REAL-TIME MEASUREMENT OF EPA REGULATED

HON COMPOUNDS AND ENVIRONMENTAL POLLUTANTS USING SIFT-MS

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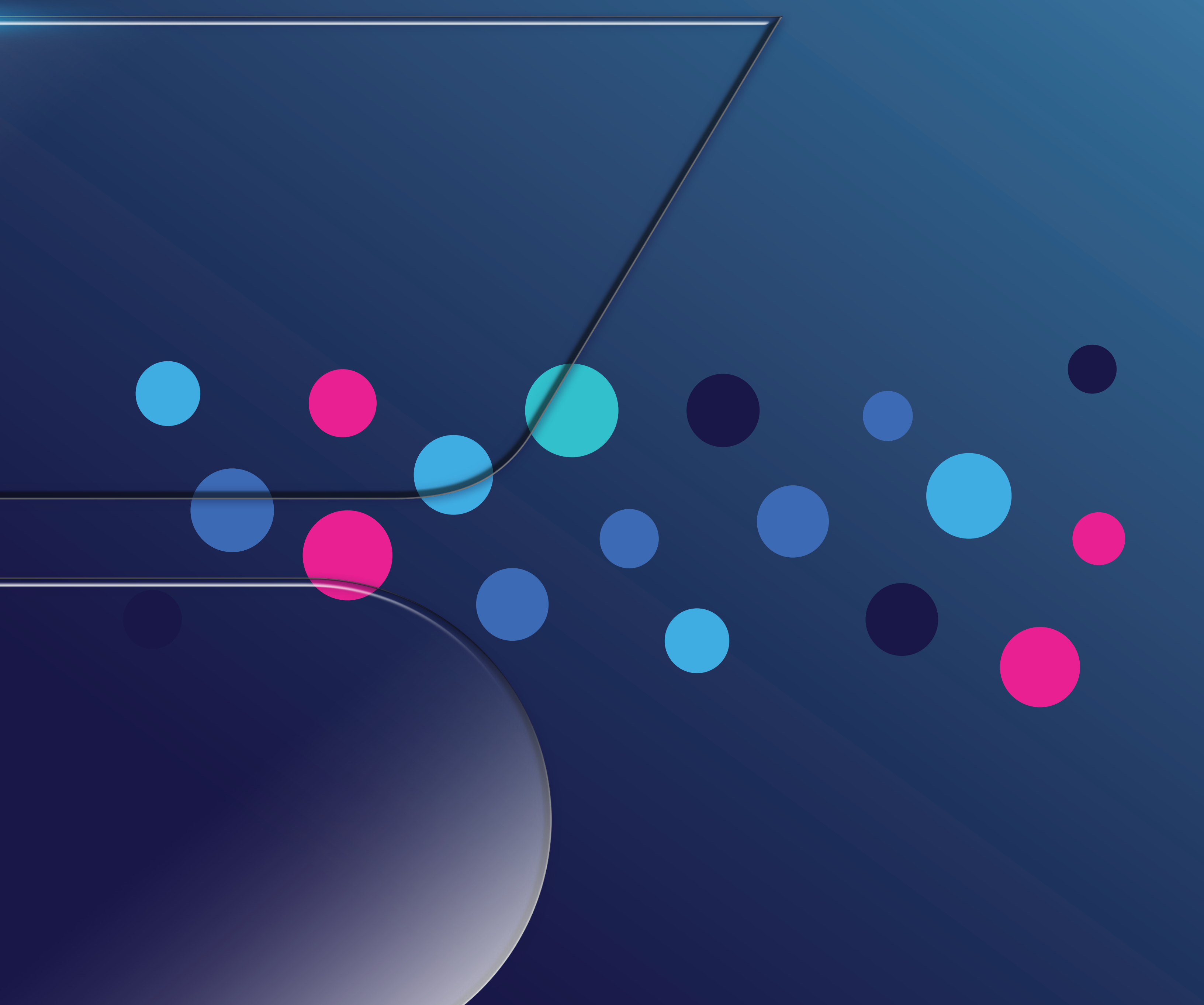


Summary

Method detection limits (MDLs) have been determined for the newly regulated HON (Hazardous Organic NESHAP (National Emission Standards for Hazardous Air Pollutants)) compounds, which validate selected ion flow tube mass spectrometry (SIFT-MS) as an effective solution for measuring these toxic volatile organic compounds (VOCs) and other environmental pollutants in ambient air, whether at the fenceline or in a mobile setting. SIFT-MS offers unparalleled speed, sensitivity and ease of use for environmental monitoring applications.

