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Identification of Off-Odor Compounds in Fragrance-Free, Cosmetic Face Wipes Using Sensory Directed Analysis

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Keywords

Off-odors, Fragrance, Cosmetics, Thin Film-Solid Phase Micro-extraction (TF-SPME), Selectable $^{1}D/^{2}D$-Gas Chromatography-Olfactometry/Mass Spectrometry ($^{1}D/^{2}D$-GC-O/MS), Sensory Directed Analysis (SDA)

Abstract

Fragrance-free is an increasing trend in personal care products. Consumers gravitate towards these products due to allergies, sensitivities, medical conditions, maintaining a neutral work environment, and avoiding overpowering scents. When these products contain off-odors, they become much more apparent to the consumer since there is no other fragrance to mask them, resulting in complaints and brand damage. This study used thin film-solid phase microextraction (TF-SPME) in a sensory directed analysis (SDA) approach to extract off-odor compounds from fragrance-free, makeup-removing face wipes. Selectable $^{1}D/^{2}D$-gas chromatography-olfactometry/mass spectrometry ($^{1}D/^{2}D$-GC-O/MS) enabled the separation of coeluting chromatographic regions and simultaneous detection of off-odor regions of the chromatogram and mass spectra for off-odor compound identification. Identifying off-odor compounds in consumer goods is crucial for the manufacturer to pinpoint the cause, take corrective actions, and maintain brand success.

Introduction

Off-odors in materials, foods, beverages, etc., are a major problem globally that leads to consumer complaints, a perception of reduced quality, brand damage, and adverse publicity, which can be extremely costly to the manufacturer. The compounds responsible for these odors present an analytical challenge since they generally have low odor thresholds, making them difficult to identify, especially in complex matrices. As a result, the chromatographic differences that can be seen between control and complaint samples are often not the compounds responsible for the off-odors. Sensory directed analysis (SDA) is a process that utilizes gas chromatography in combination with the human nose and mass spectrometry to identify sensory-active compounds. The use of olfactory and MS detection enables the simultaneous determination of sensory-active regions of the chromatogram and mass spectral identification of the associated compounds. In many cases, the compounds of interest are sensed at the ODP but are below the instrument's detection limit.

High-capacity extraction techniques are necessary to gain the analyte mass on column needed to produce a peak signal for compound identification. In addition, the extraction technique must produce a representative extract of the odors of interest to ensure the compounds are introduced into the GC system

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for detection. This study initially explored Dynamic Headspace Large (DHS L) for extracting sensory-active compounds in the face wipes, but it could not effectively capture the off odor of interest. As an alternative, thin film-solid phase microextraction (TF-SPME) was employed as a high-capacity, solventless means of extracting analytes. The TF-SPME device is a 20 mm x 4.8 mm carbon mesh sheet impregnated with nine µL of sorptive phase. The TF-SPME devices are typically used in headspace mode for solid samples, but they can also be placed in direct contact with the samples to increase the amount of extracted compounds further. Selectable ^{1}D/^{2}D-GC-O/MS or "heart-cutting" GC was used to resolve components in the complex matrix. The system is configured with two low thermal mass (LTM) GC columns with dissimilar column phases and a valveless, software-controlled column switching device to easily implement a ^{2}D GC separation. Combining these techniques in an SDA approach enabled the identification of off-odor compounds in fragrance-free, cosmetic face wipes.

Experimental

Instrumentation

GERSTEL MPS LabWorks Platform with Dynamic Headspace Large (DHS L) and Olfactory Detection Port (ODP 4) on Agilent 8890/5977C GC-MSD with LTM option as shown in figure 1, GERSTEL Thermal Extractor (TE 2).

Figure 1: Selectable ^{1}D/^{2}D-GC-O/MSD system.

Analysis Conditions LabWorks Platform using DHS L

DHS L		
Trap		Tenax® TA
	Incubation	30 °C
	Trap	25 °C
	Volume	750 mL (50 mL/min)
TDU 2		
	Pneumatics mode	solvent venting/dry purge, 50 mL/min
	Temperature	40 °C (3 min); 720 °C/min; 250 °C (5 min)
CIS 4		
	Liner	glass bead filled
	Pneumatic mode	split 10:1
	Temperature	-120 °C; 12 °C/s; 280 °C (3 min)

Analysis Conditions LabWorks Platform using TF-SPME

TF-SPME		
	Phase	HLB/PDMS
TDU 2		
	Pneumatics mode	solvent venting/dry purge, 60 mL/min
	Temperature	40 °C (3 min); 720 °C/min; 250 °C (5 min)
CIS 4		
	Liner	glass bead filled
	Pneumatic mode	split 10:1
	Temperature	-120 °C; 12 °C/s; 280 °C (3 min)

