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A Procedure for Measuring Microplastics using Pressurized Fluid

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Supporting Information

Extraction

ABSTRACT: A method based on pressurized fluid extraction (PFE) was developed for measuring microplastics in environmental samples. This method can address some limitations of the current microplastic methods and provide laboratories with a simple analytical method for quantifying common microplastics in a range of environmental samples. The method was initially developed by recovering 101% to 111% of spiked plastics on glass beads and was then applied to a composted municipal waste sample with spike recoveries ranging from 85% to 94%. The results from municipal waste samples and soil



Waste material

Plastic residue

samples collected from an industrial area demonstrated that the method is a promising alternative for determining the concentration and identity of microplastics in environmental samples.

1. INTRODUCTION

The proliferation of plastics material is an issue of increasing global concern, as there is mounting evidence of the risks posed by microplastics in the environment. 1-5 Microplastics have been reported in marine waters, 9-12 freshwaters, 13-16 marine species, 17-20 and some terrestrial environments. 21,22 Despite this there is a lack of knowledge on the distribution of microplastics in these environments, particularly terrestrial landmasses. 6-8 In these studies, a wide variety of methods have been used to identify and quantify microplastics which can make comparisons of large-scale results difficult.²³ Experts have identified the need for an established, uniform method for measuring and reporting microplastics in environmental materials 23-25 materials²

While plastic fragments larger than 1 mm can be recovered and identified in a straightforward manner, with current methods the assay of plastic particles smaller than 1 mm is more problematic. Existing methods for the assay of microplastic fragments typically involve either a floatation or density separation step using dense salt solutions. 17,26 Although these methods have gained common usage, the procedures can suffer from a limited scope of plastics types and poor collection efficiencies. Alternative procedures involving specialized equipment and denser salts (NaI and ZnCl₂)^{17,27} have been used for sediments with some success but the denser salts are expensive and samples with high organic content, such as wastewater, have been reported to cause problems.²⁵ Enzymatic digestion, peroxide digestion and acid digestion have been reported with varying degrees of success for high organic content materials such as biota and wastewater. 25,28 Many of these methods report numbers of fragments of plastic which is important information from a risk assessment perspective but can be difficult to relate to a concentration. ^{23,29} The size of plastic particles assayed in sediments seem to have a practical limit of approximately 20–40 μ m. ^{17,30} Microplastic particles smaller than 20 μ m are of concern as they can be more readily incorporated in the biosphere through ingestion and other mechanisms.³⁰ There is also evidence that microplastics particles can absorb chemical pollutants, complicating an assessment of their environmental impacts³¹

The application of current assays for the plastic content in complex matrices such as industrial and domestic wastes are likely to be problematic. Fine plastic particles can be unintentionally generated and sequestered into materials through grinding and homogenizing, particularly in large scale composting processes. The fine plastics are incorporated into the material making it difficult to quantify and characterize. There is a need from environmental regulators for a robust analytical method with a uniform reporting unit that can quantitatively determine microplastics in environmental materials. Such a method would facilitate the monitoring of marine and terrestrial⁸ microplastics and identify priority areas for investigations.

Pressurized fluid extraction (PFE) is a technique that uses solvents at subcritical temperature and pressure conditions, principally for the recovery of semivolatile organics from solid materials. The technique has achieved acceptance as a standard extraction technique (U.S. EPA Method 3545A)³² and is commonly utilized in environmental laboratories for the extraction of organic pollutants from soils, sediments and wastes. The authors considered that by optimizing PFE

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conditions, it may be possible to quantitatively extract and analyze plastics from environmental samples. A technique based on the extraction of plastics through either partially emulsifying or solubilizing plastics would have a significant advantage over existing physical separation procedures as the process would be unlikely to be affected by particle sizes. Smaller particles would be expected to be more readily extracted with such a process, theoretically enabling the assay of even submicron particles. This work presents method performance characteristics and two case studies using the developed method for the measurement and identification of microplastics.

2. EXPERIMENTAL SECTION

The plastic materials used were high density polyethylene (HDPE) (Aldrich # 434272), polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (PS) (Aldrich 200557), and poly(vinyl chloride) (PVC) (Aldrich #18621–25G). The materials were powders typically 50 μ m in diameter with the exception of PS which had a mean size of approximately 1 mm. Other plastics used were polyethylene terephthalate (PET), and polypropylene (PP) which were obtained from various plastic packaging materials and containers. The materials were cut and filed or ground, and sieved through a 1 mm sieve. The identity of the materials was confirmed by a Nicolet 6700 FTIR spectrophotometer (Thermo) prior to use. These five plastics were selected as test materials as they account for approximately 80% of consumed plastics and over 90% of nonrecycled plastics, based on Australian usage data. 33

A municipal solid sample collected from a waste facility in Sydney was also used for method validation. The facility collects and processes household waste and typically uses separation, grinding, pasteurization and stabilization. A number of soil samples collected near an industrial site were also used for a case study.

