Electronic Sensor Technology

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zNose™

Technical Report

BACKGROUND

Plastics are used as containment vessels for a wide variety of products and readily absorb organic compounds. These organic compounds can easily taint the products within the containment vessel leading to unpleasant odors and a loss of product. The compounds 2,4,6 Tribromophenol (TBP) and 2,4,6-tribromoanisol (TBA) are particularly difficult because they have very low odor thresholds, typically less than 1 picogram per milliliter of air. TBP is commonly used as a fungicide in wood and fiber. TBP is methalyated into TBA by metabolic processes of bacteria.

The important physical properties of TBP and TBA are listed in Table I. Also shown are the homologues trichlorophenol (TCP) and trichloroanisole (TCA). TCA has nearly the same 'earthy' or 'mold' smell, an equally low odor threshold, and is a major taint in wines.

Table I

	TCP	*TCA*	*TBP*	*TBA*
Sat. Vapor Pressure				
micro-mmHg	**8**	**22.8**	**0.303**	**0.644**
ppm	**1.053**	**3.006**	**0.039**	**0.076**
ng/mL	**8.5**	**26**	**0.53**	**1.08**
Mol. Wt.	**197.45**	**211.48**	**330**	**344.83**
Odor Threshold				
pg/mL		**0.05**		**0.03**

Objective

An assessment of TBP/TBA odor delectability in plastics and wood using an ultra-fast, short column gas chromatograph called the zNose™ was performed. The objective was to assess analytical performance of the zNose™ and to develop a quick and portable method for screening plastic and fiber/wood materials prior to their use.

The zNose™

The zNose is designed to sample, analyze and quantify the chemical composition of any odor, fragrance, or vapor in seconds with part per trillion sensitivity and universal selectivity. Instruments are produced in two basic configurations, handheld and bench-top, as shown in Figure 1 and Figure 2. Both types are portable and operate from 110/220 VAC. The only consumable, helium gas, is supplied from either a re-chargeable or disposable cartridge within each instrument.

Figure 1- The Model 4200 zNose provides handheld performance and maximum measurement flexibility.

Figure 2- The model 7100 zNose uses a single benchtop enclosure which can also be integrated for unattended process control and monitoring.

Direct Sampling Methods

A heated inlet (200°C max) and an internal pump allow the zNose™ to directly sample and quantify volatile (<C15) and semi-volatile (>C15) organics in ambient air spanning the range C4 to C24 (relative to n-alkanes). Volatile compounds are best measured using a sample needle and septa sealed vial as shown in Figure 3. As the zNose™ removes a small amount of vapor for analysis a venting needle maintains atmospheric pressure within the vial. Vapors of known concentration can be easily created and used to calibrate the instrument directly in vapor pressure units (ppm or ppb). Because vapor pressure is dependent upon temperature accurate measurements require temperature control and for this a 2-zone vial heater is available. The 2-zone heater, shown in figure 4 is designed to minimize condensation on the septa and to allow for accuracy in comparing the concentration of organics in solid as well as liquid samples.

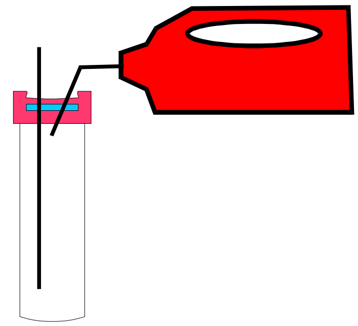

Figure 3- Direct vapor measurement method, C4 to C15, using septa vials.

