretreatment, laser of different wavelength may be used to avoid the interference. Otherwise, the sample should be analyzed by FTIR.

3.5. In Raman analysis, there are two ways to improve the signal to noise ratio. One is to raise the power of laser, the other is to increase signal integration time. However, if the laser power is too strong to cause irreversible damage to the sample, it may cause poor reproducibility of the Raman spectrum.

4. Equipment and Materials

4.1. Standard test pieces: such as polystyrene from instrument built-in or commercially available standard for confirmation the performance of FTIR.

4.2. Silicon chip: single crystal silicon with a crystal orientation of <100> for calibration of Raman spectrometer.

4.3. Plastic microbeads standard: commercially available standards with known purity.

4.4. Screen: stainless steel, aperture 5 mm (4 mesh).

4.5. Filter: stainless steel, aperture 0.05 mm (325 mesh).

4.6. Washing bottles.

4.7. Glass bottles: about 500 mL in volume.

4.8. Balance: accurate to 0.01 g.

4.9. Oven: to control the temperature at 50 ~ 60 ℃.

4.10. Glass or metal stir bar.

4.11. Tweezers: metal tweezers

4.12. Conical flask: about 500 mL in volume.

4.13. Dry cabinet: electronic, dry dish or others able to dry.

4.14. Disc: aluminum foil.

4.15. Filtration device: thin film filter funnel.

4.16. Pumping device.

4.17. Fourier Transform Infrared Spectrometer (FTIR)

 4.17.1. Attenuated Total Reflection (ATR) detection mode, ATR crystal with a range of 550 to 4000 cm^{-1}.

 4.17.2. Spectral range 550 to 4000 cm^{-1}.

 4.17.3. Resolution ≦ 4 cm^{-1}.

 4.17.4. Software with functions of spectrum comparison and calculation of similarity index.

4.18. Raman spectrometer.

 4.18.1. Equipped with at least one laser light source, and the light source matched grating and filter , the maximum output power of the laser should be no less than 10 mW.

 4.18.2. Spectral range 500 to 3200 cm^{-1}.

4.18.3. Software with functions of spectrum comparison and calculation of similarity index.

5. Reagents

Deionized water

6. Sampling and Preservation

Samples are collected in the form of original package and stored at room temperature.

7. Procedures

7.1. Sample pretreatment:

7.1.1. Take 0.5 to 3 g of the sample into a glass bottle containing about 200 mL of warm deionized water and well-mixed the sample with water.

7.1.2. Pass the solution through a 5 mm (4 mesh) screen and collect the filtrate in a conical flask. Omit this step if the microbeads are significantly less than 5 mm.

7.1.3. Pour the filtrate into a filtration device equipped with a 0.05 mm (325 mesh) stainless steel filter. After filtration, rinse the filter several times with deionized water.

7.1.4. Remove horizontally the filter containing the microbeads using a metal tweezers and place the filter on an aluminum foil disc.

7.1.5. Place the aluminum foil disc in an oven at 50 to 60 ° C for about 30 minutes to remove residual moisture. Extend sample drying time if the follow up FTIR analysis indicates the interference of water.

7.1.6. Analyze the dry solid microbeads by FTIR or Raman spectrometer. Store the sample in a dry cabinet if not analyze right after.

7.2. Analysis of dry solid microbeads

7.2.1. FTIR analysis

(1) Make sure that the instrument database contains the reference spectrum of common plastics such as polyethylene, polypropylene, polyethylene terephthalate, polymethyl methacrylate, nylon and polylactic acid. If it is needed, one can build his own data base using the standards.

(2).Before the analysis, calibrate the instrument with standard test pieces using the procedures provided by instrument manufacture.

(3)Analyze the sample with attenuated total reflection method. Clean the probe with appropriate solvent before taking the background spectrum.

(4) Scan the instrument from 550 to 4000 cm^{-1}.