A pressurized fluid extractor (Dionex ASE-350) with 34 mL stainless steel cells was used. High temperature Viton o-rings (Dionex #056325) were used in the end-caps. Glass fiber filters (Dionex # 056781) were used in the cell base. High purity solvents such as methanol, hexane and dichloromethane (Suprasolv, Merck, Germany) were evaluated. Except where it is mentioned, samples were extracted using solvent, temperature, pressure and other parameters as outlined in Table 1.

Table 1. Optimized Extraction Conditions for PFE

| parameter | pre-extraction | microplastics extraction |
|-----------------------------|----------------|--------------------------|
| extraction solvent (°C) | methanol | dichloromethane |
| extraction temperature (°C) | 100 | 180 |
| heating time (min) | 5 | 9 |
| static time (s) | 5 | 5 |
| cycles | 3 | 2 |
| rinse volume (%) | 45 | 80 |
| purge time (s) | 75 | 75 |
| system rinse volume (mL) | 15 | 15 |

The solvents were removed from the extract residues by evaporation under a stream of nitrogen (Reacti-Therm, Thermo, US). Dried residues were examined by a Nicolet 6700 FTIR bench equipped with a Smart iTR (Thermo) for identification of plastic type. The single bounce ATR consisted of a diamond ATR crystal with ZnSe lens (active sample area of 1.5 mm^2 , penetration depth of $2.03 \mu m$ at 1000 cm^{-1}). Spectral information was collected over a wavenumber range from 4000

to 600 cm⁻¹ (32 scans at 4 cm⁻¹ resolution). The identity of plastic type was accomplished by comparing the sample spectrum against the library spectra using a correlation algorithm in OMNIC 8.2 software (Thermo). The software provides match values ranging from 0 (no match) to 100 (match).

A combustion method based on Australian Standard 1038.8.1 was used to determine total chlorine in the soils, semivolatile organochlorine compounds were determined using GC-MS based on U. S. EPA method 8270, and soluble chloride was determined using ion chromatography based on APHA Method 4110.

Standard laboratory quality control procedures were followed for the case studies, including spikes, replicates and method blanks.

3. RESULTS

3.1. Method Development Using Glass Beads and Municipal Waste Material. Instrument conditions were optimized using plastic spiked onto glass beads (4 mm, Crown Scientific Australia). The typical cell loading was 10-20 mg of plastic material and approximately 40 g of glass beads. After evaluating various solvents (water, acetone, hexane, DCM) and temperatures in the range of 60- 200 °C, a twostep extraction procedure was developed. An initial extraction step was devised using methanol at a temperature of 100 °C to remove all the extractable semivolatile organic compounds such as fats and oils. Extracts recovered from the methanol extraction were found to contain none of the spiked plastics. The second extraction used dichloromethane to recover the microplastic fraction. Pressurized fluid extraction using dichloromethane at a cell temperature of 100 °C and a pressure of 1500 PSI as specified in USEPA method 3545A³² was found to quantitatively recover PET and PS from glass beads, however PP and PE yielded poor recoveries. Optimum extraction temperatures for these plastics was determined to be 180-190 °C. An extraction temperature as low as 160 °C was sufficient to extract PE, however long-term usage under these conditions with a high sample loading of PE can cause blocking of a 100 μ m frit in the static valve. The use of higher extraction temperatures of 180-190 °C and reduced loading of plastic material prevented this problem occurring.

The optimized extraction conditions are presented in Table 1. Slight variations in instrument parameters did not have a significant effect on the performance of the extraction.

The optimized extraction conditions were used to recover the spiked plastics from the glass beads. The collected DCM extracts were evaporated to dryness and were measured gravimetrically. Recovery results, as shown in Table 2, show greater than 100% recovery for many of the samples indicating positive interference, however results for laboratory control blanks showed average microplastic content of 0.09 mg (SD = 0.17, n = 3). It is possible, the plastics may have encapsulated some of the solvent and caused greater than 100% recovery but the recoveries were within typical environmental laboratory acceptance criteria of 80%-120% for organic analytes and therefore considered satisfactory.

