

Off-Odor Detection Utilizing Gas Chromatography- Mass Spectrometry/Olfactometry (GC-MS/O)

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Introduction

Muddy/earthy odor from plastic bottles used for packaging medicine or in wine bottle corks, stinky sulfurous smell in hand lotion, oxidized-burnt hair aroma in dairy: off-odors destroy consumer confidence and present challenging problems for the food/ beverage/ cosmetics/packaging industries. Odors frequently are intermittent, are perceived differently by individuals (various descriptors), and are difficult to reproduce. Sources may be one or many trace level (parts per million, $\mu\text{g}/\text{mL}$), or ultra-trace level (parts per billion, ng/mL , or lower) aroma active chemicals introduced during manufacturing, shipment, or storage. To add to the complexity of the problem, often it is unclear whether off-odors originate from packaging or product.

GC-MS/O Gas chromatography- mass spectrometry coupled with olfactometry (GC-MS/O) allows for rapid odorant identification without having to sort through the plethora of other chemicals that originate from a food/ cosmetic/ package that have absolutely nothing

to do with the off-odor problem, but lead to expensive, time consuming sensory and analytical dead ends.

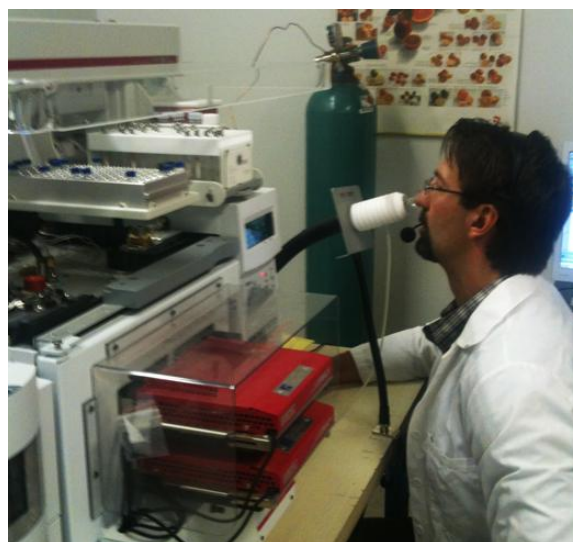


Figure 1 GC effluent is split in half and an aroma judge rates intensity and character of odorous components present. The other half of GC effluent is directed to the mass spectrometer for simultaneous detection (same retention time)

Method of Operation

A laboratory standard for more than 30 years, a gas chromatograph separates complex mixtures of volatile and semi-volatile chemicals by chemical properties, e.g. boiling point or polarity. Once separated, chemicals are pushed along by an inert gas into a detector. With gas chromatography- mass spectrometry/ olfactometry, the flow of chemicals is split with one-half directed to a mass spectrometric detector (MSD), and the remaining half flowing through a heated tube where they are mixed with humidified air (**Figure 1**). An odor panelist (trained aroma judge) sniffs the chemicals as they depart the heated/ humidified tube and the odor intensity plus description are recorded at the same time as the MSD records chemical fragmentation pattern and abundance. The result is an aromagram that resembles a chromatogram only the peaks represent odor

intensity vs. time. The aromagram is superimposed upon the MS total ion chromatogram (graph of total ion abundance vs. time). Identities of potential problem odorants may be quickly deciphered by concentrating on the small percentage of peaks that exhibit odor. For example In **Figure 2** below, if the offending odor was described as similar to stinky dirty socks, the responsible chemical may have been a combination of valeraldehyde and isovaleraldehyde, two short chain aldehydes with odors similar to their better known acidic cousins, valeric and isovaleric acids.

Sometimes an odor will be moderate or strong, but yet the responsible chemical is not clearly identifiable. This happens most frequently with chemicals that have very low odor thresholds. Researchers (1, 2) have defined an aroma value or flavor value as per **Equation 1**.

Equation 1 Aroma activity or flavor value =
[Chemical concentration of odorant in product or package/ Aroma threshold]

In other words, if the concentration of chemical that emanates from a product is greater than the odor threshold (threshold is defined as the amount of chemical necessary to elicit odor perception), the chemical contributes a noticeable aroma. If the threshold is very, very low, as is the case for certain chemicals such as ethyl mercaptan, also known as ethane thiol, (260 pg/mL or parts per trillion; 3) or tribromoanisole (4pg/mL, or parts per trillion; 4), then when analyzing a sample by GC-MS/O there may be a prominent odor detected by the odor judge, but there may not be a

corresponding MS peak. In this case additional methods are utilized to identify the unknown chemical odorant. This may be accomplished by increasing the concentration of the unidentified chemical utilizing longer extraction times with solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), or adsorbent tubes. Other methods include running the mass spectrometer in a more sensitive mode, selective ion monitoring (SIM), or utilize another type of detector such as a flame photometric detector in the case of sulfur components. Another option available is

GC x GC where short increments of primary column effluent are collected in a modulator and then sent to a secondary column for enhanced separation (5).

