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A REVIEW OF SOME EXPERIMENTAL
MEASUREMENTS ON DETECTORS FOR TRACE
CHEMICALS IN THE ATMOSPHERE

R. D. Shelton, et al

USA Ballistic Research Laboratories
Aberdeen Proving Ground, Maryland

July 1975

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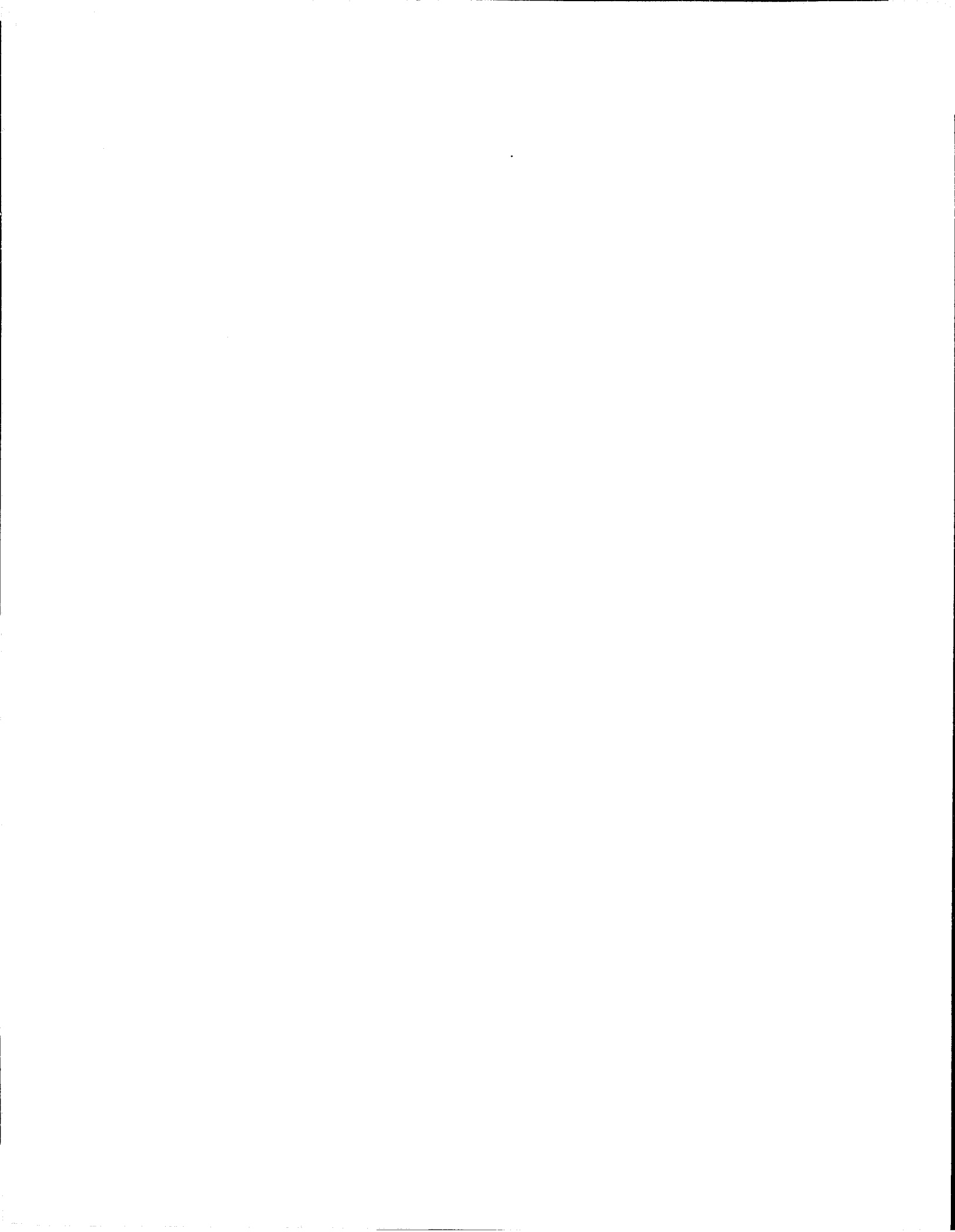
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THE ATMOSPHERE

R. D. Shelton
W. A. Wall

NCJRS

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I. INTRODUCTION

Almost anything done by man results in some effluent which becomes airborne from the scene of activity. The effluent may be in the form of particles, aerosols, or gas molecules. For example, a man driving a car would result in the emission and stirring-up of dust and the evolution of aerosols and gas molecules. The effluents created by man are of great interest to governments for reason of atmospheric pollution, police surveillance, and military intelligence, as well as for a number of scientific applications.

Certain types of illnesses are evident by smell to an experienced physician. By using instruments sensitive to effluents evolved through the skin, lungs, and excretory system, much can be learned about the metabolism of an individual. In particular, it has been found possible to determine specifically the drug used by an unconscious overdose victim^{1, *}, such as opiates, barbituates, amphetamines and hallucinogenic drugs, by rapid analysis of urine samples with a sensitive mass spectrometer. In some areas there has been intense concern with the illicit manufacture of LSD and heroin. Suitable detectors carried by motor vehicles or aircraft can be used to sniff out the source of vapors characteristic of this type of manufacture. Men, smoking cigarettes or using an internal combustion engine, create large numbers of condensation nuclei which are readily detected by a miniaturized and instrumented form of the classic Wilson Cloud Chamber. Housing facilities used by terrorists for the manufacture of illegal munitions can be identified by the effluent from the explosive used. Finally, a large number of military and industrial operations evolve trace materials which permit an identification and location of the source. Although the initial effort was concerned with the location of enemy personnel hidden by heavy cover impenetrable to radar IR or visual detection, a number of other uses appeared later in the areas of environmental monitoring, industrial safety, medicine, and law enforcement.

During the several years preceding its disestablishment, the U.S. Army Land Warfare Laboratory examined a number of detectors for trace chemicals in the atmosphere and acquired considerable data on their performance in the search for personnel, explosives, and illicit drugs. The following discussion is a summary of what was learned.

In the search for sources of trace chemicals in the atmosphere, two general techniques may be used. One involves carrying the sniffer around until the desired effluent is detected and working upwind until the source is found. The other technique, which has a great operational

¹ USA Land Warfare Laboratory Annual Progress Report, 30 Jun 74, p. 185, AD 920 231L.

* Referenced reports of the USA Land Warfare Laboratory are available from the National Technical Information Service, US Department of Commerce, P.O. Box 1553, Springfield, VA 22151, or from the authors in some cases.

advantage but considerable technical difficulty, views the vapor cloud from a distance and traces it back to the source, much as the eye connects a trail of smoke to the stack putting it forth. The first technique may be called direct sensing and the second remote sensing. Direct sensing requires a passage of the detector through the effluent cloud and the search pattern is dictated by weather and terrain conditions. Remote sensing depends on some form of electromagnetic radiation, and may be either active or passive, depending on whether the radiation comes originally from the sensor system, as in radar, or from the effluent cloud, as in thermal imaging.

The ideal sensor for trace chemicals would be an optical device, like a pair of binoculars, which would superimpose an image of the effluent cloud on an image of the natural terrain. If this could be arranged, the problem of source identification and location would be very similar to that of locating a fire by following the smoke plume.

It should be pointed out that infrared and high frequency radar detectors are much like conventional optical devices in their inability to penetrate foliage and masonry, i.e., they are line-of-sight. On the other hand, almost every human activity loads the atmosphere with an identifying signature which cannot be hidden as easily as personnel.

Effluent detectors are characterized by sensitivity and specificity. Sensitivity is defined as the least concentration detectable under ideal conditions. It is the threshold or liminal concentration for which detection is possible and is conveniently expressed as the number of molecules of interest per billion molecules of background gas, usually considered to be air. Specificity is the capability of the instrument to determine what substance caused it to respond, and it is about this property that most of the debates are held.

It is possible for an instrument to respond well to a number of chemicals, perhaps best to those of least interest, but to be highly useful in an environment which is likely to offer only one of them. For example, a gasoline detector in a motor housing may be sensitive to a number of organic compounds but be quite useful because it is unlikely to encounter any of these compounds except gasoline in a situation of importance. On the other hand, this detector might not be useful if the objective was to find hoards of gasoline in an urban environment. The following discussion is concerned with information which is likely to be of importance to those seeking sensitive detectors of trace chemicals in the atmosphere but makes no claim to delineate for each instrument where it might be best applied.

Perhaps the greatest single contribution to the development of detectors with high sensitivity and specificity is the use of membranes that are strongly selective in their permeability to different gases. This selectivity, with a suitable pumping configuration, can raise the relative concentration of the gas being detected by several orders of magnitude. This improves both sensitivity and specificity.

II. CALIBRATION SYSTEM

After a number of techniques for trace chemical detection had been tried in the field, a grant from the National Science Foundation, (NSF) as part of the Presidential Internship Program, made it possible to begin careful calibration of several instruments relative to each other and to standard equipment. The NSF-Army agreement contained a provision that two postdoctorates work for a year in an area that could be militarily useful but also have application in the world outside DOD, so that employment opportunity would be good when the postdoctorate appointment was over. It was decided that the calibration of the trace chemical detectors developed by the Land Warfare Laboratory would satisfy the NSF and Army goals.

