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Abstract

To date, the most reliable method for searching for illicit materials in containers involves manual unloading of the cargo and careful screening of each item by manual inspection. Because of limited resources, relatively few containers can be examined in this manner. For example, 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. Only about 20 percent of that cargo passes through overseas ports such as Hong Kong, where U.S. inspectors are being stationed. Although the situation poses a clear and present danger, efforts to contain the problem have proven to be daunting not only for the U.S. but also for countries worldwide.

Current sensor capabilities to detect the presence of substances such as cocaine are fairly limited; in many cases, the best "technology" continues to be trained dogs. Manufactured sensors are often designed for use in specific environments and are capable of identifying 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. There is a need for a field able instrument that can rapidly pre-screen containers and allow customs officers to distinguish between innocent and suspicious cargo. In addition, any detection system developed must be portable to measure systems and humans without compromising on the quality of measurements. In this paper, the development of a solid state integrating acoustic detector with direct column heating electronic nose, called the zNose™ is described. The results of this work demonstrates for the first time that an electronic nose can be used in the field to quantitatively characterize and measure cocaine vapors as well as its volatile by-products, methyl benzoate and ecgonidine esters. Specific details such as repeatability, accuracy and precision are verified using laboratory-simulated experiments. In addition, the application of this device to explosive and nerve gas detection is also being explored.

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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. There is a need for a field able instrument that can rapidly pre-screen containers and allow customs officers to distinguish between innocent and suspicious cargo. A typical cargo container requires approximately 15 man-hours to inspect.

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 illicit or hazardous materials. 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.

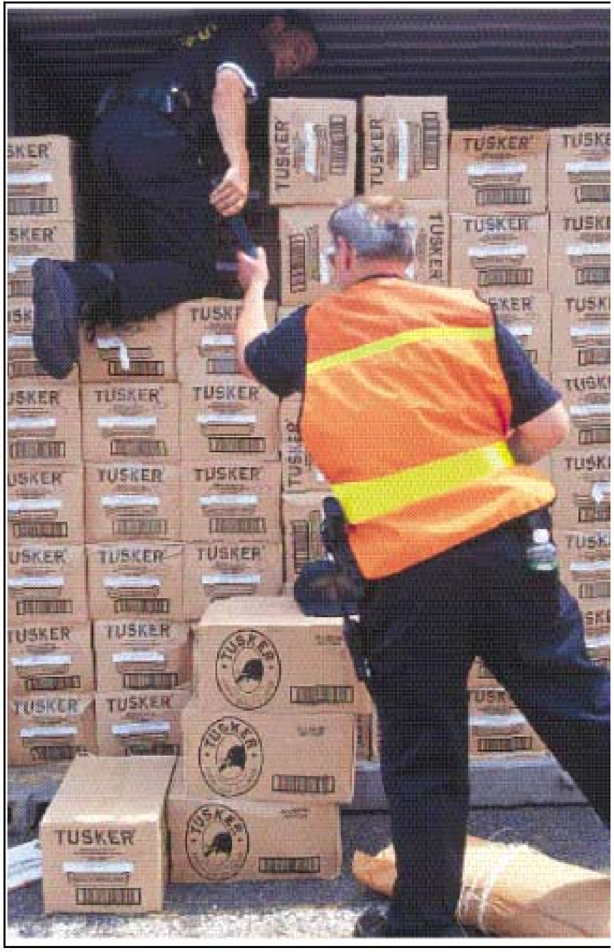


Figure 1- Nearly 15 man-hours are required inspect a single cargo container.

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 drugs of abuse, and even the cargo itself provide 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.

