Analysis of Odors from Explosives using an Electronic Nose

Edward J. Staples, Electronic Sensor Technology

Electronic Noses and Bomb Detectors

Conventional bomb detectors are designed to respond to only energetic materials , e.g. nitrates, and not to detect other background chemicals in odors. Conversely electronic noses are designed to respond to all chemicals within an odor. Based upon this distinction electronic noses might not be considered good bomb detectors where there are strong background odors. On the other hand bomb detectors might not be very good electronic noses because they are blind to many important environmental and olfactory chemicals. However, the diversity of today's terrorist threats (explosive, chemical, and biological) makes it increasingly apparent that there is a role for electronic noses with the ability to quickly learn and recognize threat vapors of any kind.

Sensitivity is not the issue since electronic noses like the zNose® and bomb detectors like ion-mobility spectrometers (IonTrack IMS) have essentially equal speed and sensitivity to explosive compounds. Specificity is the issue and users should understand the different role each type of instrument can undertake as part of an integrated security, force protection, or general law enforcement screening or investigative mission.

New Analytical Tool for Odor Measurements, the zNose®

A new type of ultra-fast gas chromatograph, the zNose® is able to perform analytical measurements of volatile organic vapors and odors in near real time with part per trillion sensitivity. Because of its picogram sensitivity it is a useful tool for detecting energetic materials (explosives) involving volatile organics of all kinds. The zNose® separates and quantifies the organic chemistry of odors through ultra-high speed chromatography in 10 seconds. Using a patented solid-state mass-sensitive detector, picogram sensitivity, universal non-polar selectivity, and electronically variable sensitivity has been achieved. An integrated vapor preconcentrator coupled with the electronically variable detector, allow the instrument to measure vapor concentrations spanning 6+ orders of magnitude. A portable zNose®, shown in Figure 1, is a useful tool for onsite odor and ambient air measurements.

How the zNose® Quantifies the Chemistry of an Odor

A simplified diagram of the zNose® system shown in Figure 2 consists of two parts. One section uses helium gas, a capillary tube (GC column) and a solid state detector. The other section consists of a heated inlet and pump which draws ambient air into the instrument. Linking the two sections is a "loop" trap which acts as a preconcentrator when placed in the air section (sample position) and as an injector when placed in the helium section (inject position). Operation is a two step process. Ambient air (odor) is first sampled and organic vapors collected (preconcentrated) on the trap. After sampling the trap is switched to the helium section where the collected organic compounds

Figure 1- zNose® technology incorporated into 3 commercial instruments.

are injected into the helium flow. The organic compounds pass through a GC column with different velocities and exit the column at characteristic times. As they exit the column they are detected and quantified by a solid state detector.
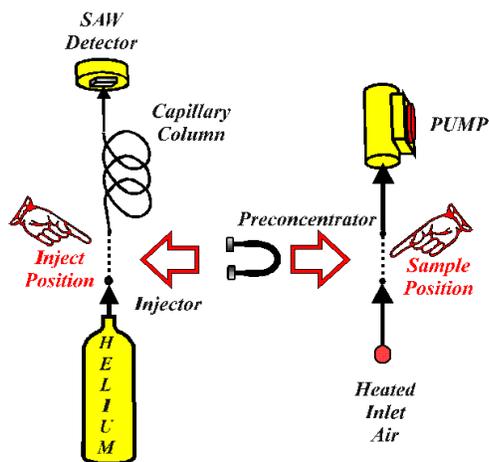

Figure 2- Simplified diagram of the zNose® showing an air section on the right and a helium section on the left. A loop trap preconcentrates organics from ambient air in the sample position and injects them into the helium section when in the inject positron.

A high speed gate array processor controls the processing of odor samples and includes electronic flow control, timing, electronic injection, and temperature control for the column, inlet, detector, and other parts of the instrument.   The user interface can be a laptop computer or any remote computer using a wireless modem (1 mile range). A software program allows users to select appropriate measurement methods and to identify specific energetic compounds found in explosives from a library of Kovats indices.

Energetic Compounds

The chemistry of explosives involve what are called energetic compounds because they readily decompose with shock or high temperature. Some important characteristics of six common energetic compounds found in explosives are listed in Table I.