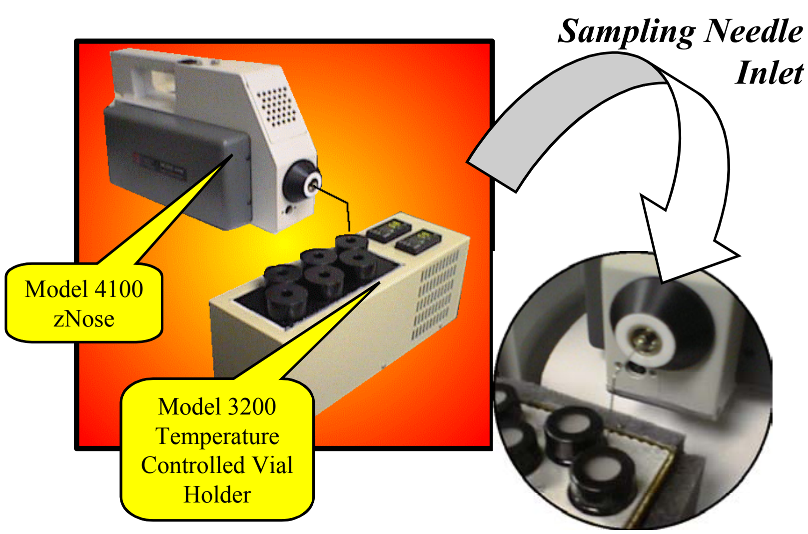

Figure 4- Consistent vapor measurements are possible using 2-zone (top and bottom) temperature controlled septa-vial heater and zNose™ with side-ported sampling needle attached to the luer inlet of the instrument.

Semi-volatile organics (>C15) are characterized by low vapor pressure and a strong desire to adhere to cool surfaces such as vials and sample needles. Consequently, measurement of semi-volatile vapors, such as TBP and TBA, surrounding objects such as plastic pellets and wood or fiber materials is best done by direct sampling with the heated inlet of the zNose™. In this case the mass (nanograms or picograms) of each compound within a vapor sample is measured relative to the response obtained by directly injecting a known amount of that compound directly into the inlet of the zNose™ as shown in Figure 5.

Using direct sampling the zNose™ inlet sample flow is typically 30 milliliters per minute. Sampling air containing 1 nanogram per liter of TBA requires only 1 milliliter of air or just 2 seconds to collect 1 picogram of TBA. However to achieve the same sensitivity as a human, 30 picograms per liter, direct sampling requires 333 times longer or more than 10 minutes to again collect 1 picogram of TBA. To achieve higher signal to noise (e.g. 10 to 1) and higher sensitivity, indirect sampling methods are a more practical approach.

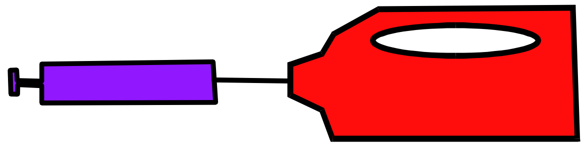

Figure 5- Direct injection of a known mass provides a simple calibration method for quantifying the concentration of semi-volatile compounds in odors.

Indirect Sampling Methods

The low odor threshold of TBA/TBP, 30 picograms per liter, was confirmed by sampling residual vapor concentrations in 40-milliliter septa-vials. The zNose™ cannot directly detect the presence of TBA at these concentrations without excessive sample time. To measure TBA and TBP at picogram per liter levels an indirect sampling method is used. The method requires an additional preconcentration stage using a sampling flow 150-200 milliliters per minute. The 2-step process is shown in Figure 6.

Indirect sampling is accomplished by attaching an open tubular desorber (OTD) accessory to the zNose™. In this method, an OTD sampling tube, called a SlickStick™, is attached to the inlet of the instrument. The sampling tube can be filled with an absorbent such as Tenax™ or glass wool. Using the zNose™ sample pump, ambient vapors are preconcentrated at high flow (150-200 milliliters per minute) and room temperature. Step one sampling can be several minutes although detection levels of below picograms/liter concentrations of TBA/TBP are achieved using a 2-minute sample time. The second step of the indirect method raises the temperature of the SlickStick™ to approximately 170^{o}C and the preconcentrated TBA/TBP is desorbed into the inlet of the zNose™ where it is collected and analyzed using low flow sampling (30 milliliters per minute) for approximately 10-20 seconds.

