APPLICATION NOTE

MONITORING OF OZONE PHOTOCHEMICAL PRECURSORS

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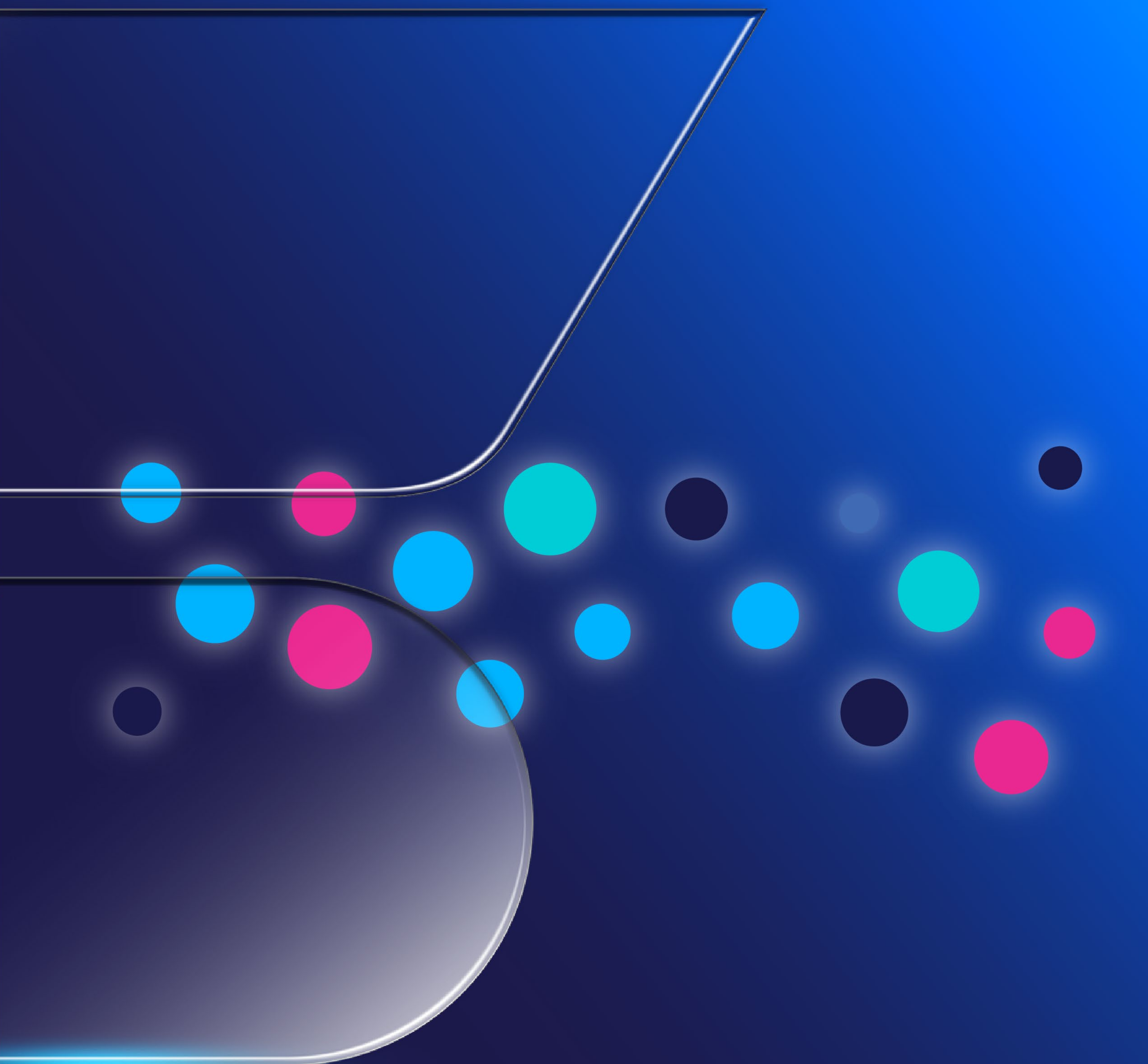


