APPLICATION NOTE

FT-IR, IR Microscopy

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FT-IR Microscopic Analysis of Microplastics in Bottled Water

Introduction

Bottled water is marketed as being the clean and pure alternative to drinking tap water. However, there is increasing opposition to the use of single-use plastic bottles and the fact that they end up in the environment either as intact bottles (since they take years to degrade), or as secondary microplastics when they do break down into smaller pieces and particles. A recent study also reports that microplastic particles have been detected in several brands of bottled drinking water.[1] The effects on human health from microplastics are still to be determined, but the presence of microplastics, potentially containing priority organic pollutants (POPs), in food and beverages is a major concern. Analysis of bottled water can determine the presence, identity, size and number of microplastics present.

Infrared (IR) spectroscopy is the primary analytical technique for the identification of polymers and the use of IR microscopy allows for the detection and identification of microplastics down to particles of only a few microns in size. This application note describes the analysis of several different brands of bottled water using the PerkinElmer Spotlight 400 FT-IR Imaging system.

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Sample Preparation for IR Microscopy

The IR microscopic analysis of a range of microplastics from different sources requires the samples to be clean from any sample matrix interference, and the individual particles or fragments to be isolated. In some cases, such as microplastics present in sediments, the sample cleanup can be a significant process. However, in the case of bottled water samples there is no sample cleanup required, just the separation of the microplastics from the aqueous matrix. This can be achieved by simple filtration of the sample using an appropriate filter that is suitable for IR measurements. The optimum filter types for IR microscopy have been determined to be either silver membrane, gold-coated polycarbonate or laser-etched silicon filters.[2] The silicon filters are best if the sample is to be measured in transmission, all three types are suitable for reflectance measurements.

Experimental

Five anonymized brands of (plastic) bottled water were purchased locally in the UK in order to test for the presence of microplastics. A tap water sample was also tested. Sample volumes of 500 mL of each sample were vacuum filtered using a 600 mL Advantec flask fitted with a 13 mm glass filter holder. 13 mm membrane filters (Sterlitech Corp.) with pore sizes in the range 1-5 microns were used. These pore sizes allow rapid filtration and will retain microplastics in the size range down to a few microns, the size limit of IR microscopy due to diffraction limitation. For bottled water testing it was sufficient to use 13 mm diameter filters since the sample matrix is generally clean and there are only a small number of particles to filter. The 13 mm filters were placed directly into the IR microscope sample slide holder of the Spotlight 400 (Figure 1) for reflectance measurement and visible image surveys collected for each complete filter.

Figures 2a and 2b show the complete visible image survey, using reflectance illumination, of a bottled water sample and a tap water sample on 13 mm diameter gold coated polycarbonate filters.

A range of dark particles can be observed distributed across the filter from the bottled water sample. The tap water sample has a considerable number of particles and fibers visible.

After the visible image survey has been collected decisions were made as to whether the whole sample is imaged or if individual particles are scanned. A whole IR image of a 13 mm filter can take between one and five hours depending on the spatial resolution, spectral resolution and the sensitivity required. However, if there are only a few particles on the filter, taking an IR image is not necessary, since scanning individual particles can be performed within a few seconds per particle using a single point mode. In the case of the tap water sample, where there are hundreds of particles then taking an IR image was the most sensible approach. The scan conditions are shown in Table 1 for single point and IR imaging measurements performed on these samples.

Figure 1. PerkinElmer Spotlight 400 FT-IR Imaging system.

