

RAPID DETERMINATION OF VOLATILE COMPOUND CONTENT USING MULTIPLE HEADSPACE EXTRACTION-SIFT-MS

Combining the power of direct analysis using selected ion flow tube mass spectrometry (SIFT-MS), with the matrix-independent multiple headspace extraction (MHE) methodology, volatile compounds are quantified absolutely and economically. This application note describes the application of MHE-SIFT-MS to detection of C₁-C₁₀ aldehydes and other oxygenated volatile organic compounds (VOCs) in paperboard.

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INTRODUCTION

Pharmaceutical and food products are susceptible to contamination from volatile compounds present in packaging – whether from polymeric materials, printing inks, or paperboard. These compounds can also migrate through multiple layers of packaging, so it is critical to evaluate each material on a regular basis.

Traditional analytical techniques applied to trace volatile compound analysis typically involves significant sample preparation and low throughput. This is particularly true for multiple headspace extraction (MHE), which in principle provides a straightforward approach to determination of absolute concentrations of volatile compounds in solid matrices (such as packaging materials), independent of matrix effects. However, MHE requires a multiple-step analysis for each sample, as the name implies. This means that it is an expensive technique to employ in traditional routine testing, because conventional VOC analysis methods are based on relatively slow gas chromatography (GC) or liquid chromatography (LC). The current outcome for these techniques therefore, is that MHE is used in situations where it is the only option for the product, and only

limited product screening will be conducted.

This study evaluates the application of MHE-selected ion flow tube mass spectrometry (MHE-SIFT-MS) to the measurement of volatile compounds in paperboard, which is “rich” in volatile short-chain aldehydes. MHE-SIFT-MS is found to provide several benefits over traditional approaches due to its application of direct headspace analysis using soft chemical ionization:

1. Higher sample throughput,
2. Simple analysis of polar and non-polar volatiles, and
3. Elimination of derivatization, pre-concentration and other sample preparation steps.

These benefits make MHE-SIFT-MS analysis very economical.

METHOD

1. The SIFT-MS technique and its automation

The first application note in this series (Rapid Screening of Volatile Compounds in Paperboard using Static Headspace SIFT-MS) gives an introduction to SIFT-MS and its application to automated analysis. See references 1-3 for more information on SIFT-MS.

2. Multiple headspace extraction (MHE)

Static headspace analysis provides concentrations that can be correlated with actual quantities in the sample itself only with difficulty, due to matrix-dependent interactions with volatile compounds or byproducts. The multiple headspace extraction (MHE) technique⁴ is a headspace technique that calculates the total concentration from a limited number of consecutive headspace analyses by recognizing that the decrease in concentration over multiple headspace measurements is exponential. A headspace concentration is generated, the concentration measured and then flushed or vented and a new headspace generated (Figure 1). Typically six cycles are utilized in complete analysis of one sample, which makes it a very costly technique when coupled with GC-

MS, with each measurement taking tens of minutes. By utilizing rapid SIFT-MS measurement instead, headspace regeneration becomes the rate-limiting step, but with GERSTEL's PrepAhead software, multiple headspace samples can be analyzed in parallel.

3. Samples and analysis conditions

Random paperboard samples were supplied by Mpact, South Africa. Sample "2" from the first application note was used in the present MHE study (odor rating 3). Replicates of paperboard sample 2 (linear dimensions 21 cm x 4 cm; mass 1.3 grams) were placed in four 20mL headspace vials and incubated at 75 °C for 20 minutes, followed by a 3-minute post-measurement flush. Headspace was sampled with a 2.5mL headspace syringe heated to 150 °C, and injected at a flowrate of 50 $\mu\text{L s}^{-1}$ into the SIFT-MS instrument's inlet together with the make-up gas, giving a total flow rate of ca. 420 $\mu\text{L s}^{-1}$. Due to the rapid SIFT-MS analysis, 10 MHE cycles were measured for each replicate sample, but only cycles 1-6 were utilized in calculations according to the conventional approach used with GC-MS.⁴

RESULTS AND DISCUSSION

Figure 2 shows the headspace concentration data (in ppbv) obtained for measurement cycles 1, 6, and 10 for all four replicate samples, together with the mean of the replicates. The relative standard deviations (RSDs as a percentage) are summarized in Table 1. Generally RSDs increase as a function of reducing volatility and/or concentration as analyte recovery becomes more challenging at very low ppb levels. Nevertheless, for all compounds repeatability is excellent for injections 1 to 4.

Calculation of the volatile concentrations in the paperboard itself is undertaken after visually confirming that the data conform to expectations. Example plots of the six MHE injections used in the calculation are shown in Figure 3 for acetaldehyde and nonanal, which roughly span the volatility and concentration range encountered in this study. The logarithmic plots show pleasing linearity.

