

The How and Why of Electronic Noses

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WITNESSING THE SWIFT ADVANCES in the electronic means of seeing and hearing, scientists and engineers scent a market for systems mimicking the human nose. Already commercial systems from several companies are targeting applications, present and potential, that range from quality assurance of food and drugs to medical diagnosis, environmental monitoring, safety and security, and military use.

The harnessing of electronics to measure odor is greatly to be desired. Human panels backed by gas chromatography and mass spectrometry (GC/MS) are helpful in quantifying smells, but they are time-consuming, expensive, and seldom performed in real time in the field. So it is important that these traditional methods give way to a speedier procedure using an electronic nose composed of gas sensors.

To be sure, gas sensors have been around for many years. But today's electronic nose technology goes several steps farther. Arrays of sensors that respond to a wide range of compounds are used, as well as advanced pattern recognition and artificial intelligence techniques, which enable users to readily extract relevant and reliable information. So-called electronic noses--systems that detect and identify odors and vapors, typically by linking chemical sensing devices with signal-processing and pattern-recognition subsystems--go for US \$20 000 to \$100 000 in Europe, the United States, and Japan, predominantly for laboratory use.

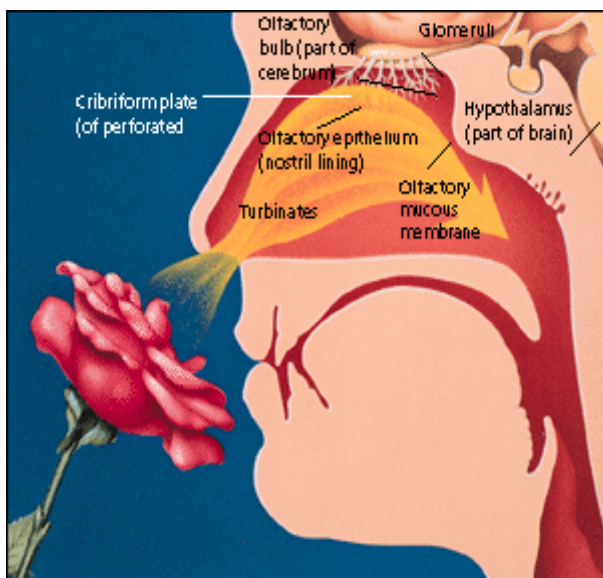
Advances in the technology have been made ever since the early 1980s when researchers at the University of Warwick in Coventry, England, developed sensor arrays for odor detection. Focused primarily on the sensor aspect of the problem, the initial research explored the use of metal oxide devices. Later work at Warwick University explored the use of conducting polymers. In both, sensing is based on conductivity changes. Those early efforts have spawned several commercial enterprises. In August 1991, the pioneers organized an advanced research workshop in Reykjavik, Iceland, sponsored by the North Atlantic Treaty Organization. The workshop accelerated interest in the field, and by now there are many groups around the world working on electronic nose technology.

The Warwick pioneers envisioned an actual electronic equivalent of the mammalian olfactory system and dubbed their primitive analogs of it the electronic nose. So even though the electronic system resembles its biological counterpart none too closely, the "electronic nose"--or E-nose--label has been widely adopted around the world.

The biological nose

To attempt to mimic the human apparatus, researchers have identified distinct steps that characterize the way humans smell [see "Design for smelling" by Wolfgang Göpel and Tilo Weiss]. It all begins with sniffing, which moves air samples that contain molecules of odors past curved bony structures called turbinates. The turbinates create turbulent airflow patterns that

carry the mixture of volatile compounds to the thin mucus coating of the nose's olfactory epithelium, where ends of the nerve cells that sense odorants show up [Fig. 1].



[1] *The human perception of odors begins with sniffing, which brings air samples that contain odorant molecules past curved bony structures in the nose called turbinates. These last create turbulent airflow patterns that allow the mixture of volatile organic compounds (VOCs) to reach a thin mucus layer coating the olfactory epithelium. The sensory cells for detecting odorants are part of the epithelium.*

The volatile organic compounds (VOCs) basic to odors reach the olfactory epithelium in gaseous form or else as a coating on the particles that fill the air we breathe. Particles of less than 1 μm across, each a potential carrier for adsorbed odorous VOCs, can linger in still air for weeks on end. And VOCs reach the olfactory epithelium not only from the nostrils but also from the mouth when food is chewed.

As VOCs and particles carrying VOCs pass over the mucus membrane lining the nose, they are trapped by the mucus and diffuse through to the next layer, namely, the epithelium, where the sensory cells lie in wait. The cells are covered in multiple cilia--hair-like structures with receptors located on the cells' outer membranes. Olfactory cells are specialized neurons that are replicated approximately every 30 days.

Defining terms

Atomic mass profile: the pattern of the mass of particles from a compound, expressed in units of atomic mass.

Electronic nose, or E-nose: a system that uses the pattern of response of an array of gas sensors to identify an odor.

Gas chromatography: an analytical method that separates a gaseous mixture of chemical compounds into its molecular constituents. The mixture is borne through a tube (called a

column) by a pure, inert carrier gas. In transit, the molecular constituents each undergo different delays, and therefore emerge at the outlet of the column as a series of constituent compound pulses, or peaks.

Mass spectrometry: an analytical method of measuring the masses of different ions formed by the ionization of a molecule. Ions are either deflected by magnetic fields or separated by dc and radio-frequency fields.

Odor: a sensation generated when odorant (gas) molecules interact with receptors on cilia on the olfactory neurons in the (human) nose.

Odor detection threshold: the minimal concentration at which an odorant gas may be detected by a subject sniffing it; also known as the absolute threshold of odor sensation.

Odor recognition threshold: the minimum concentration at which an odor is correctly identified by a subject. In practice, the value can be determined by computing, over a representative population, the concentration at which 50 percent of individuals can identify the odor.

Odor unit: the odor concentration at the detection threshold is 1.0 odor unit/m³, as defined by the European Standard (EN) Technical Committee 264. Higher concentrations may be expressed in terms of multiples of the concentration at the detection threshold.

Odorant: a chemical compound or mixture of chemical compounds that, when sniffed by a person (or animal), engenders the sensation of an odor. For example, charred wood is an odorant that produces a burnt odor.

Odorant concentration: the ratio of the number of odorant molecules to the total number of molecules in the gas sample being analyzed. [Note: concentration is presented here in accordance with sensor industry practice, with abbreviations such as ppm, ppb, and ppt, used for parts per million (10⁻⁶), per billion (10⁻⁹), and per trillion (10⁻¹²), respectively. These abbreviations are not recommended by the International System of Units. Ed.]

Olfaction: the sense of smell.

Olfactometer: an instrument for measuring the sensitivity of the sense of smell. It delivers vapors of odorants at controlled concentrations to the nose of a human sniffer.

Olfactory neurons: nerve cells sensitive to odor. They reside in a thin layer (called the olfactory epithelium) on the roof of the nasal cavity.

QCM sensor: a member of the piezoelectric family of sensors that is configured as a mass change-sensing device. This quartz crystal microbalance type consists of a resonating disk with metal electrodes on each side.

