

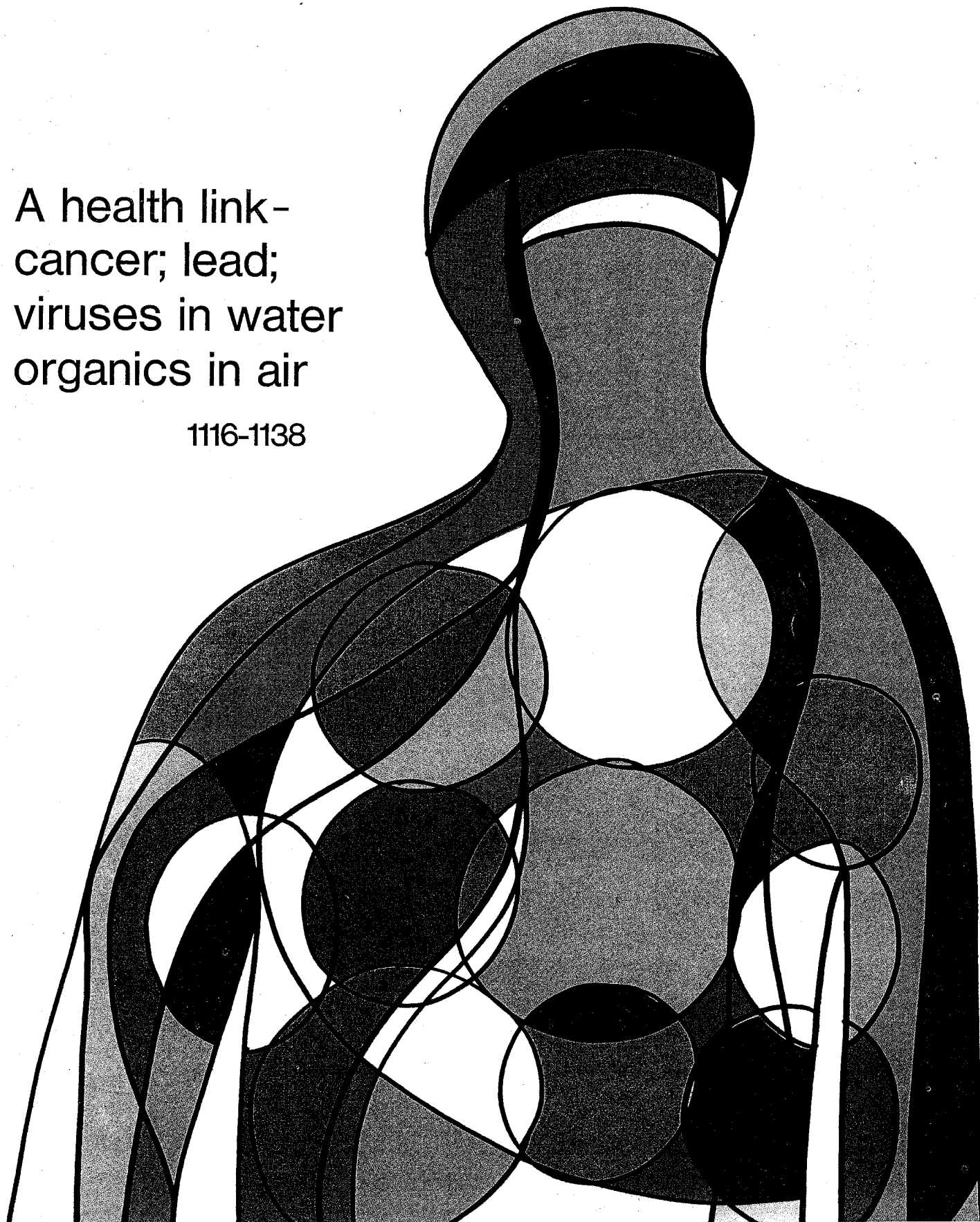
Environmental

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A health link-
cancer; lead;
viruses in water
organics in air

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Monitoring organic vapors

A portable mass spectrometer can be used in the field to detect thousands of these materials at the parts per billion level in the ambient and workplace air environments

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The problems involved in measuring and identifying organic compounds in the environment have been of constant concern to the environmental scientist. Industrial hygiene, an allied area, which is concerned with occupational health in the workplace, is experiencing many of the same problems. The more stringent regulations, requiring specific compound identification, have forced both groups to use sophisticated instruments that were seldom used in the past.

