

## Comparing Odor Evaluation Technologies

Traditional analytical approaches to odor evaluation like mid-IR spectrometry and gas chromatography are highly selective, achieving either spectral or temporal separation. Recently, two new players have emerged which may eventually supplant the traditional technologies. Both lack the specificity of the above techniques, relying instead on chemometrics, primarily pattern recognition algorithms, to establish the relationship between instrument response and sample composition. The so-called electronic nose, first commercialized in 1993, employs a series of discrete solid state sensors, such as conductive polymer, metal oxide, or piezoelec-

tric devices. Mass spectrometers specifically configured for rapid headspace analysis were introduced in 1998. Both the e-nose and the headspace MS instruments are aimed at a wide variety of flavor and fragrance applications and seek to augment or even replace human sensory evaluation.

The purpose of this note is to provide background for matching instrument type with application needs. In particular, the HP 4440A Chemical Sensor, a headspace MS instrument, is shown to avoid many of the limitations of the competing e-nose technologies.

**Table 1. Comparison of Odor Evaluation Technologies**

Technology	Average Throughput	Primary Advantages	Primary Disadvantages
Mid-IR Spectrometry	High (0.5 minutes/sample)	<ul style="list-style-type: none"> <li>• Structural information</li> <li>• Easy on-line implementation</li> </ul>	<ul style="list-style-type: none"> <li>• Aqueous samples require special cells</li> <li>• Non-linear response to many analytes</li> <li>• Difficult to determine trace analytes</li> </ul>
Gas Chromatography	Low (15+ minutes/sample)	<ul style="list-style-type: none"> <li>• Linear response</li> <li>• Excellent selectivity</li> <li>• Can analyze less volatile materials</li> </ul>	<ul style="list-style-type: none"> <li>• Column fouling, bleed</li> <li>• Increasing resolution increases analysis time</li> <li>• Short and long term drift</li> </ul>
Solid state sensors	Moderate (5-15 minutes/sample)	<ul style="list-style-type: none"> <li>• Responds to a variety of analytes</li> <li>• Minimal sample preparation</li> <li>• Can be miniaturized</li> <li>• Easy on-line implementation</li> </ul>	<ul style="list-style-type: none"> <li>• Sensor poisoning</li> <li>• No structural information</li> <li>• Time consuming calibration</li> <li>• Short and long term drift</li> <li>• Alcohol and water interfere</li> </ul>
Headspace Mass Spectrometry	Moderate (3-5 minutes/sample)	<ul style="list-style-type: none"> <li>• Responds to all volatiles</li> <li>• Structural information</li> <li>• Minimal sample preparation</li> <li>• Fast method development</li> </ul>	<ul style="list-style-type: none"> <li>• Cannot distinguish optical isomers</li> <li>• Vacuum pump required</li> <li>• Subject to tuning inconsistencies</li> </ul>

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## Selecting a Technology

Several sometimes conflicting criteria must be considered when choosing an odor evaluation approach. For example:

- *Timing of Data Collection* - Must data be collected on-line? If not, how soon after a sample is collected should the analytical results be available?
- *Sensitivity, Selectivity and Stability* - What range of analyte concentration or property value can be expected? What are the possible interferences or matrix effects? How important is day-to-day reproducibility? How important is instrument-to-instrument reproducibility?
- *Cost and Benefit of Analysis* - What is the total cost of running the instrument including maintenance, methods development, sample handling, operator training and disposables?

Some features of the different analytical approaches are listed in [Table 1](#).

## Comparing New Technologies

In the e-nose and headspace MS instruments, there are noteworthy similarities and dissimilarities in functional features. In both cases, the sample is introduced as a thermally equilibrated vapor. Both device types also output a vector of responses; however, the physical processes which give rise to those responses are significantly different.

In a mass spectrometer, the various compounds in a narrow plug of sample vapor are ionized and fragmented, with each compound producing a characteristic fragmentation pattern. These ion fragments are filtered by the mass analyzer (for example, a quadrupole) then detected by an electron multiplier. The output vector is a mass spectrum.

