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GC/MS – Polymode Ionization – Environment

A Sample Prep-Free Analysis of Perfluorinated Carboxylic Acids with *"SMCI+"* using Negative Chemical Ionization

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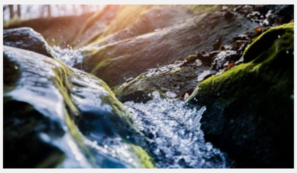
Abstract

Perfluorinated carboxylic acids (PFCAs) are man-made compounds that are extremely persistent in the environment. Although PFCAs could be detected with gas chromatography/mass spectrometry technique using electron ionization and positive chemical ionization analysis modes, the sensitivity of detection may be suboptimal. Since PFCAs compounds consist mainly of electronegative fluorine elements, the detection sensitivity of PFCAs with GC/MS could be further improved with negative chemical ionization mode. This *Technology Brief* introduces a simplified approach to directly analyze PFCAs with negative chemical ionization mode, which is achieved through the usage of a *polymode ionization* setup, consisting of a direct sample probe with innovative reagent gas source and ion source. The new *polymode ionization* setup could simplify the workflow to achieve preliminary identification of PFCAs to support current efforts in environmental and substance monitoring.



Keywords:
Polymode Ionization, Negative Chemical Ionization, Perfluorinated Carboxylic Acids, Direct Sampling

Analyzing PFCAs with GC/MS in negative chemical ionization mode enables higher sensitivity for better environment monitoring

Highlights

- *"SMCI+"* setup enable direct and quick qualitative GC/MS analysis of PFCAs without the need for tedious derivatization steps
- *"SMCI+"* setup delivers convenience and safety to carry out negative chemical ionization and requires only common laboratory solvent as reagent gas
- Detection sensitivity of PFCAs can be improved by using negative chemical ionization supported by *"SMCI+"*

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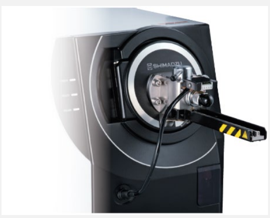
Direct Sample Inlet



Solvent Mediated Chemical Ionization (SMCI)

1. INTRODUCTION

Perfluorinated carboxylic acids (PFCAs) are commonly labelled as "the forever chemical". These compounds are extremely persistent in the environment. PFCAs are man-made and do not occur naturally in the environment. The prolonged accumulation of PFCAs in humans, wildlife, and the environment can lead to potentially adverse effects.

The pervasive use of PFCAs in manufacturing processes and its broad exposure has since come to the attention of regulators such as the US Environmental Protection Agency and the European Environmental Agency. A recent study has also indicated that long carbon chain PFCAs are detected in human breast milk and infant formulas. Despite numerous attempts to restrict the use of PFCAs, the lack of alternatives and international free trades necessitate the need for constant environmental and substance monitoring.

PFCAs are compounds of the formula $C_nF_{(2n+1)}CO_2H$. Due to the presence of a carboxyl functional group, it is necessary to perform derivatization prior to analysis with the gas chromatography/mass spectrometry (GC/MS) technique. The usage of a direct probe as a sample inlet in GC/MS provides an alternative technique that eliminates the need for tedious sample preparation. This benefit paves the way for a quick and direct method to achieve preliminary detection and identification of PFCAs.

In addition, as PFCAs are fluorinated compounds, negative chemical ionization mode could improve the detection sensitivity. This article demonstrates the application of a direct probe in conjunction with a solvent mediated chemical ionization (SMCI) operated under negative chemical ionization (NCI) mode for the analysis of six types of PFCAs. The NCI mass spectra of PFCAs generated by SMCI units will be evaluated.

2. EXPERIMENT

2.1 Analytical Setup

The analytical results in this report were generated using a Direct Sample Inlet (DI) probe in conjunction with a SMCI unit. The combination of DI with SMCI unit is hence known as *"SMCI+"* in this article (Figure 1).

The DI probe is designed to be able to fit a miniature sample vial at its tip. The sample vial is thereafter placed close to the ion source and subsequently heated up according to a temperature program. The chemicals in the sample vial are hence volatilized and ionized in the ion source.

On the other hand, the SMCI unit enables positive and negative chemical ionization (PCI and NCI) modes with conventional PCI/NCI ion sources and methanol as the reagent gas. Usage of methanol allows safe (i.e., it eliminates the use of flammable and toxic reagent gases such as methane, isobutane and ammonia) and convenient adoption of PCI/NCI modes in routine GC/MS analysis.

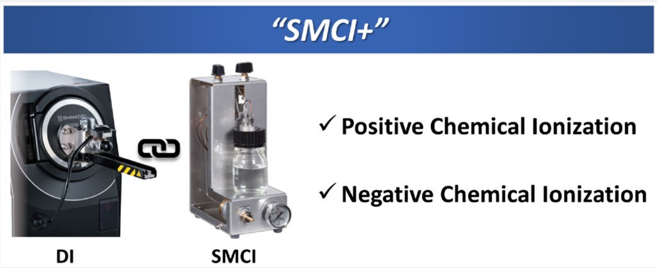
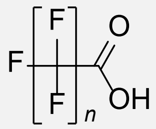


Figure 1. Polymode ionization setup of "SMCI+"

A total of 6 PFCAs including perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorotridecanoic acid (PFTriA) and perfluorotetradecanoic acid (PFTA).



