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# Identification of Off-Odor Compounds in Paper Products using Thin Film Solid Phase Microextraction (TF-SPME) and GC-MS/O

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## Keywords

LabWorks Platform, Thin Film Solid Phase Micro-Extraction (TF-SPME), Gas Chromatography-Mass Spectrometry-Olfactometry (GC-MS/O), Olfactory Detection, Off-Odor Compounds, Sniff Port.

## Abstract

In this study, Thin Film Solid Phase Microextraction (TF-SPME) with a divinylbenzene/polydimethylsiloxane coating (DVB/PDMS) was used to extract off-odor compounds from paper product samples. The use of gas chromatography-mass spectrometry directly coupled with olfactory detection (GC-MS/O) enabled simultaneous detection of off-odor regions of the chromatogram and mass spectral identification of off-odor compounds. Identification of off-odor compounds in consumer goods is crucial for the manufacturer in order to identify the cause, take corrective action, and thereby maintain brand acceptance and success.

## Introduction

Off-odors in materials, food, beverages, and consumer goods in general, are a major problem globally; they lead to consumer complaints, a perception of inferior quality, brand damage, and adverse publicity. Complaints and a damaged reputation can be extremely costly to the manufacturer and can diminish the value of the brand. The compounds responsible for off-odors typical-ly present an analytical challenge since they generally have low odor thresholds making them difficult to identify especially when present in complex matrices. As a result, the chromatographic differences found between control and complaint samples are often unrelated to the off-odors. The use of an Olfactory Detection Port (ODP) coupled with gas chromatography-mass spectrometry (GC-MS) enables simultaneous identification of off-odor regions of the chromatogram and mass spectral determination of the off-odors. In many cases the compounds of interest are detected at the ODP, but are present in amounts below the limits of detection of the analytical instrument. High capacity extraction techniques must therefore be used to gain more mass-on-column and produce sufficient signal for compound identification.

Thin Film Solid Phase Micro-Extraction (TF-SPME) is an extension of regular SPME with increased surface area and phase volume, both of which lead to improved analyte recovery and higher overall sensitivity of the analysis. The TF-SPME device is a 20 mm x 4.8 mm carbon mesh sheet impregnated with a sorptive phase. For solid samples, the TF-SPME devices are typically used in headspace mode but they can also be placed in direct contact with solid samples to speed up and further increase analyte recovery.

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## Experimental

*Instrumentation*
GERSTEL Labworks Platform with Olfactory Detection Port (ODP 4) on Agilent GC-MSD

*Analysis Conditions LabWorks Platform*

| | |
|---|---|
| TF-SPME | PDMS/DVB |
| TDU 2 | splitless |
| | 40 °C (0.5 min), 720 °C/min to 250 °C (3 min) |
| CIS 4 | glass wool packed liner |
| | solvent vent (50 mL/min), split 10:1 |
| | -120 °C (0.2 min), 12 °C/sec to 280 °C (3 min) |
| ODP 4 | transfer line: 280 °C |
| | mixing chamber: 150 °C |

*Analysis Conditions GC*
Agilent 8890 GC

| | |
|---|---|
| Column | 30 m Stabilwax-MS (Restek) |
| | $d_i$=0.25 mm, $d_f$=0.25 µm |
| Pneumatics | He, $P_i$ = 13.5 psi |
| | Constant Flow 1 mL/min |
| Oven | 35°C (2 min), 10°C/min to 240°C (3 min) |

*Analysis Conditions MS*
Agilent 5977 MSD

| | |
|---|---|
| full scan | 40 – 350 amu |

*Sample Preparation*
Five paper products (Samples 1-5) were obtained from the manufacturer. Two products, samples 1 and 2, were control samples with no off-odors. The other three, samples 3-5, were complaint samples with an off-odor described as fishy/amine and pool liner/rubbery. A 0.5 g sample was cut from the center of each product and placed into a 10 mL screw-capped vial in direct contact with the TF-SPME device and left overnight (16 hours). The TF-SPME devices were subsequently placed into conditioned TDU tubes for analysis.

