

## Appendix C

# Vapor Detection Systems

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### *Gas Chromatography With Chemiluminescence*

**Sponsor:** Federal Aviation Administration (FAA) Technical Center; Department of State; both supporting contracts with Thermedics, Inc.

**Status:** Hand-held unit is in production for U.S. Department of State and other buyers. Prototype for "walk-in" style of detector for airport concourse security is being built for FAA but is not yet formally tested.

**Funding:** Approximately \$7 million from the Department of State since 1985 and approximately \$5 million from the FAA since 1984, plus some private funding (\$6 million) from Thermo Electron Corp., the parent of Thermedics.

#### Basic Operating Principle and Goals of Concept

These devices use gas chromatography, a fully mature technology, to separate a sample of molecules from a carrier gas and to isolate molecules of different chemical compounds from each other. The sample is taken with a portable hand-held collection unit that heats up the sampled surface with infrared lamps and sucks air from near the surface.<sup>1</sup> Heating is important, since vapor pressure increases by a factor of 10 for every increase of 10 °C.

The sample is then injected into chromatographic columns, which consist of thin tubes lined with a material that absorbs or dissolves the molecules of interest, thereby retarding their passage through the column. Different molecules are slowed to different degrees. The material with the least affinity for the column substrate will go through fastest and those with increasing affinity will traverse the column in longer times. Residence time within the column can be adjusted by varying such factors as column length and temperature. Furthermore, since different materials are released from the column at different times, this technique allows mixtures of material to be resolved. With proper calibration, the residence time of a given type of molecule within a given column is predictable and can be used to identify the molecule.

At the termination of the separation process, column contents are heated to pyrolyze the explosive compounds into fragments, among them nitric oxide (NO). The

chemiluminescent reaction of nitric oxide with ozone (O<sub>3</sub>) is well known<sup>2</sup> and yields photons that can be detected by conventional means<sup>3</sup>. This signal is analyzed by a microprocessor to determine if it meets predetermined criteria for alarm. The timing of photon detection can be used to identify those explosive compounds present, since each compound has a characteristic speed of migration through the column.

While this strategy relies on familiar instruments and well-known chemical reactions, it is by no means an insignificant task to perfect the operational parameters so that minute quantities of material can be successfully and reliably recognized within a few seconds. Through a proprietary combination of column lengths and temperature cycles, the manufacturer of this device, Thermedics Inc. of Woburn, MA, claims to be able to detect plastic explosives rapidly. Independent tests have also shown that the device has this capability. The company also ran tests that appear to show that their walk-in booth, based on the same technology, responds to plastic explosives hidden under one layer of clothing.

#### Technical Description

The only difference between the hand-held and walk-in models is the sample collection step. In the walk-in device, an individual to be tested stands in a booth where air is vigorously blowing. The velocity of the air is sufficient to cause at least the outer layer of clothing to be agitated. Simultaneously, the subject's skin and clothing are warmed by infrared heaters. This facilitates the escape of any target molecules. The air currents are collected through a series of funnels positioned in a vertical array in the back of the booth.

The hand-held device consists of two units: a testing unit and a collector. The testing unit is about the size of a 55-gallon drum and contains the chromatographic columns, chemiluminescent reaction chamber, and all the display instrumentation. The collector, which is about the size of a large hand-held vacuum cleaner, contains a suction device and is adapted to be placed against or near an object to be tested. The head of the collector unit includes a heat source and appropriate ducting to direct the resulting air stream onto a preconcentrator. This unit consists of a high surface area substrate made of a material onto which active molecules (which would include any explosives) in the air stream attach themselves while inert materials are blown past. At appropriate intervals, mole-

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<sup>1</sup>The walk-in portal unit samples quite differently and is discussed separately. Except for the sampling, the two units are essentially the same.

<sup>2</sup>P.N. Clough and B.A. Thrush, "Mechanism of Chemiluminescent Reaction Between Nitric Oxide and Ozone," *Trans. Faraday Soc.*, 63,915 (1967).