In the US Army Land Warfare approach, the first step was to establish a calibration system which would provide vapor samples of a variety of chemical compounds of interest at known concentration levels. This capability would enable the evaluation of a number of commercial and military trace detection systems against a common base.

The key ingredient in the measurements to be discussed below is the dilution system depicted in Figure 1, which could be accurately calibrated to supply a number of chemical vapors, at concentrations as low as one part per billion, to the detector under test.

The first stage of the dilution system consists of a thermogravimetric analyzer (TGA) and a heated mixing tube. The TGA is an electrobalance which directly measures changes in weight of a sample as a function of temperature or time. It incorporates a furnace assembly which allows temperature programmed measurements on sample evolution to be performed. For the experiments on sensitivity, the temperature of the sample is held constant and is selected to provide a suitable evolution rate of sample into the vapor state. An inert gas is allowed to flow at a constant rate over the sample as it evolves. A knowledge of the flow rate of the inert gas and the evolution rate of the sample permits calculation of the concentration of the sample - inert gas mixture emerging from the TGA. On exit from the TGA the gas mixture enters a heated glass line having an approximate length of one meter. To minimize adsorption of the sample, dilution line surfaces are maintained at the highest temperature which does not effect thermal degradation of the sample. Diffusion and other mixing processes will have established a fairly uniform concentration over the line cross section as the mixture reaches the end of its travel in the line.

In order to obtain sufficiently low concentrations of sample vapor in a purified gas, a second stage of dilution is utilized. A mixture of fixed concentration is allowed to flow through the first stage for a sufficient time to reduce losses due to adsorption. A fraction of this flow is then diverted into the second stage of the dilution system. The flow rate of the mixture from the first to second stages is controlled by pressure difference across the orifice connecting the two stages. The surface of

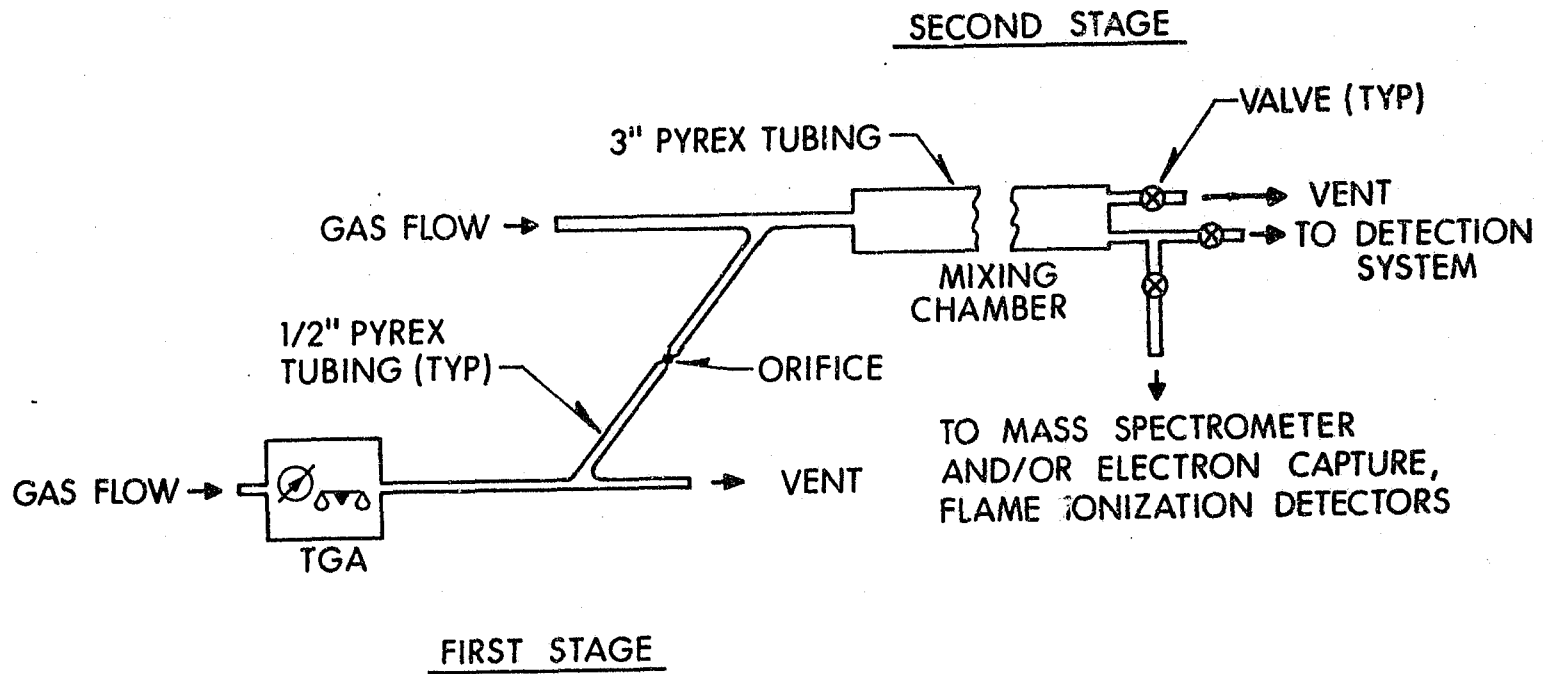


Figure 1 Diagram of the Two-Stage Dilution System



the second stage as well as of the connecting line is also heated to an appropriate temperature of the sample under investigation. The second stage has a purified carrier gas flowing through it at a rate which is generally 10^3 to 10^5 greater than the flow rate through the orifice. Beyond the junction point of the two flows, there is a 3.3m length of heated glass tubing with a 75mm diameter. Diffusion and turbulent mixing are expected to have produced an approximately uniform concentration of this mixture as it reaches the end of this section. Located at this end is an entrance port through which a detector probe can be inserted to sample the final mixture. The concentration of this final mixture is calculated from a knowledge of the two flow rates and of the concentration in the first stage mixture.

The electron capture and flame ionization detectors of a gas chromatograph were calibrated for response to low concentrations of materials of interest in solutions. The dilution apparatus has been arranged so that a portion of the flow exiting from the dilution system can be diverted directly (without passing through a G.C. column) into either or both of the G.C. detectors. It is possible to monitor the rise of the concentration of the sample material, as the walls of the dilution system approach an equilibrium condition for adsorption-desorption processes, and verify the actual concentration of the mixture emerging from the system and seen by a detection system. A portion of the flow can also be diverted to a quadrupole mass spectrometer having a Llewellyn membrane separator. This instrument was calibrated independently for several materials of interest by means of commercially prepared gas mixtures whose contents were verified by an independent analytic laboratory. In general, the increment in signal at the relevant mass/charge numbers is directly proportional to the concentration of sample presented to it. The mass spectrometer allows confirmation of the concentration of the final mixture as well as verification of its integrity.

III. CONDENSATION NUCLEI DETECTORS

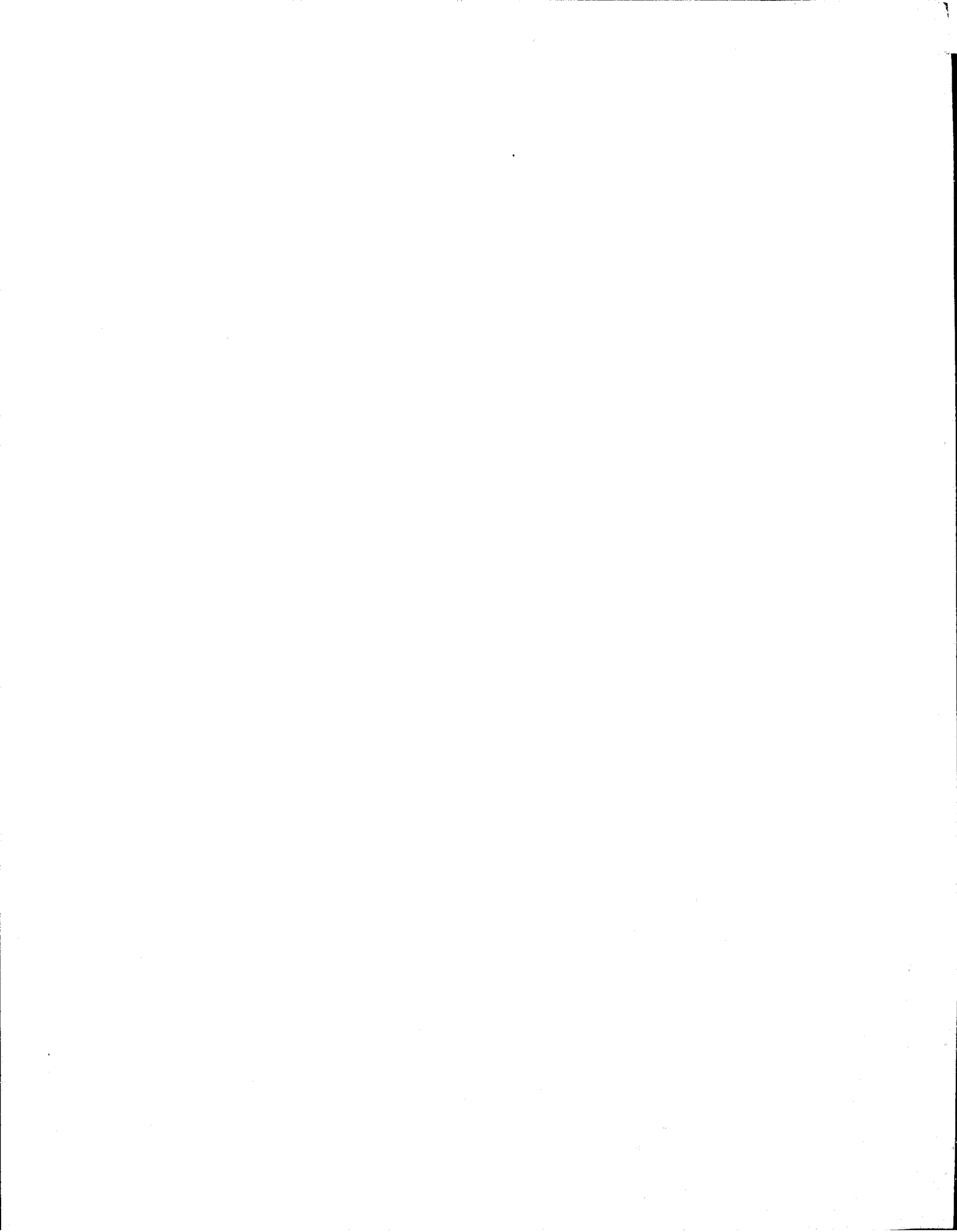
In certain changes of state, such as evaporation, liquefaction, or solidification, the change will not take place as soon as the energy constraints are satisfied, but will undergo a delay until some suitable inhomogeneity is introduced. This remarkable phenomenon of nucleation is the reason that stones are added to stills for obtaining pure water and is the basis for such sensitive detectors as the Wilson Cloud Chamber and the hydrogen bubble chamber, which can detect the ionized track of a single high energy subnuclear particle. The Wilson Cloud Chamber operates on the principle that air saturated with water vapor becomes super-saturated when it expands and cools, and condenses its excess water on any available ion or aerosol. These points of condensation are called condensation nuclei. The condensed water droplets are much larger than the condensation nuclei and can be detected easily by optical means, such as the scattering of light. The Wilson Cloud Chamber can be miniaturized, instrumented, and made to operate several times a second so that an almost continuous reading of the density of condensation nuclei can be made. It is also possible