*Sample Introduction*
Samples were desorbed in splitless mode under a 50 mL/min helium flow at 250 °C for 3 minutes. Analytes were cold trapped in the CIS 4 inlet at -120 °C in the glass wool packed liner. When desorption was complete, analytes were transferred to the GC column in split mode (10:1) by heating the inlet rapidly to 280 °C.

*Olfactory detection*
For GC-O analysis the GC/MS was equipped with an Olfactory Detection Port (ODP 4). The column effluent was split 2:1 between the ODP 4 and mass spectrometer respectively. The ODP transfer line temperature was 280 °C. The mixing chamber was kept at 150 °C and purged with humidified nitrogen to prevent olfactory fatigue caused by dehydration of the nasal mucous membranes.

## Results & Discussion

The chromatographic profiles of all samples were very similar. However, the compounds N,N-dimethylformamide, 2-furanmethanol, and phenol were identified and were present in higher abundance in the complaint samples as shown in table 1. Peak areas were normalized to the peak areas for sample 1. No odor was detected at the ODP for 2-furanmethanol or phenol in any of the samples, indicating that these two compounds are not responsible for the off-odors detected. However, an odor described as rubbery/amine was sensed at the ODP for N,N-dimethylformamide in samples 3-5 only. While also present in the control samples, N,N-dimethylformamide was below the odor threshold and not contributing a detectable off-odor in those samples.

**Table 1:** Relative peak areas for selected analytes.

| Sample → | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| N,N-Dimethylformamide | 1.00 | 0.58 | 7.33 | 8.28 | 6.00 |
| 2-Furanmethanol | 1.00 | 0.94 | 4.65 | 1.95 | 12.01 |
| Phenol | 1.00 | 0.67 | 2.84 | 2.31 | 3.51 |

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A distinct fishy, amine aroma was detected from 2.94 – 3.25 min at the ODP, but no peak was present to allow identification. In addition, there were several other sections in the chromatogram in which a fishy or rubbery off-odor was detected, but either no peak was present or positive identification of the mass spectrum could not be made. The descriptors and retention times for these off-odor sections are shown in table 2.

**Table 2:** Aroma descriptors for off-odors in complaint samples.

| Start RT [min] | Stop RT [min] | Descriptor | Identity |
|---|---|---|---|
| 2.94 | 3.25 | fishy, amine | trimethylamine |
| 3.78 | 3.91 | fishy | |
| 7.53 | 7.58 | rubbery | |
| 10.96 | 11.14 | rubbery, amine | N,N-dimethylformamide |
| 20.03 | 20.12 | pool liner, rubber | |

To increase sensitivity a representative complaint sample, sample 5, was extracted with four TF-SPME devices, which were desorbed using multi-desorption mode and combined into a single GC/MS run. Figure 1 shows the overlay of the peaks from 2.1 – 7 min from the thermal desorption of a single vs. four TF-SPME devices.

