A Microanalytics White Paper

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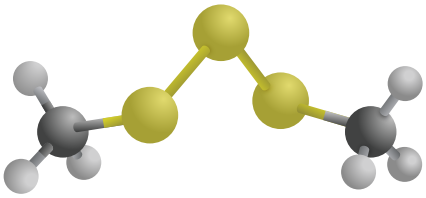

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Addressing the TBP/TBA odor issue

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Imported wood pallets have come under fire recently for allegedly imparting odors to the products being stacked and distributed on them. Several product recalls have been announced recently due to consumer complaints about moldy or musty odors that have been associated with nausea, stomach pain, vomiting and diarrhea. Fingers are being pointed toward a chemical called tribromophenol (TBP) which continues to be used as a wood preservative in certain countries to control fungi, pests, etc.

Although TBP has been banned in the United States, Europe and Canada as a fungicide, it is still being used in South America. During times of domestic wood supply shortages, TBP-treated pallets can end up in the domestic distribution channel.

Adverse financial/brand impact

Microanalytics has been involved in a number of projects where a by-product of TBP microbial metabolism, 2,4,6-tribromoanisole (TBA), has been identified as the cause of the off-odor. Results from these projects demonstrate that TBA can be absorbed by both corrugated shipping cases and the primary plastic bottles/jars contained inside. Additionally, entire physical structures (warehouses, plants, etc.) can also be affected.

TBA contamination can have significant financial impact. Examples include:

- major pharmaceutical product recall with an impact of hundreds of millions of dollars.
- manufacturer of surgical gowns had to replace all of the warehouse sheetrock and reseal the floor.
- bottled water brand absorbed the musty odor, rendering it unsellable.
- other consumer products stored in the same warehouse can become contaminated.

Because contamination can be instantaneous and can quickly spread to other pallets, truckloads and even physical plants, it is critical that the problem be identified as quickly as possible to minimize financial impact and damage to brand equity. Warehouse personnel should be particularly sensitive to any odd odors emanating from pallet loads.

How contamination occurs

Contamination from TBA occurs upon direct contact with the source or from the air in an enclosed area.

Pallets that are shipped across national borders must be phytosanitary compliant. This means that the materials used for the construction of the pallets cannot support invasive species of insects and plant diseases. Pallets must either undergo a heat-treatment or chemical fumigation process to be compliant. This is when TBP can potentially be introduced.

Odor chemistry

A class of organic compounds called haloanisoles is known to cause a “musty,” “moldy” and/or “earthy” smell in many different types of materials. These compounds contain at least one halogen atom as part of their chemical composition. Haloanisoles are the by-product of microbial metabolism in products that have been treated with halophenols. This conversion process is called biomethylation or O-methylation. Of specific interest are the compounds 2,4,6-trichloroanisole (TCA) and 2,4,6-tribromoanisole (TBA). These compounds are extremely aromatic and have a very low odor threshold. A TBA concentration in the parts per quadrillion range can provide the characteristic odor.

Halophenols are the precursor compounds needed for the formation of haloanisoles. One of these halophenol compounds, 2,4,6 tribromophenol, is used as fungicide, flame retardant, wood preservative and an antiseptic agent. It is also used as a chemical intermediate in the preparation of other flame retardant materials. Thus, halophenolic compounds can be readily found in many areas of the manufacturing and shipping processes.

AromaTrax® System pinpoints odorants

As a respected leader in sensory analysis, Microanalytics has been actively working with brand owners to address TBP/TBA issues. The AromaTrax® GCMS-Olfactometry System combines state-of-the-art technology with the human nose to identify specific chemical odorants—down to parts per trillion or quadrillion. The analysis employs multidimensional gas chromatography, mass spectrometry and olfactometry.

To isolate and measure the odorant, first collection needs to take place. In this case, a small sample can be taken from the pallet, packaging material and/or air samples can be collected from the problem area.

The samples are then processed through a headspace solid phase microextraction (SPME) procedure to collect the volatile organic compounds. The same SPME fiber is used to transfer the sample to the inlet of the gas chromatograph which performs the chemical separation of the compounds. The mass spectrometer is used for the identification of the compounds that are being separated while the olfactometry detector allows for the determination of the odor causing compound or compounds.