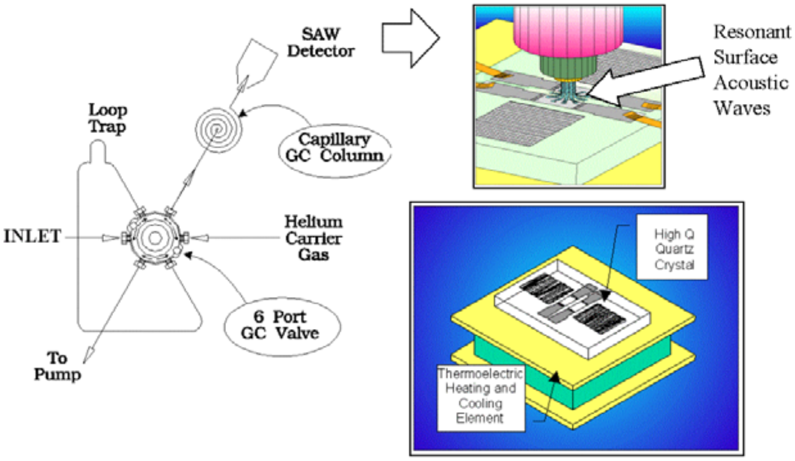


Figure 4- Diagram of high speed GC and details of SAW detector.

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.

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.

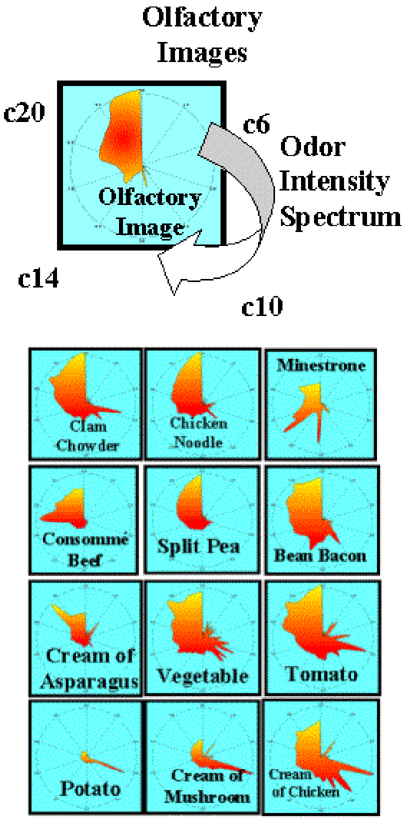
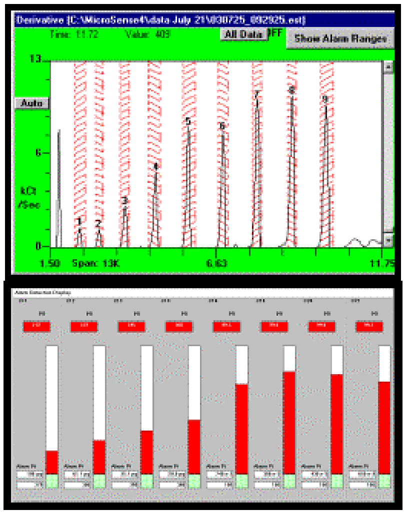
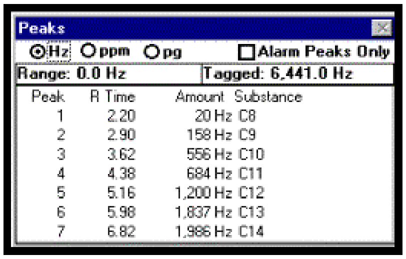


Figure 5- VaporPrint™ olfactory images


Derivative [C:\MicroSense4\data July 21\030725_092925.est]

Sensor Calibration


Peaks

● Hz ○ ppm ○ pg ☐ Alarm Peaks Only

Range: 0.0 Hz | Tagged: 6,441.0 Hz

Peak	R Time	Amount	Substance
1	2.20	20 Hz	C8
2	2.90	158 Hz	C9
3	3.62	556 Hz	C10
4	4.38	684 Hz	C11
5	5.16	1,200 Hz	C12
6	5.98	1,837 Hz	C13
7	6.82	1,986 Hz	C14

Figure 6- Virtual Chemical Sensor Arrays

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.

