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LABORATORY EVALUATION OF DETECTORS OF EXPLOSIVES' EFFLUENTS

J. E. Cline
J. R. Hobbs
A. E. Barrington
Transportation Systems Center
Kendall Square
Cambridge, MA. 02142

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16. Abstract

This document contains the classification, technical description and laboratory evaluation of five commercial detectors for explosives' effluents. It includes an outline of operating principles, test and evaluation procedures. The evaluation is based on laboratory tests at TSC, tests at Logan Airport and in another government laboratory. The five detectors are the Varian Chemical Vapor Analyzer (mass spectrometer), Franklin GNO Plasma Chromatograph, Panametrics Panatek 3000 Leak Detector (Electron Capture Detector), Hydronautics Vapor Trace Analyzer (gas chromatograph) and RPC bioluminescence detector. The descriptive and technical details of the five commercial detectors are summarized in Appendix A. The results of a novel investigation to determine the mass spectrometer signature of dynamite effluent are presented in Appendix B.

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PREFACE

The work described in this report was performed in the context of an overall program at the Transportation Systems Center concerned with the assessment of various techniques for Civil Aviation Security. The program is sponsored by the Department of Transportation through the Office of the Secretary of Transportation.

Table of Contents

List of Illustrations

1.0 Introduction

It is the purpose of this report to present a classification and comparative technical evaluation of five commercial instruments for effluent detection. Four of these instruments were purchased and tested extensively at TSC under laboratory conditions; the fifth was tested only briefly in another government facility for a preliminary sensitivity evaluation.

2.0 Classification of Effluent Detectors

The instruments evaluated in this report, shown in Figure 1, fall into three groups, according to the detection technique employed: (1) Ionic Mass Separation - in this method an air sample containing the effluent is ionized, the ions are separated by electric or magnetic forces and the presence of the effluent is established from a characteristic instrumental signature measured electrically; (2) Electron Capture Detection - in this method, negative ions of the effluent in an air sample are produced preferentially and measured electrically. For improved specificity, physical separation of the gas sample by a membrane or chromatographic column may precede the ionization process; (3) Detection of Bioluminescence - in this method, the light level produced by a special strain of marine bacteria is changed by the presence of explosives effluent. The change and/or rate of change of light level produces a characteristic signature which is measured electrically. A more detailed description of these techniques follows.

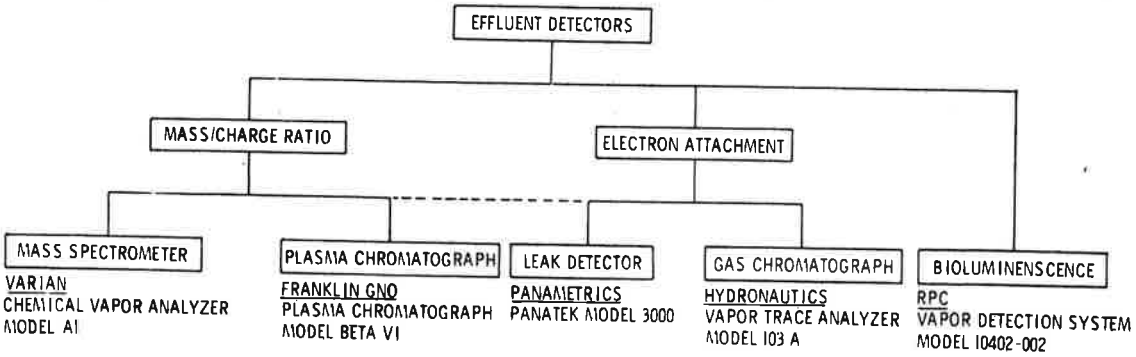


Figure 1 Classification of Effluent Detectors

2.1 IONIC MASS SEPARATION

If molecules of a sample containing a mixture of gases are charged electrically (ionized), it is possible to perform a separation of these charged molecules (ions). The mechanism of ion formation and subsequent ion separation depends on the ambient pressure at which a particular ionic mass analyzer is operated. If ionization occurs at an ambient pressure equal to or below 10^{-4} torr, discrete ionized molecules of the various constituents of a gas sample are produced, as are ionized fragments of these molecules. No significant collisions between ions and neutral molecules occur, and analysis is performed by accelerating the ions in an electric field and separating them according to their mass/charge ratio in an electric or magnetic field. If ionization occurs at atmospheric pressure, charged molecules can collide with other charged or neutral molecules leading to the formation of charged clusters of molecules. Such clusters can be accelerated electrically, but their motion is impeded by collision with neutral molecules of the ambient gas. Separation and identification of charged clusters depends not only on mass/charge ratio but also on a factor termed "mobility", which in turn depends on the applied electric field and the operating pressure in the analyzer. The instrumental signatures of the various constituents are generally complex and, in only the simplest cases, are identifiable without some data processing.

