Size-resolved identification and quantification of micro/nano-plastics in indoor air using pyrolysis gas chromatography-ion mobility mass spectrometry

Mahin Hashemihedeshi¹, Ethan Haywood¹, Daniel C. Gatch², Liisa Jantunen³, Paul A. Helm⁴, Miriam L. Diamond⁵, Frank L. Dorman⁶,⁷, Lindsay S. Cahill¹, Karl J. Jobst¹,*

¹ – Department of Chemistry, Memorial University of Newfoundland, 45 Arctic Ave., St. John’s, NL, Canada, A1C 5S7
² – Gerstel, 701 Digital Drive, Linthicum Heights, MD, USA, 21090
³ – Environment & Climate Change Canada, 6248 8th Line, Egbert, ON, Canada, L0L 1N0
⁴ – Ontario Ministry of the Environment, Conservation and Parks, 125 Resources Road, Etobicoke, ON, Canada M9P 3V6
⁵ – Department of Earth Sciences and School of the Environment, University of Toronto, 22 Ursula Franklin St., Toronto, Ontario, Canada, M5S 3B1
⁶ – Waters Corporation, 34 Maple St., Milford, MA, USA, 01757
⁷ – Department of Chemistry, Dartmouth College, Hannover, NH, USA

Abstract

Humans are exposed to differing levels of micro-/nanoplastics (MNPs) through inhalation, but few studies have attempted to measure <1 µm MNPs in air, in part due to a paucity of analytical methods. We developed an approach to identify and quantify MNPs in indoor air using a novel pyrolysis gas chromatographic cyclic ion mobility mass spectrometer (pyr-GC×IMS). Four common plastic types were targeted for identification, namely (polystyrene (PS), polyethylene (PE), polypropylene (PP), and polymethyl methacrylate (PMMA). The method was applied to size-resolved particulate (56 nm-18µm) collected from two different indoor environments using a Micro-Orifice Uniform Deposit Impactors (MOUDI) model 110 cascade impactor. Comprehensive two-dimensional separation by GC×IMS also enabled the retrospective analysis of other polymers and plastic additives. The mean concentrations of MNP particles with diameters <10 µm and <2.5 µm in the laboratory were 47 ± 5 and 27 ± 4 µg/m³ respectively. In the private residence, the concentrations were 24 ± 3 and 16 ± 2 µg/m³. PS was the most abundant MNP type in both locations. Approximately 57-67% of MNPs were characterized by particle diameters <2.5 µm, and 50-60% of the total particulate matter in the private residence was plastic. Non-targeted screening revealed the presence of plastic additives, such as TDCPP (Tris(1,3-dichloro-2-propyl)phosphate) whose abundance correlated with that of polyurethane (PU). This is consistent with their use as flame retardants in PU-based upholstered furniture and building insulation. This study provides evidence of exposure to MNPs which constitute over half of PM2.5 indoors and underlines the need for further study of this route of exposure to MNPs and the plastics additives carried with them.

*Corresponding author: kjobst@mun.ca

Keywords: Micro-/nanoplastics, Ion mobility-mass spectrometry, Cyclic ion mobility, Indoor pollution, Persistent organic pollutants, Indoor dust

https://doi.org/10.26434/chemrxiv-2023-rvnn0 ORCID: https://orcid.org/0000-0002-7687-6629 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0
1. Introduction