ABSTRACT

Accurate and continuous monitoring of atmospheric ozone precursors is crucial for effective air quality management. This study demonstrates the application of selected ion flow tube mass spectrometry (SIFT-MS) for real-time, high-frequency monitoring of volatile organic compounds (VOCs) and nitrogen dioxide (NO_2) using SyftEnviro software. Unlike traditional methods that require complex sample preparation and extensive lab analysis, SIFT-MS provides near-instantaneous measurements, enabling rapid response to pollution events. With broad capabilities, a single SIFT-MS instrument has the potential to replace three separate units in a typical monitoring station by combining the ability to measure VOCs, carbonyls, and NO_2. By seamlessly integrating weather station data SyftEnviro unlocks the speed, simplicity, and sensitivity of SIFT-MS measurements for improved air quality assessments and policy decisions.

INTRODUCTION

Photochemical smog has been a growing issue for large cities and industrial centers globally since the middle of the 20th century. Smog forms when sunlight drives chemical reactions between nitrogen oxides (NO_x) and volatile organic compounds (VOCs) resulting in ground level ozone, which then oxidizes chemicals in the air, resulting in the formation of secondary organic aerosols (SOAs). While ozone provides a beneficial UV shield in the stratosphere, when present at ground level it has major harmful impacts on human health (Zhang et al., 2019). This is particularly problematic for large urban centers, as human activity is increasingly responsible for the elevation of atmospheric NO_x and VOCs to dangerous levels. However, industrial processes and vehicle emissions are not the only causes of photochemical smog: VOCs are also emitted from biogenic sources – evidence for this can be seen in the ‘blue hazes’ that form over forested areas in summer such as the Blue Mountains (Australia) and Smoky Mountains (USA) (Wayne, 2000). This highlights the difficulty that regulatory bodies face when attempting to combat smog formation with sensible emissions policies.

As the emission sources of problematic compounds vary, measurement techniques must change to gain a full picture of the system. In response to the steadily growing risk that photochemical smog poses, regulatory bodies have instituted increasingly complex legislation to implement progressively more comprehensive monitoring programs for the chemical precursors to ozone. Preeminent among these is the United States Environmental Protection Agency’s 40CFR part 58, which has provided the framework for how air quality monitoring networks are designed and operated worldwide. The mechanism for ozone formation involves multiple steps and can be affected by various factors which mean that an in-depth understanding of the chemical composition of the atmosphere is necessary to implement effective mitigation strategies. These monitoring programs employ complicated and expensive methodologies to achieve full coverage of the compounds of concern, requiring countless workhours to ensure data quality. For example, the typical methodology for measuring carbonyls, a subset class of VOCs, involves a derivatization step, whereby the sample is loaded onto a DNPH impregnated cartridge, then eluted with organic solvent before analysis via HPLC (EPA, 2019). The status quo for other VOC measurements involves either cryogenic preconcentration (EPA, 1999), followed by dehumidification, or an 8-hour sampling time into an evacuated cylinder (EPA2023). These steps add complexity, cost, potential for error, and a measure of uncertainty. SIFT-MS eliminates all this, achieving the necessary sensitivity with direct sampling of whole air in real time.

Selected ion flow tube mass spectrometry (SIFT-MS) is well suited to photochemical monitoring, compared to the incumbent techniques: SIFT-MS is easier to install, simpler to operate, easier to maintain, requires fewer interventions, and provides data at a much greater frequency. This application note describes the application of SIFT-MS to photochemical monitoring and demonstrates how reliable data is produced simply, facilitated by the new SyftEnviro software. The SyftEnviro software package is designed as a simplified interface for performing real-time volatile compound analysis using a Syft Tracer™ instrument in a mobile or stationary installation, supported by real-time geospatial mapping and weather station integration. It allows users to set up methods, collect, and interpret data for fast decision making. This is achieved by centralizing product status, data visualization, and product control into a unified user interface.