The recovered plastic residues were analyzed by FTIR to confirm their identity. The residues were different in appearance to the spiking material indicating changes during hot solvent dissolution/emulsification and reprecipitation process. 34,35 The FTIR spectra of the residues were found to be similar to the original spiking material and could readily be

Table 2. Recovery Data Using Spiked Glass Beads

| | | а | . () | | |
|--------------|-------------------|-----------------------|-------|-------|----------------------|
| | spike amount (mg) | | | | (-1) |
| plastic type | r | recovered amount (mg) | | | average recovery (%) |
| HDPE | 11.8 | 12.4 | 49.9 | 48.3 | 102 |
| | 12.9 | 13.0 | 49.4 | 45.1 | |
| | | | | | |
| PP | 37.4 | 44.0 | 7.7 | 12.7 | 101 |
| | 36.3 | 42.6 | 8.1 | 13.2 | |
| | | | | | |
| PVC | 19.5 | 18.5 | 47.1 | 50.3 | 111 |
| | 25.6 | 19.8 | 49.0 | 51.3 | |
| | | | | | |
| PS | 17.9 | 19.2 | 10.30 | 10.81 | 107 |
| | 20.8 | 20.4 | 11.48 | 11.63 | |
| | | | | | |
| PET | 20.8 | 20.9 | 42.2 | 54.8 | 111 |
| | 24.3 | 22.2 | 46.5 | 61.9 | |
| | | | | | |

identified using a standard FTIR database, indicating that no significant chemical changes has occurred during the extraction processes. Evidence for the spectral similarity between the extracted plastic residue at 195 $^{\circ}$ C and the original spike material is presented in Figure 1.

3.2. Method Validation Using a Municipal Waste Sample. The optimized extraction procedure was validated on a sample collected from a municipal waste processing facility. Some characteristics of the waste material are presented in Table 3.

Prior to the assay for microplastics the material was dried, sieved to remove particles greater than 1 mm, then ground with a mortar and pestle to promote homogeneity prior to subsampling. The sample size extracted was 2 g. The remaining space in the cell was filled with glass beads. The collected dichloromethane extracts were evaporated to dryness, rinsed with methanol (washing discarded), weighed and analyzed by FTIR for plastic identification. Replicate analysis of the dried residue found an average microplastics concentration of 23 000

Table 3. Composted Waste Material Characteristics (Typical Range)

| moisture content (% w/w) | 22-30 |
|-----------------------------------|-------|
| ash content (% w/w, dry weight) | 30-45 |
| oil and grease (g/kg, dry weight) | 28-70 |

mg/kg (SD = 2000, n = 7). A typical FTIR spectrum of the residue from a waste processing facility is shown in Figure 2. The residue was typically found to be an amorphous material that can break up into flakes. FTIR traces from different spots on the material indicated homogeneity of the extracted plastic. Each FTIR trace is collected from an area of 1.5 mm², defined by the area of the diamond crystal. Additional tests to confirm the residue as plastic were loss on ignition and optical microscopy. These results and micrographs of a typical plastic residue are included in the Supporting Information document.

A more detailed analysis of the FTIR spectra (Figure 3) indicated the presence of polystyrene and polycarbonate in the samples. The detection of polycarbonate indicated that the method may be applicable to a wider range of plastic materials than initially validated.

The precision and accuracy of the analytical method was verified by spiking the municipal waste material with known amounts of selected plastics (10–50 mg). Recoveries were estimated by subtracting the previously calculated total microplastics content of the material from the spiked amount. The recovery results are shown in Table 4. Average recoveries were found to be greater than 80% in municipal waste material, which contained a wide range of chemical and physical contaminants including fats and oils, organic carbon, heavy metals, cations, anions, plastics and glass.

3.3. Case Study—Microplastic in Soils Collected from an Industrial Area. The validated method was used in a case study with the purpose of identifying the source of very high chlorine levels in soil samples collected from around a Sydney industrial area. A field fluorescence assay indicated high levels of chlorine, however semivolatile organic testing found no

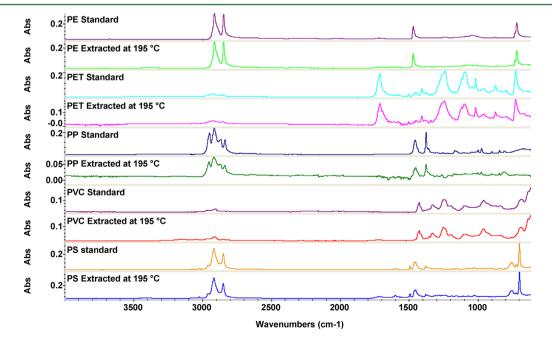


Figure 1. Comparison of FTIR spectra of extracted plastic with the spike material.

