

## Detection of Phenol in Water and Air 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 aromas.

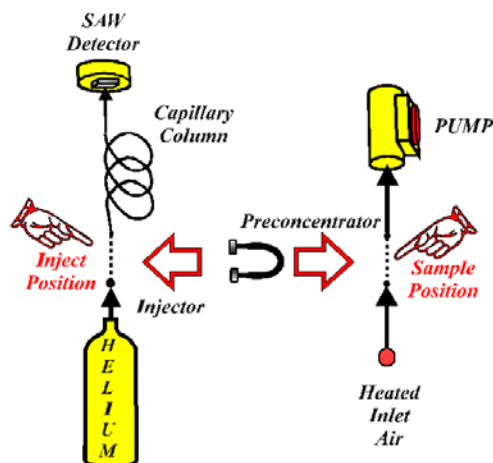
A new type of electronic nose, called the zNose®, is based upon ultra-fast gas chromatography, simulates an almost unlimited number of specific virtual chemical sensors, and produces olfactory images based upon aroma chemistry. The zNose® is able to perform analytical measurements of volatile organic 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 environmental tool for quantifying the concentration of phenol in air and water samples.



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

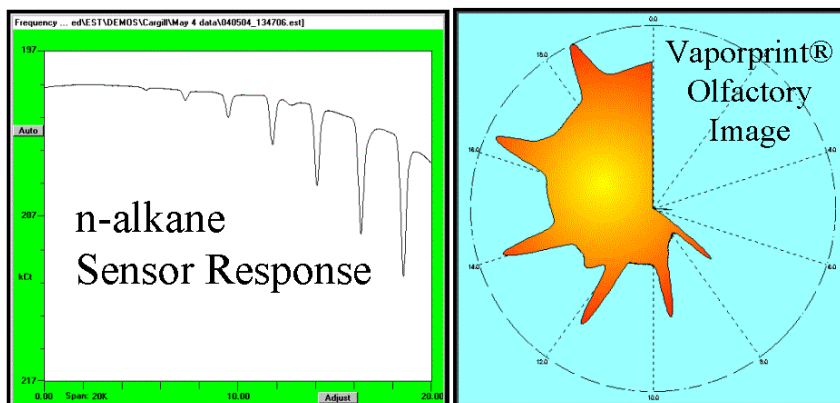
## How the zNose™ Quantifies the Chemistry of Aromas

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 (aroma) 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. Aroma 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 C6-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 (C6 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.

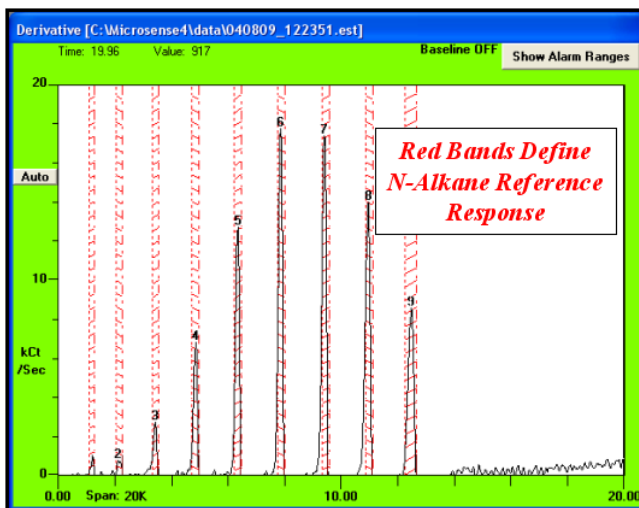


Figure 4 - Chromatogram of n-alkane vapors C6 to C14).

## Properties of Phenol

Physical properties of phenol are shown in Figure 5. Although it is relatively volatile is also is very soluble in water which accounts for the low Henry's constant and at room temperature, only 0.00136% will partition into the air from water as headspace vapor.

