ODOR CHARACTERIZATION

AT A GELATIN FACTORY, USING SIFT-MS*

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Instrumental odor analysis is challenging due to the chemical diversity of many important odorants (and their short lifetime in sampling media), the high sensitivity required, and the dynamic nature of the odor itself (due, for example, to changing wind conditions or human activity). Conventional sensor-based and chromatographic technologies are poorly suited to the task. Selected ion flow tube mass spectrometry (SIFT-MS) is a revolutionary direct mass spectrometric technology that provides comprehensive real-time odor analysis through high-sensitivity detection and quantitation of all odorants (e.g. aldehydes, amines, organosulfur compounds, and volatile fatty acids). In this application note, the SIFT-MS is evaluated for odor source characterization at a gelatin factory, together with benchmarking of the effectiveness of an ultraviolet (UV) photolysis technology used for odor mitigation. SIFT-MS is very effective in both applications.

Introduction

Odors can have a significant influence on quality of life. However, to establish acceptable standards for odor emissions, the human nasal response alone cannot be relied on because it is subjective and variable.[1-5] Instrumental detection of odors, although not subject to the variability of the human nose, is challenging due to the chemical diversity of the odorants, the high sensitivity that is required for identification and monitoring, and sudden changes in atmospheric conditions. Conventional sensor-based and chromatographic techniques are not well suited to the task of monitoring odors due to the rapidly changing and variable nature of the emissions.[6-10] In this application note, we evaluate a direct-analysis mass spectrometric technique, selected ion flow tube mass spectrometry (SIFT-MS), for odor analysis at a gelatin factory. SIFT-MS applies very soft chemical ionization to analyze odorants direct from air to sub-part-per-trillion-by-volume concentrations) (pptV) in real time (that is, analysis is conducted without pre-concentration or chromatography).[11-14] Gelatin is a mixture of peptides and proteins produced by partial hydrolysis of collagen that is extracted from the skin, bones and connective tissue of animals such as cattle, chicken, pigs, and fish.[15-17] The process of conversion of animal byproducts into gelatin is accompanied by odor production. Hence a gelatin factory provides an ideal industrial case study for odor source profiling. In 2017, the Gelita factory in question also evaluated a Neutralox® photoionization plant[18-19] that utilizes UV light to photo-convert odorant molecules such as sulfides, mercaptans and ammonia in to non-odorous species. Efficacy of deodorization was also investigated using SIFT MS.

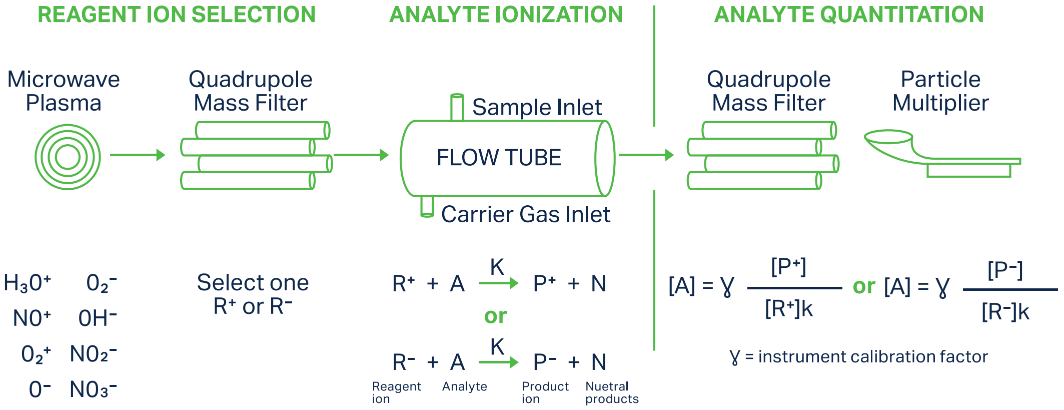
Method

1. The SIFT-MS technique

SIFT-MS11-14 (Figure 1) uses soft chemical ionization (CI) to generate mass-selected reagent ions that can rapidly quantify VOCs to low parts-per-trillion concentrations (by volume, pptv).12-14 Eight reagent ions (H_3O^+, NO^+, O_2^+, O^-, OH^-, O_2^-, NO_2^- and NO_3^-) obtained from a microwave discharge of moist or dry air, are now applied in commercial SIFT-MS instruments. These eight 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 allows for real-time analysis of air samples at trace and ultra-trace levels without pre-concentration, and results compare well with gas chromatography mass spectrometry (GC-MS).[20]

