A Complete Solution for Aroma Characterization

Introduction
The sense of smell is pervasive to our everyday lives, enhancing pleasurable experiences, adding to the enjoyment of culinary experiences and warning of possibly unpleasant events with the detection of off-odors. Many memories are also triggered by smell as the olfactory bulb is part of the brain’s limbic system. Although odors and scents can be subjective, understanding what comprises them is increasingly important.

The new GC SNFR™ Olfactory Port enables food, beverage, flavor and fragrance producers to characterize even the most complex aromas by capturing sensory evaluation and correlates that human interaction with analytical data from a PerkinElmer GC/MS system.
A Complete Solution Package

The GC SNFR Olfactory Port is the latest addition to PerkinElmer’s comprehensive suite of innovative gas chromatography solutions and is seamlessly integrated to a PerkinElmer Clarus® GC, using Swafertm technology, and a Clarus SQ 8 mass spectrometer for best in class sensitivity. By adding the TurboMatrix™ headspace sample handling option, users have a flexible and convenient technique to extract and transfer to the GC odor vapors from samples that cannot be directly injected into the GC column. Samples such as fruit, coffee, hops, various textiles and petroleum based materials or those with high water content can easily be analyzed without complicated extraction steps. The volatile compounds in the sample matrix are effectively transferred to the gas chromatograph leaving the heavy bulk of the sample behind in the sample vial.

With the classical headspace technique, only a very small fraction of the total vapor is transferred to the GC column. The extraction performance of the headspace system is further enhanced through the inclusion of adsorbent trap technology, which enables all or most of the sample vapor from the vial to be collected, concentrated and transferred to the GC column. This HS Trap sampling system can improve detection limits by a factor of up to x100 and so, very importantly, deliver higher amounts of each compound to the olfactory port to aid their detection by the operator.

The complete package is shown schematically in Figure 1.

While no other detectors are shown, it is possible to add further detector options, up to a maximum of two, in the GC in addition to the MS and SNFR port.

GC SNFR Olfactory Port

The GC SNFR Olfactory Port is a device that allows a fraction of the GC column effluent to flow through a narrow transfer line and be presented through a nose piece to the operator’s nose. In this way, it’s possible to monitor the smell of compounds as they elute from the GC column at the same time as they are processed by the MS and other detectors that may be present. This provides a very powerful means of correlating analytical data with sensory perception – simultaneously getting both an objective and a subjective interpretation of sample aromas.

The GC SNFR system consists of a heated silica transfer line from the GC, which provides an inert path from the column to the nosepiece. The eluent is then mixed with humidified air at the inlet to the glass nosepiece to prevent drying of the nasal passages during prolonged monitoring. A concentric airflow provides efficient compound transport with no condensation. The GC SNFR Olfactory Port, shown in Figure 2 has independent controls for water temperature and air flow to a maximum of 500 mL/min. Its glass nosepiece is designed to be adjustable in the vertical and longitudinal directions, providing greater comfort during long analysis runs. Its nosepiece is easily cleaned with a sanitizing wipe or it can be removed for additional cleaning. Labs can provide each analyst using the system with their own personal nosepiece for a cleaner, healthier testing environment. The GC SNFR nosepiece is odor free and designed not to roll should the user remove it for cleaning.

Figure 3 shows the metal collar of the GC SNFR, which allows an efficient thermal connection of the nosepiece to the transfer line. The humidified air is introduced at the base of the collar to promote an annular flow around the column eluent. Due to these features, there is no condensation in the nosepiece.
Swafer Technology

Swafer™ technology is a flexible micro channel device for heart-cutting and split flow manipulation. The GC SNFR Olfactory Port uses the S-Swafer as a post column splitting device to distribute the effluent from the column at a constant pressure. This provides a stable flow of gas into each detector and the GC SNFR Olfactory Port. The addition of a second pressure source regulates the splitting and maintains the outlet flows independent of column head pressure. Independence from column head pressure increases the options available to a chemist with respect to flow rate in the separation as there is no requirement that the column flow also satisfies the detector flows. Split ratios and flows are a result of the selected transfer line geometries to each detector and the GC SNFR Olfactory Port and carrier gas pressure.