Introduction

There are over 200 chemical plants in the United States producing chemicals that pose a significant cancer risk to nearby communities. These are known as HON facilities. In January 2024, the US Environmental Protection Agency (EPA) enacted a rule mandating fenceline monitoring of six toxic VOCs produced by these facilities: ethylene oxide (EtO), chloroprene, benzene, 1,3-butadiene, ethylene dichloride, and vinyl chloride. Action levels for these compounds, established by the new regulations, are thresholds for annual average air concentrations; if these levels are exceeded at the fenceline, facilities must identify and address the pollution source to effectively manage hazardous emissions.

SIFT-MS offers real-time, direct monitoring of VOCs and inorganic compounds in air. SIFT-MS has been adopted by governmental agencies and industry worldwide for environmental monitoring. For example, the South Korean government agencies have relied on SIFT-MS for years to monitor toxic VOCs at both federal and state levels (Langford et al. (2023a)). Recently, the US EPA has also adopted SIFT-MS for use in mobile laboratories across real-time mobile monitoring applications.

In response to the new HON Rule, Syft Technologies has developed robust methods for sampling these toxic VOCs. These methods have achieved MDLs in the low- to mid- part per trillion by volume (pptV) range, validating SIFT-MS as an excellent solution for monitoring these compounds as well as other compounds in ambient air. With SIFT-MS, users get real-time monitoring that will connect emissions to specific events, giving a deeper understanding of plant operations while still meeting regulatory requirements.

Method

In SIFT-MS, real-time specificity is achieved by the combination of rapidly switchable reagent ions and various reaction mechanisms to distinguish multiple compounds in a single analysis. Reliable quantification of target compounds is provided by mass spectrometric detection combined with library records of ion molecule reaction rate constants.

This work uses a SIFT-MS instrument (Syft Tracer) operating with nitrogen carrier gas and equipped with a high-performance inlet (HPI). The HPI provides direct sample analysis, minimizing loss of volatiles. Samples were prepared by diluting reference standards in clean, humid air to produce a consistent flow at the concentration of interest with 40-50% relative humidity. Samples were delivered to the HPI with a flow past arrangement.

Library entries were used to create one-minute methods for each of the compounds. For compounds

Table 1. Action levels for HON compounds.

Analyte	Molecular Formula	HON Action Level (µg/m³)	HON Action Level (pptV)
Benzene	C_6H_6	9	2770
1,3-Butadiene	C_4H_6	3	1335
Choloroprene	C_4H_5Cl	0.8	217
Ethylene oxide	C_2H_4O	0.2	109
Vinyl chloride	C_2H_3Cl	3	1155
Ethylene dichloride	$C_2H_4Cl_2$	4	990

**µg/m³ to pptV conversion at 20 °C.*

that were reactive with more than one reagent ion, all rapid reactions were included in the methods. For methods using both positive reagent ions (H_3O^+, NO^+ and O_2^+) and negative reagent ions (O^-, OH^-, O_2^-, NO_2^- and NO_3^-), the total measurement time was 2 minutes; with 1 minute allocated to each phase.

MDLs were determined using US EPA procedure EPA 821-R-16-006 (US EPA (2016)).

EtO quantitation with H_3O^+ is known to be affected by the presence of its isomer acetaldehyde (Swift et al. (2023)). The method tested here included a subtraction for acetaldehyde based on acetaldehyde's reactivity with NO^+. The EtO MDL was measured in the presence of 2.5 ppbV acetaldehyde, to ensure the MDL results were representative of analysis of a realistic environmental sample.

Results

In addition to the HON compounds, MDLs were also determined for other environmentally important compounds. The MDLs in Table 2 and Table 3 represent what is achievable for each compound in one minute with the SIFT-MS system.

Table 2. Comparison of MDLs using SIFT-MS with HON compound action levels. Results are for one-minute methods using a single reagent ion, except for EtO.