At Microanalytics, a preliminary olfactory identification of TBA can be made in a relatively short period of time, while the verification can take hours. The testing can be performed on the pallet material itself or on any type of material that is contaminated.

Case history example

A gas chromatogram acquired from a TBA contaminated sample is shown in ***Figure 1***. This chromatogram shows the complexity of the analysis. Each of the peaks in the chromatogram represents a single volatile organic compound that originated from the sample. For many of these compounds, the concentration in the sample is too low for olfactory detection. Also, the gas chromatogram acquired from an uncontaminated sample would be nearly identical. The question that needs to be answered is which of these peaks, if any, is associated with the foul odor due to TBA.

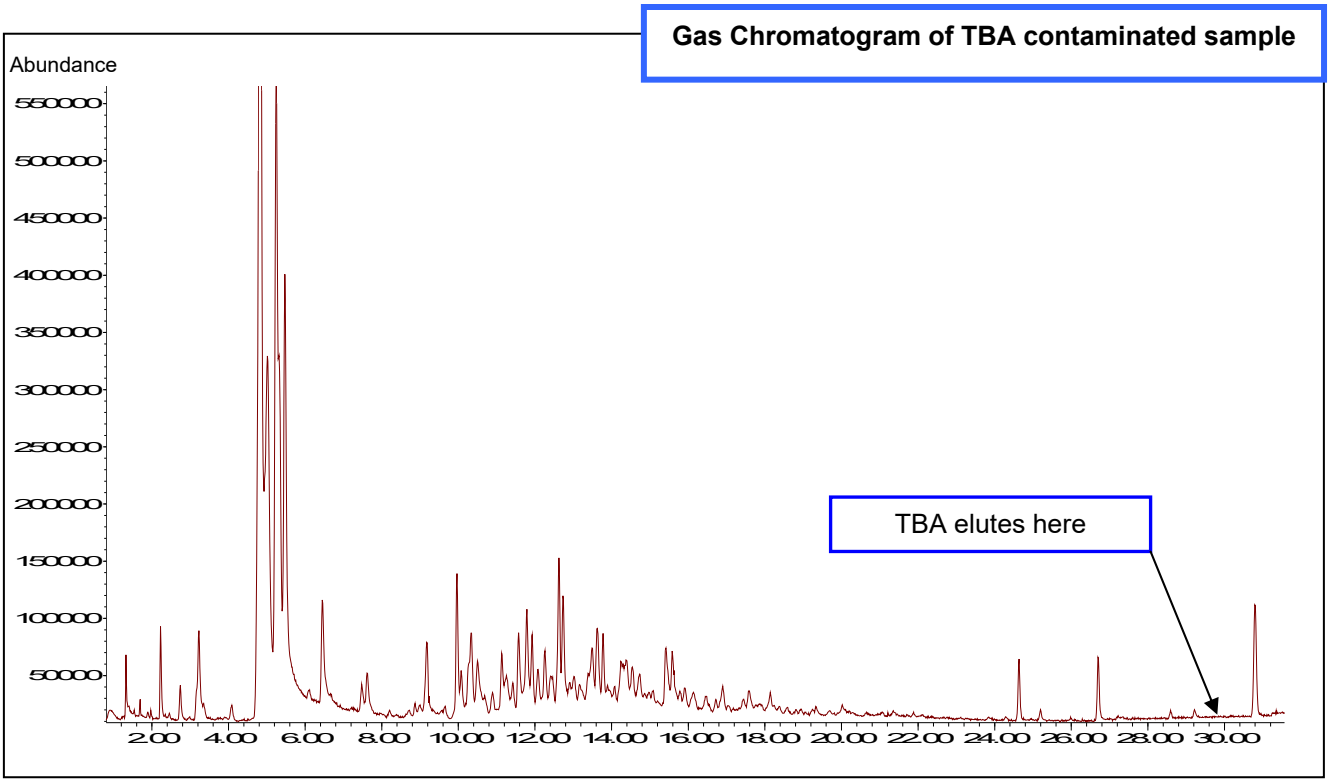

Figure 1. A gas chromatogram acquired from a TBA contaminated sample. The arrow indicates the area of the chromatogram where TBA would elute from the GC column.