METHODS

A Syft Tracer™ i3 SIFT-MS instrument operating on nitrogen carrier gas was installed at Syft Technologies head office in Christchurch, New Zealand. To allow for unimpeded airflow, a 15-m length of high purity, PFA sample line was routed from the roof of the building to a pump, via a back pressure regulator, configured to allow a continuous flow of ~2 SLPM outdoor air past the inlet of the SIFT-MS instrument. From this flow, the instrument was set up to receive 25 sccm via a heated PFA capillary. Immediately adjacent to the sample line inlet, an Airmar WeatherStation 200WX was installed to monitor the temperature and wind speed/direction. SyftEnviro software (Figure 1) was employed to integrate these data streams.

Figure 1: SyftEnviro software interface.

Targeted SIFT-MS analysis of VOCs was conducted using selected ion monitoring (SIM) mode. The target list was adapted from the EPA list of priority and optional compounds stipulated in 40 CFR 58, the specific reagent and product ion pairs used in the method are shown in Table 1. Data visualization utilized R version 4.4.2, using the open-source R package: openair.

Analyte	Molecular Weight ($gmol^{-1}$)	Reagent Ion	Product Ion Formula	Branching ratio (%)	Product Ion m/z (Secondary Ion m/z)
1,3-butadiene	54.09	NO^+	$C_4H_6^+$	100	54
		O_2^+	$C_4H_6^+$	70	54
acetaldehyde	44.05	NO^+	CH_3CO^+	100	43 (61)
acetone	58.08	H_3O^+	$C_3H_7O^+$	100	59 (77)
		NO^+	$C_3H_6.NO^+$	100	88
acetylene	26.04	O_2^+	$C_2H_2^+$	100	26
benzaldehyde	106.12	H_3O^+	$C_7H_6O.H^+$	100	107 (125)
		O_2^+	$CH_3H_5O^+$	30	105
		O_2^+	$CH_3H_6O^+$	70	106
benzene	78.11	NO^+	$C_6H_6^+$	81	78
		NO^+	$C_6H_6.NO^+$	19	108
		O_2^+	$C_6H_6^+$	100	78
butene†	56.11	NO^+	$C_4H_8.NO^+$	60	86
carbon tetrachloride	153.82	H_3O^+	$C^{35}Cl_3^+$	44	117
		H_3O^+	$C^{35}Cl_2{}^{37}Cl^+$	42	119
		NO^+	$C^{35}Cl_3^+$	44	117
		NO^+	$C^{35}Cl_2{}^{37}Cl^+$	42	119
		O_2^+	$C^{35}Cl_3^+$	44	117
		O_2^+	$C^{35}Cl_2{}^{37}Cl^+$	42	119
ethanol	46.07	H_3O^+	$C_2H_5O.H^+$	100	47 (65)
		NO^+	$C_2H_5O^+$	100	45 (63)
ethylene	28.05	O_2^+	$C_2H_4^+$	100	28
formaldehyde	30.03	H_3O^+	CH_3O^+	100	31 (49)
isooctane	114.23	H_3O^+	$C_8H_{17}^+$	22	113
		H_3O^+	$C_8H_{18}.H_3O^+$	32	133
		NO^+	$C_8H_{17}^+$	93	113
isoprene	68.12	H_3O^+	$C_5H_8.H^+$	100	69
		NO^+	$C_5H_8^+$	100	68
		O_2^+	$C_5H_7^+$	45	67
		O_2^+	$C_5H_8^+$	45	68
nitrogen dioxide	46.01	O_2^+	NO_2^+	100	46
pinene	136.23	H_3O^+	$C_6H_9^+$	39	81
		H_3O^+	$C_{10}H_{16}.H^+$	61	137
		NO^+	$C_{10}H_{16}^+$	77	136
		O_2^+	$C_7H_9^+$	56	93
propylene	42.08	H_3O^+	$C_3H_6.H^+$	100	43
		O_2^+	$C_3H_7^+$	100	42
styrene	104.15	H_3O^+	$C_8H_8.H^+$	100	105
		NO^+	$C_8H_8^+$	100	104
		O_2^+	$C_8H_8^+$	100	104
tetrachloroethylene	165.83	NO^+	$C_2{}^{35}Cl_3{}^{37}Cl^+$	42	166
		O_2^+	$C_2{}^{35}Cl_4^+$	32	164
		O_2^+	$C_2{}^{35}Cl_3{}^{37}Cl^+$	42	166
		O_2^+	$C_2{}^{35}Cl_2{}^{37}Cl_2^+$	21	168
toluene	92.14	H_3O^+	$C_7H_8.H^+$	100	93
		NO^+	$C_7H_8^+$	100	92
		O_2^+	$C_7H_8^+$	100	92
total C_3-alkylbenzenes	120.19	H_3O^+	$C_9H_{12}.H^+$	100	121
		NO^+	$C_9H_{12}^+$	100	120
		O_2^+	$C_9H_{12}^+$	85	120
xylenes and ethylbenzene	106.17	H_3O^+	$C_8H_{10}.H^+$	100	107
		NO^+	$C_8H_{10}^+$	100	106
		O_2^+	$C_8H_{10}^+$	90	106

