Homeland Security, Olfactory Images, and Virtual Chemical Sensors

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Abstract

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 approach using ultra-high speed gas chromatography now allows for the creation of arrays of virtual chemical sensors with non-overlapping responses. In addition, high-resolution 2-dimensional olfactory images allow many complex odors to be easily recognized. Long term stability coupled with picogram sensitivity may lead to the successful application of artificial intelligence and neural networks to detect and recognize an unlimited number of chemical vapors. A portable chemical profiling system for homeland security applications incorporating an ultra-high speed chromatography column, a solid-state sensor, a programmable gate array microprocessor, and an integrated vapor preconcentrator is described.

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. Hence there is a need to develop screening methods, which will be quick and cost-effective. The nature of the current threat is such that an almost unlimited number of possible target chemicals could be used to carry it out. It is, therefore, imperative that sensor technology be highly adaptive. Electronic noses can play a major role in preventing catastrophic terrorism and in minimizing the impact of attacks, if and when they do occur. Adaptive virtual sensor arrays have the potential to thwart terrorist activities in the planning stage as well as before or during attempted attacks. They can also help identify suspicious cargo and, 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). In this paper, an electronic nose using a single solid-state sensor that is able to create an unlimited number of specific virtual chemical sensors for chemically profiling odors in cargo containers is described.

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, and the problem of dealing with it 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 that can create an unlimited number of specific virtual chemical sensors for chemically profiling odors in cargo containers is described. 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

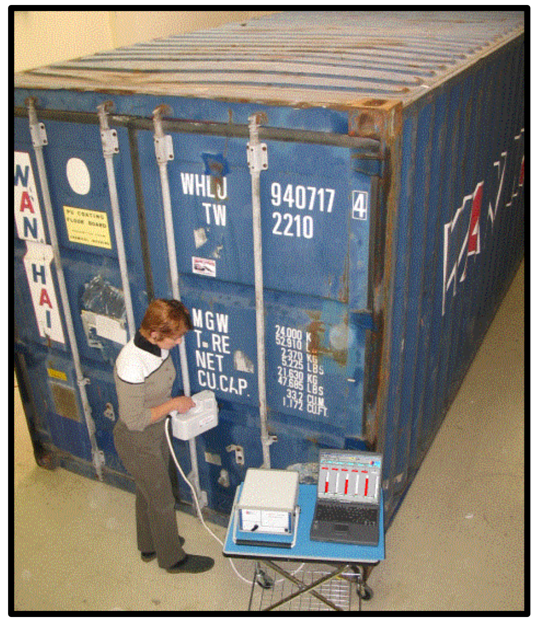

Figure 3- Vapors are sampled by inserting a probe attached to the inlet of the instrument into a small re-sealable hole in the container.

The chromatograph system (Figure 4) contains a minimum number of parts. The system is designed to generate temperature programming a directly heated capillary column at rates as high as 18^{o}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.

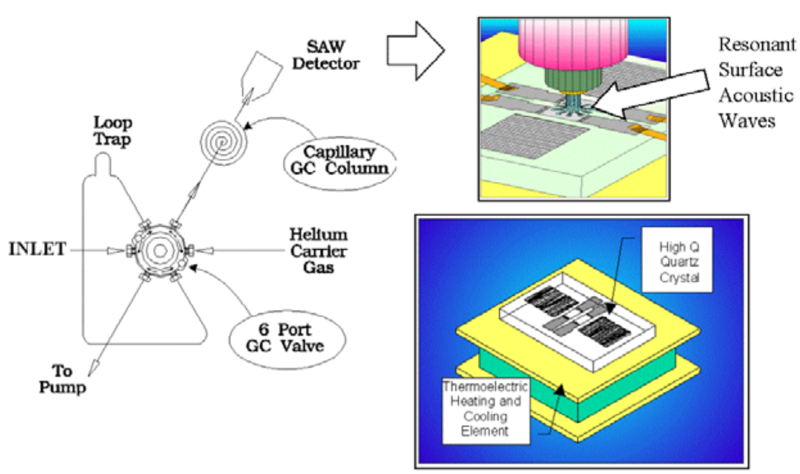

Figure 4- Diagram of high speed GC and details of SAW detector.