Profiling of Cargo Container Odors

Odors From Cocaine

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 are much more difficult because their vapor pressure is extremely low. However due to the chemical process by which cocaine is produced it is often found that there are many impurities as well as natural decomposition products, which can be quite volatile and provide a biomarker for the presence of this drug. The following compounds have been identified[1] in unadulterated illicitly produced cocaine: ecgonine, ecgonine methyl ester, benzoylecgonine, *trans*-methyl cinnamate, *cis*-methyl cinnamate, ecgonidine (anhydroecgonine) methyl ester, methyl benzoate, benzoic acid, acetone, ether, ethanol, and water.

The chemical odor signature of cocaine in a cargo container was tested using approximately 100 kilograms of cocaine placed on a table in the middle of the container as shown in Figure 7. Cocaine itself produced little or no detectable vapors at ambient temperatures and significant vapor concentrations could only be detected when the temperature of the container was above 50^{o}C or when air was blown into the container so as to create a suspension of particles containing cocaine.

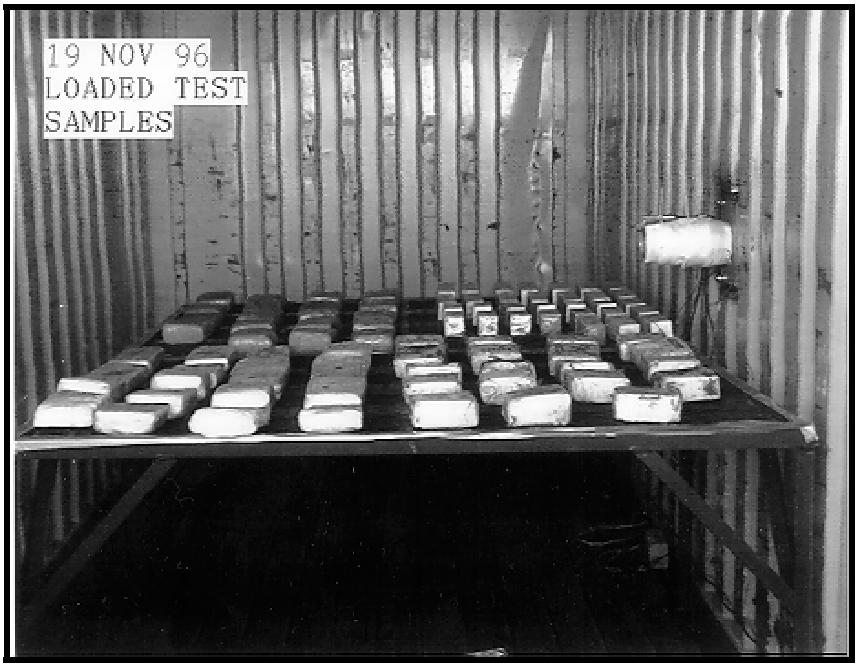


Figure 7- Cargo container loaded with 1 kilogram packages of cocaine.

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[1] T. Lukaszewski and W. K. Jeffery, "Impurities and artifacts of illicit cocaine", Journal of Forensic Sciences , vol. 25, No. 3 (1980), pp. 499-507.

When particles of cocaine were present in the air the chemical odor signature was as shown in Figure 8. Cocaine is the dominant peak with a Kovats index of 2202.