Humans spend >90% of their time indoors\(^1\). There, exposure to microplastics (diameters <5 mm)\(^3\) and nanoplastics (diameters <1 µm)\(^4\) is inevitable via inhalation of indoor dust and ingestion of food contaminated by dust fall\(^5\). Aside from microplastics produced by the unintentional degradation of larger plastics, we are also exposed via indoor pathways to microplastics produced for commercial purposes, including microfibers released from our clothing, furniture, and other everyday household items\(^6\). Young children are likely to be disproportionately exposed due to more frequent hand-to-mouth contact\(^7\) with the floor and other surfaces where dust accumulates and from crawling. Of particular concern is particulate matter (PM) with diameters <10 µm and especially <2.5 µm which are likely to remain airborne\(^1\), thereby posing a greater risk of inhalation where they can penetrate deeply into the lungs. Nanoplastics are small enough to translocate from the lungs into the bloodstream\(^8\), where they can accumulate in tissues and organs\(^9,10\). There is mounting evidence that these exposures can cause adverse respiratory effects, including lung cancer\(^11\). Despite these concerns, the occurrence of <10 µm microplastics and <1 µm nanoplastics in indoor air and their potential impact on human health remains unknown\(^6\). A limited number of studies have reported on airborne microplastics indoors\(^12-15\), however none have measured particle sizes <1 µm\(^16\).

Research on nanoplastics has been enabled by techniques that have long been employed for the characterization of inorganic nanoparticles. The morphology\(^17\) of an environmental micro-/nanoplastic (MNPs) particle can be visually characterized by microscopy methods such as scanning electron microscopy-energy dispersive X-ray (SEM-EDX)\(^18\), transmission electron microscopy (TEM)\(^19\), atomic force microscopy (AFM)\(^20\) and stimulated emission depletion (STED)\(^21\) microscopy. To determine the size of MNPs, there are scattering methods such as dynamic light scattering (DLS)\(^22\), asymmetric flow field-flow fractionation with multi-angle light scattering or total organic carbon (AF\(_4\)-MALS\(^23\) or AF\(_4\)-TOC\(^24\)) and nanoparticle tracking analysis (NTA)\(^25\). Spectroscopy methods used for chemical identification of MNPs include surface enhanced Raman (SERS)\(^26, 27\), Raman tweezers\(^28, 29\), Fourier transform infrared (FTIR)\(^30\), X-ray photoelectron (XPS)\(^31\) spectroscopy and photo induced forced microscopy (PiFM)\(^32\). These techniques can be useful for characterizing particles but they typically involve characterizing individual particles which is very time-consuming, as well as subjective visual assessments that are often restricted by particle size.
Mass spectrometry (MS) is an alternative technique used for identifying and quantifying the composition of MNPs in complex samples. MS, in principle, is not limited to the size of the particle and can be combined with other (chromatographic) techniques. Single particle inductively coupled plasma (SP-ICP)\textsuperscript{33, 34} enables the quantification of the number of MNPs, but this requires functionalizing the nanoparticles with heavy metals, such as gold (Au) or Holmium (Ho). Matrix-assisted laser desorption/ionization (MALDI)\textsuperscript{35} is a powerful technique for the analysis of intact molecules with high molecular weights. This method can quantify plastic particles directly through MS. However, it cannot identify and quantify plastics and their additives simultaneously.

Most MS-based approaches involve thermal decomposition methods, such as pyrolysis, or similar destructive techniques that target the products of decomposition. Pyrolysis can be performed in combination with ambient ionization techniques such as direct analysis in real time (DART)\textsuperscript{36,37} or following separation by gas chromatography (GC)\textsuperscript{38} or liquid chromatography (LC)\textsuperscript{39}. Wang et al.\textsuperscript{39}, used LC-MS to quantify polycarbonate (PC) and polyethylene terephthalate (PET) by depolymerization in sludge and indoor dust samples. Pyrolysis-gas chromatography (pyr-GC) is a popular thermal decomposition method that can provide structural information about the polymer changes, as well as insights into the presence of polymer additives. It has typically been coupled to single quadrupole MS\textsuperscript{40, 41}. Recently tandem mass spectrometry (MS/MS)\textsuperscript{42}, and high resolution time-of-flight (ToF)\textsuperscript{43} platforms have also been hyphenated with pyr-GC, which can increase sensitivity, selectivity and enable the detection of a greater number of pyrolysis products that constitute an MNP’s chemical fingerprint\textsuperscript{36}.

