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Application of an ODP Performance Checkout Procedure and a Demonstration of using the GERSTEL ODP 4 for Sniff and Trap Work

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Abstract

Gas Chromatography-Olfactometry (GC-O) is an essential technique in aroma analysis. Olfactory detection is often performed in parallel with GC detection, for example, using a mass spectrometer. To ensure that an Olfactory Detection Port (ODP) is installed properly and is in good working condition, a performance checkout procedure is required. An ODP checkout standard has therefore been developed and its application is discussed in this document. The latest generation GERSTEL ODP, the ODP 4, can be used as a sniff port for olfactory detection using the human nose, including for calibrated olfactory assessors, and can also be temporarily fitted with an adapter for a sorbent tube to be inserted at various chromatographic retention times to trap GC eluate for further enrichment or analysis. An example of this function is presented in this work.

Introduction

To study fragrances in pharmaceuticals and personal care products, or flavors in food and beverages, sensory analysis using human assessors is essential, since the odor character of a compound cannot be deduced from its chemical or physical properties. To correctly determine the odor character of each compound in the fragrance or flavor mixture, gas chromatography coupled with mass spectrometry and olfactometry (GC-MS/O) is often employed to separate and determine aroma compounds simultaneously by a mass spectrometer, to obtain mass/concentration information, and by an Olfactory Detection Port (ODP) with a human assessor for odor information. Various GC-O methodologies are available, such as dilution to threshold, detection frequency and direct intensity, to determine the relative odor impact across the range of odor-active volatile compounds [1]. For instance, in an earlier application note, key aroma impact compounds in a bourbon sample were successfully identified using aroma dilution analysis which is a dilution to threshold approach [2].

A performance checkout procedure can provide assurance that the ODP is correctly set up and in good operating condition for GC-MS/O analysis work. An ODP performance checkout standard should meet the following requirements: (1) it must contain at least 2 different aroma-active compounds, which are easily distinguished by most human assessors; (2) the two compounds must be easily and quickly separated by GC columns of different polarities; (3) the aroma profiles must be pleasant with strong sensory impressions. When the checkout standard has been injected, the compounds are separated by GC and elute to the ODP and another GC detector simultaneously, enabling cross referencing between sensory information from the assessor at the ODP and the detector signal, such as, for example, a mass spectrum for the compound in question. The combined information is used to validate the performance of the installed ODP.

Instead of sniffing the eluted compound at the ODP, it can be trapped and stored on an adsorbent tube. Such a function can be useful for a variety of purposes: (1) to keep the trapped compound or fraction for later sensory evaluation; (2) to perform multiple collections of the same GC compound(s) over a series of GC runs for subsequent enhanced detection, MS identification or sensory perception at the ODP; (3) to re-inject the trapped compounds onto a column with different properties such as different polarity (also known as offline GC-heartcutting); (4) Selective trapping of certain fractions of the chromatogram to study synergy effects.

A performance checkout procedure for the ODP 4 is described and carried out and the trapping efficiency using the ODP 4 fitted with adsorbent tube adaptor is studied in this application note.

Figure 1: GERSTEL ODP 4 fitted with adsorbent tube adaptor for GC eluate collection.

Experimental

Instrumentation

GERSTEL LabWorks Platform with Olfactory Detection Port ODP 4 on GC 7890 and MSD 5977 (Agilent).

Software

Maestro Software, ODP Recorder, Enterprise Edition, Olfactory Data Interpreter ODI, AromaOffice ^{2}D (GERSTEL), MassHunter Version 7 (Agilent).

Analysis Conditions LabWorks Platform

Thermal Desorption TDU 2

Tube type	Tenax TA
Pneumatics mode	splitless
Temperature	30 °C; 120 °C/min to 250 °C (2 minutes)

CIS 4 Inlet (liquid injection)

Liner type	packed with deactivated glasswool
Carrier gas	helium
Pneumatics mode	splitless; split 20:1
Temperature	250 °C

CIS 4 Inlet (with TDU)

Liner type	packed with deactivated glasswool
Pneumatics mode	solvent venting, splitless
Vent flow	50 mL/min
Split flow	60 mL/min @ 2.01 min
Temperature	-30 °C (1 min); 120 °C/min to 250 °C (5 min)

ODP 4

Transfer line	250 °C
Mixing chamber	200 °C
Purge	humidified nitrogen
Split ODP: MSD	1:1
ODP fraction collection	Tenax TA adsorbent, +/- 0.2 min of a peak.

