Testing for Anisols and Phenols in Ambient Air, Wood, and Paint Samples with the zNose®

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Summary

Samples of ambient air (tedlar bags), wood, and dried paint were tested for the presence of trichloroanisole (TCA), trichlorophenol (TCP), tetrachloroanisole (TeCA), tetrachlorophenol (TeCP), pentachloroanisole (PCA), pentachlorophenol (PCP), tribromoanisole (TBA), and tribromophenol (TBP) using an ultra-fast gas chromatograph called the zNose®. The zNose® system contains an integrated vapor preconcentrator allowing direct sampling of ambient air or air samples in tedlar bags. Wood and paint samples were placed in septa-sealed 40 mL vials, heated to 40^{o}C, and their headspace vapors sampled. Methanol extracts of paint samples were also tested by direct injection into the inlet of the zNose®.

Introduction

Chemical sensor arrays, called eNoses, have interested wine producers for some time, yet physical sensors have limited performance because of overlapping responses and physical instability. However, using ultra-high speed gas chromatography, a different kind of electronic nose has been achieved. With chromatography, arrays of virtual chemical sensors with non-overlapping response are possible. Long-term stability and picogram sensitivity in a solid-state sensor now enable quantification and recognition of volatile compounds in seconds. Portability, high speed, and virtual chemical sensors, specific to anisols and phenols, make the zNose® an effective tool for quality control.

Description of the zNose®

A portable zNose™ is shown in Figure 1. The high performance of the instrument is achieved by using a new type of solid-state GC detector with picogram sensitivity and a directly heated capillary column capable of programmed temperature ramping at rates as high as 20^{o}C/second. A typical chromatographic analysis of ambient air takes can be done in 10 seconds and measurements repeated at 1-minute intervals.

Figure 1- Portable zNose™ vapor analyzer

Using only resonant sound waves, the solid-state sensing element provides sensitivity comparable to an electron capture detector yet is non-ionic and non-specific enabling it to detect all organics regardless of polarity. Radioactive elements or high voltage ionization sources are not used. The ability to detect compounds universally enables the zNose® to characterize a wide range of aromas and chemicals.

Standard Response and Calibration

An aroma standard or perfume of n-alkanes is used to calibrate retention time and allows the instrument to recognize known chemicals and/or chemical groups (odor signatures) based upon Kovats indices. Response factors for individual compounds, such as TCA, are based upon injection of standards directly into the inlet of the instrument as shown in Figure 2. Linearity and sensitivity for TCA is shown in figure 3.

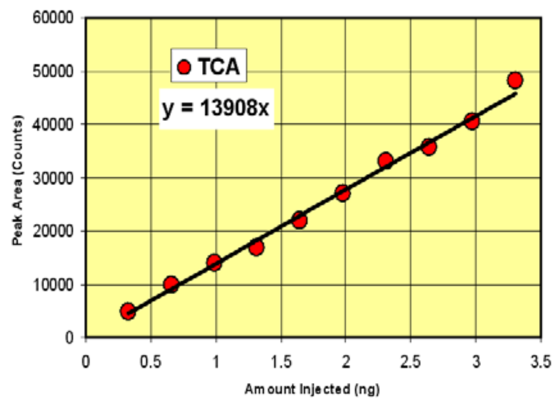

Figure 2- Direct injection of standards *Figure 3- N-point calibration for TCA response*

Graphically defined regions shown in red in Figure 4 define virtual sensors specific to target anisols and phenols. This figure shows vertically offset chromatograms corresponding to injection of three different standard mixtures.

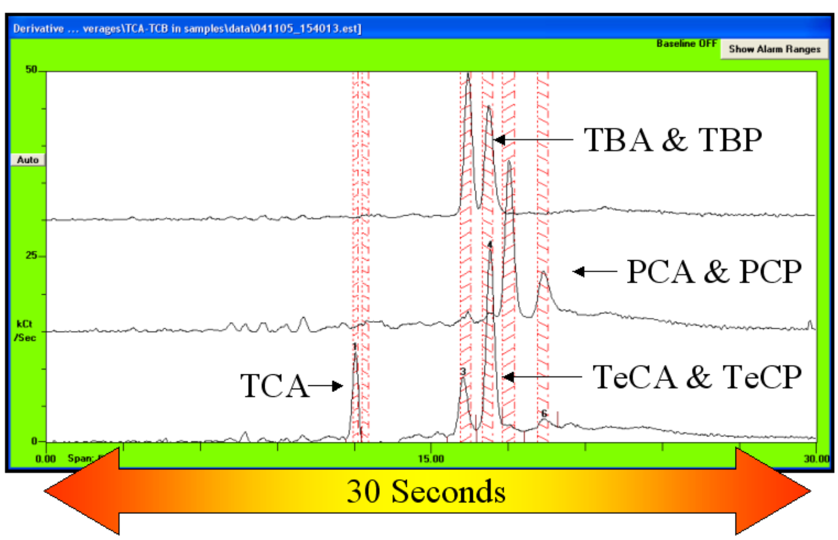

Figure 4- Vertically offset responses to anisole and phenol standards.

