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RAPID ODOUR SCREENING OF PAPERBOARD USING STATIC HEADSPACE-SIFT-MS

Combining the power of direct analysis using selected ion flow tube mass spectrometry (SIFT-MS) with static headspace (SH) analysis, diverse odour compounds – such as short-chain organic acids, aldehydes and reduced sulfur compounds – are detected and quantified rapidly and economically. Processing the instrumental data using multivariate statistics enables a preliminary evaluation to be made of the correlation with odour panel ratings. SH-SIFT-MS shows promise as an instrument-based odour rating technique, with a throughput of at least 12 samples per hour in the current configuration.

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INTRODUCTION

Paperboard contain chemically diverse volatile organic compounds (VOCs) that arise from both the natural sourced materials and subsequent processing. A number of these compounds impart odours to the products, including short-chain aldehydes and organic acids, as well as reduced sulfur compounds.

The traditional approach to quantifying odour uses a trained sensory panel, which is expensive. Viable instrumental alternatives for determining are few:

- The gold-standard VOC analysis methods (gas chromatography, GC, gas chromatography-olfactometry, GC-O, and liquid chromatography, LC) struggle with the diversity of compounds and require significant simple preparation – including derivatization for the short-chain aldehydes and organic acids.
- Electronic noses are subject to significant drift, susceptible to contamination and false positive readings, and cannot identify individual odour components.
- Traditional direct mass spectrometric (DMS) methods are too harsh or not selective enough to profile all odour compounds.

Selected ion flow tube mass spectrometry (SIFT-MS), on the other hand, is a direct mass spectrometry (DMS) that eliminates chromatography and applies soft chemical ionization, and in doing so can selectively detect and quantify a very wide range of odour compounds in real time.

In this application note, we make a preliminary investigation of the correlation between traditional odour ratings for paperboard and instrumental analysis using SH-SIFT-MS coupled with multivariate statistical analysis.

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. Samples and analysis conditions

Random paperboard samples were supplied by Mpact, 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 flowrate of 50 μL s^{-1} into the SIFT-MS instrument's inlet together with the make-up gas, giving a total flow rate of ca. 420 μL s^{-1}.

Replicate measurements of each sample were not made in this study because between-sample repeatability is very good (see application note, Rapid Determination of Volatile Compound Content using Multiple Headspace Extraction-SIFT-MS). To obtain necessary replicates for statistical analysis, individual data from the sample injection were extracted.

SAMPLE CODE	1	2	3	4	5	6	7	8	9	10	11
ODOUR RATING	3	3	2	2.25	2.5	2.5	2.75	2.75	2.75	2.5	1.5
ODOUR LABEL IN FIGURES	OR 3	OR 3	OR 2	OR 2.25	OR 2.5	OR 2.5	OR 2.75	OR 2.75	OR 2.75	OR 2.5	OR 1.5

Table 1. Paperboard sample codes together with their odor ratings and the labeling convention used in the figures.

3. Multivariate statistical analysis

The SIFT-MS SIM data were treated using multivariate statistical analysis to determine the ability of SIFT-MS to discriminate between the paperboard samples.

The multivariate statistical methodology utilised was Soft Independent Modelling by Class Analogy (SIMCA), which was developed by Wold in the 1970s.[4] SIMCA applies principal component analysis (PCA) to the whole dataset and to each of the classes with the end goal of creating a model that discriminates each class from the others. The Infometrix® Inc. (Bothell, WA) implementation of the SIMCA algorithm in the Pirouette software package was employed here.

Three types of output from the SIMCA analysis are presented in this report:

1. **Class projections:** These three-dimensional plots show how each sample falls with respect to the three most important principal components derived from PCA on the entire data set. Each user-defined class shows the sample with the same colour and a 'cloud' representing the calculated space in which all samples of the class are expected to lie. Better class separations lead to more confident assignment of unknown samples to a predefined class, if a suitable one exists.
2. **Interclass distances:** These are a measure of the separation between classes. A value of three (3) is usually considered acceptable for class separation.[5] Sometimes the class separability indicated by these distances is not apparent in the three-dimensional class projection plot.
3. **Discriminating power:** This parameter helps variables to be identified that provide the most discrimination between the classes. A variable with larger discriminating power has greater influence on separating the classes than one with a small discriminating power. There does not appear to be a set threshold value above which a discriminating power is considered "good", because these values vary strongly with interclass distance.

RESULTS AND DISCUSSION

The instrument data used in this study are shown in Table 2. These data differ from those given in the first application note in this series because they include several additional target compounds, blanks were not subtracted, and concentration data were not corrected for dilution on injection into the SIFT-MS instrument. The limited sample set investigated here utilised the same blanks and dilutions, which means that they are irrelevant to the multivariate statistical analysis.

