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The zNoseÔ, A New Electronic Nose Using Acoustic Technology

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Abstract - A new Electronic Nose using a single, uncoated, high Q surface acoustic wave resonator is described. The commercial expression of this technology, the zNose™, is now providing an on-line quantitative measure of quality for food, beverages, cosmetics, and other manufacturers of aromatic products. The zNose™ can provide a recognizable visual image of specific vapor mixtures (fragrances) containing possibly hundreds of different chemical species in 10 seconds or near real time. At the same time this new nose is able to speciate and quantify the individual chemicals (hydrocarbons mainly) present in any vapor, odor, or smell. Because the new acoustic technology is quantitative it is the only electronic nose technology to be validated by the US EPA.

An array of sensors simulating the human olfactory response has become known as an eNose [Ref. 1]. An eNose provides a vectorial image in N-dimensional space (where N equals the number of sensors) of specific vapor mixtures (fragrances) containing possibly hundreds of different chemical species. eNoses have only a few sensors, produce responses which are not correlated, multiple sensors respond to the same vapor e.g. overlap, and their sensitivity is very poor. In the chemical sense, an eNose using quasi-specific sensor arrays may never be a quantitative measurement instrument.

However, a new approach, based upon fast chromatography and a single high Q acoustic sensor, solves these problems by simulating a virtual sensor array containing hundreds of orthogonal (non-overlapping) sensors. Analysis of any odor is accomplished by serially polling a virtual sensor array or spectrum of retention times. For a zNose™ system, sensor space is defined mathematically by assigning unique retention time slots to each sensor.

The zNose™ is fast (10 seconds), operates over a wide range of vapor concentrations, and has picogram sensitivity. Sending a stream of helium gas and the vapors of interest through a specially coated column causes the vapor's constituent chemicals to split up and travel at different velocities. Emerging from the column at different times, each constituent absorbs and desorbs onto the surface of an acoustic detector, which changes its frequency of vibration depending on how much of the particular chemical is present. There are many successful applications of this new acoustic technology. Food and beverage, pharmaceutical, and cosmetic companies are using the zNose™ to monitor the quality of their products. The acoustic sensor can also be used to detect pollutants, explosive materials and other volatile and semi-volatile compounds with part-per- trillion sensitivity.

Introduction

An array of sensors simulating the human olfactory response has become known as an electronic nose [1]. Electronic noses, called eNoses, utilize non- or weakly specific arrays of physical sensors to produce an N-dimensional response (where N equals the number of sensors) of specific vapor mixtures (fragrances) and this response can be analyzed by principal component analysis. Unfortunately, eNoses using uncorrelated sensor arrays only produce chaotic patterns that cannot be recognized except with sophisticated computer software. Unable to speciate, this type of electronic nose can not be calibrated with chemical standards and therefore is not accepted for use in quantitative scientific methods of measurement.

The development of a solid state integrating acoustic detector [2] with direct column heating [3] has produced a different type of electronic nose, called the zNose™, which can be used to perform quantitative scientific testing of any vapor, odor, smell, or fragrance in seconds. zNose™ instruments are now commercially available as handheld or benchtop style instruments as shown Figure 1.