Mass spectrometry and gas chromatography-mass spectrometry are becoming two of the most popular and useful techniques available to the environmental chemist and industrial hygienist. Basically two reasons, high sensitivity and definitive identification, account for this popularity. The modern mass spectrometer is capable of detecting organics in the nanogram (10^{-9} g) and even picogram (10^{-12} g) range.

This sensitivity combined with the capability to identify specific sample materials in the presence of the many interfering compounds in an otherwise normal background often makes mass spectrometry the only applicable technique for monitoring abnormal materials in the environment. A recent augmentation of the technique, adding substantially to its utility, is the minicomputer-based dedicated data system. This has allowed for an efficient means of collection, reduction, and analysis of large volumes of data thus making feasible, for many laboratories, an instrument that was once considered only a tool of research.

Although the conventional mass spectrometer has gained a strong foothold in the environmental laboratory, it does not easily lend itself to portability and field use. It would, however, make an excellent field monitor if the problems involving size and weight could be overcome. Its sensitivity, specificity, and flexibility would allow it to replace many of the specific monitoring systems now in use.

For the past year, the U.S. Army Environmental Hygiene Agency has been using just such an instrument in the areas of industrial hygiene and air pollution monitoring. The system has proven extremely useful and has often provided information unobtainable by any other instrumental technique.

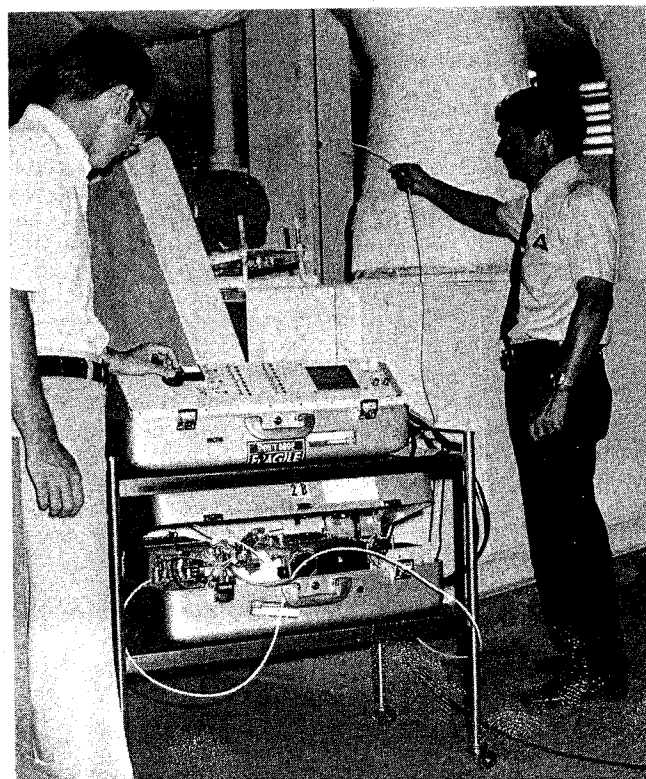
Background

The portable vapor detection system, based on a portable mass spectrometer, was developed for the U.S. Army Land Warfare Laboratory by Varian Associates under the technical

direction of H. Clay McDowell. The original purpose of the project was to develop an instrumental system capable of detecting the presence and movement of concealed personnel. A mass spectrometer was chosen as the heart of the system because of its fast response and specificity of detection. Masses, indicative of organic compounds emitted by the human body, were monitored via specific or multiple ion detection and the processed data were displayed on an integral CRT (cathode ray tube) monitor. The presence and intensity of these masses, above background, demonstrated the presence of target personnel and to some degree their distance from the instrument.

