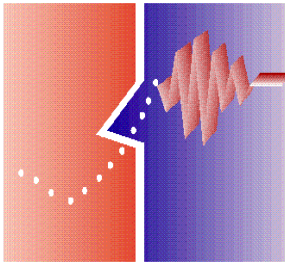


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Odor Detection and Analysis using GC/SAW zNose[®]



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Abstract

New analytical methods for detection and analysis of odors are needed for quick evaluation of odor problems. An important requirement for an odor profiling system is that it must recognize odors based upon their full chemical signature. 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.

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. A library of retention time indices for chemicals allows for the creation of hundreds of specific virtual chemical sensors. Virtual chemical sensors combined with odor profiling can be an effective method for recognizing the presence of odorous emissions. Chemical libraries and electronic odor profiles allows users to quickly distribute signatures of odorous vapors of any kind. 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, the application of zNose, as a useful environmental tool for quantifying volatile organics in ambient air is presented.

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Odor Assessment with an Electronic Nose

Conventional odor assessment methods use subjective human panels to evaluate ambient air samples collected in tedlar bags and a summary report using human descriptors such as foul, sweet, pungent, etc. is produced. These reports are useful but difficult to interpret and are certainly not quantitative.

A complimentary odor analysis method using an electronic nose called the zNose[®] is shown in Figure 1. This portable instrument is able to perform analytical measurements of volatile organic vapors and odors in near real time. Separation and quantification of the individual chemicals within an odor is performed in seconds. An integrated vapor preconcentrator coupled with the electronically variable sensitivity, allow the instrument to measure vapor concentrations spanning 6+ orders of magnitude. In internal pump samples ambient air at ½ milliliter per second and thus the volume of directly sampled air samples is only 5-10 milliliters. Even with such small volume air samples the instrument is able to achieve sensitivity in the low ppb and even ppt concentration ranges.

A handheld air sampler consisting of a battery operated sample pump and a tenax[®] filled probe enables organic compounds associated with odors to be remotely collected. Examples of odors being remotely collected are shown in Figure 2. Using a sample flow of 1 liter/minute allows much larger volumes of air to be tested than with by direct sampling. After sampling the tenax probe is removed from the handheld sampler and then inserted into the inlet of the electronic nose where the collected organic compounds are desorbed and measured.

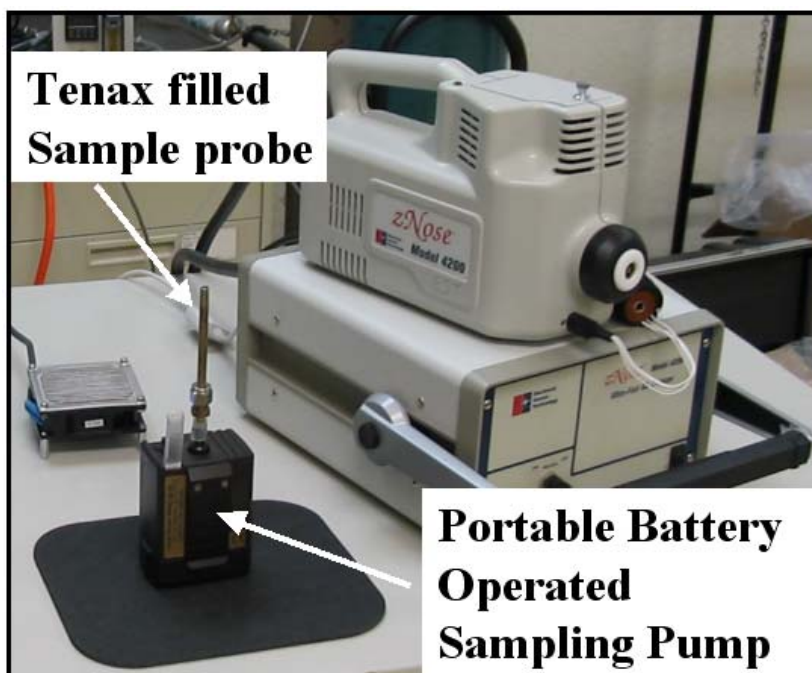


Figure 1- Portable zNose[™] odor analyzing system and battery operated air sampler.



