HORIBA

Raman Spectroscopy

Analysis of Synthetic Polymer Microparticles (microplastics) in hand sanitizers using ParticleFinder™ and IDFinder™

Application Note

Pharmaceuticals
Cosmetics
RA86

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Abstract: Since October 2023, the European Union has enforced restrictions on the intentional use of microplastics in products such as cosmetics and self-care items. Using the example of hand sanitizer, this application note demonstrates how to evaluate whether the product contains synthetic polymer microparticles covered by this restriction. Three different hand sanitizers from various countries were analyzed, demonstrating the presence of microplastics measuring from 20 to 100 microns in one of them.

HORIBA provides a full solution for microplastics analysis, including high-performance Raman microscopes, a filtration kit, ParticleFinder™ software for automatic particle analysis, and IDFinder™ software for the automatic identification of multiple spectra.

Keywords: Raman Microscopy, ParticleFinder™, IDFinder™, Microplastics, Hand sanitizer.

Introduction

Since October 2023, the European Union has enforced restrictions on the intentional use of microplastics in certain products, including cosmetics and self-care items [1]. According to these restrictions, particles considered as microplastics must be excluded from products if they meet the following criteria:

- Consist of synthetic polymers
- Solid
- Insoluble in water
- Not biodegradable
- Measure less than 5 mm

In the case of microplastic beads used as exfoliating components, the regulation is straightforward and strict: they should no longer be included in formulations. However, the situation is less clear for other ingredients consisting of synthetic polymers. While they may be classified as microplastics in their pristine form, significant changes can occur once they are added to the hydroalcoholic solvents of liquid formulations. Therefore, it is essential to evaluate their fate after the final usage of the finished product [2].

In this application note, we demonstrate the classical approach for microplastics analysis applied to hand sanitizers, which have become part of our daily routine since the COVID-19 crisis. The objective is to simulate the use of hand sanitizers and evaluate whether particles considered as microplastics remain on our hands after its using. Raman microspectroscopy is recognized as one of the reference methods for microplastics analysis, providing detailed information on the chemical identity, size, morphology, and number of particles in a sample [3]. In this application note, we demonstrate the typical workflow for microplastics analysis, from sample preparation to data treatment, using the full solution provided by HORIBA.

The workflow involves several key components:

- Sample Preparation: Utilizing HORIBA's filtration kit, samples are prepared for analysis by filtering and isolating microplastic particles.
- Raman Microscopy: The latest generation of Raman microscopes, LabRAM Soleil, is used for high-resolution imaging and spectral analysis.
- Automated Particle Analysis: Dedicated software, ParticleFinder™ and IDFinder™, facilitates fully automated analysis of particles, including their identification and characterization.

This integrated approach ensures precise and efficient analysis of microplastics, making it an invaluable tool for researchers and industry professionals concerned with the presence of microplastics in various products.

Instrument and methods

Samples preparation

Three hand sanitizers, referred to as Sample 1, Sample 2, and Sample 3, originating from different countries, were selected for microplastic analysis. A volume ranging from 25 to 50 ml of each sample was diluted in ethanol and filtered through Silicon (Si) filters (SMART MEMBRANES, www.smartmembranes.com) with varying porosities using HORIBA's filtration kit. The exact sampling volume, ethanol quantity, and filter porosity are detailed in Table 1.

For the blank filtration, the same filtration conditions were replicated; however, instead of adding a sample, 50 ml of distilled water was used.

Table 1: Filtration conditions for each sample and blank.

Sample	Blank	1	2	3
Volume of sample (ml)	50	50	25	50
Volume of Ethanol (ml)	50	50	75	50
Filter pore diameter (µm)	5	5	10	10

Raman analysis

The Raman analysis was performed using the LabRAM Soleil™ Raman microscope. For particle analysis, including automated Raman spectra acquisition, particle counting, and size characterization, ParticleFinder™ software was utilized.