Table 1: Compounds selected for monitoring including measured product ions.

RESULTS AND DISCUSSION

In air pollution studies, the fluctuation of pollutant levels based on the time of day and day of the week can provide valuable insights into their potential sources. For instance, emissions from road vehicles typically follow consistent daily and weekly patterns. In contrast, industrial emissions or pollutants from natural sources, such as sea salt aerosols, may exhibit significantly different trends. The nitrogen dioxide concentration data collected in this study demonstrate such daily and weekly trends, shown in Figure 2. When the level of NO_2 is plotted by hour and normalized to the mean value, a clear pattern emerges where peaks can be observed corresponding to weekday rush-hour as Christchurch inhabitants start their vehicles to get to work.

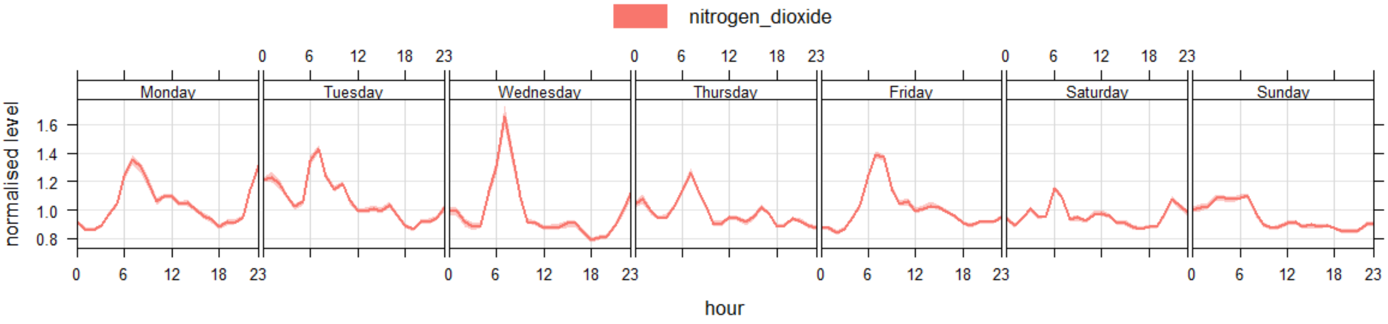


Figure 2: Normalized nitrogen dioxide concentration. Note the spikes during weekday morning rush hour.

The distribution of VOCs around the Syft office, and the correlation between concentration and the compass point wind direction, demonstrate how the emission sources can be isolated easily and quickly. Using typical monitoring methods, these trends can take months to determine, as each data point requires a minimum of 8 hours to collect. SIFT-MS massively increases the frequency with which pollution data are collected. With this data density, the emission trends and phenomena can be teased out in a matter of days. Figure 3 shows how higher than average concentrations of biogenic volatile organic compounds (BVOCs) occurred at the analyzer when light winds carried them from their source: the large city green space: Hagley Park, to the northwest of the sample inlet. Complementarily, instances of high anthropogenic compounds (AVOCs) primarily arose from winds from the northeast, exactly aligning with the closest busy street intersection of St Asaph St and Montreal St, where many vehicles spend time idling at stop lights throughout the day.