In an e-nose, a carrier gas sweeps the sample vapor through the chamber(s) where its components interact with sensor substrates. Depending on the sensor type, a sensor property (e.g., its resistance) is altered by the sample to produce a time dependent response. The output vector is assembled from a user specified number of

response points (e.g., the maximum) from every sensor.

## Flexibility

When purchasing an e-nose, you must specify the number and type of sensors to incorporate. Depending on the vendor, your choices may be limited. Some vendors furnish only one type of sensor; others provide a small number of possible combinations.

With mass spectrometry, preconfiguration is unnecessary. For example, a typical quadrupole MS can scan from 2 - 800 amu. The user adjusts the scan range (i.e., chooses the number and type of sensors) at run time based on the particulars of the sample.

Time spent developing methods is minimal for the HP 4440A. One or two experiments are usually sufficient to determine the appropriate mass range and sample heating parameters; a method may be developed and samples run in a single day.

## Sensitivity and Selectivity

Amount of sample volatilized, headspace vial temperature, and the scan range determine the sensitivity of a MS. The instrument can also be operated in selected ion monitoring (SIM) mode to increase sensitivity. The sensitivity of solid state sensors is determined by their type, the flow rate over the sensor, the analyte, and temperature.

E-nose sensors are subject to interference from water and alcohol in the sample, reducing not only the sensitivity to other constituents but also the sample throughput by requiring a lengthy recovery time. Moreover, e-nose sensors can be poisoned by strongly-adsorbing materials, such as sulfur-containing compounds. Analogous effects are not observed in mass spectrometry. To the extent that a solvent, say, produces a large, even overwhelming signal at one or several m/z settings, the performance at other m/z settings is unaffected.

## Stability

E-nose sensors are known to be subject to short and long term drift due to changes in relative humidity. In addition, individual sensors have to

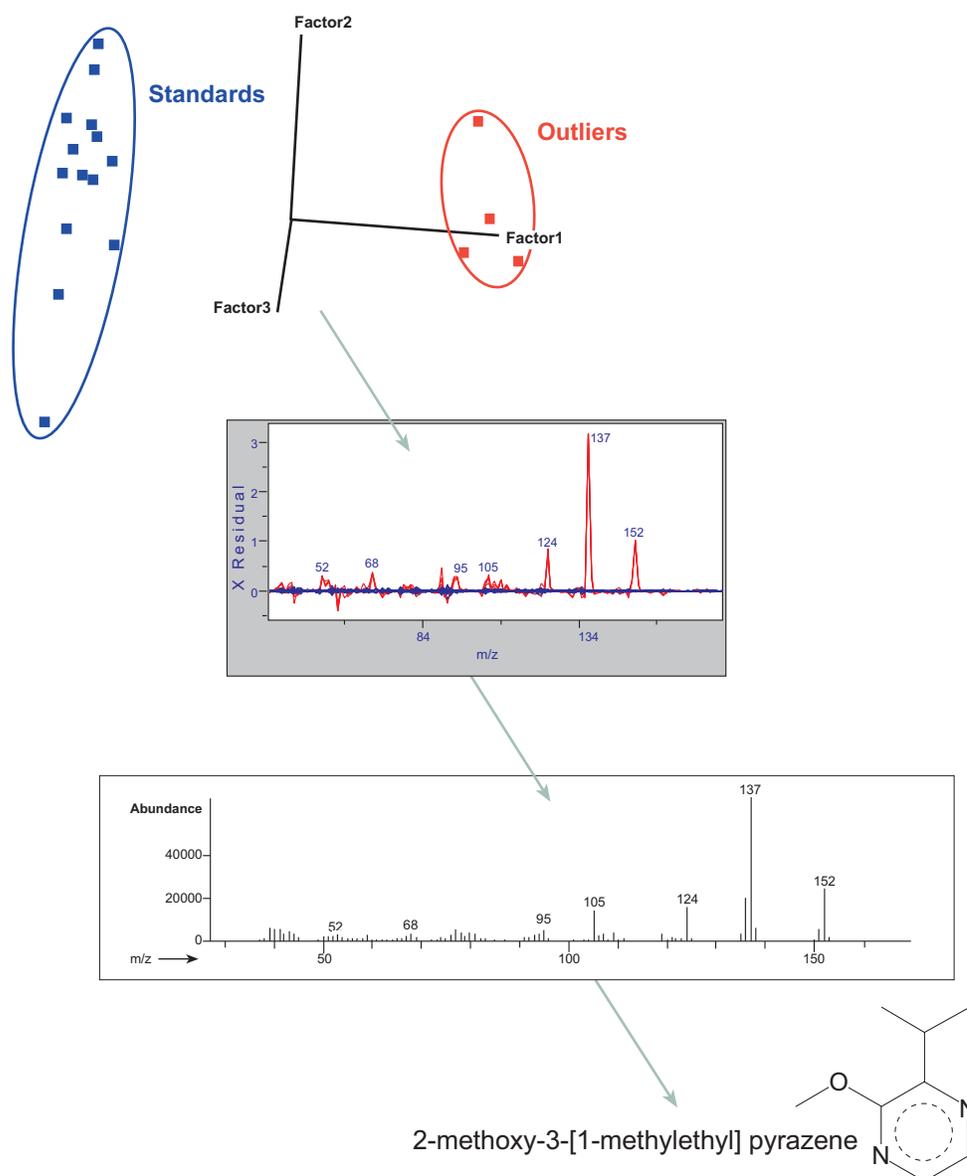
be replaced periodically. Mass spectrometers have been designed to minimize effects of changes in the external environment; a high degree of stability is a requirement for any analytical technique which relies on standard library searching.