Dark-field illumination was employed to enhance the optical contrast of the particles on the Si filter, facilitating their automatic localization with ParticleFinder™. Once the particles were located in the image, the Raman spectrum of each particle was recorded using a 785 nm laser. Only particles with a circle equivalent diameter between 20 and 100 µm were considered for Raman analysis to enable fast scanning.

The filter was analyzed in a so-called "Dynamic mode," meaning that the following analytical sequence was automatically repeated for each field of view of the optical objective:

- Image acquisition
- Automatic particle localization
- Raman spectra recording

This approach is well-suited for large filters, minimizing the risk of particle displacement due to external factors and ensuring high precision in localization and particles size characterization.

Figure 2: LabRAM Soleil Raman microscope

Figure 1: Filtration apparatus: glass funnel, glass support base, silicone stopper, glass flask, and vacuum pump.

Data treatment

Apart from baseline correction, no additional processing was applied to the spectra. The spectra identification was performed using IDFinder™ software. The spectra were compared with a dedicated spectral library, and a matching score called the Hit Quality Index (HQI) was assigned to each spectrum. Pearson's correlation was used to calculate the HQI (Figure 3). The compound with the highest HQI was considered the chemical identity of the particle. The minimum acceptable score for automatic particle identification was set at 65%.

Index	X pos	Y pos	Diameter	Image	Spectrum	Class	HQI
Filter min						Set	
Filter max							
8	-1554.23	-1474.45	51.95			PET	95.55
9	-1599.87	-1381.73	41.68			PET	96.01
10	-1291.53	-1334.15	42.22			PET	96.34
11	1365.65	4163.71	31.85			PE	92.74
12	-1818.79	156.75	48.32			PE	93.32
13	1348.68	4163.02	48.16			PE	93.68
14	3787.97	4232.36	36.15			PE	94.14
15	-1532.50	4305.78	45.14			PE	94.49
16	-2535.19	3038.06	37.05			PE	94.89
17	-1447.58	-3495.88	34.06			PE	94.97
18	-1442.76	-3496.38	47.31			PE	95.20
19	1486.85	3683.19	29.93			PE	95.59
20	-2542.12	3046.33	29.73			PE	95.62
21	-1098.75	-205.11	77.39			PE	95.66
22	-2112.91	3375.23	70.39			PE	95.88
23	-1918.40	1813.55	40.27			Cellulose	91.06
24	-2537.77	-2419.63	47.45			Cellulose	91.14
25	-2034.61	1676.55	43.73			Cellulose	91.25
26	-3787.87	275.60	34.45			Cellulose	91.31
Mean	91.71	701.32	48.96				93.74
StDev	2257.15	2543.25	13.34				1.68
Median	-1061.25	488.25	47.31				93.53

Figure 3: Information about each particle is resumed in a table. Each spectrum is compared with dedicated spectral library, the component with the highest matching score (Hit Quality Index, HQI) is mentioned in a column "Class".

The spectral library was customized to include spectra of the 10 most abundant polymers (listed in Table 2) and common non-plastic materials (such as Si, amorphous carbon, cellulose, proteins, $CaCO_3$, and TiO_2, etc.). It should be noted that the above-mentioned list forms the basic content of the spectral library adapted for microplastics analysis, which can be supplemented with other organic and inorganic compounds expected to be present in the samples.

Table 2: List of most abundant polymers included in basic spectral library for microplastics analysis.

Polymer	Abbreviation
Polyethylene	PE
Polypropylene	PP
Polyethylene terephthalate	PET
Polycarbonate	PC
Polystyrene	PS
Polytetrafluoroethylene	PTFE
Polyvinyl chloride	PVC
Polyamide	PA
Polymethyl methacrylate	PMMA
Polyurethane	PU

Results

Figure 4 presents optical images of three filters corresponding to the analysed samples and a blank filtration. Compared to the blank sample, significantly more particles were detected in the analyzed samples, with fibers visible in Samples 2 and 3.