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.

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 allow the use of a chemical library and electronic odor profiles to be shared by many users. Users can quickly distribute and share odor profiles of cargo, new threats, or contraband of any kind.

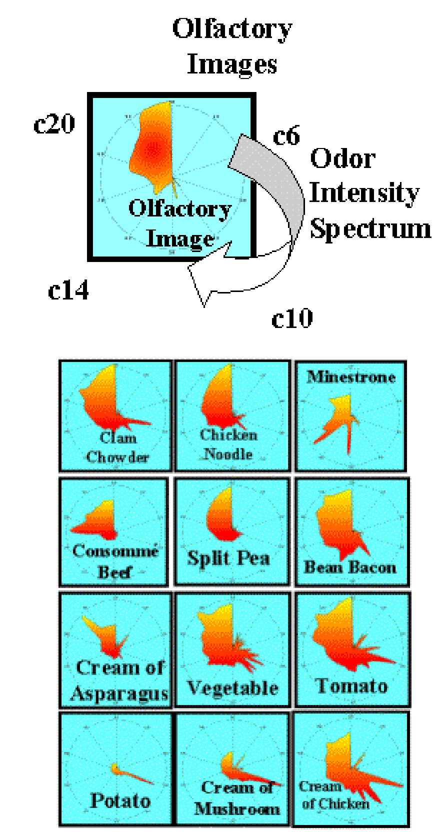

Figure 5 - VaporPrint™ olfactory im-

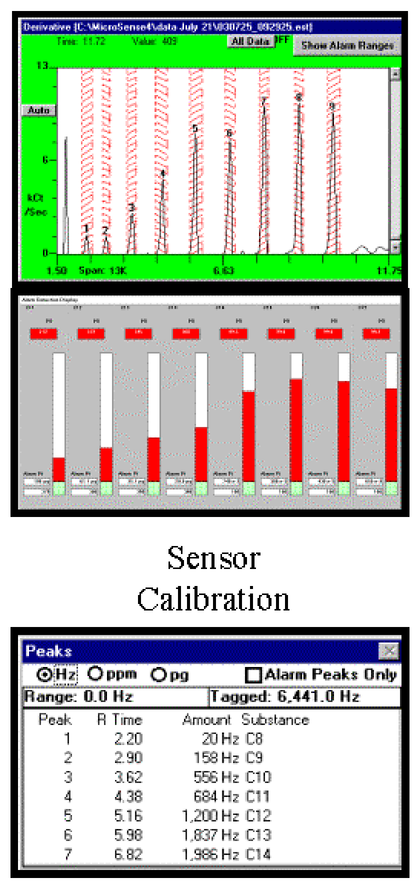

Figure 6- Virtual Chemical Sensor Arrays

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 the way 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 un-packaged C4 is shown in Figure 7. The RDX response (peak 7) may not be seen easily, but the volatile taggant (peak 1) can be detected without any difficulty..

Not all explosives contain a nitrogen base. Hence they cannot be detected with conventional explosive trace detectors. One explosive of this type is triacetone triperoxide (TATP). Even though this has the explosive power of RDX, it contains no nitrogen. This was the compound that was used by the shoe-bomber Richard Reid. It is also one that is commonly used by human bombers in Israel. The chemical odor profile of TATP crystals is quite simple as shown in Figure 8. Like NG, DNT and TNT, TATP is very volatile and fugitive emissions of this explosive can easily be detected in cargo containers.