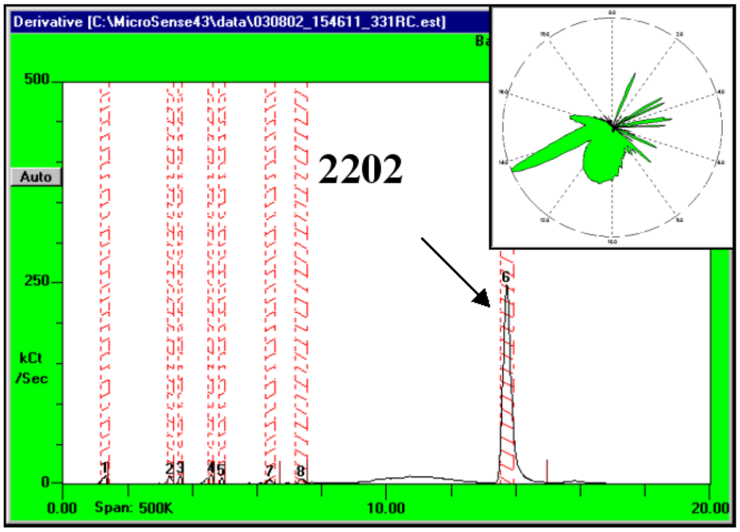


Figure 8- Chemical odor signature when particles of cocaine were present in the air.

Without disturbing the air within the container and allowing vapors to reach equilibrium it was found that there was a pronounced odor consisting of five volatile compounds as shown in Figure 9. Peak number 4, identified as methyl benzoate (Kovats index = 1124) is a natural decomposition by product of cocaine and is sometimes called doggy cocaine because it is used to train canines to detect cocaine.

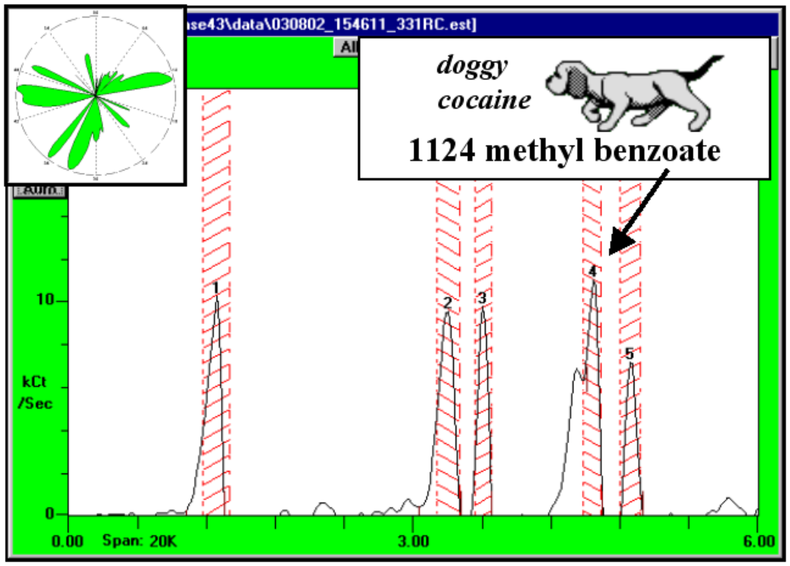
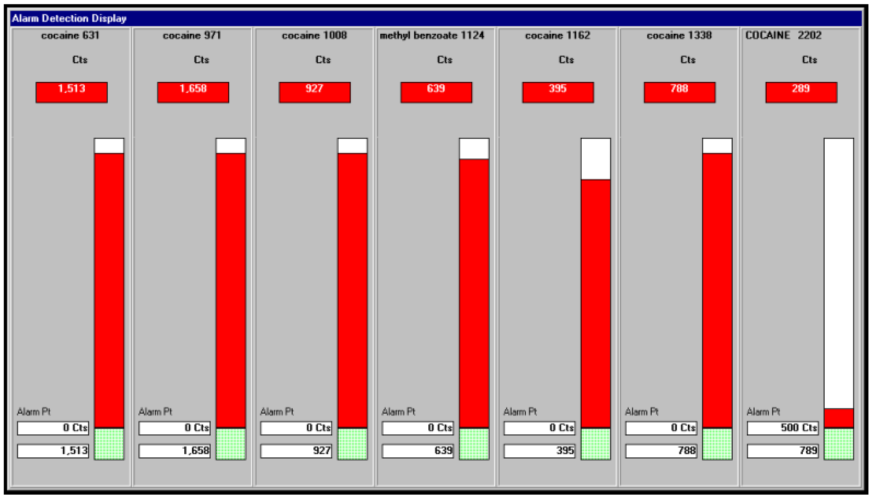


Figure 9- Volatile compounds from cocaine produced a distinct and recognizable chemical signature.