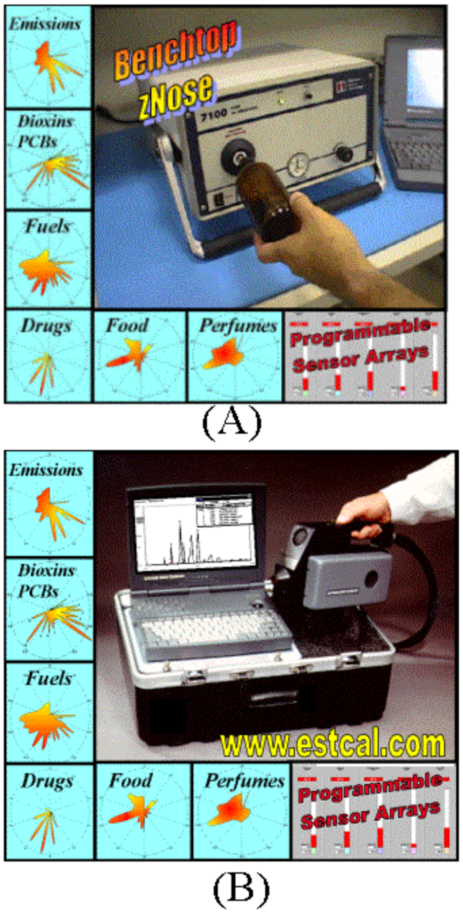
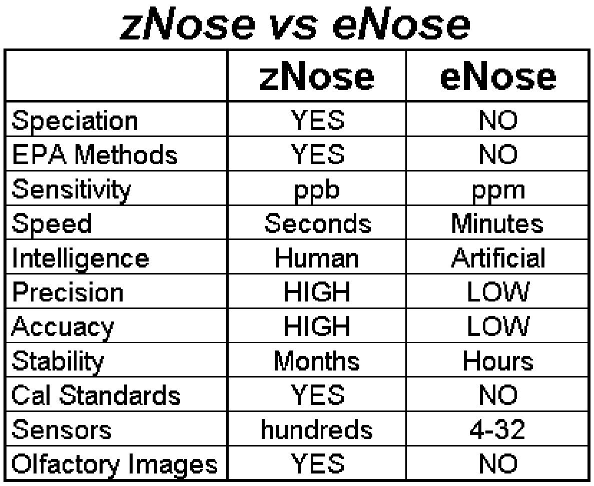


Figure 1- zNose Ô commercial instruments come as benchtop (A) or handheld (B) instruments. Both versions are fully portable and contain their own helium gas supply.

The zNose™ is able to speciate chemical vapors with precision, accuracy, and 10 second speed [4,5,6] and the performance of this new zNose™ technology has been verified by the US EPA Environmental Technology Verification (ETV) program [7]. These results demonstrate for the first time that an electronic nose can be used in the field to quantitatively characterize and measure environmental pollutants according to accepted scientific principles.

Features, which distinguish the two types of electronic noses, are tabulated in Figure 2. Because chromatographic speciation is achieved, calibration standards can be used according to EPA methods. Since only one physical sensor is used sensitivity is quite high with part per billion levels being typical for volatile organics in air or water. As expected with good chromatography, precision and accuracy are high. Unlike chemically coated sensors, which are known for their instability, the solid state acoustic detector is able to maintain calibration for months. Finally, the zNose™ is able to produce high-resolution visual olfactory images, which can be easily recognized by human operators.



zNose vs eNose

	zNose	eNose
Speciation	YES	NO
EPA Methods	YES	NO
Sensitivity	ppb	ppm
Speed	Seconds	Minutes
Intelligence	Human	Artificial
Precision	HIGH	LOW
Accuacy	HIGH	LOW
Stability	Months	Hours
Cal Standards	YES	NO
Sensors	hundreds	4-32
Olfactory Images	YES	NO

Figure 2- Comparison of zNose Vs eNose technology characteristics.

New Electronic Nose

The new zNose™ quantifies the olfactory response by simulating hundreds of speciated chemical sensors spanning a continuous range (chromatogram) of retention time. The electronic nose system diagram is depicted in Figure 3. Input vapors, odors, smells, or fragrances from either air, water, or solids enter the system through a temperature-controlled inlet and are preconcentrated for a carefully measured period of time. The concentrated vapors are injected as a short pulse into a temperature programmed capillary column. The dispersed column effluent then passes to a SAW integrating detector, which records the time and amount of each chemical response.

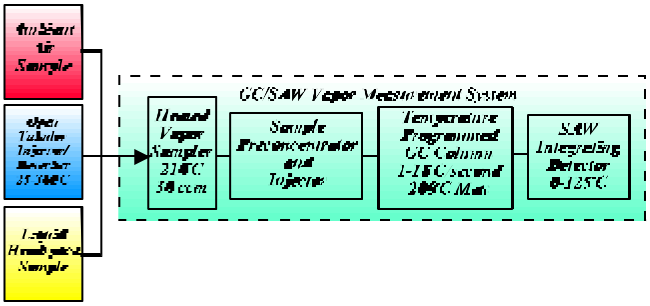


Figure 3- GC/SAW system diagram.

The electronic nose uses a two step process to analyze vapors. The first step samples ambient inlet vapors and concentrates them in a Tenax trap. Sample preconcentration is carefully controlled to produce a repeatable and accurate collection of ambient vapors for analysis in the second step.

