

# Revolutionizing PFAS Detection in Air: High Sensitivity and Versatility with the Vocus Aim Reactor

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## Introduction

Per- and polyfluoroalkyl substances (PFAS) are man-made chemicals widely used in various industrial and consumer products for their water- and oil-resistant properties [1]. Despite being produced since the 1940s, these compounds have only gained global attention in the last decade due to their adverse effects on human health. These molecules, often labeled as 'forever chemicals' because of their resistance to natural degradation and ability to bioaccumulate in organisms, have been found in air, surface waters, oceans, soils and even in remote Arctic regions [2]. In addition, elevated concentrations of PFAS have been detected indoors, indicating an important exposure pathway for humans [3].

According to [CompTox](#), a chemical database maintained by the U.S. Environmental Protection Agency, there are nearly 15 000 synthetic PFAS chemicals. The emergence of new PFAS and the simultaneous release of next-generation PFAS-like

compounds pose significant obstacles for environmental scientists and regulators. Keeping pace with new sources, developing dedicated analytical methods, and understanding their toxicological effects is challenging. As a result, the majority of these substances are not yet subject to regulatory monitoring under current environmental laws, especially considering their direct measurement in ambient air.

The low concentration of these compounds complicates their analysis and requires highly sensitive analytical detection methods. Traditional methods employed for gas-phase sampling have predominantly relied on offline analytical methods. These methods involve the use of passive or active air sampling devices that collect samples onto filters and/or sorbents with subsequent laboratory analysis [4]. While essential, these methods face significant limitations in directly addressing the issue at its source. For example, the long collection periods together with the time-intensive nature of the sample

analysis hinder a comprehensive understanding of the sources and dynamics of these pollutants in the air. Additionally, offline methods are typically targeted, detecting only known compounds, which limits their ability to identify new or emerging contaminants. To gain insight into the release of these contaminants into the atmosphere and understand their sources and transport mechanism, real-time measurement techniques can be employed, which allow for the detection of a wide range of compounds.

#### Direct PFAS Analysis via Chemical Ionization

Chemical ionization (CI) using iodide as a reagent ion has recently emerged as a promising technique for the real-time detection of PFAS in air [4-6]. TOFWERK's versatile [Vocus Aim](#) (adduct ionization mechanism) reactor employs a soft ionization approach, which minimizes fragmentation and hence preserves the parent molecular ion. When coupled with time-of-flight mass spectrometer (TOFMS, TOFWERK), this approach enables an accurate assignment of molecular formulas of the detected ions with a time resolution of one second with unprecedented sensitivity.

This study aims to demonstrate the applicability of the Vocus Aim reactor as a tool for real-time

quantitative PFAS detection in air and bring this innovative technique to a broader audience beyond the scientific community. This technique directly analyzes air without the need for sample collection or pre-separation, distinguishing it from traditional methods.

To obtain quantitative data, a reliable calibration method for PFAS is essential. Typically, chemical ionization can be calibrated using a multicomponent gas cylinder for compounds with high enough vapor pressure and limited reactivity. Alternatively, certified permeation tubes with known permeation rates can be used, but the availability of these standards is limited. For less volatile molecules, solutions of known concentration can be prepared and evaporated using commercially available [liquid calibration systems](#) (LCS). However, these devices have extensive surfaces where very low volatile molecules can adhere, causing long response times and risking permanent contamination from toxic compounds, such as PFAS [7]. To address these challenges, our objective is to demonstrate a standardized and robust calibration method, including calibration factors, detection limits, and humidity dependencies for these emerging contaminants, and comparing this method with a recently reported calibration

approach [3]. Additionally, we evaluated two ion chemistries available within the Aim reactor: iodide and nitrate. This approach is also extended to other emerging contaminants, such as pesticides, which pose similar challenges in gas-phase measurement and calibration due to their high toxicity and contamination issues.

