Detection of Volatile Organic Compounds in Odors from Plastics Using the zNose®

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Electronic Noses

Conventional electronic noses (eNoses) produce a recognizable response pattern using an array of dissimilar but not specific chemical sensors. Electronic noses have interested developers of neural networks and artificial intelligence algorithms for some time, yet physical sensors have limited performance because of overlapping responses and physical instability. eNoses cannot separate or quantify the chemistry of odors.

A new type of electronic nose, called the zNose®, is based upon ultra-fast gas chromatography, simulates an almost unlimited number of specific virtual chemical sensors, and produces olfactory images based upon aroma chemistry. The zNose® is able to perform analytical measurements of volatile organic vapors and odors in near real time with part-per-trillion sensitivity. Separation and quantification of the individual chemicals within an odor is performed in seconds. Using a patented solid-state mass-sensitive detector, picogram sensitivity, universal non-polar selectivity, and electronically variable sensitivity is achieved. An integrated vapor preconcentrator coupled with the electronically variable detector, allow the instrument to measure vapor concentrations spanning 6+ orders of magnitude. In this paper a portable zNose®, shown in Figure 1, is shown to be a useful tool for quantifying the concentration of volatile organic compounds in odors produced by plastic objects.

Figure 1- Portable zNose® technology incorporated into a handheld instrument

How the zNose™ Quantifies the Chemistry of Odors

A simplified diagram of the zNose™ system shown in Figure 2 consists of two parts. One section uses helium gas, a capillary tube (GC column) and a solid-state detector. The other section consists of a heated inlet and pump, which samples ambient air. Linking the two sections is a "loop" trap, which acts as a preconcentrator when placed in the air section (sample position) and as an injector when placed in the helium section (inject position). Operation is a two step process. Ambient air (odor) is first sampled and organic vapors collected (preconcentrated) on the trap. After sampling the trap is switched into the helium section where the collected organic compounds are injected into the helium gas. The organic compounds pass through a capillary column with different velocities and thus individual chemicals exit the column at characteristic times. As they exit the column they are detected and quantified by a solid state detector.

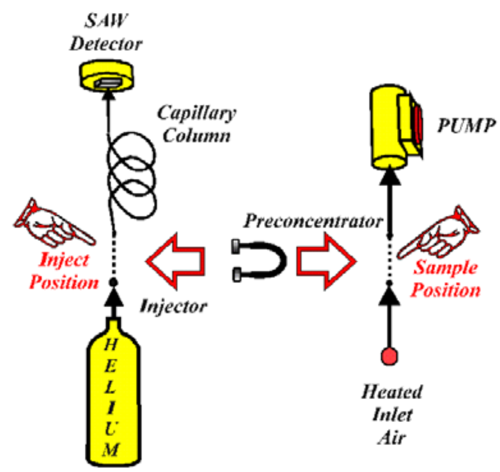

Figure 2- Simplified diagram of the zNose™ showing an air section on the right and a helium section on the left. A loop trap preconcentrates organics from ambient air in the sample position and injects them into the helium section when in the inject position.

An internal high-speed gate array microprocessor controls the taking of sensor data which is transferred to a user interface or computer using an RS-232 or USB connection. Odor chemistry, shown in Figure 3, can be displayed as a sensor spectrum or a polar olfactory image of odor intensity vs retention time. Calibration is accomplished using a single n-alkane vapor standard. A library of retention times of known chemicals indexed to the n-alkane response (Kovats indices) allows for machine independent measurement and compound identification.

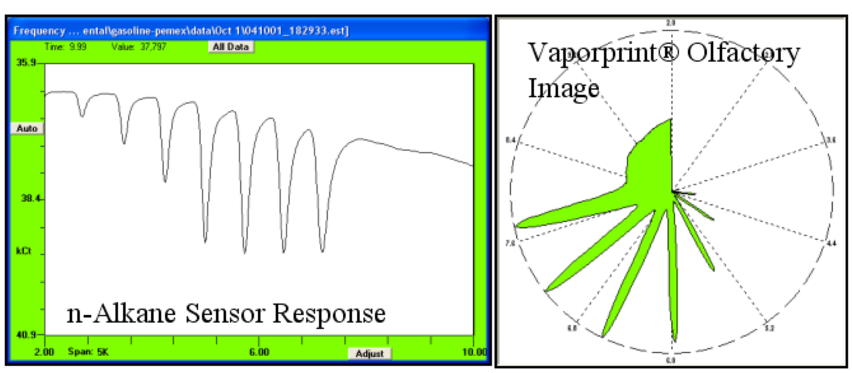

Figure 3- Sensor response to n-alkane vapor standard, here C7-C14, can be displayed as sensor output vs time or its polar equivalent olfactory image.

