Safeguarding Ports with Chemical Profiling

Ultrahigh-speed gas chromatography (GC) is a powerful method for analyzing odors, fragrances, and chemical vapors produced by explosives, chemical and biological weapons, contraband, and hazardous industrial materials. A new chemical-profiling system directly measures odor concentration and intensity with an integrated GC sensor. Using a solid-state surface-acoustic-wave (SAW) sensor with electronically variable sensitivity, it identifies the chemical species in the vapors inside cargo containers and determines their concentrations in 10 s with picogram sensitivity. Although the system is useful for sampling any accessible container, it currently holds immediate significance for America's ports.

The problem

The United States now inspects 4% of the 6 million shipments that arrive at more than 100 U.S. ports annually, double the 2% before the attacks on New York and Washington, DC, on September 11, 2001. About 20% of those 6 million shipments pass through overseas ports, such as Hong Kong, Tokyo, Rotterdam, and Antwerp, where the United States has stationed U.S. customs inspectors. According to the Department of Homeland Security (DHS), cargo worth $1.2 trillion, or half of U.S. imports, arrives by sea; the rest enters from Canada and Mexico. Cargo containers pose a clear and present danger as a means for terrorist attacks or the smuggling of weapons of mass destruction. Yet, addressing the problem is daunting.

Current sensor capabilities are limited, and in many cases, the best technology for practical use remains trained dogs. Manufactured sensors are often designed for use in specific environments and are selective for only one or two chemicals. Yet, because there is a spectrum of possible threats, inspectors need sensor systems that can detect and identify a large number of possible chemicals. In addition, these sensor systems need a number of subsystems, including sample collection and processing, presentation of the chemicals to the sensor, and sensor arrays that recognize and distinguish different chemical profiles.

The zNose Model 4200 (Electronic Sensor Technology, LP, Newbury Park, CA) can create an unlimited number of specific virtual chemical sensors for profiling odors. This portable system incorporates an ultrahigh-speed chromatography column, a solid-state sensor, a programmable gate-array microprocessor, and an integrated vapor preconcentrator. The sensor system produces high-resolution, two-dimensional images in the form of radial charts. These images represent the olfactory information unique to many complex odors, including those from explosives, contraband drugs of abuse, hazardous chemicals, and even life-forms (Figure 1).

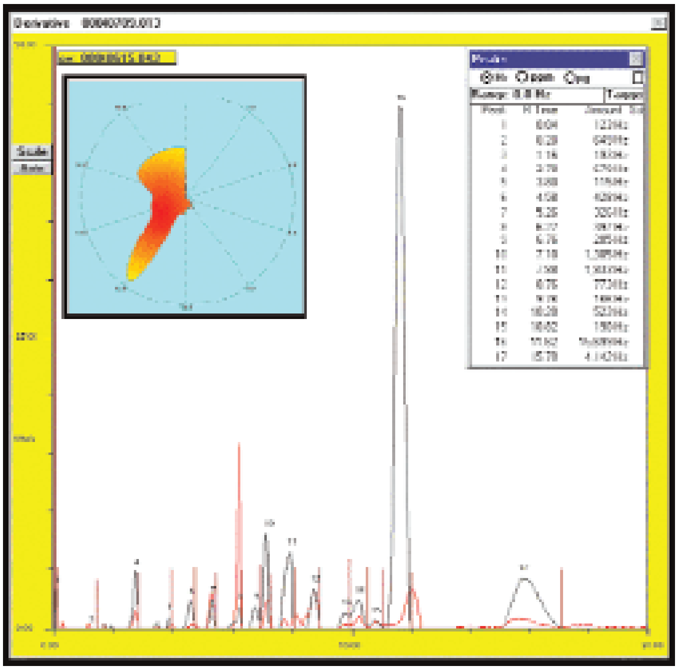

Figure 1. A two-dimensional radial chart (top left) can represent the full chemical signature of a complex odor, where radial distance is proportional to concentration of a species and radial angle is proportional to elution time through a gas chromatograph. The large peak in this *E. coli* bacteria chart is due to a high concentration of indole.