to achieve the same effect aerodynamically with a continuous air flow. Either type can measure accurately the condensation nuclei density from the low level of the cleanest jungle, about 500 nuclei/cm³, to the high level on a busy city street, over 1,000,000 nuclei/cm³. The condensation nuclei detector is especially sensitive to combustion processes, such as those in cigarette smoking, brush burning, and internal combustion engines. It was used in the Republic of Vietnam to seek terrorists, encamped by day under heavy jungle canopy, where they were invisible to infrared and radar detectors, and in World War II to search for submarines. It was not possible to calibrate it with the chemical dilution system shown in Figure 1, because it is sensitive to condensation nuclei rather than chemical molecules.

IV. ELECTRON CAPTURE DETECTORS

A number of detectors are based on the principle that the flow of electrons between two electrodes is attenuated if electrons are captured and prevented from reaching the anode by gas molecules moving between the electrodes. Usually a low energy beta source such as Ni⁶³ or H³ is located in the vicinity of the electrodes and produces a standing current by ionization of an inert carrier gas. The anode is connected to a high impedance electrometer capable of measuring very small currents. Such detectors can have DC or pulsed modes of operation, with the former corresponding to a constant potential across the electrodes, the latter to a periodic potential of duration from μ seconds to tenths of m seconds. Generally, the pulsed mode is preferable, because of its greater sensitivity and linear range.

The Model 58 Explosive Detector, distributed by Ion Track Instruments of Waltham MA, is a pulsed mode electron capture detector using a dimethyl silicone rubber membrane to pass molecules of interest from an incoming air stream to a stream of argon which flows through the detector head, as shown in Figure 2. Molecules with a strong electron affinity, such as halogenated hydrocarbons and explosives, are readily detected. A TNT concentration of 4 parts per billion gave a full scale deflection on this explosive detector and it is estimated that 0.2 parts per billion could be easily detected. The response of this detector to selected compounds is shown in Table 1.



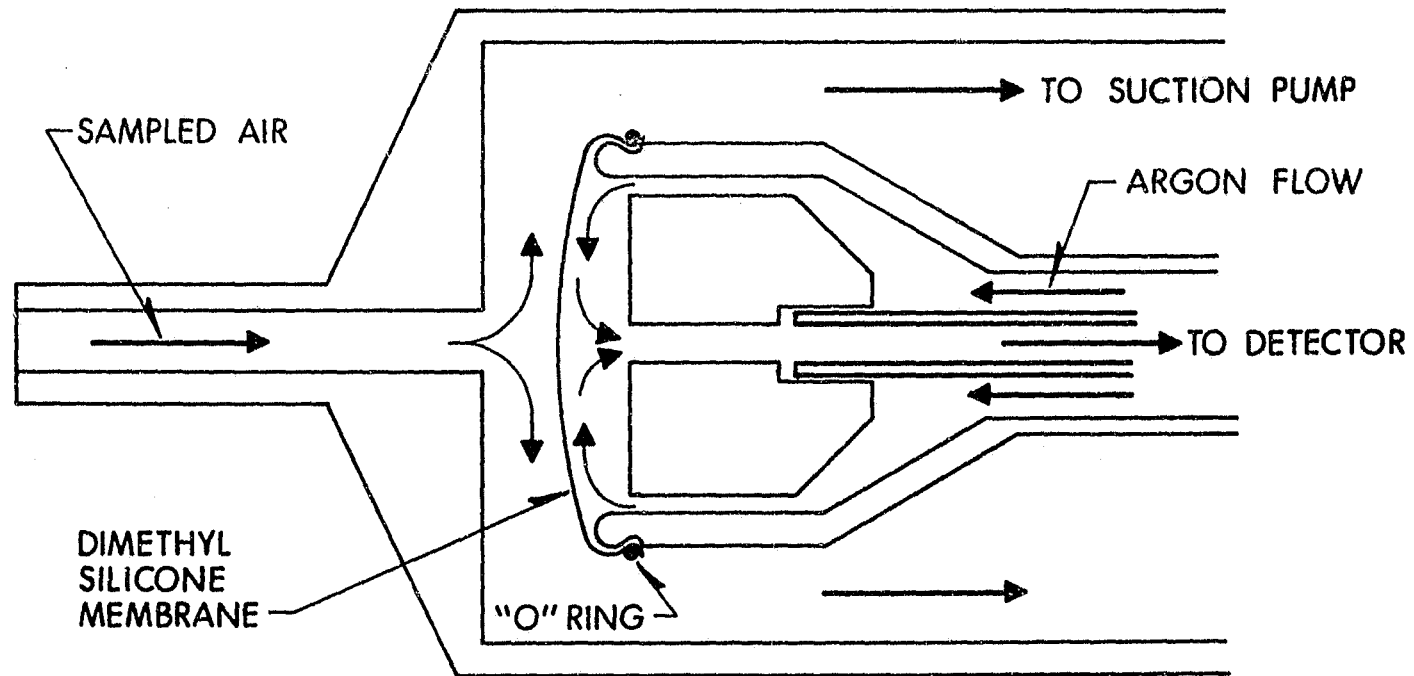


Figure 2

Cross Section of Probe and Membrane Concentrator of Gelignite and Explosive Detectors

Table 1

Response of Model 58 Gelignite Detector
to Selected Compounds

<u>Drugs</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
Cocaine	No	W	No	No
Heroin	W	W	No	No
Heroin (Street)	No	No	No	No
Marijuana	W	W	No	No
Morphine Sulphate	No	No	No	No
<u>Explosives</u>				
Black Powder	S	S	S	S
C-3	S	S	S	S
C-4	S	S	M	W
Comp B	W	M	M	W
Dynamite, Gelatin, 40%	S	S	S	S
Dynamite, Gelatin, 50%	S	S	S	S
Dynamite, Gelatin, 60%	S	S	S	S
Dynamite, Red Cross	S	S	S	S
Flex - X	S	M	M	W
Ethylene Glycol Di-Nitrate (EGDN)	S	S	S	S
Octol	S	S	S	W
PE-2	S	S	W	W
PEIN	W	W	W	No
Pentolite	No	No	M	No
PETN	S	M	W	W
PL - NP - 10	S	M	W	W
RDX, Comp A-3	S	M	W	No
RDX (BRL)	M	No	No	No
SEMTEX - H	S	M	W	W
Tetryl	M	S	W	W
Tetryl, British	S	M	M	W
TNT (BRL) (Military Grade)	W	M	S	W
TNT, Granular (Military Grade)	S	S	M	W
Nitroglycerine - Lactose	S	S	S	S
<u>Common Compounds</u>				
Citrus Fruit, Grapefruit	M	No	No	No
Fertilizer, 10-8-7, Liquid	S	No	No	No
Gasoline (ARCO Regular) (Getty)	S	S	S	M
Heating Oil	No	No	No	No
Water, Distilled	W	No	No	No
Silicone Compound, MIL-S-8660B	S	W	No	No
Sugar	No	No	No	No

Table 1

Response of Model 58 Gelignite Detector
to Selected Compounds (Cont'd)