Receptor: a molecular structure on the surface of a nerve cell to which specific compounds can bind; also a sensory nerve terminal that responds to stimuli.

SAW sensor: another piezoelectric sensor that is a surface acoustic wave device. It operates at much higher frequencies than QCMs do.

Vapor trap: a means of concentrating odorants in a gas sample.

Volatile organic compound (VOC): an organic (carbon-containing) compound that can exist in vapor phase at room temperature. Such compounds are the primary constituents of odorant mixtures that stimulate the mammalian sense of smell.

The transformation of a molecule into an odor begins when this odorant molecule, as it is called, binds to a receptor protein. The event initiates a cascade of enzymatic reactions that result in depolarization of the cell's membrane. (Ion pumps within the cell's membrane keep the cell polarized in its rest, or steady state, with a typical rest potential of about 90 mV across the membrane.) There are more than 100 million protein receptors in all, and perhaps 1000 types. For example, one receptor type is sensitive to a small subset of odorants, one of which is the organic compound octanal.

The sensory cells in the epithelium respond by transmitting signals along neural "wires" called axons. Such an axon first traverses a small hole in a bony structure in the base of the skull, known as the cribriform plate. Then the rest of the neuron wends its way to the brain's olfactory bulb, where it terminates in a cluster of neural networks called glomeruli.

The 2000 or so glomeruli of the olfactory bulb represent the first tier of central odor information processing. All sensory neurons containing a specific odorant receptor are thought to converge on two or three glomeruli in the olfactory bulb. Note that olfactory sensory neurons in the epithelium can each respond to more than one odorant. It is therefore the pattern of response across multiple glomeruli that codes olfactory quality.

Olfactory information ultimately arrives higher up in the brain, first at the hypothalamus, which also processes neural signals related to food intake, and then at still higher processing centers. The use of noninvasive techniques to study the brain suggest that different chemical stimuli activate different brain regions to different degrees.

As the new electronic technology emerges, conventional approaches to measuring odor are challenged. As noted earlier, current methods generally involve either the use of human odor panels to quantify and characterize the odor or gas chromatography and mass spectrometry to precisely identify the odorants producing it.

The concentration of an odor may be expressed as a multiple of either its detection or its recognition threshold. The detection threshold is defined by the American Society for Testing and Materials (ASTM) as the lowest concentration at which an odor is first detected--recognition is not necessary--by 50 percent of humans sniffing it. The detection threshold is considered the absolute threshold of sensation for an odor. The odor concentration at this threshold is defined to be 1.0 odor unit/m³. The value is established by averaging the responses over a population of individuals.

Panels of trained human "sniffers" are the gold standard of odor measurement. The recognition threshold is defined by ASTM as the lowest concentration at which an odor is first identified by 50 percent of the population sniffing an odorant. In this case, positive identification of the odor is required. The recognition threshold is often 5-10 odor units, or 5-10 times as high as the detection threshold.

Gas chromatography and mass spectrometry have also been used to identify the chemical constituents of an odorous mixture. Air samples are collected in special canisters or bags and taken to the laboratory for analysis afterward. The odorant may be concentrated--in the field or laboratory--by using a vapor trap consisting of an absorbent material or cryogenic device.

In either case, a measured volume of the sample is forced through the trap, where odorant molecules are removed from the gas sample and collected on the absorbent material or cryogenic surface. Heating the trap releases the concentrated molecules rapidly into the gas chromatograph.

Borne along on a small volume of a pure carrier gas, which flows through the column at a constant rate, the sample passes through the column to a detector [see "Some gas chromatography and mass spectrometry basics"].

Some gas chromatography and mass spectrometry basics

A common type of gas chromatography (GC) column consists of a small capillary tube with an interior diameter of about 25 to 250 μm and a length of 1 to 30 meters. The inside wall of the hollow tube (the column) is coated with a thin polymeric film, from one-tenth to a few micrometers thick.

As odorants travel down the tube, the film interacts with the mixture, impeding its progress toward the outlet. The transport time delays of the various molecular constituents of the mixture vary with their vapor pressure and solubility, causing them to separate as they emerge from the column outlet.

Think of it as an auto race in which all the contestants begin at the same time in a group, but stretch out and arrive in single file at the finish line. Similarly, the transport time delay generates a molecular spectrum of constituents emerging from the end of the GC column.

A sensor at the end of the column generates a peak-shaped current response with the emergence of each of the constituent gases (elutes). The most common sensor is a flame ionization detector in which a flame heats a small gap between two wires, such that each constituent gas produces an electric current as it passes through the flame. The height and area of the peaks is a measure of the mass of each of the odorant constituents.

Furthermore, the molecules eluting from the column can be fragmented in a mass spectrometer (MS) to produce a characteristic pattern that aids in their identification. In the MS, each constituent compound molecule is ionized, typically by an electron beam, and the energy absorbed by the molecule in effect breaks it into fragments.

Just how a molecule fragments depends on its chemical structure and mode of ionization. These ions are injected into a mass filter that separates them according to their mass-to-charge ratio, yielding a quantitative measurement of each ion. The mass spectrum that results can be used to identify the original molecule.

The combination of a gas chromatograph followed by a mass spectrometer makes a powerful analytical tool. In brief, the GC column separates an odorant mixture into its molecular constituents, and the MS generates a mass spectrum for each peak.

The spectra are typically compared to spectra contained in a large chemical database to help identify the specific chemical compound in each constituent peak.

The spectrum of labeled peaks with the concentration information from the gas chromatograph column is then used to distinguish the odorant mixture in the original sample.

--H.T.N., S.S.S., & R.G.O.

Why electrify the nose?

Enter the gas sensors of the electronic nose. This speedy, reliable new technology undertakes what till now has been impossible--continuous real-time monitoring of odor at specific sites in the field over hours, days, weeks, or even months.

An electronic device can also circumvent many other problems associated with the use of human panels. Individual variability, adaptation (becoming less sensitive during prolonged exposure), fatigue, infections, mental state, subjectivity, and exposure to hazardous compounds all come to mind. In effect, the electronic nose can create odor-exposure profiles beyond the capabilities of the human panel or GC/MS measurement techniques.

The electronic nose is a system consisting of three functional components that operate serially on an odorant sample--a sample handler, an array of gas sensors, and a signal-processing system. The output of the electronic nose can be the identity of the odorant, an estimate of the concentration of the odorant, or the characteristic properties of the odor as might be perceived by a human.

Fundamental to the artificial nose is the idea that each sensor in the array has different sensitivity. For example, odorant No. 1 may produce a high response in one sensor and lower responses in others, whereas odorant No. 2 might produce high readings for sensors other than the one that "took" to odorant No. 1.

What is important is that the pattern of response across the sensors is distinct for different odorants. This distinguishability allows the system to identify an unknown odor from the pattern of sensor responses. Each sensor in the array has a unique response profile to the spectrum of odorants under test. The pattern of response across all sensors in the array is used to identify and/or characterize the odor.

Sensing an odorant

In a typical electronic nose, an air sample is pulled by a vacuum pump through a tube into a small chamber housing the electronic sensor array. The tube may be made of plastic or stainless steel.