Compound	MDL (pptV)	HON Action Level (pptV)
Vinyl chloride	460	1170
1,3-Butadiene	60	1360
Benzene	50	2820
Ethylene oxide	105[†]	110
Ethylene dichloridde	260	990
Chloroprene	145	220[‡]

[†] *EtO MDL over 30 minutes in presence of 2.5 ppbV acetaldehyde (see Discussion).*

[‡] *There is a second, lower chloroprene action level (83 pptV) for HON facilities collocated with neoprene production sources (see Discussion).*

Discussion

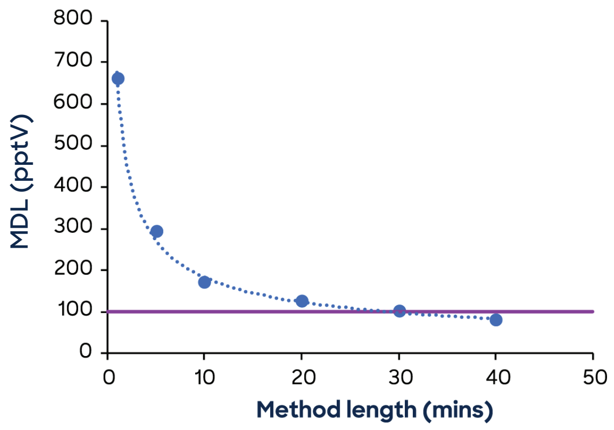
The MDLs presented in Table 2 and Table 3 reflect the capabilities of single-compound SIFT-MS methods conducted over one minute (30 minutes for EtO). All the HON compounds have MDLs below the EPA action level for fenceline monitoring.

Table 3. MDLs for environmentally important compounds using SIFT-MS. Results are for one-minute methods using a single reagent ion.

Compound	MDL (pptV)
Toluene	25
Xylenes and ethylbenzene	55
Hydrogen sulfide	125
Trichloroethylene	165
Nitrogen dioxide	65
Sulfur dioxide	200
Trans-1,2-dichloroethylene	100
1,3,5-trimethylbenzene	65
Ammonia	595
Acetaldehyde	35
Formaldehyde	595
Methyl bromide	90
n-butane	250
Acrolein	120

The new EPA regulations for fenceline monitoring of the HON compounds stipulate that alternative monitoring methods must achieve MDLs at least one-third of the action level for the monitored compounds. 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.

Figure 1. EtO MDL in the presence of 2.5 ppbV acetaldehyde as a function of method length. The HON action level is marked by the horizontal line.



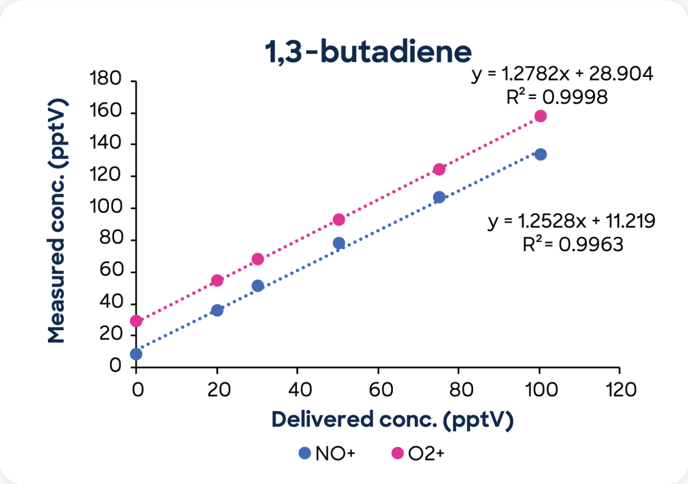
EtO provides a great example of how adjusting method length can significantly enhance an MDL. A substantial dataset of real EtO one-minute scan data was aggregated over time, allowing for the calculation of MDLs for these aggregated datasets. For EtO, the MDL with a 1-minute method exceeds the HON action level. Figure 1 demonstrates the enhancement in the EtO

MDL achievable by increasing the method duration.

The MDL for EtO drops below the HON action level when the method length exceeds 30 minutes. To achieve an MDL of one-third of the action level, the method length would need to be extended to about 3 hours. This duration is significantly shorter than the 24-hour average concentration measured by the standard canister method for EtO, allowing for multiple high-precision samples to be collected within the required 24-hour period. Similarly, extending the chloroprene method duration to five minutes effectively lowers the MDL for chloroprene from 145 pptV (Table 2) to below the secondary action level of 83 pptV relevant to facilities collocated with neoprene production sources.