Figure 2- Battery operated remote sampler can be used to collect vapors from many different types of odors.

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 (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.

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. 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. The time derivative of the sensor spectrum 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.

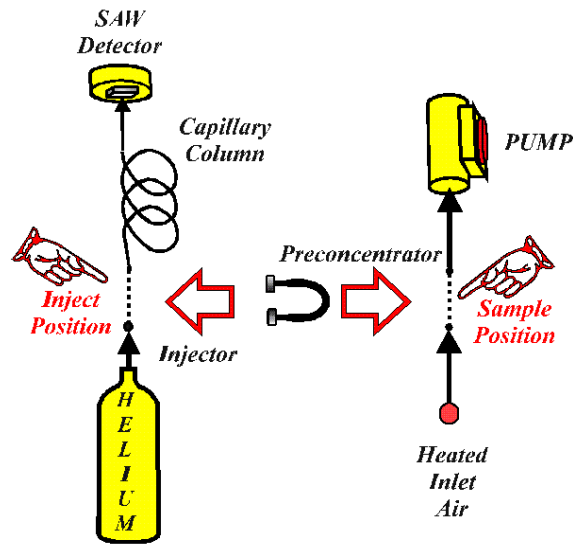


Figure 3- Simplified diagram of the zNose™ showing an air section on the right and a helium section on the left. A loop trap pre-concentrates organics from ambient air in the sample position and injects them into the helium section when in the inject position.

Kovat's Indices (n-Alkanes)

Machine-independent retention times (Kovat's indices) for known odoriferous compounds are determined by retention time comparisons with vapors from an n-alkane vapors as shown in Figure 4. As an example phenol has an index of 988, slightly less than decane (C10), which has an index of 1000. The indices for trichloroanisole (TCA) and trichlorophenol (TCP) are 1330 and 1377 respectively because their corresponding response peaks lie between those of C13 and C14. Instrument software automatically displays Kovats indices for all compound peaks detected in an odor.

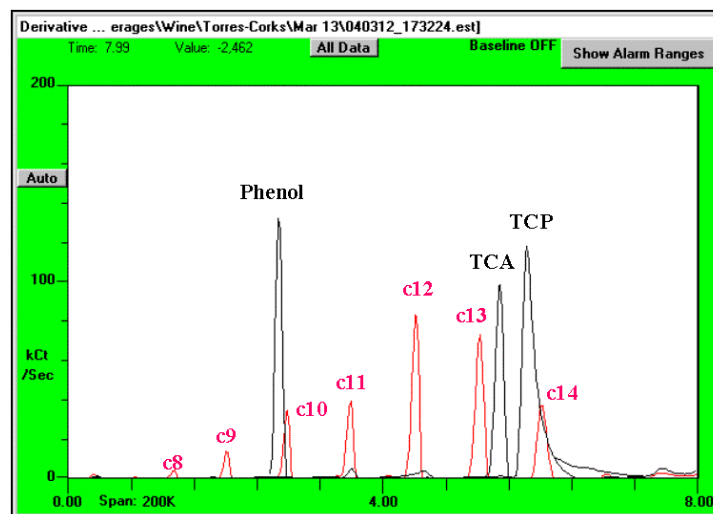
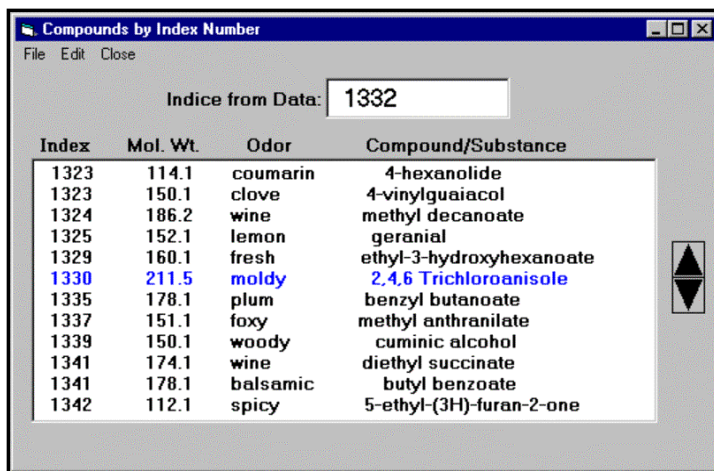


Figure 4- Kovats retention time indices are made relative to n-alkanes (in red).