Figure 4 shows the concentrations (in $\mu\text{g g}^{-1}$) of the various oxygenated VOCs in paperboard sample 2 for all four replicates. In addition, the results obtained from averaging the data are also shown. Agreement between these approaches is very good. These data are also summarized in Table 2, together with the RSDs across the replicates. RSDs less than 10% are good for this type of analysis and at low-ppb headspace concentrations (e.g.

nonanal and decanal), acceptance criteria are typically 20%.

CONCLUSIONS

This study demonstrates that MHE-SIFT-MS is a very powerful new methodology for rapid determination of volatile compounds in paperboard. Not only does SIFT-MS provide a four-fold increase in sample throughput compared to MHE-GC-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 small aldehydes without any need for derivatization or pre-concentration. MHE-SIFTMS can facilitate enhanced quality control through faster screening of a wider range of volatiles.

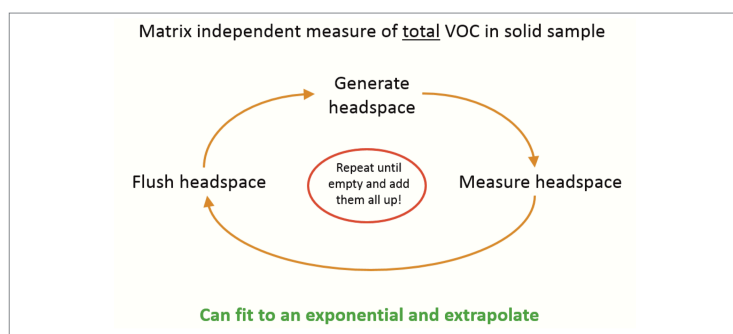


Figure 1. Schematic representation of the MHE technique.

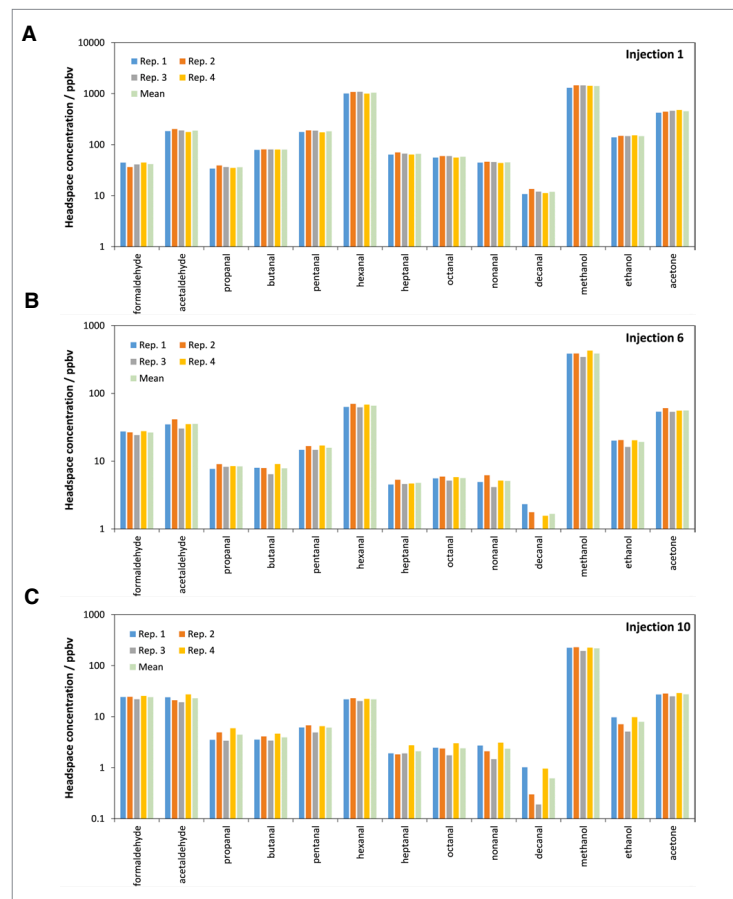


Figure 2. Measurement repeatability across all target compounds for the (a) first, (b) sixth, and (c) last (tenth) injections in the MHE procedure. Headspace concentrations (in ppbv) for the four replicates are shown, together with the mean, on a logarithmic scale.

Table 1. Relative standard deviations (RSDs as a percentage) obtained for the four replicate samples for all analytes across 10 MHE injections.