Chemical profiling

An important requirement for a chemical-profiling system is that it recognize odors and fragrances on the basis of their full chemical signature—the combination of all the chemicals in an odor—which is unique to each substance producing the odor. Unlike a trace detector, it must see everything and miss nothing. The portable chemical-profiling system can speciate and quantify the vapor chemistry inside a cargo container in 10 s.

A library of retention-time indices for chemicals—which give the specific time required for each of its indexed chemicals to pass through a chromatograph's column—allows the creation of hundreds of specific software-generated virtual chemical sensors. These virtual sensors, combined with odor profiling, can be a cost-effective screening method for shippers and inspectors alike

Vapors in a cargo container are sampled by inserting a tube attached to the inlet of the instrument through a small opening in the container door. The chromatography system (Figure 2) contains a minimum number of parts. A small capillary trap filled with Tenax, which acts as a vapor sponge, collects and preconcentrates sampled vapors before injecting them into the GC capillary column, which is then heated at rates as high as 18 °C/s to move heavier compounds through it. A key component of the system is a solid-state SAW detector, which can detect quantities as small as 1 pg. The sensitivity of the 0.1 × 0.1-in. detector chip depends on the SAW temperature, which is electronically controlled by a Peltier thermoelectric element. The SAW sensor is

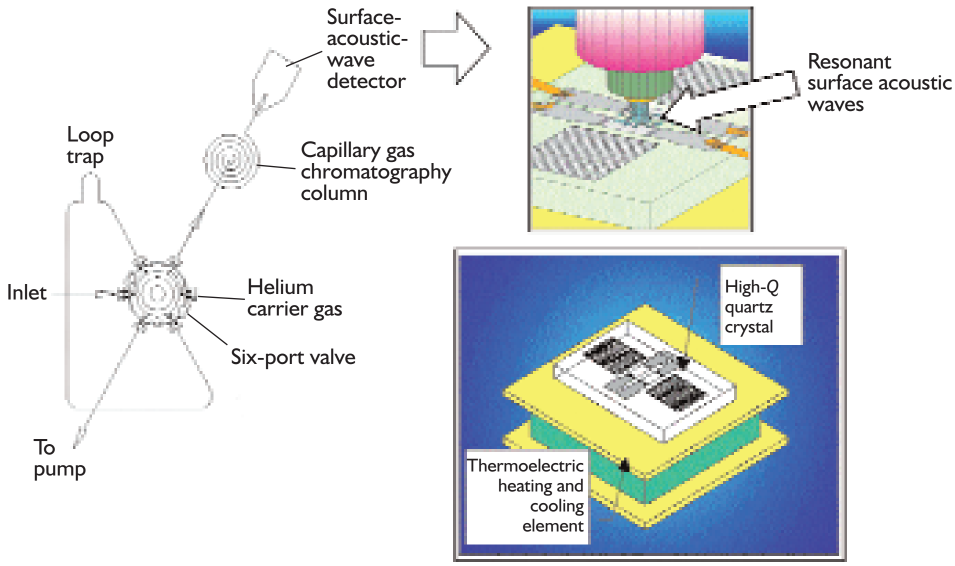

Figure 2. Gas species pass through the ultrahigh-speed gas chromatography column and condense on the surface-acoustic-wave crystal, whose fundamental frequency changes according to the mass of the species.

nonionic and nonspecific. It directly measures the total mass of each chemical compound as it exits the GC column and condenses on the SAW crystal surface, which causes a change in the crystal's fundamental acoustic frequency. Odor concentration is directly measured with this integrating type of detector, which, unlike flux detectors, physically captures each chemical. A conventional chromatogram, or column flux, is obtained from a microprocessor, which continuously calculates the derivative of the SAW frequency.

Plotting the sensor's frequency change (radial) versus elution time (angle) produces a high-resolution, two-dimensional olfactory image called a VaporPrint (Figure 1, top left). Such images display the entire odor chemistry as radial charts, which enables the chemical-profiling system to recognize complex odors on the basis of their full chemical signature.

Different chemicals have different retention times, a feature that allows the creation of hundreds of specific virtual chemical sensors, each of which acts as a trace detector for a specific chemical (Figure 3b).

