SIFT-MS:

A POWERFUL ANALYTICAL TOOL FOR WASTEWATER ODOR ANALYSIS

Vaughan S. Langford
Syft Technologies Limited, Christchurch, New Zealand

Abstract

Wastewater treatment plant (WWTP) odor is complicated due to the variable process inputs and complex biochemistry. WWTP odor has frequently been attributed to hydrogen sulfide (H_2S), despite the presence of other odorous species that may have lower odor thresholds. In this application note, the performance of selected ion flow tube mass spectrometry (SIFT-MS) is evaluated for analysis of odors from diverse sources at a modern WWTP. The soft chemical ionization employed in SIFT-MS provides detection and quantification of a wide range of potential odorants to below, or close to, the human odor detection threshold (ODT). SIFT-MS provides comprehensive, quantitative profiling of odor sources and can identify operational abnormalities. In particular, the results presented demonstrate that methyl mercaptan is almost always a more significant odorant at this WWTP than hydrogen sulfide and confirm that the relative abundances of these odorants vary significantly. Finally, SIFT-MS shows promise for instrument-based sensory analysis of odor concentration.

Note: This application note is derived from an open-access article published in Environments (Langford et al. (2020)); full details can be found there. The original article won the Ronald Hicks Memorial Award from Water New Zealand (https://www.waternz.org.nz/RonaldHicks) in 2021. "This award will be made to the author(s) of an article or paper considered significant in solving or clarifying sewage treatment or water pollution problems in New Zealand."

INTRODUCTION

Modern metropolitan wastewater treatment plants (WWTPs) typically process a variable mixture of both industrial wastewater (so-called trade wastes), residential (domestic) wastes, and runoff from rainfall. The organic content, chemical content, and high microbial load in influent, and throughout much of the wastewater treatment process, mean that odor mitigation is important. Mitigation strategies include containing odorous air using sealed lids, enclosing in an air-tight structure, and ducting the air through biofilters in which microbes metabolize the odorants. Odor regulation ensures that WWTPs are not an odor nuisance to nearby business and residential areas, and this is supported through both human sensory and instrumental odor measurement.

Despite the process complexities, hydrogen sulfide has consistently been used by industry as the primary indicator of odor, even though other odorous compounds (e.g., methyl mercaptan) are usually present and have lower odor thresholds (Suffet *et al.* (2004)). Use of hydrogen sulfide as the sole odor indicator has its challenges because it is not always present and its correlation with perceived odor is inconsistent (Braithwaite (2019)). More sophisticated measurement techniques are required to better represent complex odors from the complex and variable wastewater treatment processes.

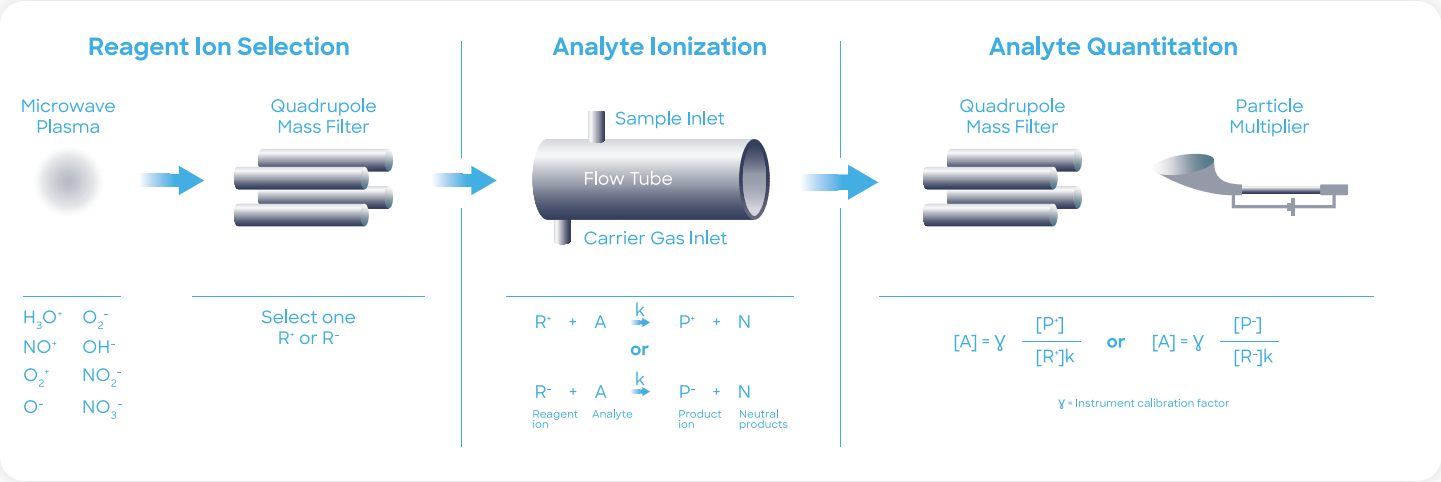
This application note summarizes the results obtained in the first published study of SIFT-MS measurement of odorants at a WWTP in parallel with a human sensory panel (see Langford *et al.* (2020) for full details). The study demonstrates that the combination of broad-spectrum analysis, high sensitivity, and high selectivity of SIFT-MS make it an effective odor monitoring tool for WWTPs.