For all the HON compounds, SIFT-MS has dramatically better temporal resolution than the EPA specified methods – passive and canister sampling – facilitating better source identification in the event of the concentration exceeding the action level.

Figure 2. 1,3-Butadiene low concentration calibration showing excellent linearity down to low pptV concentrations.



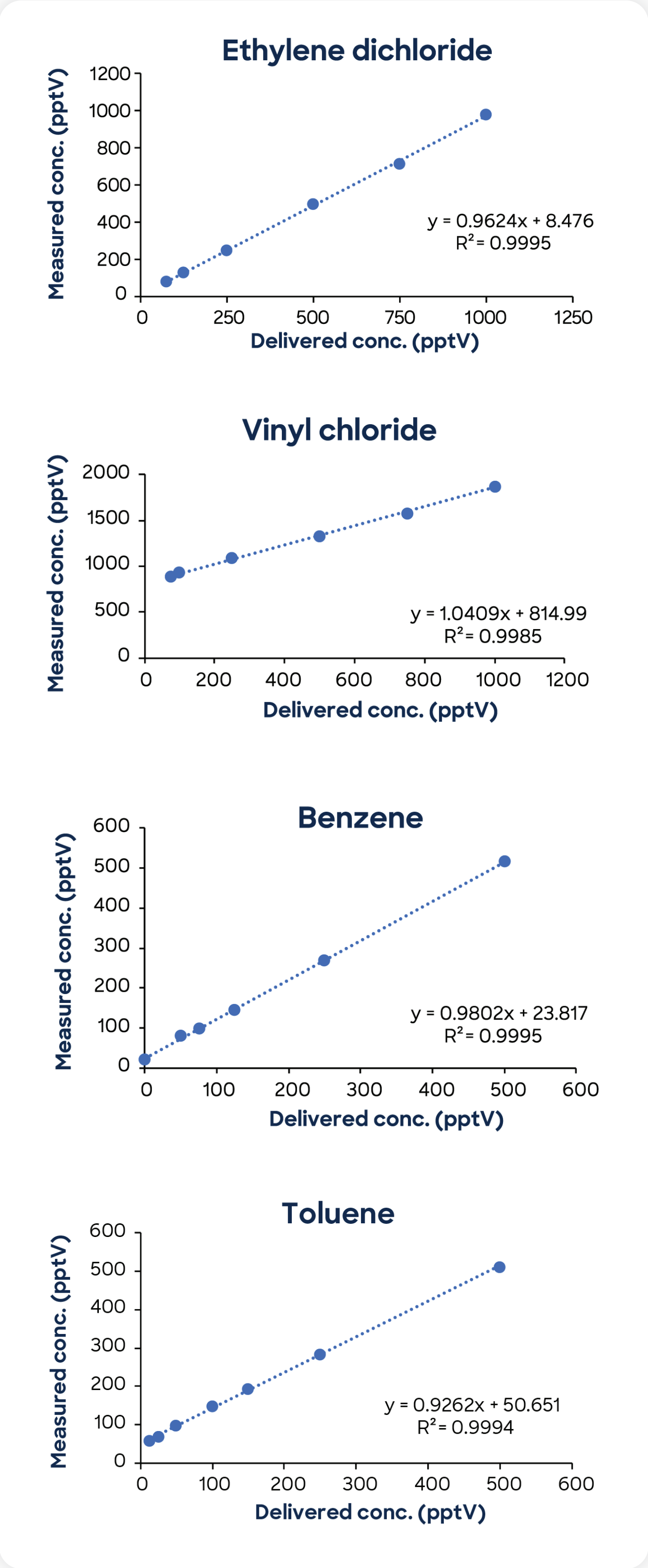
The EPA procedure states that MDLs can be estimated by examining the region of the calibration where there is a significant change in sensitivity, i.e., a break in the slope of the calibration. To support the MDLs in Table 2 and Table 3 which were measured at a single concentration, low concentration calibrations were also performed for each compound down to low pptV levels. An example is shown in Figure 2 for 1,3-butadiene.

