Chemical Profiling Cargo with an Ultra-High Speed Gas Chromatograph, Olfactory Images, and Virtual Chemical Sensors

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Abstract

Ultra-high speed gas chromatography is a powerful analytical method for analysis of odors, fragrances, and chemical vapors produced by explosives, chemical and biological weapons, contraband, and hazardous industrial materials. A portable chemical profiling system incorporating an ultra-high speed chromatography column, a solid-state sensor, a programmable gate array microprocessor, and an integrated vapor preconcentrator is described.

Using ultra-high speed chromatography, chemical vapors within containers can be speciated and their concentration measured in less than 10 seconds with picogram sensitivity using a SAW sensor with electronically variable sensitivity. Odor concentration and intensity are measured directly with an integrating GC sensor. The solid-state sensor produces high resolution 2-dimensional olfactory images unique to many complex odors. Examples involving odors from explosives, contraband drugs of abuse, hazardous chemicals, and even biological life forms are presented.

An important requirement for a chemical profiling system is that it must recognize odors and fragrances based upon their full chemical signature. Unlike a trace detector, it must see everything and miss nothing. 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 hazardous materials. Chemical libraries and electronic odor profiles allows users to quickly distribute signatures of hazardous materials or new threat vapors of any kind.

Chemical sensor arrays 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. Using ultra-high speed gas chromatography, arrays of virtual chemical sensors with non-overlapping response are possible. Long term stability coupled with picogram sensitivity may lead to the possibility of applying artificial intelligence and neural networks to detect and recognize an unlimited number of threat vapors.

Introduction -The Problem

The U.S. now inspects 4 percent of the 6 million shipments that arrive at more than 100 ports, twice the 2 percent before the Sept. 11 attacks in 2001. About 20 percent of that cargo passes through overseas ports such as Hong Kong, where U.S. inspectors are being stationed. Cargo worth $1.2 trillion, or half of U.S. imports, arrives by sea. The rest comes from Canada and Mexico. There is a clear and present danger yet the problem is daunting.

Figure 1- Nearly 7 million cargo containers come into U.S. ports from overseas every year. Officials say it would be impossible to examine every one of them.

Current sensor capabilities are fairly limited; in many cases, the best “technology” for practical use continues to be trained dogs. Manufactured sensors are often designed for use in specific environments and to be selective for only one or two chemicals. Yet because there is a spectrum of possible threats, sensor systems are needed that can detect a large number of possible chemicals. In addition, sensor systems need a number of different subsystems, including sample collection and processing, presentation of the chemicals to the sensor, and sensor arrays with molecular recognition.

In this paper, an electronic nose using a single solid-state sensor is able to create an unlimited number of specific virtual chemical sensors for chemically profiling odors in cargo containers. Virtual sensor arrays and recognizable olfactory images for explosives, hazardous substances, drugs of abuse, and even the cargo itself provides a cost effective screening tool for shippers and inspectors alike. In support of container security protocols, odor profiles can also be attached to an electronic manifest file and forwarded to authorities at the country of destination for comparison purposes.

Chemical Profiling with High Speed Gas Chromatography

A portable chemical profiling system (Figure 1) incorporating an ultra-high speed chromatography column, a solid-state sensor, a programmable gate array microprocessor, and an integrated vapor preconcentrator is able to speciate and quantify the vapor chemistry within a cargo container in 10 seconds. Vapors within the container are sampled by inserting a sampling tube attached to the inlet of the instrument through a small opening in the container door (Figure 2).