	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
<u>Gun Related Compounds -</u>				
<u>Cleaners, Preservatives, Coatings</u>				
Compound, Heavy	No	W	No	No
Corrosive Protective Compound (MIL-C-16130)	S	S	M	No
Cosmoline	W	W	No	No
Grease, Automotive & Artillery (MIL-C-10924)	No	No	No	No
Gun Oil	M	S	W	No
Gun Slick	No	No	No	No
Rust Inhibiting Grease, RIG Universal	No	No	No	No
Solvent, Nitro-Powder, Hoppe's	S	S	S	S
<u>Chemical Compounds of Interest</u>				
Acetic Acid (Glacial)	S	S	S	M
Acetic Anhydride	S	S	S	M
Acetone	M	M	W	W
Ammonium Hydroxide	W	No	W	No
Benzene	No	No	No	No
Citric Acid	No	No	No	No
Dimethyl Sulfoxide	S	S	S	M
Ether	S	S	S	M
Ethyl Alcohol	W	W	No	No
Pyruvic Acid	S	S	S	S
Potassium Chloride	No	No	No	No
Match Heads	No	No	No	No

Key:

- I - Signifies Range x 10, Temperature 50°C settings on detector
 II - Signifies Range x 10, Temperature 100°C
 III - Signifies Range x 10, Temperature 150°C
 IV - Signifies Range x 50, Temperature 150°C
- S - Strong response, where deflection of meter $\Delta \geq 40$
 M - Medium response, where deflection of meter $40 > \Delta \geq 20$
 W - Weak response, where deflection of meter $20 > \Delta \geq 5$
 No - No response, where deflection of meter $5 > \Delta$

V. THE ION MOBILITY SPECTROMETER

The ion mobility spectrometer (IMS) was invented and designed, under the name Plasma Chromatograph, by the Franklin GNO Corporation and considerably improved, from the diagnostic viewpoint, by the Franklin Institute.

The interior configuration of the IMS is diagrammed in Figure 3. Air is continuously drawn into the instrument and swept past a Ni^{63} beta emitter. The beta particles ionize molecules in the air and, in turn, the ions may interact with other molecules. Although the kinetics involved are quite complicated and not completely understood, the net result is a region of ionized molecules near the shutter grid at the entrance of the drift tube. The drift tube has a cylindrical shape and a radially-independent electric field is imposed along its axis. However, the shutter grid acts as a gate to prevent ions from randomly entering the tube. When the grid is "opened", ions of the proper charge accelerate into and down the drift tube, undergoing multiple collisions with neutral molecules, and eventually being collected and measured as a current by a fast electrometer. The mobility of an ion depends on a number of factors such as its mass, charge, effective ionic size, and so forth. It has been claimed that ionic mobility differences would result in a separation of ionic species into envelopes whose time of flight would characterize the species, analogous to the retention times of gas chromatography.

The IMS operates in a continuous mode, with the shutter grid opening for a fraction of a millisecond every 25.6 milliseconds, and with a detection mode for either positive or negative ions. Data are visually displayed on an oscilloscope in the form of a spectrum of current versus time over the 25.6 millisecond period. A live or instantaneous spectrum may be introduced into storage at any time and the stored spectrum can be displayed simultaneously with the live spectrum. Those spectra toward the left side of Figure 4 are typical clean air spectra. It is believed that the "air peak" is due to ions chiefly of the form $(\text{H}_2\text{O})_n \cdot \text{H}^+$ in the positive detection mode, $(\text{H}_2\text{O})_m \cdot \text{O}_2^-$ in the negative detection mode. These ions are termed reactant ions, because they can interact with trace molecules in the air to produce additional ionic species. Even when such interactions occur, the area under the spectral curve remains constant corresponding to a conservation of the charge available for detection.

The spectrum of the IMS is electronically broken up into 256 intervals, each interval corresponding to 0.1 millisecond. Since the spectral area remains constant, the appearance of new features in the spectrum due to the detection of some vapor is accompanied by the reduction in size or disappearance of original features. The IMS has an alarm circuit which can be activated to monitor the live spectrum at as many as four arbitrary intervals. Positive or negative increments on the signal, at preselected intervals relative to a stored spectrum, then trigger an alarm light. This circuitry was developed under the assumption that each compound has a unique and recognizable spectrum. Unfortunately, this is not the case. The spectrum of a compound actually is strongly dependent on the vapor concentration presented to the detector.



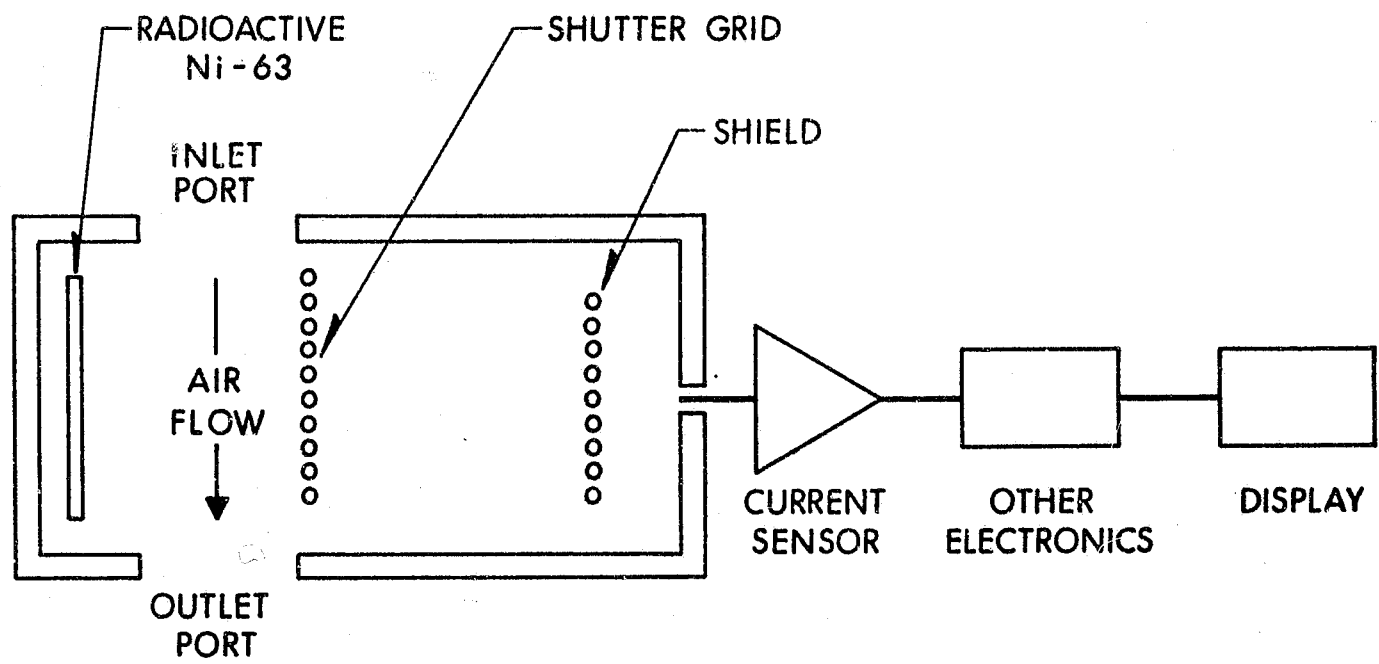


Figure 3 Schematic of Ion Mobility Spectrometer Cell

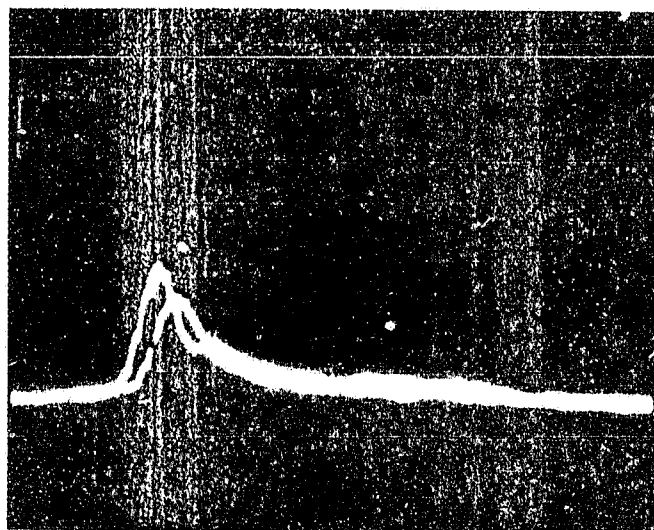


Figure 4(a) Spectra* of Ion Mobility Spectrometer for Acetic Anhydride at 5 ppb

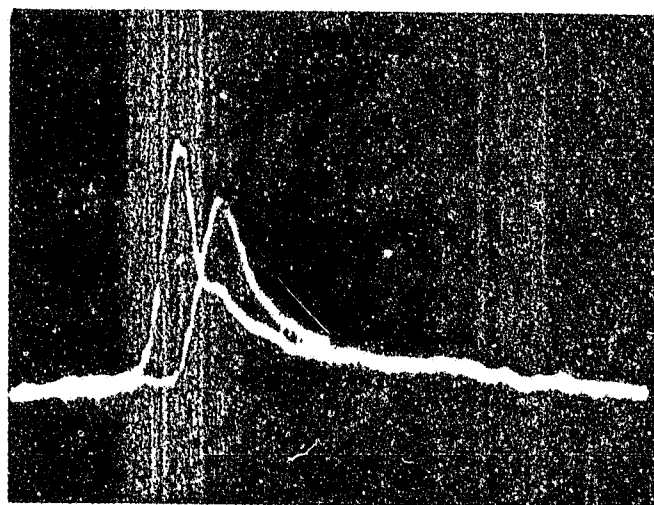


Figure 4(b) Spectra* of Ion Mobility Spectrometer for Acetic Anhydride at 15 ppb

*Clean air spectrum to the left is stored and used as a reference.