The development cycle of the portable vapor detection system started with breadboard feasibility in 1968. Although

Leaks. Persons check the escape of materials from ducts



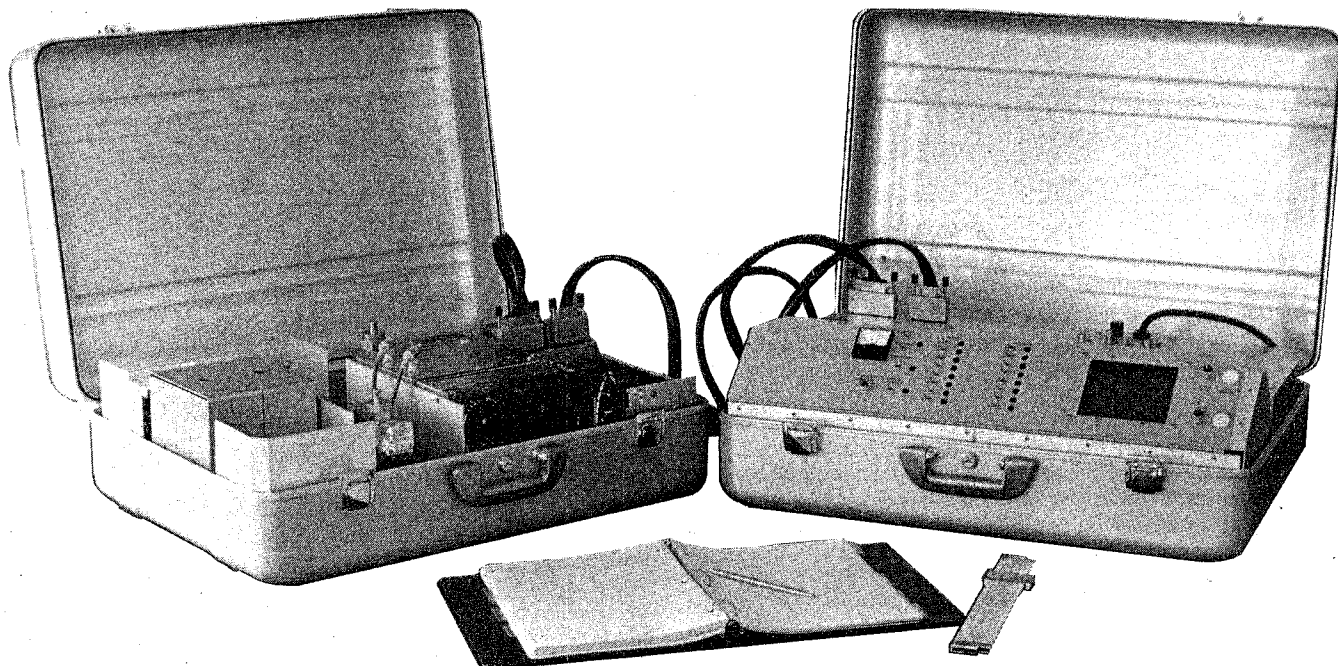


Figure 1. Suitcase (right) shows the operator's control panel and CRT monitor; suitcase (left) with protective insulation and covers removed shows the quadrupole analyzer and its vacu-

um system (in the center and upper right-hand portions), and the membrane separator and its vacuum canisters (in the lower left-hand portion)

development was essentially complete by 1970, small improvements were made through 1973 and consisted mainly of the replacement of some electronic components with "state of the art" ones as they became available. This ongoing development resulted in a lighter weight package with a high degree of electronic reliability. Weight and durability are especially important since the system usually travels as excess baggage on commercial airlines. Even though the initial development contract has been satisfied, continued improvement is imminent. An integrated gas chromatograph and an "idiot proof" color CRT display are to be added later this year. The addition of the GC will greatly increase our capability in water pollution monitoring and a color change of the data peaks on the video display at preset concentration levels will make the instrument a "technician level" system. Operation of the system in the field while unattended via an acoustic coupler from the agency is also envisioned.