Chemical Analysis (Chromatography)

The time derivative of the sensor spectrum (Figure 3) yields the spectrum of column flux, commonly referred to as a chromatogram. The chromatogram response (Figure 4) of n-alkane vapors (C7 to C14) provides an accurate measure of retention times. Graphically defined regions, shown as red bands, calibrate the system and provide a reference time base against which subsequent chemical responses are compared or indexed. As an example, a response midway between C10 and C11 would have a retention time index of 1050.

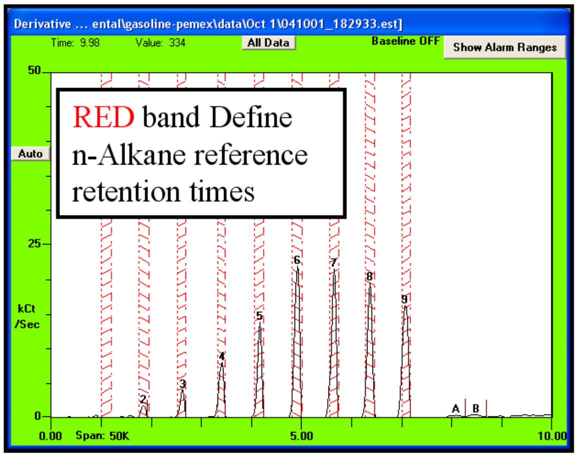

Figure 4 - Chromatogram of n-alkane vapors C6 to C14).

Odors from Plastics

Odors from synthetic material, including soft plastics and vinyl, rubber, polyester, rayon, and nylon can produce unpleasant odors and may also contain chemicals harmful to people. Solvents and other plasticizers may continue to outgas long after the plastic object has been formed. Often chemicals such as toluene, benzene, 1,1,1-trichloroethane, chloroform, styrene, formaldehyde, phenol, and alcohols are given off. Plasticizers (phthalates) left over in the material (did not react) after the manufacturing process will outgas and produce distinctive odors as well.

Figure 5- Plastics are a necessary part of the modern environment and serve many useful purposes.

Sampling Vapors from Plastics at Room Temperature

Using a side-ported sampling needle attached to the inlet of the zNose, Figure 6, odors and chemical vapors within the vial can be sampled and chemical concentrations quantified in a controlled and predictable manner. Four plastic rods, were separated into two groups of two rods each. Sample no. 2 produced a distinctive and unpleasant odor while sample no.1 rods produced only a very slight odor.

Odors from each of the four rods were measured by sampling vial headspace vapors. Sampling removed approximately 10 milliliters air from the 40 mL vial.

Vertically offset chromatogram results for each sample group are shown in Figure 7. Sample 1 produced only 4 distinct chemicals while sample 2 produced 8 at much higher concentration measured in peak area (counts).

Figure 6- Direct headspace sampling of chemical odors produced from plastic samples placed in a septa-sealed vial.