METHOD

1. SIFT-MS and its automation

This work utilized a Syft Technologies Voice200*ultra* SIFT-

Figure 1. Schematic diagram of SIFT-MS – a direct, chemical-ionization analytical technique.



MS instrument operating on helium carrier gas. SIFT-MS (Figure 1) uses soft chemical ionization (CI) to generate mass-selected reagent ions (Smith *et al.* (2020)) 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 (Hera et al. (2017)). These reagent ions react with 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.

In this study, the SIFT-MS instrument was operated in selected-ion monitoring (SIM) mode. The reported target compound list is summarized in Table 1, while full SIFT-MS method details are given in Langford et al. (2020). Quantitation of most compounds was carried out from the LabSyft Compound Library. However, hydrogen sulfide, methyl mercaptan, ethyl mercaptan plus dimethylsulfide, and dimethyl disulfide were calibrated against certified gas mixtures (CAC Gas, Sydney, Australia) to improve accuracy. Blank bags were filled with odor-free scrubbed air used in olfactometry and provided a baseline of contamination from the sampling method.

To facilitate comparison of the SIFT-MS data with the sensory results, concentrations were converted to odor activity values (OAVs). This is achieved straightforwardly by dividing the SIFT-MS concentration measurement for a given compound by its odor detection threshold (ODT). See Langford *et al.* (2020) for literature sources of ODTs and a discussion of how these were selected in the frequently encountered situation of poor agreement between different workers.

2. Sensory panel

Olfactometry was conducted at the Watercare Laboratory Services Odor Laboratory (Auckland, New Zealand). Odor concentrations (in odor units m^{-3}; OU m^{-3}) were determined using dilution olfactometry according to AS/NZS 4323.3:2001. An Olfasense olfactometer (Kiel, Germany, www.to-evolution.com) was used with four to six panelists.