Table 1- Common Energetic Compounds found in Explosives

Explosive	CAS No.	Formula	Molecular Weight	density	vapor pressure	Decompose
NG	55-63-0	C3H5N3O9	227.0872	1.6	4×10^{-3}	120°C
DNT	121-14-2	C7H6N2O4	182.1354	1.521	1.47×10^{-4}	300°C
TNT	118-96-7	C7H5N3O6	227.133	1.654	5.5×10^{-6}	240°C
PETN	78-11-5	C5H8N4O12	316.1378	1.77	1.2×10^{-8}	141°C
RDX	121-82-4	C3H6H6O6	222.117	1.82	4.1×10^{-9}	170°C
Tetryl	479-45-8	C7H5N5O6	287.1452	1.73	4×10^{-10}	220°C

The molecular structures of the six compounds are shown in Figure 3.   Structures can be open or closed (aromatic) and molecular weights are typically above 200. For detection purposes perhaps the most important characteristics are the vapor pressure and decomposition temperature. Low vapor pressure compounds tend to adhere to cool surfaces and require careful control of instrument temperatures. However, if temperatures are too high compounds like NG and PETN will decompose before they can be detected.
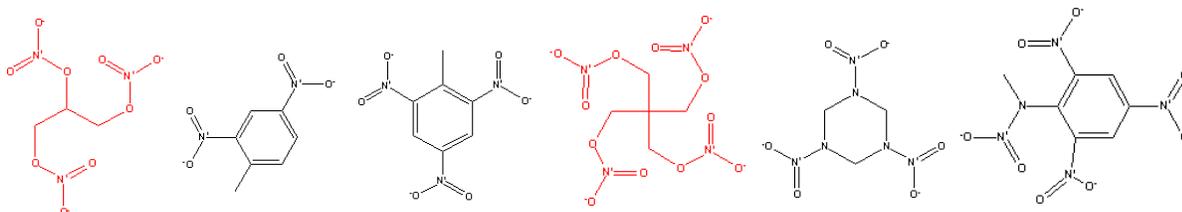

Figure 3- Molecular structure of nitroglycerine (NG), dinitrotoulene (DNT), trinitrotoluene (TNT), Pentaeryth-ritoltetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), and trinitrophenyl-n-methylnitramine (Tetryl). Open structures (shown in red) are more likely to decompose compared with closed aromatic ring structures.

The lower vapor pressure of these compounds means there concentration in ambient air will also be low. If explosives are contained in an enclosure with cool surfaces the vapor concentration may be even lower than saturated values due to partitioning effects. The saturated equilibrium ambient air concentration of TNT, RDX, and PETN as a function of ambient temperature is shown in Figure 4.   At room temperature there are approximately 100 picograms of TNT per milliliter available for detection. NG and DNT have even higher concentrations available for detection. However, PETN and RDX produce less than 1 picogram per milliliter and hence are much more difficult to detect as vapors.   For these compounds it is easier to use a wipe to extract material from surfaces and then to thermally desorb the compounds as vapors into the detection system.
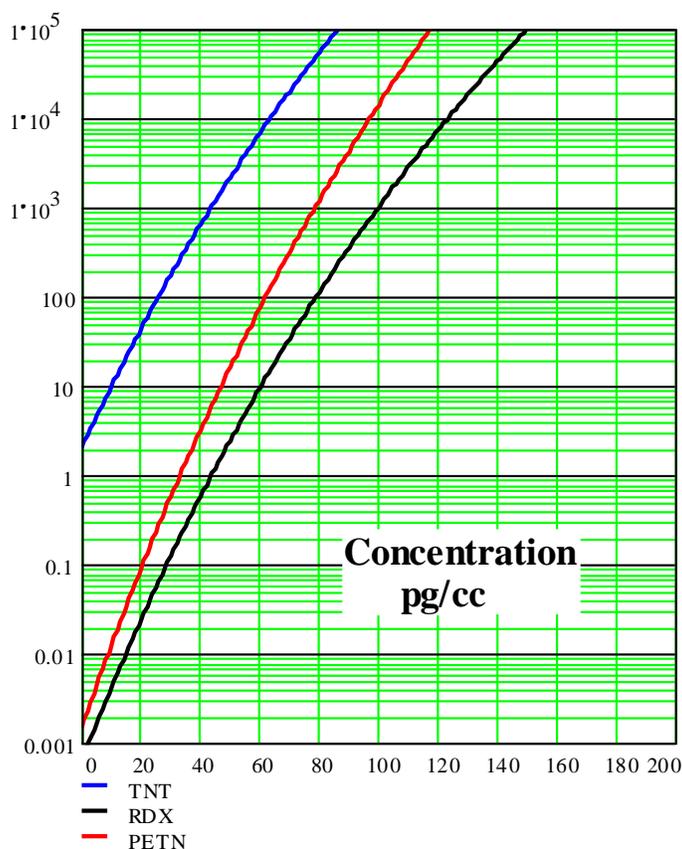
Figure 4- Using the Antoine equation the equilibrium vapor concentration of energetic materials can be plotted as a function of ambient temperature.

