PFAS Emissions and Formation from Fluorinated Compounds

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PFAS, or per- and polyfluoroalkyl substances, play a crucial role in various aspects of modern life and find widespread application across diverse industries [1]. One notable area of use is in semiconductor manufacturing, where PFAS are used for producing components that are integral to semiconductor fabrication processes. Given the growing concerns and regulations surrounding PFAS emissions and their environmental and health impact [2], the routine monitoring of PFAS sources will be of growing importance as regulations aim to reduce the global PFAS burden.

Experiment setup

Figure 1 shows the experimental setup for the thermal release of PFAS from PFA tubing which is widely used due to its unique chemical properties. Approximately 5g of PFA tube was placed within a heated stainless-steel oven, continuously flushed with 2 liters per minute of UHP nitrogen gas. The oven was directly connected to the inlet of a chemical ionization mass spectrometer (Vocus B2), and the temperature within the oven was linearly increased from 100 to 330 °C at a rate of around 2 °C per minute. The resulting emissions were detected using the fast polarity switching capabilities of the Aim reactor, coupled to the Vocus B2, to capture emissions through online measurement of both positive and negative analyte ions.

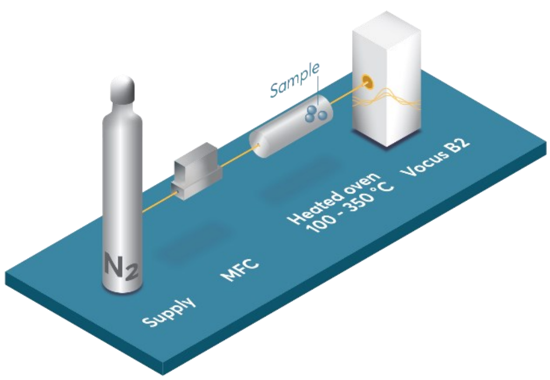

Figure 1. Experimental setup used in this study.

Results

All relevant PFAS compounds were detected as the parent molecule clustered with iodide reagent ions or as their deprotonated anion [3]. Compounds were identified based on their chemical formula through precise mass-to-charge ratio measurement and isotopic patterns made possible by fragmentation-free ionization. Figure 2 (top) shows a time series of representative PFAS compounds such as PFBA, PFHxA, and PFOA (blue trace), where the observed signal began increasing at 150 °C and continued to rise until ~250 °C. At higher temperatures, the signal decreased, suggesting that decomposition mechanisms begin to play a significant role. As the emitted PFAS compounds degraded, we observed the appearance of various known fluorinated degradation products as hydrofluoric acid and TFA (red trace) as well as non-fluorinated compounds such as fulminic acid (HCNO) as shown in black (Figure 2). Similar results have also been reported previously [4].

The mass defect plot in Figure 2 (bottom) shows total material emissions at three different temperature points. At ~100 °C, marking the beginning of heating process, minimal PFAS emissions were observed from the sample. At ~250 °C, elevated PFAS emissions were observed including long chain perfluoroalkyl carboxylic acids (PFCAs) with carbon chain length of 9 - 18. After exceeding 250 °C, various fluorinated and non-fluorinated compounds were observed at elevated levels. These non-fluorinated compounds are representative of various plasticizer products. Volatile hydrocarbon emissions as measured by benzene cations remained low at all temperatures investigated here.

