SIMPLE, RAPID ANALYSIS OF PACKAGING FOR VOLATILE MOSH AND MOAH CONTAMINANTS

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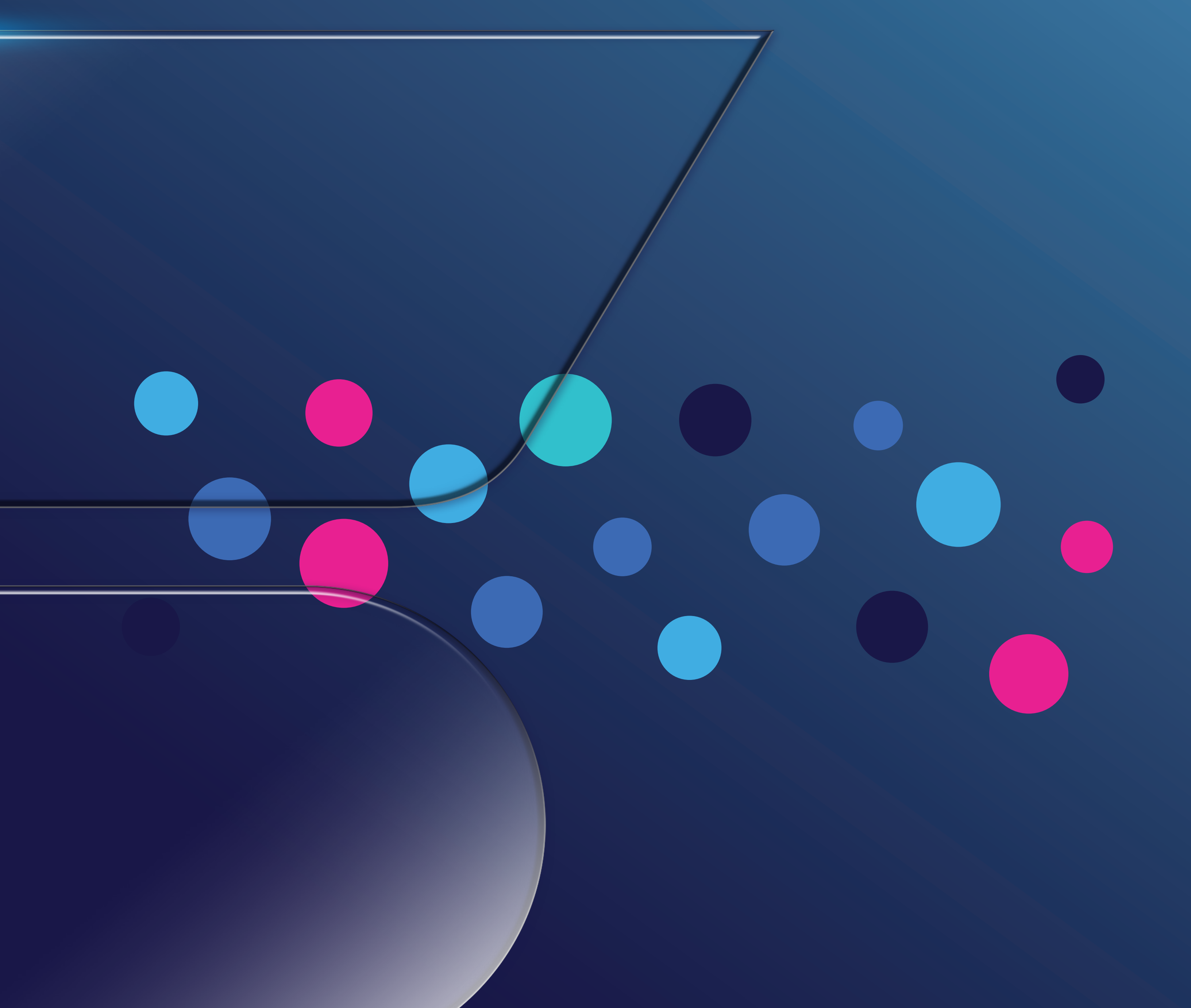


Abstract

Mineral oil hydrocarbons (MOH) may contain carcinogenic and mutagenic impurities and hence national and regional food safety authorities require that food ingredients, finished products, and packaging materials be tested. Comprehensive analysis of MOH is very challenging and time consuming. This application note demonstrates that automated headspace-SIFT-MS analysis has the potential to screen larger sample numbers for the volatile MOH fraction, providing a rapid indication of packaging material contamination. As benzene has also recently been found to be problematic in commercial products, it was included in the method and the concurrent quantitative measurement of benzene is also reported. Headspace-SIFT-MS can screen over 220 samples per day for the volatile fraction – nearly seven-fold more samples than the routine liquid and gas chromatography method.

