Gas Chromatograph Mass Spectrometer GCMS-TQ™8050 NX

Application News

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

- Environmental Monitoring -

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User Benefits

- "*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+*"

■ 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.

■ Measurement Conditions and Samples

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 (Fig. 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

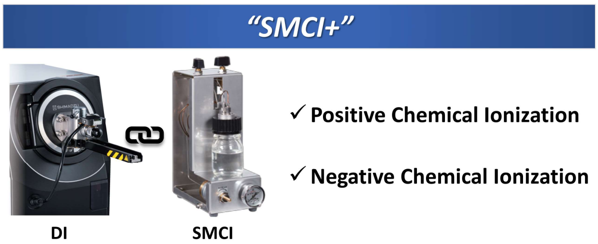
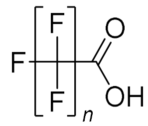


Fig. 1 *Polymode Ionization* setup of "*SMCI+*".



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

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.

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).

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. A mixture sample was prepared by introducing 1 µL of each standard solution into a DI sample vial. The samples were left to dry before analysis.

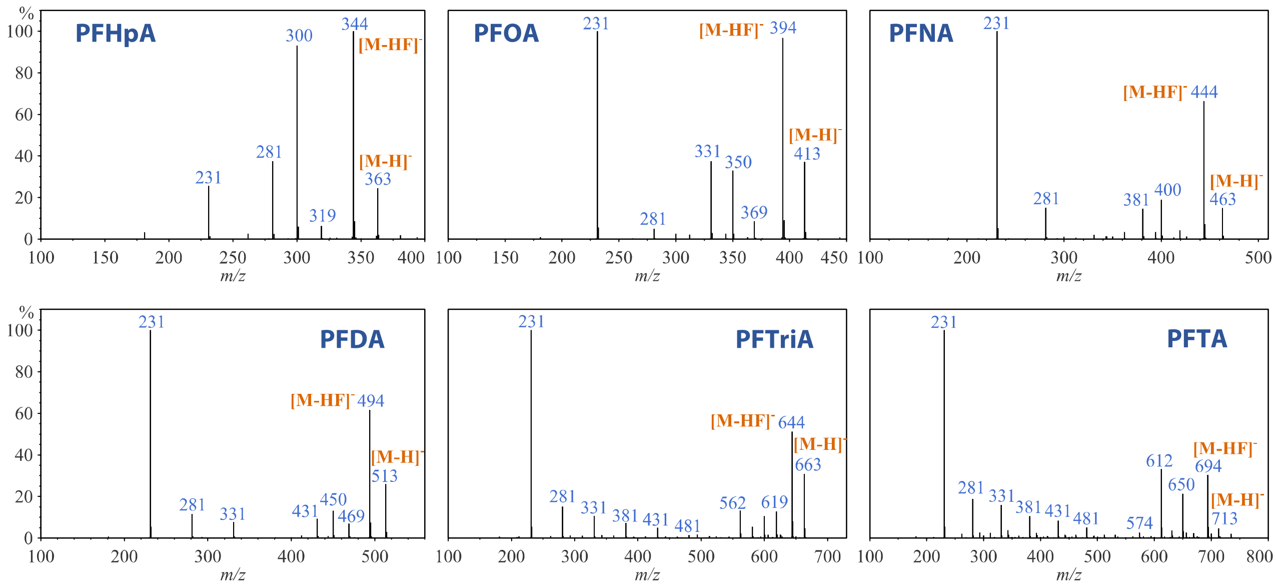


Fig. 2. NCI mass spectra of PFCAs collected with “*SMCI+*”.

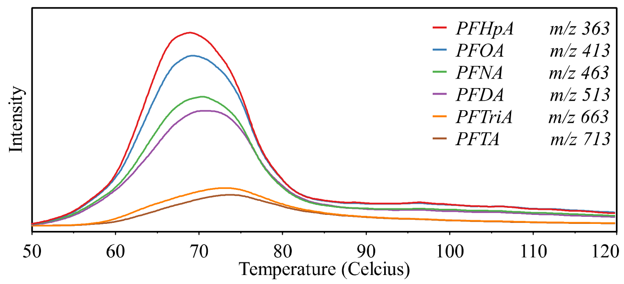


Fig. 3. EIT profiles of [M-H]- ions from NCI mode of “*SMCI+*” for a mixture of PFCAs.

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.

■ Results and Discussion

“*SMCI+*” (NCI) Mass Spectra.

The NCI mass spectra of the PFCAs are shown in Fig. 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+*” (Application News JMST-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 Fig. 3. By tracing the extracted ion thermogram (EIT) profiles of $[M-H]^-$ ions, the PFCAs were observed to elute within 100 °C.

■ 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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