Retention-time indices of known chemicals, developed using the established passage times of *n*-alkanes as the timing standard, combined with a chemical library and electronic odor profiles, enables users of the system to quickly distribute and share odor profiles of cargo, new threats, or contraband worldwide.

Explosive odors

Because the SAW sensor is nonspecific, it can detect and quantify the vapor concentration of almost any explosive, independent of its chemical makeup. Not all explosives contain a nitrogen base and, as a result, conventional trace detectors cannot identify them. The probability of detecting explosives from the odors in a cargo container depends on the container's temperature, the vapor pressure of the explosive chemicals, and how they are packaged. Hence, plastic explosives such as Semtex and C4, which contain high-molecular-weight chemicals—for example, pentaerythritol tetranitrate and cyclotrimethylene trinitramine—are rarely detectable by vapor-phase measurements.

Because of this insensitivity, and by international accord, all manufacturers of plastic explosives now include a volatile taggant compound such as 2,3-dimethyl-2,3-dinitrobutane (DMNB) or mononitrotoluene, which enables their identification by vapor-detection systems and canines. The complete chemical odor profile, olfactory image, and virtual sensor array response of unpackaged C4 is shown in Figure 3. The RDX response (peak 7) is difficult to see, and it is much easier to detect the volatile taggant DMNB (peak 1).

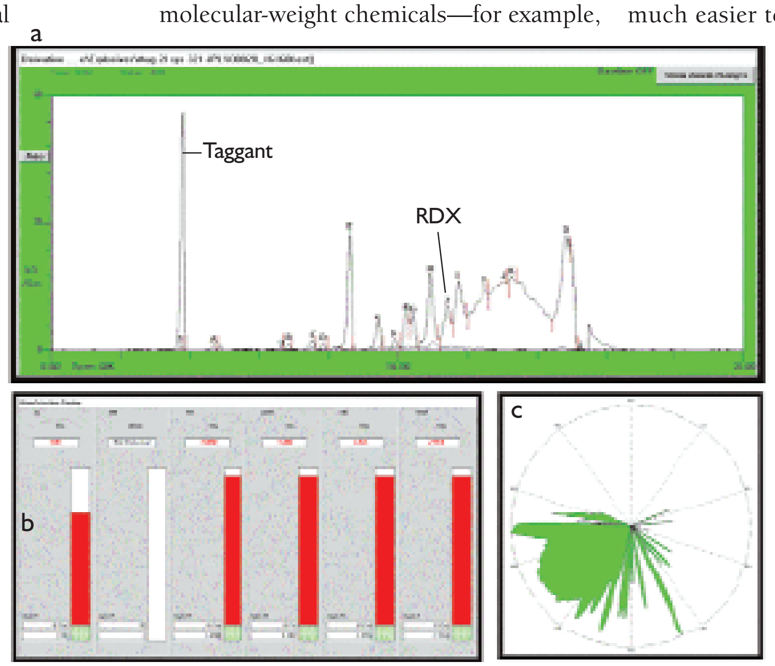

Figure 3. Plastic explosive C4 is identified by its chemical odor profile (a), virtual sensor array response (b), and olfactory image (c). The peak (no. 7 in a) for high-molecular-weight cyclotrimethylene trinitramine (RDX) is more difficult to detect than the taggant (peak 1).

Another plastic explosive is triacetone triperoxide (TATP), which has an explosive power (velocity = 5,300 m/s) similar to that of RDX (velocity = 8,380 m/s). Human bombers commonly use TATP for attacks in Israel, and the shoes of Richard Reid contained this compound when he tried to blow up an American Airlines flight over the Atlantic Ocean in December 2001. Just like nitrogen-containing explosives, TATP is highly volatile, and its vapors can easily be detected in cargo containers.

Contraband

Some illicit drugs have distinctive odors, such as the mono- and diterpenes released by marijuana, which canines and the zNose 4200 can easily detect. Others, such as cocaine and heroin, are more difficult to detect because they have extremely low vapor pressures. A virtual sensor array can screen a container for such contraband. Virtual sensors can be created by using odors from samples of the drugs or by selecting specific compounds from the system's chemical library.