INTRODUCTION

Mineral oil hydrocarbons (MOH; European Food Safety Authority, EFSA(2012)) are derived primarily from crude oil, but may also be synthesized from coal, natural gas, and biomass. MOH are typically in the C_{10} to C_{50} range and can be present in food through environmental contamination, machinery lubricants, processing aids, food additives, and food contact materials (FCMs). Mineral oil aromatic hydrocarbons (MOAH) are minimized in food-grade MOH products (compared to technical mineral oils, which may contain up to 35% MOAH) due to potential carcinogenicity and mutagenicity. Food-grade mineral oils are therefore comprised largely of mineraloil saturated hydrocarbons (MOSH).

MOH are extremely complex mixtures and tend to elute from standard chromatographic analyses as a broad band, rather than resolving individual components (EFSA (2012)). Moreover, testing for them in food products adds another layer of complexity (Bratinova and Hoekstra (2019)), for which a highly sophisticated automated sample preparation and analysis solution has been commercialized (liquid chromatography-gas chromatography-flame ionization detection/mass spectrometry (LC-GC-FID); GERSTEL), delivering a throughput of two samples per hour.

For this application, headspace SIFT-MS has a throughput of 12 samples per hour (Perkins and Langford (2021)) and a demonstrated ability to analyze volatile organic compounds (VOCs) at high sensitivity (Perkins and Langford (2022a)). Chromatography-free direct analysis of the more volatile component of MOH may enable workflows to be further optimized through rapid pre-screening. FCMs are suspected to contribute significantly to total consumer exposure (EFSA (2012)), especially from paper and board packaging. These products are experiencing a resurgence due to the reduced use of plastic packaging, and therefore FCMs provide the ideal proof-of-concept scenario for evaluating headspace-SIFT-MS.This study demonstrates the suitability of automated headspace-SIFT-MS analysis for rapid screening of paper- and polymer-based packaging materials for volatile (C_{10} to C_{16}) signatures of MOHs. Additionally, quantitation of lower molecular weight aromatics is reported due to recent concerns about benzene in various consumer products (Bettenhausen (2022), Valisure (2022)).

Figure 1. Headspace SIFT-MS enables high-throughput screening of FCMs for benzene and volatile MOH, providing enhanced quality control and quality assurance.