In step 2 the trap is rapidly heated and release vapors are re-focused on the head of the relatively low temperature (40°C) capillary column. Then the column temperature is programmed to follow a linear rise to its maximum temperature causing the different chemical species in the sample to be released, travel through the column, and collect on the surface of a temperature controled surface acoustic wave (SAW) crystal.

The acoustic sensor, a SAW crystal, shown in the upper right of Figure 4, consists of an uncoated 500 MHz acoustic interferometer or resonator bonded to a Peltier thermoelectric heat pump with the ability to heat or cool the quartz crystal. Coatings are not used because they reduce the resonator Q, introduce instability, and require excessive time for equilibrium. The temperature of the quartz substrate is held constant during chromatography and provides a method for adjusting the sensitivity of the detector.

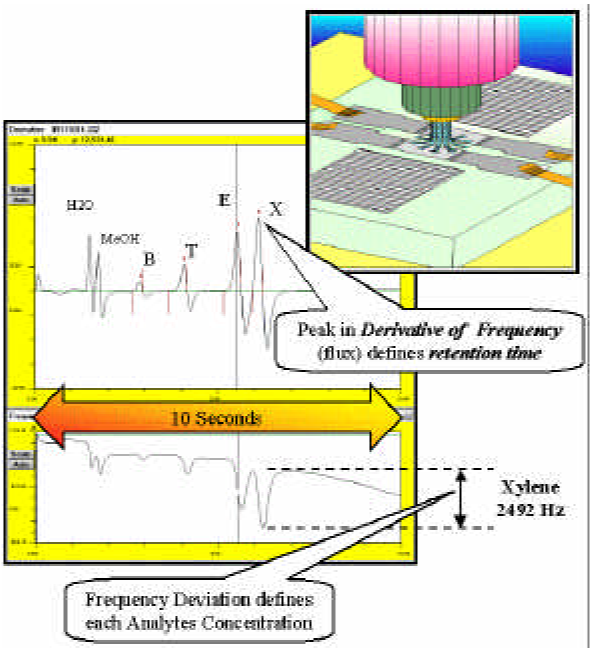


Figure 4- Absorption and desorption of analytes onto SAW crystal creates a frequency chromatogram (lower trace). The derivative of frequency chromatogram produces a flux chromatogram for determining retention time.

System Calibration and Virtual Sensors

The zNose™ only needs electrical power to operate since it carries its own supply of helium in a tank capable of supplying enough gas to capture more than 300 VaporPrint™ images. The instrument includes Windows® software to supply macro instructions to the internal programmable gate array (PGA) microprocessor.

In all scientific measurement methods, reliable and accurate calibration standards are used. An accurate calibration standard for the zNose™ is a tedlar bag filled from a certified high pressure tank of known vapor concentration. In Figure 5, a tedlar bag is filled with a known concentration of benzene-toluene-ethylbenzene-Xylene (BTEX) vapor which provides a reliable BTEX calibration standard.

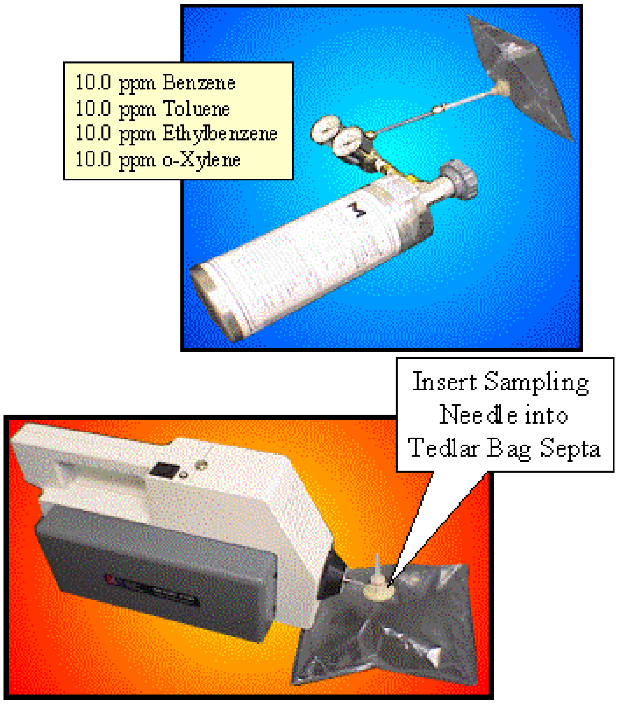


Figure 5-Using a certified tank of vapors to fill tedlar bags with standard concentrations of calibration vapors.