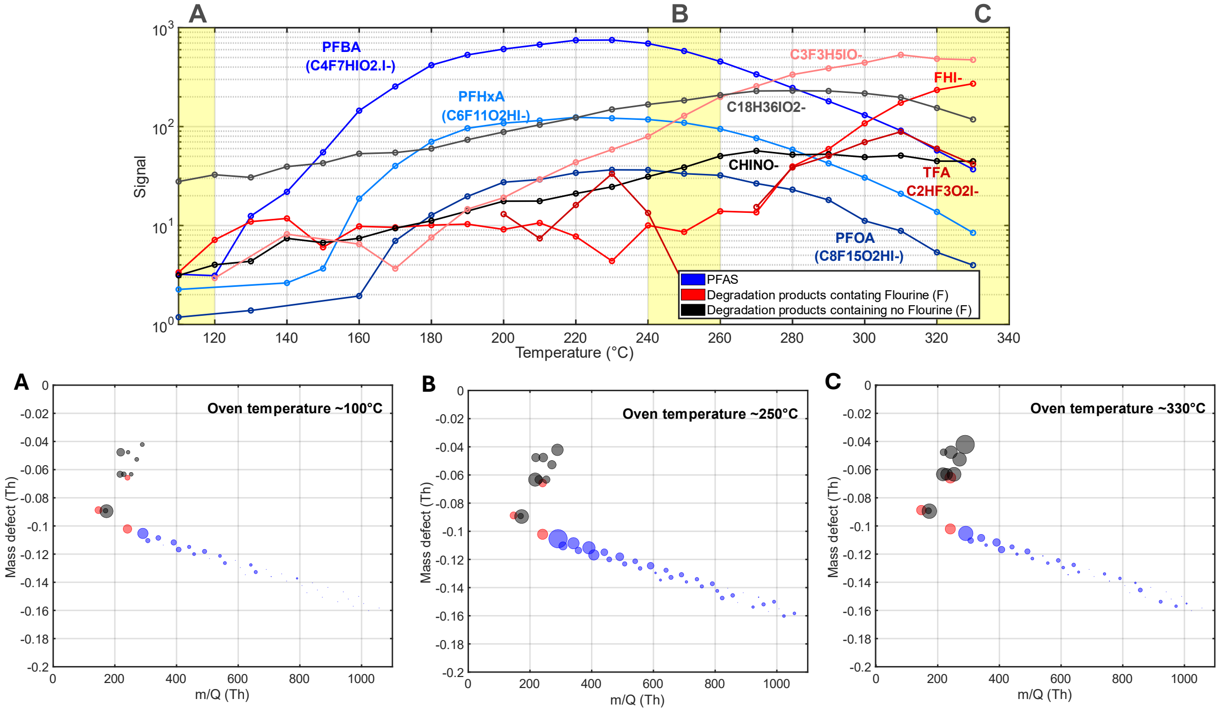

Figure 2. Time series of some compounds emitted from the material as a function of oven temperature (top) and mass defect plots showing total emissions at three temperature points: 100°C (A), 250°C (B) and 330°C (C).

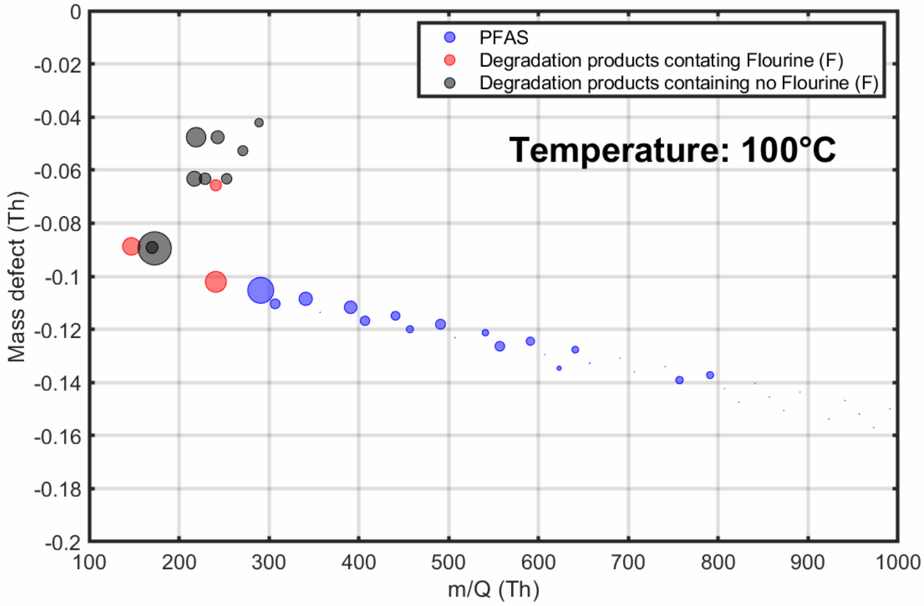

Figure 3. Evolution of material emissions depicted as a function of temperature.

Conclusion

We demonstrated that Vocus B series with iodide reagent ions enabled real-time monitoring of PFAS emissions from PFA tubing in the gas phase. While the hydrocarbon emissions of PFA is extremely low, the comprehensive nature of the Vocus B series is likely critical for other material offgassing applications. Comprehensive emissions and thermal degradation information is vital for optimizing processes and ensuring compliance with regulatory standards, especially for high performance materials which are exposed to a wide range of process and environmental conditions.

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References

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