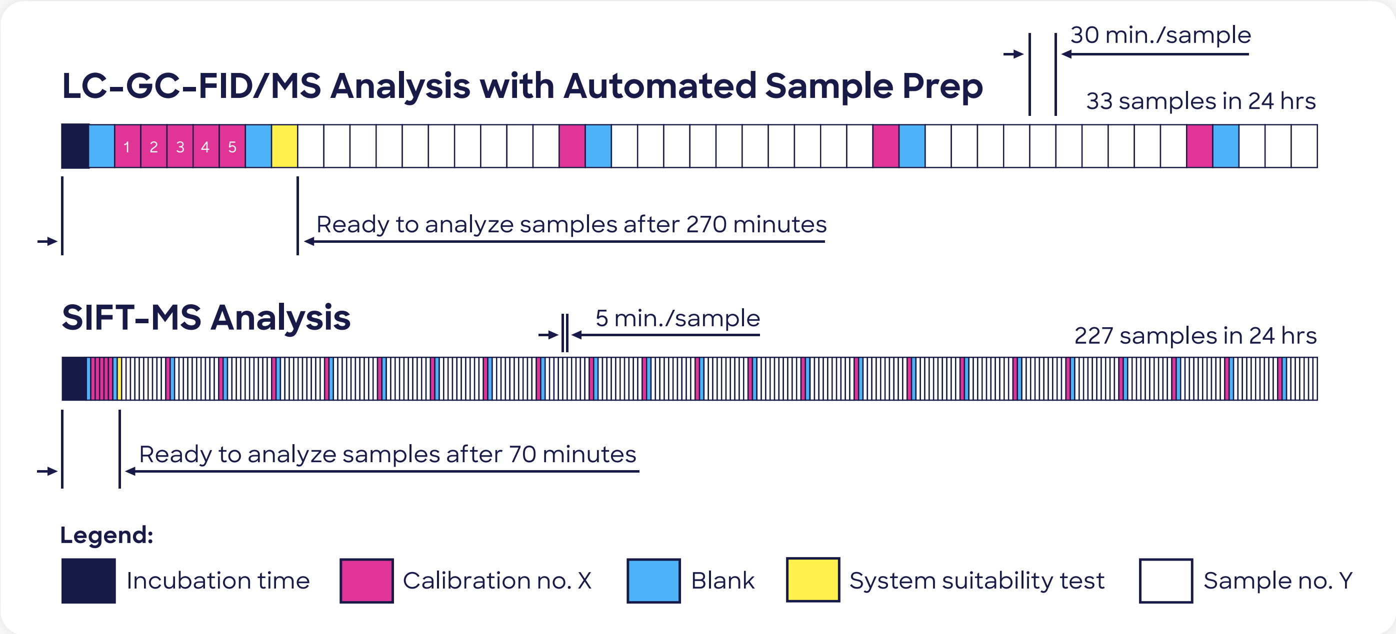
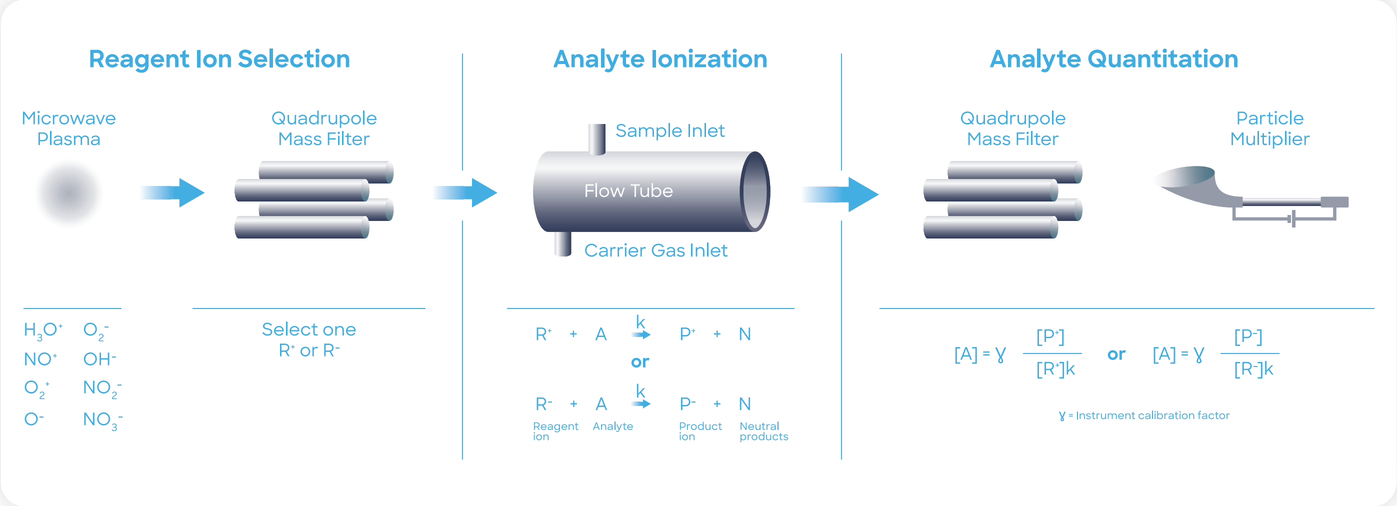


Figure 2. Schematic diagram of SIFT-MS – a direct, chemical-ionization analytical technique.



Method

1. The SIFT-MS technique

This work utilized a Syft Technologies Voice200*ultra* SIFT-MS instrument operating on helium carrier gas. SIFT-MS (Figure 2) 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.

Automated MHE analysis was carried out using a SIFT-MS instrument coupled with a multipurpose autosampler (MPS Robotic Pro, GERSTEL; Mülheim, Germany). The autosampler was controlled using GERSTEL's Maestro software. Samples were incubated at 80 °C for 45 min. in a GERSTEL agitator. Headspace was sampled using a 2.5-mL headspace syringe (heated to 150 °C) and subsequently injected at a flow rate of 50 µL s^{-1} into the SIFT-MS instrument's autosampler inlet (heated to 150 °C) *via* a self-sealing GERSTEL septumless sampling head. Since the nominal sample flow into the SIFT-MS instrument is 420 µL s^{-1}, a make-up gas flow (ultra-high purity nitrogen) is also introduced through the sampling head. This 10-fold dilution is accounted for in the final concentration calculations below. The analysis time for each sample was 120 s.

2. Taget Compounds

For both MOSH and MOAH compounds, carbon numbers up to C_{16} were targeted in these experiments. However, the data suggest that at an incubation temperature of 80 °C higher carbon numbers may be measurable, and this should be explored in future work (e.g., to C_{20}). Note that some of these compounds are not currently in the Syft compound library for SIFT-MS; they were detected using parameters derived from reaction trends observed for analogs that are in the library.