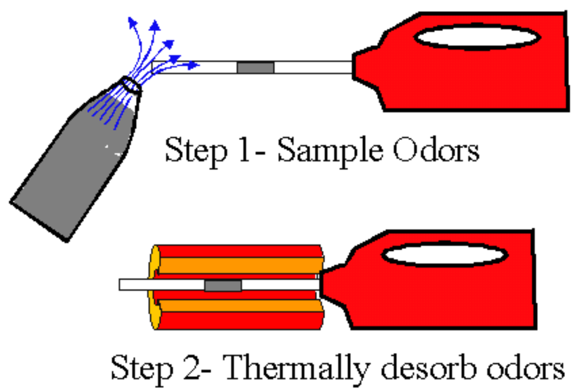

Figure 6- Preconcentrating odors and then thermally desorbing them into the zNose(tm).

Analytical Performance of the zNose™

To evaluate the ability of the zNose™ to detect TBP/TBA, chemical standards of known concentration in methanol are used with the direct sampling method. Two initial stock solutions, 8 milligrams per milliliter for TBP and 7.2 milligrams per milliliter for TBA were first produced. Serial dilution was then used to create test solutions containing 2 nanograms/µliter and 1.8 nanograms per µliter of each. Injecting 0.2 µliters directly into the inlet of the zNose™ during a sampling of ambient air produced the chromatogram shown in Figure 7.

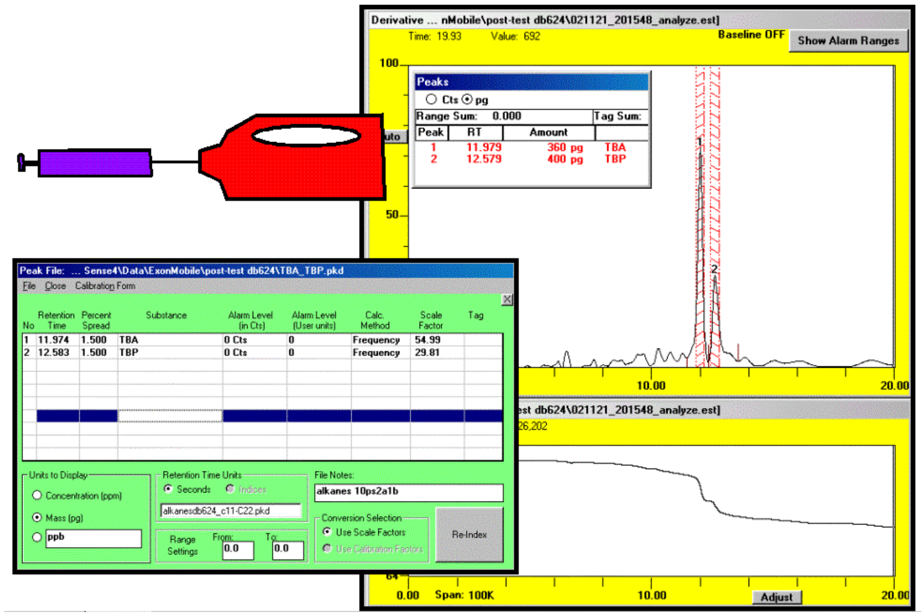

Figure 7- zNose™ detector response (lower) and derivative chromatogram (top) obtained by injecting 0.2 µliter of standard methanol solution.

Retention time bands associated with each compound and detector response factor, defined as the area in counts for each compound peak divided by the amount injected, allow for calibration and quantitative vapor measurements. In this case the response factor for TBA was 54.99 count/picogram and 29.01 counts/picogram for TBP.

The zNose™ system response to specific compounds is stored in a subprogram peak file listing the retention time and response factor as shown in Figure 7. Retention time can also be measured relative to the n-alkanes and listed as Kovats Indices rather than time. The detector noise floor is typically less than 10 counts, although background vapors typically limit delectability to 1 picogram for TBA and TBP.

