Monitoring produced gases from PFAS removal technologies

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are highly toxic contaminants hazardous to both environmental and human health. Removal of PFAS is essential to help keep the population safe.

Many PFAS removal technologies break down compounds into smaller components which can be captured or neutralized *e.g.*, hydrogen fluoride (HF), carbon dioxide and water. However, if this process does not happen under the correct conditions, products of incomplete destruction (PIDs) are created.

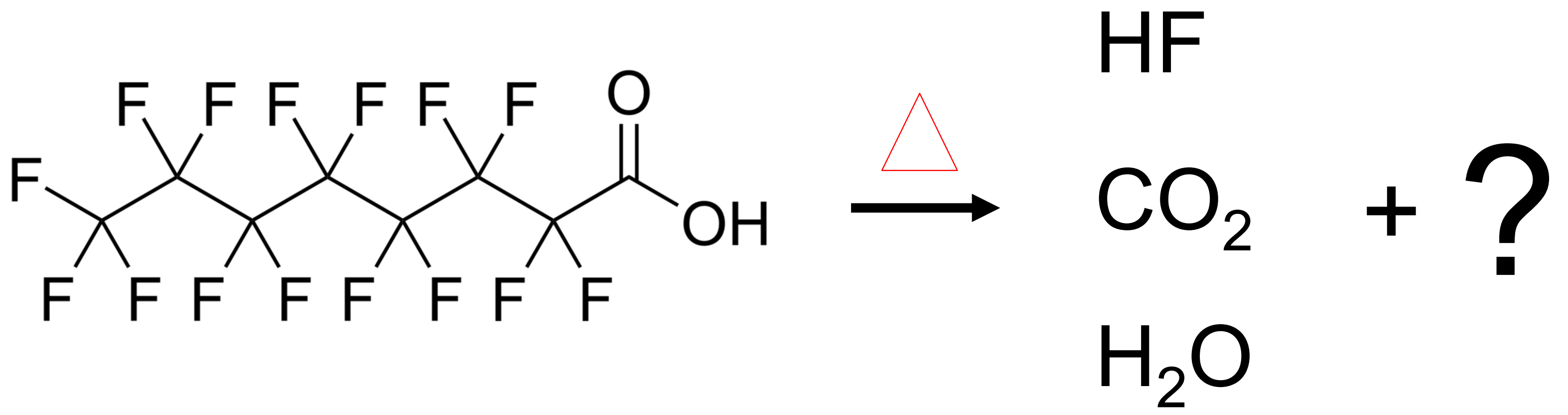
Products of incomplete destruction

PIDs are volatile PFAS species that have their own damaging effect upon the environment. This means that PFAS destruction must be monitored to ensure complete destruction has occurred.

The smallest PID is CF_4, an exceedingly volatile freon and potent greenhouse gas. To destroy it, a temperature of 1440°C for over one second is required. However, CF_4 is challenging to monitor due to its volatility.

Global networks which monitor CF_4 currently require extremely specialized equipment in order to reach background concentration levels.

In this study, we show that commercially available thermal desorption equipment can be used to monitor CF_4 and other priority PFAS from destruction sources.



Sources

The sources which will need to be monitored include:

- Municipal waste facilities
- Hazardous waste facilities
- Thermal oxidisers
- Sludge incineration
- Bio-solid incineration
- Novel PFAS destruction technologies
- And others…

Figure 1: Municipal waste incineration plant. PFAS are contained in a huge number of household and workplace items. When these items are disposed of, they will typically go to landfill or for incineration. If they are incinerated, there is the potential for PIDs to be produced.