N-Alkane Odor Standards

An odor standard of n-alkanes is used to calibrate not only sensitivity of the electronic nose but also it's specificity. Specificity is what allows the instrument to recognize known chemicals and/or chemical groups (odor signatures) and to deliver the appropriate alarms.   The zNose® is an ultra-fast GC which separates and measures the concentration of the individual chemicals of an odor directly, typically in 10 seconds. Individual chemicals are recognized by their retention time relative to the retention times of linear chain alkanes. Tabulating the retention times and detector counts (cts) provides a quantitative measure of an odor's chemistry.

To calibrate the instrument requires only that a known amount of each alkane be introduced into the instrument. For alkane numbers above 14 (and explosive compounds) this is best done by the three step process depicted in Figure 5. A glass tube is attached to the inlet and a known amount of alkanes dissolved in methanol are injected. A short drying (step 2) removes the volatile solvent vapors but leaves the semi-volatile alkanes (or explosives) attached to the walls of the tube. The final step is to heat the tube to vaporize the semi-volatiles and then collect them in the preconcentrator trap of the zNose®.
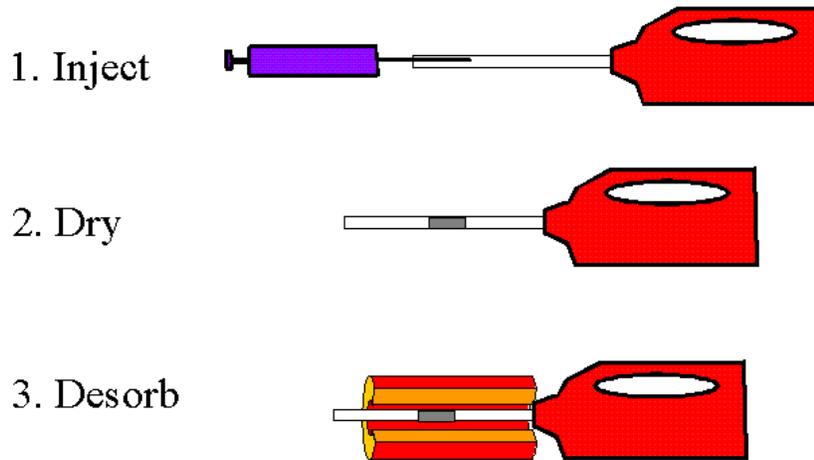
Figure 5- Three step calibration process for semi-volatiles and explosives using the zNose®.

The retention time of chromatogram peaks are referenced then indexed to the retention time of a standard vapor mixture of linear chain n-alkanes.   Shown in Figure 6 is the standard vapor response obtained using a calibration vapor containing C11 through C22 alkanes as well as DNT and TNT. Retention times are expressed as indices relative to the n-alkane peaks. DNT has an index of 1537 (between C15 and C16) and TNT has an index of 1707 (slightly above C17) in this chromatogram.
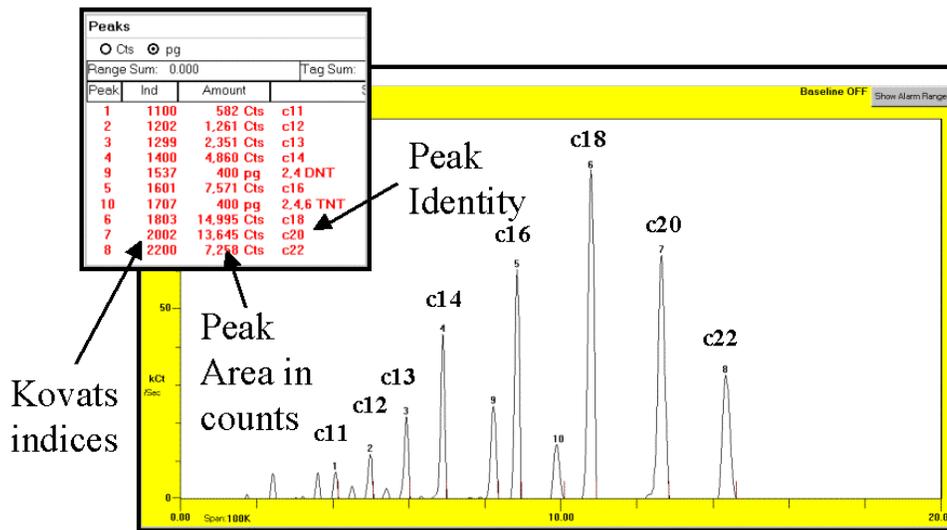