In this study, the benzene alkyl derivatives were targeted as representative of the MOAH class. These aromatic compounds were primarily targeted via their H_3O^+ and NO^+ reaction chemistry, as shown in Table 1, because these ions give a convenient total for a given carbon number. For benzene and toluene, O_2^+ was utilized because it yields no fragments and hence is highly sensitive. The naming convention used here for aromatics higher than toluene refers to the number of carbons in the side chains. For example, the total concentration measured for the sum of ethylbenzene and the xylene isomers is referred to as "C_2-alkylbenzenes".

The MOSH class was targeted via alkanes containing 10 to 16 carbon atoms (C_{10} – C_{16}) using the 'parent' product ions of NO^+ and O_2^+ (Table 1). NO^+ is typically more sensitive than O_2^+, but inclusion of the latter is necessary for paper-based samples due to the presence of aldehydes that share the NO^+ product ion. Each measurement represents a total of the alkanes of a given carbon number (e.g., "C_{10}-alkanes" includes n-decane and all its branched variants).

Table 1. Target compounds (or sums of compounds), their molecular weight, and reagent ion-product ion pairs used in the method (ion formula and mass-to-charge ratio, m/z).

Target Compounds		**H_3O^+**		**NO^+**		**O_2^+**	
Name	**MW / g mol^{-1}**	**Formula**	**m/z**	**Formula**	**m/z**	**Formula**	**m/z**
Benzene	78			$C_6H_6^+$	78	$C_6H_6^+$	78
Toluene	92	$C_7H_9.H^+$	93	$C_7H_8^+$	92	$C_7H_8^+$	92
C_2-Alkylbenzenes	106	$C_8H_{10}.H^+$	107	$C_8H_{10}^+$	106		
C_3-Alkylbenzenes	120	$C_9H_{12}.H^+$	121	$C_9H_{12}^+$	120		
C_4-Alkylbenzenes	134	$C_{10}H_{14}.H^+$	135	$C_{10}H_{14}^+$	134		
C_5-Alkylbenzenes	148	$C_{11}H_{16}.H^+$	149	$C_{11}H_{16}^+$	148		
C_6-Alkylbenzenes	162	$C_{12}H_{18}.H^+$	163	$C_{12}H_{18}^+$	162		
C_7-Alkylbenzenes	176	$C_{13}H_{20}.H^+$	177	$C_{13}H_{20}^+$	176		
C_8-Alkylbenzenes	190	$C_{14}H_{22}.H^+$	191	$C_{14}H_{22}^+$	190		
C_9-Alkylbenzenes	204	$C_{15}H_{24}.H^+$	205	$C_{15}H_{24}^+$	204		
C_{10}-Alkylbenzenes	218	$C_{16}H_{26}.H^+$	219	$C_{16}H_{26}^+$	218		
C_{10}-Alkanes	142			$C_{10}H_{21}^+$	141	$C_{10}H_{22}^+$	142
C_{11}-Alkanes	156			$C_{11}H_{23}^+$	155	$C_{11}H_{24}^+$	156
C_{12}-Alkanes	170			$C_{12}H_{25}^+$	169	$C_{12}H_{26}^+$	170
C_{13}-Alkanes	184			$C_{13}H_{27}^+$	183	$C_{13}H_{28}^+$	184
C_{14}-Alkanes	198			$C_{14}H_{29}^+$	197	$C_{14}H_{30}^+$	198
C_{15}-Alkanes	212			$C_{15}H_{31}^+$	211	$C_{15}H_{32}^+$	212
C_{16}-Alkanes	226			$C_{16}H_{33}^+$	225	$C_{16}H_{34}^+$	226

Note that concentrations are reported as part-per-billion by volume (ppbV) in the headspace. Determination of the quantity of MOSH or MOAH components in the packaging samples can be achieved using multiple headspace extraction (MHE), for example (Perkins and Langford (2022b)).

3. Samples

A variety of polymer and paper-based samples were analyzed in this feasibility study (Table 2). Sample sizes utilized for polymers and paper were 1 g and 0.5 g, respectively, placed in 20 mL headspace vials. A single replicate of each sample type was analyzed.