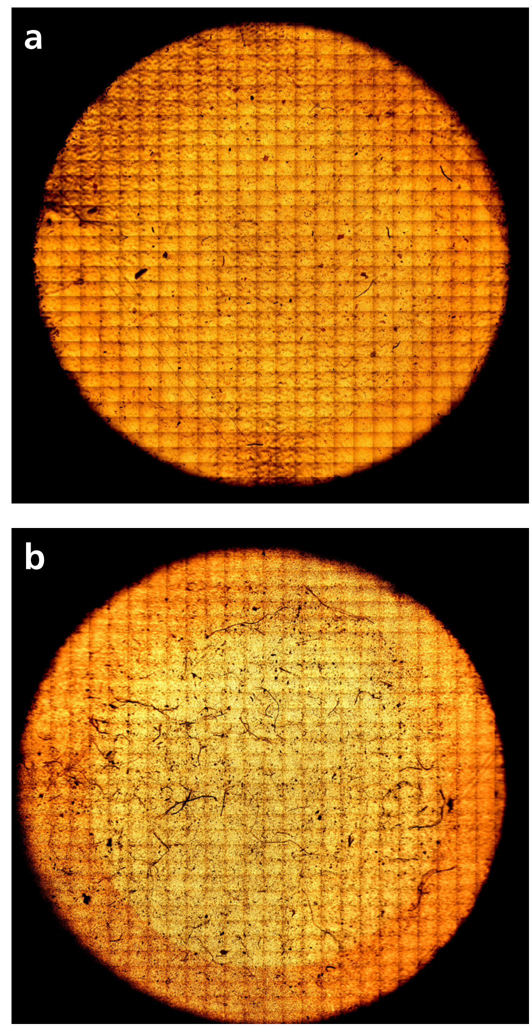

Figure 2. (a) Visible image survey of bottled water sample filtered onto gold-coated polycarbonate filter. (b) Visible image survey of tap water sample filtered onto gold-coated polycarbonate filter.

Table 1. Measurement parameters for Single Point and Image mode.

	Point Mode	Imaging
Resolution	8 cm^{-1}	Typically 8 or 16 cm^{-1}
Aperture Size	Maximized for each particle	6.25 or 25 um pixel size
Number of Scans	16 per particle	1 or 2 per pixel
Analysis Time	10 seconds per particle	50 minutes upwards for 13 mm filter

Typical contaminant materials that were discovered in the water samples are either fibers or single particles. Some examples are shown in Figure 3 below:

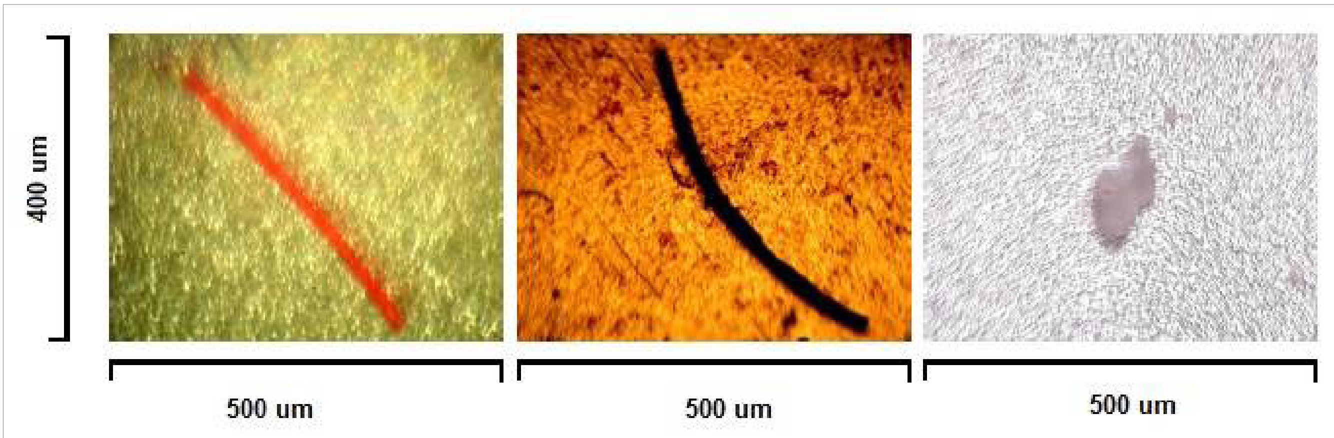

Figure 3. Examples of fibers and particles extracted from bottled water.