Injection Number	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Nonanal	Decanal	Methanol	Ethanol	Acetone
1	8.1	4.8	5.3	1	3.8	3.9	4.1	3.4	2.2	8.9	4.5	3.3	4.6
2	9.5	5.7	6.9	4.4	4.7	5.9	6.9	8.7	6.2	9.6	6.1	4.4	3.8
3	6.5	5	2.7	5.5	3	4.4	3.6	3.6	6.8	5.6	1.5	2.9	1.3
4	7.3	6.3	5.6	4.2	4.6	3.6	4.4	2.1	6.2	7.9	2.1	3.5	2.5
5	7.3	5.5	4.1	7.1	7.1	4.3	8.1	5.7	8.3	21.4	6.4	12.8	5.8
6	5.2	11.1	5.8	12	6.8	5	6.5	5.2	14.3	27.9	7.6	9.2	5.1
7	1.1	8.2	7.4	8.8	6	4.2	8.8	8	7.9	101.1	6.9	12.2	4.8
8	5	10	8.6	2.7	6.5	4.2	7.8	6.4	9.9	22.5	4.9	7.9	3.6
9	5.4	8.5	12.8	7.6	5.9	3.5	10	16	10.6	37.3	4.8	14.1	7.3
10	5.5	13.5	23.8	12.5	11.7	4.6	18.1	18.6	26.4	60.7	6.5	24.7	5.4

Table 2. Concentrations of volatiles (in $\mu\text{g g}^{-1}$) found in paperboard sample 2 using MHE-SIFT-MS. Concentration data and RSDs for the four replicate analyses are shown.

Parameter	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Nonanal	Decanal	Methanol	Ethanol	Acetone
Rep 1	0.088	0.164	0.043	0.088	0.218	1.338	0.102	0.108	0.100	0.035	1.954	0.079	0.328
Rep 2	0.104	0.182	0.05	0.088	0.237	1.429	0.113	0.115	0.105	0.037	2.012	0.082	0.345
Rep 3	0.078	0.154	0.045	0.083	0.226	1.397	0.102	0.111	0.095	0.028	1.893	0.074	0.341
Rep 4	0.093	0.164	0.048	0.093	0.227	1.361	0.102	0.112	0.100	0.030	2.267	0.086	0.362
Mean (1-4)	0.091	0.166	0.047	0.088	0.227	1.381	0.105	0.111	0.101	0.032	2.032	0.08	0.344
SD (1-4)	0.011	0.01	0.002	0.003	0.007	0.035	0.005	0.003	0.005	0.004	0.142	0.004	0.012
%RSD (1-4)	11.8	6.1	5.2	4.0	2.9	2.5	4.3	2.3	4.7	11.4	7.0	5.6	3.5

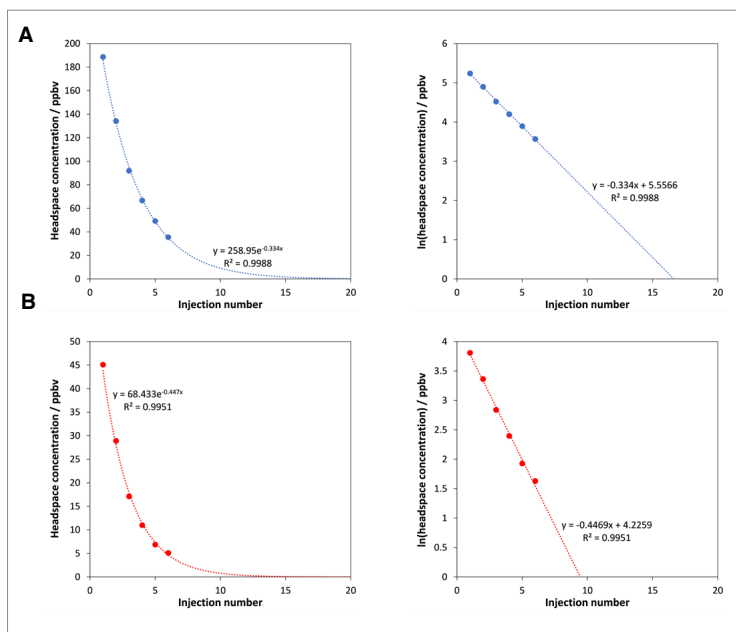


Figure 3. Example plots of the MHE injections for (a) acetaldehyde and (b) nonanal, showing the linear and logarithmic variants and associated fits used to calculate concentrations in the paperboard sample.

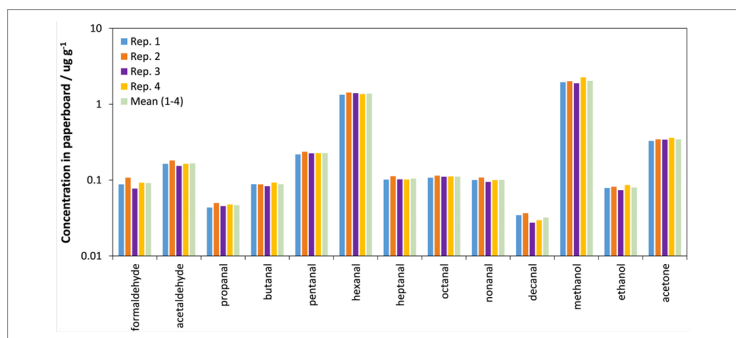


Figure 4. Repeatability of concentration measurements (in $\mu\text{g g}^{-1}$) for the four replicate analyses on sample 2. The mean calculated from averaging the final result from the individual MHE analyses is also shown. Note the concentration scale is logarithmic.

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