### Experimental

Calibration measurements were performed using a [Vocus 2R equipped with an Aim reactor](#) with a measuring frequency of 0.5 Hz. Details of the reactor can be found [elsewhere](#) [8]. The reactor was operated at 50 mbar and a temperature of 50 °C for both iodide and nitrate ion chemistries. Liquid calibration standards of PFAS were prepared in methanol, methyl

acetate, and dichloromethane with concentrations ranging from 0.2 to 4 mg L<sup>-1</sup> to investigate potential solvent dependency in the calibration outcomes. To evaluate the differences between single and continuous injections of liquid standards, a 250 µL glass syringe (Hamilton) and a syringe pump (KD Scientific) were used. The injection rates tested ranged from 20 µL per hour to 800 µL per hour. Single injections involved introducing a specific volume of the liquid standard at once, while continuous injections maintained a steady flow of the liquid standard over time. This comparison aimed to determine which method provided more consistent and accurate calibration results by assessing the precision, stability, and reproducibility.

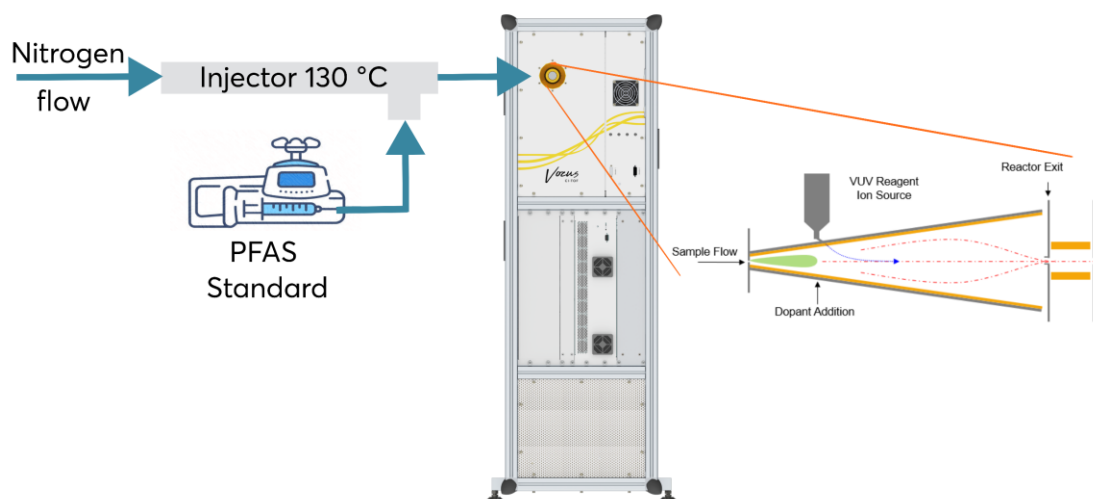


Figure 1. Experimental set-up used in the calibration of the PFAS.

The sample was introduced into a 130 °C heated 0.5- inch OD Sulfinert tubing at a 90° angle through a GC septum into the injection point. The tubing was encapsulated with a heating element, allowing for easy sonication or replacement of the tubing itself if needed. The injector was continuously flushed with 2 sLPM of UHP N<sub>2</sub>, with the excess flow directed to the exhaust. Figure 1 shows the experimental setup used during the calibrations. As the Aim reactor allows switching between reagent ions, subset of the chemicals was calibrated in both iodide and nitrate modes.

## Results

Using the calibration set-up discussed above, in Table 1 we report calibration factors and limits of detections (LODs) for 2 fluorotelomer alcohols (FTOHs), 11 perfluorinated carboxylic acids (PFCAs), pentachlorophenol and 4, 4 DDT. The LODs were measured in both nitrogen and ambient air to assess potential interferences based on the dilution medium of the injected solutions. The 1 Hz LODs were within 10% between the matrices and established to be a few parts per trillion (ppt).

*Table 1. Iodide CIMS emerging contaminants calibration summary. All calibration factors are reported in counts per second (cps) per part per trillion by volume (pptv) and normalized per million counts of total reagent ion signal.*

Compound	Calibration factor (ncps ppt <sup>-1</sup> )	LOD 1s (ppt)	LOD 1min (ppt)	LOD 1min (ng/m <sup>3</sup> )
TFA	4.30	30.0	4.0	18
6:2 FTOH	5.40	1.6	0.3	6
8:2 FTOH	5.50	1.5	0.2	4
PFBA	5.29	1.3	0.2	2
PFPeA	5.92	1.7	0.2	2
PFHxA	5.27	0.9	0.1	1
PFHpA	4.29	1.0	0.2	3
PFOA	2.77	1.3	0.3	6
PFNA	1.86	2.0	0.3	6
PFDA	0.77	3.0	0.5	11
PFUnA	0.36	3.4	0.5	13
PFDoDA	0.16	4.7	0.7	19
PFTriDA	0.06	7.6	1.2	36
PFTeDA	0.03	6.5	1.0	32
DDT	0.29	5.0	0.7	10
Pentachlorophenol	0.29	14.0	2.0	22