The response of the IMS to various chemicals is shown in Table II. It can detect several chemicals at concentrations of a few parts per billion, but the specificity is so poor that there is no way to tell which of a myriad of chemicals is being detected. The spectrum of a compound, a sample of which is shown in Figure 4, is dependent upon its concentration, so that there is no characteristic spectrum for a given compound. Except in special circumstances, where one needs a sensitive detector for a known chemical and where no other chemicals are likely to be, the IMS is not an operationally useful detector. It could, however, be an excellent research instrument for studying molecular ion interactions at atmospheric pressures.

VI. ELECTRIC QUADRUPOLE MASS SPECTROMETER

Varian Associates of Palo Alto, CA have developed a portable electric quadrupole mass spectrometer capable of resolution of one mass number^{2, 3}. It incorporates a unique Llewellyn membrane separator which permits direct atmospheric sampling and provides the interface between the high vacuum of the mass spectrometer and the atmosphere being sampled. This membrane preferentially passes a number of organic molecules while providing a barrier to the permanent atmospheric constituents. These systems have operated successfully in rotary and fixed wing aircraft and in automotive vans.

The foreline vacuum is provided by a liter canister of zeolite, which is sufficient for eight hours of field operation. The system can be re-stored for reuse by pumping down after each day of operation.

Control, calibration and programming of the system is performed by a minicomputer, which can be programmed to look at the full mass/charge range from 12 to 350 or to sum up to 15 mass peaks which characterize a substance to be detected. A catalog of 16 such unique signatures can be stored in the instrument for comparison with unknown samples encountered during a field operation. Instantaneous output is displayed on a CRT and stored by tape or chart recorders.

The portable electric quadrupole mass spectrometer, with its associated inlet system and computer, can positively detect and identify a large number of trace chemicals in the atmosphere down to concentrations of a few parts per billion, or less. Research in other types of membranes could improve this capability.

²U.S. Army Land Warfare Laboratory Technical Report, LWL-CR-03P68. AD 511 364L.

³U.S. Army Land Warfare Laboratory Technical Report, LWL-CR-03P68C.
AD 782 844/5GI.

Table 2 Response of Ion Mobility Spectrometer
to Selected Compounds

<u>Selected Compounds</u>	<u>Positive Ion Response</u>	<u>Negative Ion Response</u>
<u>Drugs</u>		
Cocaine	Yes	No
Heroin	Yes	No
Heroin (Street)	No	No
Marijuana	No	No
Morphine Sulphate	No	No
<u>Explosives</u>		
C-3	No	No
C-4	No	No
Comp B	No	No
Dynamite	No	Yes
Dynamite, Gelatin, 40%	No	Yes
Dynamite, Gelatin, 50%	No	Yes
Dynamite, Gelatin, 60%	No	Yes
Dynamite, Red Cross	No	Yes
Flex-X	No	No
Ethylene Glycol Di-Nitrate (EGDN)	No	Yes
Octol	No	No
PE-2	No	No
PEIN	No	No
Pentolite	No	No
PETN	No	No
P1-NP-10	No	No
RDX, Comp A-3	No	No
RDX (BRL)	No	No
Semtex - H	No	No
Tetryl	No	No
Tetryl, British	No	No
TNT (BRL)	No	No
TNT, Granular	No	No
Nitroglycerine - Lactose	No	Yes
DNT	Yes	Yes
<u>Common Compounds</u>		
Citrus Fruit, Grapefruit	Yes	No
Fertilizer, 10-8-7, Liquid	Yes	No
Gasoline (ARCO Regular) (Getty)	Yes	Yes
Water, Distilled	No	No
Silicone Compound, MIL-S-8660B	No	No

Table 2 Response of Ion Mobility Spectrometer
to Selected Compounds (Cont'd)

<u>Selected Compounds</u>	<u>Positive Ion Response</u>	<u>Negative Ion Response</u>
<u>Gun Related Compounds</u>		
Compound, Heavy	No	No
Corrosive Protective Compound (MIL-C-16130)	No	No
Cosmoline	No	No
Grease, Automotive & Artillery (MIL-C-10924)	No	No
Gun Oil	No	No
Gun Slick	No	No
Rust Inhibiting Grease, RIG Universal	No	No
Solvent, Nitro-Powder, Hoppe's	Yes	No
<u>Chemical Compounds of Interest</u>		
Acetic Acid (Glacial)	Yes	Yes
Acetic Anhydride	Yes	Yes
Acetone	Yes	Yes
Ammonium Hydroxide	Yes	Yes
Citric Acid	No	No
Dimethyl Sulfoxide	Yes	Yes
Ether	Yes	No
Ethyl Alcohol	Yes	No
Pyruvic Acid	Yes	Yes
Benzene	Yes	No

Some results of tests⁴ with the portable electric quadrupole mass spectrometer are given in Table III. This instrument is the most specific of all the detection systems evaluated, and is surprisingly sensitive because of the Llewellyn three stage membrane separator system.

VII. THIN FILM DETECTORS

Thin surface films of platinum, chromium, and gold, plated on metal oxide surfaces, exhibit a change of electrical resistance as molecules of trace gases are adsorbed on the surface. A small, portable, battery-powered unit was developed by ENMET Corporation, Ann Arbor, MI to sample ambient air continuously in environments where trace chemicals from known manufacturing processes could be injurious to health⁵. Ethylene glycol dinitrate and nitroglycerin were detectable at levels of 1-2 parts per million in air. A small piece of dynamite in a briefcase was easily detected if the case was opened slightly.

Detectors of this type can be made more selective in response by using several surfaces of different metal films or by using several surfaces of the same metal held at different temperatures, or both. Although it is probable that a high degree of specificity will not be obtained, this type of detector can be highly useful in environments where the possible trace chemicals are known and an economical, sensitive, and reliable alarm system is necessary.

VIII. BIOLUMINESCENT DETECTORS

Almost all living organisms respond overtly to a number of weak chemical stimuli in their environment, but the easiest response to instrument is possibly the light output from a class of luminescent marine microorganisms. It is an impressive experience to walk into a dark room stocked with these microorganisms and be greeted with a sudden increase in luminescence, occurring in less than a second. This light output can be easily converted by a photocell or photomultiplier into an electrical signal which can be processed electronically.

A number of luminescent microorganisms show considerable sensitivity perhaps down to parts per billion, but are not very specific. Just as a hungry person will salivate when assailed with any one or more of a large number of food odors, a luminescent microorganism will show an interest or disinterest in a large number of trace chemicals in the air. Significant progress⁶ has been made in producing strains of bacteria with more

⁴U.S. Army Land Warfare Laboratory Technical Report, LWL-TR-74-86. AD 922 188L.

⁵U.S. Army Land Warfare Laboratory Technical Report, LWL 74-11, AD 917 291L.

⁶U.S. Army Land Warfare Laboratory Technical Report, LWL-CR-01C69.

Table 3 Results of Sensitivity Measurements on
Quadrupole Mass Spectrometer

<u>Compound</u>	<u>Sensitivity</u>	<u>Comments</u>
Acetic Anhydride	4 ppb	Measured with gas mixtures <u>and</u> dilution system.
Perchloroethylene	0.1 ppb	Extrapolated from measurements with gas mixtures <u>and</u> dilution system.
TNT	25 ppb	Measured with dilution system.
Cocaine	74 ppb	Measured with diluted system.

specific responses and in working two or more strains concurrently to provide more information about an unknown odor. It is possible, for example, to expose three selected strains of bacteria to a given odor and have two emit more light and the third emit less light.

The response of two strains of bioluminescent detectors to a number of chemicals is listed in Table IV. Quantitative measurement in the dilution facility showed that the threshold level of TNT for this particular detector combination was 30 parts per billion with a three to one signal to noise ratio. Although greater sensitivity is probable for this type of detector, its sensitivity to such a large number of chemicals will in many situations make it difficult to have confidence about what was detected but may not be a problem in some special situation where chemicals other than the ones of interest would not be present.

IX. ANIMAL CAPABILITIES

The phenomenal sensitivity of animal olfactory systems to selected odors has been the subject of much curiosity and investigation. Dogs have been used for centuries for tracking and hunting, and pigs have been used to seek truffles in France. Recent problems with explosives, drugs and buried cadavers have renewed the interest in using dogs in police detection work. Trained detector dogs have been calibrated in the dilution facility against known chemical sensors⁷ for ethylene glycol dinitrate (EGDN). EGDN is an ingredient in commercial dynamites and, due to its relatively high vapor pressure, is the predominant vapor of dynamite. The results were complicated by the facts that dogs are unique creatures with wills of their own and that EGDN is not their favorite odor.

Two male German sheperds and one female Standard Poodle were trained by the Southwest Research Institute (SWRI) to examine three sampling funnels for the presence of EGDN. Each dog was trained to sit at a funnel containing EGDN or to return to the handler if no EGDN was present. During a given trial, as described above, EGDN was supplied to one or none of the sampling funnels by the system depicted in Figure 1. In a positive trial, one funnel had EGDN; in a negative trial, no funnel had EGDN.