Analysis Conditions Agilent 8890 GC with LTM

Pneumatics	He; P_i = 335.17 psi constant pressure (^{1}D) ramped pressure (^{2}D)
Column 1	30 m DB-5MS UI (Agilent) d_i = 0.25 mm, d_f = 0.25 µm LTM format
Column 2	30 m DB-WAX (Agilent) d_i = 0.25 mm, d_f = 0.25 µm LTM format
Oven	250 °C (isothermal)

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Analysis Conditions ODP 4

Transfer line	250 °C
Mixing chamber	150 °C
Split	2:1 ODP:MSD

Analysis Conditions Agilent 5977C MSD

Mode	Full scan, 40-350 amu

Sample Preparation

One control and two complaint makeup removing face wipe packages were purchased from local stores.

One face wipe was placed into a 1-liter DHS L canister. The face wipe was incubated at 30 °C for 2 minutes and then extracted for 15 minutes with 50 mL/min helium flow for a total trap volume of 750 mL. The analytes were trapped at 25 °C on a Tenax TA®-packed tube.

An HLB/PDMS TF-SPME membrane was placed between the layers of face wipes in the face wipe package. The sample was extracted for 2 hours at room temperature. After extraction, the TF-SPME membrane was placed in an empty thermal desorption tube for analysis.

Sample Introduction

Samples were desorbed in solvent venting mode with a 60 mL/min helium flow at 280 °C for 3 minutes (Tenax TA®) or 250 °C for 5 minutes (TF-SPME). Analytes were trapped in the CIS 4 inlet on a glass bead-filled liner at -120 °C. When desorption was complete, analytes were transferred to the column in split (10:1) mode by heating the inlet rapidly to 280 °C.

Olfactometry

GC-O analysis was performed with the column effluent split 2:1 between the ODP 4 and MS. The ODP transfer line was heated to 250 °C. The mixing chamber was heated at 150 °C and purged with humidified nitrogen to prevent olfactory fatigue and nasal dehydration.

Results and Discussion

A sensory panel was conducted on each sample to compare the odor of the control and complaint samples. The control sample had minimal odor and was described as fresh, floral, and soapy. The complaint samples had an off-odor described as rancid and fishy. The samples were initially extracted using DHS L. The Thermal Extractor (TE) was used to smell the total odor released from the sorbent tubes to confirm if DHS L successfully extracted the off-odor. Figure 2 shows the TE setup where the Tenax® TA tube was heated with no nitrogen flow to desorb the volatiles from the sorbent. Then, the flow was applied to allow the analyst to smell the total odor profile of the extract. The DHS L extract had a very low odor, and the analysts questioned whether the off-odor was present. The DHS L extract was injected into the GC-O/MS instrument. The fishy, rancid odor was not detected at the ODP; only a few odors were detected that were described as soapy, floral, and fruity.

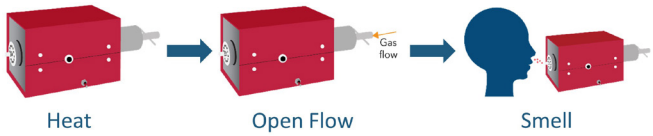

Figure 2: TE setup for smelling the total odor of sample extract.

While the sampling parameters could be optimized to create a more representative extract, an alternative approach was needed due to the limited number of complaint face wipes. Instead, a TF-SPME membrane was placed between the layers of face wipes in the package and left to extract for two hours. The TF-SPME membrane was evaluated with the TE, and the fishy, rancid odor was easily detected. When the TF-SPME membrane was thermally desorbed on the GC-O/MS instrument, the latter half of the chromatogram was highly overloaded. However, a fishy, rancid odor was detected in two early regions at the ODP, as shown in Figure 3.