Table 2. *Polymer and paper-based samples analyzed in this study, together with sample identification details.*

Sample Type	Virgin or Recycled	Cleanliness or Grade	Identifier used
High-density polyethylene (HDPE)	Virgin	Scientific grade	HDPE - Scientific
	Virgin	Craft grade	HDPE - Craft (Economy)
	Recycled	Clean	HDPE - Reclaim - Clean
	Recycled	Dirty	HDPE - Reclaim - Dirty
Polypropylene (PP)	Virgin	Scientific grade	PP - Scientific
	Virgin	Craft grade	PP - Craft (Economy)
	Recycled	Clean	PP - Reclaim - Clean
	Recycled	Clean (consumer best case)	PP - Reclaim - Cons. Best
	Recycled	Clean (consumer worst case)	PP - Reclaim - Cons. Worst
Polyethylene terephthalate (PET)	Virgin	Scientific grade	PET - Scientific
	Virgin	Craft grade	PET - Craft (Economy)
Polyethylene (PS)	Virgin	Scientific grade	PS - Scientific
Cardboard (2 samples)	Not known	Unprinted portion sampled from printed boxes	Cardboard - 1 Cardboard - 2
Paper (3 samples)	Virgin A4 paper	Clean, new paper	Paper - 1 Paper - 2 Paper - 3

Results and Discussion

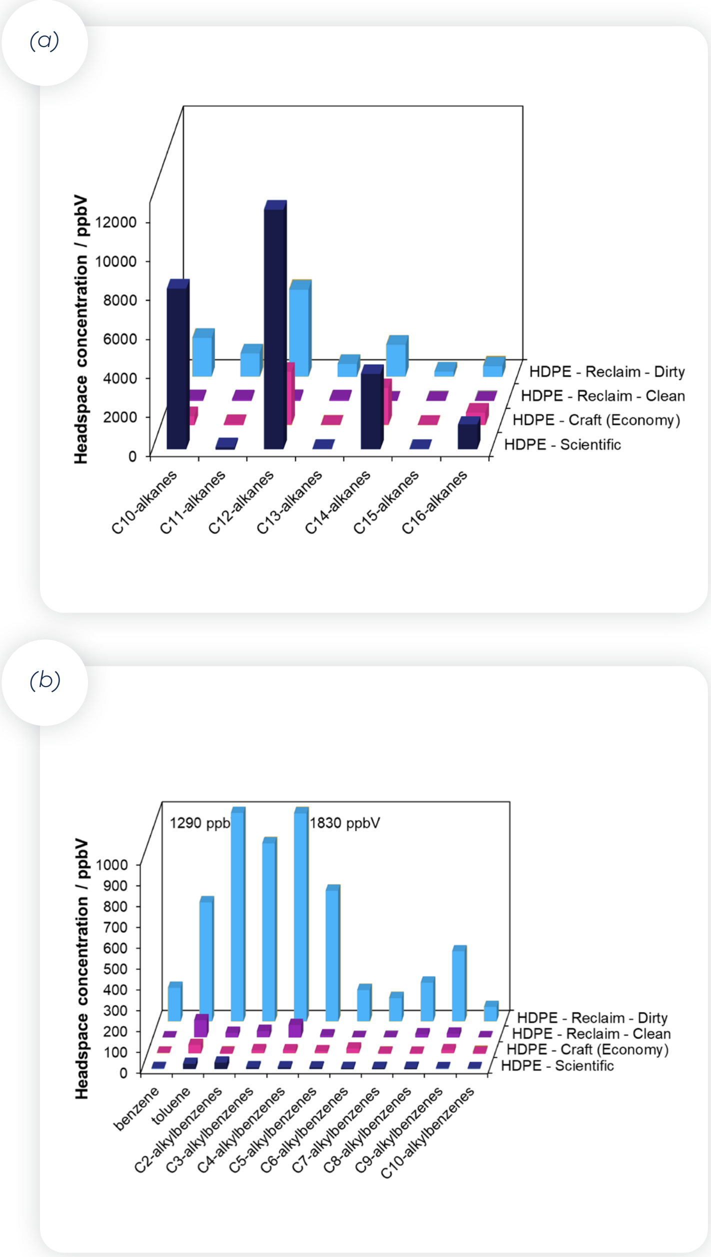
This section summarizes and discusses the results obtained for each sample type (Table 2). The concluding subsection discusses the benzene results obtained across the sample types.

1. High-Density Polyethylene (HDPE)

The MOSH and MOAH results obtained for the HDPE samples are summarized in Figure 3. Alkanes of even carbon number dominate due to polymer synthesis from ethylene (these are visible as dominant features in SIFT-MS full scan spectra of HDPE; see Langford and Perkins (2022)). For all but the "clean" reclaimed HDPE, these concentrations of C_{10}, C_{12}, C_{14}, and C_{16} are significant and could contribute significant MOSH residue to any product that they contain.

