

Screening Total Organic Fluorine in Solid Samples Using a Pyroprobe

Application Note

Environmental

Abstract

This application note highlights the use of the Pyroprobe 6150 for the analysis of Total Organic Fluorine (TOF), PFAS as a screening tool.

Author:

John W Scott¹

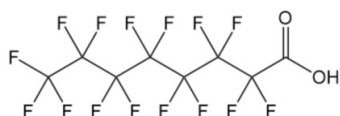
Wei Zheng²

Introduction

Standard methods for measurement of per- and polyfluoroalkyl (PFAS) utilize liquid chromatography-tandem-mass spectrometry (LC-MS-MS). This technique is specific for targeted PFAS, very sensitive, highly accurate, and precise. However, it is expensive and time-consuming to perform. The diverse range of fluoropolymers in use and the existence of thousands of individual species of PFAS preclude the use of LC-MS-MS as a practical first option for extensive analysis and decision-making. Therefore, there is an urgent need for a universal, rapid, and cost-effective PFAS screening tool that can support large-scale sampling, analysis, and field-level decision-making. Such a screening tool would greatly complement the available targeted LC-MS-MS methods. To address this need, a pyrolysis-gas chromatography mass spectroscopy (PY-GC-MS) technique has been developed with an intended use as a screening tool for PFAS laden solid materials and fluoropolymers.

Experiment Setup

The PFAS reference materials used for this study were sourced from Sigma-Aldrich chemical company and were of technical grade. Specific PFAS targeted in this study included, Perfluorobutanoic acid (PFBA), Perfluorobutanesulfonic acid (PFBS), Perfluorohexanoic acid (PFHxA), Perfluorohexanesulfonic acid (PFHxS), Perfluorooctanoic acid (PFOA), Perfluorooctanesulfonic acid (PFOS), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluorododecanoic acid (PFDoA), and Perfluorooctanesulfonamide (PFOSA). Each reference material was dissolved in methanol such that a concentration of 10 µg of total fluorine of each species was achieved. Twenty µL of each solution was added to DISC tubes for analysis at 1000°C.



Pyroprobe 6150

DISC:

Dry: 70°C 60 sec

Py: 1000°C 60 sec

Interface: 300°C

Transfer Line: 325°C

Valve Oven: 300°C

GC-MS

Column:

5% phenyl (30m x 0.25mm x 0.25 µm)

Carrier: He 1.00 mL/min, 5:1 spl

Injector: 330°C

Oven: 40°C for 0.9 min 30°C/min to 330°C

Source: 250°C

Mass Range: 35-250amu

Results and Discussion

All ten species of PFAS analyzed by PY-GC-MS displayed an instrument response in the region of 2.5 minutes to 3.0 minutes. The mass spectra obtained for these peaks were all similar and included intense response for ions m/z 69, 81, 100, 119, and 131 and matched well with the reference spectrum for tetrafluoroethylene and hexafluoropropylene. Figure 1 presents the chromatograms and mass spectra for PFOA and PFOS.

To demonstrate linearity, PFOA and PFOS reference materials were prepared at five concentrations (0.075 ng, 0.75 ng, 7.5 ng, 75 ng, and 1500 ng) as total organic

¹Senior Chemist, ²Environmental Chemist

The Illinois Sustainable Technology Center, Prairie Research Institute at the University of Illinois

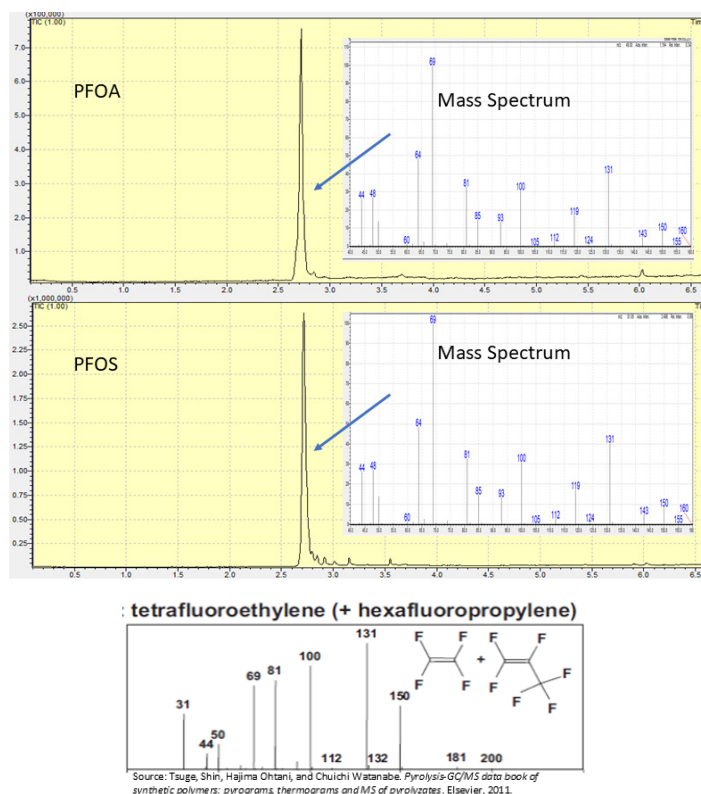


Figure 1. Chromatograms and Mass spectra for PFOA (top) and PFOS (center) and reference spectrum (bottom) for Analysis by Py-GC-MS.