Applications

Because of the inherent flexibility of the mass spectrometer, the system was ideally suited for a number of other projects. It underwent extensive field testing to determine its usefulness in detecting military explosives. The instrument was mounted in both fixed and rotary wing aircraft and flown over TNT (trinitrotoluene) melting operations in order to determine if the system could detect the plume given off by molten explosives. It was discovered that the more volatile MNT (mononitrotoluene) and DNT (dinitrotoluene) components present in TNT could easily be detected and thus provide information as to the locations of enemy explosive reclamation facilities.

Several other applications projects were also undertaken. In one, the system was installed in a Volkswagen Microbus. This resulted in a highly mobile system capable of detecting chemical effluents of military and environmental interest. Another project involved the analysis of drugs and drug metabolites in body fluids.

When the U.S. Army Land Warfare Laboratory was disestablished in 1974, the U.S. Army Environmental Hygiene Agency obtained, on loan, one of two mass spectrometer-based, portable vapor detection systems that had been delivered. For the past year, the agency has been involved in eval-

uating its utility in monitoring and detecting environmental and industrial hygiene pollutants.

The instrument package

The portable vapor detection system is housed in two heavy-duty aluminum suitcases. One contains the control panel and data display, the main power system, and a miniaturized general purpose computer. The quadrupole mass spectrometer, its vacuum system, and the specialized inlet system are housed in the other case. During operation, the two cases are interconnected and operated via switch commands from the control panel (See Figure 1). Although the system incorporates many unique features, the inlet system and the digital computer are probably the greatest contributions to its portability and success.

The inlet system consists of a dual section Llewellyn silicone membrane separator, a sample pump, and two interstage pumping canisters. Each separator section itself is a 3-stage device with each of the two sections operated at different temperatures (See Figure 2). In normal vapor sensing operations, the higher temperature section is normally set by thermostat at 60°C while the lower one is slightly above ambient. These temperatures are suitable for those materials that are sufficiently volatile to furnish partial pressures within the detection range of the system (nominally greater than 10^{-6} torr). For less volatile materials, the higher temperature section is used alone and is heated under external control (maximum operating temperatures 230°C). The interstage pumping requirements for the separator are met by two stainless steel canisters each of which contains 1 kg of specially processed zeolite. Upon evacuation, these canisters can meet the separator vacuum requirements for a normal day's operation thus precluding the inconvenience of transporting a mechanical pump to the investigation site. Normally the interstage canisters are pumped down on a daily basis by using a small fore pump; this procedure requires about one hour. The system can, however, sustain standby periods of up to three days without being replenished.

During operation, a small pump pulls ambient air across the face of the outer membranes of the separators at approximately 1 liter/min. Since the dimethyl silicone membrane material is more permeable to organic molecules than to the

air gases, the relative concentration of transmitted sample is increased at each stage of the three-stage separator. Sample enrichment is compounded multiplicatively with each successive stage and, typically, is about 10^6 . With ambient concentrations of 1 ppb the enrichment presents the spectrometer with a sample to air ratio of about 10^{-3} , which is easily managed by the dynamic range of the system. The small amounts of air gases that pass the first two membranes are quite effectively removed by the zeolite canisters. Depending on the volatility of the material to be analyzed, either a Teflon or heated probe may be used for sample collection. A high-temperature liquid inlet system is also available.

Spectrometer

The UTI Model 100B quadrupole analyzer used in the system is a very precise mechanical assembly. Therefore, the analyzer rods must maintain their alignment within 0.0001 inch. Since external forces on the rod assembly could alter alignment, the analyzer structure is floated within the vacuum housing. A radial clearance of 0.001 inch in its mounting prevents external forces from distorting the structure but still constrains its motion when the suitcase is subjected to shock loads.