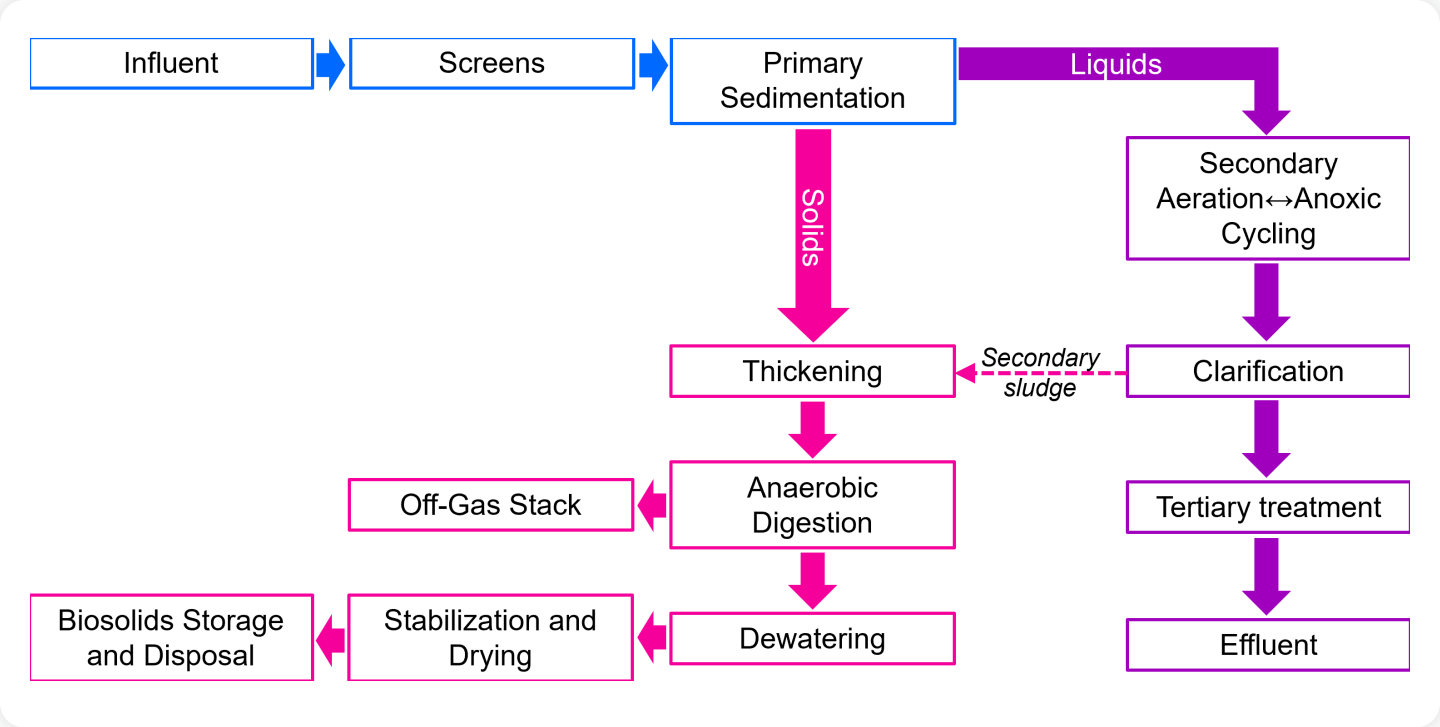
3. Samples

The odor survey was conducted at a modern New Zealand WWTP over the Southern Hemisphere summer and early fall/autumn period (December 2018-April 2019). Figure 2 provides an outline of the processing of the industrial and residential wastewaters at this plant. The olfactometry study focused on odor emission sources post-treatment at the plant, with parallel samples collected for SIFT-MS chemical analysis in the same sampling material (nalophan bags). Sampling procedures were conducted in accordance with the relevant Australian/New Zealand standard for each odor source.

Table 1. Compounds targeted using SIFT-MS and reported in Langford et al. (2020).

Compound Class	Target Compounds
Sulfur-containing	Hydrogen sulfide, methyl mercaptan, dimethyl sulfide + ethyl mercaptan, dimethyl disulfide, dimethyl trisulfide, allyl methyl sulfide, diethyl disulfide, carbon disulfide, propyl mercaptans, butyl mercaptans
Nitrogen-containing	Ammonia, methylamine, dimethylamine, trimethylamine, diethylamine, triethylamine, isopropylamine, putrescine, cadaverine, indole, skatole, pyridine
Aldehydes	Formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, heptanal, nonanal, decanal, benzaldehyde, heptadienal, decadienal
Ketones	Formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, heptanal, nonanal, decanal, benzaldehyde, heptadienal, decadienal
Alcohols	Ethanol, propanol isomers, butanol isomers, cresol isomers, 2-methylisoborneol, geosmin
Hydrocarbons	Toluene, ethylbenzene + xylenes, C_3-alkylbenzenes, C_4-alkylbenzenes, decane, undecane, dodecane
Monoterpenes & derivatives	Monoterpenes (total), carvone, dihydrocarvone, thymol
Chlorine-containing	Dichlorobenzene, chlorophenol isomers

Figure 2. Schematic diagram of the process at the WWTP investigated in this study.



RESULTS AND DISCUSSION

In this section, the most significant results from Langford *et al.* (2020) are presented and discussed. The full article gives a more detailed analysis of the SIFT-MS and human sensory results.