Examples For example in **Figure 2** the large “green” odor detected at 9:20 was identified as hexanal. This was confirmed by analyzing an authentic chemical standard (purchased from Sigma Aldrich, Saint Louis). The first odor peak

on the aromagram was described as musty, stinky, sulfur; however there was no good mass spectra library match for this aroma peak. Because of the odor descriptor and the experience of the odor judge, there was a good chance this odor was a sulfur component. A logical next step was to further concentrate the sample and analyze the sample with the MSD in SIM mode.

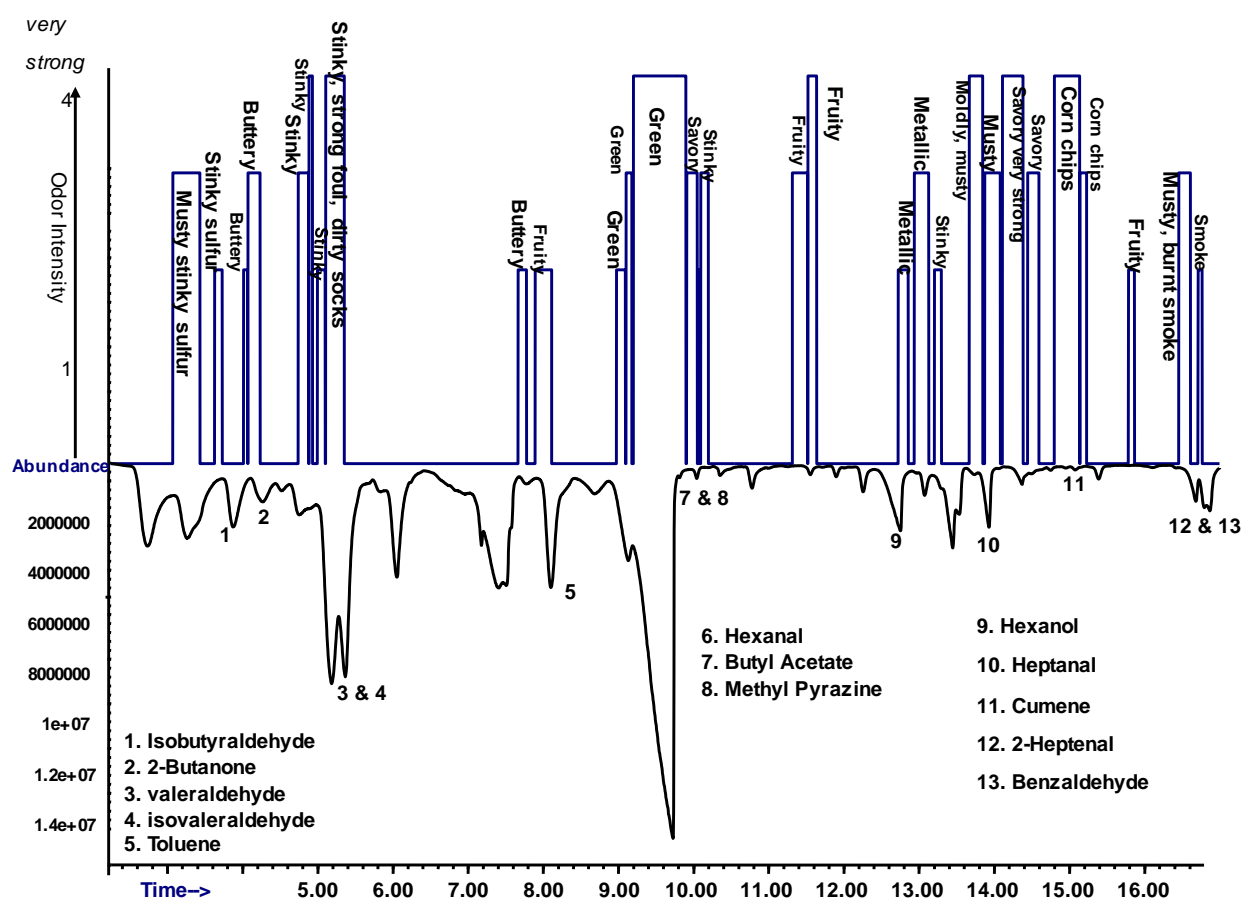


Figure 2 GC-MS/O analysis of sample headspace

Another possibility to aid in unknown component identification was to utilize a retention index. Because the retention time for this odor was known, a retention index (such as

Kovats, **Equation 2**) could be calculated using the retention times of straight chain alkane standards that bracket the unknown component’s retention time (6). Published lists

of volatile component's Kovats index values obtained from different stationary phase

capillary columns are available for reference and some are available online (7).

Equation 2 Kovats Index calculation

$$I = \left[\frac{t_{r(\text{unknown})} - t_{r(n)}}{t_{r(N)} - t_{r(n)}} \right] * (100 \times z) + (100 \times n)$$

I = Kovats retention index,

n = smaller alkane number of carbon atoms

N = larger alkane number of carbon atoms

z = difference in number of carbon atoms: smaller and larger alkane,

tr = retention time.

Summary

Off-odor problems can be very expensive due to loss of consumer confidence and resultant loss of significant market share. It is far better to identify offending problematic odors utilizing

tools that permit rapid and accurate detection, and then identify where the odors were first introduced into the product/ packaging. Once this is understood, appropriate steps to prevent odor formation may be implemented.

Volatile Analysis Corporation is available to assist with off-odor detection and resolution.

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