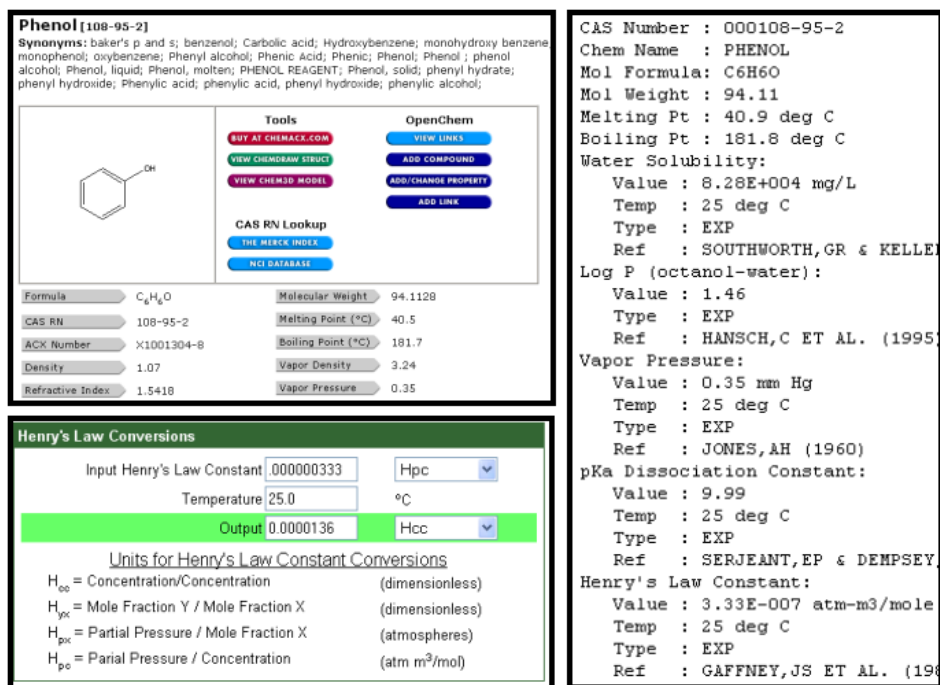
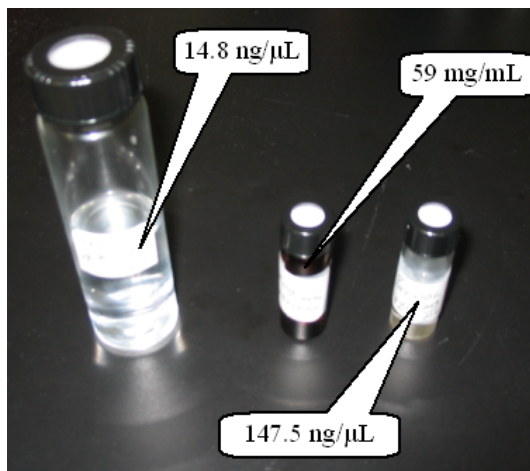


Figure 5-Physical properties of Phenol.

## Phenol Standards

A stock solution of phenol in methanol, made by dissolving 177 mg phenol crystals in 3 mL of methanol (59 mg/mL), was used as a master calibration mixture. Two additional standards at 147.5 nanograms/microliter (ng/mL) and 14.75 nanograms/microliter were produced by serial dilutions.



## Calibration by Direct Injection

The zNose was calibrated by injecting a known amount of phenol directly into the inlet of the instrument while sampling ambient air as shown in Figure 7. The calibrated response of the system to an 11.8-nanogram injection of phenol with an indexed retention time of 1085 is shown in Figure 8. The response of the zNose®, 1017 counts/nanogram, was linear with increasing amounts of phenol as shown in



Figure 7- Calibration by directly injecting a known mass of phenol

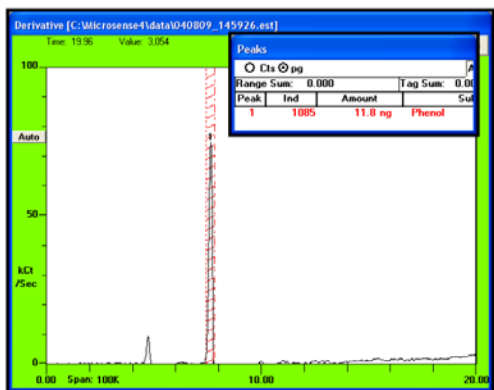


Figure 8- Response to direct injection of 11.8 nanograms of phenol.