During the gas chromatographic analysis, the scientist senses the individual compounds as they are presented at the olfactory “sniff” port. The scientist utilizes the AromaTrax software to characterize the type of odor and the intensity of the odor as a function of retention time to create an aromagram. The aromagram acquired from this contaminated sample is shown in ***Figure 2***. While there are many compounds which give rise to some type of odor, the large peak in the aromagram at approximately 30 minutes is due to TBA.

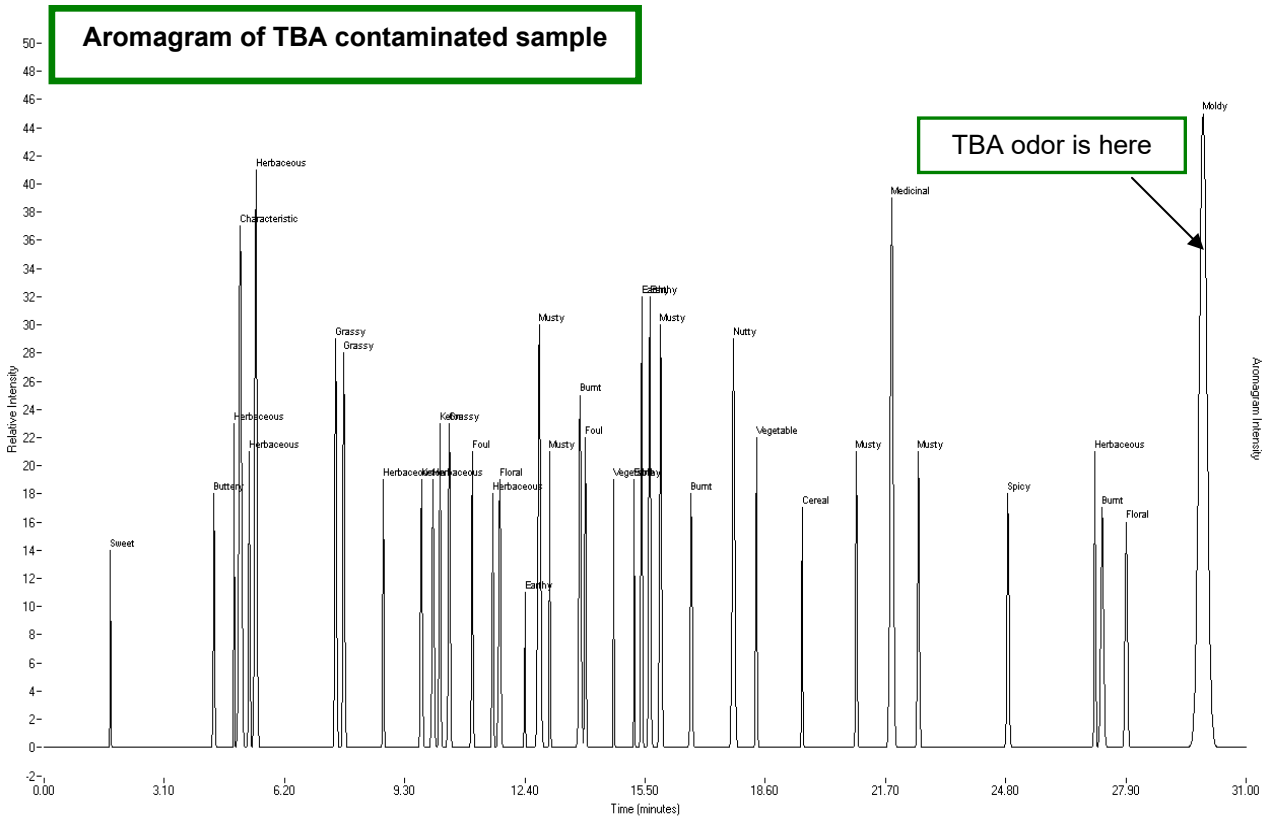

Figure 2. An aromagram acquired from a TBA contaminated sample. Each of the peaks represents a compound in the sample with a low odor threshold.