### Answering *WHY?* Questions

The patterns produced by e-nose sensors have no chemical meaning. On the other hand, a mass spectrometer generates directly-interpretable chemical information. Following multivariate analysis of the headspace MS data, evaluation of the spectral residuals may provide further insight. For instance, the residual of an out-of-

spec sample may be searched against a mass spectral library.

The scenario shown in [Figure 1](#). has several steps. First, the chemometrics software identifies deviations from the standard, shown at the top of the figure as outliers on a PCA scores plot. Next, a residuals plot (essentially a spectral subtraction) highlights the mass fragments that make the outliers unusual. As the third step, these ion intensities can be searched parametrically or used in GC/MS to determine a retention time and authentic spectrum of the contaminant, which can, in turn, be identified by library search, as demonstrated at the bottom of the figure.



**Figure 1.** Analyzing off-odor fragrance samples with the HP 4440A leads directly to the identification of the offending substance, a pyrazene.

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## Linearity

Mass spectrometer detectors respond linearly over four orders of magnitude, and the speed of response allows signal averaging, minimizing variation due to minor fluctuations in sample introduction. Built-in diagnostics alert the user if the system becomes overloaded.

In contrast, e-nose sensors have small linear ranges, typically no greater than 2 orders of magnitude. Also their response is time-dependent. The user must choose a small number of time points from each sensor trace for data analysis and assume these are optimal.

## Software and Support

ChemStation software manages the HP 4440A Chemical Sensor, including its collection and display of data. Integrated with it are two software products from Infometrix. Pirouette, easy to use and thoroughly documented, implements established chemometric approaches to the creation and optimization of multivariate models. InStep performs automated, unattended predictions with those models.

Training in chemometric theory and practice is offered regularly in Europe, the Americas and Japan. Applications support labs for the HP 4440A have been established on both coasts of the United States and in Europe.

## Conclusions

Optical spectroscopy, chromatography, solid state sensors and mass spectrometry all play distinct roles in odor applications. However, a headspace mass spectrometer appears to offer many advantages over both traditional and new technologies. When bad samples are detected

during the course of routine analysis, this system can lead quickly to a probable identification of chemical components causing the trouble, so that appropriate action can be taken to minimize the negative financial impact.

## References

The articles and books listed below contain information regarding the background technologies for e-nose and headspace mass spectrometer devices.

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