High vacuum, within the source and analyzer, is maintained by an 11 liters/sec ion pump with resulting pressures of 10^{-7} to 10^{-6} torr. Power for the ion pump is supplied by the main power supply while the system is in operation and by a small external source during standby periods. During transit, three Leclanche lantern batteries, connected in series, will supply ion pump power for 24–48 hours.

The ion source is of the closed, electron impact type and is patterned after the Alpert ionization vacuum gauge. Dual filaments are provided for redundant electron supply. The ionizer will usually function for several hundred hours even after the failure of one of the two filaments. Normal electron energy is approximately 70 eV. The ionizer, the mass spectrometer, and the electron multiplier are protected from over pressure damage by an adjustable vacuum interlock.

One of the major problems in examining an unknown and uncontrolled mixture of samples lies in the dynamic range of detection required. This is compounded by the fact that in a normal background situation, and in the presence of samples, peak intensities may vary by a factor of 100 or more. To accommodate this problem, an autoranging electrometer was specially designed for the system. Coupled to the continuous dynode electron multiplier the system, when operating at a fixed gain setting, achieves a dynamic detection range of more than 1000.

Digital system

The operation and control of the vapor detection system is entirely under digital control. Analog data from the spectrometer is digitized and processed by the computer while digital operational commands are transmitted analogically to the spectrometer.

The computer was specially designed and developed in order to accommodate size, weight, and power constraints. It was designed around the Intel 8008 microprocessor and utilizes 1792 8 bit words of Read Only Memory (ROM) and 1024 8 bit words of Random Access Memory (RAM). The ROM contains the stored programs for instrument operation and data display while the RAM is used for data and program variables. A hardware multiply and divide capability substantially increases the computers overall speed for processing data.

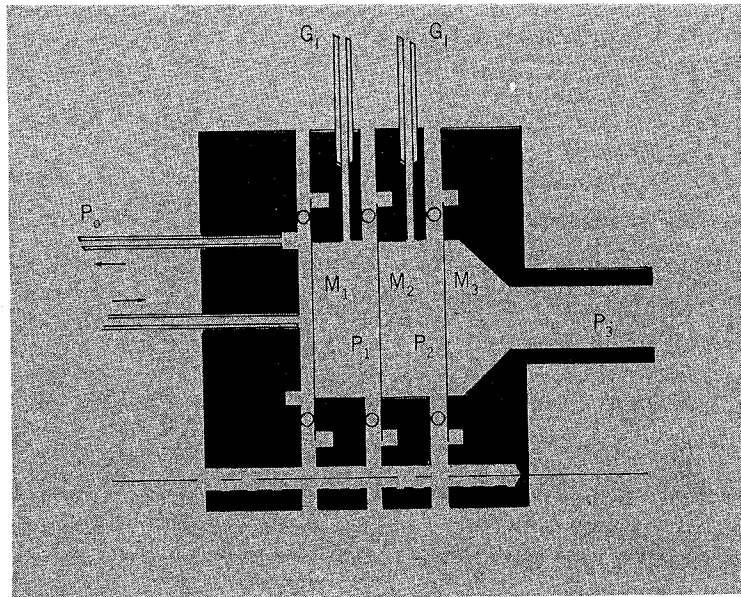


Figure 2. Diagram of one of the three-stage silicone membrane separators. Pressure decreases from P_0 (sample inlet) to P_3 (spectrometer inlet). Membranes M_1 , M_2 , and M_3 are supported by gold-plated nickel and stainless steel screens on their low pressure sides. Air gases that penetrate M_1 and M_2 are removed by their respective zeolite canisters G_1

Since all operational programs are stored in reprogrammable ROM, protection is complete. Neither manipulation of the panel switches nor power outages can disable the stored program, which adds a level of protection for the novice operator.

Operation

Three modes of operation are available with the system. One, a full scan from mass 10 to 346, is seldom used in the field as a separate oscillographic recorder would be required. A partial scan mode and a specific or multiple ion detection mode, however, output directly to an integral television monitor.