Rapid switching between reagent ions provides high selectivity, because the multiple reaction mechanisms

***Figure 3.** Schematic diagram of SIFT-MS – a direct chemical-ionization analytical technique.*



* *Adapted from "Comprehensive Instrumental Odor Analysis Using SIFT-MS: A Case Study" by M. Askey, V.S. Langford, M.J. McEwan, H.A. Barnes, J.G. Olerenshaw, Environments, 2018, 5, 43; doi:10.3390/environments5040043*

Figure 2. Aerial photograph of the Gelita factory site in Christchurch, annotated with the different processing sites from which samples were taken.

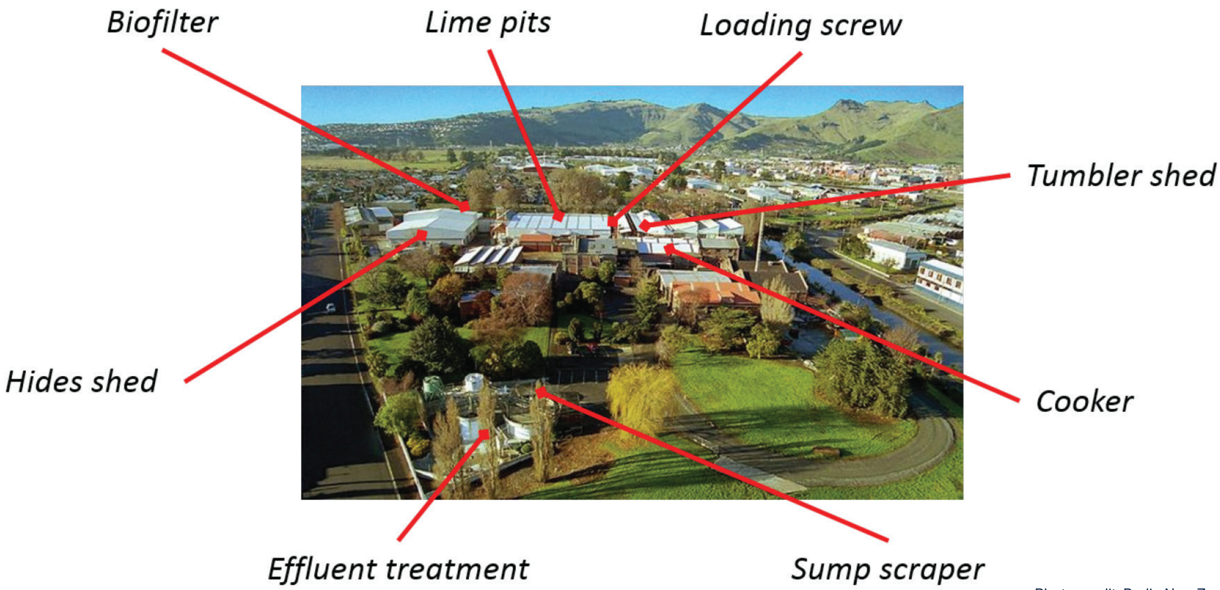


Photo credit: Radio New Zealand

2. Samples and analysis conditions

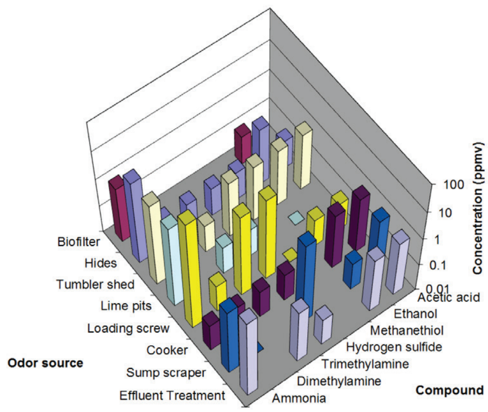
For the present work, samples were collected in Tedlar sample bags (SKC Inc., Eighty-Four, PA, USA) from the Gelita site and analyzed by the SIFT-MS instrument. Each bag was flushed three times with zero air and analyzed as a blank prior to emptying and sample collection at the Gelita site. Bags were analyzed within two hours of collection to minimize losses of odorants. Data presented here represent blank-corrected concentrations based on subtraction of the blank values for the specific sampling bag, due to the variable low-ppb background in the bags.21,22