As a result of the increased signal, the peak was identified as trimethylamine. However, there was not enough signal increase in the other regions of interest in the chromatogram to identify other off-odor compounds.
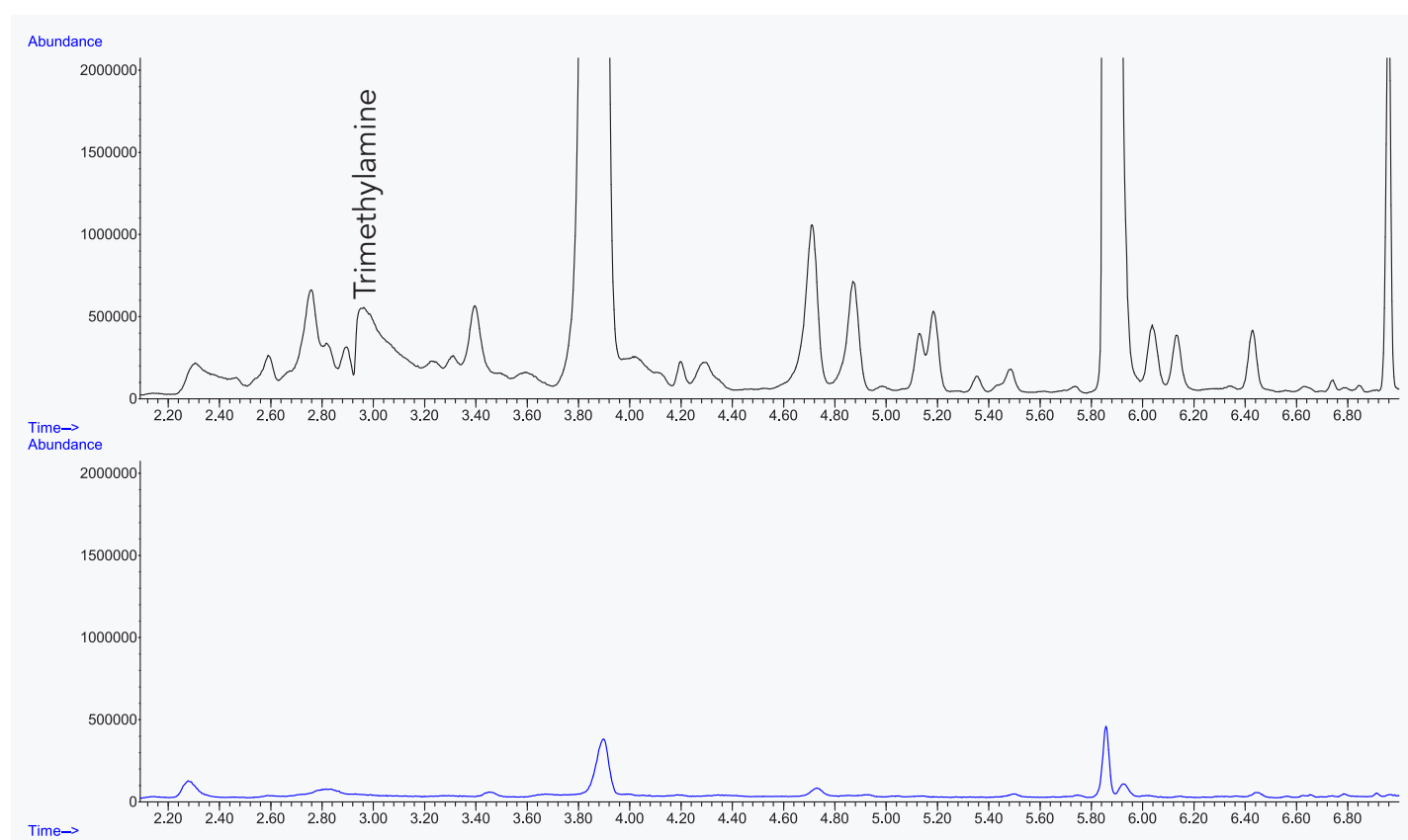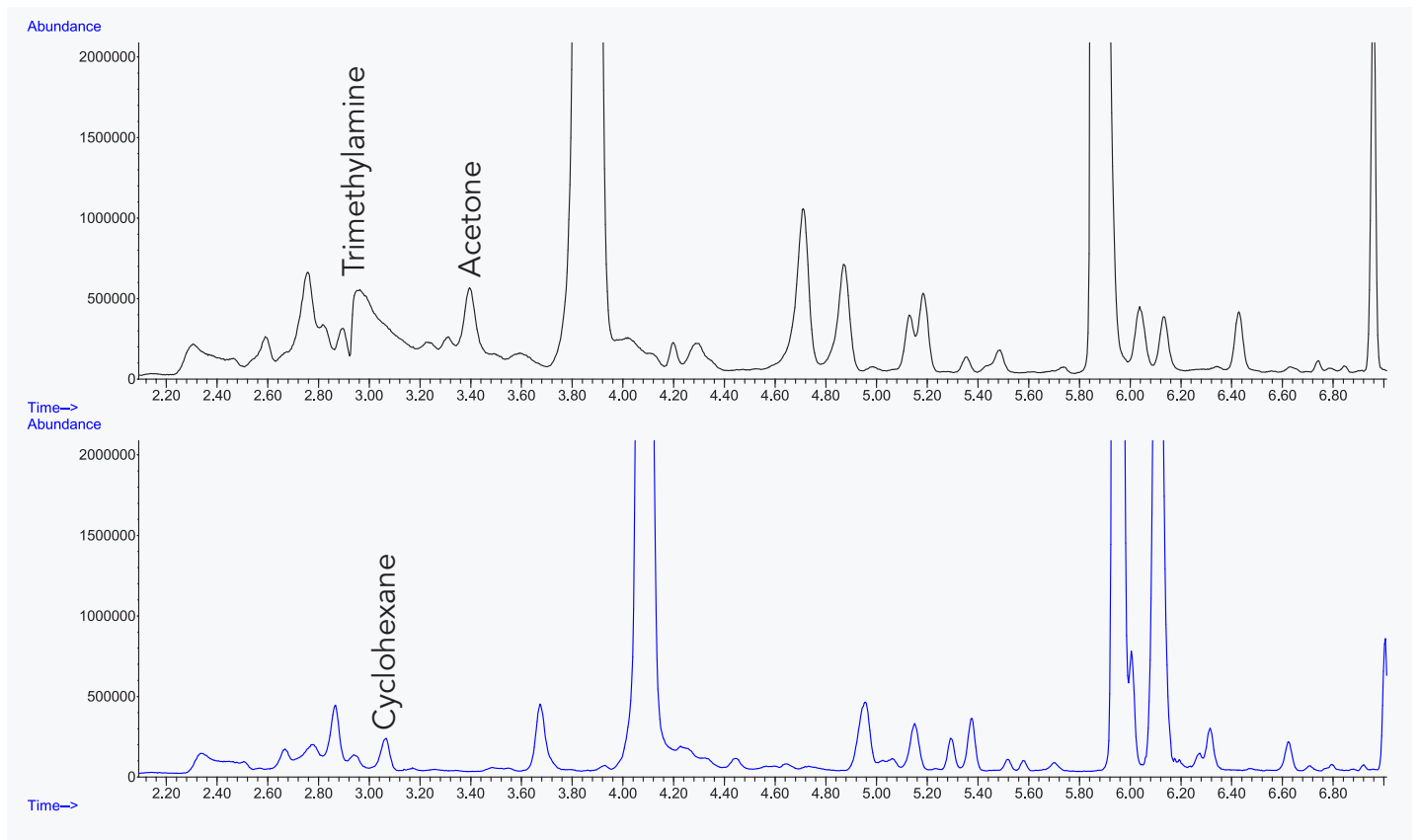


**Figure 1:** Stacked view of sample 5 chromatograms obtained from thermal desorption of a single TF-SPME device (blue) and of four TF-SPME devices in multi-desorption mode (black).

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To confirm that trimethylamine was the compound producing the off-odor, a representative control sample, sample 1, was also extracted with four TF-SPME devices that were desorbed in multi-desorption mode. There was no fishy odor detected in sample 1. Figure 2 shows the overlay of the peak from 2.1 – 7 min in samples 1 and 5. While two smaller peaks appear in sample 1, neither matches the mass spectrum for trimethylamine.



**Figure 2:** Stacked view of chromatograms, each obtained from thermal desorption in multi-desorption mode of four TF-SPME devices used to extract sample 1 (blue) and sample 5 (black).

## Conclusions

This study has demonstrated the ability of the GERSTEL Labworks Platform to perform TF-SPME extractions and GC-MS/O to identify off-odor compounds from paper products. Multi-desorption mode can be used to thermally desorb multiple TF-SPME extractions into a single GC-MS run to increase the mass-on-column and produce sufficient peak signal for compound identification. This approach could be readily used for troubleshooting incidences of off-odors in a variety of sample types.