Figure 6- Retention time calibration using n-alkane response C11 to C22. Peak retention times are listed as Kovates indices and concentration in counts except for where response factors are known.

Kovats Indices of Common Explosives

The retention times and Kovats indices of energetic compounds were obtained by direct desorbtion with a methanol solution containing known concentrations and measuring the resulting odor chemistry with a zNose® as shown in Figure 7.   The Kovats indices for each of the 6 common explosives are tabulated in Table 2.
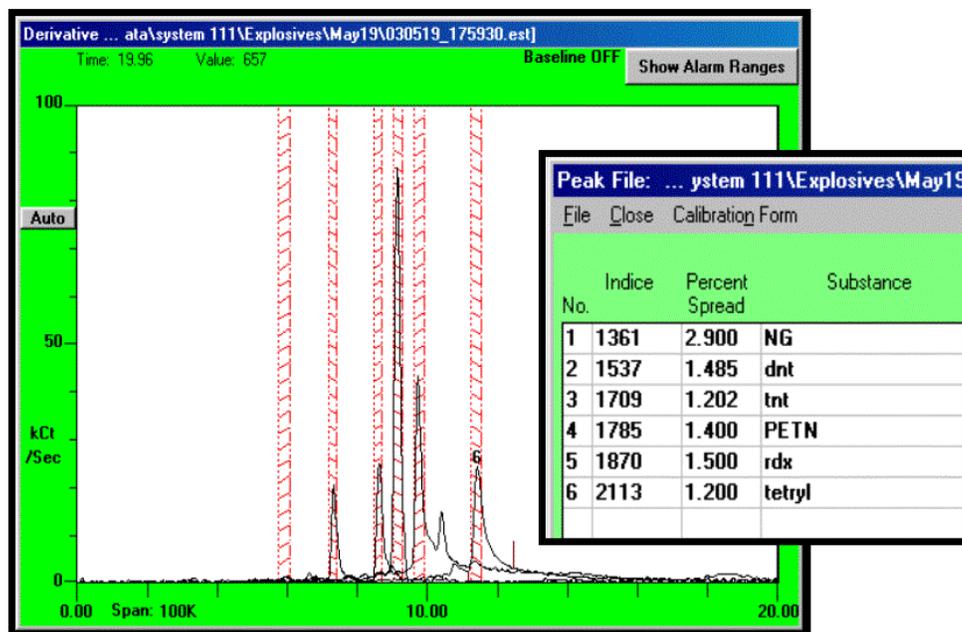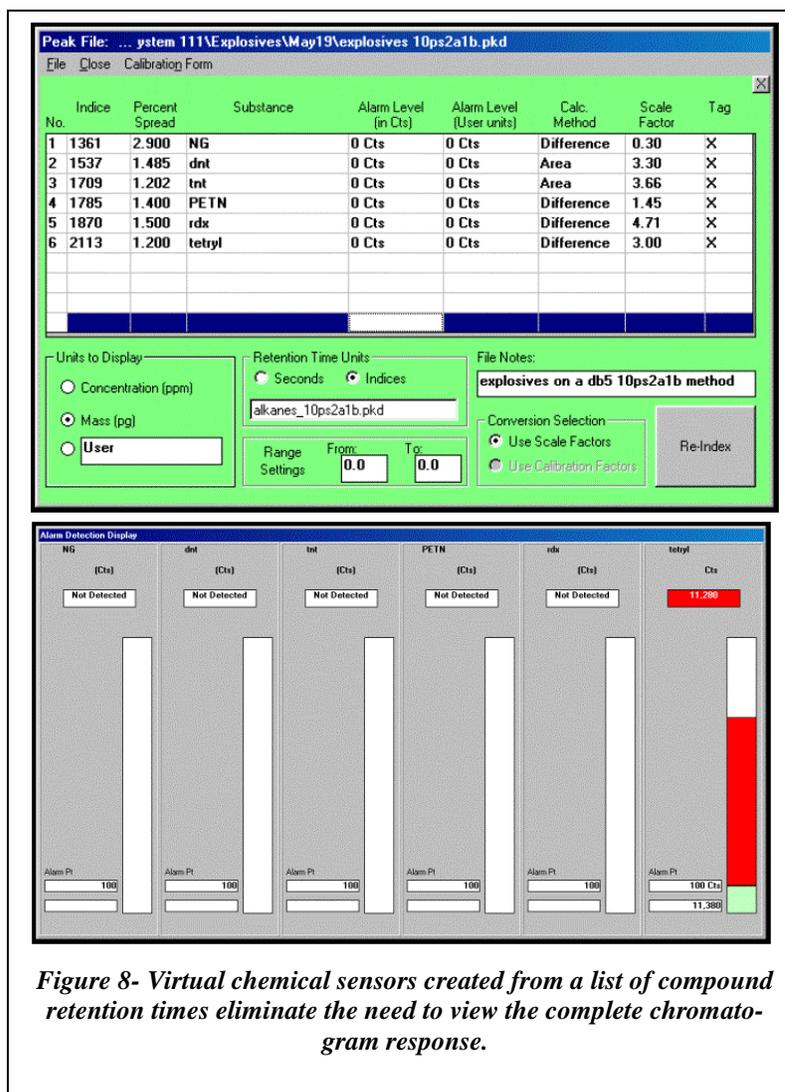