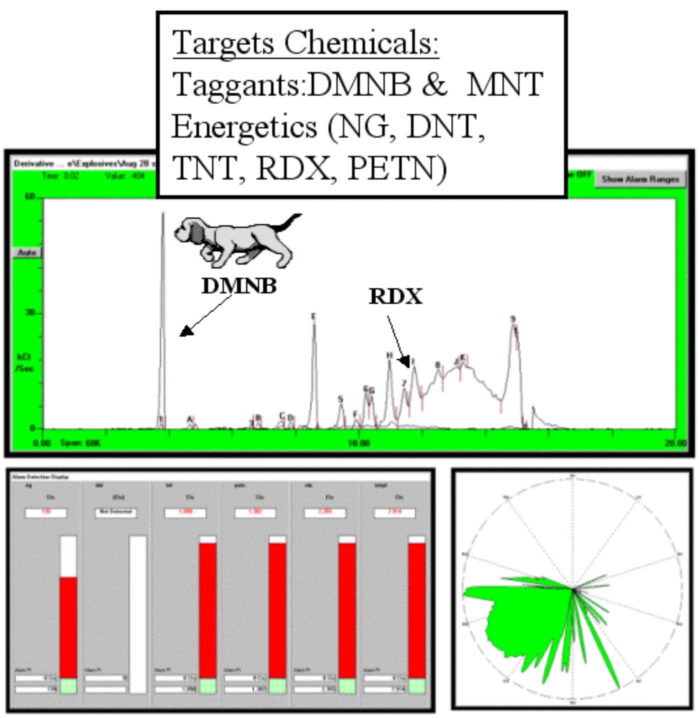

Figure 7- Chemical odor profile of C4 explosive.

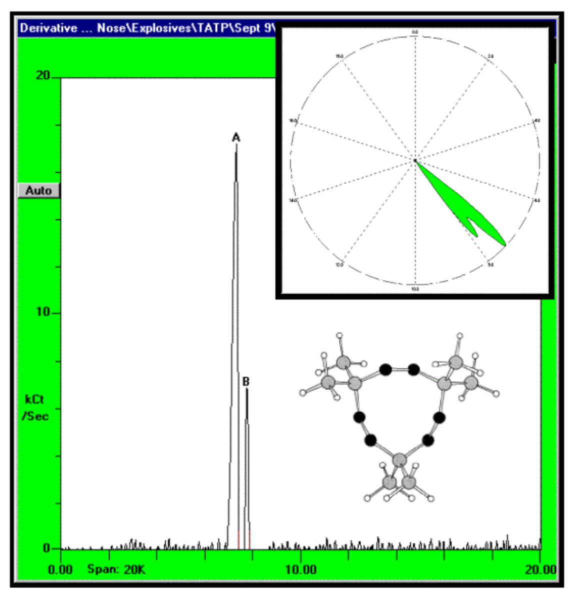

Figure 8- Chemical odor profile of TATP

Odors From Contraband Drugs

Some contraband drugs like methamphetamine and marijuana produce odiferous compounds such as THC and cannabinol, which are detectable in the vapor phase by canines as well as a GC 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 can be used to screen a chemical odor profile for specific target compounds.

The chemical odor signature of cocaine in a cargo container (Figure 9) was tested using packaged 1-kilogram bundles. Cocaine produced little or no odor signal at ambient temperatures but could be detected when particles were suspended within the ambient air. However, training canines to detect the more volatile compounds associated with cocaine and heroin has proven to be an effective technique and works equally well with GCs. For cocaine, a natural by-product is methyl benzoate, commonly referred to as doggy-cocaine because it is used to train canines. The presence of methyl benzoate is clearly visible in the room temperature odor profile shown in Figure 9.