MOAH residues are lower than MOSH residues, though in the "dirty" reclaimed HDPE they are significant – including benzene. Benzene is not detectable in "clean" reclaimed HDPE, however is at low ppbV levels in both virgin samples.

Figure 3. Headspace concentrations (in ppbV) determined using automated SIFT-MS for (a) MOSH and (b) MOAH compounds in various HDPE samples.

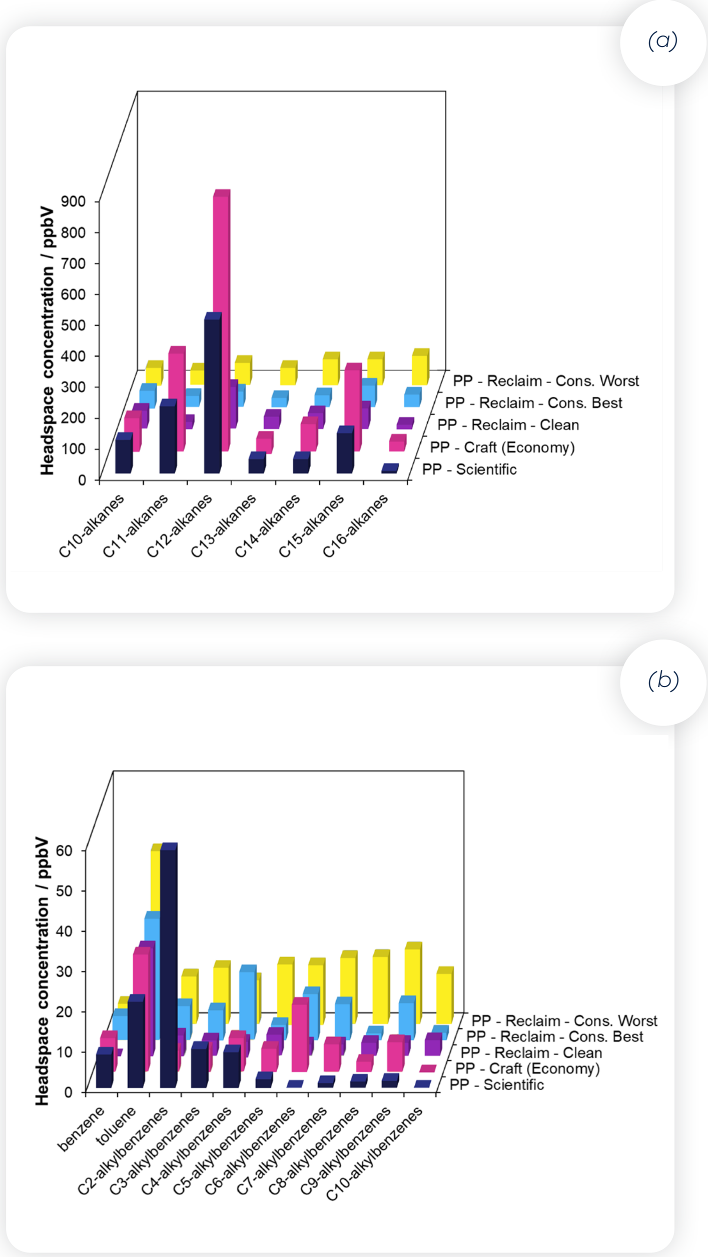


2. Polypropylene (PP)

Figure 4 shows the MOSH and MOAH results obtained for the five PP samples. The C_{12} and C_{15} features are prominent in the MOSH data for virgin samples due to partially polymerized propylene, but at much lower levels than the residues observed for HDPE (Figure 3). Interestingly, significant C_{11} alkanes are present as well. MOSH components are generally at lower concentrations in the reclaimed products, but this trend reverses for the highest molecular weight analyzed here (C_{16}).

All samples have some aromatic (MOAH) content (especially C_1 to C_5), but benzene (C_0) is only elevated in the reclaimed PP – interestingly in "best case" as well as "worst case" samples, and at similar levels for each.