<sup>3</sup>See U.S. Patent No. 3,763,877 issued Oct. 9, 1973 entitled "Fluid Flow Control System."

cules are released by warming the preconcentrating device. For the hand-held device, this operation is performed after the device has been clamped into the testing unit.

The expelled gases pass through a series of chromatographic columns specially designed to facilitate separation of the target molecules from the carrier gas and from each other. The chemiluminescent reaction is performed on the columns' effluents. Lights on the operator's panel indicate which, if any, explosive has been sensed. A more informative display is also available in the form of a video monitor, which shows the chromatogram (a chart on which the time of arrival for each compound appears as a peak) as well as a hard copy from a thermal printer.

### Potential and Shortcomings

Opinions on the merits of this device vary considerably with the customer. This device is one of the few sniffers on the market that claims to be able to detect pure plastic explosives. In a maintenance-plagued test of a prototype device conducted on real luggage in February 1989, the FAA reported that the hand-held system did not perform well.<sup>4</sup> However, more recent tests, both in the United States and abroad, including some in an airport environment, have produced far better results. Further FAA testing has been done, but the results have not yet been released.

The experience of the State Department has been far more positive. The State Department was interested in a different set of criteria than was the FAA. High throughput was not as important in the State Department's application as it is in an airport environment. State was also willing to accept a higher percentage of false positives because the inconveniences associated with such readings were less serious for their purposes. They wanted a device that could be easily operated by technically unsophisticated foreign nationals. For these reasons they were attracted to the Thermedics products. Tests conducted for the State Department showed certain maintenance problems (apparently resolved now) but confirmed the sensitivity of the device to plastic explosives and concluded that the device had promise. One foreign country, investigating this device for purposes and using methods not originally envisioned by the manufacturer, has reported very favorably on its performance. In December of 1989, they were given the use of a Thermedics machine for a few weeks and they proceeded to try it out in every possible environment: airports,

harbors, border crossings, and post-blast forensic work. They were impressed with the machine's ability (unique, in their opinion, among the "sniffers" they had tested) to respond accurately to the plastic explosives. They found the machine insufficiently rugged, in its current state of engineering, and too slow to operate effectively in a high throughput situation such as the baggage area of an airport. However, significant improvements have recently been achieved and field testing within the past year has shown far superior performance with respect to maintenance and operation. The ability of this device to identify an explosive was superior to that of other analytical techniques now used. Several other countries have also tested this device, and a number of foreign sales have been made, some for airport use.

The hand-held device is in commercial production and sells for about \$150,000 (including an extra chemistry module) under the tradename EGIS II.

The device operates remarkably quickly for a gas chromatography. The gas traverses the chromatographic column very quickly and subsequent signal analysis can be completed in about 30 seconds. Some customers find this speed acceptable, but current performance of the walk-in booth (due to slow sample collection time) would not meet FAA concourse throughput requirements unless several units were operated in parallel, or a completely independent prescreening technique were used, or unless several individuals were scanned at the same time. Because it is capable of identifying which explosive compound has been detected, this system is very useful for post-blast forensic investigations. Some tests have also shown an increased effectiveness using the wipe-down technique: wiping a suspect object or person with a paper cloth, and then sampling the cloth.

Information on the current sensitivity of this device to interferants and false alarms was not available, although tests on earlier units found false alarms due to local contamination to be a problem. The manufacturer asserts that the current production devices have very low susceptibility to interferants. Another problem might be that the chemiluminescent reaction is reported to be not particularly sensitive. However, the sampling and collection of these machines is very efficient. Furthermore, the technique is quite selective relative to other vapor detection techniques, allowing the detector to operate at sensitivities that appear to be competitive with these other methods.

<sup>4</sup>The manufacturer claims that this test is not representative of the performance of this device and that the current model performs better. Further, some problems were claimed, also by the manufacturer, to be due to cross-contamination in the FAA's laboratory rather than to the machine's performance.