1. Evaluation of ability to discriminate all samples independent of odour rating

The ability of SH-SIFT-MS to discriminate the samples in Table 1 independent of the odour panel's ratings was evaluated simply by assigning each of the samples its own class in the SIMCA algorithm (for example, sample 1 was class 1, sample 2 was class 2, and so on through to sample 11 (class 11)). The class projections are shown in Figure 1, providing a two-dimensional view of the separation. The interclass distance metrics are summarised in Table 3, showing overall that reasonable separation is achieved. Red cells show where separation is incomplete (less than 3) according to convention.

The dominant compounds contributing to separation of the paperboard samples are summarised in Table 4. Other than methanol, the list is dominated by the short-chain aldehydes, although the volatile fatty acids, hydrogen sulfide and the sesquiterpenes also contribute.

2. Evaluation of the correlation between odour ratings and SH-SIFT-MS analysis

Table 1 summarises the odour ratings obtained for the 11 paperboard samples using a trained sensory panel. Odour and instrument correlation was carried out by creating classes for each of the six odour ratings. Figure 2 summarises the results obtained from SIMCA analysis of these paperboard samples. Methanol and several aldehydes again dominate the list of compounds that are most effective at discriminating between odour ratings. The most odorous samples (odour rating 3; samples 1 and 2) and least odorous (odour rating 1.5; sample 11) are readily distinguishable from all of those in the 2 to 2.75 range. For this range, there is some overlap. However, overall reasonable prediction potential is provided in this preliminary study.

Identical (or even similar) odour ratings obtained using sensory panels (e.g. Table 1) can arise from dissimilar odour descriptors attributed by trained odour panelists, because all the sensory information is distilled as a single parameter.

Table 2. Concentrations of volatiles (in parts-per-billion by volume, ppbv) found in the headspace of paperboard samples.

n.d. = not detected.

	SAMPLE										
COMPOUND	1	2	3	4	5	6	7	8	9	10	11
formaldehyde	30.8	12.7	13.5	14.1	16.8	11.9	13.7	13.9	12.5	13.3	17
propanal	6.51	16	17.6	19.8	18.9	12.3	15	12.7	10.5	9.38	13
butanal	7.28	24.6	27.5	31.1	29.8	17.6	22.5	19.1	18.5	15.1	18.2
pentanal	10.5	88.2	87.6	107	93.4	51.3	75.6	74.4	51.4	42.4	43.7
hexanal	32.1	368	311	371	284	237	271	303	194	150	133
heptanal	4.33	18.4	21.1	22.5	15.2	16.1	25.4	10.4	15.4	11.3	24.5
octanal	6.09	12.8	16	14.9	10.5	17	26.7	9.18	14	11.5	19.5
nonanal	6.75	10	10.2	9.67	9.44	11.7	15.1	8.56	8.31	7.15	11.9
decanal	2.09	4.28	3.23	3.07	3.56	2.98	3.42	3.93	3.09	3.45	6.08
furfural	1.76	1.68	1.45	1.72	2.38	1.2	2.07	2.78	2.27	1.66	2.84
acetic acid	14.3	20.1	12	21.8	19.7	35.6	29.4	41.6	14	9.69	5.13
propanoic acid	23.1	46.7	37.4	53	47.7	45.7	35.7	56.6	13.7	10.5	12.2
acetone	100	115	134	139	151	107	113	98.1	109	91.6	105
methanol	146	319	486	580	886	329	436	362	785	958	1250
ethanol	97.3	89.2	80.1	84.8	82.4	71.1	59	57.4	93.5	90.6	83.8
tert-butyl alcohol	8.99	13.3	15.2	18.2	16.8	12.3	16	11.6	18	16.3	14.9
1-hydroxy-4-ethylbenzene	1.24	1.68	1.59	1.15	1.27	1.47	2.22	0.91	1.25	1.29	0.91
gamma-nonalactone	0.8	0.81	0.9	2.4	1.29	0.57	0.76	1.13	3.16	2.56	1.06
gamma-decalactone	1.07	1.77	1.58	1.69	1.83	2.21	2.95	1.72	1.69	1.77	2.01
hydrogen sulfide	1.87	2.59	3.29	4.05	5.15	2.95	2.53	3.11	4.05	5.1	6.5
dimethyl disulfide	1.06	3.84	2.77	3.89	2.74	3.18	2.46	2.72	2.03	2.16	2.22
dimethyl trisulfide	3.21	8.65	8.99	8.45	7.8	7	11.5	9.11	7.16	6.33	6.03
N-nitrosomorpholine	1.16	4.94	8.21	7.33	6.37	4.48	5.67	2.79	5.29	5.65	6.83
sesquiterpenes	1.22	10.6	7.3	4.43	5.46	2.78	5.5	1.36	2.21	1.46	0.52

This is in fact the case for the samples analyzed in this evaluation – samples with the same odour rating do not necessarily have the same odour descriptors. Use of a single value for odour rating provides a special challenge for analytical instrumentation since there is less reliance on individual chemical markers of a particular odour, and rather more on discriminating between profiles. By coupling SIFT-MS with multivariate statistical analysis, this challenge can be addressed effectively – at least in terms of separating odour ratings at an integer level.