Next, the sample-handling unit exposes the sensors to the odorant, producing a transient response as the VOCs interact with the surface and bulk of the sensor's active material. (Earlier, each sensor has been driven to a known state by having clean, dry air or some other reference gas passed over its active elements.) A steady-state condition is reached in a few seconds to a few minutes, depending on the sensor type.

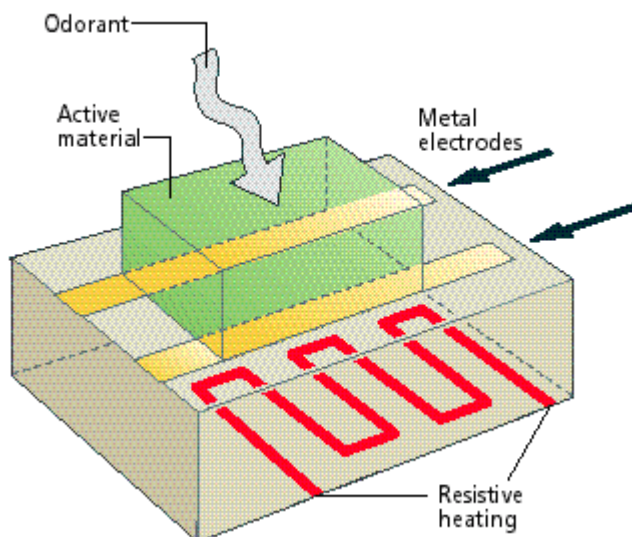
During this interval, the sensor's response is recorded and delivered to the signal-processing unit. Then, a washing gas such as an alcohol vapor is applied to the array for a few seconds to a minute, so as to remove the odorant mixture from the surface and bulk of the sensor's active material. (Some designers choose to skip this washing step.)

Finally, the reference gas is again applied to the array, to prepare it for a new measurement cycle. The period during which the odorant is applied is called the response time of the sensor array. The period during which the washing and reference gases are applied is termed the recovery time.

Starring the array

The sensor array is clearly the key element. As shown in Table 1, electronic nose sensors fall into five categories: conductivity sensors, piezoelectric sensors, MOSFETs, optical sensors, and spectrometry-based sensing methods.

There are two types of conductivity sensors: metal oxide and polymer, both of which exhibit a change in resistance when exposed to volatile organic compounds [Fig. 2]. Of the two types, metal oxide semiconductors have been used more extensively in electronic nose instruments and are widely available commercially. Typical offerings include oxides of tin, zinc, titanium, tungsten, and iridium, doped with a noble metal catalyst such as platinum or palladium.



[2] In a conductivity sensor, the usual active material is metal oxide or a conducting polymer. The electrodes may be platinum, aluminum, or gold, while the substrate may be of silicon, glass, or plastic. The heater, used only for metal oxide, is normally a platinum metal trace or wire. The interaction with VOCs alters the conductivity of the active material. The change in resistance across the electrode pair is then measured with a Wheatstone bridge or other circuitry [not shown].

The doped semiconducting material with which the VOCs interact is deposited between two metal contacts over a resistive heating element, which operates at 200 °C to 400 °C. At these elevated temperatures, heat dissipation becomes a factor in the mechanical design of the sensing chamber. Micromachining is often used to thin the sensor substrate under the active material, so that power consumption and heat dissipation requirements are reduced. As a VOC passes over the doped oxide material, the resistance between the two metal contacts changes in proportion to the concentration of the VOC.

The recipe for the active sensor material is designed to enhance the response to specific odorants, such as carbon monoxide or ammonia. Selectivity can be further improved by altering the operating temperature. Sensor sensitivity ranges from 5 to 500 parts per million. The sensors also respond to water vapor, more specifically, to humidity differences between the gas sample being analyzed and a known reference gas used to initialize the sensor.

The baseline response of metal oxide sensors is prone to drift over periods of hours to days, so signal-processing algorithms should be employed to counteract this property. The sensors are also susceptible to poisoning (irreversible binding) by sulfur compounds present in the odorant mixture. But their wide availability and relatively low cost make them the most widely used gas sensors today.

1. Electronic nose sensor technologies						
Sensor type	Principle of operation	Fabrication methods	Availability	Sensitivity	Advantages	Disadvantages
Metal oxide	Conductivity	Microfabricated	Commercial, many types	5-500 ppm	Inexpensive, microfabricated	Operates at high temperature
Conducting polymer	Conductivity	Microfab, electroplating, screen printing	Commercial, special order only	0.1-100 ppm	Operates at room temperature, microfabricated	Very sensitive to humidity
Quartz crystal microbalance (QCM)	Piezoelectricity	Screen printing, wire bonding, MEMS	Commercial, several types	1.0-ng mass change	Well-understood technology	MEMS fabrication, interface electronics
Surface acoustic wave (SAW)	Piezoelectricity	Microfab, screen printing	Commercial, several types	1.0-pg mass change	Differential devices can be quite sensitive	Interface electronics
MOSFET	Capacitive charge coupling	Microfab	Commercial, special order only	Parts per million	Integrated with electronic interface circuits	Odorant reaction product must penetrate gate
Optical	Fluorescence, chemoluminescence	Dip coating, MEMS, precision machining	Research	Low parts per billion (ppb)	High electrical noise immunity	Restricted availability of light sources
Gas chromatography	Molecular spectrum	MEMS, precision machining	Commercial, new offering	Low ppb	Potential analytical accuracy	Sample concentration required
Mass spectrometry	Atomic mass spectrum	MEMS, precision machining	Commercial, new offering	Low ppb	Potential analytical accuracy	Sample concentration required
Light spectrum	Transmitted light spectrum	MEMS, precision machining	Research	Low ppb	Sample not consumed	Requires tunable quantum-well devices

MEMS = microelectromechanical system

Conducting polymer sensors, a second type of conductivity sensor, are also commonly used in electronic nose systems. Here, the active material in Fig. 2 is a conducting polymer from such families as the polypyrroles, thiophenes, indoles, or furans. Changes in the conductivity of these materials occur as they are exposed to various types of chemicals, which bond with the polymer backbone. The bonding may be ionic or, in some cases, covalent. The interaction affects the transfer of electrons along the polymer chain, that is to say, its conductivity. A given compound's affinity for a polymer and its effects on the polymer's conductivity are strongly influenced by the counter-ions and functional groups attached to the polymer backbone.

In order to use these polymers in a sensor device, microfabrication techniques are employed to form two electrodes separated by a gap of 10 to 20 μm . Then the conducting polymer is electropolymerized between the electrodes by cycling the voltage between them. For example,

layers of polypyrroles can be formed by cycling between -0.7 and +1.4 V. Varying the voltage sweep rate and applying a series of polymer precursors yields a wide variety of active materials. Response time is inversely proportional to the polymer's thickness. To speed response times, micrometer-size conducting-polymer bridges are formed between the contact electrodes.

Because conducting polymer sensors operate at ambient temperature, they do not need heaters and thus are easier to make. The electronic interface is straightforward, and they are suitable for portable instruments. The sensors can detect odors at sensitivities of 0.1 parts per million (ppm), but 10 to 100 ppm is more usual.