Compound Identification: Chemical Odor Library

Instrument software contains a library of over 700 chemical compounds and their human odor descriptors based upon Kovat's indices. Clicking on an unknown peak displays the nearest library compound entry. Human odor perceptions for each compound can help in identification of the compound. The library is user-expandable and a typical entry for TCA, which has a moldy odor, is shown in Figure 5.



Index	Mol. Wt.	Odor	Compound/Substance
1323	114.1	coumarin	4-hexanolide
1323	150.1	clove	4-vinylguaiacol
1324	186.2	wine	methyl decanoate
1325	152.1	lemon	geranial
1329	160.1	fresh	ethyl-3-hydroxyhexanoate
1330	211.5	moldy	2,4,6 Trichloroanisole
1335	178.1	plum	benzyl butanoate
1337	151.1	foxy	methyl anthranilate
1339	150.1	woody	cuminic alcohol
1341	174.1	wine	diethyl succinate
1341	178.1	balsamic	butyl benzoate
1342	112.1	spicy	5-ethyl-(3H)-furan-2-one

Figure 5- A chemical library based upon Kovat's indices and human odor perception is useful for identification of unknown compounds.

Virtual Chemical Sensors with Alarms

A technique of creating virtual chemical sensors simplifies the measurement of specific malodorous compounds. Virtual sensors (e.g. phenol, TCA, and TCP) are user defined by placing bands or zones (shown as red hatching) over the target compounds as shown in Figure 6. With alarm levels specified, the chromatogram display is converted into an array of virtual chemical sensors shown on the right.

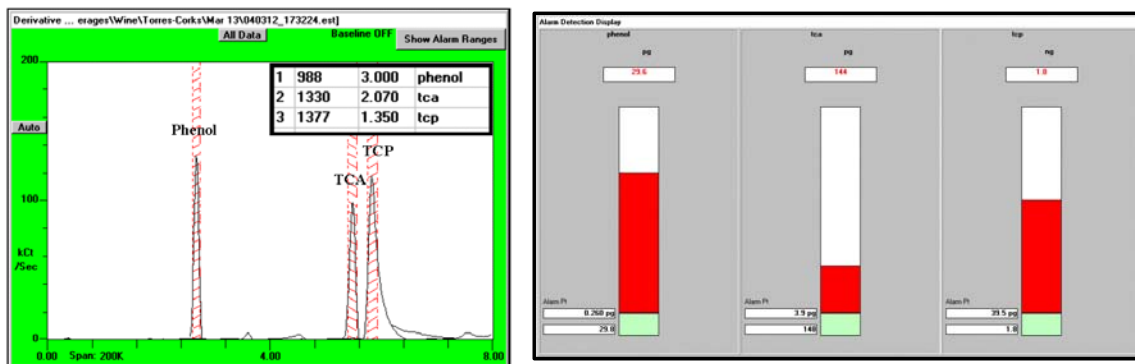


Figure 6- Virtual chemical sensors with user selectable alarm levels simplify measurements.

Quantification of Odor Measurements

The concentration of different compounds in odors can be measured by calibrating the instrument with chemical vapor standards or by direct injection of target compounds. Sampling air from a tedlar bag with a known vapor concentration of target compounds is shown in Figure 7-A. After a known amount of standard vapor has been preconcentrated the collection probe is transferred to the inlet of the instrument (B) and a temperature controlled heater (C) used to release the trapped compounds so then can be transferred to the internal preconcentrator and injected into the GC for analysis..