Figure 9. The minimum detection limit for phenol was 10 picograms.

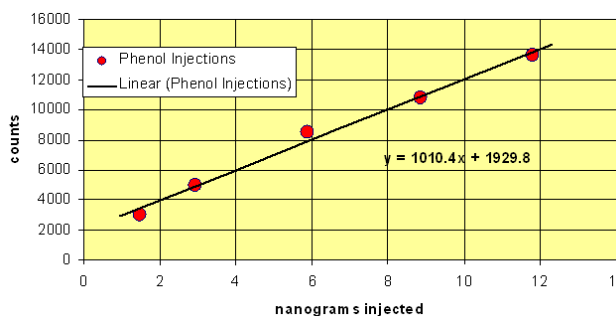


Figure 9- Linearity of Phenol response.

## Vapor Calibration Standard

A phenol vapor standard (590 picograms/milliliter) was created by injecting 10  $\mu\text{L}$  of standard solution (147.5 ng) into a 250 mL bottle. Using a side-ported sampling needle attached to the inlet of the zNose<sup>®</sup>, 3.17 mL vapor samples were extracted and quantified. Offset replicate samples are shown in Figure 11. An insert plot shows the vapor concentration in the bottle following the injection.

A maximum of 750 pg per sample indicated 40% recovery due to absorption of phenol on the walls of the bottle. The minimum vapor detection limit for phenol was approximately 800 parts per trillion (ppt) or 3.25 nanograms/Liter.



Figure 10- Phenol Vapor Standard

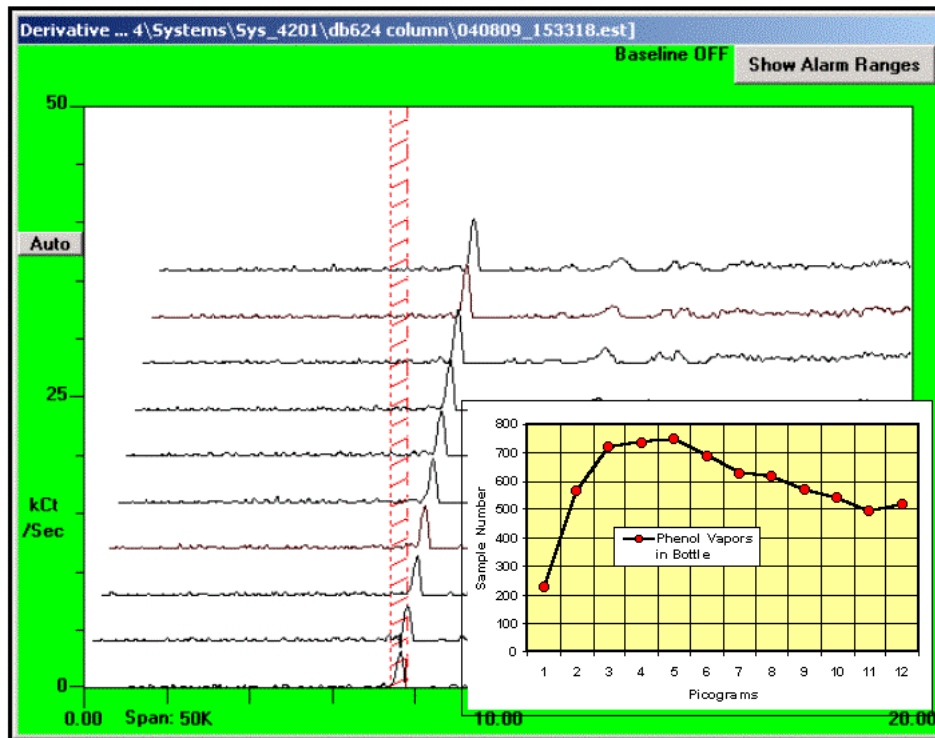
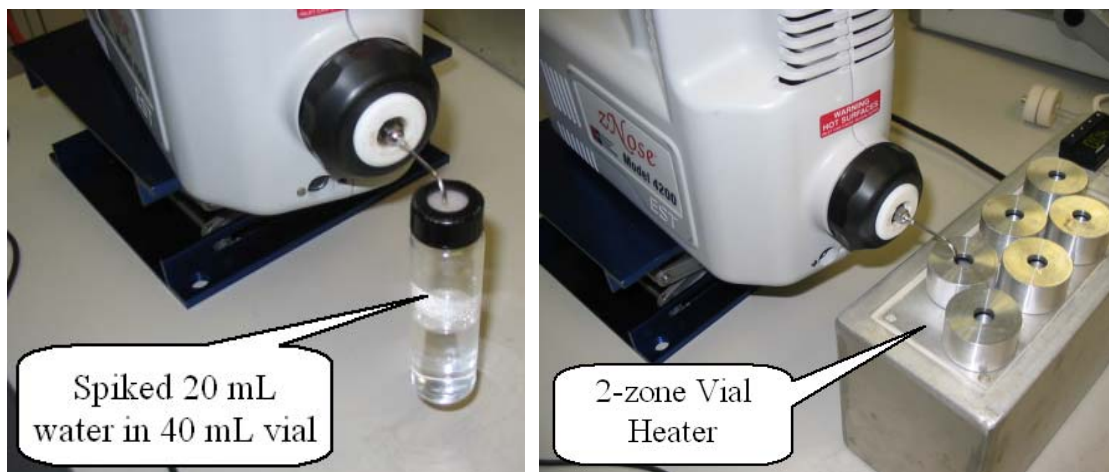


