

RAPID SCREENING OF VOLATILE COMPOUNDS IN PAPERBOARD USING STATIC HEADSPACE-SIFT-MS

Combining the power of direct analysis using selected ion flow tube mass spectrometry (SIFTMS) with static headspace (SH) analysis, diverse volatile compounds — such as organic acids, aldehydes and reduced sulfur compounds — are detected and quantified rapidly and economically. This application note describes the application of SH-SIFT-MS to the detection of very diverse volatiles in eleven paperboard samples with analysis times of less than one minute per sample.

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INTRODUCTION

Wood-based products such as paperboard contain chemically diverse volatile organic compounds (VOCs) that arise from both the natural sourced materials and subsequent processing. These include terpenes, aldehydes, organic acids, and reduced sulfur compounds. Applying conventional chromatographic methods to these diverse species involves significant sample preparation – including derivatization for the short-chain aldehydes and organic acids – and specialized columns for the low molecular weight organosulfur species. This means that screening of paperboard products using traditional methods is expensive and not feasible for implementation on a wide scale.

Direct mass spectrometry (DMS) that eliminates chromatography and applies soft chemical ionization has potential to provide rapid, economic screening of paperboard products. Of the available DMS methods, selected ion flow tube mass spectrometry (SIFT-MS) is unique because it has eight rapidly switchable standard reagent ions that detect the widest range of compounds and provide maximum selectivity.

This study applies SH-SIFT-MS to the measurement of a wide range of volatile compounds in paperboard. With sample throughputs of up to 20 samples per hour, SH-SIFT-MS screening of paperboard is very economical.

METHOD

1. The SIFT-MS technique

SIFT-MS^{1,2,3} (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). 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).⁴

Rapid switching between reagent ions provides high selectivity, because the multiple reaction mechanisms provide additional independent measurements of each analyte. The multiple reagent ions also help to remove uncertainty from isobaric overlaps in mixtures containing multiple analytes.

Targeted analyses were run in Selected Ion Mode (SIM) using a Voice200ultra SIFT-MS instrument (Syft Technologies, Christchurch, New Zealand). Analytical methods were created using the Method Editor module in the LabSyft software package from Syft Technologies.

2. Automated SIFT-MS analysis

In SIFT-MS, the capability for rapid direct analysis of a sample provides unique opportunities for high-throughput headspace analysis, irrespective of whether the task is routine VOC monitoring or the analysis of chromatographically challenging species, such as

ammonia and formaldehyde. In contrast to chromatographic techniques that require rapid injection to achieve good peak shapes and temporal separation, SIFT-MS simply requires steady sample injection for the duration of the analysis – that is, sample injection and analysis occur simultaneously (Figure 2).

Automated headspace analysis was carried out at Anatune's laboratory using the above SIFT-MS instrument coupled with a GERSTEL MPS2 autosampler (GERSTEL, Mülheim an der Ruhr, Germany). Samples were first incubated in a GERSTEL agitator prior to sampling of the headspace and subsequent injection into the SIFT-MS instrument through a GERSTEL septumless sampling head. A make-up gas flow was also introduced through the sampling head to maintain the standard, nominally 25 sccm sample gas flow into the SIFT-MS instrument.

The GERSTEL MPS2 autosampler was controlled using GERSTEL's Maestro software. In addition to controlling the injection into the SIFT-MS instrument, the Maestro software's PrepAhead function allows for optimal scheduling of pre-injection preparation steps, such as syringe flush or incubation. This ensures that the highest sample throughput is achieved for the conditions described in this application note (Figure 3). In this figure, the different colors represent different actions that the autosampler undertakes, including vial movements, incubation, sample injection and syringe flushing. With the hardware and method conditions used here, throughputs of at least 12 samples per hour are achieved.

3. Samples and analysis conditions

Random paperboard samples were supplied by Mpack, South Africa (Table 1). Paperboard samples (21 cm x 4 cm; 1.3 grams) were placed in 20-mL headspace vials and incubated at 60 °C for 15 minutes. The headspace was sampled with a 2.5-mL headspace syringe heated to 150 °C, and injected at a flow-rate of 50 $\mu\text{L s}^{-1}$ into the SIFT-MS instrument's inlet which has a total flow rate of ca. 420 $\mu\text{L s}^{-1}$. All concentration data are corrected for dilution on injection into the SIFT-MS instrument, with the exception of the data in Figure 4.