When strong EGDN samples were interspersed with samples containing no EGDN, the dogs identified the strong samples 100% of the time but mis-called 5% of the samples without EGDN. When the EGDN level was reduced to 110 parts per billion, positive and negative samples were identified correctly 55% of the time. If the dog had no sense of smell and only guessed at each of the three funnels in a random sequence with no bias

⁷Herbert M. Gage and William A. Wall, USA LWL TR-74-14, "An Investigation of the Sensitivity of Trained Detector Dogs for Vapors of the Explosive EGDN", May 74. AD 920 663L.

Table 4 RPC Bioluminescent Detector Test Results, Summarized

<u>Chemical Compounds of Interest</u>	<u>TNT⁽¹⁾ Sensor</u>	<u>Dynamite⁽²⁾ Sensors</u>
<u>Drugs</u>		
Cocaine	No	No
Heroin	No	No
Heroin (Street)	No	No
Marijuana	No	No
Morphine Sulphate	No	No
<u>Explosives</u>		
Black Powder	Yes	Yes
C-3	Yes	No
C-4	Yes	No
Comp B	Yes	Yes
Dynamite	Yes	Yes
Dynamite, Gelatin, 40%	Yes	Yes
Dynamite, Gelatin, 50%	Yes	Yes
Dynamite, Gelatin, 60%	Yes	Yes
Dynamite, Red Cross	Yes	Yes
Flex - X	No	No
Ethylene Glycol Di-Nitrate (EGDN)	Yes	Yes
Octol	Yes	No
PE-2	No	No
PEIN	No	No
Pentolite	No	No
PETN	No	No
PL - NP - 10	No	No
RDX, Comp A-3	No	No
RDX (BRL)	No	No
SEMTEX - H	No	No
Tetryl	No	No
Tetryl, British	No	No
TNT (BRL)	Yes	No
TNT, Granular	Yes	No
Nitroglycerine on Lactose	Yes	Yes
<u>Common Compounds</u>		
Citrus Fruit, Grapefruit	No	No
Fertilizer, 10-8-7, Liquid	No	No
Gasoline (ARCO Regular) (Getty)	Yes Yes	Yes Yes
Heating Oil	No	No
Water, Distilled	No	No
Silicone Compound, MIL-S-8660B	Yes	Yes
Sugar	No	No

Table 4 RPC Bioluminescent Detector Test Results,
Summarized (Cont'd)

<u>Chemical Compounds of Interest</u>	<u>TNT⁽¹⁾ Sensor</u>	<u>Dynamite⁽²⁾ Sensors</u>
<u>Gun Related Compounds - Cleaners, Preservatives, Coatings</u>		
Compound, Heavy	No	No
Corrosive Protective Compound (MIL-C-16130)	Yes	No
Cosmoline	No	No
Grease, Automotive & Artillery (MIL-C-10924)	No	No
Gun Oil	No	No
Gun Slick	No	No
Rust Inhibiting Grease, RIG Universal	Yes	No
Solvent, Nitro-Powder, Hoppe's	Yes	Yes
<u>Chemical Compounds of Interest</u>		
Acetic Acid (Glacial)	Yes	No
Acetic Anhydride	Yes	No
Acetone	No	No
Ammonium Hydroxide	Yes	No
Benzene	Yes	Yes
Citric Acid	No	No
Dimethyl Sulfoxide	Yes	Yes
Ether	No	No
Ethyl Alcohol	No	No
Pyruvic Acid	No	No
Potassium Chloride	No	No
Match Heads	No	No

No - Sensor(s) did not respond with an identifying signature, i.e., no detection.

Yes - Sensor produced a signature indicating a detection.

(1) - Based on only one available sensor (negative). A matching positive TNT sensor will eliminate some of these detections.

(2) - Results based on reactions of a matched pair of dynamite sensors where detection depends on the simultaneous, significant deflections. (Positive sensor deflects in a positive direction and the negative sensor deflects in a negative direction.)

toward guessing either positive or negative, he would be right 12.5% of the time for a negative trial and 29% for a positive trial. If he always gave a positive response in the hope of a better reward, he would be right 0% of the time for the negative trials and 33% for the positive trials.

At 40 parts per billion EGDN, the dogs were correct 33% of the time for both positive and negative samples.

A number of pitfalls in this type of experiment are readily recognized. The average dog is much more interested in some odors than in others, and does not detect all odors with equal sensitivity. The concept of the average dog is about as valid as that of the average human. A bias in positive and negative responses could have been induced by training procedures, which rewarded correct positive responses with food and correct negative responses with words. The dog, having the capability to learn and associate, may have developed cues other than olfactory or have learned on a mixture of odors unknown to the trainers. The dogs could be confused by other odors in the room, including some EGDN contamination. The resolution of these kinds of conjectures must come from careful studies of animal behavior coupled with accurate laboratory measurements.

Insects were studied briefly as detectors of personnel and drugs. Hungry Mexican bedbugs can detect very low concentrations of human odor and become very excited in anticipation. The problems with such detectors were numerous, but perhaps the most inimical were psychological. The humor and derision made a serious study difficult. Maintaining a bedbug in the most effective state of hunger was an uncertain affair. Motivating a soldier to carry a detector, held out in front of him on a stick, ahead of a squad advancing upwind toward a possible enemy position, was viewed as a serious obstacle.

It was thought that fruit flies, fed in the larval stage on diets of marijuana and heroin, might as adults retain a strong interest in these drugs. The ability of fruit flies to search for and congregate on interesting sources of odor was evident, but it was also apparent that the natural interest in a number of usual foods far outweighed the unnatural interest conditioned by feeding in the larval stage⁸.

Electronic detectors can be put on the shelf and stored in a reasonably harsh environment when not in use. They are fairly consistent from one instrument to another. Animal detectors must be cared for all the time in a reasonably controlled environment and may show a dismaying individuality. There are strong social attachments possible between animals and men and there are the problems of disease, nourishment, and continued training. These factors are important in the use of animals as effluent detectors and should be considered seriously before a large investment is made.

⁸U.S. Army Land Warfare Laboratories Technical Report, LWL-CR-08B73. AD 772 965.

X. REMOTE SENSORS

A remote sensor offers the opportunity of covertly examining more space in less time from a better location. In concept, the ideal remote sensor for trace chemicals in the atmosphere should present a picture of the natural terrain with an image of the chemical plume superimposed on it. The optics should permit a large field of view for search and a small field of view for observational detail. The principal problem is to give roughly equal weight to our perception of a very tenuous plume and its background, which may be sky or landscape. There are advantages to using a passive system, i.e., one which uses electromagnetic energy available from the chemical plume and its background.

It is a general fact that electromagnetic emissions and absorptions by free molecules and atoms of a specific gas are characterized by sharp spectral lines whereas the background of the solid terrain is characterized by broader spectral distributions of emission and absorption, as shown in Figure 5. In principle, the ratio between the amount of energy received from a line characteristic of a given molecule and the general background can be varied by adjusting the bandwidth $\Delta\lambda$ associated with an observation. Suppose that a system, such as that depicted in Figure 6, admits radiation from a chemical cloud through a narrowband filter to a light amplifier in front of a TV camera. The signal from the camera is amplified and processed for desired contrast and displayed on a cathode ray tube. This would be close to an ideal system if it could be achieved.

The problems with this system are several. Good filters, with the capability of admitting several wave lengths characteristic of a given molecule while being narrow band in the regions of interest, are necessary for high sensitivity and specificity. Good filters are more easily obtained for the longer wavelengths, but detectors are better for the shorter wavelengths. Only atoms and simple molecules have the sharp spectral lines necessary to achieve a reasonable contrast between radiations from the chemical cloud and its background. Nevertheless, a number of systems, now in existence in prototype or commercial form, offer several of the features of the ideal system, and perform excellently for some applications.

The Barringer UV correlation spectrometer is a good example of an instrument which has achieved remarkable sensitivity and specificity in examining incoming radiation from a small solid angle, 3 milliradians by 10 milliradians. A correlation spectrometer permits energy from several narrow spectral regions, corresponding to emissions or absorptions characteristic of a given molecule or atom, to be examined simultaneously. The result is that an operation such as shown in Figure 7 can be conducted very efficiently. Sunlight passing through the SO₂ cloud is absorbed selectively in the ultraviolet, and the spectrometer, with its small-field of view, is designed to detect this absorption. By making orderly traverses of the terrain, a map of the SO₂ concentrations can be made.