Figure 11- Replicate samples taken on phenol vapors in bottle.

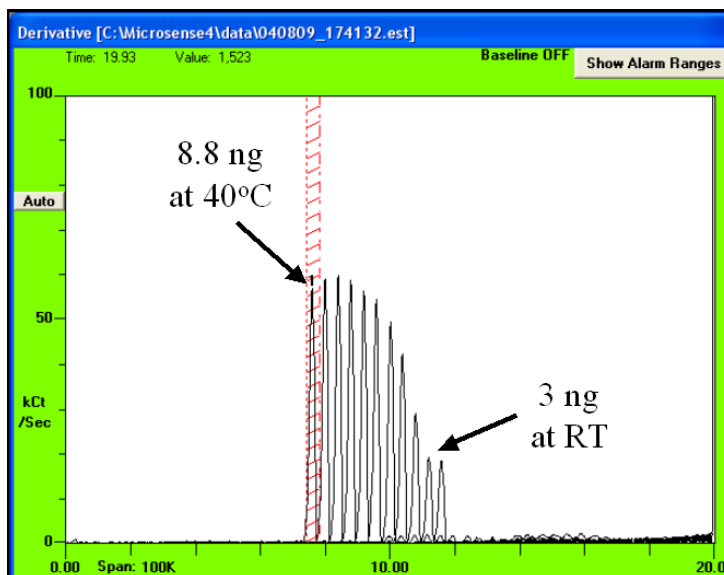
## Direct Detection of Phenol in Water

Headspace vapors from water samples (20 mL water in a 40 mL vial) were sampled directly using a side-ported sample needle attached to the inlet of the zNose® as shown in Figure 13. The concentration of phenol in headspace vapors from water at room temperature is low because phenol is very soluble in water, however, heating the water using a two-zone, top and bottom, vial heater accessory shown in Figure 14 can increase it.



*Figure 12- Direct headspace sampling of water Figure 13- Direct headspace sampling of heated water spiked with phenol*

Replicate direct sample measurements (offset in x-direction) are shown in Figure 15 for water containing 5.9-ppm phenol. At room temperature 3 ng in the 20 mL headspace was detected while raising the water temperature to 40°C increased the amount detected to 8.8 ng. Using direct sampling of water headspace vapors the minimum detectable amount of phenol in water at room temperature (590 counts/ppm) was 0.250 ppm. The minimum detectable amount of phenol in water at 40°C was approximately 100 ppb.



*Figure 14- Direct Sampling of Headspace vapors from water at two different temperatures*

## Detection of Phenol in Water Using SlickStick® Accessory

The detection limit for phenol in water can be reduced to the low ppb range by use of a 2<sup>nd</sup> stage of preconcentration combined with water heating. The external preconcentrator accessory (SlickStick®) is a tube containing tenax absorbent and attaches between the inlet of the zNose® and the side-ported sample needle as shown in Figure 15. Using the internal pump of the zNose®, headspace vapors are sampled at a higher flow rate than direct sampling (100 ccm) and for longer times without breakthrough.