Analysis Conditions GC

GC Agilent 7890

Non-polar column	DB-5MS (Agilent), d_i=0.25 mm, d_f=0.25 µm
Polar column	30 m DB-WAX (Agilent) d_i=0.25 mm, d_f=0.25 µm
Mode	He, constant flow, 1.25 mL/min
Temperature	50 °C (7 min); 60 °C/min to 230° C (2 min)

Analysis Conditions MS

MSD Agilent 5977A

Scan	29 to 350 amu

Figure 2: GERSTEL ODP 4 coupled to GC/MS system with TDU 2 and GERSTEL MPS robotic^{pro}.

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ODP Performance Checkout Procedure
A solution containing Ethyl Butyrate and Linalool dissolved in Ethanol was prepared as ODP Performance Checkout Standard (P/N: 022824-S01-SG). This solution was injected in split mode. Injection can be done at a lower split ratio or splitless mode if the odor intensity is deemed too weak.

During the GC run of the ODP Checkout standard, the ODP Recorder software was activated allowing the human assessor to record voice descriptors for the odor character of each eluted compound while using the GERSTEL Olfactory Intensity Device (OID) to indicate the intensity of the olfactory impression.

Sniff and Trap using the ODP 4
The standard solution containing the respective analytes was injected in splitless mode for trapping on a Tenax TA tube. The Tenax TA tube was subsequently desorbed in splitless mode in a TDU-CIS-GC-MS/O system.

Results & Discussion

ODP Performance Validation
Ethyl butyrate and linalool were well separated both on the non-polar (DB-5MS) column and the polar (DB-WAX) column with a short GC runtime of 12 min, as shown in figure 3. This enables a quick and easy performance checkout procedure of the installed ODP.