Figure 2- Portable chemical profiling system incorporating an ultra-high speed gas chromatograph

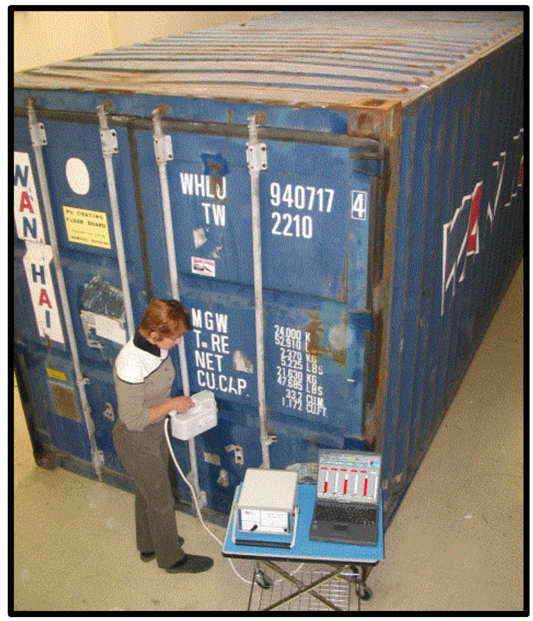

Figure 3- Vapors are sampled by inserting a probe attached to the inlet of the instrument into a small re-sealable hole in the container.

The chromatograph system (Figure 4) contains a minimum number of parts and temperature programming a directly heated capillary column at rates as high as 18°C/second produces 10 second chromatograms. A small capillary trap filled with tenax™ preconcentrates sampled vapors and injects them into the capillary column. A key component of the system is a solid-state surface-acoustic-wave (SAW) detector which has zero dead volume and can detect quantities as small as one picogram. The sensitivity of the detector chip (0.100 x 0.100 inch) is dependent upon temperature which is electronically controlled by means of a Peltier thermoelectric element.

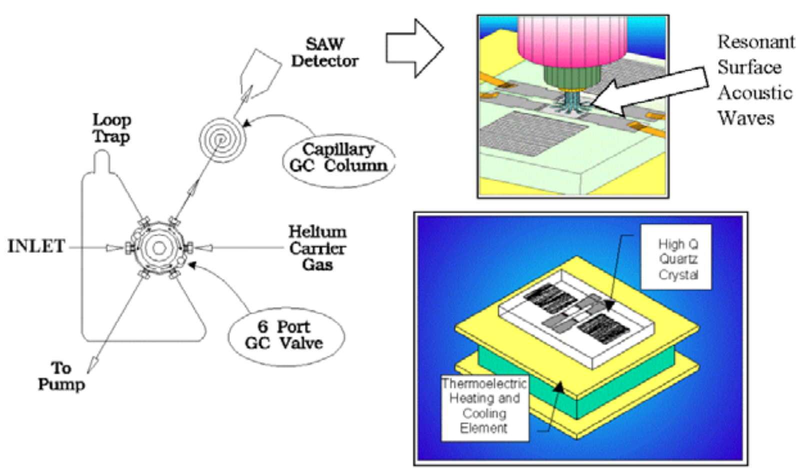

Figure 4- Diagram of high speed GC and details of SAW detector.

Olfactory Images and Virtual Chemical Sensors

The SAW sensor is non-ionic and non-specific. It directly measures the total mass of each chemical compound as it exits the GC column and condenses on the crystal surface, causing a change in the fundamental acoustic frequency of the crystal. Odor concentration is directly measured with this integrating type of detector. Column flux (conventional chromatogram) is obtained from a microprocessor which continuously calculates the derivative of the SAW frequency.

