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GC/MS – Polymode Ionization – Environment

A Sample Prep-Free Analysis of Perfluorinated Carboxylic Acids with *“Smart IS+”* and *“SMCI+”*

Written by:

Chua Chun Kiang
Tan Yu Jun
Jackie Jackie
Loo Lai Chin

Abstract

Perfluorinated carboxylic acids (PFCAs) are synthesized compounds that are extremely stable and therefore bioaccumulate. While these compounds are usually analyzed with the liquid chromatography/mass spectrometry technique, the gas chromatography/mass spectrometry (GC/MS) method can also be adopted but requires multi-step derivatization processes. This Technology Brief introduces a simplified approach to directly analyze PFCAs with GC/MS. As a result of using a combination of direct sample probe with innovative ion sources and reagent gas sources that are capable of polymode ionization, both electron and chemical ionization analysis modes can be performed. The new polymode ionization setup could deliver seamless preliminary identification of PFCAs to support current efforts in environmental and substance monitoring.


PFCAs, commonly detected in human breast milk and infant formulas, are persistent environmental contaminants known as the “forever chemical”

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

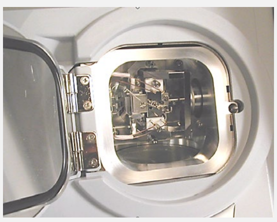
Highlights

- *“Smart IS+”* and *“SMCI+”* setups enable quick and direct qualitative GC/MS analysis of PFCAs without the need for multi-step derivatization procedures
- Gain access to both electron ionization and positive chemical ionization modes with a single *“Smart IS+”* setup
- *“SMCI+”* setup delivers convenience and safety to perform positive chemical ionization since it requires only common laboratory solvents as reagent gas

Technologies Featured

Direct Sample Inlet

Smart EI/CI Ion Source (Smart IS)



Solvent Mediated Chemical Ionization (SMCI)

1. INTRODUCTION

Perfluorinated carboxylic acids (PFCAs) are man-made compounds that do not occur naturally in the environment. These compounds are extremely persistent in the environment and commonly named “the forever chemical”. PFCAs bioaccumulate in humans and wildlife leading to potential adverse effects on the environment, human, and wildlife health.

Perfluorooctanoic acid (PFOA) is one of the most widely used PFCAs in manufacturing processes and its exposure has long caught the attention of regulators such as the US Environmental Protection Agency and the European Environmental Agency. Longer carbon chains of PFCAs are also a major concern as they were detected in human breast milk and infant formulas. While there have been enormous efforts to restrict the use of PFCAs, the lack of alternatives and international free trades hence call for 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.

This article demonstrates the application of a direct probe in conjunction with a Smart EI/CI ion source (Smart IS) or solvent mediated chemical ionization (SMCI) unit for the analysis of six types of PFCAs. The mass spectra of PFCAs generated by Smart IS and 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 Smart IS or SMCI unit. The combination of DI with Smart IS or SMCI unit is hence known as *“Smart IS+”* and *“SMCI+”* in this article, respectively (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.

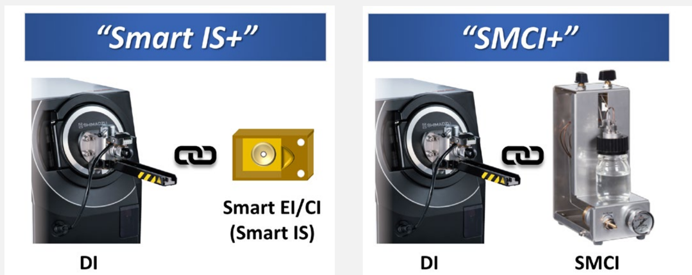
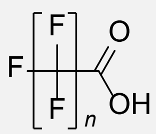


Figure 1. *Polymode Ionization* setup inclusive of *“Smart IS+”* and *“SMCI+”*

Smart IS is a 2-in-1 ion source that enables both electron ionization (EI) and positive chemical ionization (PCI) modes. PCI is achieved with the usage of isobutane gas as a reagent gas. Due to the simplicity of switching between the two different ionization modes with Smart IS, the PCI mode attained with Smart IS is referred to as quick chemical ionization (QCI).