SAMPLE CODE	1	2	3	4	5	6	7	8	9	10	11
ODOR RATING	3	3	2	2.25	2.5	2.5	2.75	2.75	2.75	2.5	1.5

Table 1. Paperboard sample codes and odor ratings.

RESULTS AND DISCUSSION

Figure 4 shows a representative profile (for sample 2) of continuous SIFT-MS analysis of headspace as it is injected into the instrument's inlet by the GERSTEL autosampler. All compounds are analyzed in one procedure using SIFT-MS, due to the soft chemical ionization that analyzes compounds directly (in contrast to chromatographic methods that usually analyze the derivatized forms). The analysis time for each sample was one minute and even more remarkable is that each measurement cycle in the time-resolved plot represents a chromatographic analysis.

All results obtained for SH-SIFT-MS screening of the eleven paperboard samples are shown in Figure 5 and summarized in detail in Table 2. Note that the current analytical method does not discriminate between isomeric forms within the sesquiterpene group; that is, a total is shown. Although the most abundant volatiles detected are methanol, hexanal, acetone, and pentanal, trace concentrations of short-chain fatty acids, reduced sulfur compounds (hydrogen sulfide and dimethyltrisulfide) and N-nitrosomorpholine are also readily detected.

CONCLUSIONS

This study demonstrates that SH-SIFT-MS is a very powerful new methodology for rapid determination of volatile compound concentrations in paperboard. Not only does SIFT-MS provide up to a 10-fold increase in sample throughput compared to SHGC-MS, but it also broadens the range of compounds detectable in a single analysis. SIFT-MS easily detects and quantifies polar species (such as the short-chain aldehydes and organic acids) and thermally labile species (e.g. the reduced sulfur compounds) without any need for derivatization, pre-concentration or headspace multiple chromatographic conditions. Hence SH-SIFT-MS can facilitate enhanced quality control through fast, economical screening of the widest range of volatiles.

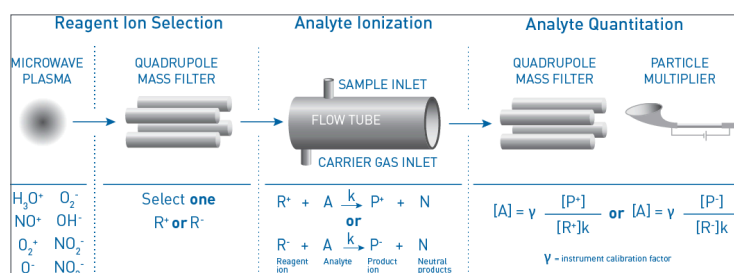


Figure 1. Schematic diagram of SIFT-MS – a direct chemical-ionization analytical technique

COMPOUND	1	2	3	4	5	6	7	8	9	10	11
formaldehyde	256	57	70	73	105	52	73	71	57	65	105
propanal	51	152	166	199	183	114	148	118	99	86	118
butanal	63	246	280	317	306	171	225	189	185	149	182
pentanal	93	910	925	1120	975	514	774	769	519	433	448
hexanal	315	3894	3300	3940	3000	2540	2870	3200	2050	1570	1390
heptanal	40	188	218	232	157	167	265	105	158	111	255
octanal	56	129	166	155	108	176	277	98	149	119	199
nonanal	60	98	105	97	95	124	152	83	82	69	127
decanal	19	42	32	28	34	31	33	39	29	28	60
acetic acid	373	323	161	174	n.d.	91	65	48	82	259	144
propanoic acid	51	196	91	184	173	159	100	223	44	31	45
acetone	941	1090	1290	1340	1470	1000	1070	902	994	831	984
methanol	1360	3220	5010	5970	9350	3360	4440	3680	8200	9950	13200
ethanol	796	713	623	665	644	528	399	385	764	735	660
tert-butyl alcohol	80	128	146	182	156	123	156	105	175	160	143
hydrogen sulfide	17	22	31	39	52	30	23	30	43	52	65
dimethyl trisulfide	26	83	90	83	77	69	112	87	68	59	57
N-nitrosomorpholine	6.7	51	84	72	64	43	54	28	57	55	70
sesquiterpenes	5.9	105	70	72	51	22	51	7.4	16	8.4	n.d.

Table 2. Concentrations of volatiles (in parts-per-billion by volume, ppbv) found in the headspace of paperboard samples. n.d. = not detected.