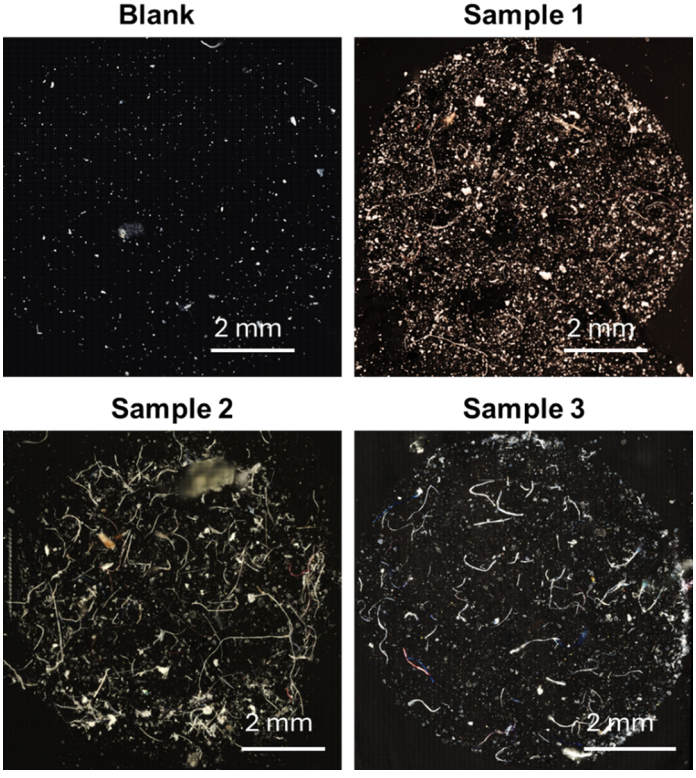

Figure 4: Optical images of analysed filters.