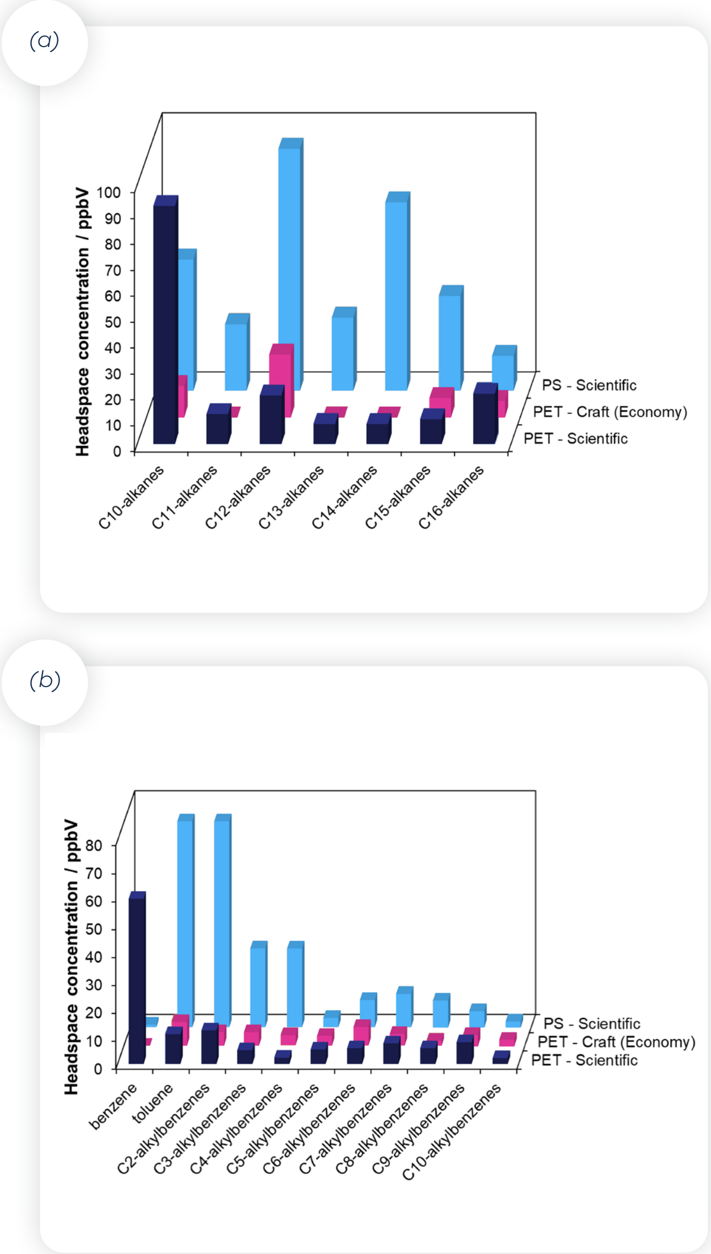
Figure 4. Headspace concentrations (in ppbV) determined using automated SIFT-MS for (a) MOSH and (b) MOAH compounds in various PP samples.



3. Polyethylene terephthalate (PET)

Only two samples of PET were analyzed (Figure 5) and these had the lowest levels of MOSH detected of any samples in this study. For MOAH, benzene was undetectable, but trace concentrations of C_1 to C_{10} alkyl aromatic compounds were detected in both samples (<12 ppbV in all cases).

Figure 5. Headspace concentrations (in ppbV) determined using automated SIFT-MS for (a) MOSH and (b) MOAH compounds in samples of PET and PS.



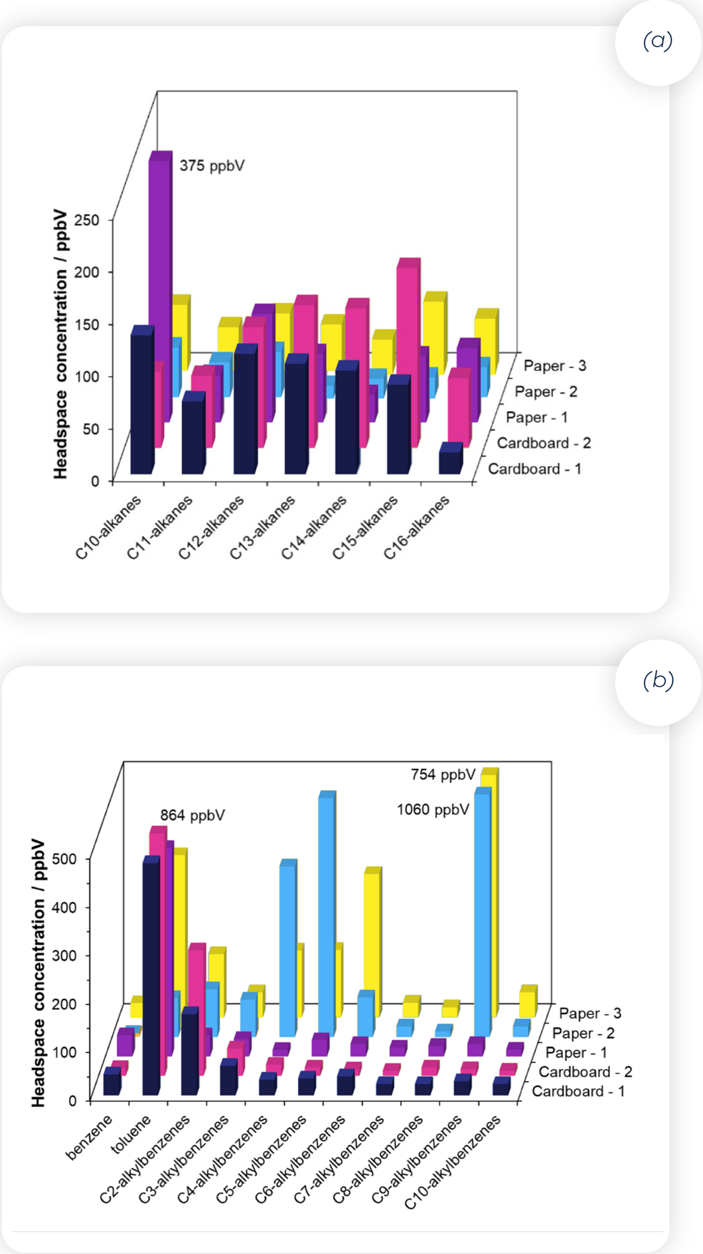
4. Polystyrene (PS)