This study reports on a method developed using pyrolysis-gas chromatography multiplexed with cyclic ion mobility mass spectrometry (pyr-GCxcIMS). Ion mobility provides additional evidence that can more accurately identify the pyrolysis decomposition products. After elution through the GC, analyte molecules are transformed into ions that travel through the mobility cell where their drift time is related to their size, shape and charge. The collision cross section (CCS), a unique identifier of an ion, can be determined from the measured drift time. The instrument also offers the capability of detecting thousands of chemical compounds, providing more detailed information on plastics \textit{and} their additives than what can be obtained using standard pyr-GC-MS. This means that plastics and plastic additives can be identified without prior knowledge of their occurrence using an approach coined non-targeted screening\textsuperscript{44, 45}. Our study aimed to: (i) to develop a quantitative method for detecting common plastics in size-resolved indoor dust particulate matter (ranging from 56 nm to 18 µm) by Pyr-GCxcIMS; (ii) to evaluate the effectiveness...
of soft ionization (APCI), tandem mass spectrometry, and ion mobility to identify plastics in these particles; and (iii) to apply the method to the indoor environment to demonstrate proof of concept that the concentration of MNPs can be determined simultaneously with the plastics additives.

2. Experimental

2.1. Chemical and Materials

Four common types of plastics, namely polystyrene (PS), polyethylene (PE), polypropylene (PP) and polymethyl methacrylate (PMMA), were selected as targets. A 25 mg/mL dispersion of PS nanoparticles (nominal size 50 nm) was purchased from Microsphere-Nanosphere (Cold Spring, NY, USA). PE, PP, and PMMA beads were obtained from Fisher Scientific (Hampton, New Hampshire, USA). The PE was used as received: the size of the microparticles ranged between 34-50 µm. The PMMA powder and PP granules were frozen with liquid nitrogen, crushed using a mortar and pestle for 15 min, and separated using a 38 µm mesh stainless steel sieve. The glass fiber filters were obtained from Cole-Parmer (Quebec, Canada). Polyurethane foam (PUF) was purchased from Tisch Environmental Inc. (Village of Cleaves, OH) to confirm the identity of PUF detected by retrospective analysis of the GCxcIMS data. Likewise, the identity of TDCPP (Tris(1,3-dichloro-2-propyl) phosphate) in the sample extracts was confirmed using a standard obtained from Wellington Laboratories (Guelph, ON, Canada).

2.2. Instrumental Analysis

Pyrolysis gas chromatographic cyclic ion mobility mass spectrometry (Pyr-GCxcIMS) experiments were performed using a Waters Cyclic IMS ion mobility mass spectrometer (Wilmslow, UK) coupled to an Agilent 8890 gas chromatograph (GC) using atmospheric pressure chemical ionization (APCI). Mass spectra were recorded between m/z 50 and 1200, enabling the detection of thousands of compounds released during thermal desorption and pyrolysis of the sample extracts. The GC inlet was equipped with a Gerstel CIS4 cooled injection system, thermal desorption unit and pyrolysis module. Automated injection of samples was achieved using a Gerstel Multipurpose-Sampler (MPS) Robotic autosampler. The analysis was performed in two-steps: First, the TDU was initially set to desorb semi-volatile compounds (SVOCs) such as plastics additives by ramping the temperature of the TDU from 50 to 320°C at a rate of 720 °C/min and then holding for 10.43 minutes. The desorbed SVOCs are then swept by helium carrier gas through a heated transfer line (held at 350°C), the CIS4 (held at 320°C) and then focused on the head of the GC column (initially held at 50°C). Separation by GC was achieved using the oven program described below. Following the TDU analysis, the sample was re-injected and pyrolyzed by raising the
temperature of the pyrolysis module to 500°C for 0.33 minutes with a follow-up time of 10 minutes at 320°C. The carrier gas used was helium (99.999%) with a flow rate of 2 mL/min on column and a 40:1 split ratio at the CIS4 injector. The split valve on the TDU was closed for all experiments.