In the partial scan mode, 14 amu (atomic mass unit) segments of the spectrum from mass 10 to 346 may be assessed via switch commands from the control panel. Access to spectral segments is relatively fast (1–3 sec) and can be accomplished at any time. Once the operator has decided upon the segment of interest, background levels may be captured and retained directly on the monitor. These retained background readings may then be compared with the current values of the peaks of interest that are displayed adjacently.

This method of display allows precise measurement of very small changes in mass amplitude. Background levels have been shown to change slowly, but large excursions can occur over a period of time. Therefore background values can be automatically updated by the computer by using a moving average of background peaks to normalize the display amplitudes. In order to accommodate a wide dynamic range, mass intensities are displayed as the square root of the detected values.

For those compounds measured on a routine basis, the specific or multiple ion detection mode is used. In the present system, 256 words of ROM are reserved for signature peaks of specific compounds. Typically 2 to 5 masses that are indicative of a target compound are programmed into the ROM and displayed as a group. Both a static and moving average background display are available (See Figure 3). Depending on the number of peaks required for identification, 7 to 14 compounds may be programmed on a single chip. The compound library can easily be expanded by programming several chips and then exchanging them as needed.

Specificity and sensitivity

Mass spectrometry is, without question, the most definitive technique available for the identification of organic compounds. Although a complete spectrum is required to identify some compounds, many can be identified on the basis of a few well chosen signature masses. Multiple Ion Detection (MID) or mass fragmentography offers two major advantages. First, it reduces the amount of data that must be interpreted by the operator, and second it increases the sensitivity of the mass spectrometer.

Since target samples are to be detected in the presence of normal background, the signature masses must be selected with care if the identification is to be truly reliable. Peaks that are common to a number of different compounds must be assigned with caution and must be augmented with other masses of the target compound which, when combined, will serve to uniquely identify the sample. In general, combinations of peaks can be found that will permit discrimination against interferences with a high degree of confidence.

Generally speaking, the average mass spectrometer will detect organic concentrations of 10×10^{-9} g/sec in the full scan mode and as little as 10×10^{-12} g/sec in the multiple ion detection mode. The quadrupole analyzer used in the portable vapor detection system is quite sensitive and operates within these ranges. The determining factor in the sensitivity of the system is the efficiency with which sample materials can be transported to the ionizer of the mass spectrometer. The inlet system with its membrane separator is more efficient in transmitting reasonably volatile organic materials at ordinary temperatures.

Less volatile materials require higher membrane temperatures; for example, TNT is best transmitted with a separator temperature of about 200°C. Inorganic materials and highly polar compounds are not transmitted as well. The mechanism that determines the facility of the membrane to transmit a substance is its solubility in the dimethyl silicone polymer.

For the majority of organic compounds having vapor pressures of greater than 10^{-5} torr, solubility in the membrane is high and detection can be made in the parts per billion range. Less tractable materials can be introduced by using higher separator temperatures. An all glass evaporator for materials of low volatility is also available. Table 1 illustrates the sensitivity of the system for several compounds in ambient air.

Uses

The U.S. Army Environmental Hygiene Agency is charged with the occupational health and safety of Army personnel and civilian contractors and protection of the environment from adverse military and contractor activities. In order to support these activities, a wealth of laboratory and field instrumentation is required. Since obtaining the portable vapor detection system last year (1974) it has been integrated into more and more activities. Its extreme flexibility has allowed it to assume the duties of many other field instruments and in some cases to accommodate areas not covered by existing instrumentation.

Some of the past and present uses for the system include:

- detection of military explosives in water by direct injection and headspace analysis
- detection of solvents used in degreasing operations
- identification of pesticides
- detection of vinyl chloride
- monitoring of cholinesterase inhibiting chemicals. The system has also been used as a general purpose mass spec-

Organic compounds, for measurement purposes, can be placed in three distinct categories:

- those relatively non-polar compounds of moderate vapor pressure that give rise to distinct, identifiable mass peaks
- those similar to category 1 except that some mass peaks are shared by a number of naturally occurring compounds
- those compounds exhibiting low vapor pressures or high polarity.