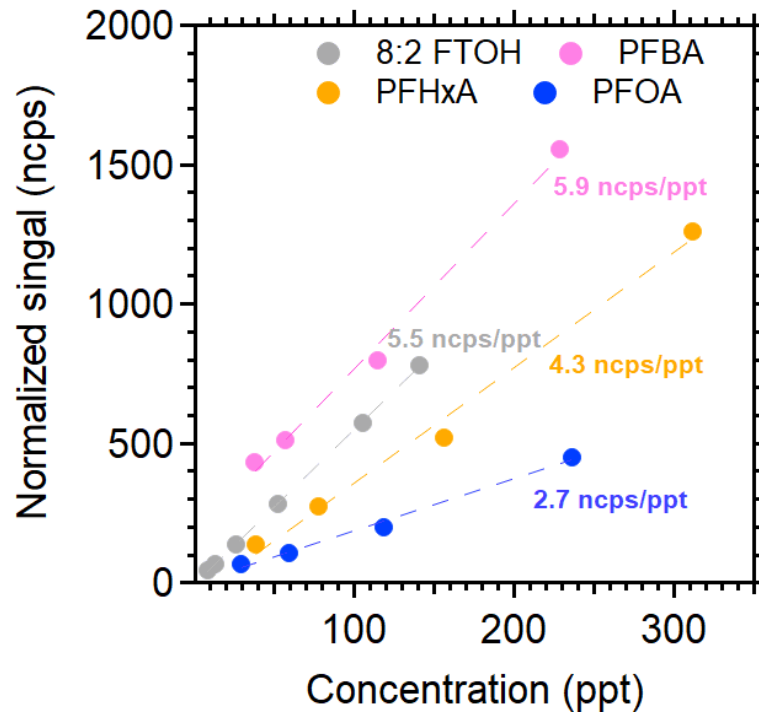


Figure 2. TOFWERK iodide Aim calibration curves for selective PFAS.

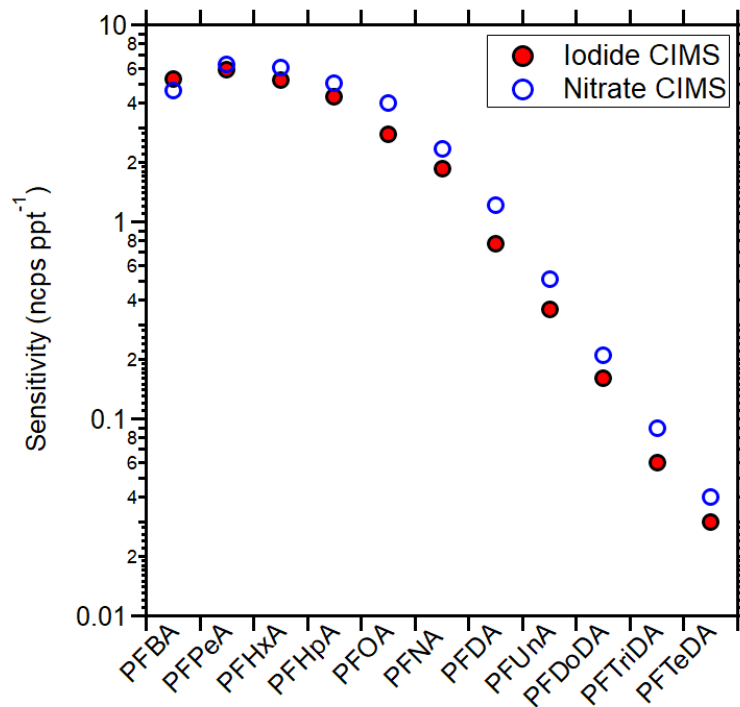


Figure 3. Measured PFCA sensitivities using iodide CIMS (red full circles) and in nitrate CIMS (blue open circles).