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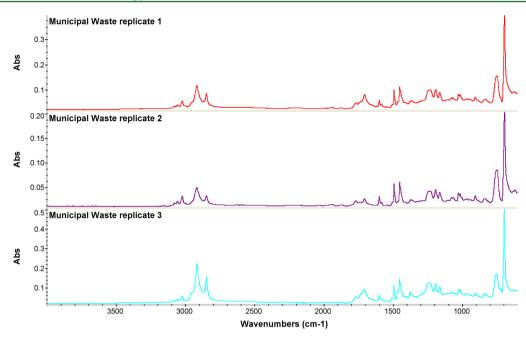


Figure 2. FTIR spectra of various areas of the extract from a waste sample.

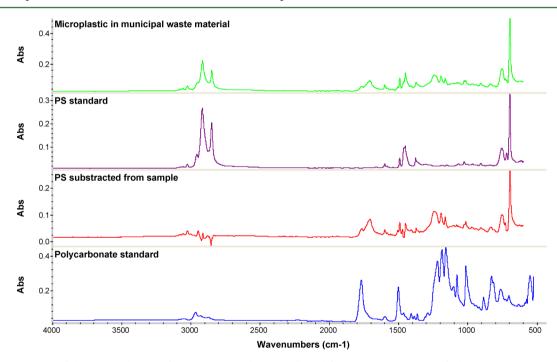


Figure 3. FTIR spectra of the extracted plastic from a composted waste collected from a waste processing facility.

organochlorine compounds in the samples. Further analysis of the soils for total chlorine using the Eschka mixture method yielded concentrations up to 30 000 mg/kg whereas water-soluble inorganic chloride values were less than 100 mg/kg. This indicated that the high chlorine may be due to the presence of nonvolatile organic chlorine compounds. As the industrial site was historically used to produce chlorinated plastics, the collected soil samples were analyzed using the developed microplastic method. The soils samples were dried at 40 $^{\circ}\text{C}$ overnight, sieved through 1 mm sieve and stored at <4 $^{\circ}\text{C}$ prior to the analysis. A sample size of 10 g was used.

FTIR analysis of the residues collected from most of the samples showed a match with the reference FTIR spectrum of

PVC. Comparison of a typical spectrum with the reference PVC spectrum is shown in Figure 4. FTIR spectra and the library search results are included in the Supporting Information that show PVC as the major component (>80% library match) in most of the soil samples. The residue FTIR spectra for two of the soil samples indicated the presence of multiple plastic types (PE and PVC and PS and PVC).

A summary of microplastic concentrations measured in a number of soil samples is presented in Table 5. The soil samples were found to contain 0.03% to 6.7% of microplastic. The microplastic concentrations were related to the vicinity of sample locations to the industrial area.

Table 4. Spike Results from a Municipal Waste

| plastic type | spike amount (mg) recovered amount (mg) | | | | average recovery (%) |
|--------------|---|-------|-------------------|-------|----------------------|
| HDPE | 9.44 | 10.29 | 30.21 | 25.75 | 87 |
| | 9.48 | 9.8 | 23.87 | 18.80 | |
| PP | 13.15 | 12.50 | 8.55 ^a | 8.07 | 84 |
| | 12.81 | 9.01 | 4.43 ^a | 6.73 | |
| PVC | 37.44 | 34.63 | 30.45 | 36.24 | 94 |
| | 36.48 | 35.40 | 27.16 | 31.05 | |
| PS | 47.95 | 45.86 | 26.87 | 43.64 | 90 |
| | 48.54 | 45.85 | 20.31 | 37.07 | |
| PET | 35.91 | 42.29 | 28.10 | 34.04 | 89 |
| | 35.99 | 44.26 | 21.08 | 25.77 | |

"low recovery in this sample was considered a random error and not used for average recovery.

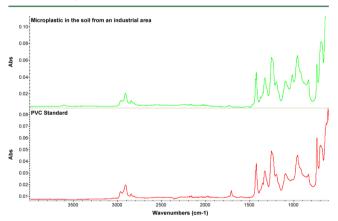


Figure 4. Typical FTIR spectral comparison between the plastic extracted from the sample and a PVC standard.

Table 5 also shows nonvolatile chlorine results that were calculated using results from total chlorine (combustion method) and water-soluble chloride (ion chromatography method). The nonvolatile chlorine results were found to correlate with microplastic results as shown in Figure 5. The good correlation between two different methods provides an additional evidence for the validity this method. The slope of the correlation curve is also consistent with an average chlorine content for common PVCs based on an assumption that PVC contains 50–60% (w/w) chlorine ³⁶

4. DISCUSSION

The results presented in this work provide evidence that a PFE based extraction method can be used to quantify and identify microplastics in a variety of environmental materials. The method is likely to be applicable to other plastic types as the preliminary results indicated that polycarbonate and polyurethane foam (PUF) can also be extracted using this method. This method was demonstrated to be applicable to municipal waste and soils, but it is likely to be applicable to a variety of other environmental matrices with minor optimization and verification of performance. The PFE technique may also be applicable to liquid matrices by an initial filtering step through glass fiber filters with subsequent PFE extraction of the filters, however this approach is yet to be verified.