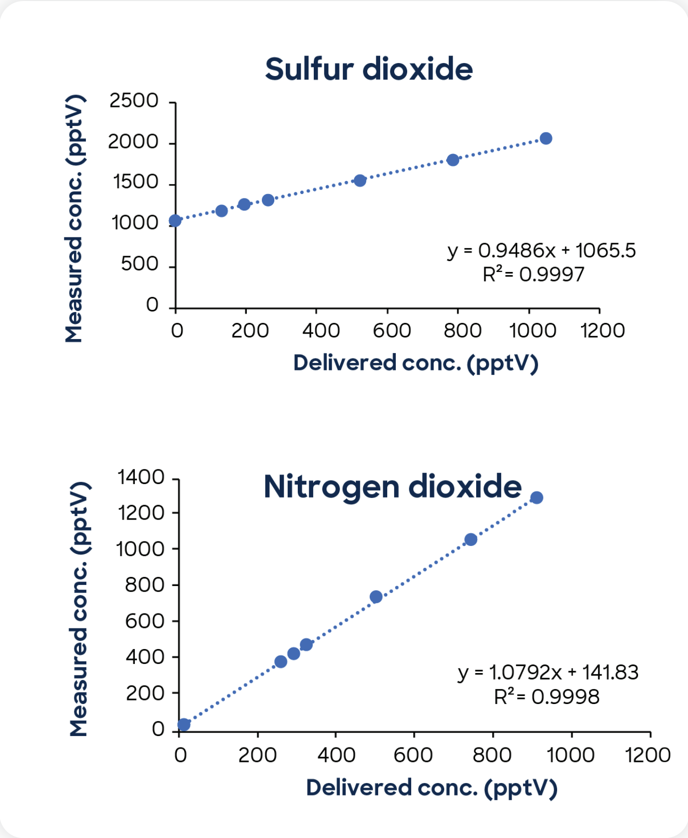
Concentrations measured using O_2^+ and NO^+ exhibit excellent linearity down to less than 20 pptV. This strong correlation shows that the 1,3-butadiene MDL presented in Table 2 is both realistic and attainable.

Additional examples of low concentration calibrations showcasing the linearity of SIFT-MS down to low pptV concentrations are presented in Figure 3.

Syft Tracer's flexibility and ability to swiftly monitor diverse chemical species at low pptV concentrations makes it the ideal choice for the monitoring of trace

Figure 3. Low concentration calibrations using simple one-minute methods exhibit excellent linearity down to low pptV concentrations.





levels of hazardous air pollutants. SIFT-MS is easy to automate, provides a simple data stream, and can operate unmonitored. It is the optimal solution for a facility aiming to go beyond basic compliance and achieve a higher standard of operational excellence. With a substantial database of ion-molecule reactions covering environmentally significant compounds, SIFT-MS is well-positioned to adapt to future regulatory challenges.

Conclusions

SIFT-MS measurements offer significant advantages over traditional techniques that require long sample collection times and off-site laboratory analysis. Unlike these methods, which can miss short-term fluctuations in pollutant concentrations, SIFT-MS provides immediate and continuous data, allowing for timely detection of hazardous compounds. This capability enhances the precision of source identification and enables quicker responses to potential environmental threats, ensuring more effective monitoring and protection of public health.

References

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Appendix

HOW SIFT-MS WORKS

SIFT-MS uses soft chemical ionization (CI) to generate mass-selected reagent ions that can rapidly react with and quantify VOCs down to part-per-trillion concentrations (by volume, pptV). Up to eight reagent ions (H_3O^+, NO^+, O_2^+, O^-, OH^-, O_2^-, NO_2^- and NO_3^-) obtained from a microwave discharge in air are now applied in commercial SIFT-MS instruments. These reagent ions react with volatile organic compounds (VOCs) and other trace analytes in well-controlled ion-molecule reactions, but they do not react with the major components of air (N_2, O_2 and Ar). This enables direct, real-time analysis of air samples to be achieved at trace and ultra-trace levels without pre-concentration. Rapid switching between reagent ions provides high selectivity because the multiple reaction mechanisms give independent measurements of each analyte. The multiple reagent ions frequently remove uncertainty from isobaric overlaps in mixtures containing multiple analytes. To calculate the concentration of the compounds, the reaction rate constant (k) from the library entry is used (Langford et al. (2023b)).

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