Literally tens of thousands of organic compounds fall into categories 1 and 2 and are therefore detectable, by the system, at the ppb level. Although a significant number of category 3 organics exist, they are usually of less importance because their low vapor pressures, at normal temperatures, would limit their concentration in the workplace or the environment.

The portable vapor detection system has, so far, met many requirements in industrial hygiene and organic environmental monitoring. The following compounds, extracted from the Threshold Limit Value (TLV) list are detectable in the ppb range and are representative of the types of compounds monitored on a daily basis.

acetic acid	formaldehyde
acetic anhydride	hexachloroethane
acetone	methanol
acrolein	methylamine
2-amino pyridine	methyl ethyl ketone
benzene	methyl isobutyl ketone
chloroform	β -naphthylamine
carbon tetrachloride	p-nitroaniline
bis-chloromethyl ether	nitrobenzene
cresol	parathion
dichloromethane	pyridine
dichloroethane	Stoddard solvent
dichloromonofluoro-	1,1,2,2-tetrachloro-
methane	ethane
diethylene triamine	tetrachloromethane
diethylamine	methylchloroform
ethanolamine	triethylamine
ethylamine	vinyl chloride
ethylenediamine	xylene

Sensitivity for some organics in ambient air with the portable vapor detection system

Compound	MW	Lower detection limit
Benzene	78	1.0 ppb ($3.2 \mu\text{g}/\text{m}^3$)
Monochloromethane	85	2.0 ppb ($1.2 \mu\text{g}/\text{m}^3$)
(MIBK)		
Paraldehyde	164	0.1 ppb ($0.7 \mu\text{g}/\text{m}^3$)
Phosphorin	224	5.0 ppb ($4.5 \mu\text{g}/\text{m}^3$)
(methyl phosphate)		
Hexane	86	5.0 ppb ($4.1 \mu\text{g}/\text{m}^3$)
Acetic anhydride	102	3.0 ppb ($2.5 \mu\text{g}/\text{m}^3$)

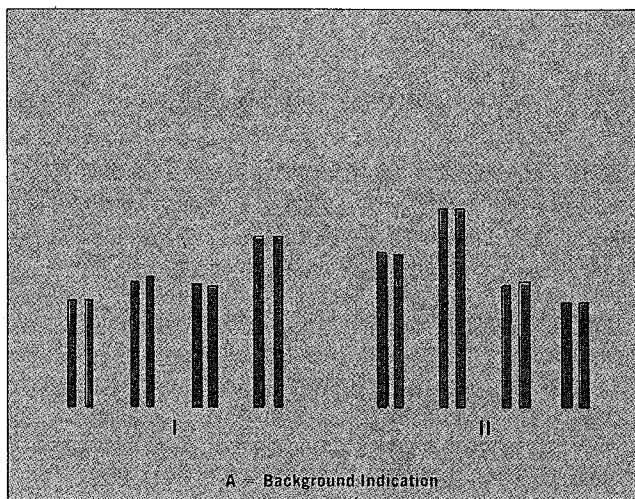
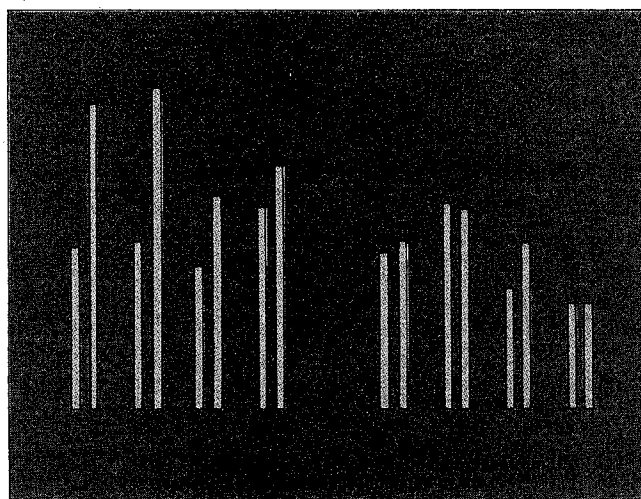