Testing Tedlar Bag Air Samples

Air samples in tedlar bags were tested and results for two different samples are shown in vertically offset chromatograms in figure 5. Tedlar bags typically contain high concentrations of phenol and acetamide shown as two major peaks on the left. Expanding the vertical scale (right side) shows low concentration trace elements.

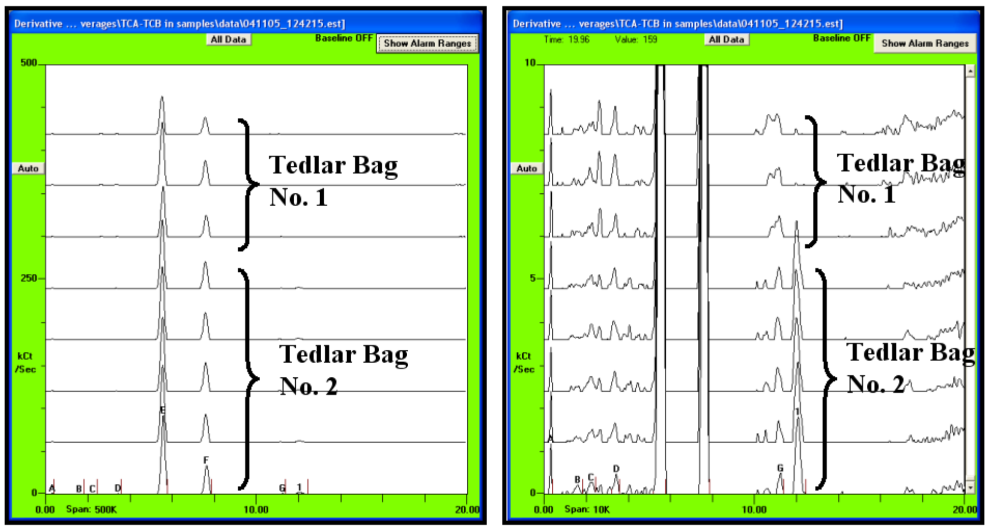

Figure 5- Replicate testing of tedlar bag air samples No. 1 & 2.

Sample No. 2 contained significant quantities of TCA while sample No. 1 did not. A more detailed view of sample 2 is shown in Figure 6 together with a listing of peak retention indices and peak areas in counts. For this analysis approximately 4 mL of air was removed from the tedlar bag. The pre-calibrated TCA sensor (Kovats index =1383) gives a reading of 97.4 picograms. This translates to an air concentration of 25 nanograms/meter^3 in the tedlar bag.

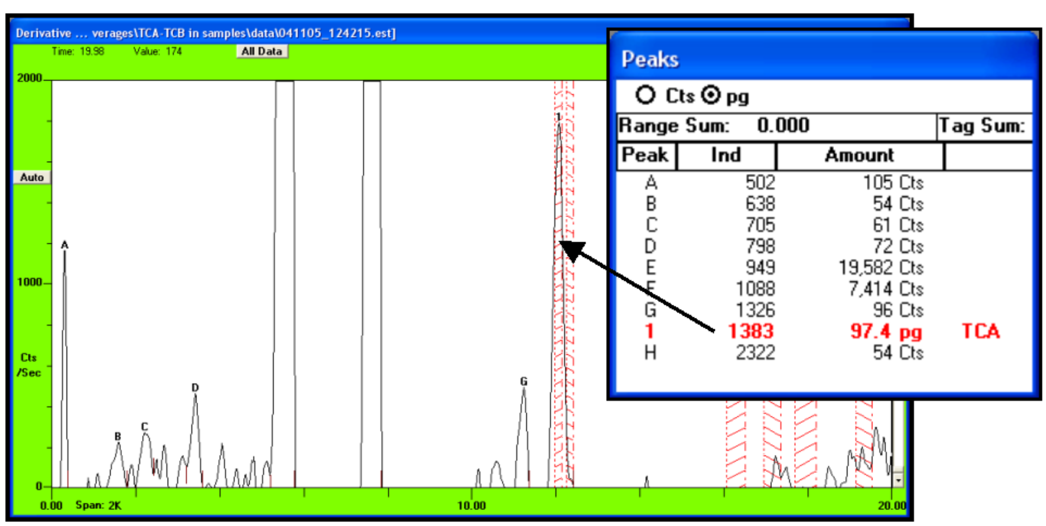

Figure 6- Chromatogram of tedlar bag air sample No. 2 showing TCA.