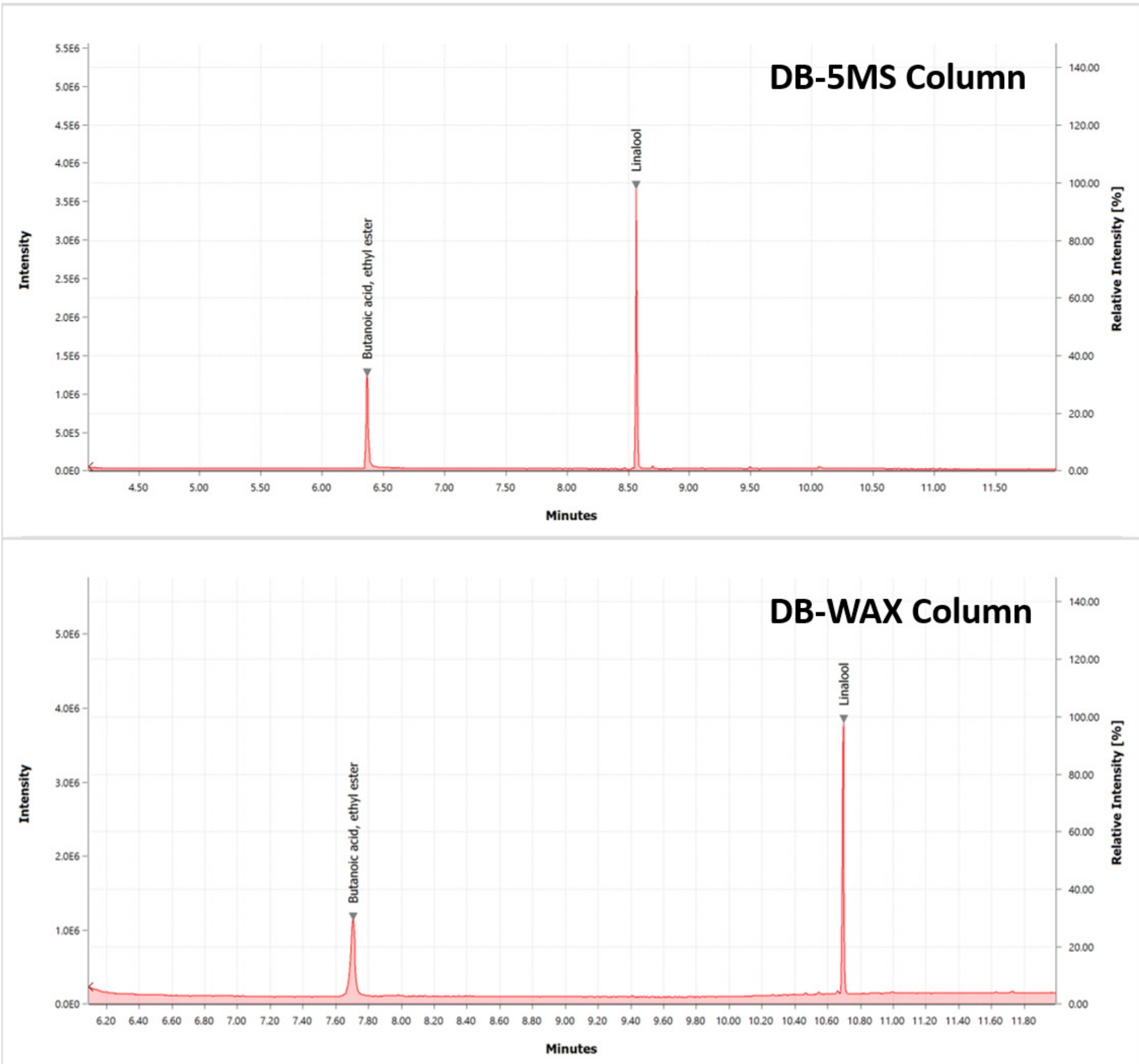

Figure 3: Chromatograms of the ODP performance checkout standard obtained on two different columns in 12 min runtime.

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A cross reference was performed using AromaOffice ²D (GERSTEL K.K.) [3], a linear retention indices database, to obtain the average reported retention indices of ethyl butyrate and linalool across different types of columns, as shown in table 1. Ethyl butyrate and linalool are always at least 3 alkanes apart (retention index differ more than 300) in all columns of various polarities, enabling quick GC method setup and a fast ODP performance checkout procedure.

Table 1: Average retention indices information from AromaOffice ²D

Column Type	Ethyl Butyrate	Linalool
Non-Polar	782	1086
Semi-Polar	798	1100
Medium Polar	841	1168
Polar	1034	1547

When the ODP recorder is used during the GC-O/MS run, multi-faceted information can be provided by the human assessor about each eluted compound: (1) Detection of an odor; (2) Time duration of the odor detection; (3) Description of the odor character; (4) Quantitation of the odor intensity/strength [1].

The combined information can be visualized in the GERSTEL Enterprise Edition Olfactory Data Interpreter (ODI) Software, overlaid with chromatographic information, as shown in figure 4. As needed, the information can be modified in the ODI Results window.