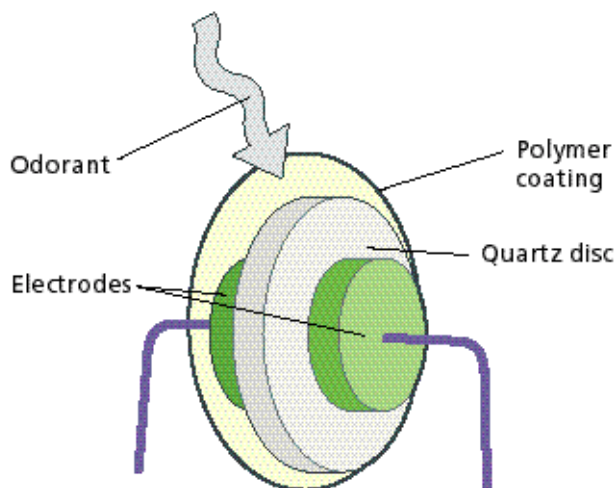
The main drawback of existing conducting-polymer sensors is that it is difficult and time-consuming to electropolymerize the active material, so they exhibit undesirable variations from one batch to another. Their responses also drift over time, and their usually greater sensitivity than metal oxides to water vapor renders them susceptible to humidity. This susceptibility can mask the responses to odorous volatile organic compounds.

In addition, some odorants can penetrate the polymer bulk, dragging out the sensor recovery time by slowing the removal of the VOC from the polymer. This extends the cycle time for sequentially processing odorant samples.

Measuring mass changes

The piezoelectric family of sensors also has two members: quartz crystal microbalance (QCM) and surface acoustic-wave (SAW) devices. They can measure temperature, mass changes, pressure, force, and acceleration, but in the electronic nose, they are configured as mass-change-sensing devices.

The QCM types consist of a resonating disk a few millimeters in diameter, with metal electrodes on each side connected to lead wire [Fig. 3]. The device resonates at a characteristic frequency (10 MHz to 30 MHz) when excited with an oscillating signal.



[3] The quartz crystal microbalance (QCM) sensor is made of a polymer-coated resonating disk, a few millimeters in diameter, with metal electrodes on each side connected to lead wire. Gas molecules adsorbed to the surface of the polymer coating increase the mass of the disk, thereby reducing its resonance frequency.

During manufacture, a polymer coating is applied to the disk to serve as the active sensing material. In operation, a gas sample is adsorbed at the surface of the polymer, increasing the mass of the disk-polymer device and thereby reducing the resonance frequency. The reduction is inversely proportional to odorant mass adsorbed by the polymer. For example, a 166- μm -thick quartz crystal cut along a certain axis will resonate at 10 MHz. If a QCM sensor made with this resonator undergoes a positive 0.01 percent change in mass, a negative shift of 1 kHz will occur in its resonance frequency. Then when the sensor is exposed to a reference gas, the resonance frequency returns to its baseline value.

A good deal is known about QCM devices. The military, for one, has experimented with them for years, using them for the detection of trace amounts of explosives and other hazardous compounds and measuring mass changes to a resolution of 1 picogram. For example, 1 pg of methane in a 1-liter sample volume at standard temperature and pressure produces a methane concentration of 1.4 ppb.

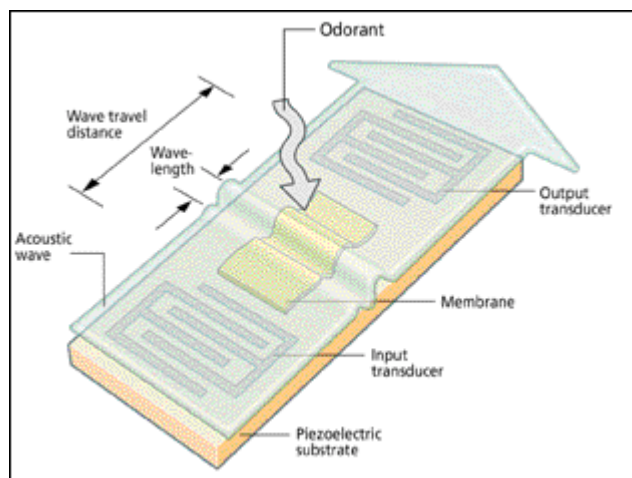
In addition, QCM sensors are remarkably linear over a wide dynamic range. Their response to water is dependent upon the absorbent materials employed. And their sensitivity to changes in temperature can be made negligible.

Tailoring the QCM for specific applications is done by adjusting its polymer coating. Fortunately, a large number of coatings is available from those developed for GC columns. The response and recovery times of the resonant structure are minimized by reducing the size and mass of the quartz crystal along with the thickness of the polymer coating. Batch-to-batch variability is not a problem because these devices measure normalized frequency change, a differential measurement that removes common-mode noise.

Care must be taken when making these three-dimensional devices by microelectromechanical system (MEMS) processing techniques. When the dimensions are scaled down to micrometer levels, the surface-to-volume ratios increase; and the larger the surface-to-volume ratio, the noisier the devices get because of surface processes that cause instabilities. Hence, signal-to-noise ratios degrade with increasing surface-to-volume ratio, thereby hampering measurement accuracy. It should be noted that this phenomenon applies to most microfabricated devices.

Traveling over the surface

QCM's cousin, the SAW sensor, differs from it in several important ways. First, a Rayleigh (surface) wave travels over the surface of the device, not throughout its volume [Fig. 4]. SAW sensors operate at much higher frequencies, and so can generate a larger change in frequency. A typical SAW device operates in the hundreds of megahertz, while 10 MHz is more typical for a QCM, but SAW devices can measure changes in mass to the same order of magnitude as QCMs. Even though the frequency change is larger, increased surface-to-volume ratios mean the signal-to-noise ratio is usually poorer. Hence, SAW devices can be less sensitive than QCMs in some instances.



[4] An ac signal applied across the input metal transducer fingers of this gas sensor creates an acoustic wave that "surfs" over the piezoelectric substrate. When the wave reaches the metal fingers of the output transducer, the ac voltage is recreated, though shifted in phase as a result of the distance traveled. The phase shift depends, among other things, on the mass and the absorption properties of the sensing polymer layer--the active membrane--which are influenced in turn by the gas molecules absorbed. [Note: the wavelength depicted has been deliberately exaggerated.]

Being planar, SAW devices can be fabricated with photolithographic methods developed by the microelectronics industry. The fact that three-dimensional MEMS processing is unnecessary makes them relatively cheaper than their QCM counterparts when large quantities are produced.