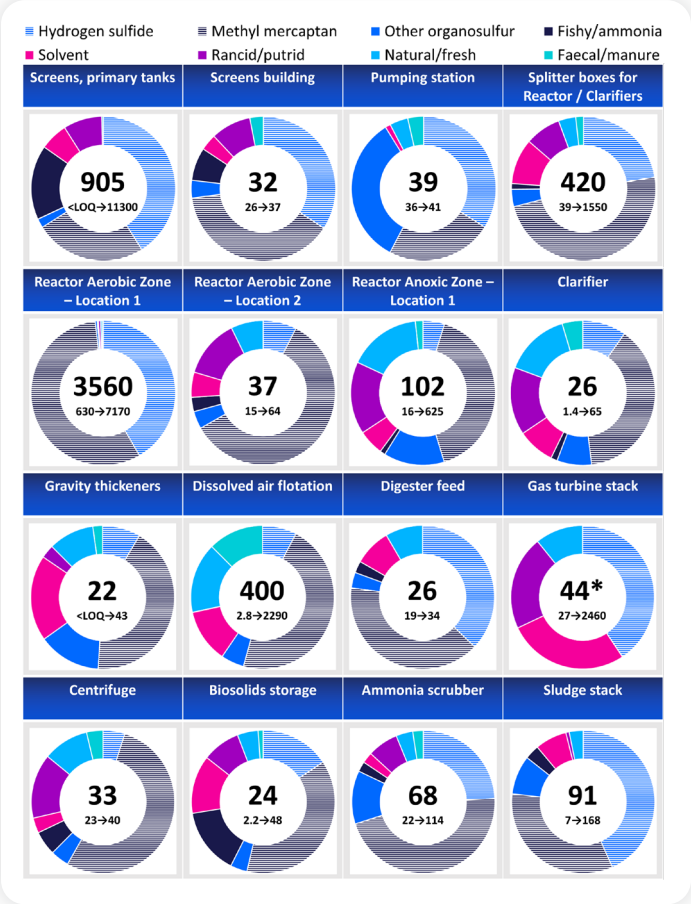
1. Characterization of odor sources

Figure 3 summarizes the odor compositions obtained using SIFT-MS for each source. For a given odor source, the mean OAV is shown as the large value in the center and was calculated from the total OAV of the individual samples from that source. The range of individual OAVs is shown in smaller point size below – a function of a very dynamic and seasonally dependent process, since in many cases samples were acquired over a period of months. The sum of hydrogen sulfide and methyl mercaptan OAVs dominated the odor for many sources. Interestingly, the relative significance of hydrogen sulfide reduces during the wastewater treatment process: it is highest in the screens and primary sewage samples. The liquid process then moves through an eight-zone alternating anoxic/aerobic step-feed reactor process to the clarifier. A reduction in hydrogen sulfide is observed as the secondary treatment process continues, both in terms of odor activity and relative contribution.