Perfluorinated Carboxylic Acid (PFCAs)

Name	Abbreviation	Formula	MW
Perfluoroheptanoic acid	PFHpA	$C_7F_{13}O_2H$	364
Perfluorooctanoic acid	PFOA	$C_8F_{15}O_2H$	414
Perfluorononanoic acid	PFNA	$C_9F_{17}O_2H$	464
Perfluorodecanoic acid	PFDA	$C_{10}F_{19}O_2H$	514
Perfluorotridecanoic acid	PFTriA	$C_{13}F_{25}O_2H$	664
Perfluorotetradecanoic acid	PFTA	$C_{14}F_{27}O_2H$	714

2.2 Experimental Condition

Standard solutions of PFCAs were prepared to a concentration of 5000 ppm in methanol. 1 µL of the standard solution was introduced into the DI sample vial for analysis. The samples were left to dry before analysis.

The DI probe was heated at 20°C /min to 100°C, then 40°C /min to 450°C and held for 7 min. The ion source temperature was set to 230°C. Negative chemical ionization with SMCI (methanol) was used. Scan mode was performed in the range of *m/z* 50-800 with a scan speed of 3333.

3. RESULTS AND DISCUSSION

3.1. "SMCI+" (NCI) Mass Spectra

The NCI mass spectra of the PFCAs are shown in Figure 2. The corresponding $[M-H]^-$ and $[M-HF]^-$ ions were observed in the NCI mass spectra for all PFCAs. The peak intensities of the $[M-HF]^-$ ions were consistently higher than the respective $[M-H]^-$ ions. The peak intensities of $[M-H]^-$ ions were observed to be at least 20% of the base peak, except for PFTA.

In comparison to PCI mode analysis with *"SMCI+"* (Technology Brief MST-204), whereby the intensities of the $[M+H]^+$ ions of the PFCAs were consistently less than 10% of the base peak, NCI was hence able to improve the detection sensitivity of PFCAs.

A distinctive peak at *m/z* 231, which corresponded to the base peak for PFOA, PFNA, PFDA, PFTriA, and PFTA, was postulated as $[C_5F_9]^+$ ion. For the longer chain PFCAs, a series of peaks differing by 50 *u* (i.e., *m/z* 281, 331, 381, 431, 481,…) could be almost certainly assigned to the loss of a CF_2 radical during the ionization process.

Subsequently, a mixture containing all PFCAs was analyzed and the total ion thermogram (TIT) is shown in Figure 3. By tracing the extracted ion thermogram (EIT) profiles of [M-H]- ions, the PFCAs were observed to elute within 100°C.

