Fast and Direct Detection of Perfluorocarboxlyic acids (PFCA) with SICRIT®-MS

Summary
- SICRIT®-MS allows for direct PFCA screening of any solid sample (formulation powders, textile samples) or coating solutions
- No sample pre-treatment necessary
- Soft ionization in negative mode
- High resolution MS data for non-target analytics

Introduction

Per- and polyfluoroalkyl compounds (PFAS), especially their carboxylic acids (PFCA), are ubiquitously used chemicals as flame retardants, surfactants, and coatings. As they are very persistent, accumulation in water and food is a result. Simultaneously, especially PFOA (perfluorooctanoic acid) and PFOS (perfluorooctanesulfonic acid) are under investigation for cancerogenic and mutagenic effects. In consequence, production and use of PFOS has been prohibited in 2009 and PFOA followed in 2019. Nevertheless, these compounds and their related substitutes as well as their degradation products will be found in any environmental sample matrix in far future.

Along with the efforts in avoiding and replacing of PFAS, quality control of textile coatings and other treated products, that are marketed as free of PFAS, becomes more and more important. From an analytical point of view, analysis of formulations and textiles is associated with tedious sample extraction and analyte enrichment. Furthermore, sampling and analyte separation is often hampered by adsorption effects and high blank values.[1]

Thus, wouldn't it be nice to have a direct, sensitive and fast technique to identify a broad variety of perfluorinated compounds instead of lengthy sample treatment and GC-MS or LC-MS/MS runs?

SICRIT® Ionization presents a versatile approach to bypass this classical workflow!

The SICRIT® ion source can be adapted to every LC-MS instrument, transforming it to an online-sensor, where samples can be analyzed by simply holding the sample of interest in front of the MS inlet!

Figure 1 - Direct MS analysis of sample headspace via SICRIT® (shown on Thermo LTQ Orbitrap).

Experimental Setup

To show the feasibility of the direct SICRIT®-MS approach, we investigated several real samples, including coating powders and coated textiles.
In this study, we utilize high-resolution full scan spectra in negative mode (mass range 50 - 750 m/z, resolution of 30.000 FWHM) obtained by an LTQ Orbitrap XL system (Thermo Fisher) allowing for non-target PFAS analysis. Of course, this technological approach can be transferred to triple quad instruments for targeted MS/MS analysis.

Different samples were analyzed for PFCA compounds with SICRIT® (Plasma settings: 1.5 kV, 15 kHz). Therefore, the headspace of coating formulations was directly measured out of plastic bags (see Figure 1). Analyte identification was performed using Thermo Xcalibur Software and a confidence window of 5 ppm.

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Results

The real samples were examined for relevant PFCAs. According to manufacturer's information, the PFAS content in the samples should be less than 1 ppm.

With SICRIT® we were able to efficiently ionize smaller perfluorinated carboxylic acid compounds in negative MS mode without fragmentation. Thus, assignment could be performed relying on dominant [M-H]⁻ species.

In Figure 2, the homologous series C3-C9 of the PFCAs, detectable in most of the real samples, is depicted. The respective observed m/z values allowing for confident identification based on exact mass are listed in Table 1.

Table 1 - Investigated PFCA species.

Compound	Sum Formula	Product ion [M-H]⁻ (M_{meas})	Difference to calculated mass (ppm)
PFBA	$C_4HF_7O_2$	212.9784	1.4
PFPeA	$C_5HF_9O_2$	262.9751	1.1
PFHxA	$C_4HF_{11}O_2$	312.9719	0.6
PFHpA	$C_4HF_{13}O_2$	362.9684	-0.3
PFOA	$C_4HF_{15}O_2$	412.9648	-1.3
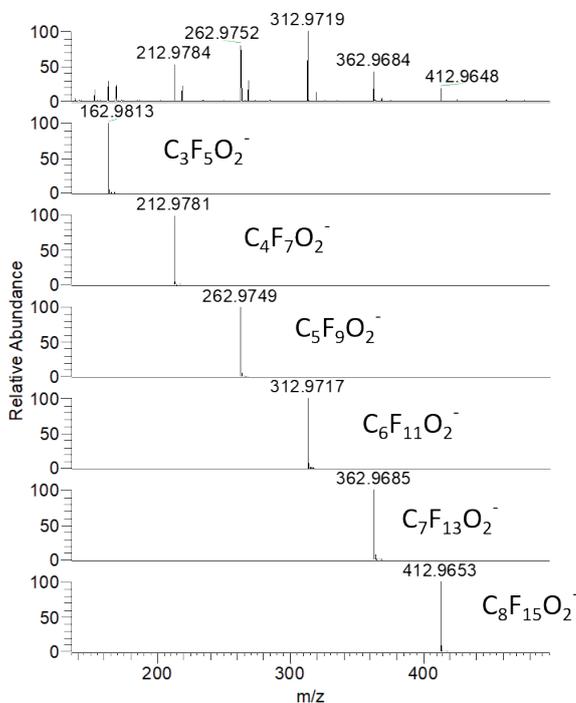
Figure 2 - High-resolution full scan spectrum of a real sample in comparison with theoretical m/z of [M-H]⁻.

Looking closer into the spectra, it was obvious, that in most of the samples the C8 species, PFOA, was not present or only detectable in very low concentrations (see Figure 3). This may lead to the suggestion, that the manufacturers are trying to find alternatives to PFOA in their formulations. Even though the shorter acids are less toxic than PFOA, extensive screening is desirable and SICRIT® can provide this.
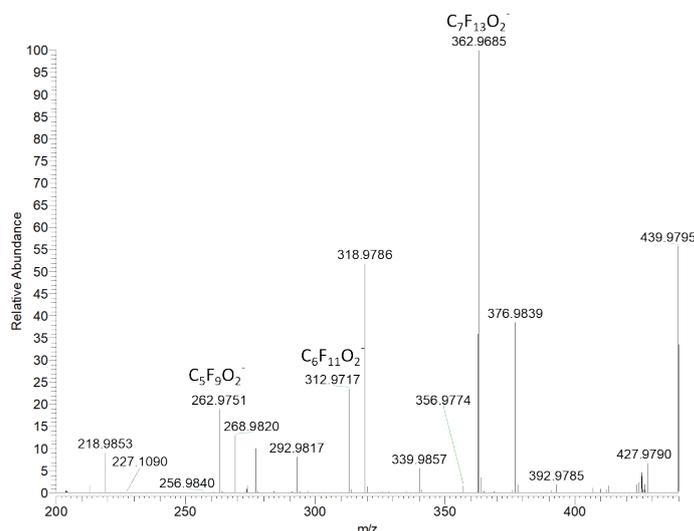
Figure 4 - Full spectrum of a real sample containingple carboxylic acids PFPeA, PFHxA, and PFHpA, but not containing PFOA.

Conclusions

SICRIT® presents a versatile new approach for direct and non-target screening of solid bulk samples, coatings, and textiles for perfluoroalkyl compounds. In negative mode, relevant PFCAs could be efficiently and softly ionized. The direct headspace sampling is dedicated for high-throughput screening of real samples. Furthermore, using a PAL autosampler, headspace sampling of solid or liquid samples may also be easily automatized. Therefore, the headspaces can be directly injected into the SICRIT® GC/SPME module in front of the SICRIT® ion source.

To sum up, this new approach may be of big interest for textile manufacturers or testing laboratories, where sample evaluation regarding PFAS content is needed and tedious sample extraction, analyte separation, and analyte derivatization is limiting the sample throughput.

References

[1] Larsen B.S.; Kaiser, M.A., Anal. Chem. 2007, 79, 11, 3966-3973.

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