The chromatographic separation is critical from an identification standpoint and from the human interaction. If the compound resolution is too close, then individual identification may be a challenge.

The Swafer configuration allows manipulation of the column flow rate and separation without impacting the active split between the mass spectrometer and the olfactory port.

Figure 4 shows a test mix of compounds separated initially with a constant pressure method and then with a ramped pressure method. The mixture was a liquid injection on to a 30 m x 0.25 mm x 0.25 micron wax column. The timing between the MS and response to the olfactory port was unchanged between the two methods.

The difference in chromatography can be observed in this example by the shift in retention time and the elution of vanillin in less than 41 minutes.

The Swafer Utility Software is helpful in identifying the tubing dimensions for the desired split control.

The selection of split ratio is heavily dependent upon the sample composition because of the difference in sensitivity between the MS and human olfactory bulb. It is entirely possible that very strong smelling compounds to which an analyst is very sensitive may be detected at extremely low concentrations and possibly at levels close to the detection limit of the MS. In such cases it is obviously desirable to have a very low split ratio (possibly less than one and in favor of the MS).

The GC SNFR Olfactory Port has demonstrated excellent performance with heavy musk compounds and vanillin, which were easily detected with no delay or condensation on the nosepiece. The timing between the nosepiece and MS is virtually simultaneous, enabling excellent correlation between analyst scent exposure and MS peak detection for accurate determination. The chosen silica dimensions provide simultaneous detection between the nosepiece and MS, enabling excellent correlation of the data.
TurboMatrix Headspace Trap
Sample Handling System

The TurboMatrix headspace trap system is an effective way to collect odor samples without complicated extraction procedures. Most importantly, the TurboMatrix will only sample those compounds that are present in the headspace for aroma characterization and will not extract non-gaseous compounds from the samples that may not be contributing to the odor experienced.

Three musk compounds were analyzed with a Tenax TA trap: \(\alpha\)-hexyl cinnamaldehyde, hexamethyltetralin and Galaxolide. The headspace conditions for the total evaporation experiment are given in Table 1.

Table 1. Headspace conditions for total evaporation experiment.

<table>
<thead>
<tr>
<th>Headspace System</th>
<th>TurboMatrix 110 HS Trap</th>
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</thead>
<tbody>
<tr>
<td>Vial Equilibration</td>
<td>210 °C for 15 minutes</td>
</tr>
<tr>
<td>Needle</td>
<td>210 °C</td>
</tr>
<tr>
<td>Transfer Line</td>
<td>210 °C, long, 0.25 mm i.d. fused silica</td>
</tr>
<tr>
<td>Carrier Gas</td>
<td>Helium at 40 psig</td>
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<tr>
<td>Dry Purge</td>
<td>5 min</td>
</tr>
<tr>
<td>Trap</td>
<td>Tenax C, 30 °C to 300 °C, hold for 5 min</td>
</tr>
<tr>
<td>Extraction Cycles</td>
<td>1 with 40 psig extraction pressure</td>
</tr>
</tbody>
</table>

The results shown in Figure 7 demonstrate the efficient transfer of these heavy base musk compounds from the Tenax TA trap through the heated transfer line to the analytical column and the MS and GC SNFR detectors.

Software Interaction

The GC SNFR Olfactory Port Narrator software is directly linked to the TurboMass™ software to ensure data continuity. As shown on a typical screen in Figure 8, the audio input is displayed with an active text box that transcribes the user narration. Also note the intensity chart, which captures input of the perceived odor intensity.

An analog joystick is provided for intensity measurement input that is then overlaid on the total ion chromatogram (TIC). The overlay enables the analyst to focus identification and analysis on those areas of the TIC that have the greatest odor impact.