On the other hand, the SMCI unit enables PCI mode with conventional PCI ion source 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 mode 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) were analyzed in this study.



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. A mixture sample of FFAs and TGs were prepared by introducing 1 µL of each standard solution into the DI sample vial. 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. Ionization mode used included EI, QCI (isobutane), and SMCI (methanol). Scan mode was performed in the range of *m/z* 50-800 with a scan speed of 3333.

3. RESULTS AND DISCUSSION

3.1 "Smart IS+" and "SMCI+" Mass Spectra

Using *"Smart IS+"* and *"SMCI+"*, the PFCAs were first analyzed with three different ionization modes, specifically EI, QCI, and SMCI, to establish the total ion thermogram profiles and mass spectra. The extracted ion thermogram (EIT) profiles of $[M+H]^+$ ion for the PFCAs collected with SMCI mode are shown in Figure 2. All the PFCAs eluted within 100°C. The consolidated mass spectra of the PFCAs collected with the three ionization modes are shown in Figure 3.

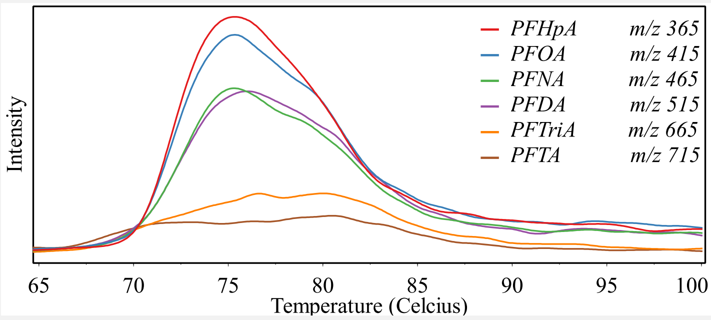
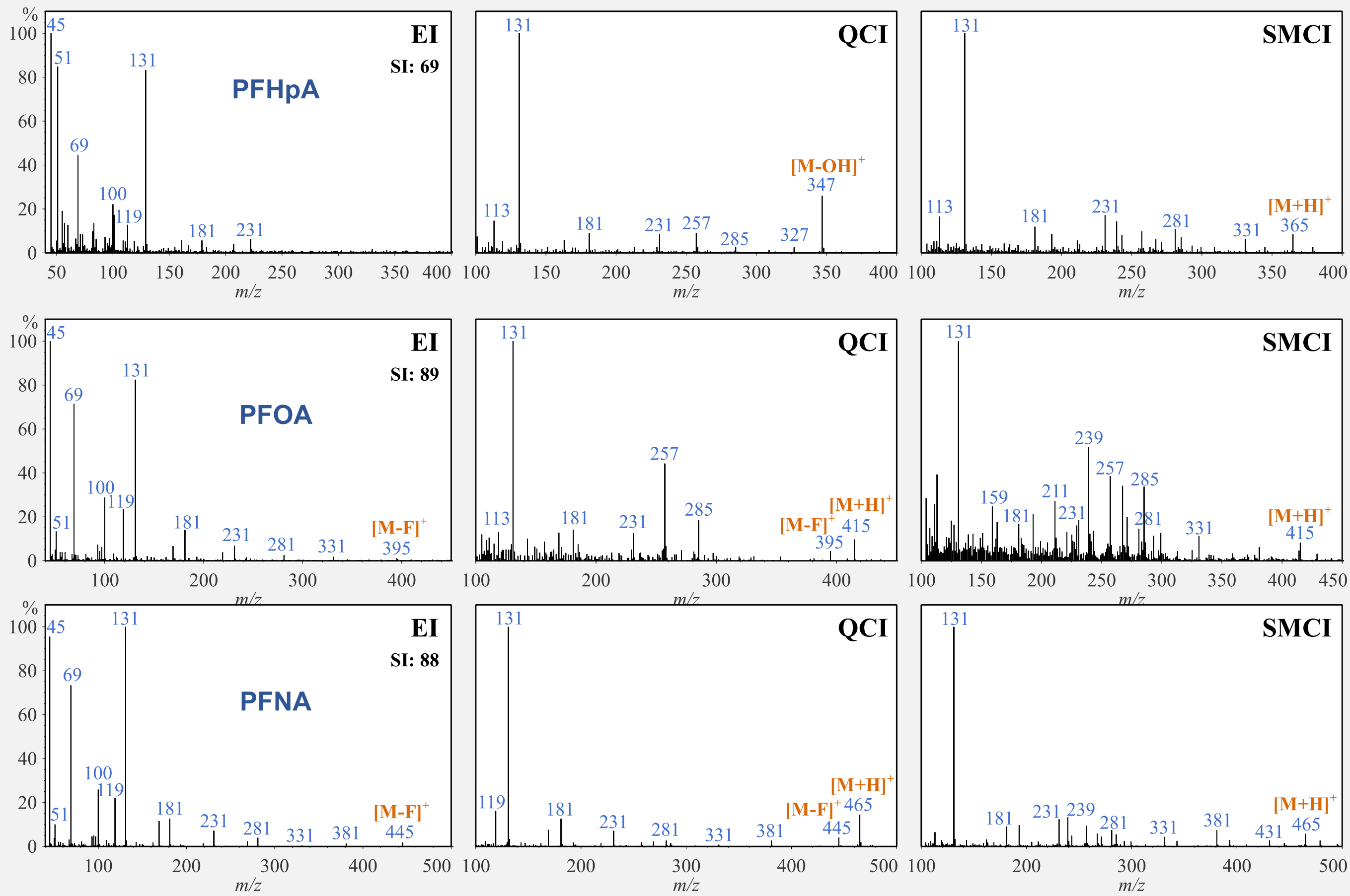