CONCLUSIONS

This preliminary evaluation demonstrates that SH-SIFT-MS has potential to provide odour ratings of paperboard samples. SH-SIFT-MS measurements coupled with multivariate statistical analysis can be used to reduce the multi-compound data set to a single parameter: the odour rating traditionally provided by a sensory panel. The combined instrumental and statistical approach used here could facilitate enhanced quality control through fast, economical screening of the widest range of volatiles

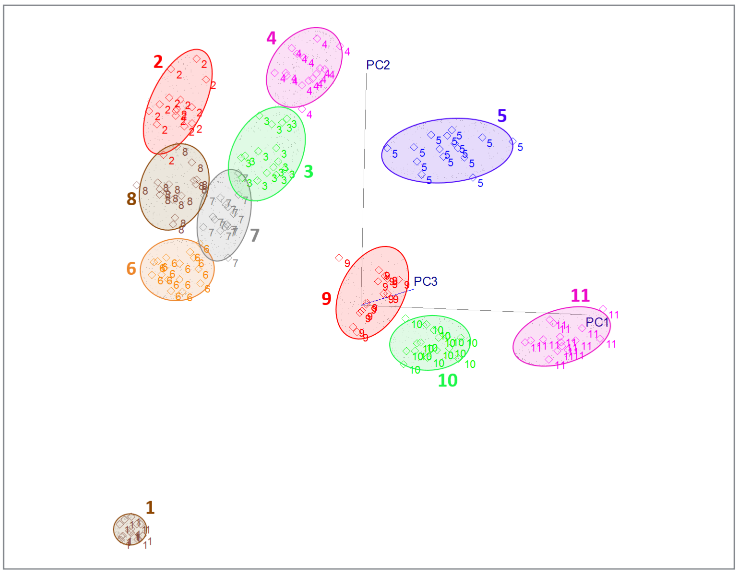
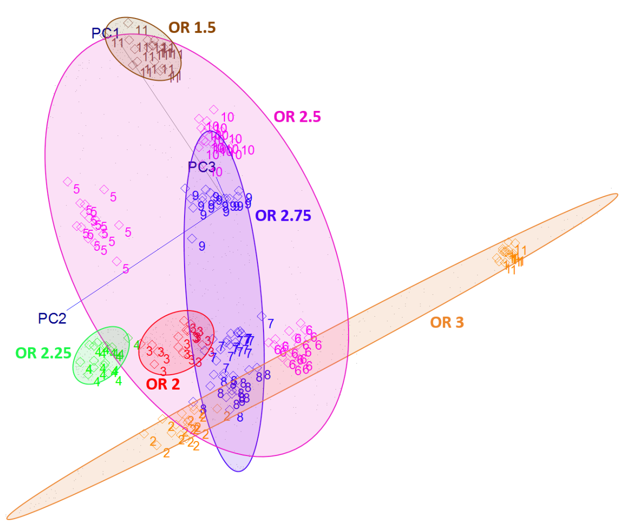


Figure 1. Class projections (obtained using the SIMCA multivariate statistical analysis algorithm) that visually indicate the degree of separation of the 11 paperboard samples.

CLASS PROJECTIONS



INTERNAL DISTANCES

ODOUR RATING	2	2.25	2.5	2.75	3
1.5	13.4	18.3	6.3	7.5	38.7
2		2.5	4.2	2.4	6.0
2.25			7.3	4.6	13.5
2.5				1.4	16.5
2.75					9.6

DISCRIMINATING POWER (DP)

COMPOUND	D.P.
methanol	2810
hexanal	669
formaldehyde	508
pentanal	482
sesquiterpenes	326
acetone	159
acetic acid	138

Figure 2. SIMCA multivariate statistical analysis of the 11 paperboard samples according to odour rating/value in Table 1.

SAMPLE	2	3	4	5	6	7	8	9	10	11
1	14.7	15.4	24.2	31.5	12.1	18.4	15.0	23.8	39.2	51.1
2		5.95	10	20.5	3.75	6.9	4.03	18	28.9	41.9
3			2.45	3.69	4.32	2.68	2.73	4.91	9.74	13.4
4				6.75	8.99	6.5	6.04	6.03	11.4	18.3
5					11.4	16.6	6.39	4.61	7.92	10.1
6						5.11	2.18	8.72	14.5	20.1
7							3.85	12.4	22.0	34.7
8								8.4	14.4	18.8
9									2.20	5.04
10										4.33

Table 3. Interclass distances (obtained using the SIMCA multivariate statistical analysis algorithm) that quantify the degree of separation of the 11 paperboard samples. Red text indicates values that are below the recognised threshold for separation (i.e. less than 3).

COMPOUND	DISCRIMINATING POWER
methanol	3370
hexanal	518
pentanal	365
formaldehyde	360
acetone	357
propanoic acid	264
heptanal	252
sesquiterpenes	230
nonanal	216
hydrogen sulfide	210
acetic acid	200

Table 4. Discriminating powers (obtained using the SIMCA multivariate statistical analysis algorithm) ranking the compounds that most contribute to distinguishing of the 11 paperboard samples.

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