IR reflectance spectra of isolated particles and fibers were measured in order to determine their identities. Many research studies that simply assess the samples by visible microscopy assume that all particles and fibers are microplastics. This is often not the case and an identification technique is essential to correctly classify the materials. Some typical spectra are shown below in Figure 4:

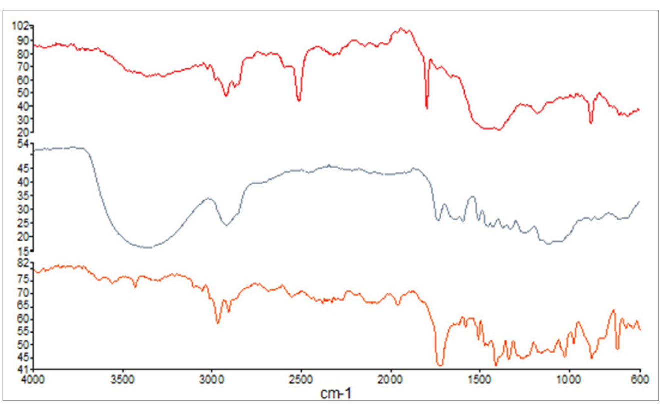

Figure 4. Spectra of typical materials found in bottled water, calcium carbonate (top), cellulose (middle), PET (bottom).

There are frequent occurrences of fibers being cellulose, other particles being calcium carbonate and the occasional "conventional" polymer such as PET, PP or PE. **By far the greatest majority are cellulose based materials.** There have been suggestions that the microplastics present in the bottled water samples originate from the bottle manufacturing process or from the action of opening the bottle causing small fragments. Plastic bottles are normally manufactured from either polyethylene (HDPE or LDPE), polypropylene (PP) or polyethylene terephthalate (PET). Of all the particles and fibers found in the five brands of bottled water, only about 5% of the materials were either PE, PP or PET. One particular brand in a particular bottle type was found to repeatedly contain these materials. Table 2 gives a summary of the number of particles found in the 500 mL samples of each of the different brands.

The tap water sample contained hundreds of particles.

The samples were also imaged at 16 cm-1 using 25 microns pixel size and two scans averaged. The image of the whole filter took approximately 100 minutes. This time could be reduced by an approximate factor of two by using single scans per pixel. The Average Absorbance image obtained from the tap water sample is shown as Figure 5.

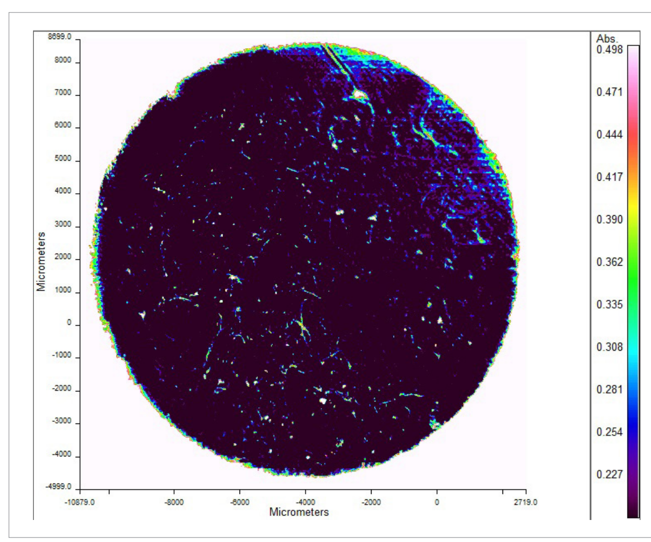

Figure 5. Average Absorbance image for tap water sample.

Table 2. Summary of bottled water samples.

Brand	B	E	S	N	T
Number of particles 20 microns or larger	16	19	14	32	17
Materials identified	Calcium carbonate, PET, cellulose, cellulose acetate	Cellulose, polyamide, polyvinyl alcohol, acrylonitrile-styrene-butadiene	Polyacrylonitrile, polyvinyl acetate, epoxy resin, PE	Cellulose, polyvinyl alcohol, PE, PET, PP	Polyvinyl alcohol, polyamide

At any point in the image there is a full IR spectrum associated with that pixel. An example spectrum is shown in Figure 6 and was identified as cellulose. In the tap water sample the vast majority of the fibers were cellulose.