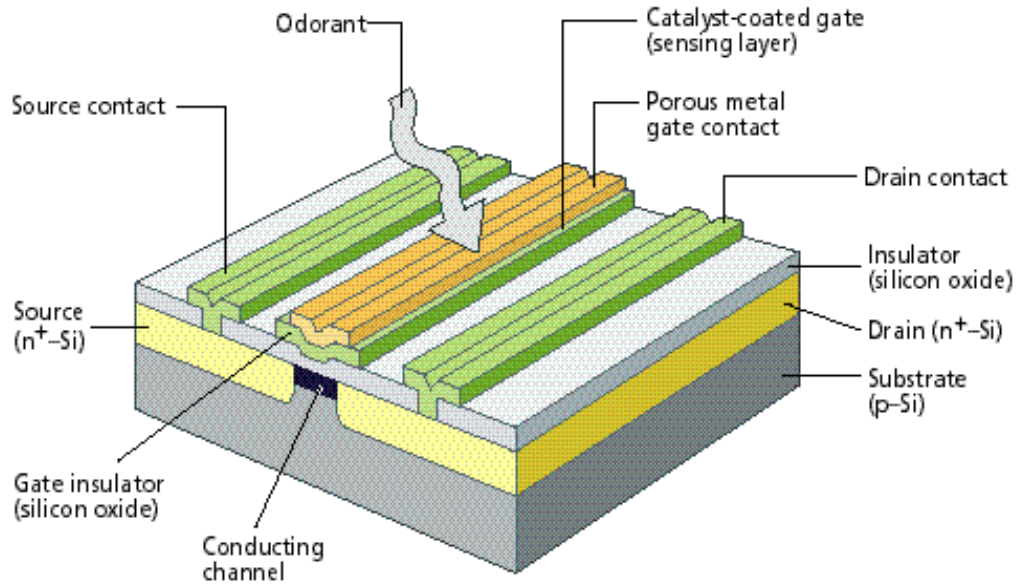
As with QCMs, many polymer coatings are available, and as with the other sensor types, differential measurements can eliminate common-mode effects. For example, two adjacent SAW devices on the same substrate (one with an active membrane and another without) can be operated as a differential pair to remove temperature variations and power line noise.

A disadvantage of both QCM and SAW devices is more complex electronics than are needed by the conductivity sensors. Another is their need for frequency detectors, whose resonant frequencies can drift as the active membrane ages.

A MOSFET catalyzed

Metal-oxide-silicon field-effect-transistor (MOSFET) odor-sensing devices are based on the principle that VOCs in contact with a catalytic metal can produce a reaction in the metal. The reaction's products can diffuse through the gate of a MOSFET to change the electrical properties of the device. A typical MOSFET structure has a p-type substrate with two n-doped regions with metal contacts labeled source and drain [Fig. 5].

The sensitivity and selectivity of the devices can be optimized by varying the type and thickness of the metal catalyst, and operating them at different temperatures. MOSFET sensors have been investigated for numerous applications, but to date, few have been used in commercial electronic nose systems because of a dearth of sensor variants.



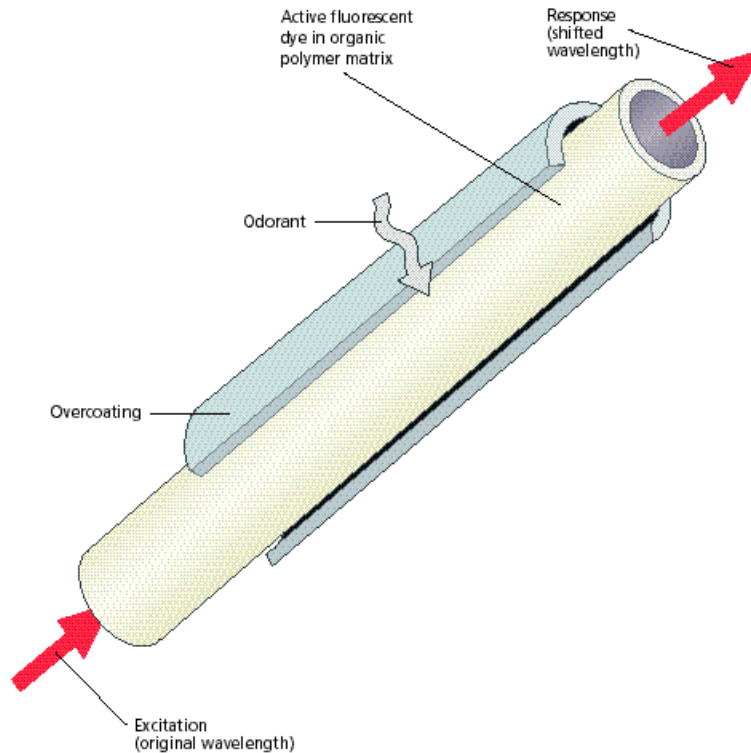
[5] The gate of this MOSFET sensor is covered by a noble metal catalyst, such as platinum, palladium, or iridium. Charge applied to the gate opens a channel for current flow from source to drain, as in any MOSFET. But VOCs sweeping over the catalyst can engender reaction products that alter the sensor's gate charge, varying channel conductivity.

The advantage of MOSFETs is that they can be made with IC fabrication processes, so that batch-to-batch variations can be minimized. The disadvantage is that the catalyzed reaction products (such as hydrogen) must penetrate the catalytic metal layer in order to influence the charge at the channel; the package must therefore have a window to permit gas to interact with the gate structure on the IC chip. Thus it is important to maintain a hermetic seal for the chip's electrical connections in harsh environments. The requirement may be satisfied by using photo-definable polymers, such as polyimide, to seal all areas of the chip that are not to be intentionally exposed to the environment. MOSFET sensors also undergo baseline drift similar to that of the conductivity sensors.

Optical-fiber sensors, yet another type, utilize glass fibers with a thin chemically active material coating on their sides or ends [Fig. 6]. A light source at a single frequency (or at a narrow band of frequencies) is used to interrogate the active material, which in turn responds with a change in color to the presence of the VOCs to be detected and measured.

The active material contains chemically active fluorescent dyes immobilized in an organic polymer matrix. As VOCs interact with it, the polarity of the fluorescent dyes is altered and they respond by shifting their fluorescent emission spectrum. When a pulse of light from an external source interrogates the sensor, the fluorescent dye responds by emitting light at a different frequency. As the source intensity is much greater than the sensor response, great care must be taken to ensure that the response photodetectors are protected from the source emissions.

Arrays of these devices with different dye mixtures can be used as sensors for an electronic nose. For example, researchers at Tufts University, in Medford, Mass., have constructed an optical system that interrogates the sensors at an (excitation) wavelength of 535 nm, and measures time and amplitude changes in fluorescence (emission) at 610 nm.



[6] Odorant optical-fiber sensors employ a glass fiber coated on its sides or ends with a thin, chemically active material containing fluorescent dyes immobilized in an organic polymer matrix. A pulse of light from an external source propagates along the fiber and interrogates the active material, with which VOCs can interact. The interaction alters the polarity of the dyes, which respond by shifting their fluorescent spectrum. For high-temperature applications, the overcoating is a protective layer, while for *in vivo* uses it is a biocompatible material.

Favoring optical-fiber sensors is the availability of many different dyes for biological research, so that the sensors themselves are cheap and easy to fabricate. It is also possible to couple fluorescent dyes to antibody-antigen binding (the recognition of a specific molecule, and only that molecule, as in the human immune system.) Thus an array of fiber sensors can have wide-ranging sensitivities, a feature not easily obtainable with other sensor types. As with other types, differential measurements can also be used to remove common-mode noise effects.

In their disfavor are the complexity of the instrumentation control system, which adds to fabrication costs, and their limited lifetime due to photobleaching. The fluorescent dyes are slowly consumed by the sensing process, the way sunlight bleaches fabric dyes.