Figure 2. EIT profile of $[M+H]^+$ ion from SMCI mode for PFCAs



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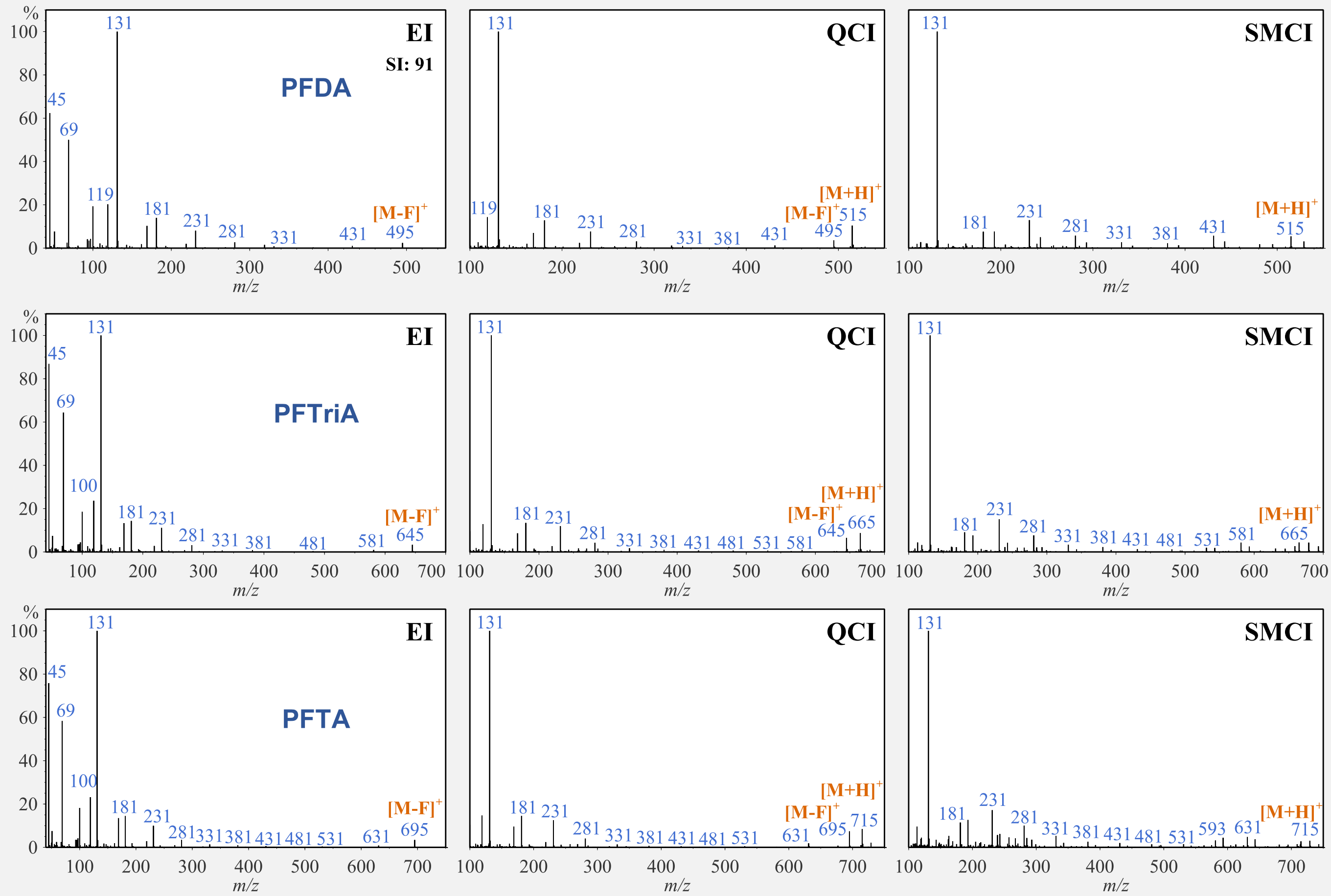