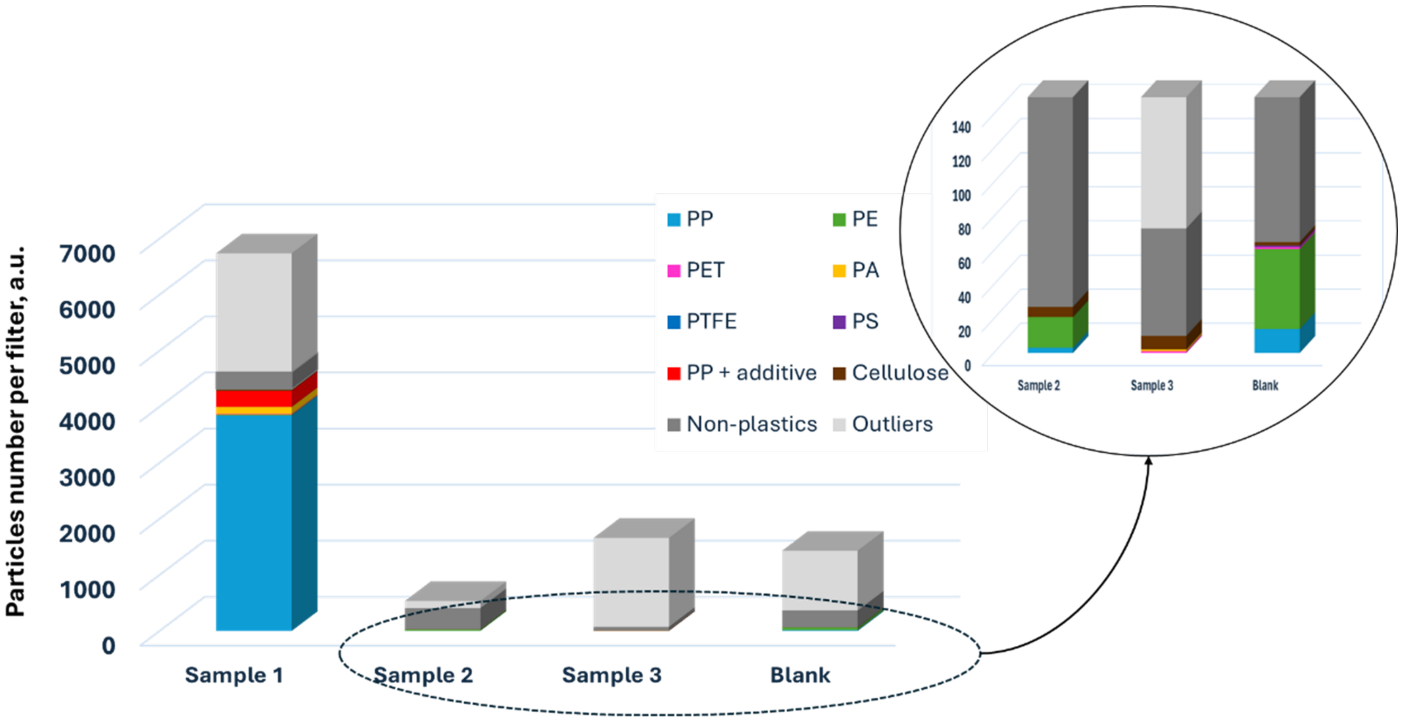

Figure 5: Results of Raman analysis for the particles measuring 20 – 100 µm.

For Raman analysis, only particles with a circle equivalent diameter between 20 and 100 microns were selected. The results of particle identification and counting are presented in Figure 5. Compared to the blank filtration, Samples 2 and 3 exhibit a similar order of magnitude in the number of plastic particles. Tens of particles of Polyethylene (PE), Polypropylene (PP), and a few particles of Polyethylene Terephthalate (PET), Polystyrene (PS), and Polytetrafluoroethylene (PTFE) were detected in both the blank and these two samples. This may be explained by slight microplastic contamination during sample preparation. For example, PE and PP were the major materials of an ethanol wash bottle, so the presence of tens of particles of these polymers was expected.

However, the presence of thousands of PP particles in Sample 1 cannot be explained by external contamination; it is attributed to the presence of these particles in the hand sanitizer itself. Most spectra identified as PP had a high matching score with Polypropylene reference spectra. However, they also showed a high score with PP-acrylic acid polymer or another polymer with a similar skeletal structure to PP, as shown in Figure 6. For simplicity, these particles were labeled as PP. Several hundred particles had spectra presenting signatures of both PP and some fatty alcohol molecules (Figure 7). These molecules may be additives to the plastic or components of the hand sanitizer itself. Thus, these particles are indicated as PP + additive in Figure 5. It should be noted that this identification may not be exact, so information about the chemical composition of the cosmetic product itself can help in data interpretation.

For simplicity, particles identified as starch, calcium carbonate, or amorphous carbon are grouped into one category called non-plastics. Most of the outlier spectra did not have a Raman signal, which was either masked by fluorescence or indicated only a silicon (Si) signal.

Therefore, the presence of microplastics was confirmed in Sample 1. As mentioned in the sample preparation section, the detected amount of microplastics corresponds to 50 ml of hand sanitizer, which represents approximately 16 single doses. Thus, approximately 400 microplastic particles in the size range of 20 to 100 µm are expected to be deposited on hands with a single dose of this hand sanitizer.