## Gas Chromatography With Electron Capture Detector (GC/ECD)

**Sponsor:** FAA  
U.S. Navy  
Canadian Government (for development work by Canadian firms)

**Status:** Workable machines are in production by several manufacturers; R&D is being done to improve selectivity and trapping, to expand the range of explosives to which the device is sensitive, and to develop improved walk-through device.

**Funding:** About \$1 million over the last 3 years.

### Basic Operating Principles and Goals of Concept

This equipment tests for low volatility, high electronegativity substances. Like the chemiluminescence device described above, these machines also make use of a chromatographic column as a first step to physically separate explosive molecules from other components of a gas stream. The detector, however, is quite different. A small radioactive source ionizes a gas mixture to form free electrons that flow towards an anode, thereby creating a constant current. Molecules emerging from the column are mixed with these electrons. Being quite electronegative, the explosive molecules will “grab” some of the electrons. Fewer electrons will then be available to flow towards the anode, and this effect is sensed as a decrease in the current. Microprocessors analyze this change to determine if it meets predetermined criteria for an alarm.

Several configurations of this detection strategy are commercially available and have found wide use throughout the world.

### Technical Description

In a typical electron capture device—for instance, the Ion Track Instruments Model 97—an air sample is aspirated into the detector and impinges on a membrane. Air and many contaminants (most critically, oxygen, halogens, and water vapor, which would foul up the detector downstream) are thereby separated from the molecules of interest, which diffuse across the membrane into a stream of argon gas. This stream is then directed into a pair of chromatographic columns. This device, however, uses two parallel GC columns, one coated with a chromatographic substrate known to retard polar (electronegative) materials such as explosives compounds and the other coated with a nonpolar substrate.

In the electron capture detector, the effluent from each of the chromatographic columns—which contains argon gas—is piped into one of a pair of detectors where it is irradiated with beta particles from a small radioactive source to yield a plasma containing  $\text{Ar}^+$  and electrons. The

electrons flow towards an anode, creating a measurable current. If highly electronegative explosive molecules are present, they will combine with some of the electrons to form negative anions, thereby depleting the available stock of electrons. This depletion is manifested as a decrease in current. If there is no change in current, or if a change occurs simultaneously in both detectors, no alarm is sounded. However, if a substance is delayed by the polar chromatographic column, the detector attached to this column will react later than the detector from the nonpolar column. If this delay occurs within a preset time window (typically 10 milliseconds or so) and other signal criteria (that vary with equipment design) are met, an alarm occurs.

Other manufacturers employ variations of this strategy. For example, a wad of adsorbent material maybe used in place of the membrane to separate sample molecules from the air stream. Another variation uses a single GC column attached to a single ECD. A microprocessor decides whether the timing and other characteristics of the signal are indicative of the presence of an explosive. The Canadian firm, Scintrex, is now marketing a dual-column device; one column is designed to respond to the EGDN-based explosives and the other to the NG/DNT group.

These devices are available either as hand-held units or as walk-through models. For example, the hand-held ITT Model 97 has been on the market since 1978 and currently costs about \$15,000. The walk-through version of this device is sold by ITT under the tradename EntryScan for about \$30,000. Other GC/ECD products include the EVD-1 manufactured by Scintrex (selling price for the dual column model, widely acclaimed for its ability to sense EGDN reliably, is about \$45,000) and Scanex Jr. from Sentex Sensing Technology of Ridgefield, NJ.

### Potential and Shortcomings

The commercial models of these devices were among those tested by the FBI in their 1988 experiments. In general, they all sensed the higher vapor pressure compounds but were unable to detect the plastics and other very low volatility materials.

While ITI claims to have detected SEMTEX with their Model 97 device, most observers feel that the device was actually responding to a contaminant (which does not appear to be reliably present in the material) rather than to the explosive itself. ITI asserts that all SEMTEX tested on the detector has shown presence of contaminants, which it states are unavoidable residues from the manufacturing process. Not all experts agree, however. ITI also claims sensitivity to Detasheet (although their detector, like the other units tested by the FBI, failed to respond consistently to this material under field conditions) and, to some degree, to U.S.-manufactured C-4. ITI claims that an

upgraded version has improved detection capability for plastic high explosives.