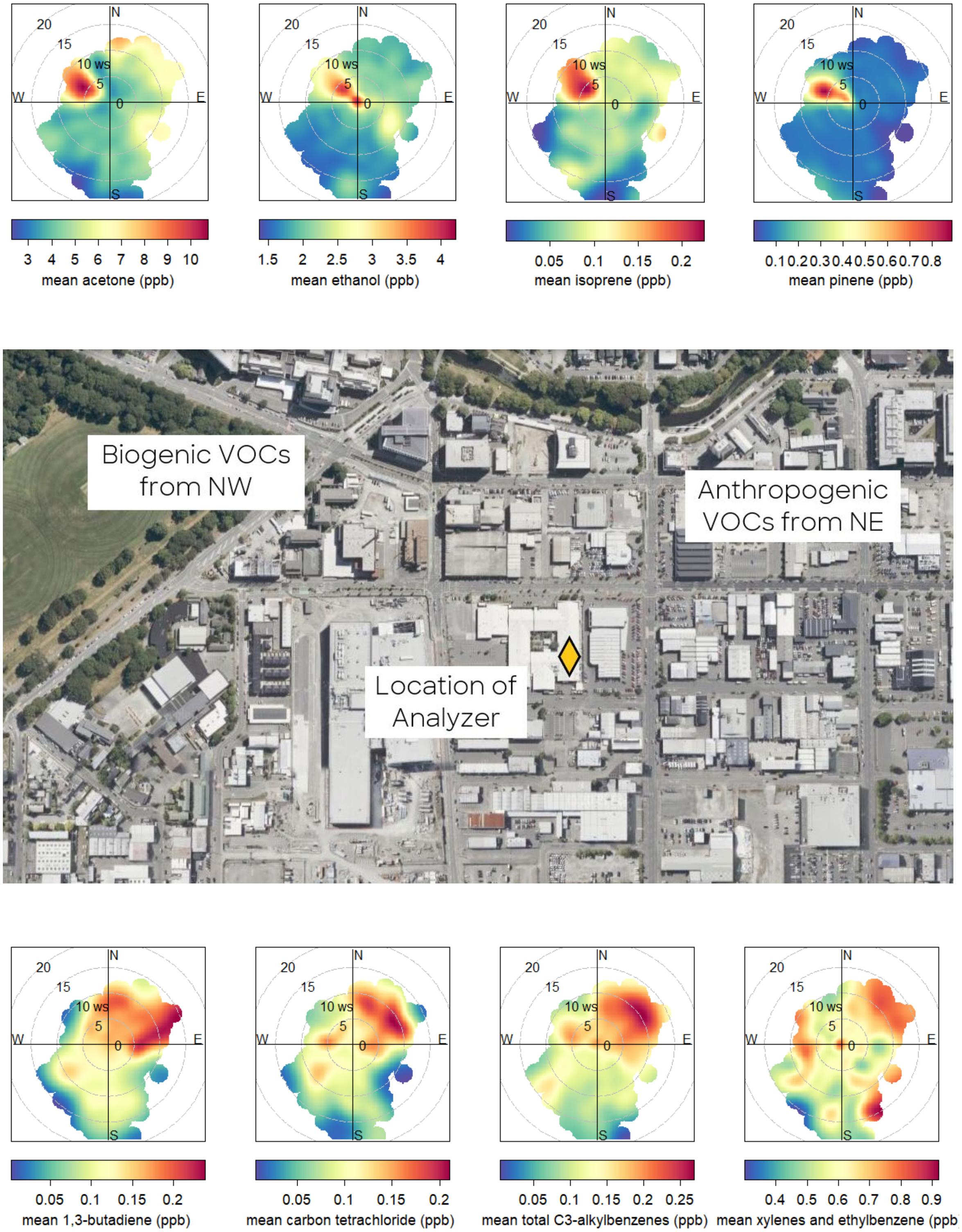


Figure 3: Polar plots of selected biogenic (top) and anthropogenic (bottom) VOCs, with a map showing analyzer location.