The chemical-odor signature of cocaine in a cargo container was tested using packaged 1-kg bundles. The cocaine produced little or no signal at ambient temperatures, and significant vapor concentrations could be detected only when the temperature of the container rose above 50 °C (Figure 4). The presence of low-vapor-pressure drugs is best detected by targeting the more volatile compounds associated with them. One natural byproduct of cocaine is methyl benzoate, commonly referred to as doggy-cocaine because it is used to train canines to detect the drug.

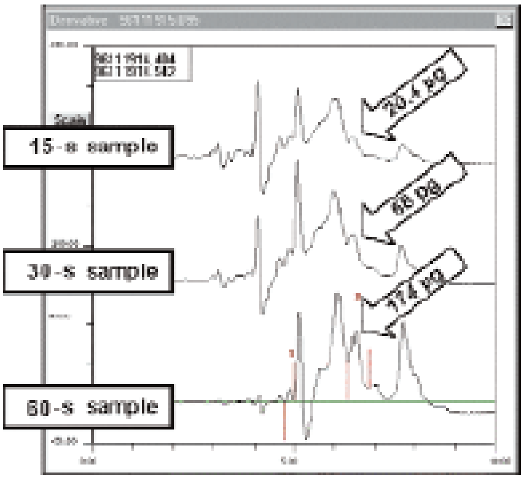

Figure 4. The chemical odor signal of cocaine in a cargo container is difficult to detect without elevated temperatures (above 50 °C) and long preconcentration times.

Hazardous chemicals are commonly present in cargo. When properly sealed, many flammable organics cannot be detected. However, even a small leak can create a dangerous and even explosive vapor, such as those from gasoline and JP-8 aviation fuel (Figure 5). Both complex substances contain many volatile organics that are not easily separated by a single-chemical sensor. However, gasoline and JP-8 do produce distinctly different olfactory images. For one thing, gasoline has more volatile compounds than JP-8. Creating a virtual chemical sensor unique to each vapor provides a convenient way to recognize the presence of either or both of them. This would be important when performing odor profiling in and around airport facilities, where JP-8 is a common background odor.

Almost all living organisms produce detectable volatile organics, which holds particular importance for our era. In recent years, smugglers have put humans inside cargo containers to slip them into the coun-

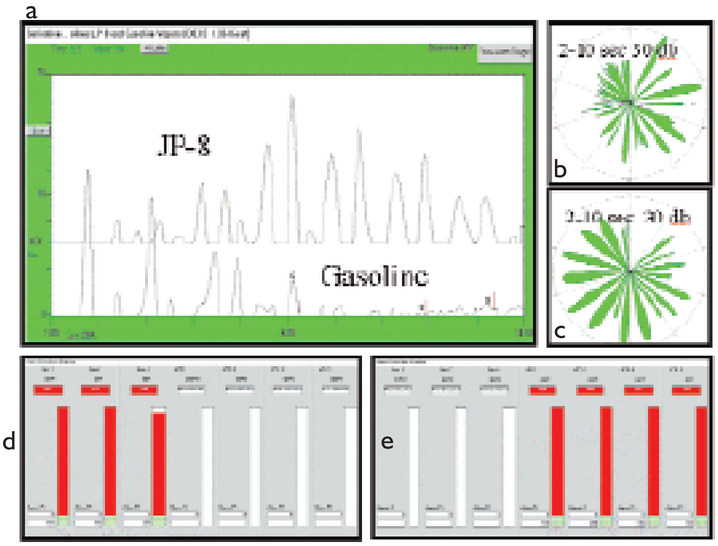

Figure 5. JP-8 aviation fuel and gasoline contain many volatile organic chemicals not easily separated by a single-chemical sensor. However, they do have distinctive olfactory images (b and c) and virtual chemical sensor arrays (d and e).

try. The presence of human cargo might be signaled by the odor of human waste, which contains a high percentage of *E. coli* bacteria. *E. coli* produce a very recognizable olfactory image, which is dominated by the chemical indole (Figure 1). The presence of molds and fungus in cargo containers can contaminate and even damage sensitive cargo. These life-forms produce distinctive olfactory images and unique, detectable chemicals called microbial volatile organic compounds (Figure 6).