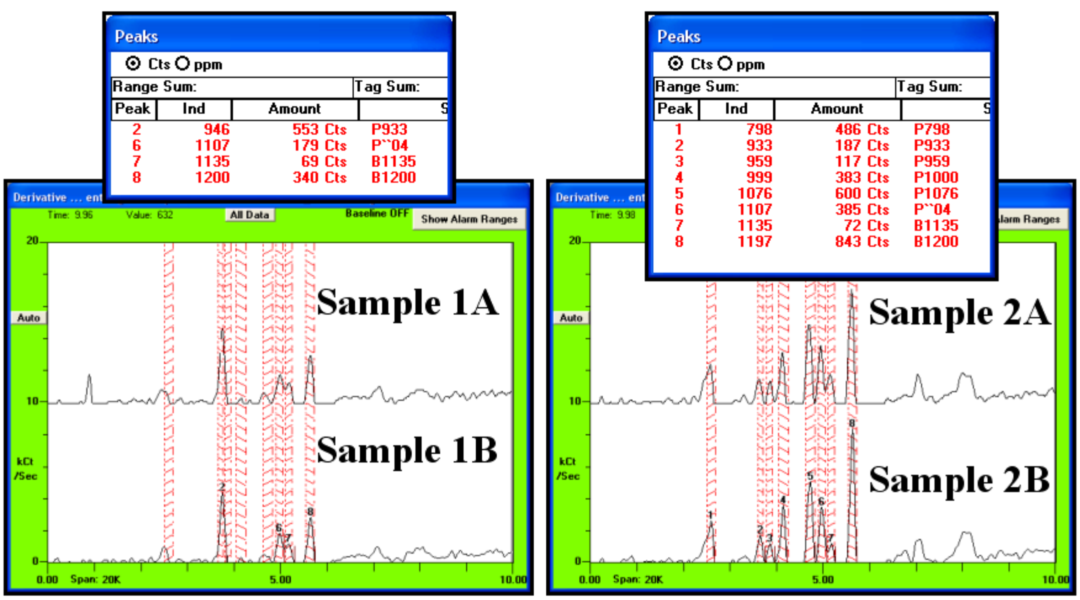

Figure 7- Vapors from samples at 23°C were evaluated using a 30 second sample time, a 10°C detector, and a 10ps2a1b method.

Testing Sample Vapors at Higher Temperature

Elevating the temperature of the plastic samples produces higher vapor concentrations which can be measured with greater precision than measurements taken at room temperature. A vial heater shown in Figure 8 was used to maintain a vial temperature of 60°C. Sample vial temperature was maintained for 10 minutes prior to sampling headspace vapors with the zNose®.

Figure 8- Direct headspace sampling of heated vials

Vertically offset chromatogram results for each sample group are shown in Figure 9. Sample 1 produced only 6 distinct chemicals while sample 2 produced 9 at much higher concentration measured in peak area (counts). The presence of additional chemicals compared with sample no. 1 can clearly be seen and is presumed these are responsible for the distinctive odor of sample 2 plastics.

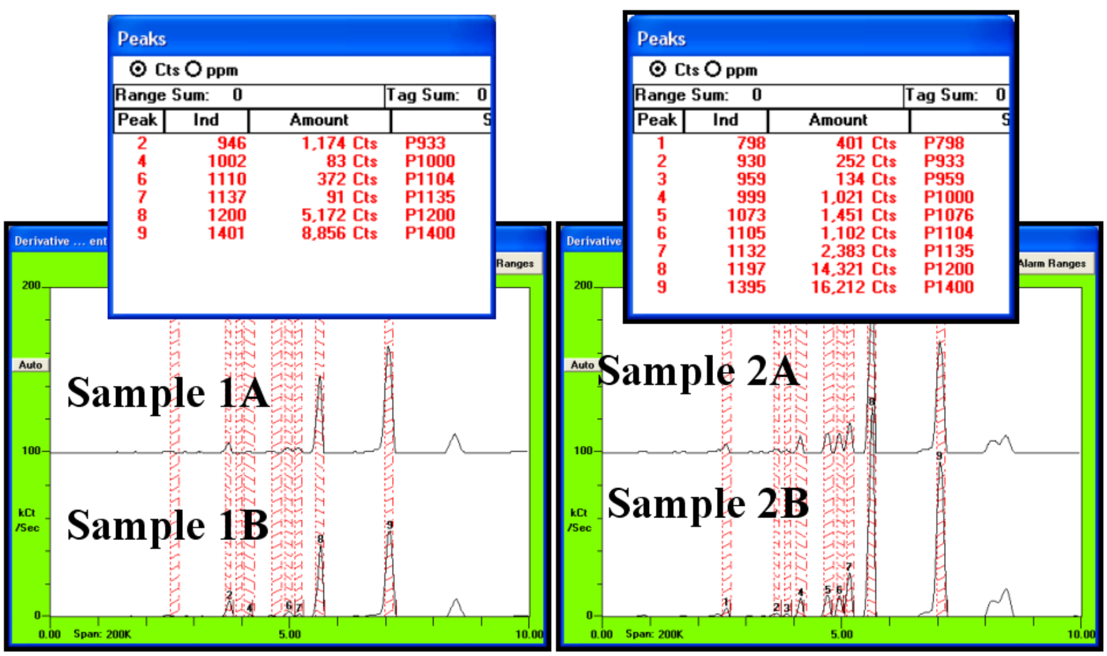

Figure 9- vapors from samples at 60°C were evaluated using a 10 second sample time, a 20°C detector, and a 10ps2a1b method.