fluorine. They were analyzed like the previous experiment, however, only m/z 69 and 131 were monitored. Figure 2 presents the instrument response of each solution versus concentration. PFOA and PFOS showed signal linearity for over 5.5 orders of magnitude regarding concentration. In addition, the coefficient of determination, r^2 , was 0.99 or greater for both PFAS and both

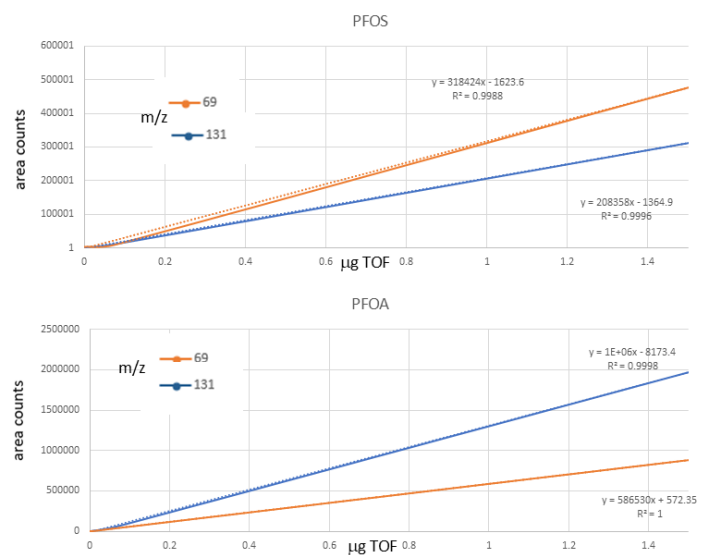


Figure 2. Instrument Response of TOF Ions (m/z 69 & 131) Versus PFAS TOF Concentration (μg).

both ions measured. Another observation made in this calibration data was a trend with regards to most abundant ions produced by Py-GC-MS as it related to class of PFAS investigated. The

carboxylic acid type PFAS, PFOA produced more ions with a m/z 131 versus 69, however the sulfonic acid type of PFAS, PFOS produced more ions with a m/z 69. The cause of this phenomenon is currently unknown; however, it is suspected to be related to the mechanism for breakdown of PFAS under thermal treatment. This finding certainly warrants further investigation and may be able to provide additional information regarding the behavior of PFAS under thermal treatment conditions.

To demonstrate the utility of this TOF method with carbon-based sorbents (activated carbon and biochars), materials were loaded with PFOA and analyzed for TOF by Py-GC-MS. This was achieved by preparing a PFOA stock solution (8 mg/L) which was used to expose 100 mg of either activated carbon, biochar, or designer biochar in 25 ml of laboratory grade water. The solution containing PFOA and sorbent were shaken at 190 rpm for 24 hours. Following exposure, the solutions were centrifuged, the solution was decanted, and the sorbent was dried under ambient conditions. The Py-GC-MS system was calibrated on m/z 131 for TOF with PFOA standards over a concentration range of 0.075 ng to 1500 ng. The sub-sample of the dried sorbent (~5 mg) was added to a DISC tube and analyzed directly following calibration. Another sub-sample of the dried sorbent was extracted with methanolic ammonium hydroxide, purified by solid phase extraction (SPE), and analyzed for PFOA by LC-MS-MS. Figure 3 presents the recovery of PFOA by the test sorbets analyzed by Py-GC-MS TOF and LC-MS-MS. The findings from analysis of both techniques agree well. Biochar alone, without modification, demonstrates poor efficiency for removal of PFOA from an aqueous media. On the other hand, designer biochar demonstrates a much better PFOA removal rate and is on par with activated carbon.

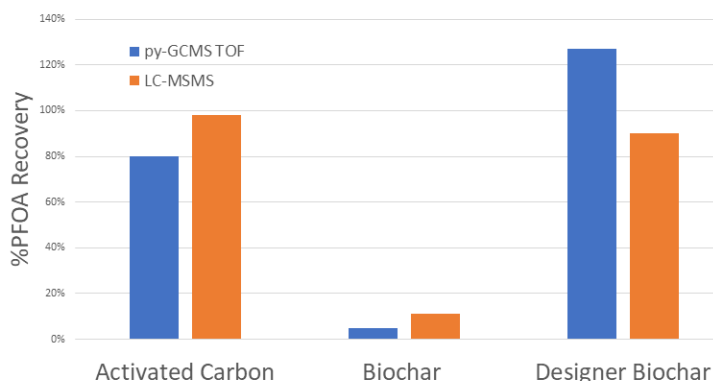


Figure 3. Comparison of PY-GC-MS and LC-MS-MS Evaluation of PFOA Adsorption Efficiency by Carbon-based Sorbents.

Conclusion

The CDS Analytical 6150 Pyroprobe combined with GC-MS offers a quick and inexpensive means for semi-quantitative analysis of total organic fluorine measurements in solid matrices. This technique has a high potential for use in screening solid materials within a fraction of time and cost that is associated with standard LC-MS-MS methods. In addition, it can detect organic fluorinated compounds that would be otherwise overlooked in targeted approaches and is not prone to interference from the presence of inorganic forms of fluorine.