In the FBI test, vulnerability to interferants varied among the detectors and apparently was related to the fine points of the preconcentration and signal processing subsystems. In the field, maintenance remains a problem. Apparently the need to deal with an inert gas bottle, a characteristic of all ECD devices, has been a problem, as has fouling by airborne particulate matter. The response time of some of these devices can be fairly slow (on the order of minutes) although others, such as the ITI 97, have a response time of less than 2 seconds. Some require a prolonged (i.e., 20 minutes) warm-up time.

Current work is aimed at improving trapping techniques to be used upstream of the ECD. In work performed for the U.S. Navy, ITI has experimented with a batch mode of operation in which the membrane is kept at a low temperature, under which conditions it functions not just as a separator but also as a preconcentrator. Recent tests of this device show promise.

Other experimental work is aimed at developing a so-called rotary trap. This is a constantly rotating, circular plate having a glassy adsorption layer. Sample air is drawn through the plate at one location. At a second location, the plate is heated to release the entrapped molecules. Additional work is being done to improve a walk-through version of this device.

### ***Ion Mobility Spectrometry (IMS)***

*Sponsor:* Technology is commercially available. Some work is being sponsored by the FBI and by the Canadian government.

*Status:* Commercially available under the Graseby trademark; marketed in the United States by Astrophysics Research Corp. of Long Beach, CA (now, EG&G Astrophysics). Similar technology is used in units marketed by Barringer, Inc. of Canada, through its U.S. subsidiary.

*Funding:* About \$100,000 over fiscal years 1989 and 1990.

#### **Basic Operating Principles and Goals of Concept**

Air containing vapor or a stream of airborne particles from an area to be tested is drawn in through a sampling probe. Air and explosive molecules diffuse through a membrane or a filter into a chamber where a sealed  $^{63}\text{Ni}$  radioactive source ionizes the sample. Periodically (about 50 times per second), small bursts of ions are released into a separation region by an electronic gating grid. Under the influence of an electric field, these ions move down a drift tube against the flow of a separation gas. The speed with which these ions move through the tube is a function of their mass, their charge, their physical shape, and the

amount of diffusion (deviation from a straight-line path). Heavier ions, such as those of explosive compounds, tend to travel more slowly than lighter, simpler ones typical of air. The drift region terminates in a collector electrode. Ions reaching this collector will cause a small current peak. The position (in time) and magnitude of this peak are analyzed by a microprocessor in order to determine the identity and concentration of the vapor being detected.

#### **Potential and Shortcomings**

In the course of the FBI test, this device operated with about the same reliability and sensitivity as the other vapor detectors examined (which were all GC/ECD devices). The machine was able to detect the higher vapor pressure explosives, nitroglycerine and DNT, but did not respond to the lower vapor pressure materials such as TNT or RDX. It was slightly more susceptible to false alarm than the other devices. Like the others, it was unable to reliably detect explosive threats in simulated real life situations.

FAA sources note that these machines operate at thermal equilibrium: the ions created by the radioactive source stay close enough together for long enough time to allow numerous molecule-molecule interactions. This can cause scrambling, whereby the ionized explosive molecules collide with other molecules and in so doing, give up their extra electrons. Such de-ionized particles would not be sensed by the machine. Also, due to the duty cycle of the grid, 99.9 percent or more of the explosive molecules never reach the detector. Given initial quantities of materials in the pico- or femtogram range, such losses can be devastating to sensitivity. Finally, even the sales literature for these machines indicates that accuracy is dependent on the training of the operator.