Analyte separation was performed with a Rtx-5 column (15 m × 0.25 mm × 0.25 μm). The initial oven temperature was set to 50°C, and then ramped to 320°C at 29°C/min and held for 5 min. Nitrogen makeup flow of ~99.99% purity at 350 mL/min was used to sweep the GC eluent exiting the column through the ion volume. APCI was initiated by a corona discharge (3 μA) in positive ion mode. The source conditions were: source temperature at 150°C, sampling cone at 40 V, extraction cone at 10 V, cone gas at 250 L/h, and auxiliary gas at 100 L/h. To internally correct the measured m/z in positive ion modes, column bleed ions (C₉H₂₇O₅Si⁺ - m/z 355.0699) were used. The cyclic ion mobility cell was operated in the single pass mode, with the separation time set to 2.0 ms and a traveling wave height of 15 V. Collision cross section (CCS) values were obtained by calibration with a set of 21 substances (aka, “major mix”) supplied by Waters Corp. (Milford, MA).

2.3. Polymer Standard Preparation

The suspension of 50 nm PS particles was received in water (25 mg/mL). A 1 mL aliquot of the PS standard was reconstituted into DCM (25 mg/mL). Stock suspensions of PMMA, PP, and PE (25 mg/mL) were made by dissolving <38 um sieved particles into toluene. Stock solutions of PS, PE, PP, and PMMA were diluted to 5 mg/mL and then combined to a suspension containing all four polymers at a concentration of 1 mg/mL in toluene. Quantitation was performed using external calibration and calibration solutions were prepared by adding 0.02 μg, 0.1 μg, 0.2 μg, 1 μg and 5 μg of each polymer onto a quartz wool bed inserted into a 40 μL quartz pyrolysis cup by serial dilution of the combined standard solution. The PS and PMMA were dissolved in toluene at room temperature, but to promote dispersion/dissolution of PE and PP during transfer steps, the stock solutions were heated to 120 °C. The polymer densities of PS, PE, PP, and PMMA were assumed to be 0.95, 1.05, 0.91 and 1.18 g/cm³, respectively. The stock solution (25 mg/mL) of PUF was prepared by dissolving it in dimethylformamide (DMF) solvent at 80 °C for 3 hours, employing a laboratory-grade magnetic stirrer.

2.4. Sampling Strategy

We sampled two indoor environments, namely a laboratory space and a private residence (both mechanically ventilated), to evaluate the developed analytical method. PM was collected using a Micro-
Orifice Uniform Deposit Impactors (MOUDI) model 110 (MSP Corporation, Shoreview, MN, USA) operated for 72 hours. Eleven samples were collected at each site with corresponding cut point aerodynamic diameters: 0.056 µm, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10 and 18 µm. Glass fiber filters (Whatman GF/F) were used to collect PM where the filters were pre-cleaned in a muffle furnace at 450 °C for 8 hours and then extracted in four cycles by accelerated solvent extraction using DCM. A PARTI5 Vacuum Pump (TSI Inc., USA) was used to draw air through the cascade impactor at a rate of 30 L/min for 72 hours at the height of 1.2 m, corresponding to the average adult breathing height. The total volume of air sampled was 129,600 L or 129.6 m³.

2.5. Extraction of Samples

The filters were extracted using a Dionex ASE 350 Accelerated Solvent Extractor (Thermo Scientific, Germany) with DCM solvent at a 100 °C extraction temperature and 1500 psi pressure. DCM was chosen as the extraction solvent due to its ability to dissolve most polymers at high temperatures. Each filter was loaded into a 10 mL stainless-steel extraction cell. Four cycles were performed on each extraction cell, using an 80% rinse volume, 250-second purge time, 9-second heating time, and 5-second static time. The resulting extract was collected in sample collection bottles, transferred to a 50 mL glass centrifuge tube, and concentrated under nitrogen until the sample volume was reduced to approx. 1 mL. The sample extract was further reduced to 200 µL in a 2 mL GC vial. 10 µL of the extract was transferred to a pyrolysis tube for Pyr-GCxcIMS analysis.