Results and Discussion

The lay-out of the Gelita factory site is shown in Figure 2 together with an overview of the surrounding neighborhood. The various operation rooms utilized by the factory are also designated. The Gelita site has been monitored using SIFT-MS technology at different times over several years. The main odors produced in the different operation rooms within the plants are summarized in Figure 3 (note the logarithmic concentration scale).

Depending on weather conditions, there have been occasions when objectional odors have permeated into the district in the vicinity of the Gelita factory. Although Gelita embarked on engineering changes to reduce odor emissions after 2005, major earthquakes in Christchurch in 2010 and 2011 disrupted this process. In 2016, the decision to evaluate odor elimination technology using a photoionization installation18,19 (Neutralox® Umwelttechnik GmbH, Hennef, Germany) was made as discussed previously.

Figure 3. Chemically diverse odor compounds from various sources at the Gelita gelatin factory that have been detected and quantified by SIFT-MS.



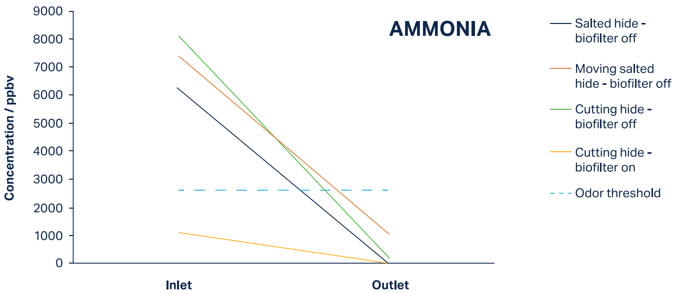
The pilot plant deodorizer unit was tested by monitoring samples collected in Tedlar sampling bags at three sites identified as odor sources within the Gelita plant. Grab samples of both inlet air and outlet air were taken from the hides shed, the loading screw and the sump scraper (see Figure 2) to assess the effectiveness of the photoionization deodorizer. The filled sample bags were delivered to the Syft Technologies Laboratory for SIFT-MS analysis – all within two hours. The odor losses due to bag absorption or diffusion are minimized by the short time to sampling for both odorized and deodorized air.21,22

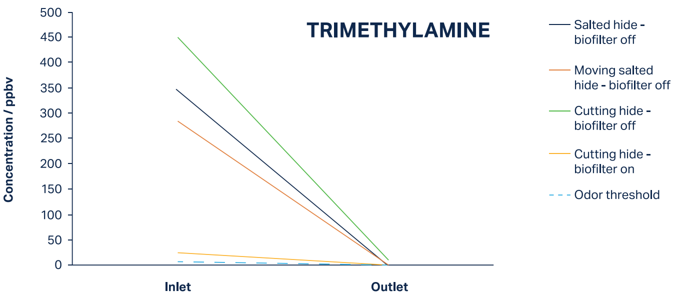
Figures 4 and 5 show the results for two of these sites: the hides shed and the loading screw. In the hides shed salted cattle hides are stored in this building before they undergo the process that extracts collagen used in the production of gelatin. Four routine activities are conducted in this shed. These are (i) delivery of salted hides to the shed; (ii) moving hides within the shed; (iii) cutting hides and (iv) transfer of hides out of the shed to the lime pits. The dashed lines show the human odor threshold in air23 and provides comparison for the SIFT-MS instrument data. It is evident that the photoionization device reduces the contamination to below the odor threshold for all odorants shown.