2.1.1 Mass Spectrometry

In mass spectrometers[1], the production of the ions and the separation to determine their mass/charge ratios occur at a pressure low enough (10^{-4} torr) to avoid any significant number of collisions between ions and neutral gas molecules. Thus, the ions produced are generally characteristic of the individual constituents. The magnitude of the ionic charge is equal to the charge of the electron (1.6×10^{-19} coulomb) or an integral multiple thereof. Therefore, the relative value of the mass/charge ratio (m/e) of specific ions is proportional to the ionic mass. Although ions

of particular compounds (CO^+, $N_2^+ \rightarrow$ m/e = 28) or ionic fragments can have nearly identical values of m/e, the yield of characteristic ionic species (i.e., the signature) of a given component is usually specific and reproducible. The numerical value of m/e is expressed in atomic mass units (AMU); it is based on the value of m/e for H^+ equal to 1 AMU.

The principal building blocks of a mass spectrometer are shown in Figure 2. They are a sample introduction system, an ion source, a mass analyzer, and an ion detector. Not shown are the various accessories, which include a vacuum pump. Once the gas sample to be analyzed is partially ionized in the ion source, the ions are sorted according to their mass-charge ratios by magnetic and/or electric fields in the mass analyzer section; and the rate at which such ions pass through the analyzer is measured by the ion detector.

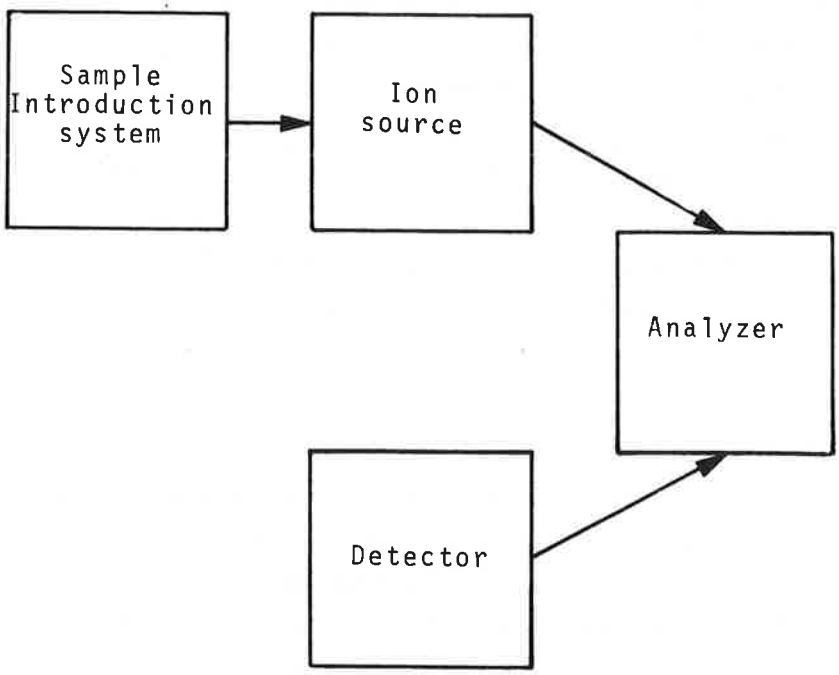


Figure 2 Principal Components of a Mass Spectrometer

In the mass spectrometer evaluated here (Varian Chemical Vapor Analyzer - Figure 3), air is continuously sampled through a three-stage membrane separator (Figure 4). As the air sample passes through successive membranes of the separator from a pressure of 760 torr to a pressure of about 10^{-6} torr required for operation of the mass spectrometer, the concentration of many trace constituents, such as the effluent from dynamite, becomes greatly enhanced. The gas sample is then partially ionized by electron impact. The analyzer section in this instrument is of the quadrupole type (Figure 5), where dc and radio frequency electric fields are applied to two pairs of symmetrically spaced rods. This type of mass analyzer is very compact and analysis can be performed in a short time. Specifically, the mass range of 250 atomic mass units can be covered at a rate of 200 AMU/sec.