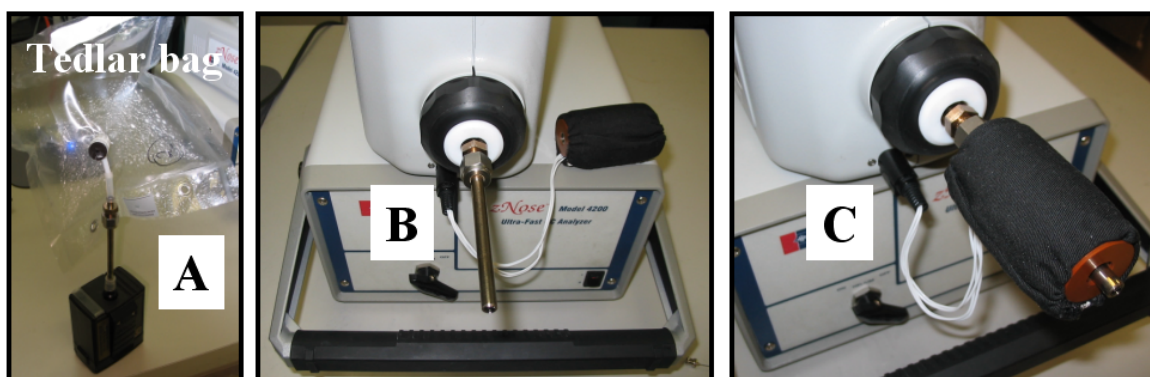


Figure 7- Standard vapors from a tedlar bag are collected by sample probe (A) which is then inserted into the inlet of the instrument (B) and heated to release the absorbed compounds (C) for analysis.

Adding a high flow preconcentrator greatly increases the sensitivity of odor measurements compared to direct sampling. This is demonstrated in Figure 8 where the response in counts from direct and indirect sampling using nearly equal sample times is compared. Using the high flow sampler a sensitivity gain of 30X is achieved.

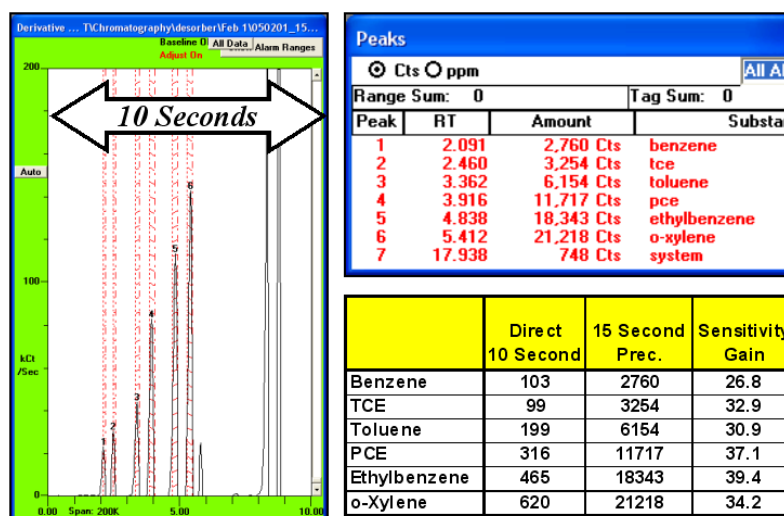


Figure 8- Sensitivity comparison of a 10 second direct sampling measurement with a 15 second high flow sampling measurement using the remote vapor collector.

Even higher sensitivity is possible using increased sample times. Sensitivity and response factors using a 1-minute sample of a low concentration vapor standard with the same six analytes is shown in Figure 9. The minimum detection level of benzene based upon signal to noise is near 1 ppb while that of o-xylene is even lower at 50 ppt. Lower detection levels can be achieved by increasing sample time.