Sample collection

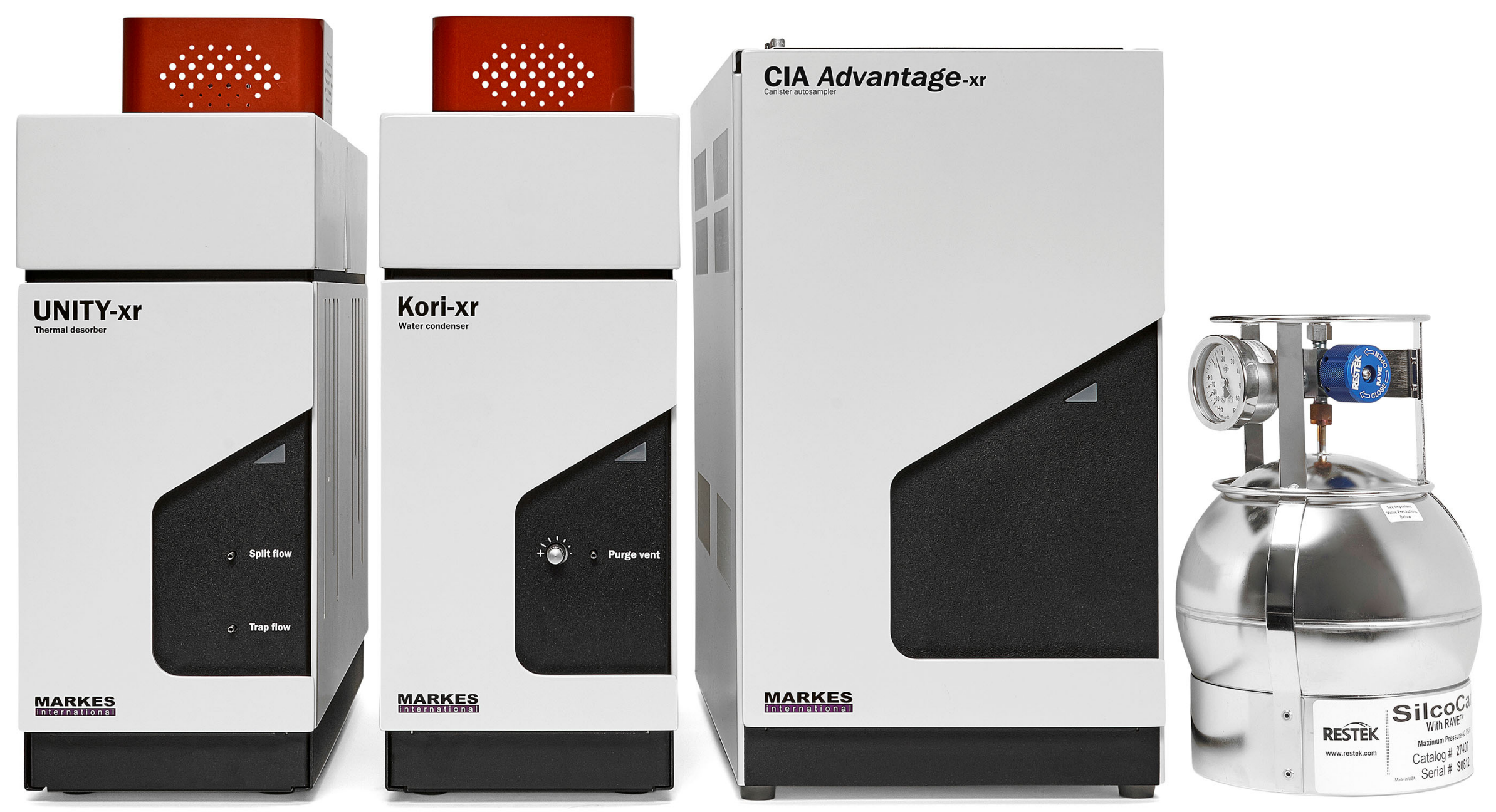
Due to the volatility of CF_4, when collecting gases from the source, stack testers will need to use a SUMMA canister. However, due to the matrix type, sample conditioning is essential. Water and HF are two matrix components which need addressing before the sample reaches the canister. Humid gas entering the canister should be non-condensing and all HF should be removed. Any HF in the sample will irreversibly damage the canister, meaning the sample won't be able to be analysed.

Sample train

Impingers can be employed to manage both HF and water, similar to how they are employed in OTM-45. Water-filled impingers will remove HF from the sample and cooled impingers will cause water to condense and be removed. Sample conditioning means that whilst SUMMA canisters can capture both polar and non-polar PFAS, only the non-polar species will be quantitated using this method.

Laboratory analysis – modified EPA Method TO-15A

Figure 2: Markes' UNITY-xr™ pre-concentrator system, Kori-xr™ water removal device and CIA *Advantage*-xr™ canister autosampler systems sitting next to a typical 6 L SUMMA canister. The CIA *Advantage*-xr™ has positions for 14 canisters, is cryogen free and is fully compliant with canister methods such as US EPA Method TO-15A.



In the lab, analysis of PIDs can be performed using a modified US EPA Method TO-15A, though the VOCs that need to be monitored are completely different. Key physical modifications to the method include using an analytical focusing trap and GC column.

Water removal is managed by the Kori-xr system as the sample is transferred to the cryogen free focusing trap. CO_2 is also present in the sample and can be managed through purging of the cryogen free focusing trap on the UNITY-xr system.