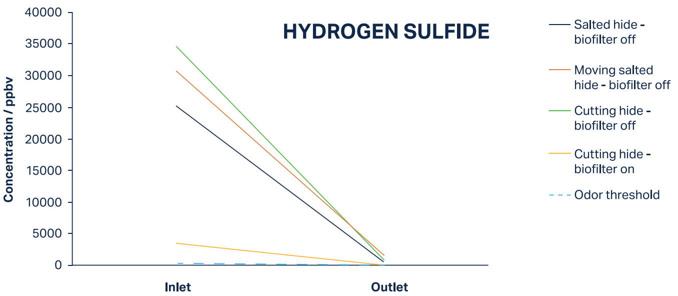
Every day, conditioned cattle hide is transferred from the alkaline lime pits via the loading screws shed to the tumblers for acidulation. The hide is conditioned with lime and caustic and is highly alkaline (pH 12). It is generally of consistent quality. Previous investigations showed that the hide transfer on the loading screw yielded high levels of ammonia and other odors typical of the lime pits from which they originate (see Figure 5), but at higher concentrations due to the agitation of the hides through the loading screw.

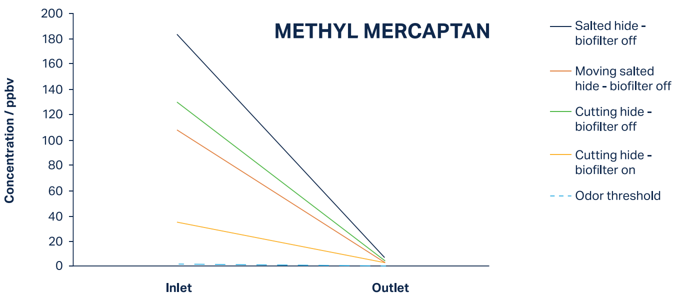
The key odorants – ammonia, hydrogen sulfide, and trimethylamine – vary significantly from day-to-day, but the Neutralox® deodorization plant is again effective in removing odors no matter what concentration enters its inlet. An exception is formaldehyde, which is both more consistent on a day-to-day basis, and shows an approximate doubling at the outlet, albeit at low concentrations. This may be due to the extent of photolysis applied. However at these levels it is not a concern for workplace exposure, the environment, or as

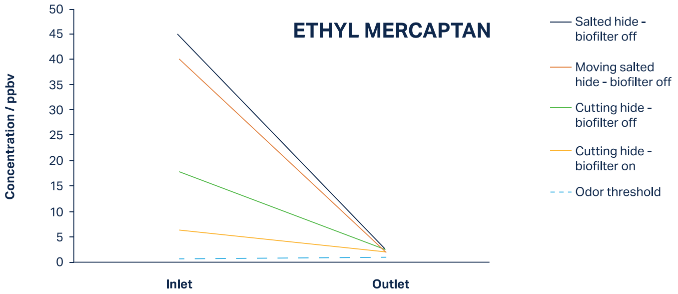
Figure 4. SIFT-MS analysis of the odor compounds before and after treatment by the Neutralox® photoionzation plant for the odorant in the hides shed. The lines shown are to guide the eye between the two SIFT-MS measurements at the inlet and exit ports of the deodorizer. The odor thresholds are from ref. 23.