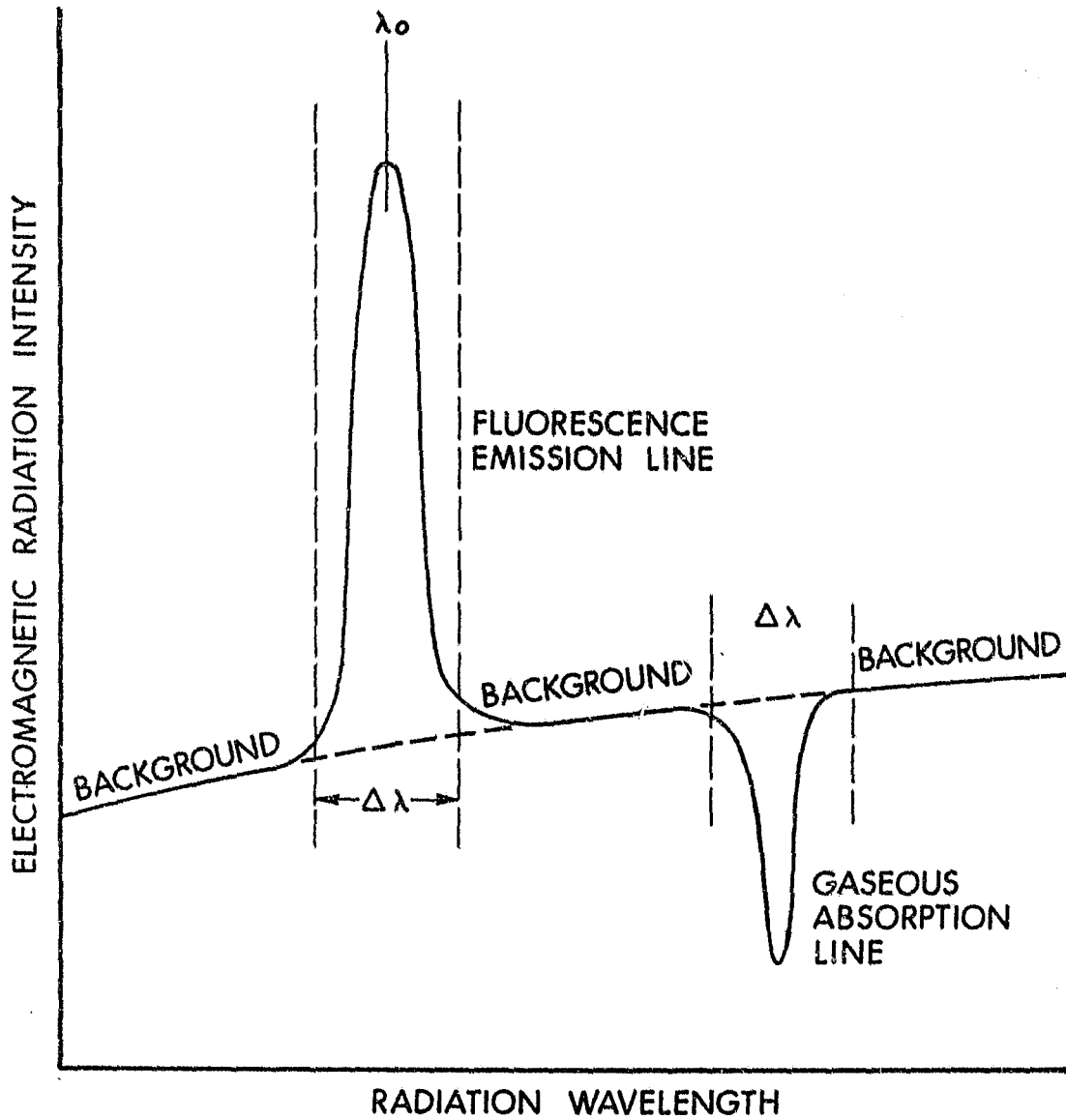
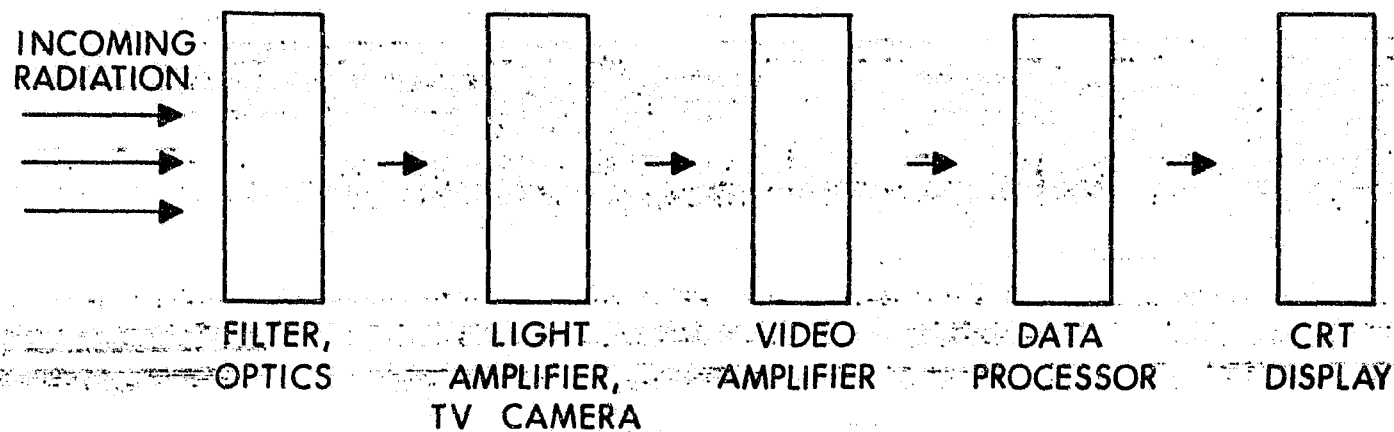
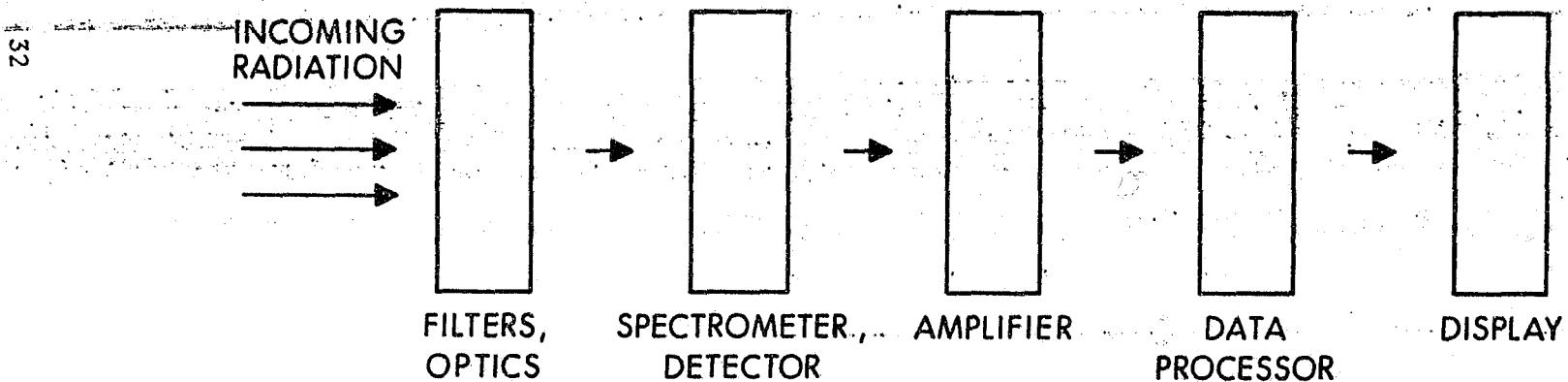


Figure 5 A Depiction of Sharp Absorption and Emission Lines in a Slowly Varying Background