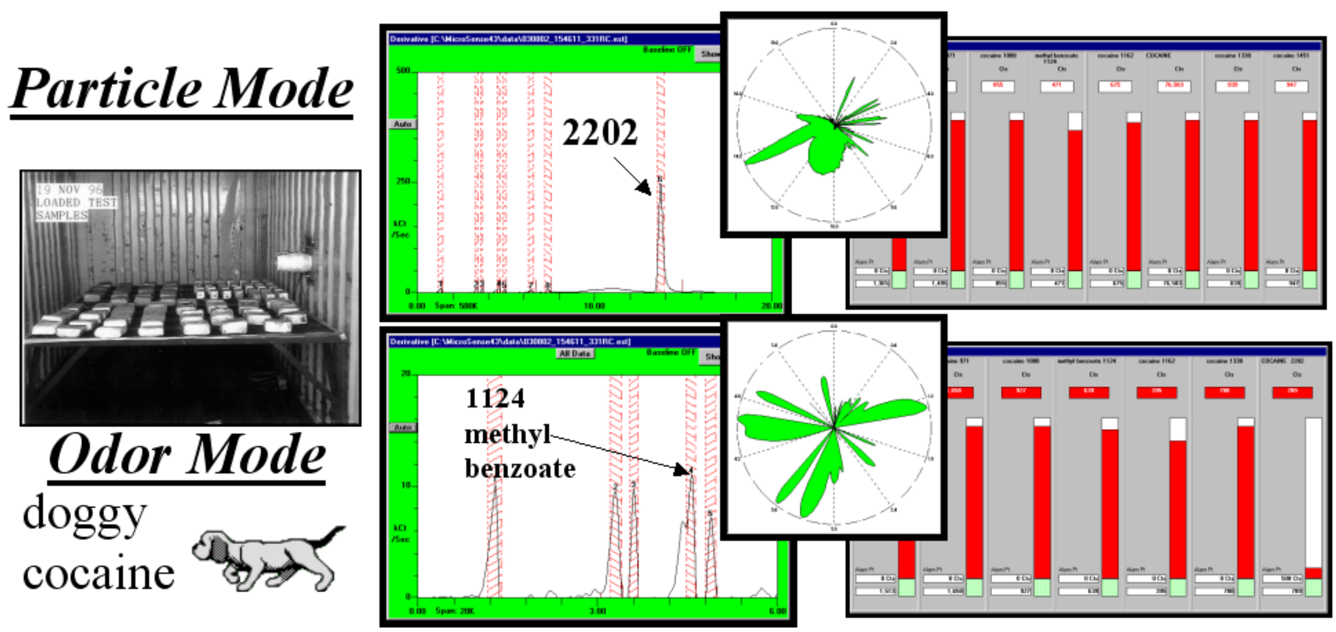

Figure 9- Cargo container loaded with 1 kilogram packages of cocaine.

Odors of Hazardous Chemicals

It is not uncommon for hazardous chemicals to be present in cargo. If properly sealed, many flammable organics may not be detected. However if a small leak does occur, it can create a dangerous and even explosive vapor. As an example, vapors from gasoline and JP-8 aviation fuel are shown in Figure 10. Both are complex substances containing many volatile organics and are not easily separated by a single chemical sensor.