Testing Wood Samples

Wood samples were placed in septa-sealed 40 mL vials, heated to 40^{o}C, and their headspace vapors sampled. A side-ported needle was attached to the inlet of the instrument and then inserted through the septa and into the vial headspace as shown in Figure 7.

Figure 7- Sampling headspace vapors of samples in heated vials

Two vertically offset replicate chromatograms of wood headspace vapors are shown in Figure 8. Although no anisols were detected, trichlorophenol (TCP) was detected in a significant amount. The TCP virtual sensor measured approximately 65 picograms in a 6 mL vapor sample. Although desorbtion and recovery models for TCP in wood prevent a precise measure of the TCP in wood concentration using headspace measurements, it is clear that the wood is contaminated. Since common bacteria can easily convert TCP into the anisole TCA, a serious odor problem may occur in areas where this wood is being used.

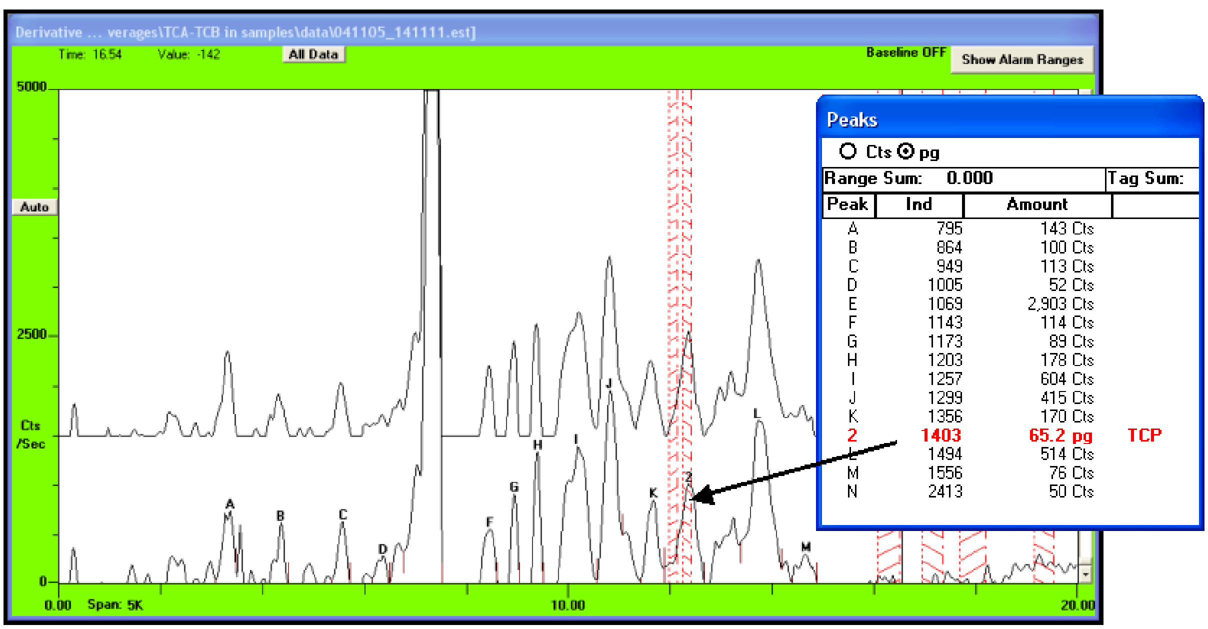

Figure 8- Two vertically offset replicate chromatograms of headspace from wood samples heated to 40^{o}C.

Testing Paint Samples

Dried paint samples were placed in septa-sealed 40 mL vials, heated to 40°C, and their headspace vapors sampled. Two vertically offset replicate chromatograms of paint headspace vapors are shown in Figure 9. A significant amount (37 pg) of trichlorophenol (TCP) and trace amounts (4 pg) of trichloroanisole (TCA) and 6 pg of tribromoanisole (TBA) were detected.