Spectral mockups

Still other approaches to developing sensor arrays have been suggested, resulting in what may be called spectrometric pseudo-sensor arrays. The first operation is to use a vapor trap to concentrate the VOCs, as is done for GC columns. The concentrated vapor is then injected into a spectrometer that generates a spectral response characteristic of the vapor. That response may take many forms, such as separated molecular constituents (as in the gas chromatograph column), atomic mass profile (as in the mass spectrometer), or transmitted light frequencies.

The last approach may be implemented by acousto-optic tunable filters (ATOFs), which alter their light-filtering characteristics in response to a change in voltage across their light-transmission path. Sweeping the voltage controlling the device effectively changes the transmission path through the filter and so changes its peak wavelength. The result is a time-varying signal that is a function of the light spectrum of the incoming source.

For all three spectrometer types, a sensor at the output detects a characteristic profile for each odorant being examined. This profile may be viewed as a uniquely varying pattern that, when sampled at various instants, creates an array of data that apparently comes from different parallel sensors; hence they may be called apparent, or pseudo, sensors. The process is like using a shift register in a computer to convert a serial bit-stream into a parallel data word.

Data points representing the pseudo-sensors can be used by signal-processing algorithms as effectively as data from the physical sensor arrays described earlier. In fact, the odorant mixture can be separated in a few seconds into constituents with analytical accuracy. On the other hand, a vapor trap is usually required to increase the sample concentration that can alter the characteristics of the odor. They also require complex electronics for instrument control.

Close to hand

Many electronic nose systems are now available, including those listed in Table 2. Since much of the early work using this technology in various applications has been carried out in Britain, many of the commercially available machines originated there, at companies such as AromaScan, Bloodhound Sensors, and EEV Chemical Sensor Systems. Other European competitors include Germany's Lennartz, France's Alpha M.O.S., and Sweden's Nordic Sensor Technologies. In the United States, there are Cyrano Sensors, Electronic Sensor Technologies, Hewlett-Packard, and MicroSensor Systems, while several Japanese companies are also developing systems.

Most of the machines listed in the table are priced from US \$20 000-\$100 000, but prices should drop in a few years as competition heats up and sensor technology improves. Most models now on the market are fairly large, none too portable, lab-type systems, but several manufacturers have said they are working on miniaturized versions.

2. Available electronic nose instruments								
Manufacturer	Place of origin	Sensortype	No. of sensors	Size of instrument	Auto-sample available?	Pattern recognition	Cost, US \$\$	How to contact
Aisense Analysis GmbH	Germany (Schweinf.)	Metal oxide semiconductor (MOS)	10	Laptop	Yes	Artificial neural network (ANN), distance classifiers (DC), principal components analysis (PCA), statistical pattern recognition (SPR)	20 000–43 000 (no auto-sampler)	www.aisense.com (49+385) 63 44-280 fax, 63 44-281
Alpha MOS–Multi Organoleptic Systems	France (Toulouse)	Conducting polymer (CP), MOS, quartz crystal microbalance (QCM) surface acoustic wave (SAW)	6–24	Desktop	Yes	ANN, discriminant function analysis (DFA), PCA	20 000–100 000	www.ALPHA-mos.com (33 +5) 62 47 53 80 fax, 61 54 56 15
AromaScan PLC	UK (Crewe)	CP	32	Desktop	Yes	ANN	20 000–75 000	www.aromascan.com. ArHome.html (44+127) 021 6444 fax, 021 6030
Bloodhound Sensors Ltd.	UK (Leeds)	CP	14	Laptop	No	ANN, cluster analysis (CA), PCA	—	www.bloodhound.co.uk/bloodhound (44+113) 233 3439 fax, 233 3433
Cyrano Sciences Inc.	United States (Pasadena, Calif.)	CP ¹	32	Palmtop ²	No	PCA	5000	www.cyrano-sciences.com
EEV Ltd. Chemical Sensor Systems	UK (Chelmsford)	CP, MOS, QCM, SAW	8–28	Desktop	Yes	ANN, DFA, PCA, proprietary algorithm	—	www.eev.com Europe: (44+1279) 871659 fax, 871662 United States: (800) 535 0606 fax, (770) 967 1854
Electronic Sensor Technology Inc.	United States (Newbury Park, Calif.)	Gas chromatography (GC) column, SAW	1	Desktop	No ³	SPR	19 500–25 000	www.estcal.com/
Hewlett-Packard Co.	United States (Palo Alto, Calif.)	Quadrupole mass spectrometry (QMS)	—	Desktop	Yes	Standard chemometrics	79 900	http://chem.external.hp.com/cag/products/hp4440.html
HKR-Sensorysysteme GmbH	Germany (Munich)	QCM	6	Desktop	Yes	ANN, CA, DFA, PCA	—	home.t-online.de/home/hkrsensor (49+89) 746 02 07 fax, 746 02 08
Lennartz Electronic GmbH	Germany (Tübingen)	MOS, QCM	16–40	Desktop	Yes	ANN, PCA, principal components regression (PCR)	55 000 ⁴	www.lennartz-electronic.de/ (49071) 93550 fax, 935530
Nordic Sensor Technologies AB	Sweden (Linköping)	Infrared (IR), MOS, MOSFET, QCM	22	Laptop	Yes	ANN, PCA	40 000–60 000	www.nordicsensortec.com (46+13) 212 900 fax, 212 905
RST Rostock Raumfahrt und Umweltschutz GmbH	Germany (Rostock)	MOS, QCM, SAW	6–10	Desktop	Yes	ANN, PCA	50 000	www.rst-rostock.de (49+381) 56-0 fax, 56-202
Sawtek Inc.	United States (Bowling Green, Ky.)	SAW	2	Palmtop	No	Proprietary	5000	www.microsensor-systems.com (407) 886 8860 fax, 886 7061

¹ The sensors are made of polymer conductive composites.

² Available summer 1999.

³ The vendor does not market an auto-sampler, but its instrument can be interfaced with third-party auto-sampling stages.

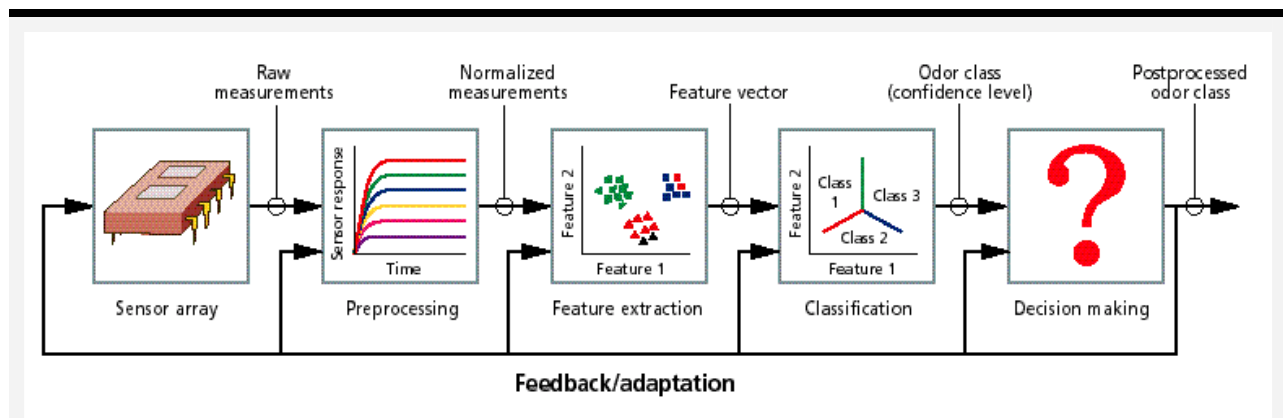
⁴ Price information upon request; prices start at about US \$55 000.