SIFT-MS has been proven to be highly sensitive and reliable for environmental monitoring, with both the South Korean government and the US EPA adopting the technology for use in mobile laboratories. Prior work at Syft Technologies (Edwards et al. (2024)) has demonstrated method detection limits (MDL), as determined by US EPA procedure EPA 821-R-16-006, for a selection of the above compounds. The MDLs in Table 2 were determined by using a 1-minute monitoring method. For any SIFT-MS method, lower MDLs are easily achieved by increasing the duration of the monitoring method - the improvement in MDL is approximately proportional to the inverse square root of the method length. These MDLs are far lower than those typically achieved by the EPA TO-17 method which requires sorbent tubes and can expect detection limits ≤ 500 pptV. The MDLs achieved by 1-minute SIFT-MS are equal to those achievable by the US EPA method TO-15a which requires large sample volumes and cryogenic preconcentration.

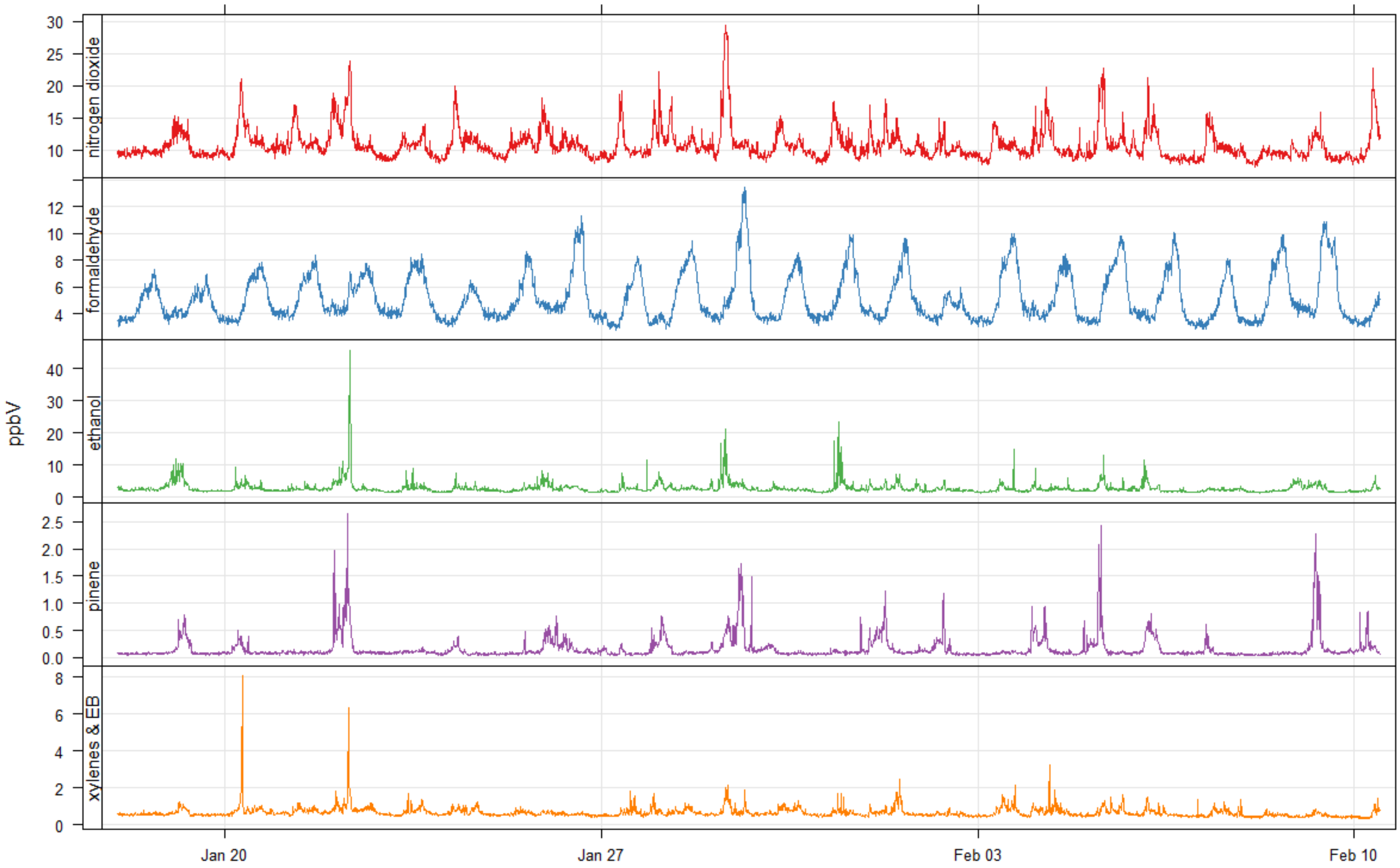
Compound	MDL (pptV)
1,3-butadiene	60
acetaldehyde	35
benzene	50
nitrogen dioxide	65
Toluene	25
total C3-alkylbenzenes	65
xylenes and ethylbenzene	55