2.6. Quality Assurance/Quality Control

The m/z and GC retention times of the pyrolysis decomposition products used for the quantitation of PS, PE, PP, and PMMA are summarized in Table 1. The accurate mass, isotope ratios and collision cross sections (CCSs) of all detected pyrolysis products fell within 5 ppm, +/- 2% of the theoretical or measured value obtained from an authentic standard. The ratio between the abundance of the pyrolysis product used for quantification (Table 1) and selected qualifier decomposition products (Table 1) deviated <20% which suggests the results of this ratio could be used for fingerprinting the results. All pyrolysis products reported herein were present at quantities that exceed the estimated method detection limits (MDL) by > 3-fold. MDLs were evaluated using 8 pre-cleaned blank filters processed using the same steps as for the samples. The MDL was calculated as 3 times the standard deviations obtained from replicate (n = 8) measurements of filter blanks. For each set of 11 filters collected during a sampling event, one procedural blank was
collected and analyzed. Polymer recovery samples (n=6) were prepared by fortifying the filters with 10 µg of PS, PE, PP, and PMMA, and then following the same extraction, and transfer steps used for all samples. Recovery, linearity and MDLs are reported in Table 2. Special care was taken during sample collection, pretreatment, and instrumental analysis to minimize potential contamination from the surrounding environment. Sample loading and drying procedures were carried out in a fume hood and nitrile gloves were worn during all steps. All glass sample containers were rinsed thoroughly with DCM before use.

2.7. Data Processing
The data were collected using Waters MassLynx 4.2 and quantitative analysis was performed using TargetLynx. In addition, GCxcIMS contour plots were generated using DriftScope (v. 3.0). Progenesis QI was used to calculate the CCS and mass of each indicator in standard and sample (see Table 1).

3. Results and Discussion
3.1. Characterization of common polymers by pyr-GCxcIMS
The identification or classification of a polymer is based on the molecular composition of the products generated during thermal decomposition or pyrolysis. Figure 1a displays the contour plot of retention time versus drift time obtained for four different MNPs (PS, PE, PP, PMMA) by pyr-GCxcIMS. Positive mode APCI was employed for this study, which Spectra acquired using APCI display abundant molecular ions and little fragmentation because this method involves ionization of the analyte molecule (M) through charge exchange with N₂⁺ or N₄⁺ radical cations generated by corona discharge which is less energetic compared to EI.

The identification of polyethylene (PE) and polypropylene (PP) can be challenging because the pyrolysis of the two polymers leads to the formation of hydrocarbons that possess identical elemental composition. Harata et. al. demonstrated the use of Py-GC-APCI for characterizing PE/PP mixtures in a complex mixture. They observed that under APCI conditions, [M+NO]⁺ adducts, and fragments generated therefrom, could be used to distinguish PE and PP. Thus, we used a lower pyrolysis temperature (500°C vs. 600°C) which resulted in higher molecular weight PE and PP decomposition products that could be separated by both GC and ion mobility.
The pyrogram obtained from PP is displayed in Figure 1b. Upon degradation, PP forms a wide range of branched and unsaturated hydrocarbons with the general formula C\(_x\)H\(_{2x-2}\), containing between 25 and 52 carbon atoms. The m/z 600.6573 ion C\(_{43}\)H\(_{84}\) was selected for quantification because of its high relative abundance. PP’s mass spectrum was dominated by the molecular ion (M\(^+\)) which, upon collision-induced dissociation (CID) decomposed by loss of a methyl as well as cleavage along the backbone: the 42 Da spacing between peaks is characteristic of the -CH\(_2\)CH(CH\(_3\))- repeating unit in PP (Fig. 2d). The pyrogram of PE was also dominated by hydrocarbons with the general formula C\(_x\)H\(_{2x-2}\), ranging from C\(_{21}\) to C\(_{42}\) (Fig. 1d). Like PP, the APCI mass spectra of the PE pyrolysis products were dominated by the molecular ion\(^{52}\). However, the pyrolysis products of PE could easily be distinguished from those of PP because (i) the CID mass spectrum of PE was characterized by fragment ions spaced 14 Da apart, consistent with its -CH\(_2\)- repeating units; (ii) the linear hydrocarbons generated from PE elute with a later retention time (RT) than the branched hydrocarbons generated by PP; and (iii) the linear hydrocarbons were characterized by larger CCSs than those of the branched hydrocarbons. Table 1 summarizes the m/z, RT and CCS measurements of the indicator compounds used in this study.