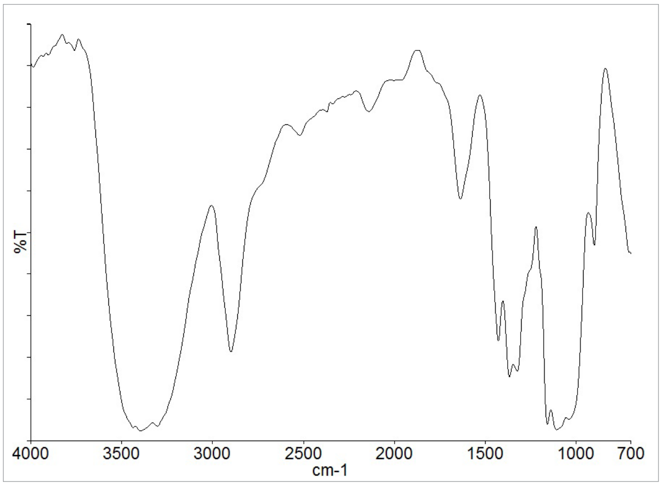

Figure 6. Typical spectrum from fibers in the tap water sample.

The IR image is based on the collection of nearly 250,000 spectra. To manually sort through the data to try to find different chemical species would take many hours. However, data processing routines allow for rapid extraction of information. The "Show Structure" command uses Principal Components Analysis (PCA) to extract the information for the different specific chemical types present within the data collected. Figure 7 shows the Score 1 image for the tap water sample. It shows clear, isolated particles from the hundreds of particles and fibers seen in the Total Absorbance plot shown in Figure 5.

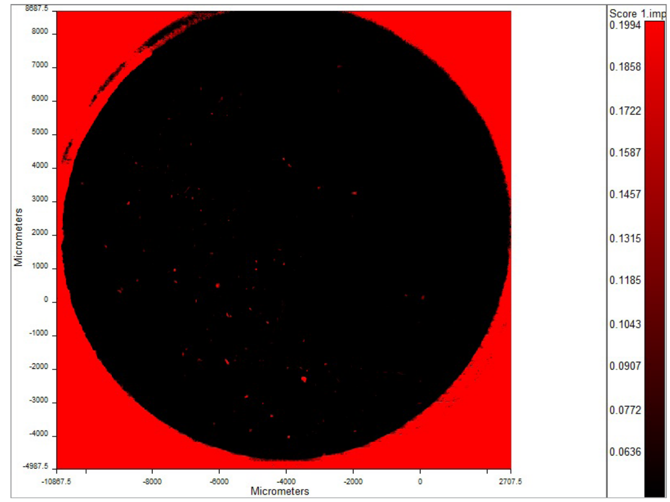

Figure 7. Scores plot 1 picking out different material present in the hundreds of particles.

Summary

IR microscopy, either using point mode or IR imaging, has been shown to be an excellent analytical technique for the detection and identification of microplastics present in bottled water, and can be applied to a much larger range of samples containing microplastics using appropriate sample collection and clean-up. All brands of bottled water contained microplastics in the size range 20-200 microns with some fibers in excess of 2 mm in length. The bottled waters contained considerably less fibers and particles than were present in the tap water sample. The types of microplastics present varied quite considerably and the vast majority were not plastic materials used in the manufacture of plastic drinks bottles. The origin of the microplastics needs to be determined within the individual manufacturer's sites to eliminate the problem, or extra filtration steps could be introduced to remove the microplastics. In addition, it needs to be determined whether the microplastics present form a health risk to consumers.

References

1. Accessible at: https://orbmedia.org/sites/default/files/FinalBottledWaterReport.pdf, August 2018.
2. "Optimizing the Workflow for Microplastics Analysis by IR Microscopy." Ian Robertson, PerkinElmer Whitepaper, 2018.

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