Overall vapor measurement sensitivity is dependent upon the size of vapor sample analyzed. The zNose™ samples odors and fragrances by preconcentrating ambient vapors at a typical flow rate of 30 milliliters/minute and for a sample time selected by user software e.g. the method. Thus, using a sample time of 10 seconds to collect and preconcentrate 5 milliliters of vapor would then have a detection limit of 1 picogram per 5 milliliters or 200 picograms per liter of air.

Odor Threshold

The ability of a human to detect trace amounts of TBP and TBA is extremely low, typically 30 picograms per liter. Experimental vapors for odor testing were created by injecting 10 nanograms of TBA or TBP into 40 milliliter vials with septa lids. Soon after injection the vapor concentration of TBA was approximately 7 picograms/milliliter and easily measured using direct sampling with a 60 second sample time. However, only 1 hour later the concentration of TBA was found to be less than 1 picogram per milliliter yet the odor remained easily detecteable by human operators.

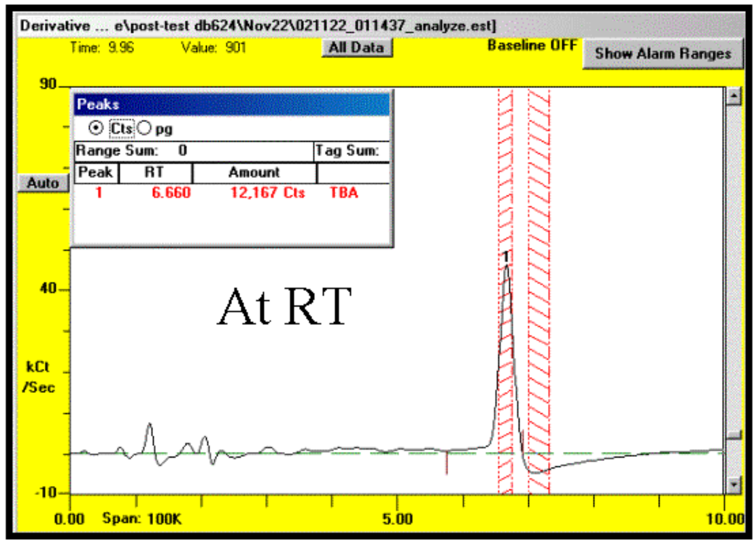

Figure 8- Direct sampling 30 milliliters of vapor from a 40 milliliter vial 2 minutes after injecting 10 nanograms of TBA produced 12,167 counts or approximately 220 picograms of TBA. (7 picograms/milliliter)

The inoculated "odor" vials provide a convenient low concentration odor standard whose concentration remained constant for many days. The concentration of TBA was subsequently measured using the indirect 2-step method and the results of a typical analysis is shown in Figure 9. The concentration of TBA in the standards was nominally found to be 0.5 picograms per milliliter.

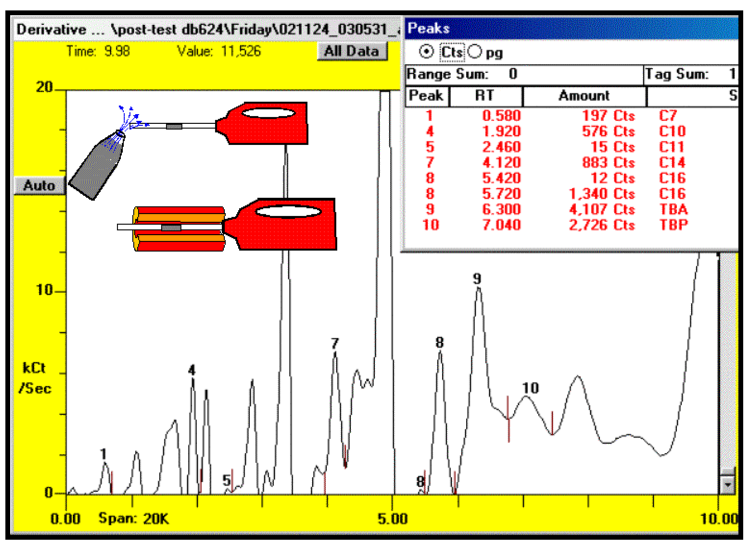

Figure 9- Indirect sampling of odor vial after 24 hours showing equilibrium concentration of TBA to be 0.5 picogram/milliliter at room temperature.