Although mass spectrometry is capable of high sensitivity, specificity depends on identification of the instrumental signature for a particular trace constituent. The complexity of this problem is illustrated in Appendix B where a study of the mass spectrometric signature of dynamite effluent is reported.

2.1.2 Plasma Chromatography

In a plasma chromatograph[2], as shown in Figures 6 and 7, the movement of ions that is used to determine their mass/charge ratios occurs at atmospheric pressure. Primary ionization is produced by electrons from a radioactive source (tritium or nickel-63). These electrons rapidly dissipate their energy to a thermal level through inelastic collision with neutral molecules. In these collisions, both positive and negative ions are produced. In normal air, depending on the degree of humidity, the predominant ions are $(H_2O)_nO_2^-$ and $(H_2O)_nH^+$. These hydrated ions react in a few milliseconds with neutral trace gas molecules to form stable complex ions. In the reaction the trace gas (parent) molecule may be fragmented and the final reaction product generally consists of hydrated parent

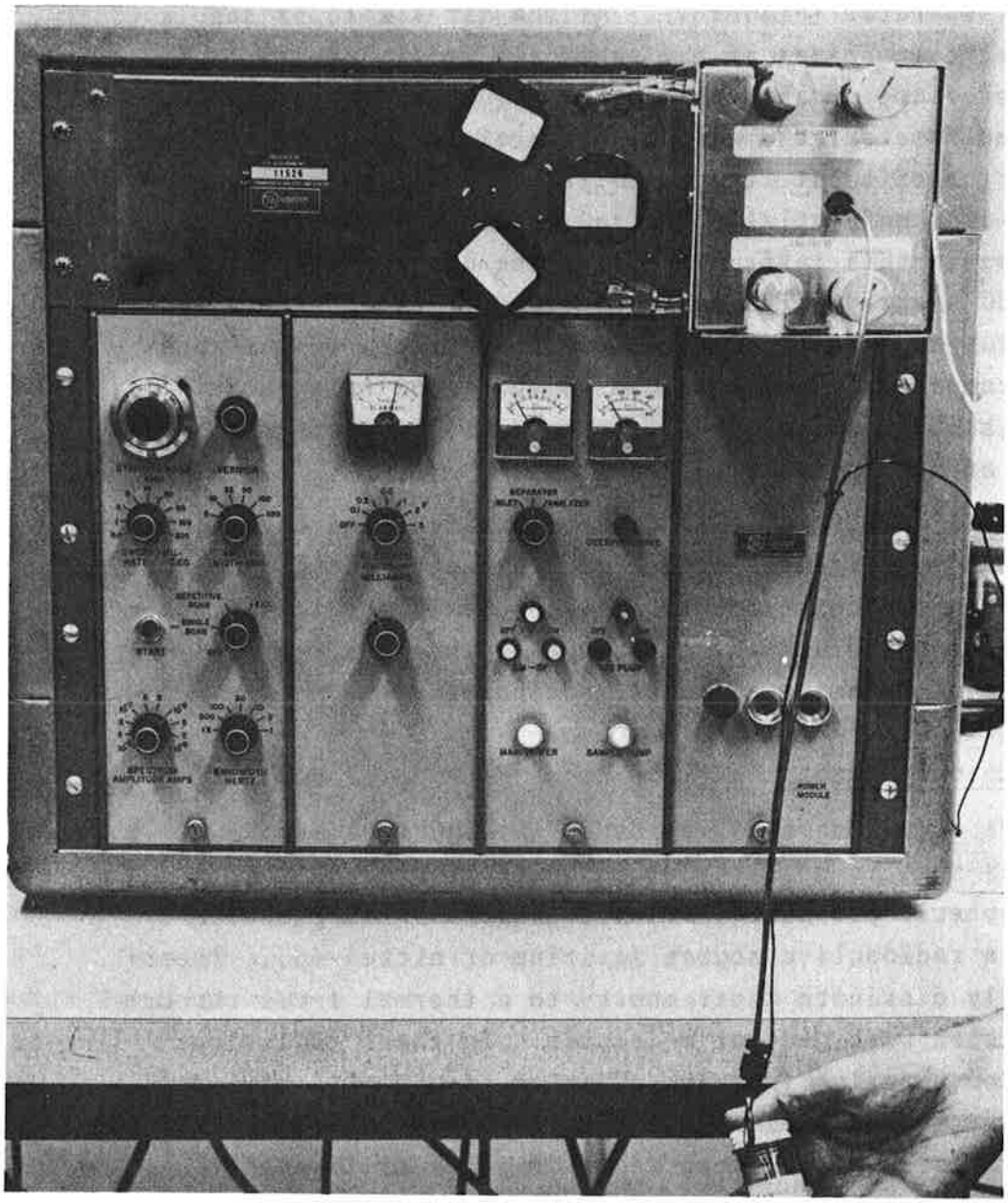


Figure 3 Varian Chemical Vapor Analyzer

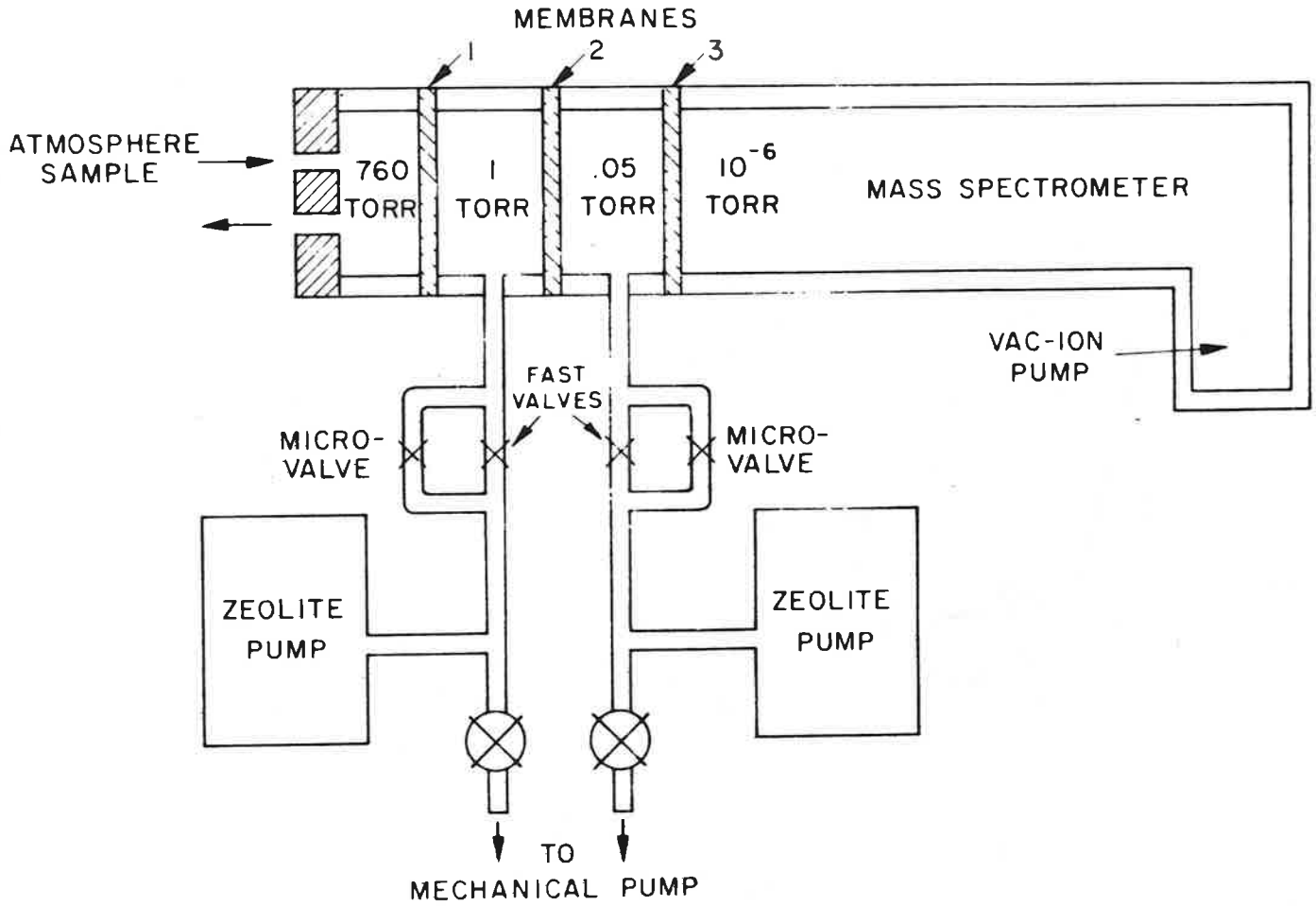