Figure 7- The retention time of a mixture containing common explosives like NG, DNT, TNT, PETN, RDX, and Tetryl were measured and compared to the retention time of N-alkane standard vapors. Peak identification windows are shown as red cross-hatched regions.

Table 2- Kovats Indices of Common Energetic Compounds

Explosive	CAS No.	Formula	Kovats Indices
NG	55-63-0	$C_3H_5N_3O_9$	1356
DNT	121-14-2	$C_7H_6N_2O_4$	1537
TNT	118-96-7	$C_7H_5N_3O_6$	1704
PETN	78-11-5	$C_5H_8N_4O_{12}$	1791
RDX	121-82-4	$C_3H_6H_6O_6$	1870
Tetryl	479-45-8	$C_7H_5N_5O_6$	2100

Virtual Chemical Sensors with Alarms

These indices, tabulated in Table 2, provide the basis for creating alarms or virtual sensors for each of the compounds. Because the retention times are relative to N-alkane vapors they are machine independent and only require knowledge of the N-alkane retention times to create a library of explosives which applies to all zNose® instruments.

Figure 8- Virtual chemical sensors created from a list of compound retention times eliminate the need to view the complete chromatogram response.

Tabulated data listings as shown in Figure 8 are used to define retention times by index rather than retention time in seconds. Response factors of each sensor and alarm window width are also defined. Thus defined, chromatographic measurements are reduced to a simple user display of six virtual sensors for the common explosive compounds together with their individual alarm levels.