Detecting Fungicide (TBP/TBA) Treated Wood

Direct preconcentration of 10 milliliters of vapors surrounding wood samples at equilibrium in a sealed bottle and room temperature easily identified the presence of TBP and TBA (Figure 12.) Translating the 674 counts of TBA and 2,320 counts of TBP into mass and dividing by the sample volume yields a TBA concentration of 1.2 picograms per milliliter and 8 picograms per milliliter for TBP.

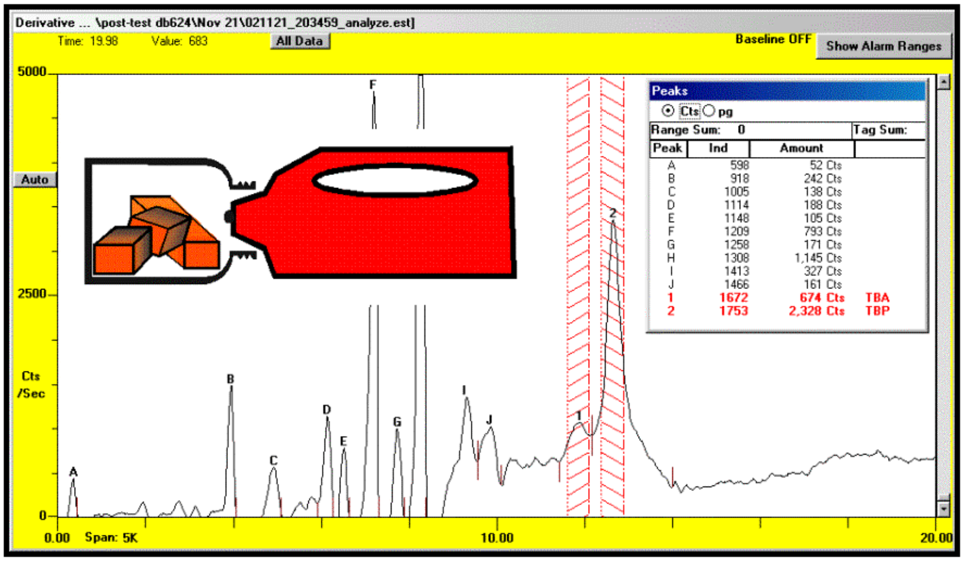

Figure 10-Directly sampled headspace vapors from wood samples in jar. (30°C detector, 10 mL sample, 10ps2a1b method, 200°C inlet 160°C valve)

Good repeatability of the direct sampling method is demonstrated by three replicate measurements chromatograms shown in Figure 12.