Calibration is performed using single or multiple (N-Point) measurements of mixtures of known analyte concentrations. A typical measurement of a mixture of BTEX, water, and methanol is shown in Figure 6. The lower trace shows the frequency of the acoustic detector while the upper trace displays the derivative of frequency.

As each analyte leaves the column it is absorbed and then evaporates from the quartz surface. The frequency of the acoustic detector decreases in proportion to the amount of vapor absorbed followed by desorption and a return to its unperturbed value. Each retention time defines one chemical sensor of a virtual five element array [8].

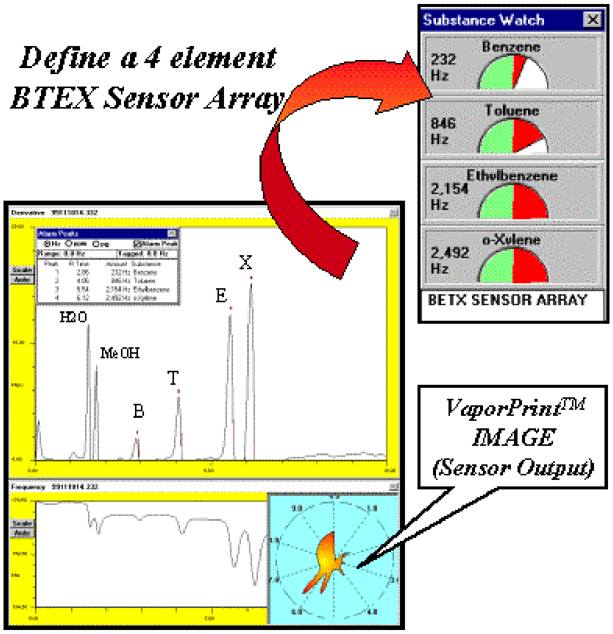


Figure 6- Creating a virtual sensor array for testing precision and accuracy.

A virtual sensor array with as many chemical sensors as needed for any odor, fragrance, or smell can be created and saved for later retrieval. Thus, for the zNose™, chemical sensor space is defined mathematically by assigning unique retention time slots to each sensor.

Precision is the ability to repeat a measurement and accuracy is the ability to obtain the correct answer. Using replicate measurements, the precision and accuracy of the zNose™ was measured. The standard deviation was less than 1-2% and minimum detection levels for toluene, ethylbenzene, and xylene were less then 10 ppb. For benzene, the MDL was approximately 20 ppb.

Because the acoustic sensor uses no coatings it is stable and very sensitive. Minimum detection levels for semi-volatile compounds typically extend well into the part-per-trillion range.

VaporPrint™ Imaging

An important new feature of this new electronic nose is the ability to produce visual olfactory images. In past sensor arrays, principal component analysis techniques to recognize relatively coarse sensor patterns were required. This approach has had limited success and provides little or no information regarding the chemistry of the fragrance.

In contrast, the acoustic sensor is able to produce a coherent, 10-second spectrum of the vapor pressure of the chemicals present in any odor or fragrance. The SAW integrating acoustic detector can produce high-resolution visual images of odor intensity (radial vector) Vs retention time (angular vector).

The zNose™ mimics olfaction by producing visual sensory images called VaporPrints™. As an example images associated with Campbell’s soup are shown in Figure 7. Humans as well as computers can easily recognize these high-resolution (500+ pixel) visual patterns. Such images allow a complex environment to be viewed and recognized as part of a previously learned image set.

A dramatic increase in olfactory perception is achieved in humans using a visual fragrance pattern response. The VaporPrint™ images show a large diversity between different odors. Their primary usage is in their ability to provide an overall view of the odor or fragrance showing the vapor (odor) concentration and characteristic shape at a glance.