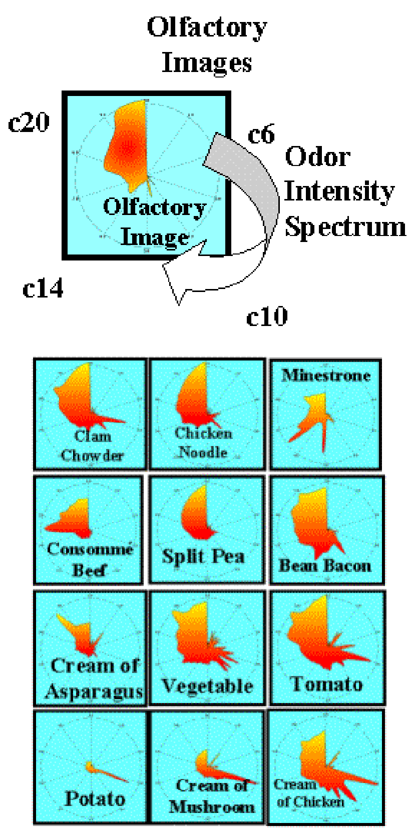

Figure 5- VaporPrint™ olfactory images

Plotting sensor frequency change (radial) vs elution time (angle) produces a high- resolution 2-dimensional olfactory image called a VaporPrint™ as shown in Figure 5. These images display the entire odor chemistry and enable the chemical profiling system to recognize complex odors and fragrances based upon their full chemical signature.

Different chemicals have different retention times and this allows for the creation of hundreds of specific virtual chemical sensors and sensor arrays for performing trace detection. Virtual chemical sensors (Figure 6) combined with odor profiles are effective methods for recognizing the signature of known hazardous materials.

Retention time indices (Kovats) of known chemicals relative to n-alkanes allows the use of a chemical library and electronic odor profiles that can be shared by many users. Users can quickly distribute and share odor profiles of cargo, new threats, or contraband of any kind.

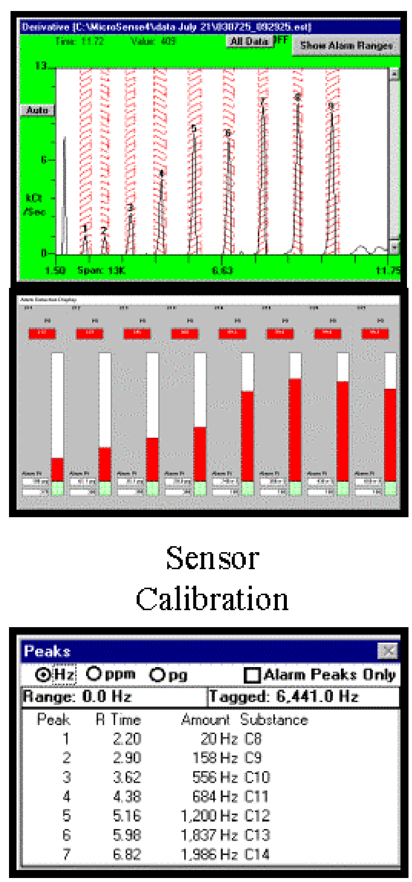

Figure 6- Virtual Chemical Sensor Arrays

Profiling of Cargo Container Odors

Odors from Explosives

Because the SAW sensor is non-specific it is able to detect and quantify the vapor concentration of virtually any explosive independent of its chemical make-up e.g. nitro or non-nitro). The probability of detecting explosives from fugitive emissions (vapor phase) within a cargo container is strongly dependent upon the temperature of the cargo container, the vapor pressure of the explosive chemicals, and how they are packaged. For this reason explosives such as Semtex and C4, which contain high molecular weight chemical explosives like PETN and RDX are rarely detectable by vapor phase measurements. Because of this, by international accord, all manufacturers of 'plastic' explosives now include a volatile taggant compound such as DMNB or MNT. This enables vapor detection systems and canines to detect these explosives. As an example, the complete chemical odor profile, olfactory image, and virtual sensor array response of unpackaged C4 is shown in Figure 7. The RDX response (peak 7) is difficult to see however is is much easier to detect the volatile taggant (peak 1).

