

# Identification of Polyfluorinated Alkyl Substances in Indoor Dust Using Gas Chromatography-cyclic Ion Mobility Mass Spectrometry

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## 1 Introduction

Poly- and perfluoroalkyl substances (PFAS) are a class of persistent organic pollutants (POPs) that have been used extensively in industry as surfactants, solvents, lubricants and flame retardants (Gluge et al., 2020) since their advent in the 1940s (USEPA). They pose a risk to the environment and to human health because they are persistent (Jones, 2021), bioaccumulative (Higgins and Luthy, 2006), and undergo long-range transport to remote regions like the Arctic (Windsor et al, 2019). Important exposure routes for humans are through inhalation of indoor dust (Zhang, He, Huang et al, 2020)(Tian, Kim, Shoeib et al, 2016) and drinking water (Guelfo and Adamson, 2018). As a consequence of the environmental and human health impacts of PFAS, parties to the Stockholm Convention have pledged to reduce the release of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). However, there are still over 12,000 other PFAS of interest to researchers (EPA Comptox database) that have evaded study and regulation.

The challenge of recognizing undocumented POPs from among the many thousands of co-extracted matrix ions is daunting. Whereas characteristic isotope patterns can reveal homologues of chlorinated and brominated POPs, per- and polyfluorinated compounds are more difficult to recognize because <sup>19</sup>F exists as a single stable isotope. A promising approach for the discovery of PFAS harnesses ion mobility. In ion mobility experiments, ions are separated according to their mobility through a gas-filled region in which the ions undergo non-reactive collisions with an inert gas like helium or nitrogen. These collisions impede the mobility of an ion, increasing its drift time relative to other ions that differ in size, shape and charge. The mobility data obtained from such an experiment can be used to calculate the ion-neutral collision cross section (CCS) of an ion. CCS is the area (Å<sup>2</sup>) around an ion that another molecule must enter in order for a collision to occur. It is a constant for each molecule and is a useful parameter for identification and comparison. Computational modelling of the CCSs of circa 20,000 industrial chemicals used in Canada and the United States suggest that any ion characterized by a CCS value less than the sum of 100Å<sup>2</sup> and one fifth of its mass is either a polybrominated flame retardant or a PFAS.

This contribution highlights a novel method for PFAS identification that has been validated by experiments with SRM 2585, a standard reference material of indoor dust. Chlorofluoro phthalimides are among those chemicals tentatively identified previously and their identities were confirmed by synthesizing a technical mixture of authentic standards. When applied to set of indoor dust samples collected from public spaces in St. John's, Newfoundland, the method revealed novel PFAS, including a range of fluorotelomer ethoxylates that have not yet been reported until now.

## 2 Experimental and computational methods

### 2.1 Sample collection and extraction

Dust was collected from the floors of 6 locations on the campus of Memorial University as well as 16 diverse locations off campus, including two hospitals, a cinema, two schools, eight commercial shopping venues, an airport, public transit and an office space. NIST SRM 2585, which contains organic contaminants found in indoor dust, was used to demonstrate the validity of the method. The dust samples were extracted using hexane, acetone, methanol and acetonitrile. The final samples were reconstituted in 50µL of hexane and analyzed using a gas chromatography-cyclic ion mobility mass spectrometer.

### 2.2 Gas chromatography-cyclic ion mobility experiments

Gas chromatography-cyclic ion mobility mass spectrometry (GC-cIMS) experiments were performed using a Waters Cyclic ion mobility mass spectrometer (Wilmslow, UK) coupled to an Agilent 8890 Gas chromatograph using atmospheric pressure chemical ionization (APCI). Analyte separation was performed with an Rtx-5 column (30 m x 0.25 mm x 0.25 µm or 15 m x 0.25 mm x 0.1 µm). The initial temperature was set to 90 °C; the oven was then ramped to 325 °C at 8.4 °C/min, and then held for 6 minutes. Sample extracts and standard solutions (1 µL) were injected in splitless mode. The inlet temperature was set to 280 °C and the helium carrier gas flow was set to 1.4 mL/min. GC eluent exiting the column was swept through the ion volume using a make-up flow of nitrogen (~99.99% purity) of 350 mL/min. APCI was initiated by a corona discharge (3 µA) in both positive and negative ion modes. The source conditions were as follows: source temperature, 150 °C; sampling cone, 40V; extraction cone, 10V; cone gas, 175 L/hour; auxiliary gas, 100 L/hour. Column bleed (C<sub>9</sub>H<sub>27</sub>O<sub>5</sub>Si<sub>5</sub><sup>+</sup> - m/z 355.0699) and background ions (C<sub>16</sub>H<sub>31</sub>O<sub>2</sub><sup>-</sup> - m/z