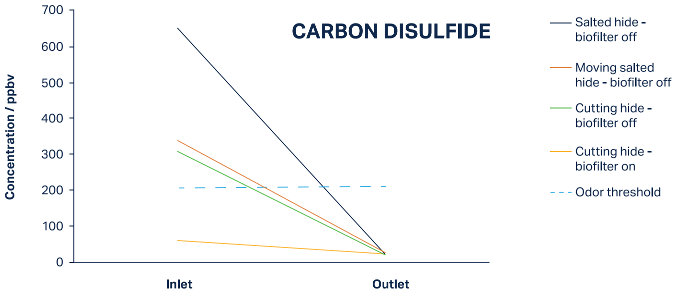


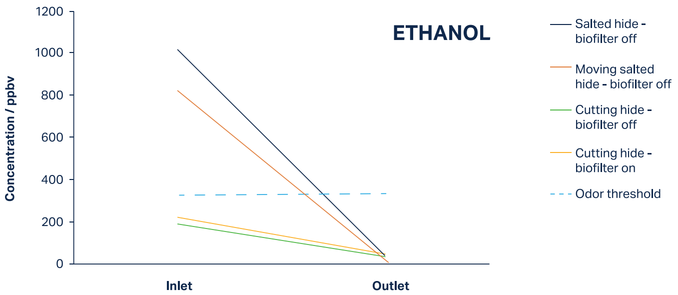


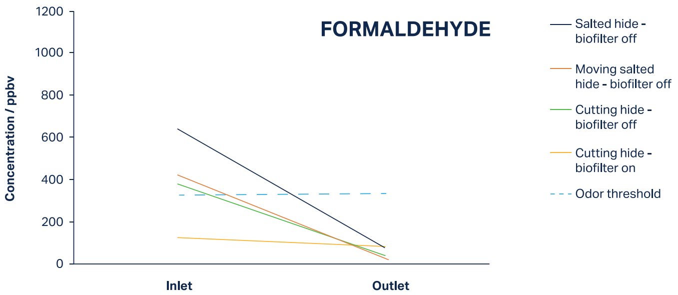






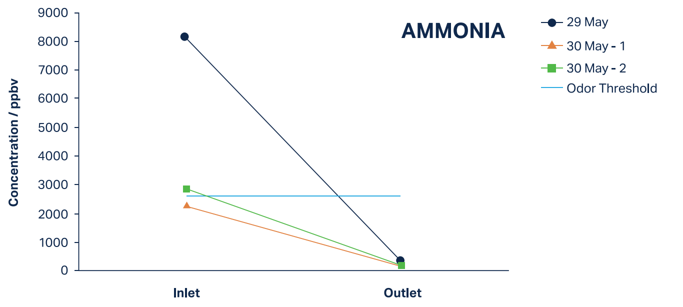


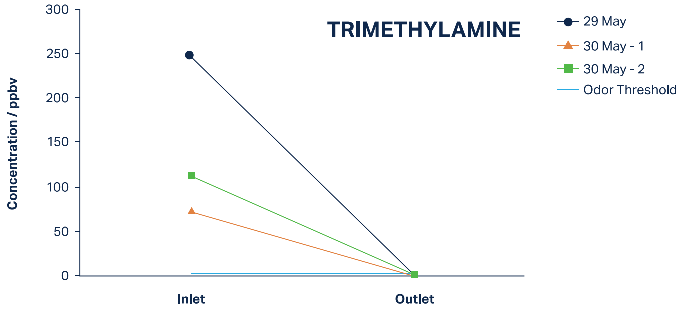


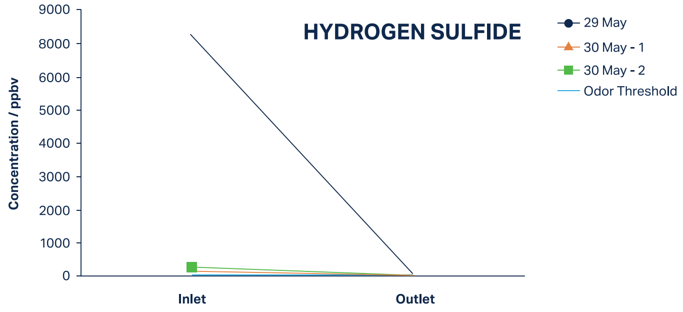


The pilot plant deodorizer unit was tested by monitoring samples collected in Tedlar sampling bags at three sites identified as odor sources within the Gelita plant. Grab samples of both inlet air and outlet air were taken from the

Figure 5. *SIFT-MS analysis of the stated odor compounds in the loadingscrew before and after treatment by the photoionization plant. The lines areshown to the guide the eye between the two SIFT-MS measurements at the inlet and exit ports of the deodorizer. The odor thresholds are from ref 28.*







Conclusions

The results presented here demonstrate that SIFT-MS is readily utilized to comprehensively and quantitatively analyze odors. The wide dynamic range of SIFT-MS means that a concentration range of over five orders of magnitude can be accommodated without dilution of the sample, enabling the instrument to detect odors directly from the source and after treatment (such as UV photolysis) without dilution or preconcentration, respectively. In the present case, up to 8 ppm of ammonia was recorded at the inlet of the Neutralox® photoionization device down to concentrations for some odors of single-digit ppbV at the outlet.

Unlike eNoses and other CMOS-based sensors, SIFT-MS readilyidentifies odorants that may have very different chemical properties and does not suffer from sensor poisoning or drift. SIFT-MS also provides significant benefits over chromatographic based techniques. The high-sensitivity, direct analysis eliminates preconcentration, derivatization, and the need for analysis on multiple chromatographic columns that complicate odor analysis in gas and liquid chromatography methods.

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