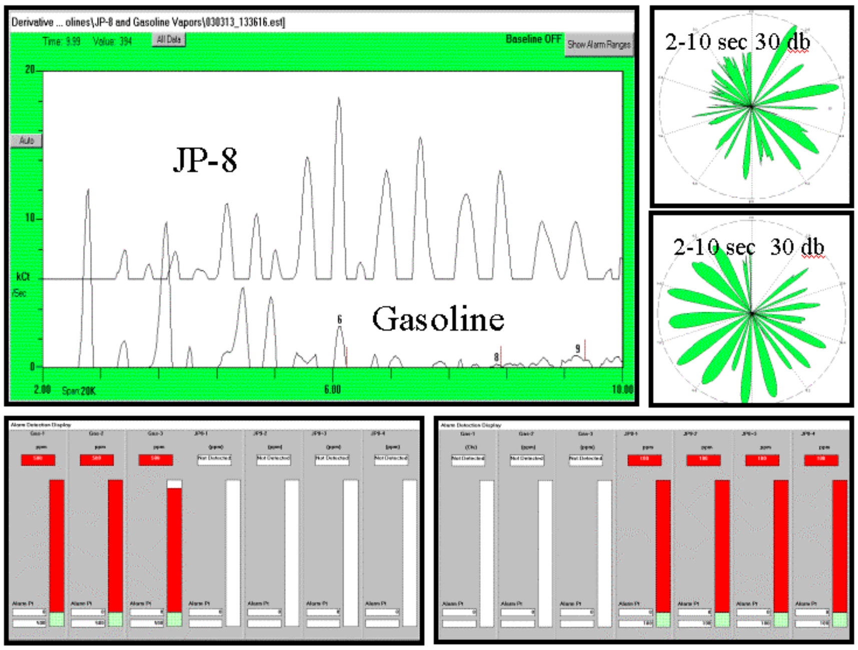

Figure 10- The chemical profiles of Gasoline and JP-8 produce easily recognizable olfactory images and can be separated using arrays of virtual chemical sensors.

However, gasoline and JP-8 do produce distinctly different olfactory images. Gasoline has more volatile compounds while JP-8 has more semivolatile compounds. Creating virtual chemical sensors unique to both is 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 11.

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 12.

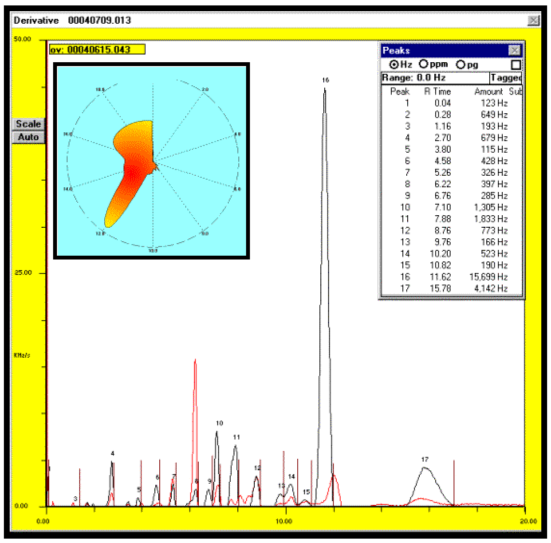

Figure 11- The chemical odor profile of e. Coli is dominated by a high concentration of indole.

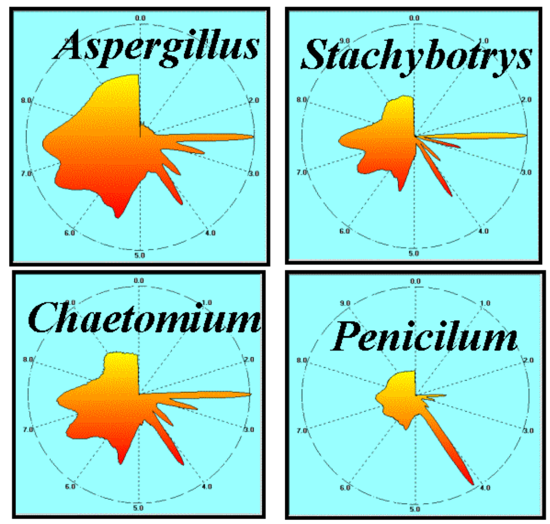

Figure 12- Olfactory images of common microbial life forms.

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 relatively inexpensive.

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. Hence there is a need to develop screening methods, which will be quick and cost-effective. The nature of the threat is such that an almost unlimited number of possible target chemicals could be used to carry it out, so it is imperative that sensor technology be highly adaptive.

Electronic noses can play a major role in preventing catastrophic terrorism or in minimizing their impacts, if and when attacks do occur,. Adaptive virtual sensor arrays have the potential to thwart terrorist activities in the planning stage as well as before or during attempted attacks. They can also help identify suspicious cargo, and 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.