Figure 3. EI, QCI, and SMCI mass spectra of PFCAs collected with "Smart IS+" and "SMCI+". SI: Library similarity index

The EI mass spectra of PFHpA, PFOA, PFNA, and PFDA were successfully matched to the NIST mass spectral library. PFOA, PFNA, and PFDA achieved a relatively high similarity index score of >80, in comparison to a low similarity index score for PFHpA. However, no mass spectral data were available for PFTriA and PFTA. Despite the lack of molecular ion peaks in the EI mass spectra, obvious $[M\text{-}F]^+$ ion was observed for all except for PFHpA.

The QCI mass spectra of the PFCAs showed a slight resemblance to their respective EI mass spectra. With the usage of PCI mode, the corresponding $[M+H]^+$ ions were observed in the QCI mass spectra for PFOA, PFNA, PFDA, PFTriA, and PFTA. Obvious $[M\text{-}F]^+$ ion peaks were also observed alongside the protonated species. For PFHpA, a prominent peak at *m/z* 347 correspondings to $[M\text{-}OH]^+$ ion was observed.

On the other hand, corresponding $[M+H]^+$ ion peaks were observed in the SMCI mass spectra for all PFCAs. The observed preference for the formation of protonated molecules for PFHpA with SMCI in comparison to QCI could be due to the difference in reagent gas used. Nevertheless, QCI provided more distinctive confirmatory ion peaks than SMCI.

In general, the analysis of PFCAs under PCI mode resulted in the formation of the base peak at *m/z* 131, which is postulated as $[C_3F_5]^+$ ion. In conjunction with this, a series of peaks differing by 50*u* (i.e., *m/z* 181, 231, 281, 331, 381, 431, 481, 531 581, 631,…) could be almost certainly assigned to the loss of a CF_2 radical during the ionization process. All in all, these peaks could serve as useful fingerprints for the preliminary detection and identification of PFCAs.

4. CONCLUSION

The *"Smart IS+"* and newly introduced *"SMCI+"* enable a direct and quick qualitative analysis of PFCAs, which conventionally requires tedious derivatization steps prior to GC/MS analysis. The "Smart IS+" setup delivers convenience in switching between electron ionization and positive chemical ionization mode of analysis.

On the other hand, the *"SMCI+"* setup delivers utmost convenience and safety to carry out positive chemical ionization since it utilizes methanol, which is a common laboratory solvent, as the reagent gas. The *"SMCI+"* setup is also capable of performing negative chemical ionization, which would further improve the detection sensitivity of fluorinated compounds such as PFCAs.

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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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