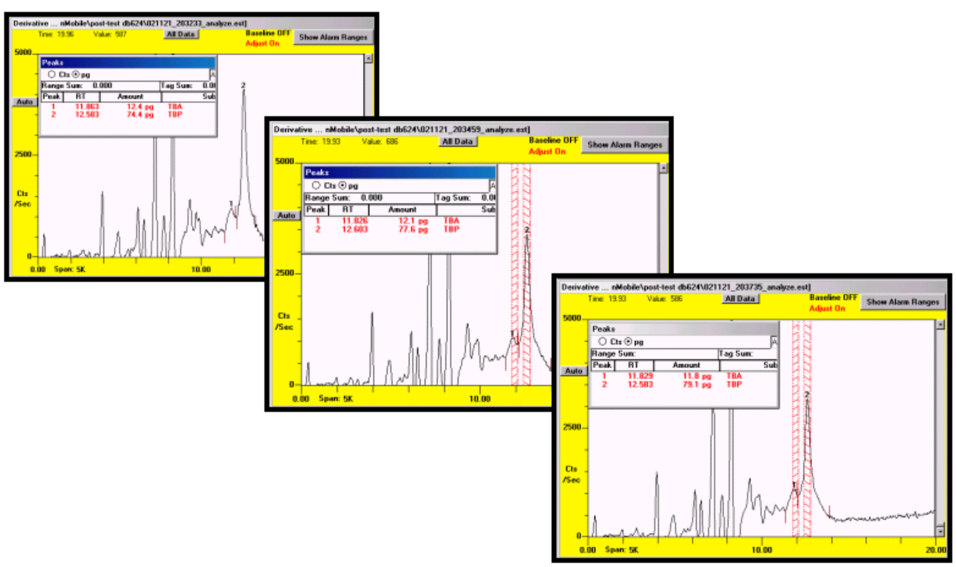

Figure 11- Replicate testing of wood headspace vapors demonstrating accuracy and precision of measurement.

Odors in Plastic Pellets

Odors associated with good and tainted plastic pellets were investigated. An initial evaluation focused on compounds in the range C4 to C14 using direct sampling and a zNose™ equipped with a db624 column for best resolving power in this range. The resulting chromatogram detected 16 volatile compounds with Kovats indices spanning 481 to 1417 as shown in Figure 13. Clearly both good and tainted plastic has a substantial but nearly identical odor chemistry in this range.

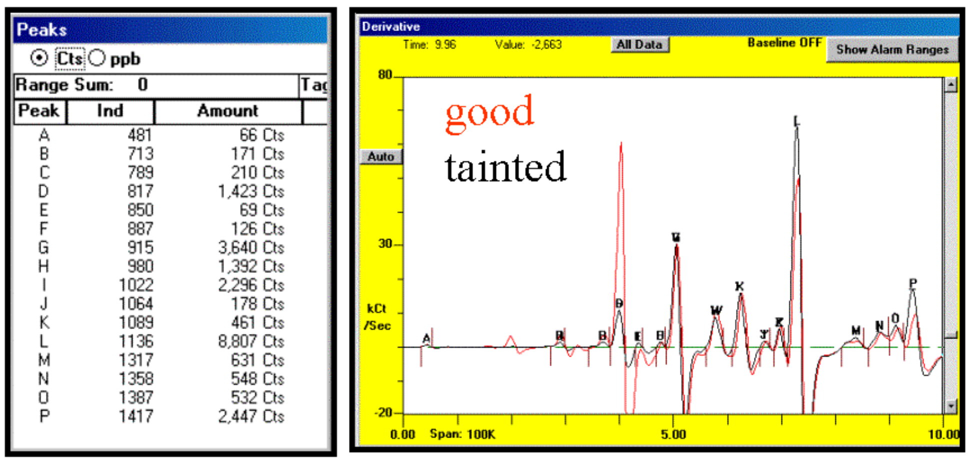

Figure 12- Primary volatile organics (C4-C14) in odors from plastic pellets

Expanding the detection range to include TBP/TBA indicated the presence of high molecular weight compounds in odors from both plastics. The presence of TBP at a concentration of approximately 1 pg/mL was indicated in both samples (Figure 14), but only in the tainted pellets was a small concentration, 0.2 pg/mL of TBA detected. Backgrouind interferrence from other compounds present in the plastic odor made quantification difficult using direct sampling at these concentration levels.