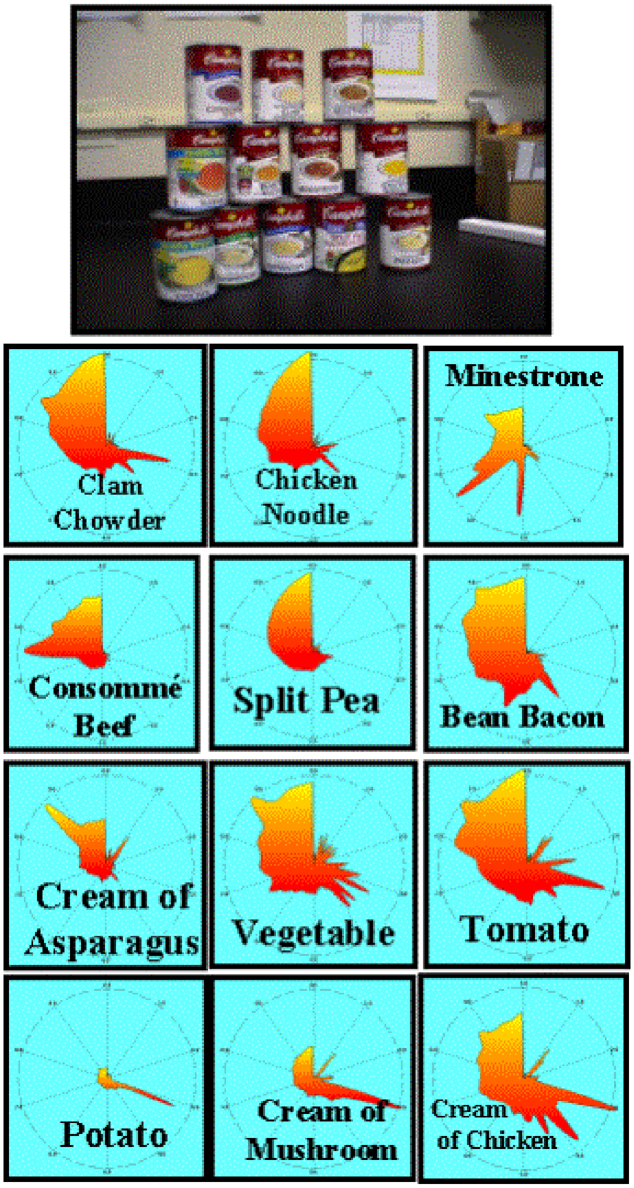
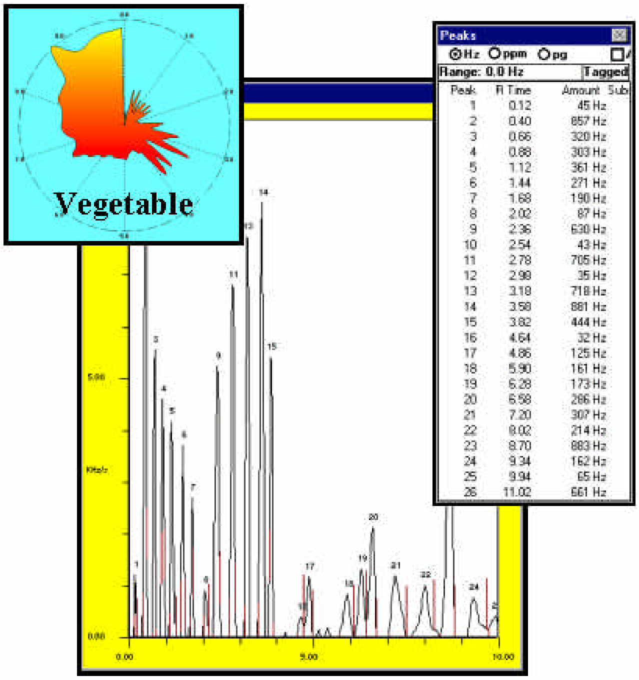


Figure 7- Soups provide a well know source of fragrances. Olfactory images, called a VaporPrint™, of different soup fragrances are shown. Radial amplitude is proportional to fragrance intensity while the angular variable represents time. Start and end time correspond to vertical in these images.

Food & Beverage Applications

The number of market applications for an electronic nose are diverse and numerous. Because the new acoustic sensor accurately measures the chemistry of vapors using an accepted analytical technique, it is the only electronic nose technology to have been accepted by government agencies like the US EPA. The ability to evaluate odors and fragrances with precision and accuracy in seconds now provides quality control engineers with the ability to analyze hundreds of samples per day [9] where previously weeks would have been required. Savings in time and labor can readily be calculated.