(5) Cove the ATR probe completely with solid microbeads and make sure that the microbeads are in close contact with the ATR probe.

(6) To improve signal to noise ratio, subtract background spectrum from the sample spectrum.

(7) Compare the sample spectrum with the reference spectrum in database. (Figure 1)

7.2.2. Raman analysis (Note):

(1) Make sure that the instrument database contains the reference spectrum of common plastics such as polyethylene, polypropylene, polyethylene terephthalate, polymethyl methacrylate, nylon and polylactic acid. If it is needed, one can build his own data base using standards.

(2) Before the analysis, verify the conditions of the instrument:

  a. Turn on the laser for a period of time (warm-up time) to make its output power stable. The warm-up time is based on the recommendation of manufactures.

  b. Single crystal silicon with crystal orientation of <100> is used for Raman analysis. The most prominent Raman peak of silicon wafer appears at 520 cm^{-1}. Calibration is needed if the deviation is more than 1 cm-1. Other standard test pieces can also be used if they can achieve the same function.

(3) Scan the instrument from 550 to 3200 cm^{-1}.

(4) Adjust the laser light intensity based on the signal strength and sample characteristics. For better signal to noise ratio, intensity greater than 1mW is recommended,

(5) Adjust the integration time based on signal strength.

(6) If it is needed, subtract background before spectrum comparison.

(7) Compare the sample spectrum with the reference spectrum in database. (Figure 2)

8. Result Processing

In FTIR or Raman analysis, the degree of similarity between sample spectrum and reference spectrum must be equal to or greater than 80% to identify the material of plastic microbeads.

9. Quality Control

Not provided

10. Precision and Accuracy

Not provided

11. References

11.1. ASTM D2124 - Standard Test Method for Analysis of Components in Poly（Vinyl Chloride）Compounds Using an Infrared Spectrophotometric Technique.

11.2. ASTM E1421 - Standard Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests.

11.3. ASTM D3677 - Standard Test Methods for Rubber—Identification by Infrared Spectrophotometry.

11.4. Environmental Protection Administration Executive Yuan, A Method for Qualitative Screening of Polyvinyl Chloride in Plastics (NIEA M906.00B), 2015.

11.5. Environmental Protection Administration Executive Yuan, Method study for the analysis of polyvinyl chloride in container accessories (EPA - 102 - HA 14 - 03 - A 197), July,2013.

Note: Operation personnel should pay attention the safety during the operation of laser.

Table 1 IR characteristic peaks of common plastic materials

Plastic material	Characteristic peaks(cm $^{-1}$)*
Polyethylene	720、1470、2850、2915
Polypropylene	1375、1455、2840、2870、2920、2955
Polyethylene terephthalate	620、960、1250、1330、1430、2910
Polymethylmethacrylate	752、841、986、1146、1188、1238、1384、1438、1728、2948、2993、3437
Nylon	934、1660、2841、2950、3080、3330
Polylactide	693、755、871、1042、1083、1128、1180、1358、1382、1453、1746、2997
Polystyrene	906、1028、1601、2850、2920、3025、3060

*The position may shift due to the purity of plastic materials

Table 2 Raman characteristic peaks of common plastic materials

Plastic material	Characteristic peaks (cm $^{-1}$)*
Polyethylene	2882、2849、1295、1128、1063
Polypropylene	2885、1460、1331、842、810
Polyethylene terephthalate	3082、1726、1615、1288、857、633
Polymethylmethacrylate	2952、2845、1729、1451、813
Nylon	2919、2871、1636、1443、1299、1130
Polylactide	3000、2947、1453、875