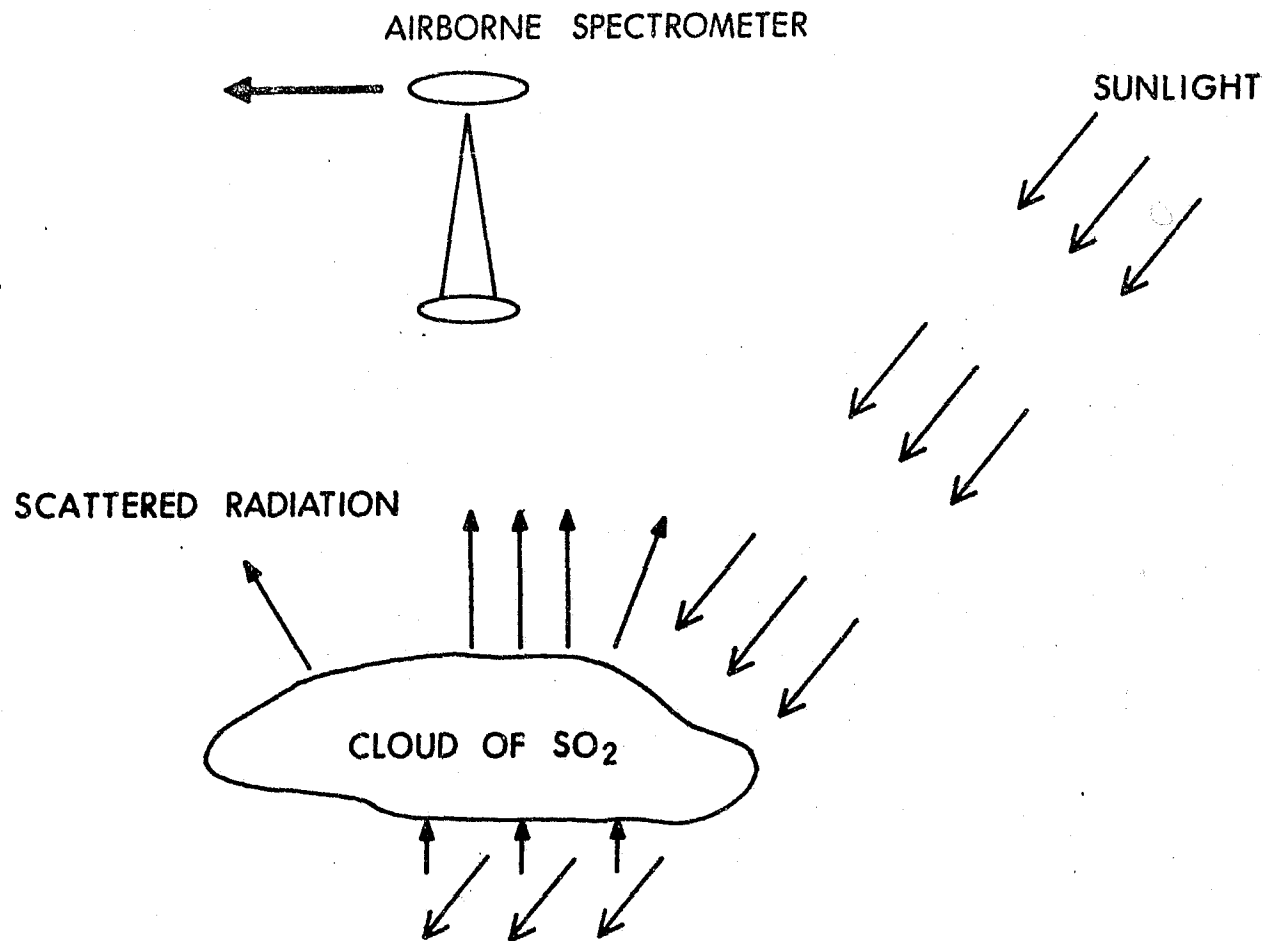


(a) A CONCEPTUAL SYSTEM FOR PLUME SURVEILLANCE



(b) A SYSTEM BASED ON SPECTROMETRY

Figure 6 Some System Concepts for Remote Sensing



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Figure 7

View of the Barringer Correlation Spectrometer to Survey the Landscape for SO₂ Emissions

The Barringer Correlation Spectrometer was adapted to detect NO₂ and used to observe internal combustion engines remotely from a tower⁹, ¹⁰. NO₂ was detected in the exhaust of a small automobile at a range of 500 meters and in the exhaust of a 30 KVA diesel generator at a range of more than 1000 meters.

Many molecules have well-defined infrared emissions and absorptions associated with the vibration-rotation energy levels. It has become possible, with the development of good optics and low-cost digital computers, to design an infrared interference spectrometer which is capable of extracting an energy spectrum from radiation arriving from a distant source¹¹. Infrared radiation, after suitable filtering to remove as much extraneous information as possible, is admitted to an interferometer, which serves the purpose of converting the spectral distribution of the incoming radiation to a time-varying electrical signal. This electrical signal is digitized and processed by computer to extract the energy spectrum of the incoming radiation. This spectrum may be correlated by computer with the stored spectrum of a chemical of interest or be used directly to identify the chemicals which modified the spectrum of the incoming radiation.

Test experience with an infrared correlation spectrometer was disappointing, but there was general agreement that most of the operational inadequacies could be removed by evident and modest engineering changes. This type of spectrometer has found useful application in infrared emission studies.

A breadboard system similar to that depicted in Figure 7 was designed to show the feasibility of thermal imaging systems. Using a narrow band filter in the 3.3-3.54 μ region and a liquid nitrogen cooled vidicon tube¹², a cloud of methane was imaged successfully in the laboratory by radiation emission from a vibration-rotation transition. Failure of the experimental vidicon tube prevented the extension of the effort to a field demonstration.

An instrument of this type has great potential for remotely locating natural gas leaks and gasoline pollution of the air by rapid aerial survey.

The use of radar techniques in active remote sensing has been considered from a number of viewpoints. Laser ranging is quite practical for determining the location of aerosol clouds. Examination of the returning laser radiation for Raman shifts unique to a specific chemical has been tried, but the fraction of returned energy associated with a given Raman transition is prohibitively small. Fluorescence and resonance scattering of laser beams may provide more return, and may provide the basis for active remote sensing systems associated with certain simple molecules and atoms.

⁹U.S. Army Land Warfare Laboratory Technical Report, LWL-CR-05C70. AD 884 736L.

¹⁰U.S. Army Land Warfare Laboratory Technical Report, LWL-CR-05C70A. AD 776 378.

¹¹U.S. Army Land Warfare Laboratory Technical Report, LWL-CR-05C70B. AD 718 210L.

¹²U.S. Army Land Warfare Laboratory Technical Report, LWL-CR-02C72.

XI. SUMMARY AND PROGNOSTICATION

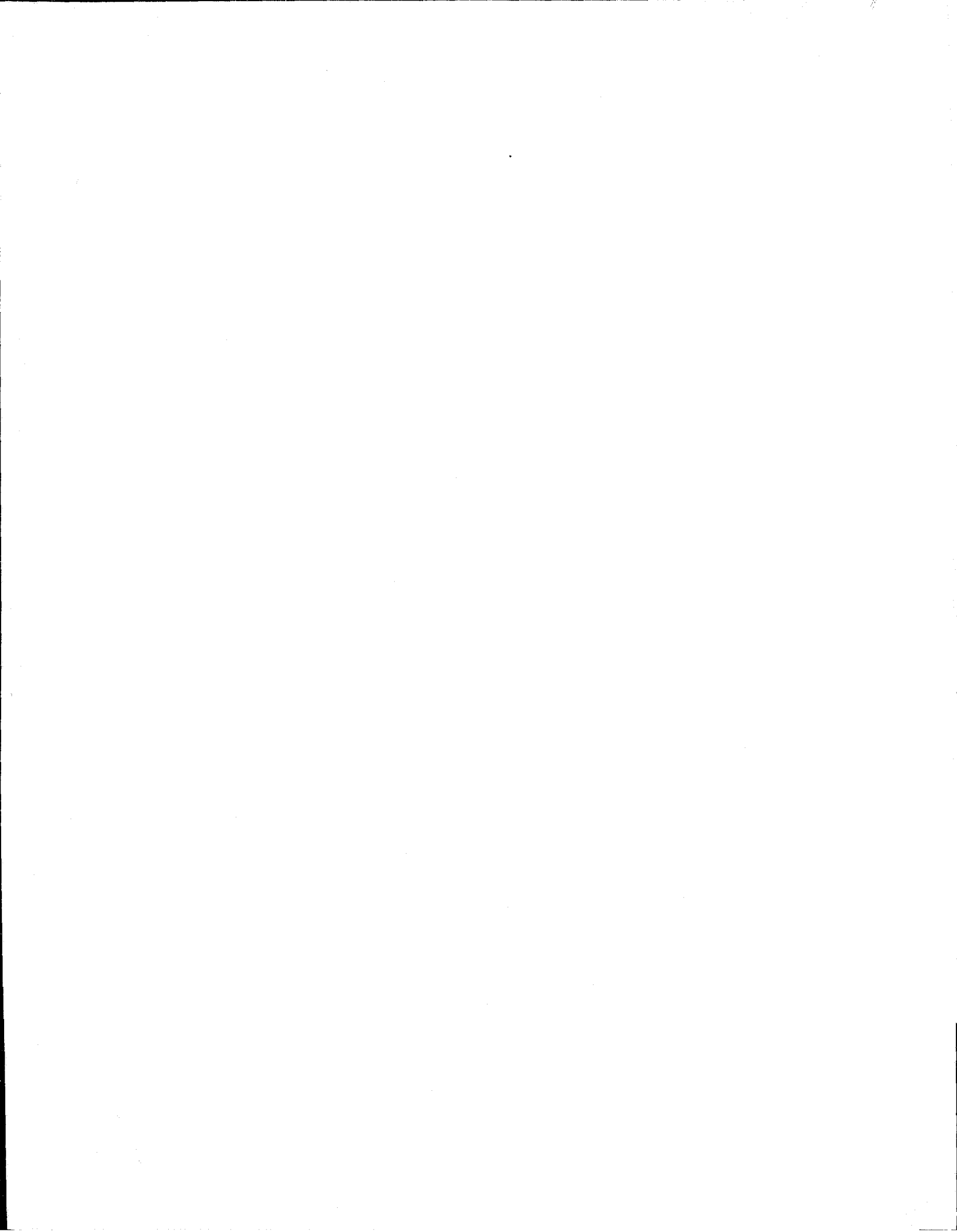
A number of sensors for trace chemicals in the atmosphere have been designed and tested for sensitivity and specificity in both laboratory and field conditions. More and better sensors will be developed as the new health and safety standards are reflected in industrial practice and as the demands of environmental legislation are implemented. Law enforcement officials will find application for a number of these in their efforts to combat continuing drug and explosive problems. The US Army will have a strong interest in these developments because of its concern for employee safety, law enforcement, and military surveillance.

ACKNOWLEDGEMENTS

This summary paper on detectors for trace chemicals in the atmosphere has borrowed freely from work, reported and unreported, by a number of people in the now disestablished U.S. Army Land Warfare Laboratory. Several of the Tables and Figures and some descriptive material were borrowed from the referenced reports of Wall and Gage. Some of the instrument developers, notably Dr. James Arnold of Varian, Dr. Sidney Fisher of Franklin Institute, Dr. R. R. Sakaida of the RPC Corporation, assisted with measurements made on their detectors, and they are due apologies for the almost cursory treatment of a situation in which they were deeply involved and to which they dedicated much time and talent. Finally, the Presidential Internship Program of the National Science Foundation made it possible for Dr. William Wall to join the Landware Laboratory and begin the work.

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