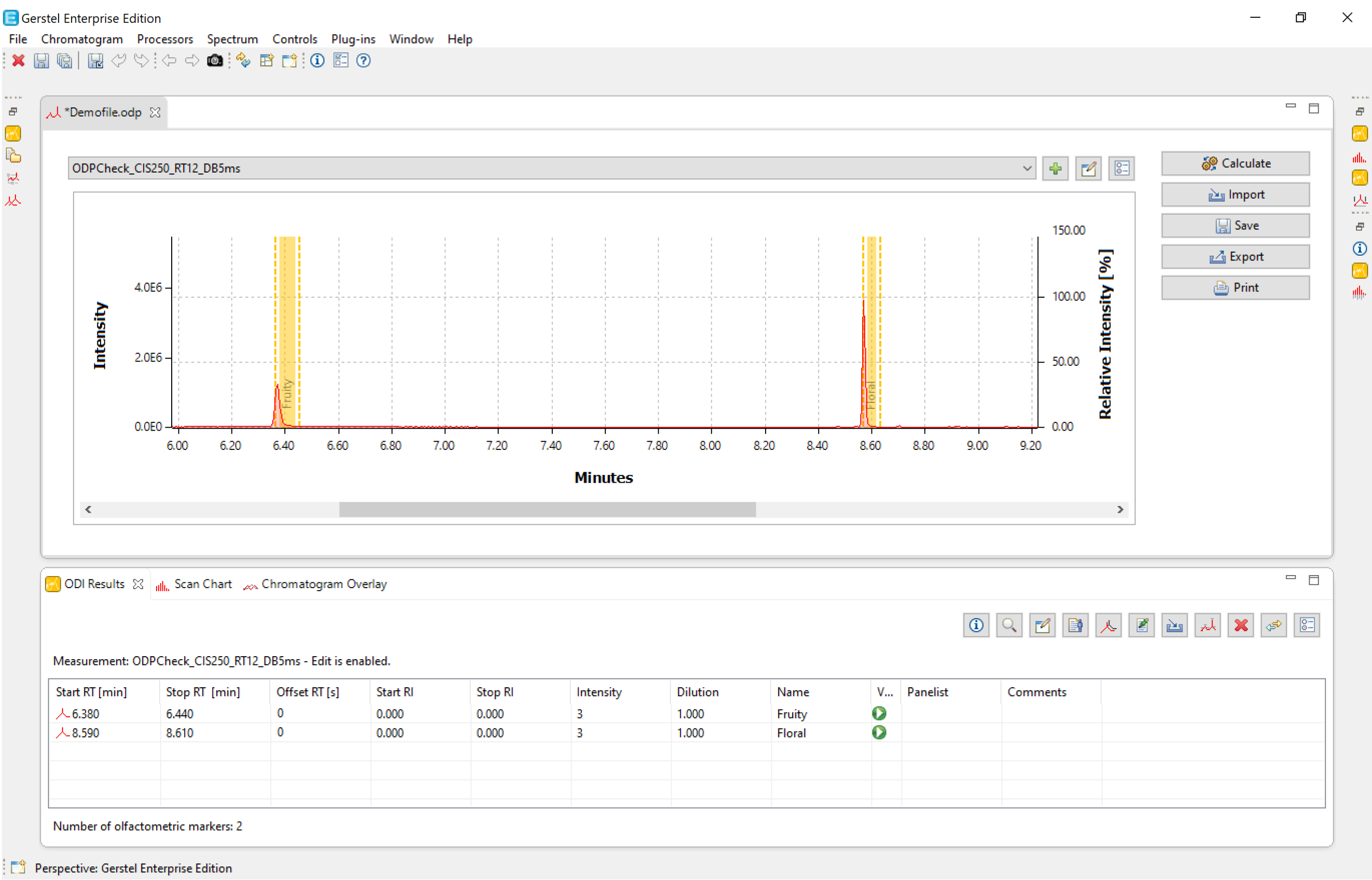

Figure 4: ODI Software view of a chromatogram/olfactogram overlay and the associated ODI results table.

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As can be observed from the overlaid chromatogram (red line) and olfactogram (yellow bar) in the top window of Figure 4, the retention time and the duration of the odor match the GC/MS peak. Also, as seen in the bottom window of figure 4, ethyl butyrate and linalool are reported by the assessor to have distinctly different odor characteristics, described as "fruity" and "floral", respectively. The descriptors in the ODI results table can easily be reviewed and edited by the assessor. Both compounds were observed to have an intensity of 3 for odor-strength (on a scale of 4 using the GERSTEL OID). The ODP can thus be concluded to be correctly installed and in good working condition for subsequent GC-O analysis work.

ODP 4 Sniff and Trap operation

Additional sensory and analytical work can be performed by using the GERSTEL ODP 4 to trap separated compounds of interest on an adsorbent tube, which is then stored in a leak-tight autosampler tray for analysis with a thermal desorption GC/MS system at a later time. In figure 5, overlaid chromatograms resulting from a linalool injection and from subsequent re-injections of the trapped compound are shown, Trapping was performed from 10.15 min to 10.45 min on a Tenax TA filled adsorbent tube attached to the ODP 4. Similar recovery was achieved from an adsorbent tube desorbed immediately after trapping and from an adsorbent tube desorbed after one week of storage.