The chemical signature from cocaine vapors was found to contain approximately 7 distinctive chemicals and that these could be used as biomarkers for the presence of cocaine. A virtual sensor array was created based upon the Kovats indices of these compounds. The target indices were 631, 971, 1008, 1124, 1162, 1338, and 2202 (cocaine). A typical sensor array response when cocaine was present is shown in Figure 10. Although the cocaine sensor response is very low the other sensors corresponding to the more volatile compounds give a clear response, which indicates the presence of this illicit drug.



	cocaine 631	cocaine 971	cocaine 1008	methyl benzoate 1124	cocaine 1162	cocaine 1338	COCAINE 2202
Cts	1,513	1,658	927	639	395	788	289
Alarm Pt	0 Cts	0 Cts	0 Cts	0 Cts	0 Cts	0 Cts	500 Cts
	1,513	1,658	927	639	395	788	789

Figure 10- Virtual sensor array for detecting volatile chemicals from cocaine.

Odors From Marijuana

Marijuana is an illicit drug, which produces a very distinctive odor, and the GC/SAW sensor response to this odor is shown in Figure 11. The sensor response can be used to produce a visual olfactory image which is easily recognized by human operators.

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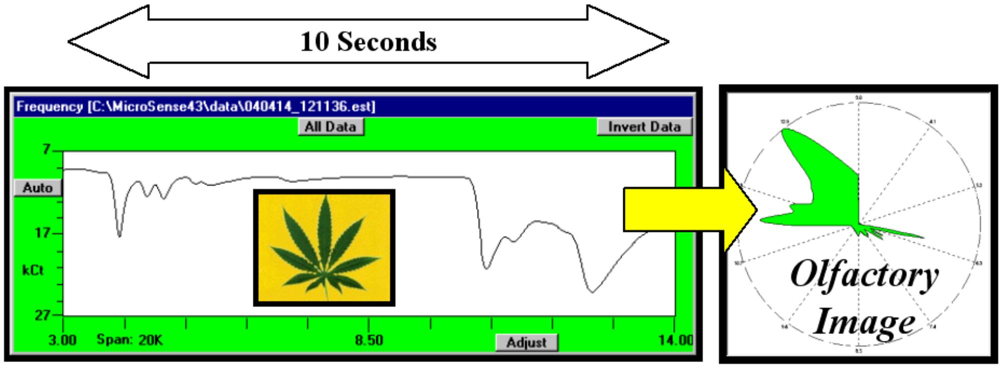
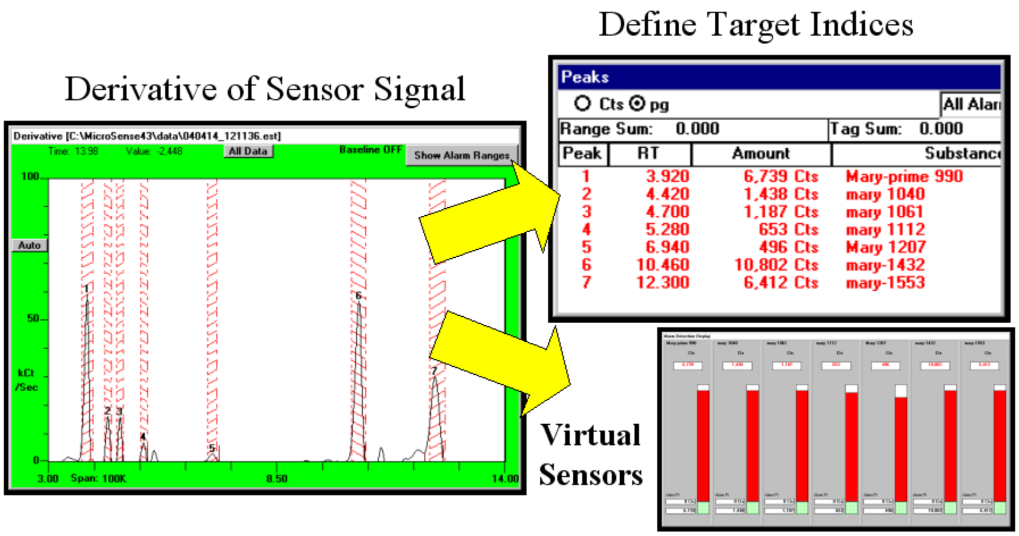