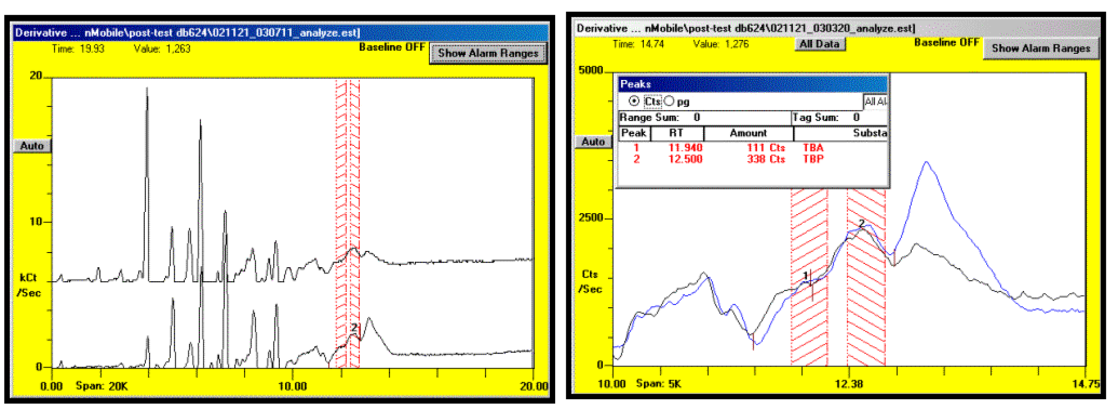

Figure 13- Sampling of odors from good and tainted plastic pellets with a 10 milliliter sample volume indicates the presence of TBA (2 pg) and TBP (11 pg).

Indirect sampling using a sample volume of 150 milliliters increased the sensitivity of the measurement as shown in Figure 14. In general the tainted plastic samples produced higher concentrations of high molecular weight compounds and TBA and TBP was detectable in the tainted plastic.

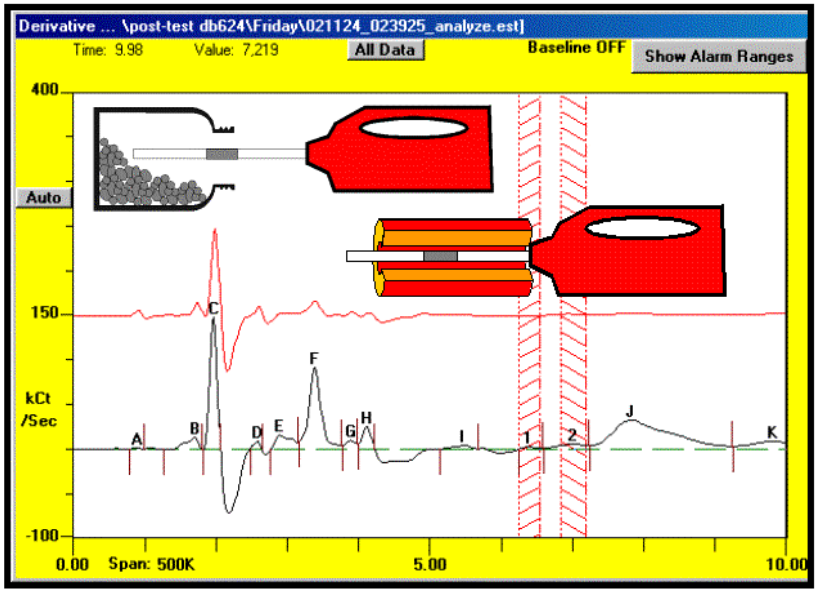

Figure 14- Offset chromatograms obtained with good (red trace) and tainted plastic pellets using a 150 milliliter sample volume.

Increasing the sample volume to 300 milliliters (Figure 15) indicated the presence of TBA/TBP in both samples but concentrations in the tainted samples are higher. In the tainted sample the concentration of TBA was 140 pg/liter and TBP was 1310 pg/liter. Their concentrations in the good plastic samples were 30 pg/liter and 400 pg/liter.