Analytical performance

Even with an optimized analytical column and focusing trap, CF_4 is still a challenging compound. Maximum sample volumes are typically 20–25 mL before breakthrough. However, compounds such as C_2F_6 can be sampled at over 1 L. To maximize sensitivity for most compounds, two analyses can be carried out, with CF_4 being quantitated in isolation at a lower sample volume.

In order to optimise the separation, a mix of ozone-depleting substances and greenhouse gases (34 compounds) was used in the absence of a PIDs gas standard being available.

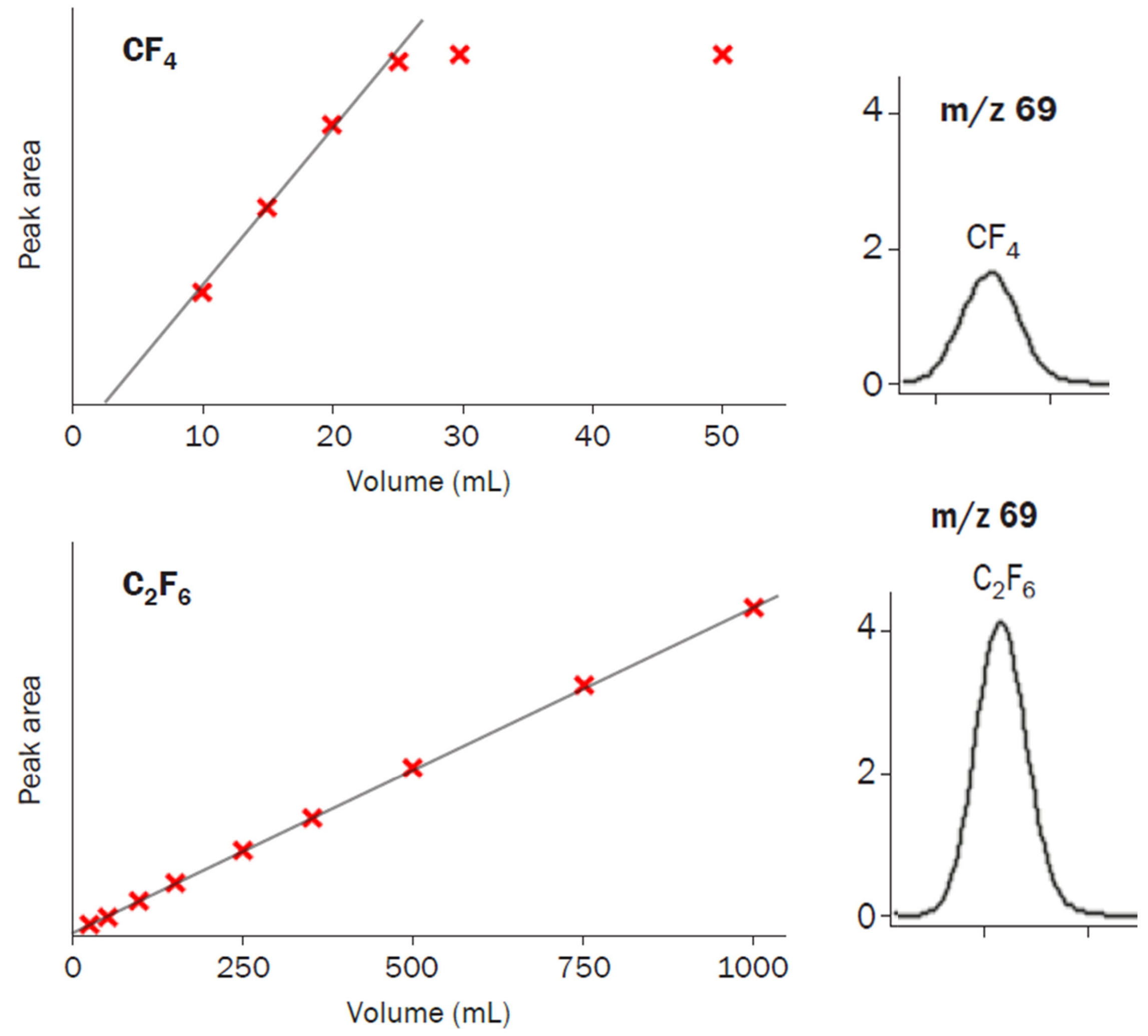
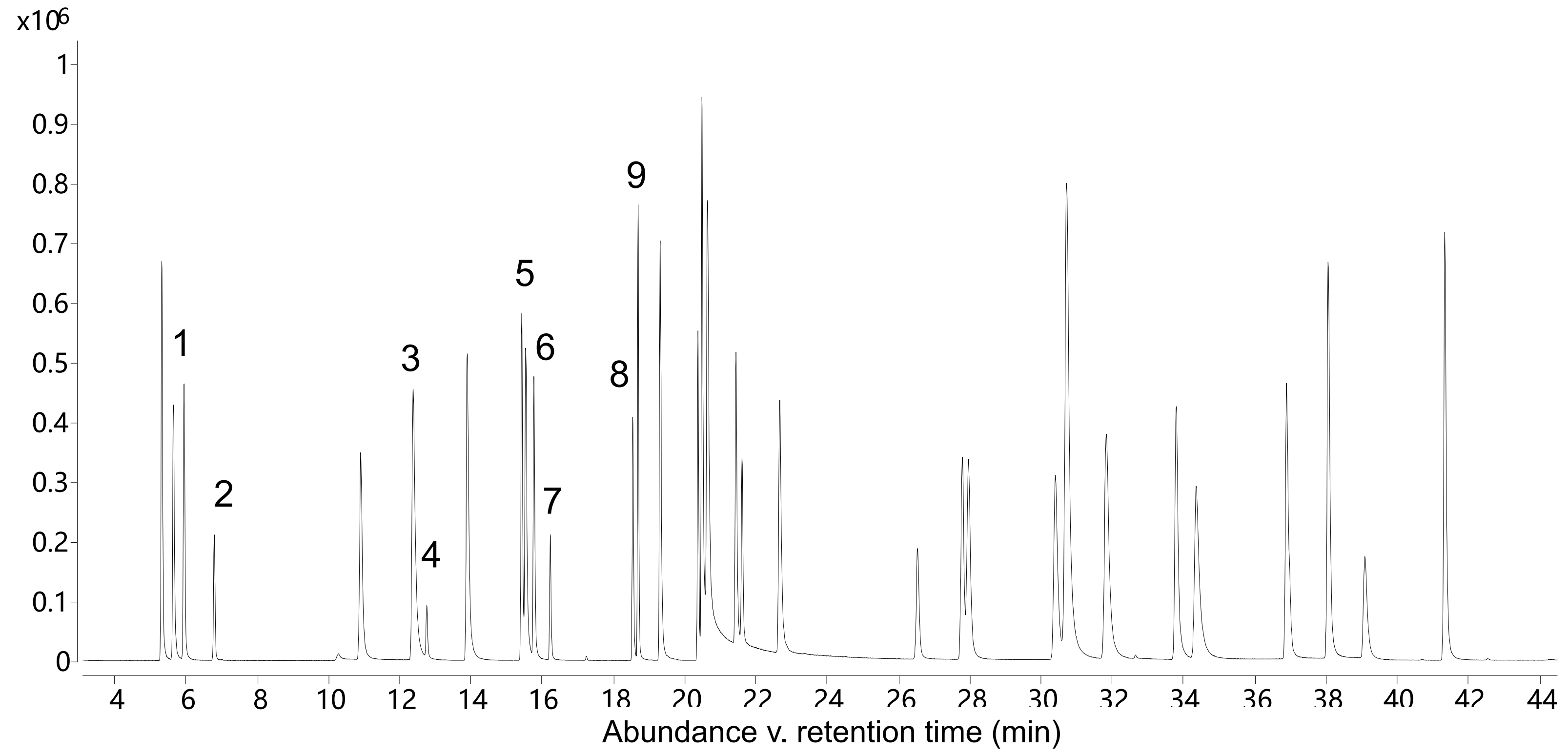


Figure 3 (left): Breakthrough testing assessing the two most volatile compounds likely to be found if destruction was incomplete. Breakthrough for CF_4 was shown to be around 20–25 mL, and at a volume of 1 L C_2F_6 still hadn't broken through.

Figure 4 (below): 34 component ODS/GHG mix with compounds thought to also be PIDs.

1) HFC-125	2) HFC-143a
3) HFC-32	4) HCFC-22
5) HFC-23	6) CFC-11
7) CFC-13	8) PFC-218
9) HFC-134a	



Conclusions

Pre-concentration and GC–MS offers practical solutions to the problems of how to monitor PFAS destruction efficiency. By using established methods as a base, laboratories can adapt to handle the requirements of these key compounds with standard hardware.

Laboratories already handling stack gas samples will be able to easily add this new requirement to their offering using the high capacity Markes CIA *Advantage*-xr system coupled to the UNITY-xr with water management from Kori-xr.

The limitations related to the retention of CF_4 can be easily managed through running a smaller volume for quantitation of the ultra-volatile compound.

Acknowledgements

Ariel Wallace, Stephen Jackson and the team at US EPA for their advice on products of incomplete destruction.