Figure 11- GC/SAW sensor response to chemicals in odors produced by marijuana.

The derivative of sensor frequency produces a chromatogram response, shown in Figure 12, clearly showing 7 major volatile compounds. The retention time of these compounds when expressed as Kovats indices can be used to define a virtual sensor array specific to the odor of marijuana. The target indices for marijuana are 990, 1040, 1061, 1112, 1207, 1432, and 1553.



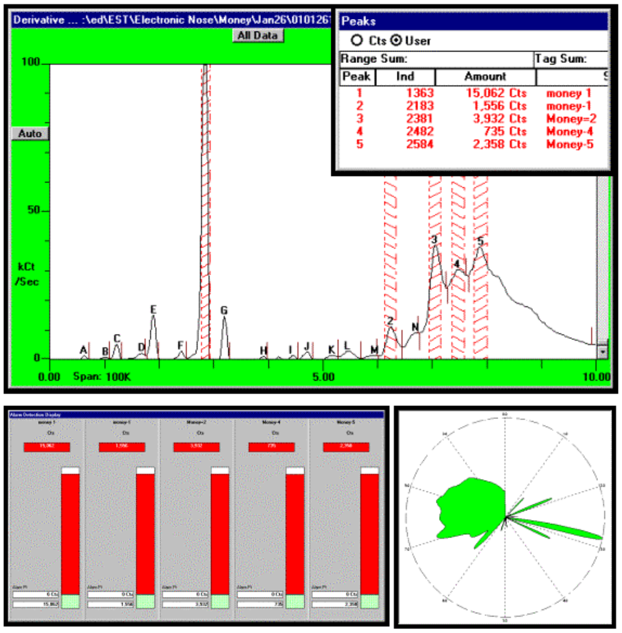
○ Cts ● pg

Range Sum: 0.000 | Tag Sum: 0.000

Peak	RT	Amount	Substanc
1	3.920	6,739 Cts	Mary-prime 990
2	4.420	1,438 Cts	mary 1040
3	4.700	1,187 Cts	mary 1061
4	5.280	653 Cts	mary 1112
5	6.940	496 Cts	Mary 1207
6	10.460	10,802 Cts	mary-1432
7	12.300	6,412 Cts	mary-1553

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 12. Using chemical odor profiling and fie virtual chemical sensors, the presence of currency can be readily identified.



○ Cts ● User

Range Sum: | Tag Sum:

Peak	Ind	Amount	
1	1363	15,062 Cts	money 1
2	2183	1,556 Cts	money-1
3	2381	3,932 Cts	Money=2
4	2482	735 Cts	Money-4
5	2584	2,358 Cts	Money-5

Figure 12- Chemical signature of money is easily recognized using virtual chemical sensors.

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 contraband drugs of abuse, currency, hazardous chemicals and explosives, and even biological life forms as well. 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

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 are 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 security. Adaptive virtual sensor arrays have the potential to identify suspicious cargo and also to thwart terrorist activities. 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 might be capable of detecting deviations from normal conditions and monitoring for chemical and biological agents.