The GC SNFR Olfactory Port Review software overlays a graphic depicting both the audio stream and the intensity data. Figure 9 shows an example. Sections of the recorded narration may be re-played by mouse-clicking on the audio stream graphic.

The musk compounds were efficiently transported through the headspace transfer line at 210 °C.

Liquid injections are also possible for essential oils or organic extracts in accordance with standard GC practice.

Environmental samples can be sampled using a thermal desorption tube and then injected with a TurboMatrix thermal desorption system.
Export of the data in the form of a comma separated value (CSV) file into a software application such as Microsoft® Excel® as shown in Figure 10 is also a simple task. The advantage of exporting the data is that it is possible to combine the perceived experience of multiple analysts to calibrate their sensitivity to a particular compound. Alternatively, the perceived odor intensities can also be overlayed in parallel to form a panel of experience from multiple analysts.

The audio recording can optionally be transcribed into a text stream and stored into a CSV file (Figure 12) for ease of reading and exporting to Microsoft® Excel®, Word® or any other suitable software package. This is achieved through the use of the Nuance® Dragon® Naturally Speaking software, which is called from the GC SNFR Olfactory Narrator software, which is included in the GC SNFR system.

Applications

The GC SNFR port is very well suited to fragrance analysis as demonstrated by the data in Figure 7 with the musk bases’ efficient transport and detection. The musk compounds demonstrate the mass range of the system application (Galaxolide with a boiling point of 304 °C) and are an important benchmark for the system application as they are somewhat ubiquitous in laundry detergents, perfumes, cosmetics and other artificially scented products.

Natural products are also readily analyzed with other applications:
- Whisky
- Hops
- Beer
- Coffee
- Food

The purpose of the analysis can be for a number of reasons including the following:
- QC check of raw ingredients
- QC check of final product
- Reverse-engineering competitive products
- Product development
- Off-flavor analysis
- Storage studies

The following pages show a few examples of typical applications.
The investigations into beer and hops were part of an ongoing quality assurance effort to characterize finished product and to source alternative raw materials. The evaluation of hops also lends itself quite nicely to the development of new beer.

Figure 15 shows a chromatogram of an alternative hop variety, Fuggles, from the Cascade hops shown in Figure 14. The information obtained from the GC SNFR olfactory port enables correlation between the user aroma experience with the qualitative and quantitative data obtained from the mass spectrometer. Decisions related to flavor and balance can then be more quickly and accurately determined.

An additional application investigated how the addition of water changed the aroma of whisky and the resulting consumer experience. Figure 16 describes the change in the headspace concentration of a malt whisky sample with the addition of 1 ml of water. Not only were the ester compounds that are characteristic of whisky enhanced in the headspace but the alcohol concentration is reduced. It is important to realize the depressive impact on the sense of smell that alcohol has in a spirit that is 40% alcohol by volume. The addition of water therefore has a twofold effect on the compounds in the headspace in that it minimizes the depressive alcohols while at the same time enhancing the concentration of the desired aroma compounds.
However, the GC SNFR Olfactory Port is not limited to food products only. Off odors are commonly found in the environment, packaging materials and polymer based materials used in shoe construction, for example. Odor investigations on large volume locations can be achieved by sampling and trapping with a thermal desorption tube prior to analysis in a similar system by replacing the TurboMatrix headspace trap with a TurboMatrix thermal desorption system.

Summary

PerkinElmer’s GC SNFR Olfactory Port is designed for high quality performance, comfort and ease of use. Integrated with the PerkinElmer GC/MS system, the GC SNFR Olfactory Port enables a clear, complete profile of food, beverage and fragrance samples. The system’s column flow independence allows great variety in analytical methodology as the detector gas input is independent of the flow through the analytical column. Sample introduction is compatible from liquid/liquid extraction, headspace, headspace trapping to thermal desorption of large volume spaces. Timing of the scent arriving at the nosepiece and MS detector is simultaneous for accurate odor determination and all sensory inputs are recorded and catalogued with analytical data for data continuity.