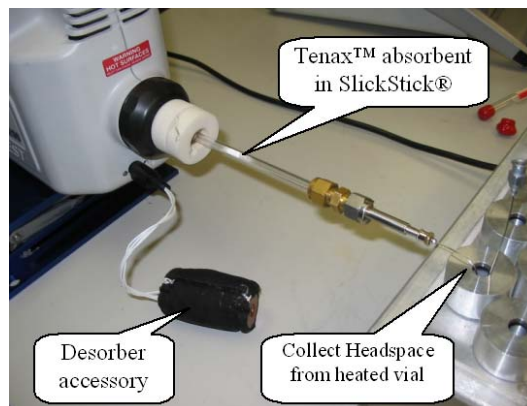


Figure 15- Sampling headspace vapors using SlickStick®

After sampling the vapors concentrated in the tenax of the SlickStick® are desorbed and collected by the internal trap of the zNose® as shown in Figure 16. The heater,



Figure 16- Desorbing into inlet sampler of zNose®

shown in black, connects to the zNose® and the desorption temperature is selectable up to 200°C by the zNose® software program.

As Shown in Figure 17, 774 pg of phenol was detected in the headspace vapors above 40°C water containing 74 ppb of phenol. With a response factor of 10 counts/ppb the minimum detection level for phenol in water is was 10 ppb.

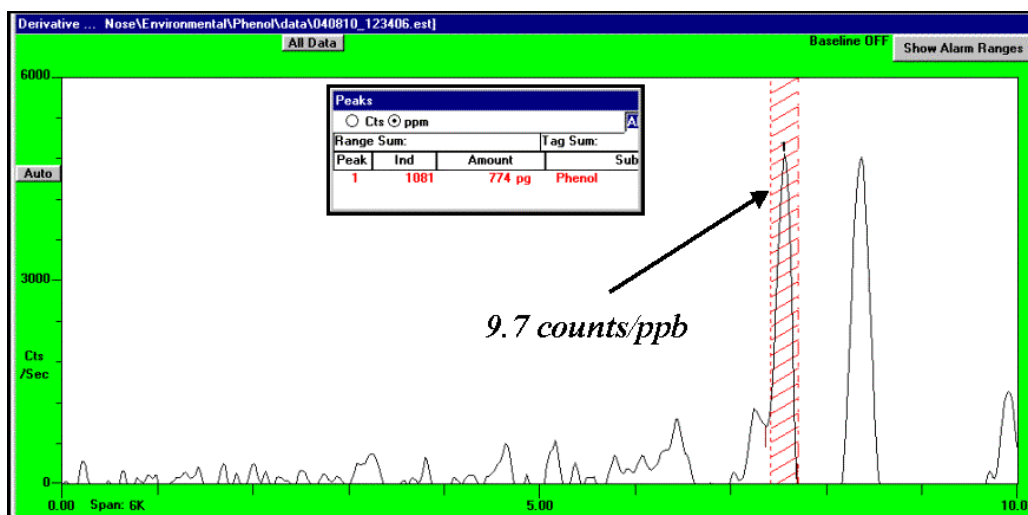


Figure 17- Detecting Phenol in water containing 74 ppb phenol.

## Summary

Detecting phenol in air and water is fast and easy using the zNose® electronic nose or portable gas chromatograph. Because phenol is a relatively volatile air concentrations well into the part-per-trillion range are possible. However, because phenol is very soluble in water headspace measurements are best performed with water samples elevated to at least 40°C. Using a 2<sup>nd</sup> stage preconcentrator accessory sampling, sampling headspace vapors with the zNose can reach minimum detectable levels of 10 ppb phenol in water. A summary chart of phenol MDL amounts is shown in Table I.

*Table I - Phenol Minimum Detection Levels*

Method	Minimum Detectable Level
Direct Sampling in Air	3.25 ng/Liter
Direct Sampling Water	
At 22.5°C	250 ppb
At 40.0°C	100 ppb
2-Stage Preconcentration	10 ppb