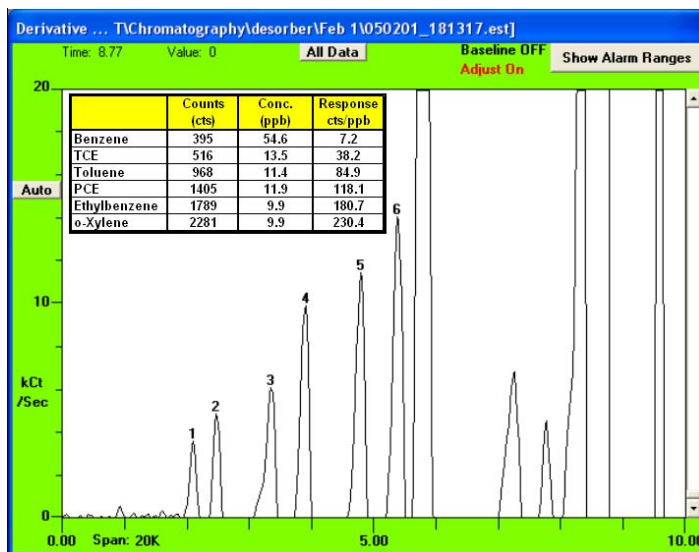


Figure 9-1 min sample of a low concentration 6-compound standard odor mixture from tellar bag.

Laboratory Ambient Air Measurements

Measurement of laboratory air near a fume hood using a 1-minute sample (750 milliliters) is demonstrated in Figure 10. The concentration of the target compounds is 8.6 ppb benzene, 83.8 ppt of TCE, 1.6 ppb toluene, 1.52 ppb PCE, 1.52 ppb ethyl benzene, and 694 ppt of o-Xylene in ambient air near the hood.

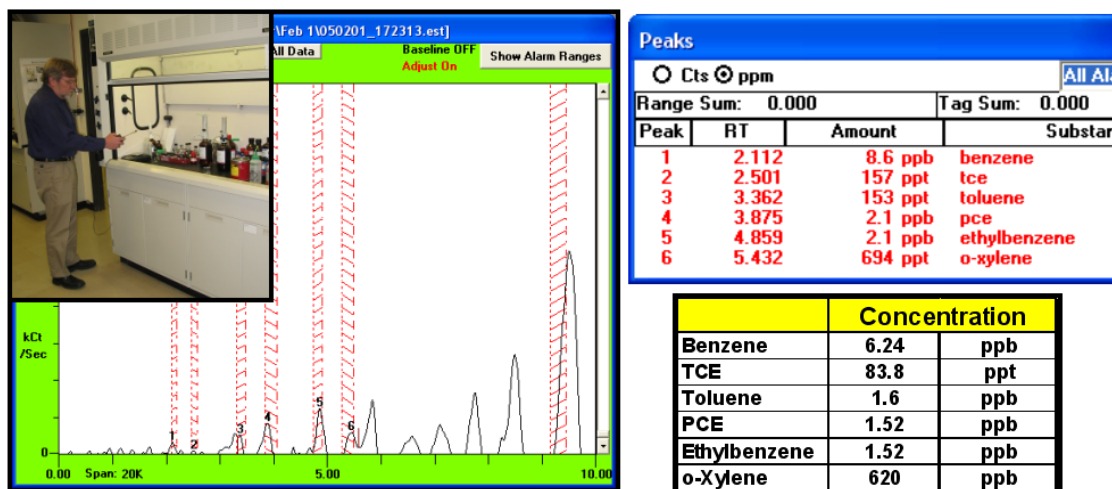


Figure 10- Measurement of laboratory odors with the remote vapor sampler.

Destructive Odors

Many offensive odors contain chemicals, which can taint and effectively destroy aromatic products such as food and beverages. The anisoles are a major source of economic loss in the wine industry and tainting from shipping containers, packaging materials, and storage areas is a major concern. These compounds originate when wood preservatives (such as pentachlorophenol and tribromophenol) are sprayed onto cut building lumber, creating a great potential source of stinky TCA (2,4,6-trichloroanisole), TBA (2,4,6-tribromoanisole), and other related compounds listed in Table I

Table I- Destructive odoriferous chemicals

	MW	VP	Kovats
2,4,6-Trichloroanisole	211.48	0.0228	1369
2,4,6-Trichlorophenol	197.45	0.008	1405
2,4,6-Tribromoanisole	344.83	0.000644	1668
2,4,6-Tribromophenol	330.8	0.000303	1727
2,3,4,5-Tetrachloroanisole	245.92	0.00319	1655
2,3,4,5-Tetrachlorophenol	231.89	0.000339	1723
Pentachloroanisole	280.37	0.000592	1774
Pentachlorophenol	266.34	0.00011	1858

To illustrate by example, odors from within a cargo container were sampled by concentrating a 2.25 liter volume of ambient air as shown in Figure 11. The sample probe was inserted into the analyzer and tested for traces of TCA, TCP, TBA, TBP, and PCP. The results, shown in Figure 12, showed 5.3 ng of TCA and 9.9 ng of TCP were present in the air sample. This amount of TCA (272 ppt) could be very destructive to any aromatic products were they to be shipped in this container.