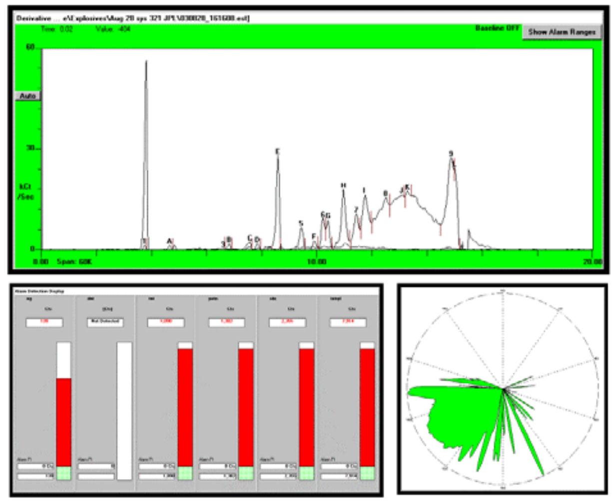

Figure 7- Chemical odor profile of C4 explosive.

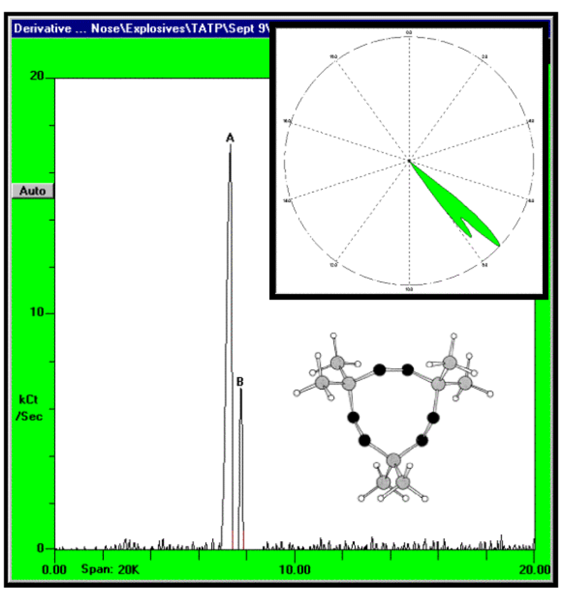

Figure 8- Chemical odor profile of TATP

Not all explosives contain a nitrogen base and because of this they cannot be detected with conventional explosive trace detectors. One explosive of this type is triacetone triperoxide (TATP) which has the explosive power of RDX yet contains no nitrogen. This compound was used by the shoe-bomber Richard Reid and is also commonly used by human bombers in Israel. The chemical odor profile of TATP crystals is quite simple as shown in Figure 7. Like NG, DNT and TNT, TATP is very volatile and fugitive emission can easily be detected in cargo containers.

Odors From Contraband Drugs

Some contraband drugs like methamphetamine and marijuana produce odiferous compounds such as THC and cannabinol which is detectable in the vapor phase by canines and the SAW based chemical profiling system. Others such as cocaine and heroin are much more difficult because their vapor pressure is extremely low. A virtual sensor array (Figure 9) is used to screen a container chemical odor profile for target compounds. The virtual sensors can be created using odors from samples of the target drugs or by selecting the specific compounds from the system's chemical library.

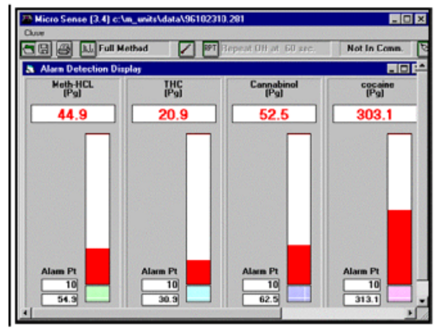

Figure 9- Virtual chemical sensor array for methamphetamine and marijuana,

The chemical odor signature of cocaine in a cargo container (Figure 10) was tested using packaged 1-kilogram bundles. Cocaine produced little or no signal at ambient temperatures and significant vapor concentrations could only be detected when the temperature of the container was above 50°C.