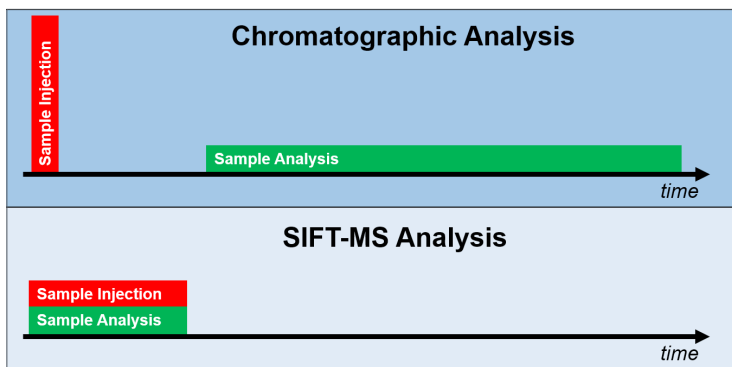


Figure 2. Graphical representation of the different sample-injection and analysis requirements of chromatographic techniques and SIFT-MS.

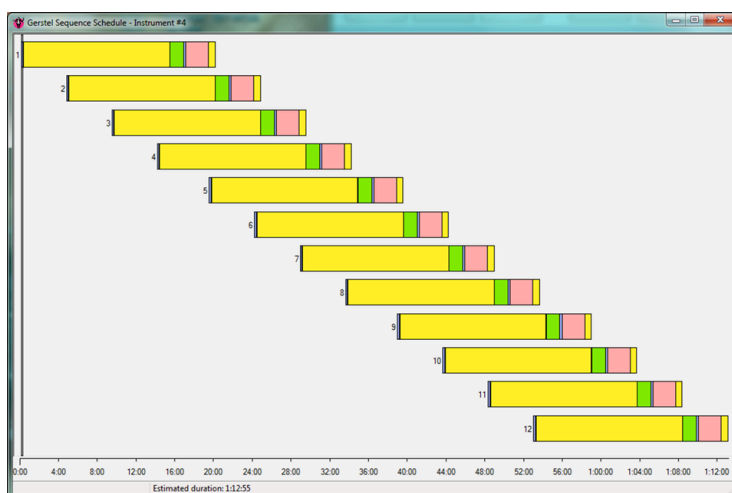


Figure 3. Sequences from the GERSTEL Maestro software for analysis of 11 paperboard samples and the blank using SIFT-MS. A throughput of at least 12 samples per hour is achieved.

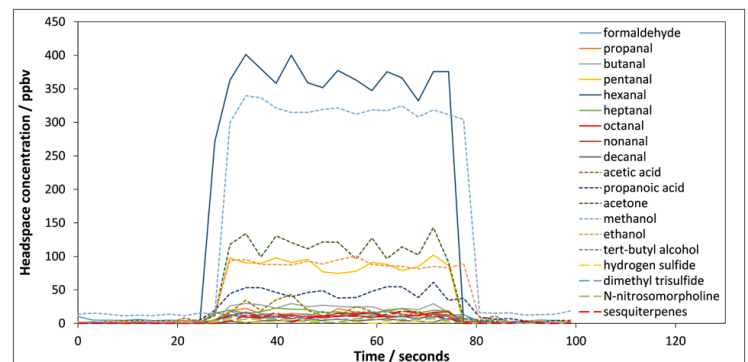


Figure 4. Representative profile (for sample 2) of SIFT-MS analysis of headspace as it is continuously injected into the instrument's inlet. Note that these data are not corrected for dilution on injection and do not have the blank subtracted. Corrected data are shown in Figure 5 and Table 2.

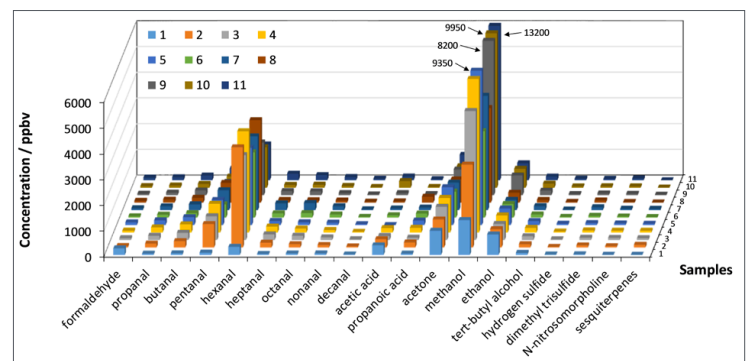


Figure 5. Static headspace-SIFT-MS analysis of eleven paperboard samples, illustrating the diverse compounds detectable in a single analysis over a wide concentration range.

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