Figure 4 Schematic Representation of Varian CVA with Membrane Separator

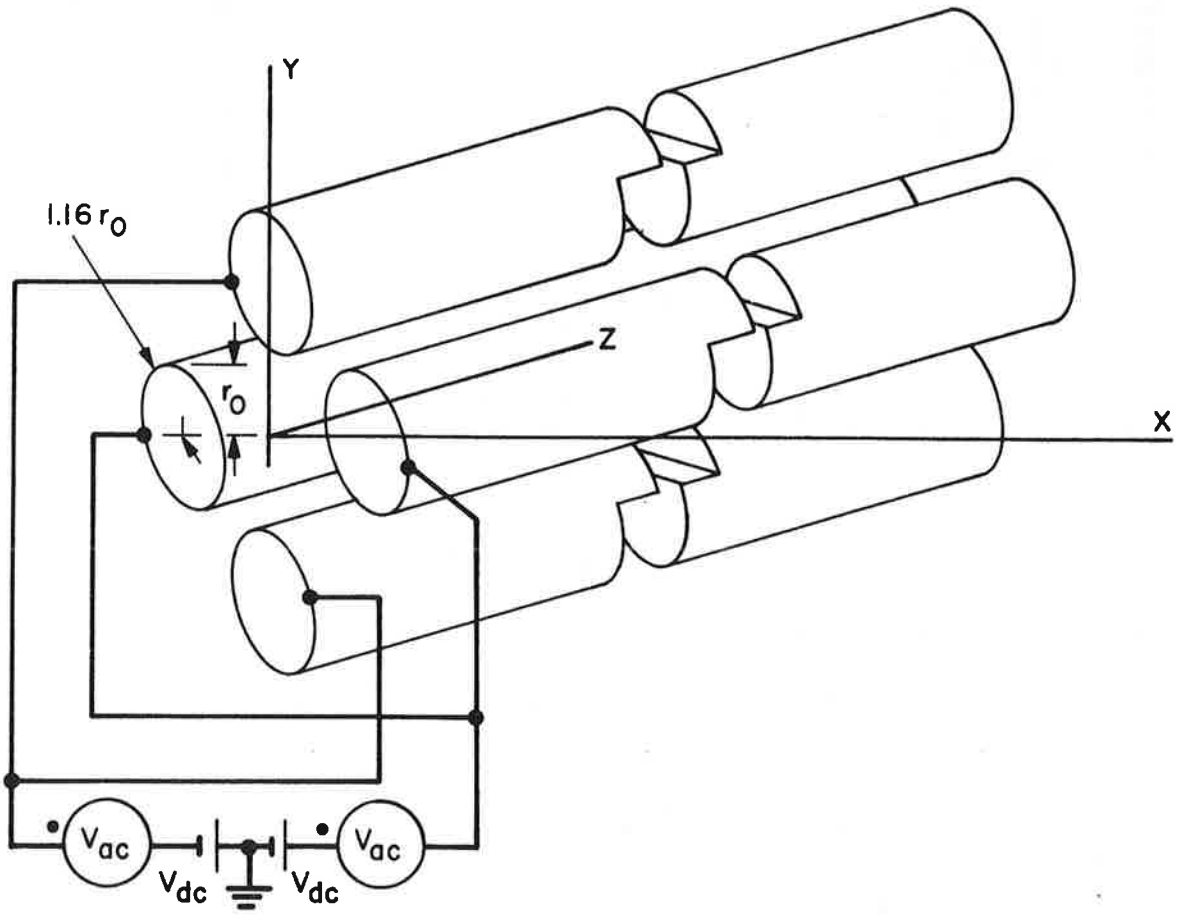


Figure 5 Quadrupole Analyzer Schematic

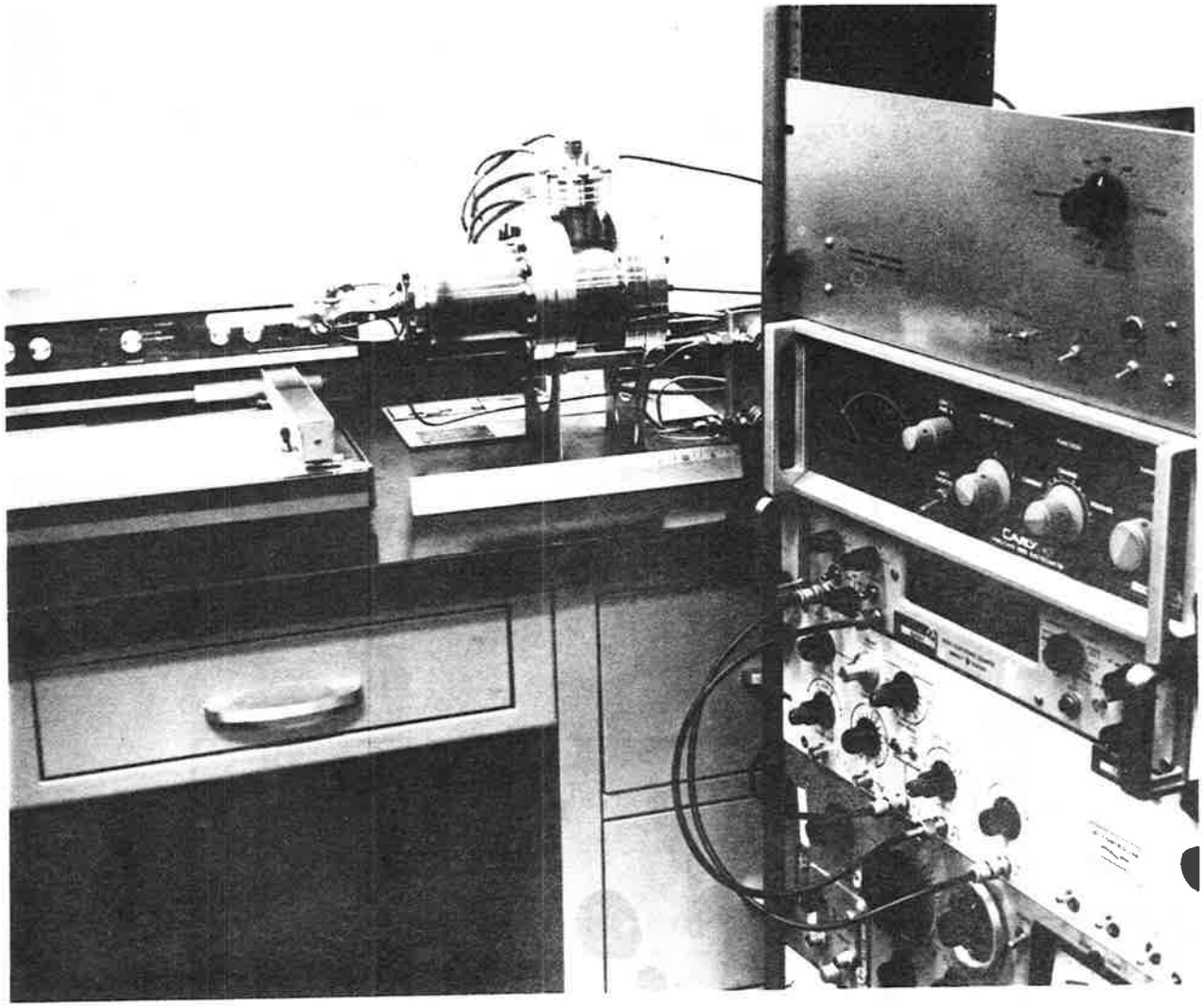


Figure 6 Franklin GNO Plasma Chromatograph

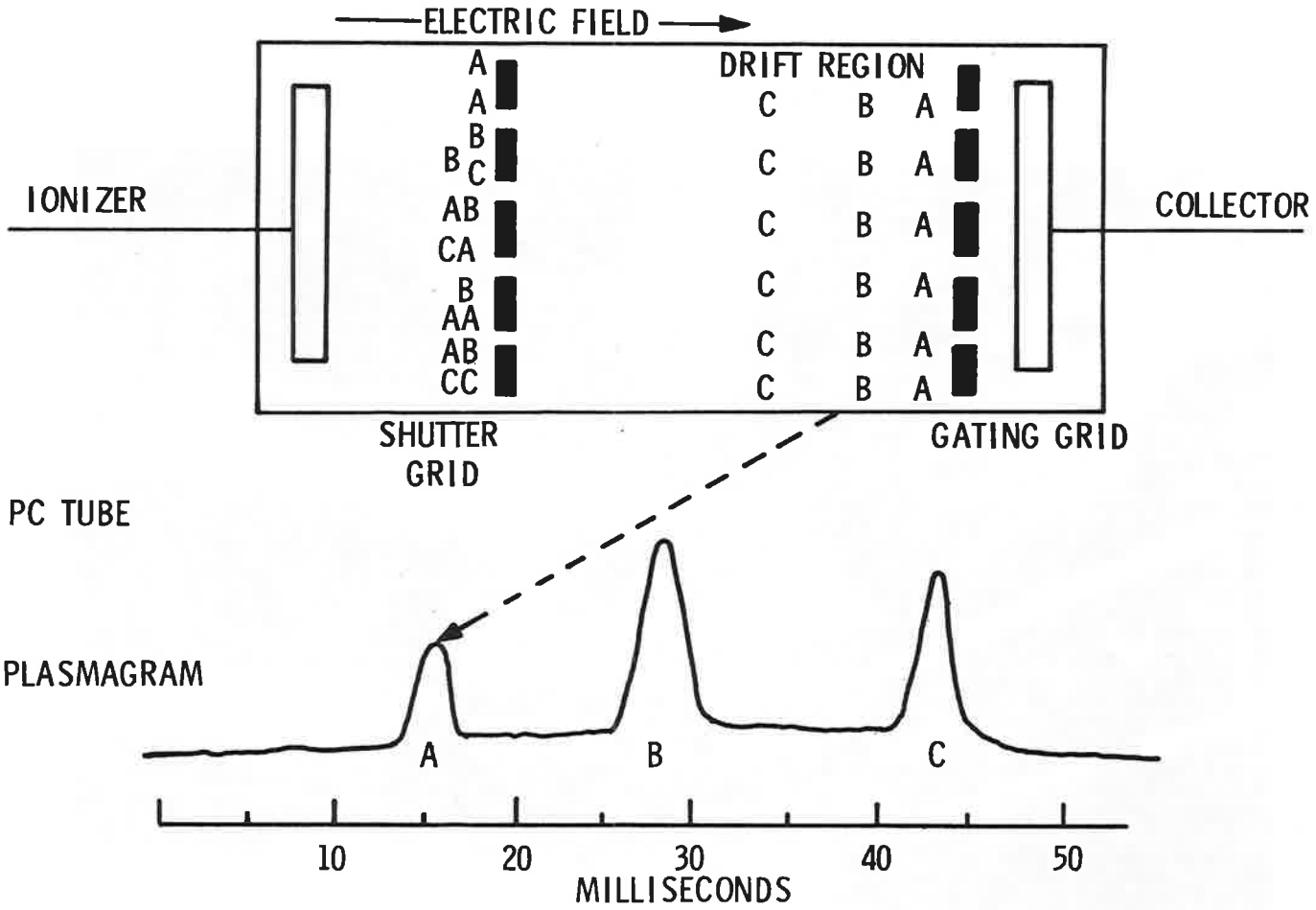


Figure 7 Operating Principle of Plasma Chromatograph

and fragment ions. Separation of the ions is accomplished in a drift region. Here the ions are subjected to an electric field while their motion is impeded by collisions with an inert gas which flows through the drift region. The instrumental signature or "plasmagram" consists of a plot of ion current as a function of drift time through the drift region. The drift time depends, in a manner not completely understood, on ionic mass, electric field in the separator, and ambient pressure, but generally the heavier ions have the longer drift time. Only preliminary data of the instrumental signature of dynamite have been reported[3]. A more detailed investigation is scheduled at TSC.

2.2 ELECTRON CAPTURE DETECTION

In an electron capture detector (Figure 8), primary ionization is produced by electrons from a radioactive source (tritium or nickel-63). These electrons rapidly dissipate their energy to a thermal level through inelastic collisions with the molecules of a carrier gas (helium or nitrogen). The thermal electrons, collected by the anode, constitute a constant (standing) current. Thermal electrons tend to attach with high probability to trace constituents having high electron affinity, if these are injected into the carrier gas. In this case, the standing current is reduced in proportion to the concentration of the trace constituents. Typical molecules which have a high electron affinity are those containing halogen or nitro-groups. Hydrocarbons as may be found in gasoline or jet fuel produce no effect.