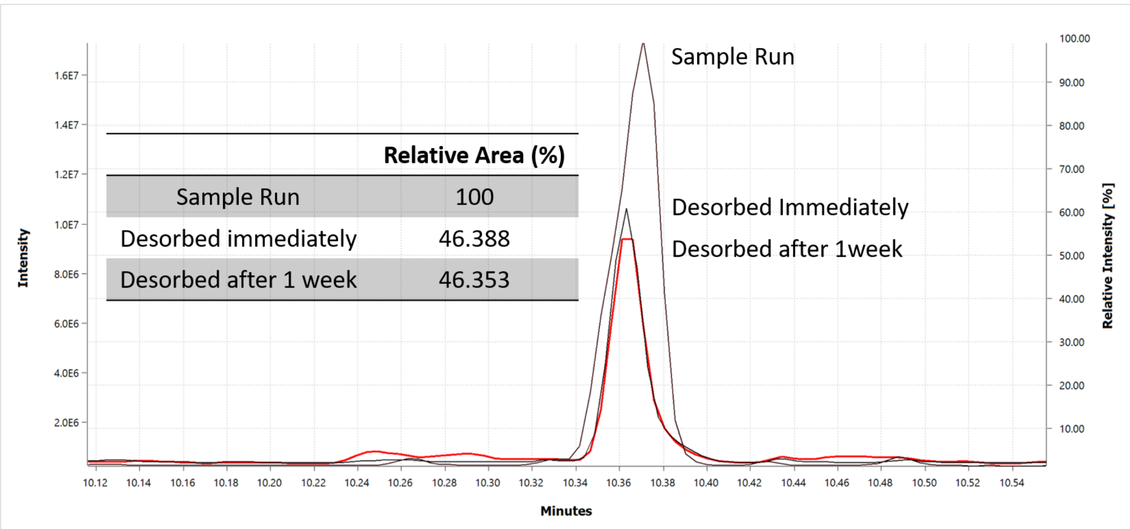

Figure 5: Comparison of a sample run and two desorption runs (immediately after trapping and one week later, respectively).

As can be observed in figure 5, the resulting peak area from the adsorbent tube desorption is approximately 50% of the peak area seen after the original injection. This is due to the 1:1 split of the GC column effluent between the ODP and the MS. Only 50% of the effluent goes to either the ODP or MS. After trapping 50%, reinjection into a similar system would result in a peak area of approximately 25% of the original signal (depending on the adsorption efficiency). If a higher response is required, trapping of the same retention fraction over multiple runs can be performed. In figure 6, a chromatogram obtained from a single trapping and a double trapping are overlaid. Trapping the same fraction over two GC runs results in 1.8 times larger peak area.

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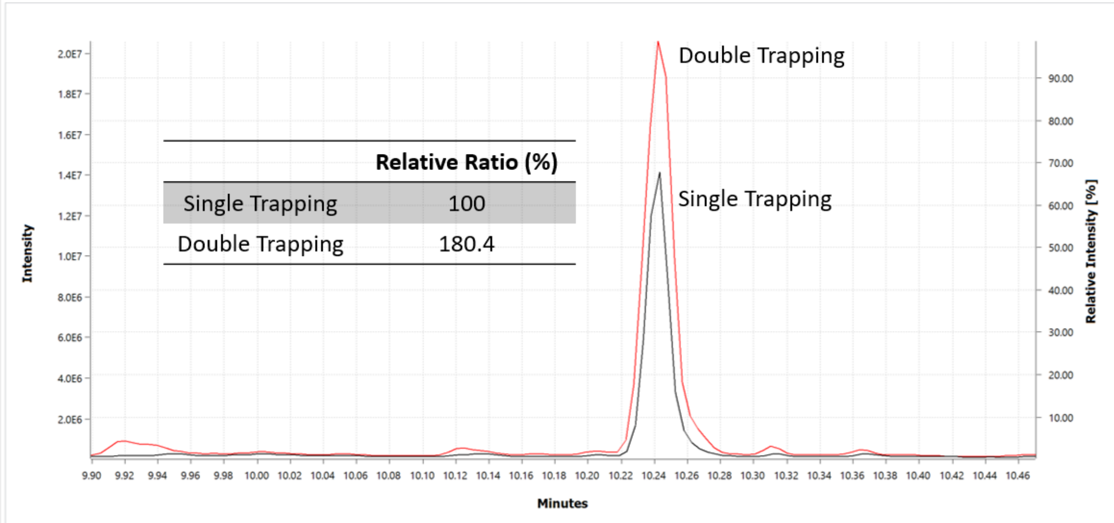

Figure 6: Comparison of single trapping and double trapping fraction collection peak areas.