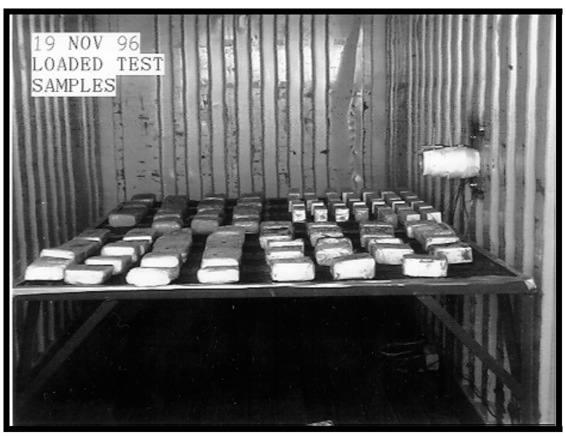

Figure 10- Cargo container loaded with 1 kilogram packages of cocaine.

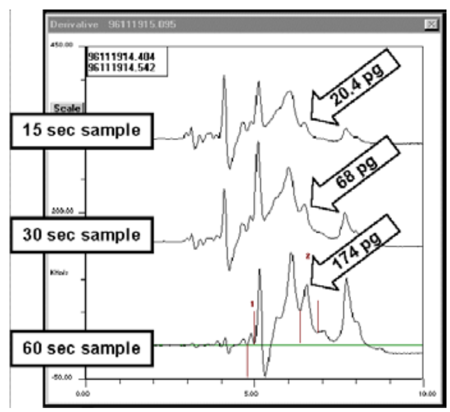

Figure 11- To detect cocaine vapors in a cargo container long sample preconcentration times and elevated temperatures must be used.

The presence of low vapor pressure drugs like cocaine and heroine is best done by targeting the more volatile compounds associated with the drugs. For cocaine a natural by-product is methyl benzoate, commonly referred to as doggy-cocaine because it is used to train canines to detect this drug. The presence of methyl benzoate is clearly visible in the room temperature odor profile shown in Figure 12.

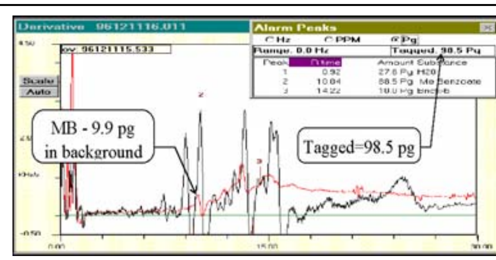

Figure 12- Volatile compounds in cargo container at room temperature.

Odors of Hazardous Chemicals

It is not uncommon for hazardous chemicals to be present in cargo. Properly sealed many flammable organics may not be detected however even a small leak can create a dangerous and even explosive vapor. As an example, vapors from gasoline and JP-8 aviation fuel are shown in Figure 13. Both are complex substances containing many volatile organics and are not easily separated by a single chemical sensor.