On the plus side, however, several groups see promise in an improved version of this device. Work at Sandia National Laboratory has established that under ideal conditions an IMS detector can find plastic explosives, being sensitive to as little as 30 femtograms of explosive, despite the built-in  $10^3$  to  $10^4$  losses caused by the duty cycle of the g-grid. Other groups from Washington State University and New Mexico State University are also working on perfecting operating parameters for this device. While most of this work is aimed at detecting trace environmental pollutants, the results are easily applicable to explosives detection.

Further, quite recently, the Canadian firm Barringer has claimed that its IMS machine can reliably detect plastic explosives by adapting the device to collect and process particles (as opposed to vapors). At least one set of independent confirmatory tests has been made at Picatinny Arsenal, U.S. Army. The device has also been tested in November 1990 by the FAA. Results have not

yet been publicly released. While this machine has been demonstrated in the laboratory and for other purposes (notably narcotics detection), field operability for explosives detection still needs to be determined.

### *Two Stage Mass Spectrometry (MS/MS—Low Pressure Glow Discharge Ionization)*

**Sponsor:** Department of Energy, work being done at Oak Ridge National Laboratory (ORNL), Oak Ridge, TN.

**Status:** First generation system operational. Theoretical work on second generation device nearly completed. ORNL wishes to transfer technology to industry for development.

**Funding:** Funded by the Department of Energy since fiscal year 1984. Funding level was about \$400,000 in fiscal year 1990. About the same amount or slightly less for each of the three previous years.

#### **Basic Operating Principles and Goals of Concept**

Each mass spectrometry stage makes use of the fact that many explosive molecules are nearly unique among natural compounds in their electronegativity, that is, their propensity to attract and capture an extra electron and thereby become negative ions. Once ionized, they can be accelerated and analyzed by subjecting them to electric and/or magnetic fields. The mass-to-charge ratios of the ions can be determined by any of a variety of means referred to collectively as mass spectrometry.

In the MS/MS explosives sniffer developed at ORNL, an air sample is drawn through a small orifice into a low-pressure chamber where an electric current flows through the sample and ionizes molecules of air and, especially, of explosives, if present. This process is called air sampling/glow discharge ionization (ASGDI). Due to various inefficiencies and the contrary properties of explosives molecules, the negative ions from the ASGDI chamber that are injected into the first stage mass spectrometer will include only 1 to 5 percent of the explosives molecules originally drawn into the chamber.

By capturing the output of the first stage mass spectrometer at a given time after injection or at a predetermined spatial location, usually a slit, the ions with particular mass-to-charge ratios are separated from the complex mixture.

Large molecules, such as the explosive compounds, can be fragmented into predictable smaller pieces. The

output of the first stage is brought into collision with a stream of neutral atoms such as helium. The impacts cause the large molecules to dissociate into smaller ions, the masses of which can be determined by a second mass spectrometer. Because it is unlikely that more than one kind of molecule will both ionize to the proper mass-to-charge ratio *and* break down into the proper fragments, this technique is considered to be very specific in detecting explosive materials and thus yields a very low false alarm rate.

#### **Technical Description**

An air sample is preconcentrated and drawn into the analysis device. optimization of these preliminary steps has not been a focus of the researchers at ORNL. Molecules in the sample are ionized at low pressure (approximately 0.8 torr) in a novel glow discharge chamber.<sup>5</sup> By operating at low pressure and in short time frames, they were able to avoid ion/molecule reactions involving analyte ions that could cause the analyte ions to transfer charges to background molecules, thereby eliminating or altering the signal.

The ions thus generated are then passed through a quadrupole mass filter: four parallel cylindrical rods that create an electrical field pattern that effectively screens out all ions except those of particular predetermined mass-to-charge ratio. The mass-selected ions are then broken into fragments by collision with helium gas. The masses of the ionic fragments are then determined using a time-of-flight spectrometer. In time-of-flight spectrometers, the ions are accelerated by applied electric fields and sent through a flight tube. Ions of different masses pass through the flight tube at different speeds.