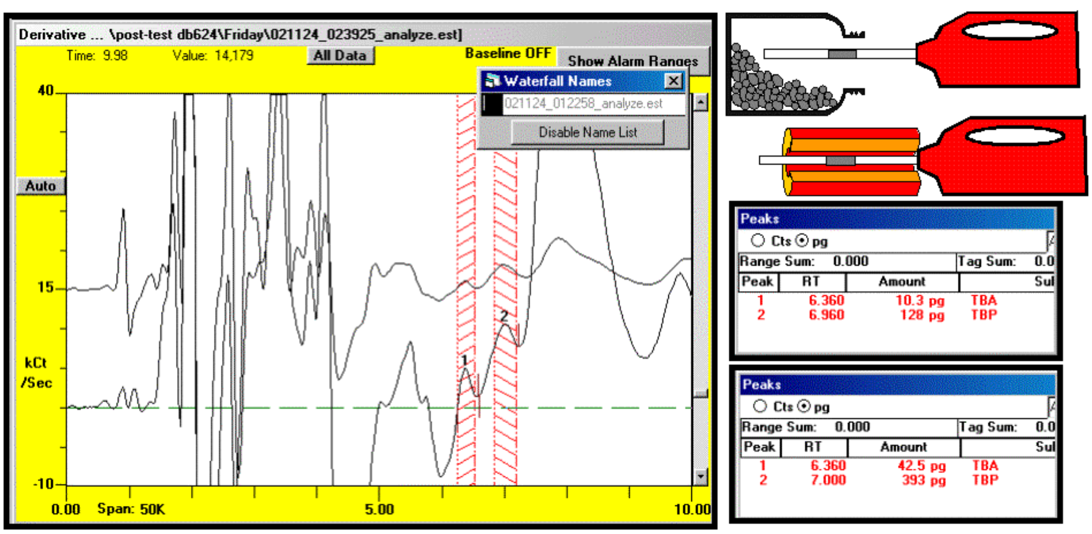

Figure 15- Expanded scale for offset chromatograms for good (top) and tainted (bottom) plastic pellets. A 300 milliliter sample volume was used.

Summary of Results

An assessment of TBA and TBP odor delectability in plastics and wood using an ultra-fast, short column gas chromatograph called the zNose™ was performed. The objective was to assess analytical performance of the zNose™ and to develop a quick and portable method for screening odors in plastic and fiber/wood materials. Quantification of odors containing TBA/TBP is made difficult because (1) low odor threshold of 30 pg/L requires picogram sensitivity, (2) low volatility and stickiness toward any surface and (3) background vapor matrix often contains other organics at significantly higher concentration than target analytes.

The zNose™ is the first electronic nose to incorporate ultra-high speed (10 seconds) gas chromatography, vapor preconcentration, and solid state vapor detection into a new analytical instrument specifically designed to measure odor chemistry. The solid state detector (with electronic sensitivity control) demonstrated picogram sensitivity. Both direct vapor sampling (30 mL/min) and indirect vapor sampling (150 mL/min) methods were investigated. Analytical performance was measured and TBA/TBP delectability was approximately 1 nanogram per liter for direct sampling while much lower delectability , 1-10 pg/L , was possible with indirect vapor sampling.

The low odor threshold of TBA/TBP was confirmed as also was the sticky nature of these materials. These compounds can easily migrate and contamination of any cool surface requires special care when performing odor measurements at picogram levels. Odors from samples of wood treated with TBP were easily identified using direct sampling and required only a 10 milliliter vapor sample. Odors from plastic pellets required indirect sampling and 150-300 milliliter vapor samples to distinguish good from tainted pellets. Indirect vapor sampling with the zNose™ was able to measure TBA/TBP in plastic odors at picogram/liter concentration levels.

The zNose™ is a very cost effective odor measurement tool when compared to the cost of conventional laboratory analyses of odor samples. Since time is costly there is a need for speed which only the zNose™ can provide. As an example, over 300 chromatographic measurements can be performed in an 8 hour period compared with less than 20 using a conventional GC instrument. Other features, like performing odor measurements on-site or in-situ working with human odor panels, offer additional capabilities to research projects involving odor management.