A manifold appeal

The electronic nose has been used in a variety of applications and could help solve problems in many fields, including food product quality assurance, health care, environmental monitoring, pharmaceuticals, indoor air quality, safety and security, and the military. However, for the electronic nose to succeed in those areas, there need to be marked improvements in technology.

The electronic nose can be applied by food manufacturers to such tasks as freshness testing, quality control, and screening of incoming raw materials, not to mention feedback control to optimize bioreactors and minimize batch variation, and monitoring for accidental or intentional contamination or mislabeling of manufactured food products.

For example, at North Carolina State University we have used an experimental prototype to analyze the odors of several types of coffee beans [Fig. 7]. We employed signal-processing and pattern recognition routines to transform and display sensor data [see "Olfactory signal processing and pattern recognition"]. Electronic nose systems are well suited to comparing final products to reference standards, even replacing human taste panels in some applications. Testing of food freshness is especially important for the elderly since their senses of taste and smell dull with advancing age.



Olfactory signal processing and pattern recognition

The task of an electronic nose is to identify an odorant sample and perhaps to estimate its concentration. The means: signal processing and pattern recognition.

For an electronic nose system, those two steps may be subdivided into four sequential stages: preprocessing, feature extraction, classification, and decision-making. But first, a database of expected odorants must be compiled, and the sample must be presented to the nose's sensor array.

Preprocessing compensates for sensor drift, compresses the transient response of the sensor array, and reduces sample-to-sample variations. Typical techniques include: manipulation of sensor baselines; normalization of sensor response ranges for all the sensors in an array (the normalization constant may sometimes be used to estimate the odorant concentration); and compression of sensor transients.

Feature extraction has two purposes: to reduce the dimensionality of the measurement space, and to extract information relevant for pattern recognition. To illustrate, in an electronic nose with 32

sensors, the measurement space has 32 dimensions. This space can cause statistical problems if the odor database contains only a few examples--typical in pattern recognition applications because of the cost of data collection.

Furthermore, since the sensors have overlapping sensitivities, there is a high degree of redundancy in these 32 dimensions. Accordingly, it is convenient to project the 32 onto a few informative and independent axes. This low-dimensional projection (typically two or three axes) has the added advantage that it can be more readily inspected visually.

Feature extraction is generally performed with linear transformations such as the classical principal components analysis (PCA) and linear discriminant analysis (LDA).

PCA finds projections of maximum variance and is the most widely used linear feature-extraction technique. But it is not optimal for classification since it ignores the identity (class label) of the odor examples in the database.

LDA, on the other hand, looks at the class label of each example. Its goal is to find projections that maximize the distance between examples from different odorants yet minimize the distance between examples of the same odorant.

As an example, PCA may do better with a projection that contains high-variance random noise whereas LDA may do better with a projection that contains subtle, but maybe crucial, odor-discriminatory information. LDA is therefore more appropriate for classification purposes.

Several research groups have recently adopted some nonlinear transforms, such as Sammon nonlinear maps and Kohonen self-organizing maps. Sammon maps attempt to find a (typically) two- or three-dimensional mapping that preserves the distance between pairs of examples on the original 32-dimensional space. Kohonen maps project the 32-dimensional space onto a (typically) two-dimensional mesh of processing elements called neurons.

Neighboring "neurons" are trained to respond to similar types of stimuli (odorants), a self-organizing behavior motivated by neurobiological considerations. Neither of these techniques makes use of class labels, so they are not optimal for pattern classification.

Once the odor examples have been projected on an appropriate low-dimensional space, the classification stage can be trained to identify the patterns that are representative of each odor. When presented with an unidentified odor, the classification stage will be able to assign to it a class label (identify the odorant) by comparing its pattern with those compiled during training.

The classical methods of performing the classification task are K nearest neighbors (KNNs), Bayesian classifiers, and, of late, artificial neural networks (ANNs). For K equal to five, for instance, the KNN classifier will find the five examples in the odorant database that are closest to the unidentified odorant and will assign the odorant class represented by a majority among those five examples.

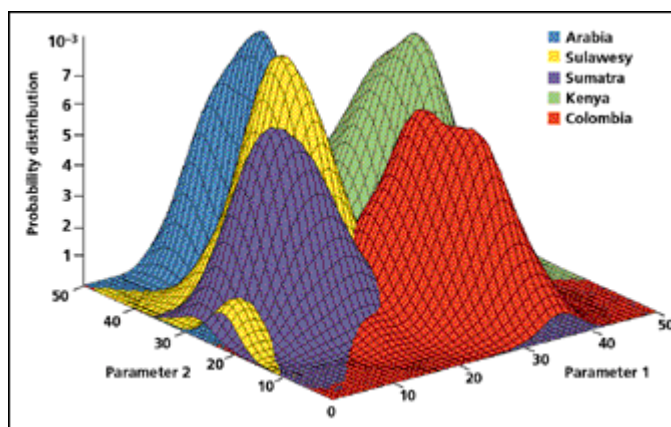
Bayesian classifiers first build a probability density function for each odor class on the low-dimensional space. When presented with an unidentified odorant, the Bayesian classifier will pick the class that maximizes the precompiled probability distribution.

A typical ANN classifier consists of two or more layers of neurons that are connected with synaptic weights--real-number multipliers that connect the outputs of neurons to the inputs of neurons in the next layer.

During training, the ANN adapts the synaptic weights to learn the patterns of the different odorants. After training, when presented with an unidentified odorant, the ANN feeds its pattern through the different layers of neurons and assigns the class label that provides the largest response.

The classifier produces an estimate of the class for an unknown sample along with an estimate of the confidence placed on the class assignment. A final decision-making stage may be used if any application-specific knowledge is available, such as confidence thresholds or risk associated with different classification errors. The decision-making module may modify the classifier assignment and even determine that the unknown sample does not belong to any of the odorants in the database.

--R.G.O.



[7] Researchers at North Carolina State University were able to tell one coffee from another in tests of discrimination techniques using metal oxide sensors. The horizontal axes are the first and second projections of a linear discriminant analysis--a feature-extraction technique. The vertical axis is the probability distribution function of each coffee over the two discriminant parameters.

Odor has been valued for centuries by physicians for diagnostic purposes. An electronic nose could be used to analyze breath, sweat, urine, and stools, and some of the commercial electronic nose systems are being tested to do that. Rapid diagnosis of acute infections through breath analysis is a high priority, as is screening of bacterial cultures for early detection of pathogens. Monitoring of body odor and wound infections in nursing homes and long-term care facilities might improve the quality of life for the elderly.