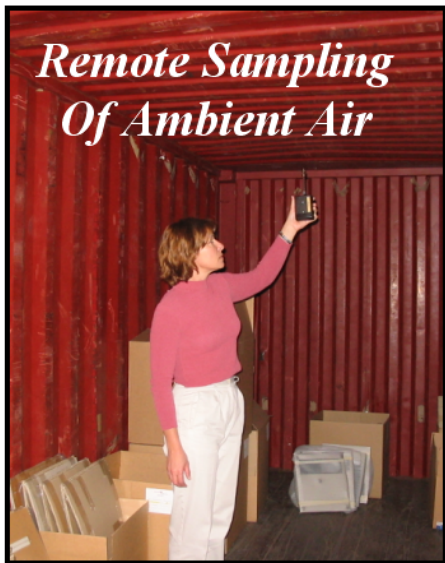


Figure 11- Odors in a cargo container.

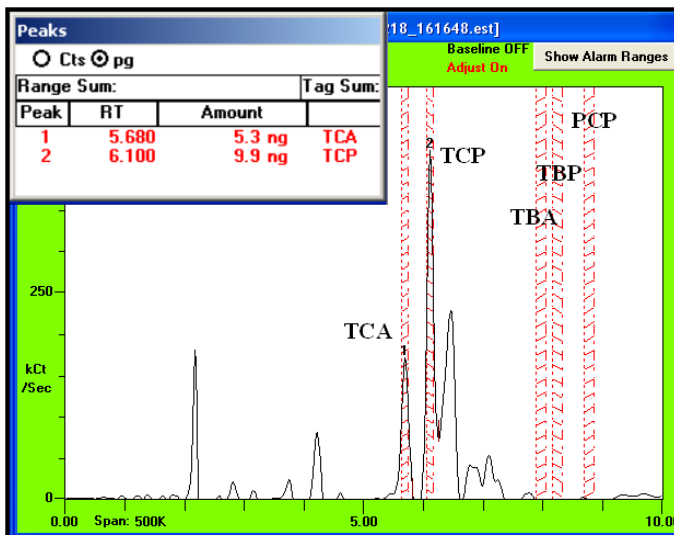


Figure 12- TCA and TCP detected in air sample.

Summary

A new analytical method for detection and analysis of odors using an ultra-high speed gas chromatograph and a battery powered remote sampler can be used to quantify odors of all kinds in remote locations in near real time. An integrated vapor preconcentrator and electronically variable solid-state sensor allow odors to be measured over a wide range of compound concentrations. Real time analytical measurements are complimentary to conventional odor assessment methods and do not replace the need for human sensory panels.

The use of a battery operated high-flow air sampler enables vapor samples to first be concentrated on Tenax[®] filled probes which are then transferred to a portable ultra-fast vapor analyzer where the collected organic compounds are desorbed and measured. Using the remote sampler, the sensitivity of odor measurements is greatly increased. Because the measurement is based upon gas chromatography, independent laboratory validation can also be carried out and results compared.

Using ultra-high speed chromatography, an almost unlimited number of specific virtual chemical sensors can be created along with chemical profiles (olfactory images), and even human odor descriptors based upon a library of odor causing chemicals using retention time indices. Chemical odor profiling combined with human odor panels can be an effective method for recognizing and eliminating sources of odorous emissions.

The odor measurement method presented in this paper can be used in a wide variety of applications. Indoor and outdoor air pollution, factories and offices for worker safety and comfort, early detection of food spoilage, food storage facilities and warehouses, sanitation and waste treatment facilities, animal farms, and even medical diagnosis based upon human and animal body odors, are just a few applications for this technology.