PS pyrolyzed into the styrene trimer (m/z 312.1878), which was the dominant compound, followed by styrene dimer (m/z 208.1252) (Fig. 1c). In source fragmentation of the trimer ion produces an intense m/z 207.1174 ion was used for quantification. The pyrogram of PMMA displayed pyrolysis products ranging from C\(_{19}\) to C\(_{34}\) (Fig. 1e). These products were associated with tetramer to heptamer molecules after the loss of the methoxy group. The mass spectra of the PS trimer ions (Fig. 2a) and the PMMA pentamer ions (Fig. 2b) displayed dissociation products that were consistent with their proposed structures.
Fig 1. a) Retention time vs drift time contour plot of PP (yellow), PE (green), PMMA (orange) and PS (pink); Extracted ion chromatograms of the decomposition products of b) PP, c) PS, d) PE, and e) PMMA; Note: “n” refers to the number of carbons in the polymer decomposition product’s structure.

Fig 2. CID mass spectra of: a) the m/z 312 ions generated by the trimer of PS; b) the m/z 500 ions generated by the pentamer of PMMA; c) the m/z 446 ions generated by the C_{32}H_{62} decomposition product of PE; d) and the m/z 600 ions generated by the C_{43}H_{84} decomposition product of PP. Note: The collision energy was 12V for PS and 20V for PMMA, PE and PP is 20V.

Table 1. Summary of pyrolysis products generated from selected polymers and their m/z and CCS measurements. The elemental compositions highlighted in bold correspond to quantification ions, whereas the remaining ions were used as qualifiers.
3.2. Method performance

Linear calibration curves were obtained from pyr-GC/MS measurements of standard PS, PE, PP and PMMA within the ranges of 0.2-5 µg for PS and 0.02-5 µg for PE, PP. The correlation coefficients, represented by $R^2$, were all $\geq 0.98$ (Table 2). Commercial PS nanospheres with a particle size of 50 nm and <38 µm of PMMA, PE, and PP were used for evaluating their recoveries. Recoveries of spiked plastic were 113 ± 19, 95 ± 25, 61 ± 29, and 114 ± 23% of PE, PP, PMMA, and PS, respectively (Table 2). The MDLs, as shown in Table 2, ranged from 0.005-0.407 µg/m$^3$.

### Table 2. Performance characteristics of the method.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Linear range (µg)</th>
<th>Linearity ($R^2$)</th>
<th>Recovery (n=6)</th>
<th>MDL (µg.m$^{-3}$) (n=8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>0.2-5</td>
<td>0.984</td>
<td>114±23</td>
<td>0.407</td>
</tr>
<tr>
<td>PP</td>
<td>0.1-5</td>
<td>0.992</td>
<td>95±25</td>
<td>0.12</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.1-5</td>
<td>0.998</td>
<td>61±29</td>
<td>0.005</td>
</tr>
<tr>
<td>PE</td>
<td>0.2-5</td>
<td>0.994</td>
<td>113±19</td>
<td>0.040</td>
</tr>
</tbody>
</table>

3.3. Quantitative analysis of PS, PMMA, PP and PE in indoor air

https://doi.org/10.26434/chemrxiv-2023-rvnn0 ORCID: https://orcid.org/0000-0002-7687-6629 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0
The concentrations of MNPs consisting of PS, PE, PP and PMMA in air samples collected from two indoor locations for each stage of the cascade impactor were determined using an external calibration curve.