By increasing the averaging time to 1 minute, the LODs were reduced by almost an order of magnitude.

Figure 2 shows the calibration curves from a single experiment for 8:2 FTOH, PFBA, PFHxA, and PFOA using iodide as the reagent ion and the syringe pump approach. Good linearity ( $R^2 > 0.98$ ) was observed for the calibrated PFAS, even at lower ppt levels, indicating the AIM reactor's excellent ability to detect PFAS in the low parts-per-trillion range.

The sensitivity of perfluorocarboxylic acids (PFCAs) was also measured using  $\text{NO}_3^-$  as the reagent ion. On average, the measured sensitivities lie within 20 % of those obtained with the iodide mode (Figure 3), indicating that using the nitrate reagent ion is similarly effective in detecting this subgroup of PFAS. For both ion chemistries, the measured sensitivities decrease with increasing size of the PFCA molecule. This is likely linked to their ability to be efficiently transferred to gas phase via this calibration approach.

The results of the evaluation of the two calibration approaches (single syringe injections of the same volume and the continuous syringe pump injection method) are shown in Figures 4. Generally, these two methods agree within 30 % for the volatile fraction of the PFAS. However, for certain molecules, high

variability in the signal response was observed with single injections of the same volume and concentration, as demonstrated in Figure 4c. Although the direct injection method is relatively simple and cost-effective, it introduces variability due to human involvement. In contrast, the syringe pump method showed improved stability in response to changes in injected flow rates, and effectively mitigated operator-induced errors. Therefore, all further results reported here rely on calibrations using the syringe pump method.

To accurately measure in environments where relative humidity (RH) fluctuates, such as ambient air, it is crucial to understand how sensitivity changes with varying humidity levels. Water can significantly impact the sensitivity of species detected by Cl, with RH-dependent sensitivities varying across compound classes. As a result, measurements in environments with varying humidity require time-consuming calibrations for different RH conditions. To mitigate this water dependence in the Aim reactor, we use a water vapor control system consisting of a regulated flow of 5 sccm of acetonitrile as a so-called dopant molecule. The dopant displaces the water molecules that would normally attach to the reagent ions, ensuring that the modified reaction