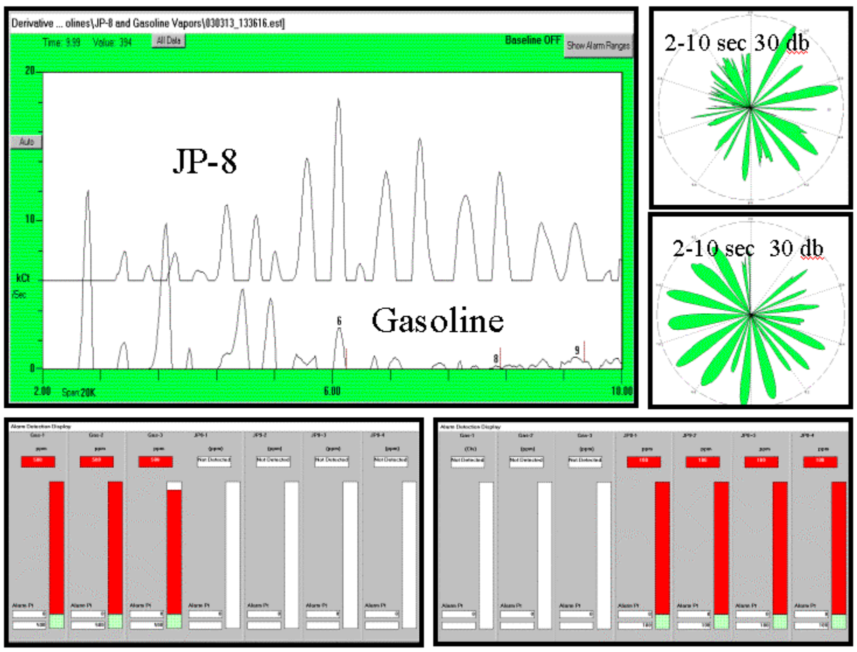

Figure 13- The chemical profiles of Gasoline and JP-8 produce easily recognizable olfactory images and can be separated using arrays of virtual chemical sensors.

However, gasoline and JP-8 do produce distinctly different olfactory images. Gasoline has more volatile compounds while JP-8 has more less volatile compounds. Creating virtual chemical sensors unique to both provides a convenient way of recognizing the difference and presence of either. This would be important when performing odor profiling in and around an airport facility where JP-8 is a common background odor.

Odors of Biological Life

Virtually all living organisms produce volatile organics which can be detected. In recent times human cargo has been smuggled inside cargo containers. The presence of human cargo might be linked to the odor of human waste which contains a high percentage of e. Coli bacteria. E. Coli produces a very recognizable olfactory image which is dominated by the chemical indole as shown in Figure 14.

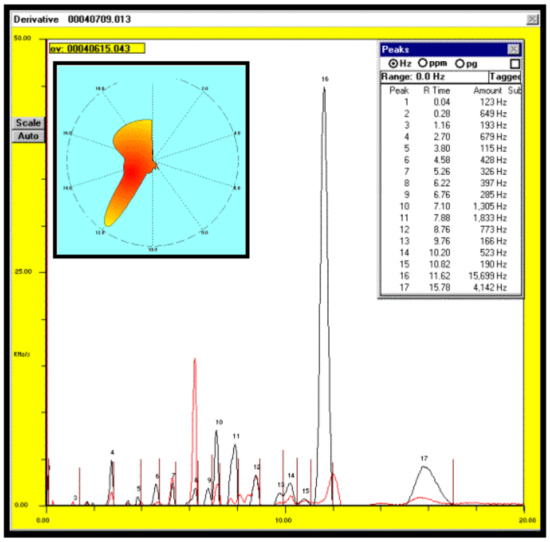

Figure 14- The chemical odor profile of e. Coli is dominated by a high concentration of indole.

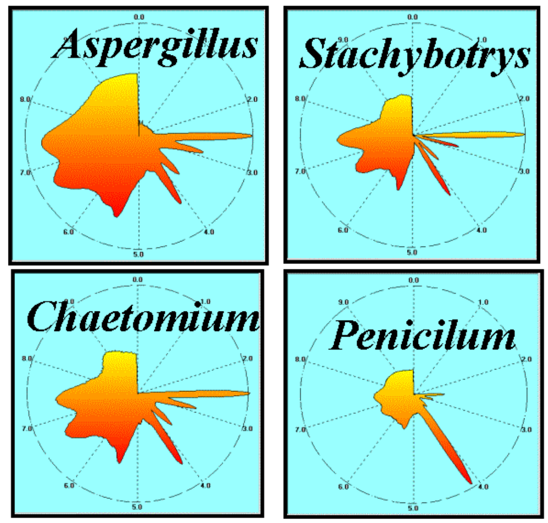

Figure 15- Olfactory images of common microbial life forms.

The presence of molds and fungus within cargo containers can contaminate and even damage sensitive cargo. These life forms produce distinctive olfactory images and unique chemicals called microbial volatile organic compounds (MVOCs) as shown in Figure 15.