**Figure 3.** The concentrations (µg/m³) of polymers A) PE, B) PMMA, C) PP and D) PS obtained from different aerodynamic cut-points (Note: PR* = Private residence). The error bars represent standard deviations of triplicate measurements.

The total mass concentrations of PM with diameters <10 µm and <2.5 µm in the lab were 47 ± 5 and 27 ± 4 µg/m³, respectively and 24 ± 3 and 16 ± 2 µg/m³ in the private residence. The World Health Organization guideline concentrations for PM₁₀ and PM₂.₅ are 15 µg/m³ and 10 µg/m³, respectively, for outdoor air pollution. While guidelines for indoor PM₁₀/PM₂.₅ exposure do not currently exist, our the measured MNP concentrations exceed the health-based outdoor guidelines which may be of concern, understanding that the chemistry and thus toxicity of indoor vs outdoor particles can be very different. A gravimetric analysis of the filters obtained from the private residence suggests that the total PM₁₀/PM₂.₅ concentrations consisted of approximately 50-60% plastic (Figure 4a).
We also calculated the number concentration (particles/m³) based on the aerodynamic cut-point size of each stage of the cascade impactor. The particle concentration of PP, PE, PMMA and PS particles with diameters <18 um approached $2.8 \times 10^8$ PP particles/m³, $1.2 \times 10^{10}$ PE particles/m³, $1.2 \times 10^8$ PMMA particles/m³, and $2.8 \times 10^{10}$ PS particles/m³, respectively. In comparison, the number concentrations in the private residence were somewhat lower than those in the lab, up to $2.2 \times 10^8$ PP particles/m³, $5.9 \times 10^9$ PE particles/m³, $1.1 \times 10^7$ PMMA particles/m³, and $1.6 \times 10^{10}$ PS particles/m³. In line with the trend observed by Dris et al.54 for particles and fibers >50 µm, the results in Figure 3 show that the number of particles increases exponentially with decreasing size. This suggests that most of the particles inhaled at the two sampling sites are characterized by small diameters (<2.5 µm), which can penetrate deeper into the lungs.

One limitation of this assumption is the fact that some polymers, such as high impact polystyrene or expanded polystyrene foam, are manufactured with a wide range of densities (0.03 to 1.25 g/cm³). Thus, the particle concentration of PS below represents a conservative estimate. Also, we assumed that all particles are spherical to simplify the analysis of number concentration, which is not necessarily true. Further, the study by Liu et. al.53 suggests that inter-stage loss of nanoparticles may occur between the inlet and one of the lower stages, ranging between 2.9 and 26.1%. Equation 1 was used to estimate the number concentrations (particles/m³) of different MNPs in the lab and private residence are shown on the secondary axes of Fig. 3.

$$C_n = \frac{6C_m}{\pi \rho d^3} \quad (1)$$

$C_n$ is for the particle concentration of MNPs (Particles/m³), $C_m$ represents the mass concentration of MNPs (µg/m³), and $\rho$ signifies the density of the previously mentioned plastics.

Interestingly, the most abundant plastic found by mass or by particle concentration was PS in both the laboratory and private residence. As described above, the styrene trimer was used as an indicator. Trimer styrene could originate from other polymers besides polystyrene (PS). For example, approximately 50% of car tires are made from various types of styrene-butadiene rubber, which may also pyrolyze to form the styrene trimer. Exchange of indoor air with outdoor air could carry road dust contaminated with styrene-butadiene rubber into the lab or private residence. However, Costa-Gomez et al.55 have shown that the outdoor concentrations of PS, using the same styrene trimer indicator, are in the low ng/m³, which is 1000-fold lower than the indoor concentrations measured in the present study.. The likely explanation for
The presence of PS in the laboratory could be that it is a relatively new space occupied in September 2021, and a significant amount of the PS may have originated from expanded polystyrene (EPS) commonly used for packaging materials. Since EPS is light weight, it is likely to remain airborne.