Odor Chemical Libraries

Computer processing of olfactory images quantifies the individual chemicals and allows the aggregate odor response to be recognized relative to a known odor standard e.g. n-alkanes. The Kovats Indices for known chemicals are stored in a library together with their odor description or perception. When an unknown odor is analyzed the reten-
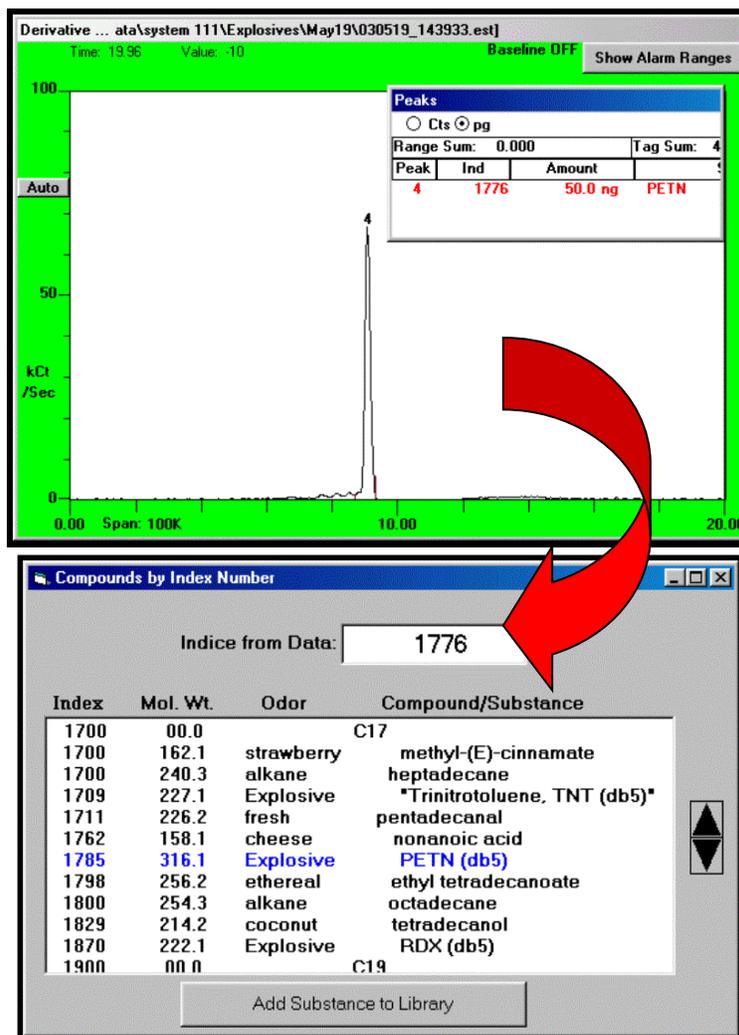

Figure 9- Software showing chromatogram response and library identification using Kovats Indices for individual peaks.

tion time of peaks are converted to Kovats indices and clicking on individual peaks with a mouse pointer brings up the nearest library entry. The lookup process is illustrated in Figure 9 using the PETN 'peak' which has an index of 1776.

Odors from Real World Explosives

Two common explosive materials are Primacord and Detasheet. PETN is the explosive core of Primacord, where it develops a velocity rate of 21,000 feet per second . Detonating cord is insensitive to friction and ordinary shock, but may be exploded by rifle fire. It also detonates sympathetically with the detonation of an adjacent high explosive. Odors from Primacord thermostated at 80° C were tested and the organic compounds detected confirm the presence of only PETN as shown in Figure 10.
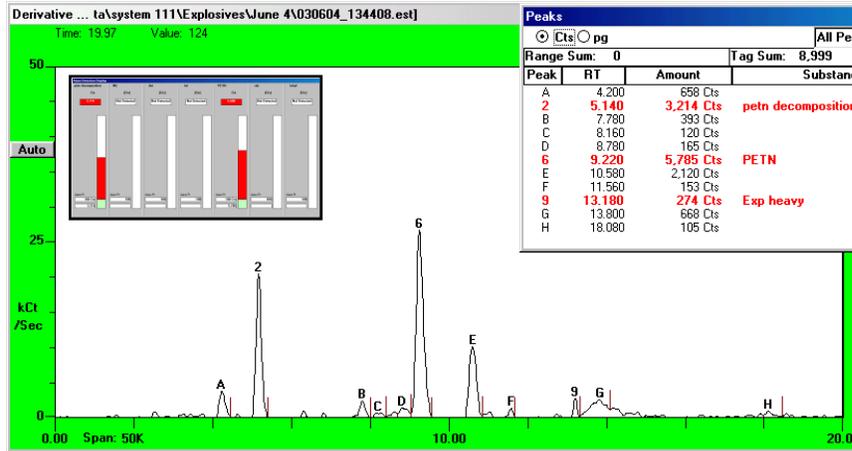