Table 2: SIFT-MS method detection limits for a subset of compounds (Edwards et al. (2024)).

The dwell time for the 53 product ions measured in this study was 100 ms, with reagent ion measurement this resulted in a cycle time of ~6 seconds. This means that a data point was measured for each of the 21 different compounds/classes every 6 seconds, 24 hours a day, 7 days per week. To achieve the required MDL, the user can simply calculate an average over a certain pre-defined period. Moreover, the dwell time for SIFT-MS methods is configurable, so the user can choose to allocate more time to compounds of greater importance or those with more stringent MDL requirements.

A massive benefit that SIFT-MS provides over conventional monitoring techniques is the ability to easily expand and adapt the number and type of VOCs being monitored, without making any hardware changes. Figure 3 includes only a small subset of the compounds that were being measured during the recent monitoring campaign, but it demonstrates the contemporaneous, independent measurement and the density of data - here averaged over 10 minutes. In any given airshed there are countless different VOCs present, the reason that speciation is important is due to their unique chemistry, different VOCs have different impacts on ozone formation. These differences are so significant that researchers have developed several different models for assessing a quantity known as OFP, ozone formation potential, which is specific to both the VOC and the system wherein it resides (National Academies of Sciences, Engineering, and Medicine, 1999).

Figure 4: Selected analytes vs. time, note the diurnal variation and independent measurement.



The ability to measure NO_2 and VOCs simultaneously is a tremendous advantage of SIFT-MS as the balance between these significantly influences the efficiency of ozone production in a complex and non-linear fashion. In NO_x-limited regions, which are often rural or remote areas with abundant VOCs but low levels of NO_x, increasing NO_2 (from the conversion of NO to NO_2) leads to more ozone production as the NO_2 photolyzes under sunlight to release oxygen atoms, which then combine with O_2 to form ozone. Conversely, in VOC-limited areas, where VOCs are the bottleneck, reducing VOC emissions can effectively reduce ozone levels. The ratio of formaldehyde (HCHO) to nitrogen dioxide (NO_2), also known as the FNR, is used to study ozone sensitivity (Goldberg et al. (2023)). The FNR is a chemical concentration-based indicator ratio that can help identify ozone chemistry sensitivities. Now for the first time, FNR can be monitored in real-time by a single instrument, where previously NO_2 would be measured using a chemiluminescence detector and formaldehyde would require derivatization before analysis via HPLC.