The repeatability of the technique was subsequently studied. The same Tenax TA trap was used to trap and desorb the same compound over three consecutive runs. The peak areas obtained show good relative standard deviation (RSD) of 2.77%, as can be seen in figure 7.

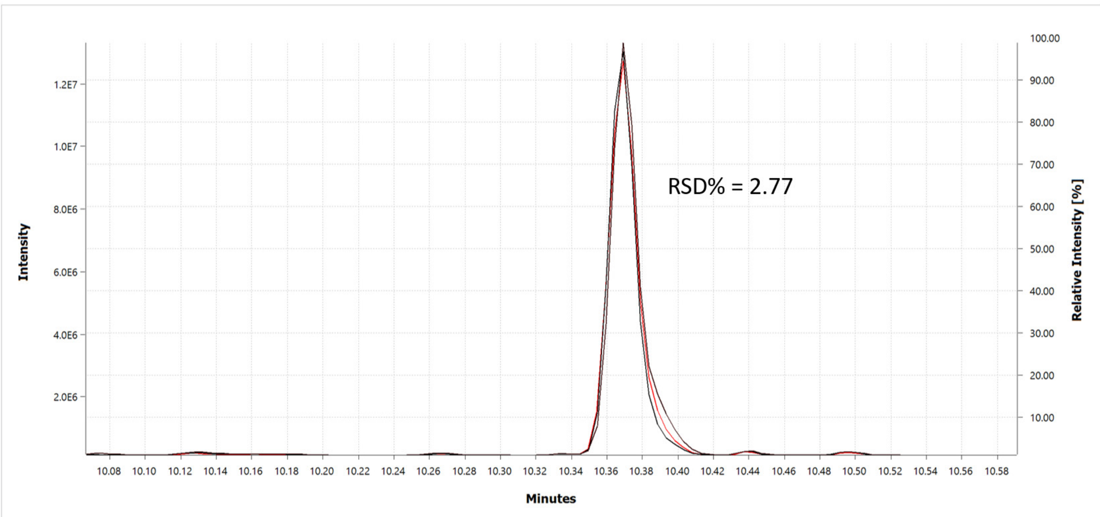

Figure 7: Repeatability achieved using the ODP 4 as fraction collector with a Tenax TA adsorbent trap.

In addition to further sensory analysis or improved overall sensitivity, the ODP 4 Sniff and Trap function can also be used for offline GC-heartcutting. Co-eluting compounds can be trapped on the absorbent tube and subsequently desorbed and analyzed on another TD-GC-MS/O system with a GC column of different polarity. As shown in figure 8, the mass spectrum obtained at the top of peak A, after separation on a DB-5MS column, includes the major ions from both ethyl guaiacol (137 and 152 ions) and cinnamaldehyde (131, 132 and 103 ions). The slightly odd peak shape of Peak A and its mass spectrum of multiple major ions provide enough cause for suspecting coelution. A run was performed to trap this peak using a Tenax TA sorbent. The fraction was then injected into a GC-MS system fitted with a more polar DB-wax column resulting in a chromatogram with ethyl guaiacol (Peak B) and cinnamaldehyde (Peak C) successfully separated.