Figure 10- Volatile organics in vapors from Detcord

Detasheet is a molded and flexible explosive consisting of RDX, PETN and plasticizing wax. Volatile organics vapors from Detasheet confirmed the presence of both as shown in Figure 11. RDX is usually used in mixtures with other explosives, oils, or waxes; it is rarely used alone. It has a high degree of stability in storage and is considered the most powerful and brisant of the military high explosives. Incorporated with other explosives or inert material, RDX forms the base for many common military explosives.
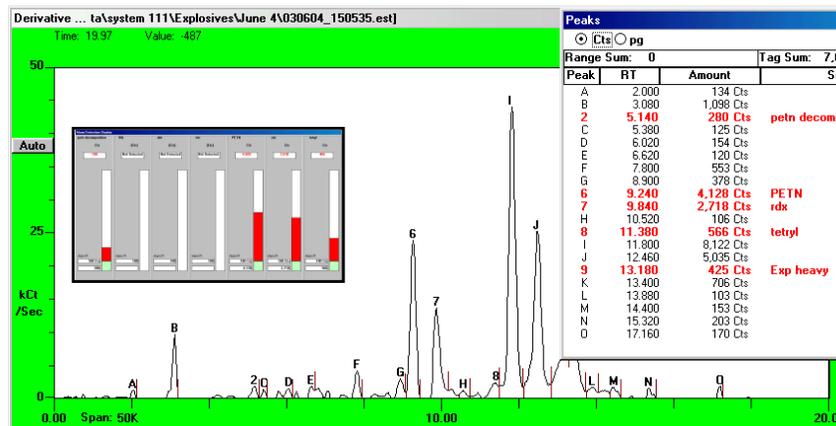

Figure 11-Volatile organics in vapors from DetaSheet

C4 is another well known explosive consisting of RDX, other explosives, and plasticizers. It can be molded by hand for use in demolition work and packed by hand into shaped charge devices. The odor of C4 explosive, shown in Figure 9, contains of RDX, PETN, TNT, Tetryl and plasticizing wax.   Even at room temperature RDX has a distinct odor consisting mainly of just one compound with an index of 1020.
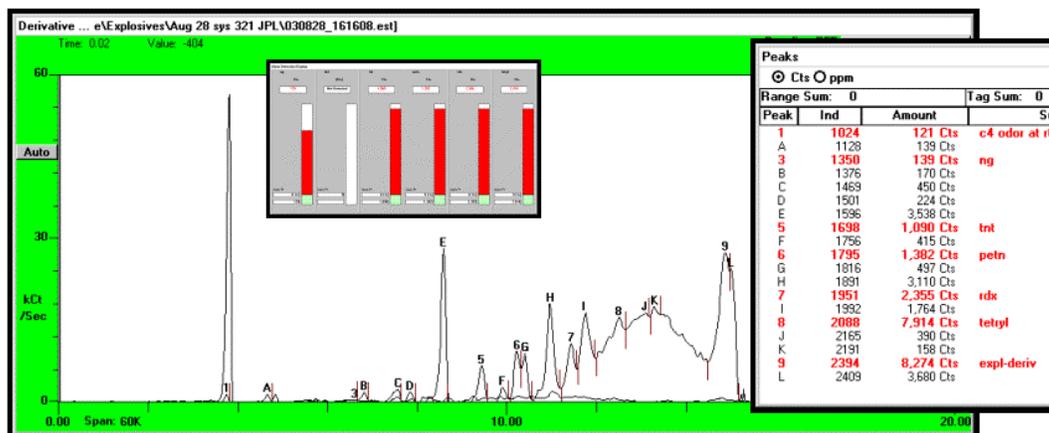

Figure 12- Chromatogram of odors from C4 showing tnt, petn, rdx, and other organic plasticizers.

Summary of Results

A new type of electronic nose based upon ultra high-speed gas chromatography and a new solid state GC detector now allows the chemistry of odors to be qluantified in near real time with high precision, accuracy, and part per trillion sensitivity. Odors from explosives were characterized and compared using chromatograms to create virtual chemical sensors for six common energetic compounds.   The sensitivity of the instrument allowed compound concentrations at part per trillion (picogram/milliliter) levels to be made.   Identification of explosive compounds is greatly simplified by indexing retention time to a single N-alkane odor standard. A library of indices also allows unknown odors to be quickly analyzed and compared to known odor signatures.

Because the electronic nose is based upon the science of gas chromatography, odor measurements can be easily confirmed and validated by independent laboratory measurements taken on quality control samples.   The ability to rapidly perform analytical measurements on odors of all kinds in real time provides first responders with a cost effective new tool for monitoring volatile organic compounds associated with explosive, chemical, or biological threats.