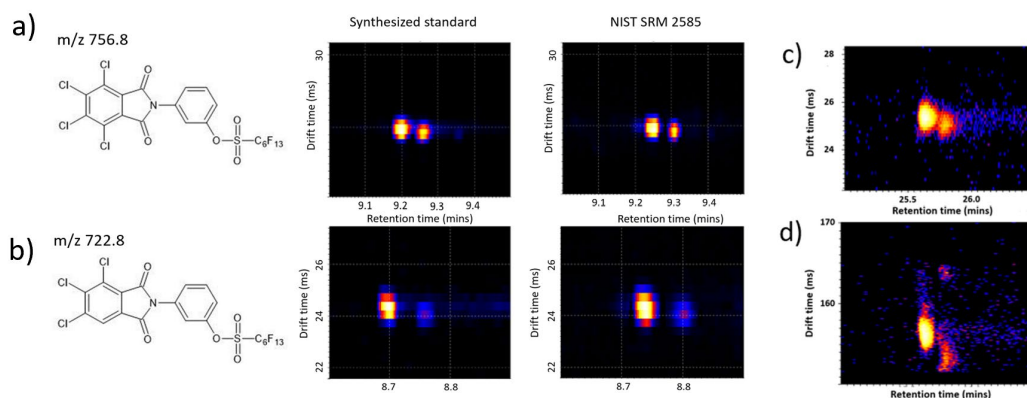


Figure 2: Retention time vs. drift time contour plots obtained from (a) the main product of the synthesis (Cl/F-1) and the same compound found in SRM 2585; and (b) a secondary product of the synthesis vis-à-vis the same compound found in SRM 2585; Retention time vs. drift time contour plot of the molecular ions  $M^{+}$  of Cl/F-1 after (c) one pass and (d) ten passes through the cyclic ion mobility cell.

The structures of two of the Cl/F phthalimides ( $C_{20}H_5NSO_5F_{13}$  and  $C_{20}H_4ClNSO_5F_{13}$ , labeled Cl/F-1 and Cl/F-2 in Fig. 1b) were confirmed using an authentic standard synthesized in our lab. Figures 2a and 2b display the drift time vs. retention time contour plots of Cl/F-1 and Cl/F-2, the primary products in the synthetic standard, alongside the same compounds detected in SRM 2585. All four contour plots display two peaks and evidently Cl/F-1 and Cl/F-2 exist as two distinct isomers which are present in both the authentic standard and in SRM 2585. A multi-pass experiment, the results of which are shown in Fig. 2d, showed that these two isomers, which have identical masses and elemental compositions, can be separated using GC-cIMS. We posit that these isomers contain linear and branched versions of the alkyl chain, and this hypothesis is supported by modeling of CCS values for different structural variations of Cl/F-1 and Cl/F-2.

After confirming the identity of the chloro/fluoro phthalimides, the methodology was applied to dust collected from six locations around Memorial University and 16 dust samples collected from diverse (public) locations in St. John's, Canada. While compounds Cl/F-1 and Cl/F-2 were not observed in these samples, several novel classes of PFAS were discovered. Halocarbons oils with the formula  $(C_2F_3Cl)_nCl_2$ , where  $n=6, 7, 8, 9$  were present in three of six locations that have recently been renovated. Environmental fate modeling has predicted that mixed halogenated n-alkanes (PXAs), are likely POPs (Li et al., 2021). The detection of chlorofluoro n-alkanes in indoor dust sample underlines the need for further study of this emerging class of pollutants. Greater than 80% of the samples contained fluorotelomer ethoxylates (see Figure 1d after filtering Figure 1c), which have attracted surprisingly little attention, and little is known about their fate in the human body or the environment. Herkert et al. (2022) have recently detected these compounds in anti-fog products and shown that they are characterized by significant cytotoxicity and adipogenic activity. To the best of our knowledge, this represents the first detection of fluorotelomer ethoxylates in the indoor environment.

## 4 Conclusions

This contribution demonstrates the successful application of a novel approach to identify per- and polyfluoroalkyl substances using GC-cIMS. Chloro/fluoro phthalimides which were detected in SRM 2585 through application of this method have been successfully characterized using GC-cIMS and the structure confirmed by synthesis of an authentic standard. When applied to a set of indoor dust samples collected from St. John's, Newfoundland and Labrador, Canada, novel PFAS were discovered, including a series of fluorotelomer ethoxylates. We suggest that this is an important application in environmental chemistry, as it is impossible to predict all of the potential structures emerging PFAS pollutants, and CCS can help reveal those that actually exist and persist in the environment.

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