Illicit-drug dealing and other illegal activities generate huge amounts of currency that cannot be transferred easily by standard methods. U.S. currency produces distinctive volatile and semivolatile compounds as well as distinctive olfactory images. Chemical-odor profiling and virtual chemical sensors can readily identify and locate currency concealed in cargo.

Advantages

Methods to detect target odors in cargo and chemically profile them have several advantages. Vapor collection from cargo containers can be rapidly accomplished and is minimally invasive. A single zNose 4200 can create an unlimited number of virtual chemical sensors—although the maximum number that can be used at one time to obtain an image with acceptable resolution is 500—and, thus, the system can quickly adapt to changing vapors. Electronic odor profiles, for example, can be attached to an electronic manifest file and forwarded to authorities at the country of destination for comparison (before and after transport) and verification.

Chemical sensor arrays have interested developers of neural networks and artificial intelligence algorithms for some time. Physical sensors, however, have limited performance because of overlapping responses and physical instability. Arrays of virtual chemical sensors, however, have nonoverlapping response, long-term stability, and picogram sensitivity, which will enable antiterrorism artificial intelligence and neural networks to quickly and automatically distinguish pat-

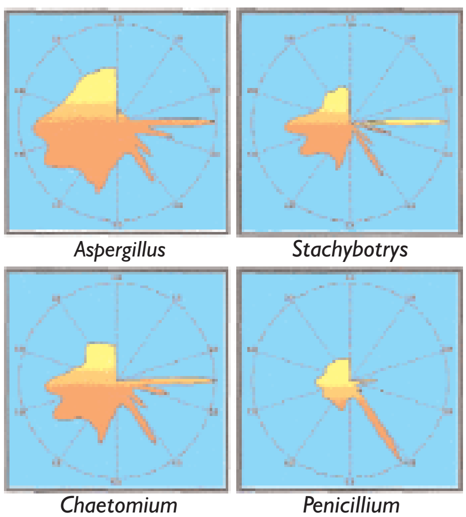

Figure 6. Molds and fungus in cargo containers, which can contaminate and damage sensitive cargo, produce detectable microbial volatile organic compounds with distinctive olfactory images.

terns of actual threats from noise or background odors with high precision.

Cargo and port security are key components of the nation's homeland security strategy, which needs the development of rapid and cost-effective screening methods. The nature of today's threat is such that an almost unlimited number of possible harmful chemicals exist for terrorists to use. This chemical diversity makes it imperative that sensor technology be highly adaptive.

Adaptive virtual-sensor arrays have the potential to thwart terrorist activities in the planning stage, and before or during attempted attacks. 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, such as subways, airports, utilities, government buildings, financial centers, and high-value industries. Virtual chemical sensors for ventilation systems capable of detecting deviations from normal and for monitoring chemical and biological agents could be coupled to rapid-shutdown procedures.

Recently, Asa Hutchinson, DHS undersecretary for border and transportation security, told a Senate hearing that "most experts believe that a terrorist attack using a container as a weapon is likely." Therefore, it is imperative that methods be found and implemented to protect containerized shipping from exploitation by terrorists. Adaptive electronic sensors can help by chemically profiling and prescreening those containers identified as high-risk.

Further reading

Additional information on cargo container security is available at http://usinfo.state.gov/is/international_security/terrorism.html, http://www.customs.ustreas.gov/xp/cgov/enforcement/international_activities/csi/, and http://www.gao.gov/terrorism.html.

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Staples, E. Detecting Chemical Vapors from Explosives using the zNose, an Ultra-High Speed Gas Chromatograph. NATO Advanced Research Workshop (ARW) on Electronic Noses/Sensors for Detection of Explosives, Oct. 1–2, 2003, Coventry, England; available at http://www.estcal.com/TechPapers/Odors_of_Explosives1.pdf.

The difference between electronic noses and trace detectors is explained at http://www.estcal.com/TechPapers/Nose_vs_Bomb_Detector.pdf.

B I O G R A P H Y

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