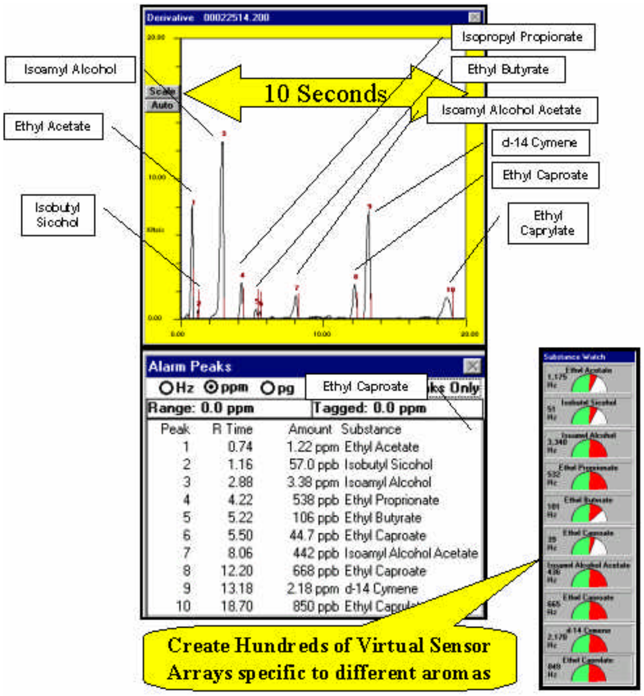
Perhaps the largest number of applications exists in the food and beverage industries because these products are strongly dependent upon aroma and taste as indicators of quality and customer acceptance. An example is depicted in Figure 8 where the compounds present in vegetable soup are shown The ability to quantify the concentration of the compounds for the purposes of quality control is unique to this new electronic nose technology.



Peak	R Time	Amount	Sub
1	0.12	45 Hz	
2	0.40	857 Hz	
3	0.66	320 Hz	
4	0.88	303 Hz	
5	1.12	361 Hz	
6	1.44	271 Hz	
7	1.68	190 Hz	
8	2.02	87 Hz	
9	2.36	630 Hz	
10	2.54	43 Hz	
11	2.78	705 Hz	
12	2.98	35 Hz	
13	3.18	718 Hz	
14	3.58	881 Hz	
15	3.82	444 Hz	
16	4.64	32 Hz	
17	4.86	125 Hz	
18	5.90	161 Hz	
19	6.28	173 Hz	
20	6.58	286 Hz	
21	7.20	307 Hz	
22	8.02	214 Hz	
23	8.70	883 Hz	
24	9.34	162 Hz	
25	9.94	65 Hz	
26	11.02	661 Hz	

Figure 8-Detailed zNose chromatogram showing more than 26 distinct chemicals in Vegatable soup which can be monitored in 10 seconds.

Another example showing the major aromatic compounds detected in a glass of wine is shown in Figure 9. In this example a sensor virtual array of chemical sensors specific to this wine (cabernet) is created and used to evaluate all other cabernet wines.