Figure 5 shows the single sample of PS analyzed in this study. Low levels of MOSH compounds were detected, while – unsurprisingly considering the monomer – some MOAH were detected (dominated by C$_1$ to C$_4$). Benzene was detectable, but at only ca. 1 ppbV.

5. Paper and Cardboard

The MOSH and MOAH results obtained for the paper-based products are summarized in Figure 6. Relatively low concentrations of all targeted alkanes are present across all samples, indicating that potential interference by aldehydes (especially of lower molecular weight) is not occurring. In contrast, samples vary markedly in the distribution of aromatic compounds, and some of these are higher than measured concentrations of the alkanes. Benzene is detected in all samples in the 7 to 43 ppbV range.

Figure 6. Headspace concentrations (in ppbV) determined using automated SIFT-MS for (a) MOSH and (b) MOAH compounds in various paper-based samples.



6. Benzene Impurities

While some of the samples analyzed in this study have revealed significant quantities of volatile MOSH and MOAH compounds, the detection of benzene in many samples (Figure 7) is of most concern due to its links to cancer and recent reports of it occurring in personal care products (Bettenhausen (2022), Valisure (2022)). As is shown in Table 1, two independent synchronous measurements of benzene were obtained and cross-compared for rejection of any interference. Furthermore, Langford, Graves, and McEwan (2014) have shown that SIFT-MS analysis of benzene agrees well with GC/MS analysis, even in complex matrices such as soil gas. These results, therefore, indicate that there is a need to expand benzene testing to packaging materials.

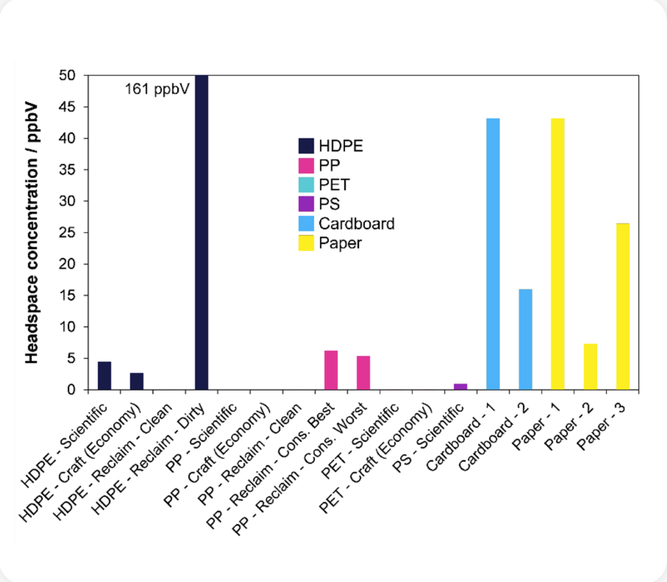


Figure 7. Benzene headspace concentrations (in ppbV) for all samples, determined using automated SIFT-MS.

Conclusions

- Simple, high-sensitivity SIFT-MS analysis readily detects volatile MOSH and MOAH compounds, including benzene.
- High-throughput automated analysis of over 220 samples per day, providing enhanced screening for volatile MOSH and MOAH.
- Low cost per sample due to simple sample preparation (no extraction, preconcentration, etc.!) and instrument operation.
- Ideally suited to quality assurance and quality control applications.
- Supports sustainability initiatives.

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