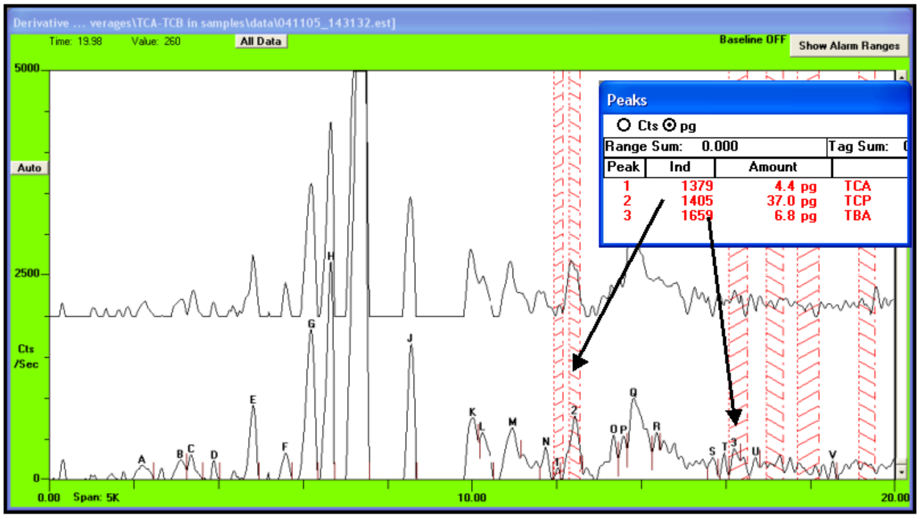

Figure 9- Headspace testing of thermally desorbed paint samples.

A better test for high molecular weight, semi-volatile compounds, is to first extract them with solvent. Five milliliters of methanol was added to the dried paint samples and then 0.5 μL injected directly into the inlet of the zNose®. The resulting chromatogram is shown in Figure 10. Significant amounts of TCA (54 pg), TCP (122 pg), TBA (255 pg), TBP (568 pg), and PCP (326 pg) were detected in the paint extract.

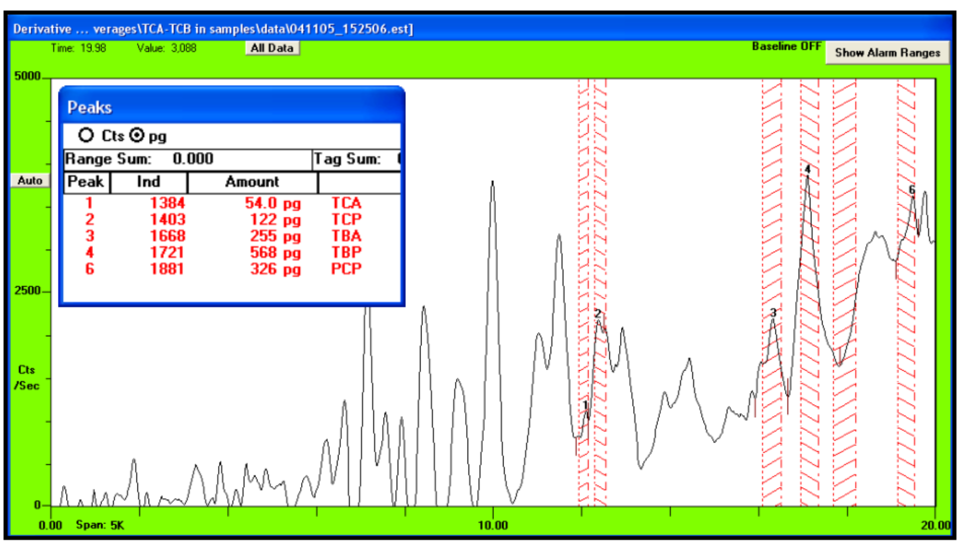

Figure 10- Extraction testing of paint samples.

Summary

The zNose® is useful tool for detecting the presence of trichloroanisole (TCA), trichlorophenol (TCP), tetrachloroanisole (TeCA), tetrachlorophenol (TeCP), pentachloroanisole (PCA), pentachlorophenol (PCP), tribromoanisole (TBA), and tribromophenol (TBP). By direct sampling of ambient air or headspace vapors from thermally desorbed wood and paint samples, the source of odor causing anisols and phenols can be quickly detected.

Portability, high speed, and virtual chemical sensors, specific to anisols and phenols, make the zNose® unique. It can be used to assess many wine production methods as well as the wine aroma itself. In addition to finished wine it could be put to good use in testing quality of wine barrels, corks, and bottles. The ability to perform literally hundreds of chromatographic analyses per day in the field represents a substantial cost savings compared to conventional long-column GC testing in the laboratory, which is slow, expensive, and certainly not portable. With the zNose® virtually any part of a winery and its production processes can be subjected to analytical testing in near real time.