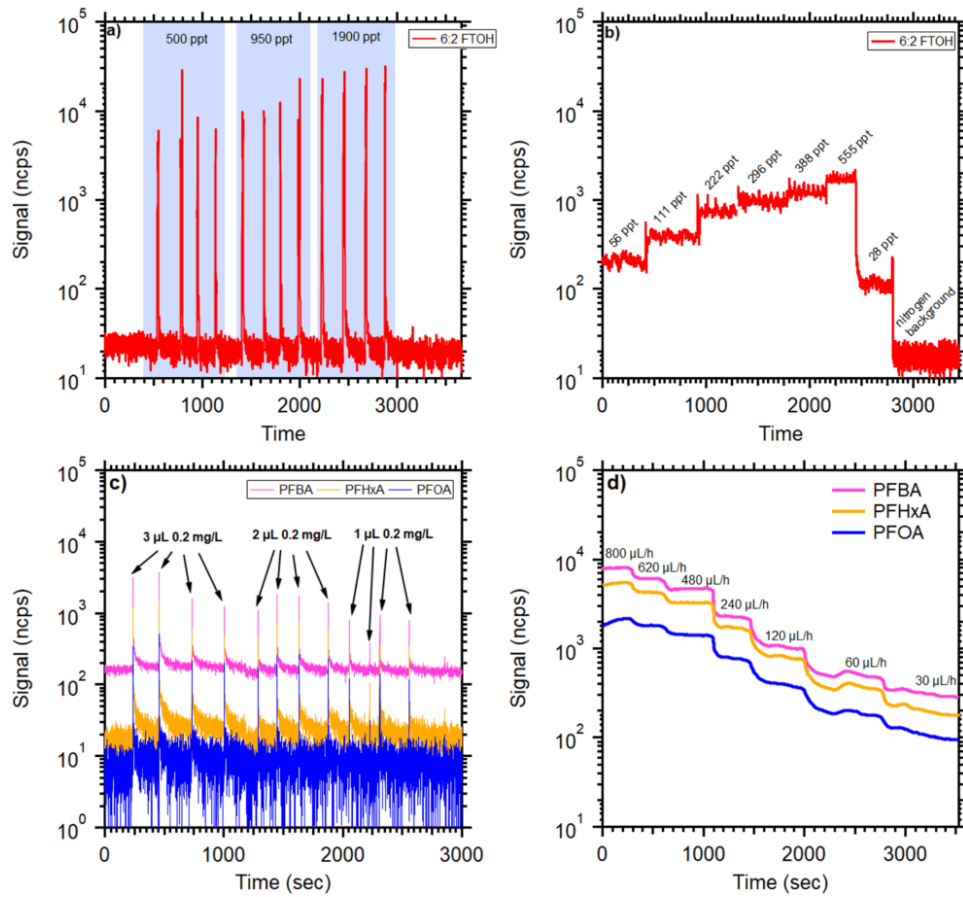


Figure 4. Comparison between direct injections (a & c) and syringe pump approach (b & d) for 6:2 FTOH and selected PFCAs. For manual injections, the same volumes of solution with increasing concentration were used. For syringe pump injection one concentration solution with varying injection rates was used. Calculated mixing ratios of 6:2 FTOH in the air are highlighted by blue shaded area.

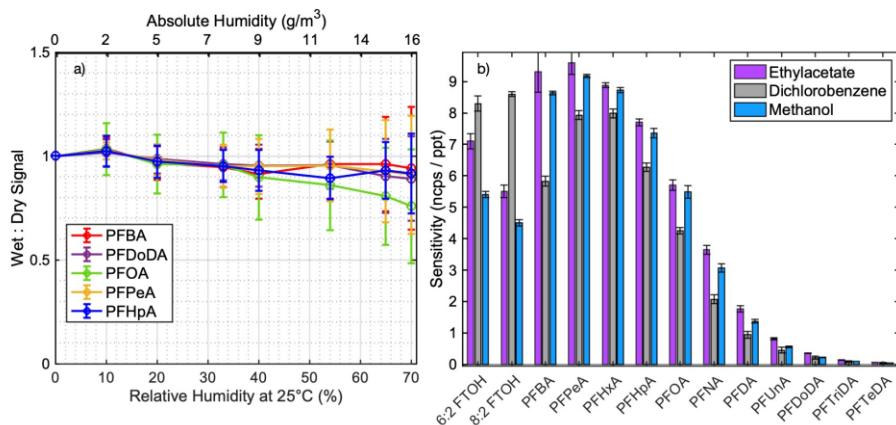


Figure 5. a) Sensitivity normalized to dry conditions as a function of increasing humidity in relative (25°C) and absolute values. The error bars represent the standard deviation, calculated from nine measurements conducted on different days. b) Sensitivity differences for various solvents.

mechanism no longer significantly depends on varying water vapor conditions. Figure 5a illustrates the relative sensitivity change for selected PFAS as a function of increasing humidity while using dopant. Our results show a minute decreasing trend. Yet, it is important to consider that the interpretation of this trend is complicated by the inherent error of the measurement, particularly concerning the reproducibility across replicates. Additionally, the variation in sensitivity increases with rising humidity levels complicates interpretation. Figure 5b illustrates the impact of matrix solvent selection on the sensitivity of PFAS detection. We observed significant deviation with dichloromethane, likely attributed to its higher volatility. Differences between methanol and ethyl acetate were minimal, with the latter emerging as the preferable choice due to its lower toxicity.

### Conclusion

We demonstrate the capability of TOFWERK Aim chemical ionization reactor to provide real-time detection and quantification of PFAS, offering temporal resolution beyond traditional offline techniques. With sensitivities ranging from 0.5 to 5 ncps/ppt and detection limits extending hundreds of ppq levels, this technique delivers

high sensitivity and specificity. While these detection limits exceed typical requirements for background monitoring of ambient air, the speed and precision of the Aim reactor make it ideal for applications such as real-time identification of volatile PFAS sources or locating potential leaks where concentrations are expected to be significantly higher. Moreover, we have shown that Aim is suitable for measurements in ambient environments with changing humidity. This technique also carries a potential for enhancing our understanding of PFAS environmental pathways through atmospheric chamber experiments, indoor air monitoring, [consumer products evaluation](#) and material emission testing. Additionally, it can facilitate regulatory monitoring of flue gases to ensure compliance with emission standards.

### Contact

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