CONCLUSIONS

- 21 different ozone precursor compounds were monitored continuously at a frequency of 1 data point every 6 seconds
- Concentration data is integrated with weather station data via SyftEnviro software aiding speed of analysis
- Detection limits for the compounds are better than or equal to incumbent EPA methods which employ complex and expensive techniques.
- The data collected demonstrate hourly, daily and weekly trends, and included speciated AVOCs and BVOCs – important for understanding emission sources.
- The number and type of compounds measured can be customized easily, without additional hardware
- Carbonyls, including formaldehyde, can be measured simultaneously with VOCs and NO_2, allowing a real-time measurement of FNR to be calculated

As the need for robust photochemical monitoring grows, SIFT-MS presents a transformative solution for researchers, policymakers, and industry stakeholders alike.

ACKNOWLEDGEMENTS

We are grateful to Dr Vaughan Langford and Dr Daniel Milligan, Syft Technologies Limited, Christchurch, New Zealand for their technical advice and ongoing support.

REFERENCES

Zhang, J., Wei, Y. and Fang, Z., (2019). Ozone pollution: A major health hazard worldwide. *Frontiers in Immunology*, 10, p.2518. doi: 10.3389/fimmu.2019.02518

Carslaw, D. C. and K. Ropkins, (2012) openair --- an R package for air quality data analysis. Environmental Modelling & Software. Volume 27-28, 52-61.

Wayne, R.P. (2000). *Chemistry of the Atmospheres* (3rd ed., pp. 422-437). Oxford University Press.

Edwards S, Silva L, Hoppens N, Pelet W, Aitcheson F (2024). Real-time measurement of EPA-regulated HON compounds and environmental pollutants using SIFT-MS. Syft Technologies application note.

U.S. Environmental Protection Agency (EPA). (2023). Compendium Method TO-15A: Determination of volatile organic compounds (VOCs) in air collected in specially-prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS). Available online: https://www.epa.gov/sites/default/files/2023-06/documents/to-15a_method.pdf

U.S. Environmental Protection Agency (EPA). (1999). Compendium Method TO-17: Determination of volatile organic compounds (VOCs) in ambient air using active sampling onto sorbent tubes. Available online: https://www.epa.gov/sites/default/files/2019-11/documents/epa-to-17.pdf

U.S. Environmental Protection Agency (EPA) (2019) Method TO-11A: Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC). Available online: https://www.epa.gov/sites/default/files/2019-11/documents/to-11ar.pdf

U.S. Environmental Protection Agency (EPA). (2021). 40 CFR Part 58: Ambient Air Quality Surveillance. Title 40 of the Code of Federal Regulations. Available online: https://www.ecfr.gov/current/title-40/chapter-I/subchapter-C/part-58

Ren, J., Xu, S., and Guo, F. (2022). Diagnosing ozone-NOx-VOC sensitivity and revealing causes of ozone increases in China. *Atmospheric Chemistry and Physics*, 22, 15035-15047. https://doi.org/10.5194/acp-22-15035-2022.

The Concept of Ozone-Forming Potential and Its Quantification. National Research Council. 1999. Ozone-Forming Potential of Reformulated Gasoline. Washington, DC: The National Academies Press. doi: 10.17226/9461.

Goldberg, D.L., Lu, X., Lamsal, L.N., Wang, Y., and Streets, D.G. (2023) 'Examining TROPOMI formaldehyde to nitrogen dioxide ratios in the Lake Michigan region: implications for ozone exceedances', *Atmospheric Chemistry and Physics*, 23(12), pp. 7867-7882. Available online: https://acp.copernicus.org/articles/23/7867/2023/ (Accessed: 17 February 2025).

Stockwell, C. E., Coggon, M. M., Schwantes, R. H., Harkins, C., Verreyken, B., Lyu, C., Zhu, Q., Xu, L., Gilman, J. B., Lamplugh, A., Peischl, J., Robinson, M. A., Veres, P. R., Li, M., Rollins, A. W., Zuraski, K., Baidar, S., Liu, S., Kuwayama, T., Brown, S. S., McDonald, B. C., and Warneke, C.: Urban ozone formation and sensitivities to volatile chemical products, cooking emissions, and NO_x upwind of and within two Los Angeles Basin cities, Atmos. Chem. Phys., 25, 1121-1143, https://doi.org/10.5194/acp-25-1121-2025, 2025

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