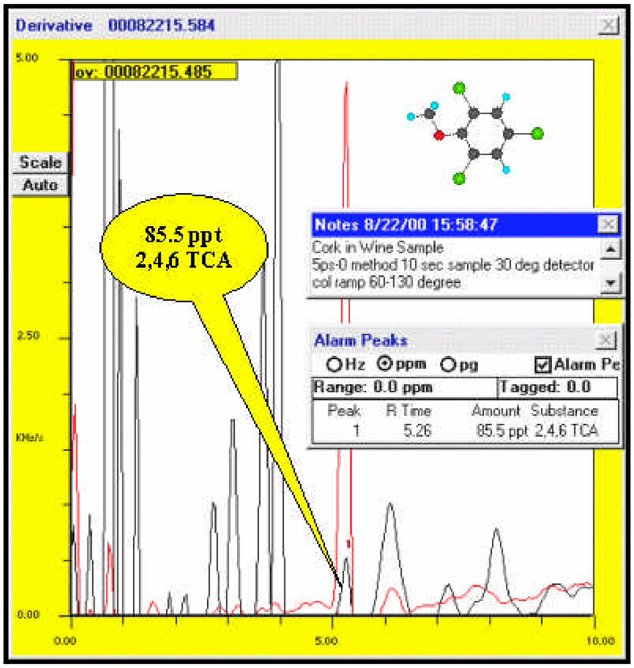


Peak	R Time	Amount	Substance
1	0.74	1.22 ppm	Ethyl Acetate
2	1.16	57.0 ppb	Isobutyl Sicohol
3	2.88	3.38 ppm	Isoamyl Alcohol
4	4.22	538 ppb	Ethyl Proprionate
5	5.22	106 ppb	Ethyl Butyrate
6	5.50	44.7 ppb	Ethyl Caproate
7	8.06	442 ppb	Isoamyl Alcohol Acetate
8	12.20	668 ppb	Ethyl Caproate
9	13.18	2.18 ppm	d-14 Cymene
10	18.70	850 ppb	Ethyl Capru

Create Hundreds of Virtual Sensor Arrays specific to different aromas

Figure 9- Analysis of the chemistry in a glass of wine allows for the creation of a virtual sensor array representing the 10 most aromatic compounds.

In a tour de force of electronic nose technology, the zNose™ has demonstrated the ability to work side-by-side with wine tasting experts in detecting TCA in cork, wine, and even in the air. For the first time an electronic nose can detect 2,4,6-trichloroanisole (TCA) in wine aroma at part-per-trillion levels in seconds. A typical TCA measurement, which demonstrates the large instantaneous dynamic range of the acoustic sensor, is shown in Figure 10. In this case TCA at part-per-trillion levels can be seen amid other compounds which part-per-million concentration levels.



Notes 8/22/00 15:58:47

Cork in Wine Sample
5ps-0 method 10 sec sample 30 deg detector
col ramp 60-130 degree

Alarm Peaks

○ Hz ● ppm ○ pg ☑ Alarm Pe

Range: 0.0 ppm | Tagged: 0.0

Peak	R Time	Amount	Substance
1	5.26	85.5 ppt	2,4,6 TCA

Figure 10- Detecting part per trillion concentrations of TCA amid part-per-million concentrations of wine aromatics requires a large instantaneous dynamic range. Here 85.5 ppt of TCA is compared with an overlay (in red) of a 1-ppb TCA standard vapor.

The zNose™ was tested with wines judged by California wine experts to contain TCA contamination and was able to identify and quantify the concentration of TCA in every case. Most samples indicated ppt concentrations of TCA consistent with the commonly accepted expert olfactory detection threshold of 5-10 ppt.

Eliminating TCA and other taints from wine is a priority at virtually with every vineyard, winery, and cork supplier in the world. One of the main reasons for corkiness in wines has been determined to be 2,4,6-Trichloroanisole (TCA). TCA smells like musty old newspapers and can destroy a good bottle of wine. According to published samplings, tainting in wine occurs in 1-2% of all bottles shipped. Such losses represent a significant waste and can adversely effect a wine's reputation and sales

Summary and Conclusions

A new type of Electronic Nose using an acoustic detector can now provide recognizable visual images of vapor mixtures (fragrances) containing hundreds of different chemical species. The zNose™ electronic nose is fast (10 seconds), operates over a wide range of vapor concentrations, has picogram sensitivity, and is easy to use and calibrate. Using visual olfactory images and virtual sensor arrays to quickly evaluate vapors and odors, the zNose™ is useful in many quality control applications involving foods and beverages.

Unlike eNoses based upon arrays of physical sensors, an acoustic system with a single integrating detector can transform the human olfactory response into a true visual response. Viewed as a virtual sensor array, the zNose™ can produce an olfaction response consistent with serially polling an array of hundreds of virtual chemical sensors. Quality control of virtually any odor or fragrance can now be achieved with speed, precision, and accuracy.

The availability of an electronic nose with the ability to maintain product quality at the part-per-trillion level is a significant breakthrough for many chemical processes. Within the food industry, the zNose™ is designed to support and not replace testing by sensory panels. Instruments can never replace the human sensor, however, the ability to quantify and understand the human perception of a smell or taste may provide valuable insights into how to define and quantify food quality in chemical terms. Once the optimum chemistry is defined, the zNose™ is able to compare and monitor the chemical composition and quality of the entire production process. In fact, no food or beverage expert panel should operate without a zNose™.

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