* The position may shift due to the purity of plastic materials

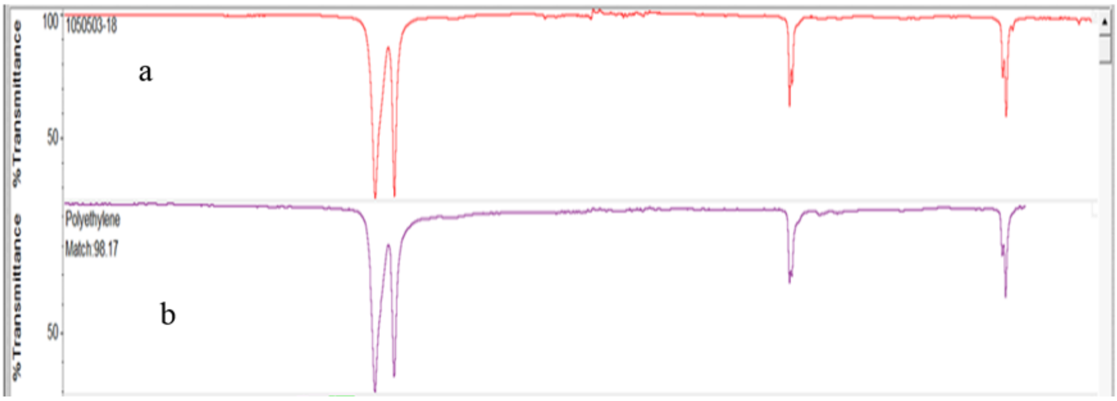

Figure 1. The detection of PE microbeads by FTIR (a) IR spectrum of plastic microbeads from a facial cleanser (b) IR reference spectrum of PE

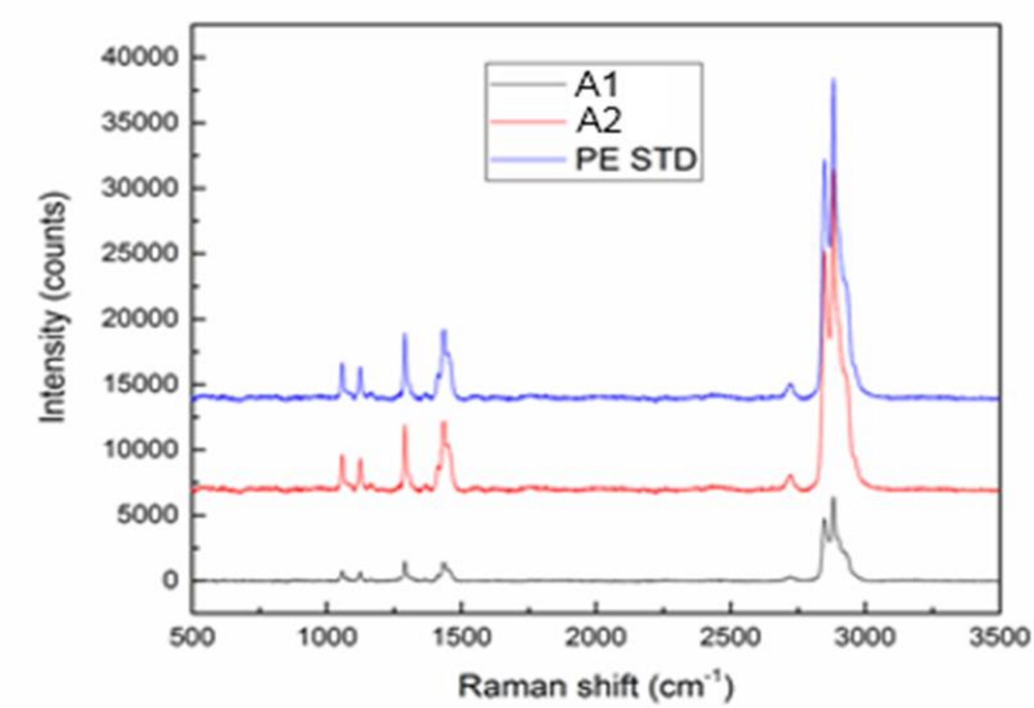

Figure 2. After sample pretreatment, the detection of PE plastic microbeads by Raman spectrometer