Contraband of Choice - Money

Money laundering is a global problem normally associated with drugs and illegal activities that generate huge amounts of currency which cannot be transacted by standard methods. US currency produces distinctive volatile and semi-volatile compounds as well as distinctive olfactory images as shown in Figure 16. Using chemical odor profiling and virtual chemical sensors can readily identify and locate currency concealed in cargo.

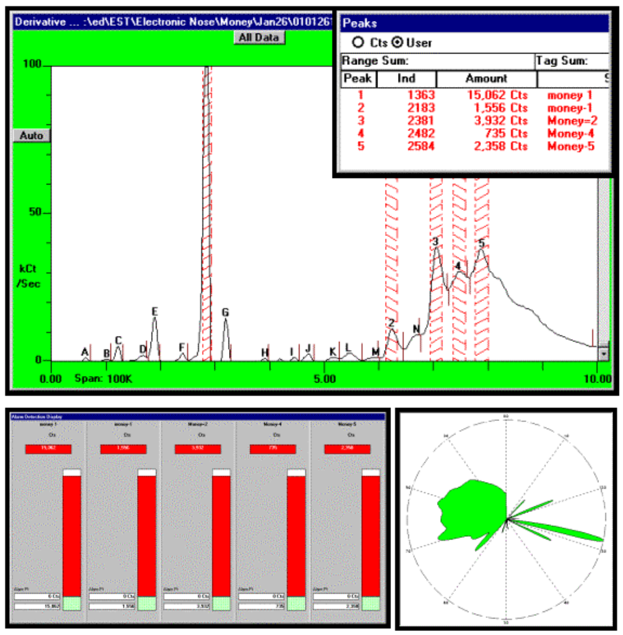

Figure 16- The smell of money can easily be recognized using virtual money chemical sensors and also by its distinctive olfactory image.

Summary

In this paper a portable chemical profiling system using high speed chromatography and a solid-state sensor has demonstrated the ability to speciate and quantify vapor chemistry in seconds. Methods to chemically profile and detect target odors in cargo have many advantages: Vapor collection from cargo containers can be rapidly accomplished and is minimally invasive. In addition the solid-state sensor system is portable and low in cost.

A non-specific sensor when coupled with chromatographic separation can produce high resolution 2-dimensional olfactory images unique to many complex odors such as from explosives, contraband drugs of abuse, hazardous chemicals, and even biological life forms. A single sensor is able to create an unlimited number of specific virtual chemical sensors and can thus quickly adapt to changing threat vapors. Virtual sensor arrays and recognizable olfactory images provide a cost effective screening tool for shippers and inspectors alike. For example, electronic odor profiles can be attached to an electronic manifest file and forwarded to authorities at the country of destination for comparison and verification

Chemical sensor arrays or 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. Arrays of virtual chemical sensors have non-overlapping response, good long term stability, and picogram sensitivity which will enable artificial intelligence and neural networks to quickly distinguish patterns of actual threats from noise or background odors automatically and with high precision.

Cargo and port security are key components of the nation's homeland security strategy. More than seven million cargo containers arrive at U.S. seaports annually, according to the U.S. government and there is a need to develop screening methods which will be quick and cost-effective. The nature of threat is such that there is an almost unlimited number of possible target chemicals so it is imperative that sensor technology be highly adaptive.

Electronic noses can play a major role in preventing catastrophic terrorism or, if attacks do occur, in minimizing their impacts. Adaptive virtual sensor arrays have the potential to thwart terrorist activities in the planning stage, before or during attempted attacks, and to help identify suspicious cargo. They may also be useful in forensic analysis to identify perpetrators after an attack. Sensors can also provide sensitive and rapid warning for the protection of fixed sites (subways, airports, government buildings, financial centers, high-value industries). For example, virtual chemical sensors for ventilation systems capable of detecting deviations from normal conditions and monitoring for chemical and biological agents could be coupled to rapid-shutdown procedures.