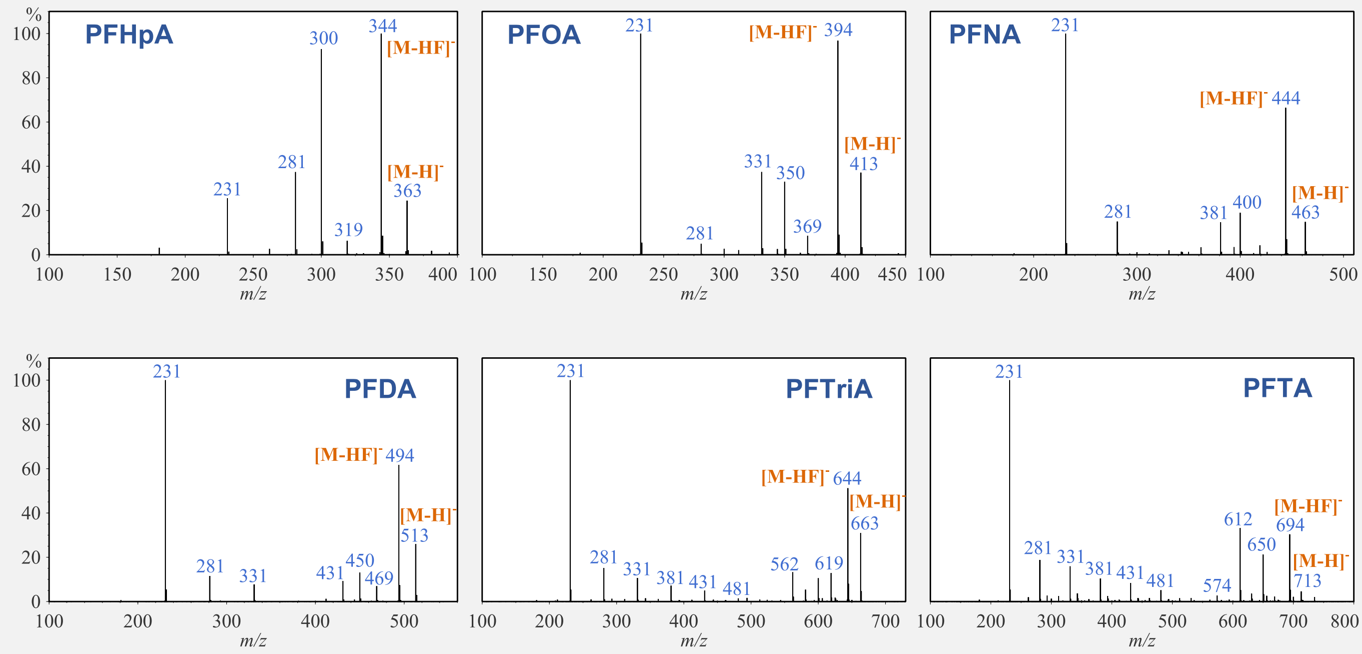


Figure 2. NCI mass spectra of PFCAs collected with "SMCI+"

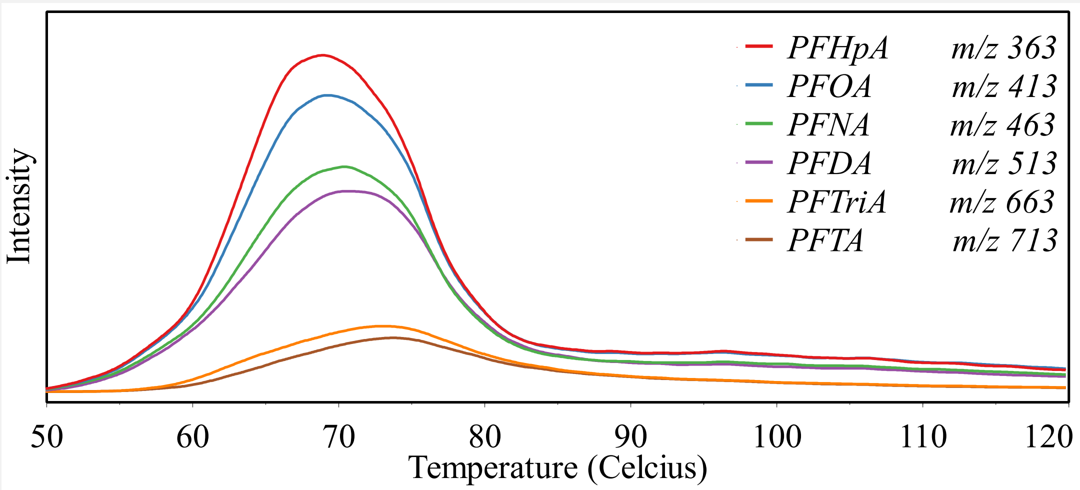


Figure 3. EIT profiles of [M-H]- ions from NCI mode of "SMCI+" for PFCAs

4. CONCLUSION

The newly introduced *"SMCI+"* enables direct and quick qualitative analysis of PFACs, which conventionally requires tedious derivatization steps prior to GC/MS analysis. The *"SMCI+"* setup delivers utmost convenience and safety to carry out negative chemical ionization since it utilizes methanol, which is a common laboratory solvent, as the reagent gas. Analysis of PFCAs with negative chemical ionization mode has further improved the detection sensitivity as compared to positive chemical ionization.

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Direct Sample Inlet (DI)

The DI unit enables samples to be injected directly into the ion source without passing through the gas chromatograph. The DI probe can be heated up to 500°C under vacuum conditions. As a result, mass spectra of high polarity and high boiling point compounds can be generated easily. The analysis is performed by simply placing the sample in a sample vial that is secured in the DI probe.

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Solvent Mediated Chemical Ionization (SMCI)

SMCI introduces headspace reagent gas from a bottle into the GC/MS ionization unit for use in positive or negative chemical ionization. Conventional chemical ionization techniques require the use of flammable reagent gas cylinders, but SMCI can be carried out with general organic solvents, such as methanol or acetonitrile, together with nitrogen or argon gas. This results in greater safety and lower running costs.

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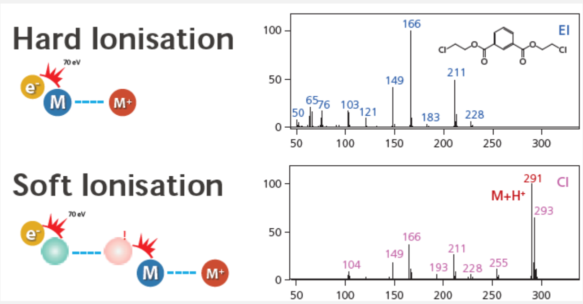
Chemical Ionization



CI is a softer ionization method than EI. Fragmentation is less likely to occur, so molecular weight information is more readily obtained. Negative chemical ionization (NCI) or negative ion chemical ionization (NICI) enables selectively measuring, with ultra-high sensitivity, chemical substances with an electron affinity, such as chlorine-based compounds.

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