Comparing Olfactory Images

High-resolution two-dimensional olfactory images together with overlaid chromatograms allow complex odor chemistry to be quickly identified and compared as shown in figure 10. Olfactory images can be plotted using linear (radial) odor intensity or logramithic odor intensity. These images can be absolute or relative to the highest chemical concentration.

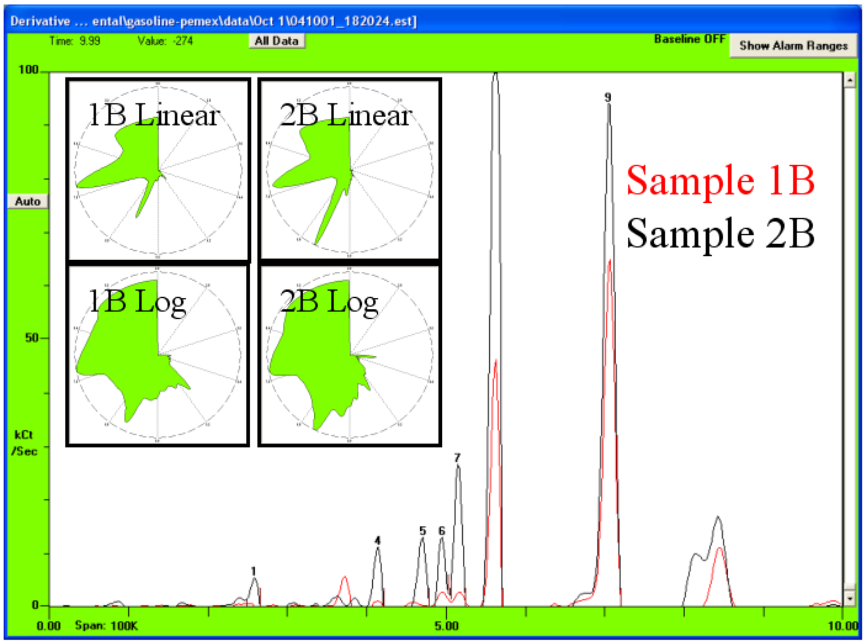

Figure 10- Vaporprint® images together with overlaid chromatograms allow complex odor chemistry to be quickly identified and compared.

The derivative of odor intensity yields chromatograms which can then be overlaid for more detailed comparisons. The odor producing chemicals in sample 2 can clearly be seen in the above chromatogram. Although not identified by name these chemicals can tentatively be identified by their unique Kovats indices 798, 1000, 1076, 1104, and 1135. Using these indices alone, the zNose® can be used as a quality control tool to either test plastic production processes or to screen plastic parts for their presence.

Summary

Quantification of odor chemistry is fast and easy using the zNose® electronic nose. Because odor chemicals are volatile, detecting air concentrations well into the part-per-trillion range is possible. However, because volatility is temperature sensitive, headspace measurements are best performed with samples elevated to at least 40°C. A summary chart of volatile chemicals by Kovats indices and their intensity in counts is shown in Table I.

Table I – Chemical Composition of Sample Odors

	Chemical Concentrations (counts)								
	Peak 790	Peak 933	Peak 959	Peak 1000	Peak 1076	Peak 1104	Peak 1135	Peak 1200	Peak 1400
Sample 1A	102	659		93		261	223	5509	10956
Sample 1B		1174		83		372	91	5172	8856
Sample 2B	685	251	116	1021	1289	1053	1699	11043	11398
Sample 2B	401	252	134	1021	1451	1102	2383	14321	16212

Odors from synthetic materials like plastics can produce unpleasant odors and may also contain chemicals harmful to people. Solvents and other plasticizers may continue to outgas long after the plastic object has been formed. Often chemicals such as toluene, benzene, 1,1,1-trichloroethane, chloroform, styrene, formaldehyde, phenol, and alcohols are given off. Plasticizers (phthalates) left over in the material (did not react) after the manufacturing process will outgas and produce distinctive odors as well. Using indices alone, the zNose® can be used as a quality control tool to either test plastic production processes or to screen plastic parts for their presence. Odor causing chemicals can now be quickly identified and remediation steps taken to improve the quality of plastic materials.