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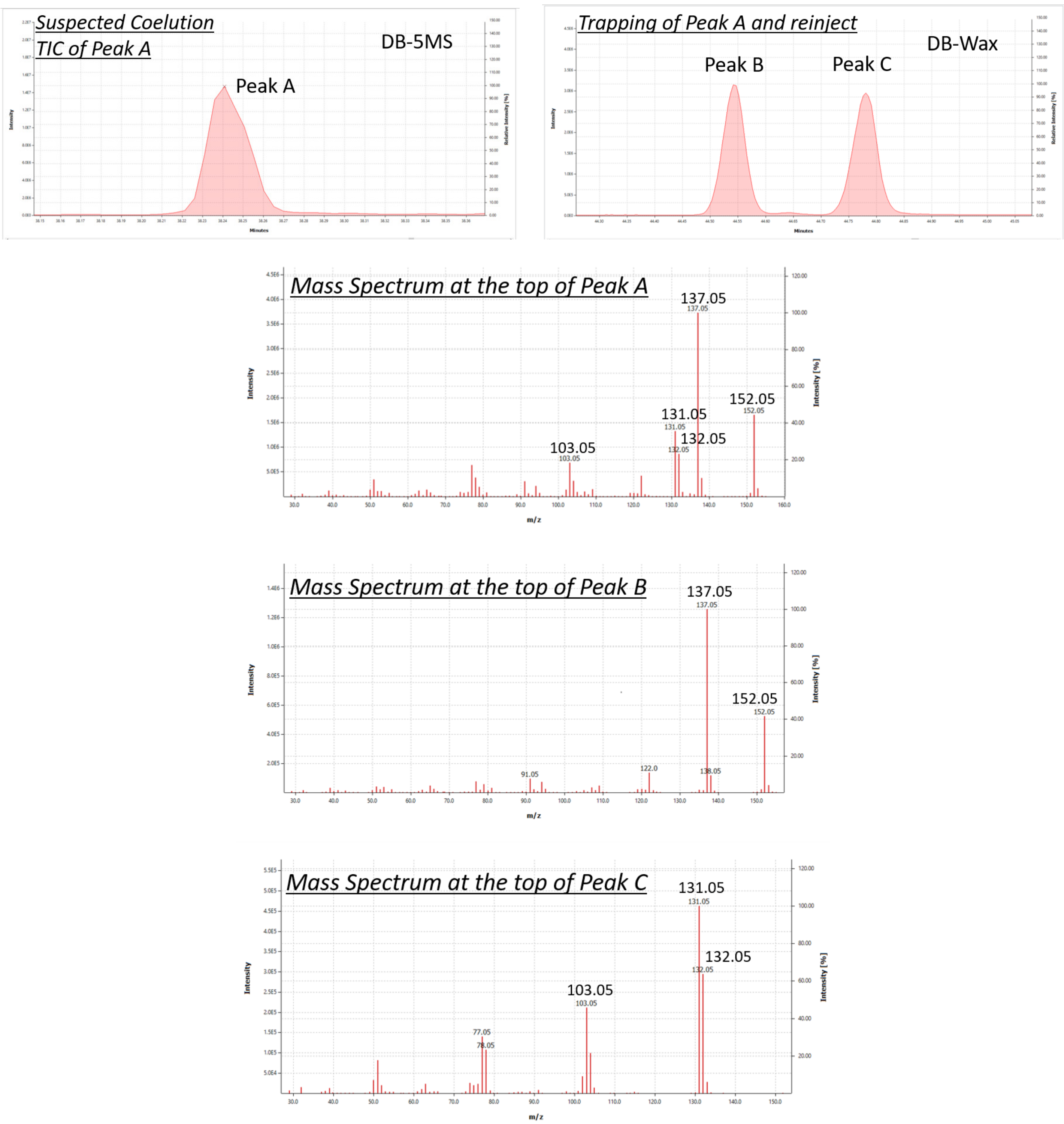

Figure 8: Cinnamaldehyde and ethyl guaiacol coeluting on a non-polar column were trapped on an adsorbent tube and subsequently separated on a polar DB-Wax column.

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Conclusions

A simple two-compound Performance Checkout standard was used to quickly verify and document the working performance of an olfactory detection port. Together with the ODP Recorder and ODI software, GC-O results obtained can easily be analyzed and reviewed with GC-MS data. The GERSTEL ODP 4 enables easy fraction collection for further sensory analysis or for subsequent separation on a different polarity GC column. The Sniff and Trap function enables offline 2-dimensional gas chromatographic separation based on simple GC-MS systems.

References

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