In a second-generation device, both quadrupole mass filters and the time-of-flight instrument have been replaced with an ion-trap mass spectrometer (ITMS).<sup>6</sup> This change promises to provide a smaller, more specific, and sturdier mass analyzer. The researchers at ORNL are currently working on perfecting techniques for injecting ions into the ITMS.

#### **Potential and Shortcomings**

This device was evaluated by Sandia National Laboratories in August 1988.<sup>7</sup> It was found to be very insensitive to interferants, even those suspected of being able to disturb the glow discharge chemistry on which the ionization of the first stage depends. The device was able to respond accurately to samples of RDX, C-4, military TNT, tetryl, the cut end of a sample of Primacord, and Detasheet, although it should be noted that the test

<sup>5</sup>See U.S. patent No. 4,849,628 issued July 18, 1989.

<sup>6</sup>Scott A. McLuck, Gary L. Glish, and Keiji G. Asano, "Coupling of an Atmospheric-Sampling Ion Source with an Ion-Trap Mass Spectrometer," *Analytica Chimica Acta* 225 (1989) 25-35.

<sup>7</sup>F.J. Conrad and D.W. Hannum, "Evaluation of the Oak Ridge MS/MS Explosives Detector," pp. 35-1 to 35-17, Sandia National Laboratories, 1988.

protocol involved near contact with the explosive sample.<sup>8</sup> Under these conditions, the device was sensitive to concentrations of explosive molecules in the range of 0.3 to 30 parts per trillion and to quantities on the order of 50-100 femtograms. No problems with maintenance or reliability were reported after the ion source had run for months at a time without breakdown or need for cleaning. Prototype versions of this arrangement have been used at ORNL. Licensing agreements have been reached with a private corporation that has plans to market a similar device as an environmental monitor and is evaluating the market for explosives detection.

### *Fluoroimmunoassay (Antigen-Antibody Reactions as a Test Technique)*

*Sponsor:* FAA Technical Center; work performed at Naval Research Laboratory (NRL)

*Status:* Beyond Proof-of-Principle. Awaiting practical testing later this year.

*Funding:* \$250,000 per year.

### **Basic Operating Principles and Goals of Concept**

A continuous flow of vapor to be tested is drawn into a preconcentrator at a rate of about 2,000 liters per minute and collected in 1 ml of aqueous solvent. The output of the preconcentrator is directed into the detection unit. This unit is a small (200 microliter) vial containing immobilized antibodies and fluorescently labeled analogs of explosive molecules. The antibody reacts with extreme specificity to only one particular explosive. If present in the sample, the explosive antigen will displace its fluorescently labeled analog, which can be easily detected downstream.

### **Technical Description**

The test takes about 1 minute. To minimize false alarms, two columns can be used in parallel, with the second column containing an irrelevant antibody/fluorophore-labeled molecule pair. Any substance that causes an alarm from both columns is obviously not reacting with the antibody but is releasing fluorescent material by another pathway. Antibodies to more than one explosive can be used simultaneously.

Other workers in this field (Westinghouse and Biometrics, Inc.) are also using antibodies to test for the presence of explosives but use a capacitive device instead of fluorescent labeling for detection.

### **Potential and Shortcomings**

Field tests are scheduled to be conducted in the near future. However, some performance characteristics can be inferred from antibody detector work in other areas. The detector is fairly inexpensive, fast, and fully automated. Because each antibody is specific to a single compound, a detection unit would need to contain antibodies to all materials expected to be encountered. Researchers at NRL claim that their device is sensitive to nanogram ( $10^{-9}$  g) quantities of material. This is substantially less sensitive than many other of the technologies discussed above. However, the investigators are now working on coupling a preconcentrator onto the front end of their device. This technique is said to be able to convert a vapor sample containing 10 ppt TNT into a 5 microliter solution, which is easily detected by their machine.

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<sup>8</sup>If the device failed to alarm under these conditions, a preconcentrator (such as a wad of quartz wool held near the explosive sample over which an air stream was drawn) was employed.

<sup>9</sup>Finnigan-Mat Corp., San Jose, CA.