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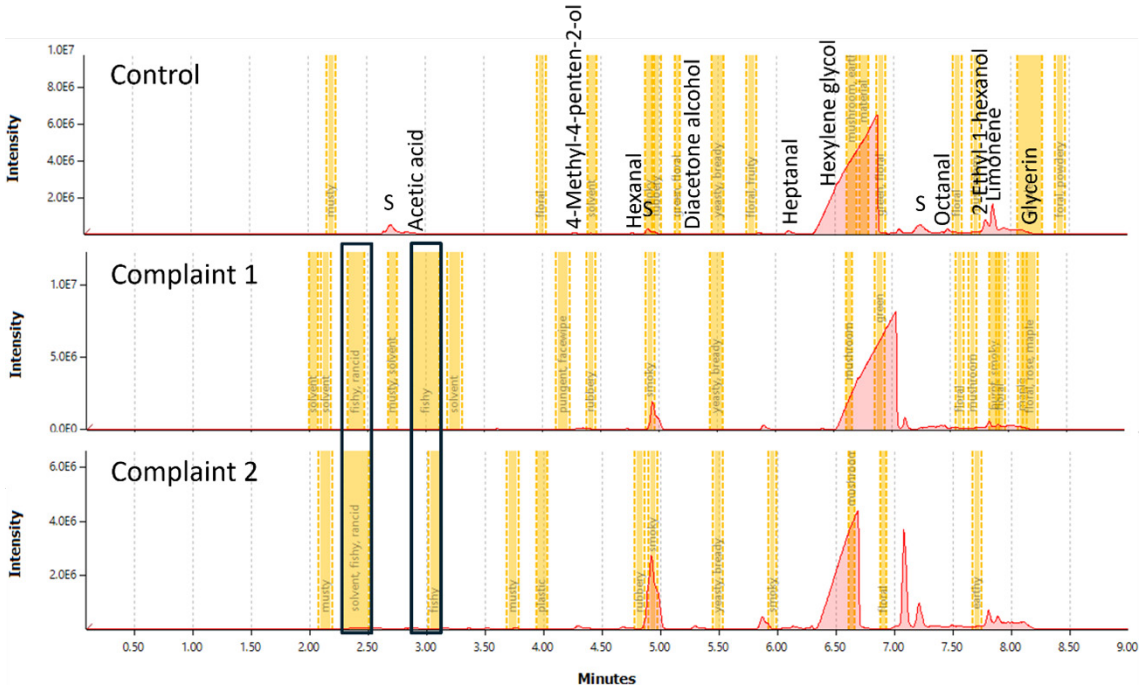

Figure 3: Stacked view of control (top) and complaint (middle and bottom) GC-O/MS data with off-odor regions marked in blue.

Since the off-odor regions eluted early in the chromatogram, the remaining injections of the samples were backflushed after 9 minutes to prevent overloading of the column and MS. The control and complaint samples were evaluated at the ODP. The two odor regions described as fishy and rancid were detected in both complaint samples but not in the control sample, as shown in Figure 3. Other odor regions in the samples were described as floral, fruity, soapy, etc., characteristic of the control face wipe aroma.

While the chromatographic profiles of the three samples are similar, there are some differences in peak abundances, as shown in Table 1. Peak areas are normalized to the peak areas in the control sample. Interestingly, most compounds decrease in abundance in the two complaint samples, including C6-C8 aldehydes, acetic acid, and limonene. Many of these compounds are described as fruity and fresh and could indicate a loss of the fresh aroma in the complaint samples. However, the olfactory data indicates that none of these compounds are present at a concentration above their odor detection threshold and are likely not contributing to the sample aroma. Only one compound, diacetone alcohol, was increased in the complaint samples compared to the control. Diacetone alcohol is a common cosmetic ingredient and is described as having a faint, minty odor [1]. Once again, the olfactory data indicates no odor is detected for this compound, demonstrating the importance of collecting olfactory data when looking for sensory-active compounds.

Table 1: Relative peak areas of compounds identified in each sample.

Compound	Control	Complaint 1	Complaint 2
Acetic acid	100	56	62
4-Methyl-4-penten-2-ol	100	86	175
Hexanal	100	46	52
Diacetone alcohol	100	151	605
Heptanal	100	43	61
Hexylene glycol	100	120	45
Octanal	100	34	30
2-Ethyl-1-hexanol	100	78	87
Limonene	100	10	14
Glycerin	100	82	99

A closer look at the chromatographic region where the two off-odors were detected shows a coeluting peak at the first region and baseline at the second. To resolve the coelution, a heart-cut was made from 2.2-2.6 minutes for additional separation on the second column. Figure 4A shows the ^{1}D chromatogram with the coeluting region at 2.4 minutes with the fishy odor. Figure 4B

shows the ^{2}D chromatogram where the peak with the fishy odor was separated and identified as trimethylamine. This was the case for both complaint samples, whereas the control sample had no fishy odor in either the first or second-dimension chromatograms, and no peak for trimethylamine was seen. A standard of trimethylamine was analyzed by ^{1}D and ^{2}D GC-O/MS to confirm that the retention time, mass spectrum, and odor matched that of the sample.