The pyr-GCxcIMS can detect thousands of chemical compounds in addition to the four polymers targeted for quantitation. Figure 5 displays the extracted ion mobilogram (Fig. 5a), extracted ion chromatogram (Fig. 5c) and mass spectrum (Fig. 5e) of toluene diisocyanate (TDI), one of the products of the pyrolysis of an air sample extract obtained from the private residence. Aromatic diisocyanates are used in the production of foams, including polyurethane foam PU. PU is a versatile polymer used in applications such as flexible foam for bedding and furniture, carpet underlay, packaging, coatings, and adhesives. When an authentic sample of PU foam was dissolved in dimethylformamide and pyrolyzed, we found that TDI is one of its decomposition products, and as shown in Figures 5b, 5d and 5f, the retention time, mobility and mass spectrum of TDI matches those obtained from the indoor air sample.

Figure 4. Concentrations of A) total PM<sub>10</sub>/PM<sub>2.5</sub> in the private residence; as well as B) PE, C) PP, D) PMMA, E) PS (μg/m<sup>3</sup>) classified as either constituents of PM<sub>10</sub>, PM<sub>2.5</sub>, or PM<sub>0.1</sub> in the laboratory and private residence. The error bars represent standard deviations of triplicate measurements.
MNPs, including PU foam, may serve as carriers of additives and small molecule pollutants, and inhalation of MNPs may be a source of exposure to these additives. PU foam could contain various flame retardants such as tris(1,3-dichloro-2-propyl) phosphate (TDCPP). Both PU and TDCPP were detected at all stages of the cascade impactor deployed to both the laboratory and private residence. We investigated whether TDCPP was used as an additive flame retardant in PU foam particles by calculating the concentration of TDCPP and PU at each stage of the cascade impactor using external calibration curves. We found a statistically significant positive correlation between the levels of TDCPP and PU PM in the lab (Pearson correlation coefficient = 0.85, p < 0.05, Figure 6a/b). TDCPP is under consideration for listing as toxic under the Canadian Chemicals Management Plan. S. Zhang noted that there are various types of flame retardants used for polypropylene, including phosphate flame retardants. In contrast, no correlation was observed for the other polymers (PMMA, PE, or PS, Fig. 6a). This results suggest that...
the method presented here can provide an indication of the presence and contributions of plastics additives identified using GCxGC-IMS.

![Table and graph]

**Fig 6.** Correlation between TDCPP and polymers in the air sample

### 4. Conclusions

We present a robust method for identifying and quantifying plastic polymers in indoor air and tested the method for PS, PE, PP and PMMA MNPs. Sampling with a MOUDI cascade impactor showed that the mass concentrations of plastic particles smaller than 2.5µm were 27 ± 4 ug/m³ in a laboratory and 16 ± 2 ug/m³ in a private residence. The results suggest that PS is the most abundant airborne MNP type in both indoor settings, possibly due to the relatively low density of PS foam. Ion mobility offers the advantage of confirming the identities of pyrolysis products by their CCSs; along with the ability to simultaneously detect thousands of other compounds, including both polymers and small molecule pollutants, present in complex samples.

### 5. Acknowledgements

This research was funded by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), the Government of Canada’s New Frontiers in Research Fund, and Health Canada. The views expressed herein do not necessarily represent the views of Health Canada. We gratefully acknowledge Elisabeth Galarneau (Environment and Climate Change Canada) for use of the MOUDI cascade impactor.
6. References


https://doi.org/10.26434/chemrxiv-2023-rvnm0 ORCID: https://orcid.org/0000-0002-7687-6629 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0