2. Identification of process anomalies

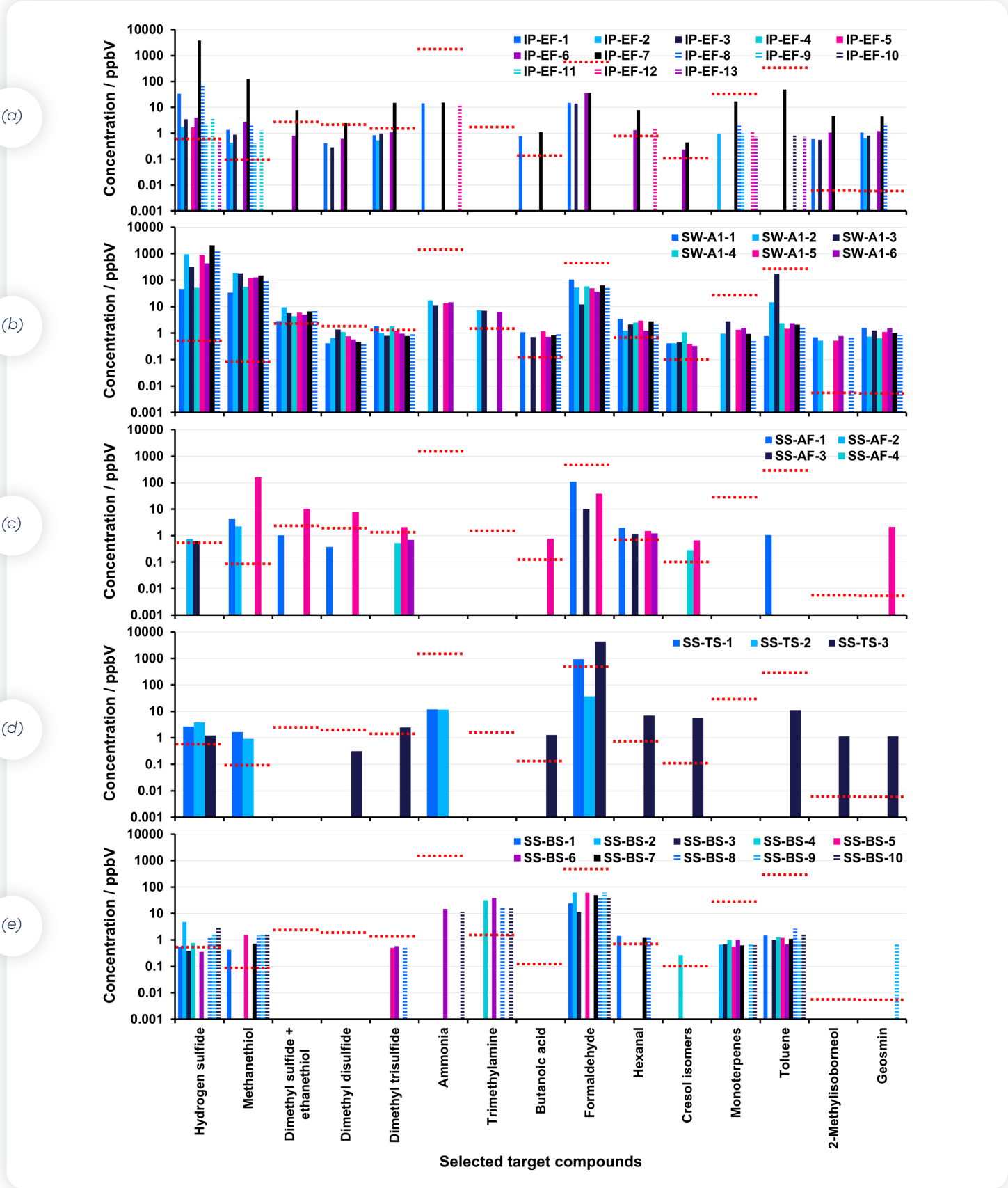
On a sample-by-sample basis, SIFT-MS rapidly detects many of the volatiles formed in biochemical processes in WWTPs. Monitoring variations in odor composition may enable operational staff to better understand process changes. Figure 4 shows examples of consistent operation (aerobic reactor, b, dissolved air flotation, c, and biofilter in biosolids storage, e), whereas there are also instances of significant variation (short-circuiting occurring in bio- or earth filters, a, where hydrogen sulfide is not an appropriate indicator,

Figure 3. Dominant odorants and odor notes for each source as a proportion of total odor activity as determined using SIFT-MS. The large number in the center of each chart is the total OAV for the individual samples averaged across the samples of that type. The small numbers show the range of total OAVs. Source: Langford et al. (2020).



and significant changes in gas combustion, d). Direct analysis onsite using a mobile SIFT-MS instrument and a biofilter hood may assist in pinpointing of short circuits in bio- and earth filters, for example, and identify areas where maintenance of odor beds is required especially where hydrogen sulfide is not an appropriate indicator.

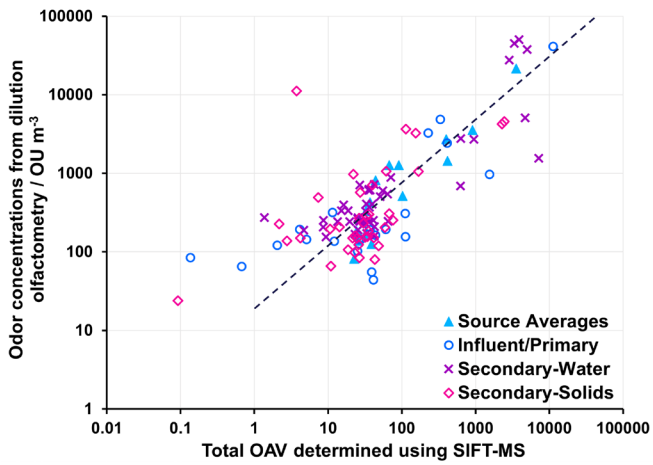
Figure 4. SIFT-MS concentration data (in ppbV on a logarithmic scale) for more significant odorants from a variety of odor sources: (a) influent biofilters, (b) reactor aerobic - location 1, (c) dissolved air flotation, (d) gas turbine stacks, and (e) biofilter at the biosolids storage location. ODTs are indicated approximately with dotted red lines. Source: Langford et al. (2020).



3. Prediction of Sensory Odor Concentration using SIFT-MS

Correlation of total OAV (determined using SIFT-MS) with the odor concentration (obtained by the sensory panel using dilution olfactometry) is shown in Figure 5. A general trend is indicated by the dashed line.