In the pharmaceutical industry, the electronic nose may serve to screen incoming raw materials, to monitor production processes, and to maintain security in storage and distribution areas. It could also test employees in critical occupations for drug use or abuse. Specialized systems can test breath and urine samples for targeted illegal compounds and byproducts. Researchers at the Duke University Medical Center in Durham, N.C., have used a commercial electronic nose with 32 conducting polymer sensors to determine the source of unpleasant odors in pharmaceuticals. The project was off limits to a human panel, which could not be exposed to the drug.

The electronic nose can serve in safety and security applications, such as hazardous alarms for toxic and biological agents, screening airline passengers for explosives, and examining vehicles for drugs and contraband at airports, border crossings, and cargo terminals.

In addition, the nose could monitor indoor air quality, as well as industrial and agricultural emissions and noxious environmental wastes. Working with a trained neural network and a properly designed database, it can vie with trained humans for far less money and for months on end.

Smart fire alarms are another potential use where hazardous combustion products can be identified. Consider a nuclear plant, where the electronic nose could monitor electrical fires in control equipment for early detection and interdiction.

Recall, too, that finding and disabling buried land mines is a high priority for the United Nations and will be a vital undertaking in dozens of nations for years to come. The electronic nose is being studied as a front-line tool in the effort to remove mines that threaten civilians.

Other battlefield applications include biological and chemical agent detection and friend-or-foe identification. Special-purpose nose systems also can be used to monitor aging warheads and artillery shells that begin to leak VOCs, anticipating the creation of explosive environments and protecting personnel who must handle these dangerous inventory items.

Keener noses in the offing

Over the last few years, the interest in electronic nose technology has increased exponentially. In the near future, therefore, expect to see instruments with multiple sensor types integrated into special-purpose devices. That will lead to systems as accurate as analytical instrumentation. In many applications, the electronic nose is configured to sample the empty space in a closed container partially filled with a liquid, such as a polluted water sample. There, expect to see additional wet chemical sensors deployed in the liquid itself.

Single-chip systems will emerge that integrate micromachined sampling units, microfabricated sensor arrays, and IC signal-processing chips [see "The electronic nose in Lilliput" by Henry Baltes, Dirk Lange and Andreas Koll]. MEMS technology will enable these systems to be mass produced and find their way into consumer products within five years.

But if those predictions are to be fulfilled, research in several areas is still needed. Perhaps the toughest problems involve sample handling, where new ways must be found to concentrate VOCs and odorant mixtures without altering how they smell. Recent efforts to integrate microfluidic systems and IC technologies hold great promise.

Another vital area is research on more sensitive sensor arrays for specific applications. For example, a 100-fold improvement in the sensitivity of conducting polymer sensors could lead to small portable electronic-nose monitors that could be the equal of the human nose in detecting odor levels from animal production facilities. There are dozens of interdisciplinary research groups around the world working to improve sensor array technology. In a sense, the future of electronic nose technology rests on progress in this area.



[8] This automated system has been designed to detect and identify the characteristics of gas samples, as well as the volatile contents of solids, liquids, and powders. At the heart of the MultiSampler-SP, from AromaScan, Hollis, N.H., is an array of 32 conductive polymer elements, plus proprietary signal acquisition and processing software.

In addition, sensor response and recovery times 10 to 100 times faster than currently available are required for many high-volume applications, such as screening vehicles for explosives, drugs, and other contraband. New arrays of detectors must also achieve long-term sensor stability, deviating less than 5 percent in their lifetime, as well as device-to-device repeatability. Otherwise it would be impossible for signal-processing databases (compiled over time during normal operation of the electronic nose system) to fill in as sensors are replaced in the normal course of maintenance.

As these databases for individual electronic nose systems mature, they may be unified into standard application-specific odorant databases. Their general availability will open the way to new ideas in information processing--using information theory to rank each sensor in the array for its contribution to assigned pattern-classification tasks. Then sensors with little to contribute can be eliminated from the array, cutting costs and improving system reliability.

For some food applications, the electronic nose will soon be augmented by an electronic tongue. It could employ the same system building blocks, except that liquid instead of gas sample handling would be involved, and the sensor array would operate in a liquid environment.

Early work on this has begun in Japan, where researchers are trying to build an electronic tongue that can identify sweet, sour, bitter, salty, and monosodium glutamate tastes. The systems have been used in quality control for producing beer, coffee, milk, tomato juice, and bottled water.

So in a few years, when you awake in the morning, your coffee maker's electronic nose and tongue may have produced that perfect cup of coffee, the one you enjoy above all others in the universe.

To probe further

The basic concepts of discriminating odorants in complex mixtures without using highly specialized sensors are covered by K. Persaud and G. Dodd in their 1982 paper, "Analysis of discrimination mechanisms in the mammalian olfactory system using a model nose" (Nature, Vol. 299, pp. 352- 55).

Sensor arrays and signal processing algorithms presented at the 1991 NATO Workshop appear in J. W. Gardner and P.N. Bartlett (eds.), *Sensors and sensory systems for the electronic nose* (Kluwer Academic Publishers, London, 1992). Also check out *Handbook of Biosensors and Electronic Noses*, ed. E. Kress-Rogers (CRC Press, Boca Raton, Fla., 1997).

An optical-fiber sensor array that can identify individual vapors is described by T. A. Dickinson, J. White, J. S. Kauer, and D. R. Walt in "A chemical-detecting system based on a cross-reactive optical sensor fiber" (Nature, Vol. 382, 1996, pp. 697-700).

Isolation of the source of unpleasant odors in a drug inhaler is highlighted in S. S. Schiffman, B. G. Kermani, and H. T. Nagle's "Analysis of medication off-odors using an electronic nose," *Chemical Senses*, Vol. 22, 1997, pp. 119-28.

An analysis of signal-processing algorithms for a gas sensor array appears in R. Gutierrez-Osuna's 1998 doctoral dissertation, "Signal processing and pattern recognition for an electronic nose" for North Carolina State University. It is available from University Microfilms Inc., Ann Arbor, Mich.

K. Toko's "Taste sensors with global selectivity" on an array made of lipid and polymer membranes was printed in *Materials Science and Engineering*, Vol. C4, 1996, pp. 69-82.

The mammalian olfactory system and membrane receptors are reviewed in depth by J. W. Gardner, P. N. Bartlett, G. H. Dodd, and H. V. Shurmer in "The design of an artificial olfactory system," *Chemosensory Information Processing*, edited by D. Schild (Springer-Verlag, Heidelberg, Germany, 1990).

A description of an electronic nose used to classify and predict the culture growth phase of two types of bacteria is presented in a paper by J. W. Gardner, M. Craven, C. Dow, and E. L. Hines titled "The prediction of bacteria type and culture growth phase by an electronic nose with a multi-layer perceptron network." It appeared in this year's *Measurement Science and Technology*, Vol. 9, pp. 120-27.

To foster activities in the field within the Institute, an electronic nose subcommittee has been established by the IEEE New Technology Directions Committee. To participate, contact t.nagle@ieee.org.

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Ricardo Gutierrez-Osuna (S) recently completed his Ph.D. in computer engineering [see *To Probe Further*]. He plans a career in medical instrumentation, artificial intelligence, and robotics.

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