Figure 3 is a combination plot of the gas chromatogram and the aromagram. The region of interest has been expanded. In this case, the concentration of the compound causing the offending odor (TBA) is at such a low concentration that it is lost in the background signal of the gas chromatogram. However, since the scientist is able to sense the offending odor in the aromagram, the individual can concentrate on that area of the chromatogram to further validate the compound identification.

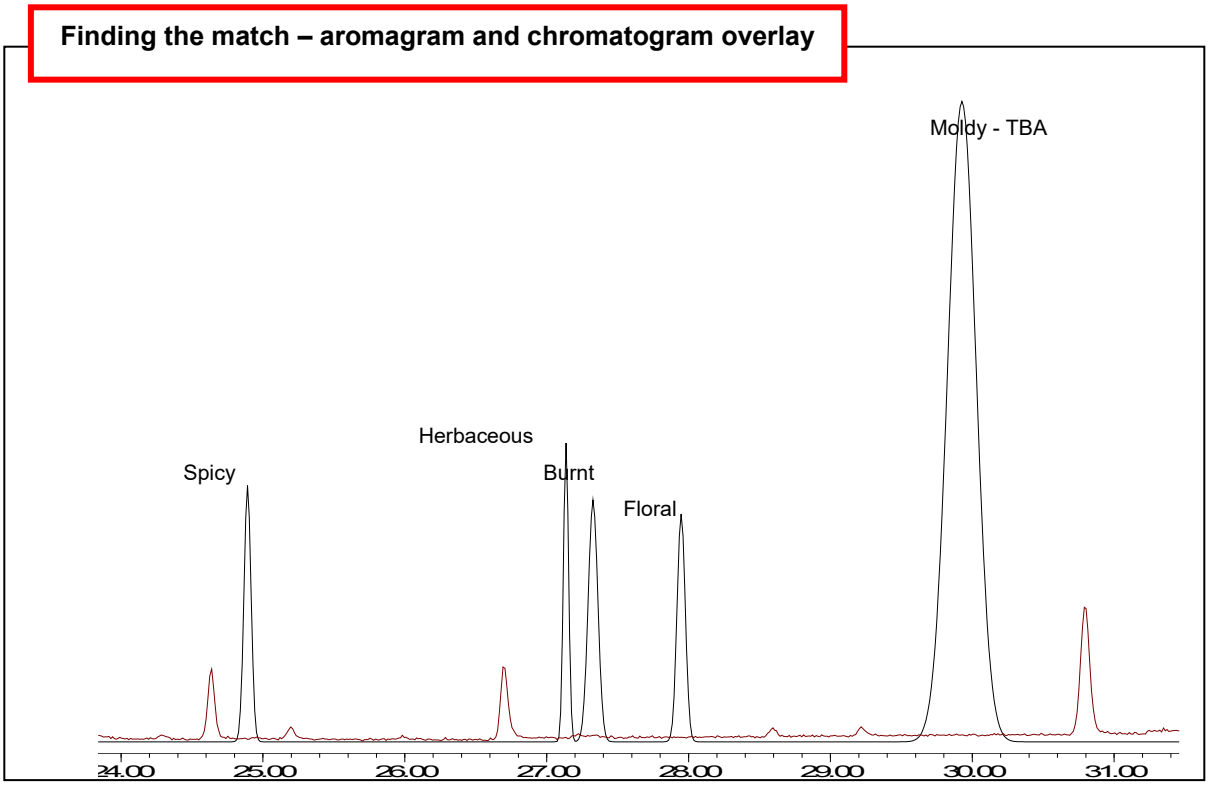

Figure 3. An expanded combination plot of the gas chromatogram (red curve) with the aromagram (black curve).

Conclusion

Microanalytics™, a subsidiary of Volatile Analysis, has developed improved approaches to identifying the source of industrial odors and can help guide strategies for neutralizing them. For addition information contact:

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