Figure 3. Diagram of CRT display for both background (A) and detection (B) situations. Signature masses for bis chloromethyl ether (I) and chloromethyl methyl ether (II) are programmed such that both compounds may be monitored si-



multaneously. The left-hand peak in each doublet is the static background level for that particular mass while the right-hand peak represents the realtime level

trometer during those times when a laboratory instrument was inoperable.

One of the most useful applications of the system is that of point source monitoring. Much of the Army work involves locating discrete sources of pollutants and toxic compounds. Because of the instrument's selectivity and fast response, it is able to measure local differences in concentration within a small area. This becomes extremely important in those cases where exposure levels differ drastically within a single work area.

A joint USAEHA-DEA (Drug Enforcement Administration) project also involves the portable vapor detection system. At this time, USAEHA is involved in a field evaluation of the system's capability in detecting the acetic anhydride plume given off by illicit morphine processing facilities. Based on earlier results, it is anticipated that the unit will be able to detect less than 1 ppb of acetic anhydride at a distance of one kilometer from the source. If the project is successful we will have an excellent weapon for combating drug traffic before it reaches the market place.

One of the most important future applications of the system may be field detection and identification of organic contaminants in drinking water and wastewaters. Some further development will, however, be required to implement this type of measurement. An integrated gas chromatograph and some additional data system capabilities will probably be required. Utility of the system will also be enhanced by developments designed to facilitate ease of operation by operators at the technician level.

Although the portable vapor detection system was designed primarily for qualitative measurement, reasonably accurate quantitative results can be obtained. Mass abundance vs. concentration curves can be constructed by measuring known concentrations of target compounds. The intensities of selected air gas background peaks can be used to adjust spectrometer gain.

Availability

At present, several companies show an interest in developing such a system. Litton Industries (Los Angeles, Calif.) is studying the feasibility of converting, for terrestrial use, the GC-MS system that will travel to Mars as part of the Viking Lander Project. Analog Technology Inc. (Pasadena, Calif.) has similar plans for their miniature quadrupole analyzer, which was developed for NASA. EPA has shown interest in this particular instrument as an environmental monitor; however, the absence of a separator or other enrichment device makes it

too insensitive for their work. Varian Associates (Palo Alto, Calif.) is also considering further development of the system.

The system currently being developed for EPA by Analog Technology Inc. is expected to sell in the \$20,000 range in production quantities. The more flexible system developed by Varian will probably be closer to \$50,000. The original Army R&D contract provided for two complete systems at a cost of \$60,000.

Although the portable vapor detection system exhibits some design limitations, it has illustrated the usefulness and flexibility of the mass spectrometer as a field monitor. Further development could make it the most powerful instrument in the field scientists' arsenal. Because of its sensitivity, specificity, and flexibility, the portable mass spectrometer may become the monitoring system of choice if exposure and pollution guidelines continue to increase the requirement to measure specific organic compounds.

The opinion or assertions contained herein are the private views of the authors and are not to be construed as official or as reflecting the views of the Department of the Army or the Department of Defense.



Joseph E. Evans is currently the East coast GC-MS specialist for Finnigan Corp. At the time of this writing, Dr. Evans was Chief of the Air Chemistry and General Support Branch, U.S. Army Environmental Hygiene Agency, Aberdeen Proving Grounds, Md. A biophysicist by training, his primary interests include biomedical and environmental applications of gas chromatography-mass spectrometry.



James T. Arnold, a physicist and senior scientist for Varian Associates, was the primary force behind the design and development of the portable vapor detection system. Dr. Arnold's primary interest involves the application of physical principles to the design of novel and innovative instrumentation for chemical measurement.