Figure 5. Odor concentrations from dilution olfactometry and SIFT-MS. Data for (a) primary, (b) secondary water, and (c) secondary solids odor sources are shown in different colors. Averaged values across all samples for a given odor source are shown with black triangles (R^2 = 0.985; slope 5.91). Source: Langford et al. (2020).



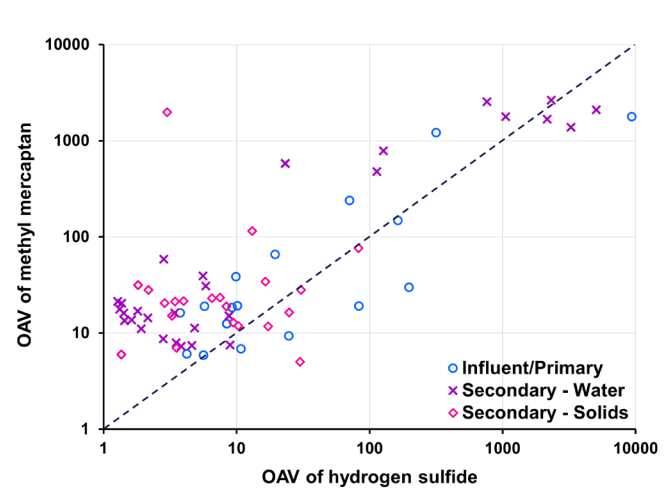
Prediction of odor concentrations determined using dilution olfactometry (i.e., OU m^{-3}) is challenging for two reasons. First, SIFT-MS is not analyzing all odorants effectively, with the absence of reliable "earthy/musty" note likely being the most significant factor. Nevertheless, a simple trend comparison of total odor activity value for the dominant odorants with odor concentration demonstrates a general correlation (Figure 5). Second, Braithwaite (2019) questions the reliability of dynamic dilution olfactometry, despite its application in numerous global standards (e.g., AS/NZS 4323.3:2001, BS EN 13725):

> *As an odor mixture is diluted, the odor notes and hedonic tones change and eventually, after sufficient dilution, the concentration of the final detectable odorant drops below its odor detection threshold so the diluted sample becomes "odorless". The amount of dilution required to reach this point is considered an indicator of the odor intensity of the initial, undiluted sample, which is problematic because the final detectable odorant may not be indicative of the odorant that dominated the odor of the undiluted sample (nor the dominant odorant in the partially diluted sample at the fenceline). Relying on dilution quantities to indicate the intensity of the total odor is crude at best and misleading at worst.*

In short, since improvements are clearly required in sensory analysis, a final judgment on the correlation of SIFT-MS data with dilution olfactometry lies beyond the scope of the present work.

Nevertheless, this study clearly demonstrates that instrumental analysis has significant benefits. For example, SIFT-MS reveals that methyl mercaptan contributes more to the odor impact than does hydrogen sulfide for certain parts of the wastewater treatment process (Figure 6), in contrast to observations that would be made with hydrogen sulfide sensors. The results presented here indicate that hydrogen sulfide measurement does not serve as a surrogate measure of methyl mercaptan. This result is clearly of value since humans are more sensitive to methyl mercaptan than hydrogen sulfide based on ODTs (0.071 and 0.41 ppbV, respectively; Nagata (2003)).

Figure 6. The relationship between the dominant sulfur odorants (hydrogen sulfide and methyl mercaptan) observed in the WWTP using SIFT-MS for the primary (blue circles), secondary water (purple crosses), and secondary solids (pink diamonds) odor sources. Note the logarithmic axes. Source: Langford et al. (2020).



CONCLUSIONS

- SIFT-MS selectively analyzes a very wide range of wastewater odorants in one simple operation, giving an objective, instrumental measure of odor character.
- SIFT-MS odor analysis is very sensitive, with quantitation limits better than, or close to, human ODTs.
- Comprehensive analysis of odor sources has potential to assist process monitoring and identify issues.
- Speciation of the most impactful odorants provides significantly greater insights than sensor technologies.
- Mobile odor monitoring option – at odor sources and boundary.

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Syft Technologies Ltd
New Zealand | +64-3-3386701

Syft Technologies GmbH
Germany | +49-6151-5201341

Syft Technologies Inc.
North America | +1-818-4504270

Syft Technologies Korea
Korea | +82-31-7056701

W: www.syft.com E: info@syft.com

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