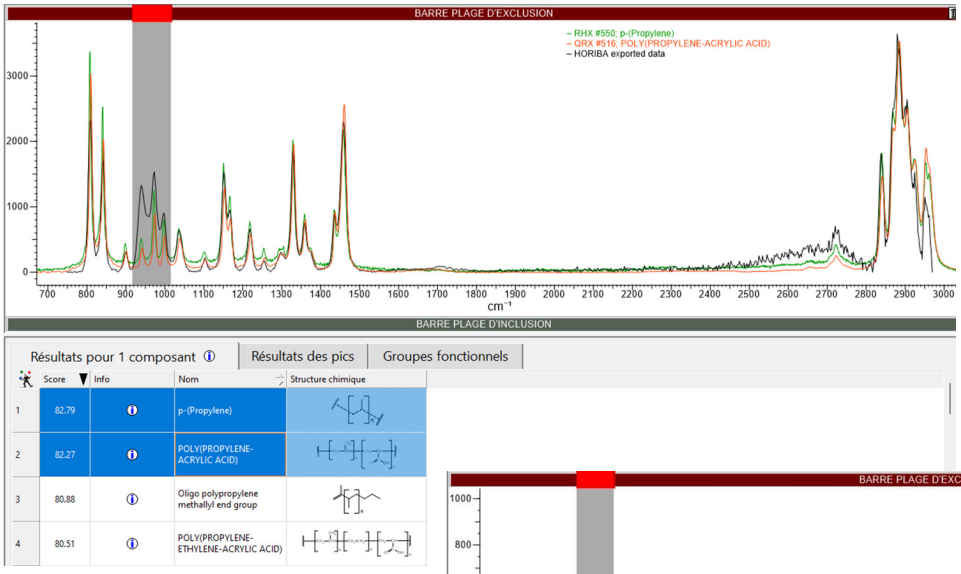

Figure 6: Matching experimental spectrum (black) identified as PP with KnowItAll Database spectra. Green and red spectra correspond to Polypropylene and Polypropylene-acrylic acid. Both spectra are similar to each other are reveal similar matching score of 82% with experimental spectrum.

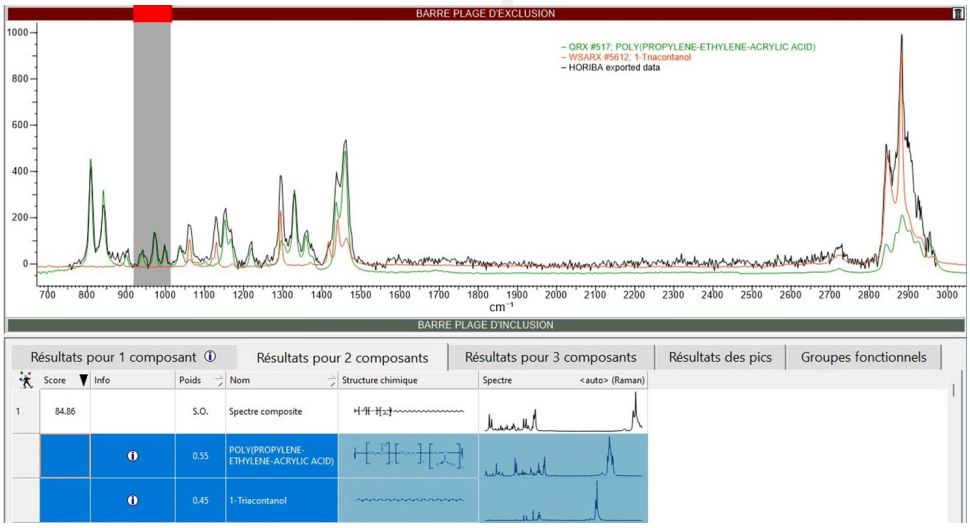

Figure 7: Matching experimental spectrum (black) identified as "PP+additive" with KnowItAll Database spectra. Green and red spectra correspond to Polypropylene-ethylene-acrylic acid and to 1-Triacontanol. Black spectrum can be deconvoluted as a sum of red and green spectra.

Conclusion

In this application note, we demonstrate the intuitive and automated workflow for microplastics analysis using Raman microspectroscopy with the latest generation of HORIBA Raman microscopes, LabRAM Soleil™, along with ParticleFinder™ and IDFinder™ software. This method enables the chemical identification and quantification of thousands of particles, including microplastics.

Three different hand sanitizers were analyzed, revealing the presence of hundreds of microplastic particles in the size range of 20 to 100 µm per dose in one of the samples. This analytical approach can be extended to microplastics analysis in any other sample subjected to the appropriate sample preparation procedure.

References

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