Table 5. Microplastic Results for Soil Samples Collected from an Industrial Area

| sample | microplastics (mg/kg) | total chlorine (mg/kg) | water-soluble chloride (mg/kg) | nonvolatile chlorine calculated ^e |
|---------|--------------------------|------------------------------|--------------------------------------|--|
| soil 1 | 800 ^a | 300 | 14 | - |
| soil 2 | 2300^{d} | 900 | 12 | 888 |
| soil 3 | 900 ^c | 500 | 11 | 489 |
| soil 4 | 500 ^b | 200 | 12 | - |
| soil 5 | 2400 ^d | 700 | 15 | 685 |
| soil 6 | 500 ^c | 400 | 28 | 372 |
| soil 7 | 9200 ^d | 4700 | 17 | 4683 |
| soil 8 | 3100^{d} | 1200 | 6 | 1194 |
| soil 9 | 13 400 ^d | 9100 | 12 | 9088 |
| soil 10 | 7700 ^d | 5800 | 19 | 5781 |
| soil 11 | 4400 ^d | 1700 | 34 | 1666 |
| soil 12 | 10 400 ^d | 5800 | 40 | 5760 |
| soil 13 | 67 500 ^d | 30 000 | 11 | 29 989 |
| soil 14 | 300 ^c | 600 | 24 | 576 |
| soil 15 | 700^c | 1100 | 28 | 1072 |
| soil 16 | 1000 ^d | 700 | 11 | 689 |
| soil 17 | 6900 ^d | 4500 | 15 | 4485 |
| | | | | |

"FTIR spectral matching identified the presence of polyethylene in the sample. "FTIR spectral matching identified the presence of polystyrene and PVC in the sample. "FTIR spectral matching identified trace amount of PVC in these samples. "FTIR spectral matching identified microplastic as PVC. "Nonvolatile chlorine = total chlorine — volatile and semivolatile organic chlorinated compounds — water-soluble inorganic chloride. Semivolatile organic chlorinated compounds have not been reported however they were found to be insignificant (<2 mg/kg).

Relationship between microplastic content and non-volatile organic chlorine

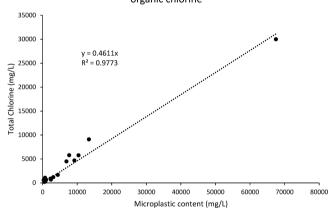


Figure 5. Correlation between the amount of microplastic and nonvolatile organic chlorine in the soil samples.

Some of the benefits of this technique include simplicity, cost, speed, and uniformity in reporting concentration results. The extraction component of the method can be fully automated, minimizing operator skill requirements. The sensitivity of the method is expected to be limited by the precision and accuracy of gravimetric techniques. The authors found that a few milligrams could be accurately measured, therefore by using larger sample amounts through multiple cell extractions or larger volume extraction cells the method should realize part per million sensitivity. The method results are directly presented as a concentration which is a more standardized basis for comparison of data than particle

numbers. The method will efficiently extract plastic particles less than 30 μ m, which can be difficult to measure by floatation and other physical separation procedures. The recovered residue is amenable to further characterization by a range of techniques such as FTIR, GC pyrolysis, thermogravimetric analysis and differential scanning calorimetry.

Some limitations to this method are the inability to measure size fractions of microplastics in samples, however it is possible to separate material into different size fractions using sieves and apply the PFE technique to those size fractions. The extraction procedure obliterates the morphology of microplastic particles, therefore physical characterization tests to assist with source attribution will not be possible on the extract residues. Similarly, samples with multiple types of microplastics will produce residues with complex FTIR spectra that may require skills in spectral deconvolution to identify constituent polymers or require advanced techniques for identification. Additional work is necessary to verify the applicability of the method to resins, adhesives and other plastics.

In conclusion, a simple pressurized fluid extraction method has been successfully evaluated and applied to the assay of five common thermoplastics in glass beads, soil and municipal waste. The method recovery and precision were deemed satisfactory to realize good quantitative data. The concentration, number, type and morphology of plastics are important information in the assessment of microplastic pollution. This PFE method is envisaged to be complementary to existing methods to deliver these information requirements.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00816.

Additional information as noted in the text (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest

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