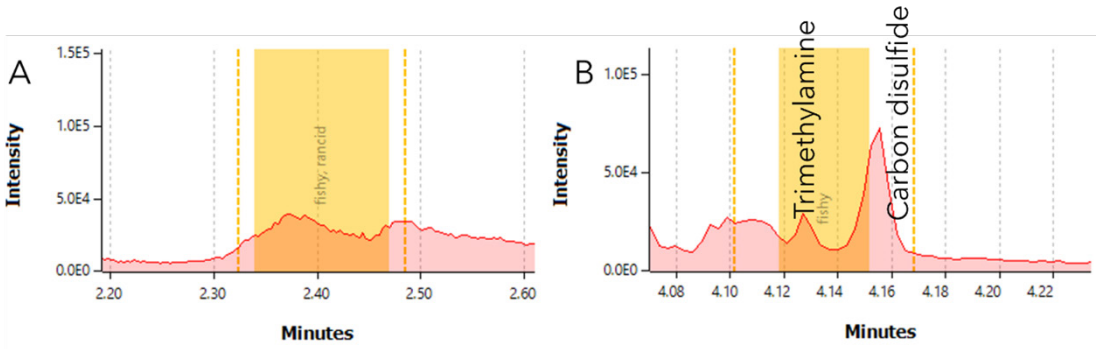

Figure 4: ^{1}D (A) and ^{2}D (B) chromatograms of the odor region of interest described as fishy and identified as trimethylamine in the complaint samples.

More analyte mass on column is needed to obtain a detectable peak signal for the second off-odor region. The ODP 4 can be easily configured for trapping onto sorbent-filled tubes. In this configuration, selective regions can be trapped on the same sorbent-filled tube multiple times while eliminating the rest of the sample matrix. Over a series of injections, six extractions of complaint 1 were used to trap the odor region between 2.95 and 3.05 minutes onto a single Tenax TA thermal desorption tube. However, upon reintroduction still, no peak signal was seen, as shown in Figure 5. This indicates that the compound responsible for the odor has a very low odor threshold, meaning it can be smelled at very low concentrations. Further trapping would be needed to obtain a detectable peak signal of this very low odor threshold compound.

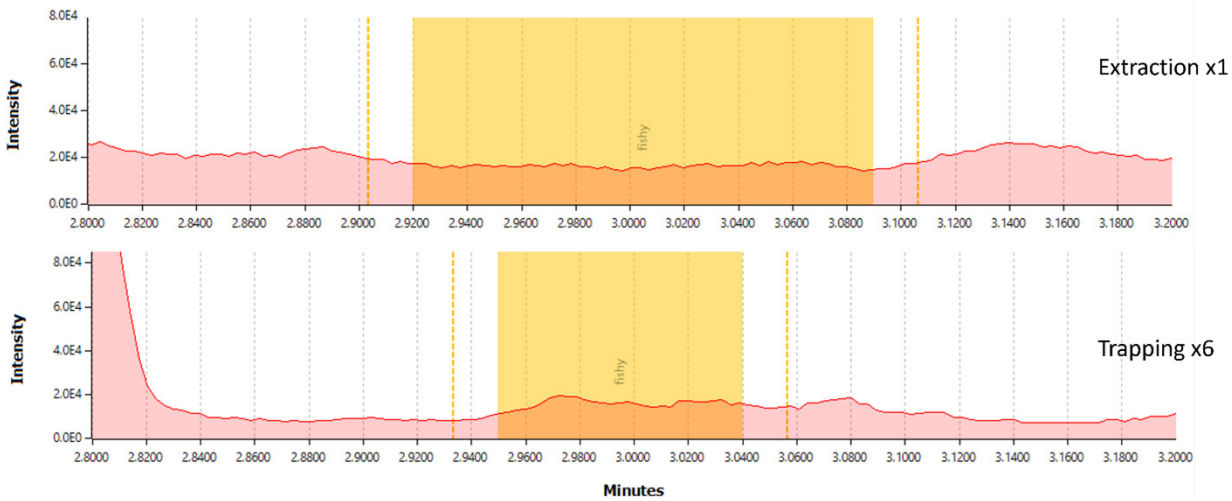

Figure 5: Stacked view of complaint sample extracted 1x (top) and extracted 6x, trapped, and reintroduced (bottom).

Conclusions

This study has demonstrated the ability of an SDA methodology to identify off-odor compounds in fragrance-free cosmetic wipes. TF-SPME membranes provided representative sample extracts for analysis, and $^{1}D/^{2}D$-GC-O/MS resolved an area of coelution to allow the identification of trimethylamine, a rancid, fishy sensory-active compound. The ODP 4 allows selective trapping of chromatographic regions of interest to increase analyte mass on column while removing the rest of the sample matrix. However, some compounds can be smelled at such low concentrations that a multitude of trapping is required. This approach could be readily used to troubleshoot off-odors in various sample types and enhance product quality and development.

References

[1] Cosmetic Ingredient Review, 2021, https://cir-reports.cir-safety.org/cir-ingredient-status-report/?id=44aac427-6c9f-4303-9b67-222b111a8db9