2.2.1 Leak Detectors

A commercial instrument, the Panametrics Panatek 3000, (Figure 9) was specifically designed for leak testing of sealed systems containing refrigerant gases which have high electron affinity. It is manufactured by Analytical Instruments, Ltd., England. Similar equipment is used in Northern Ireland by the British Army to detect gelignite (a type of dynamite). In this instrument the

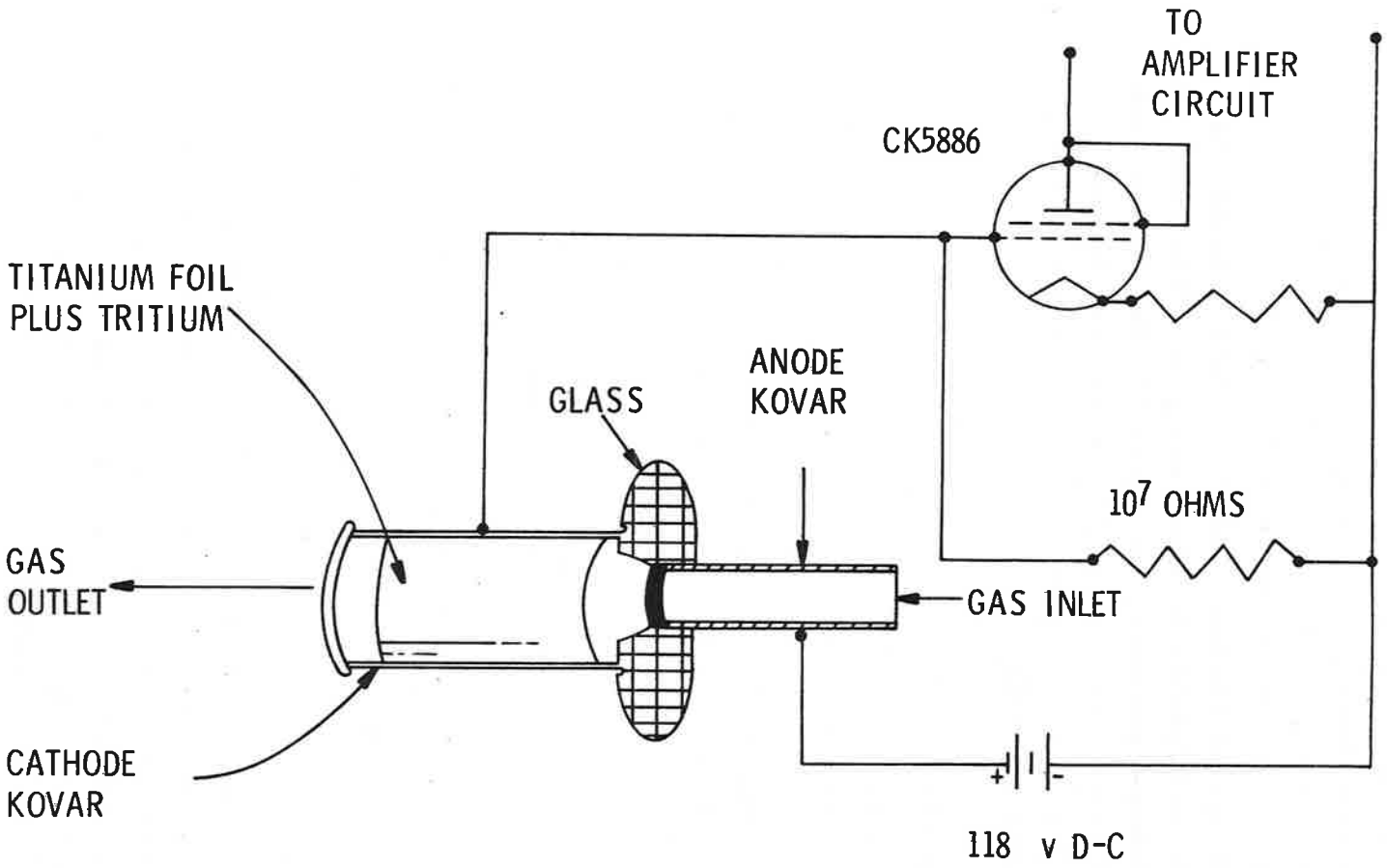


Figure 8 Electron Capture Detector

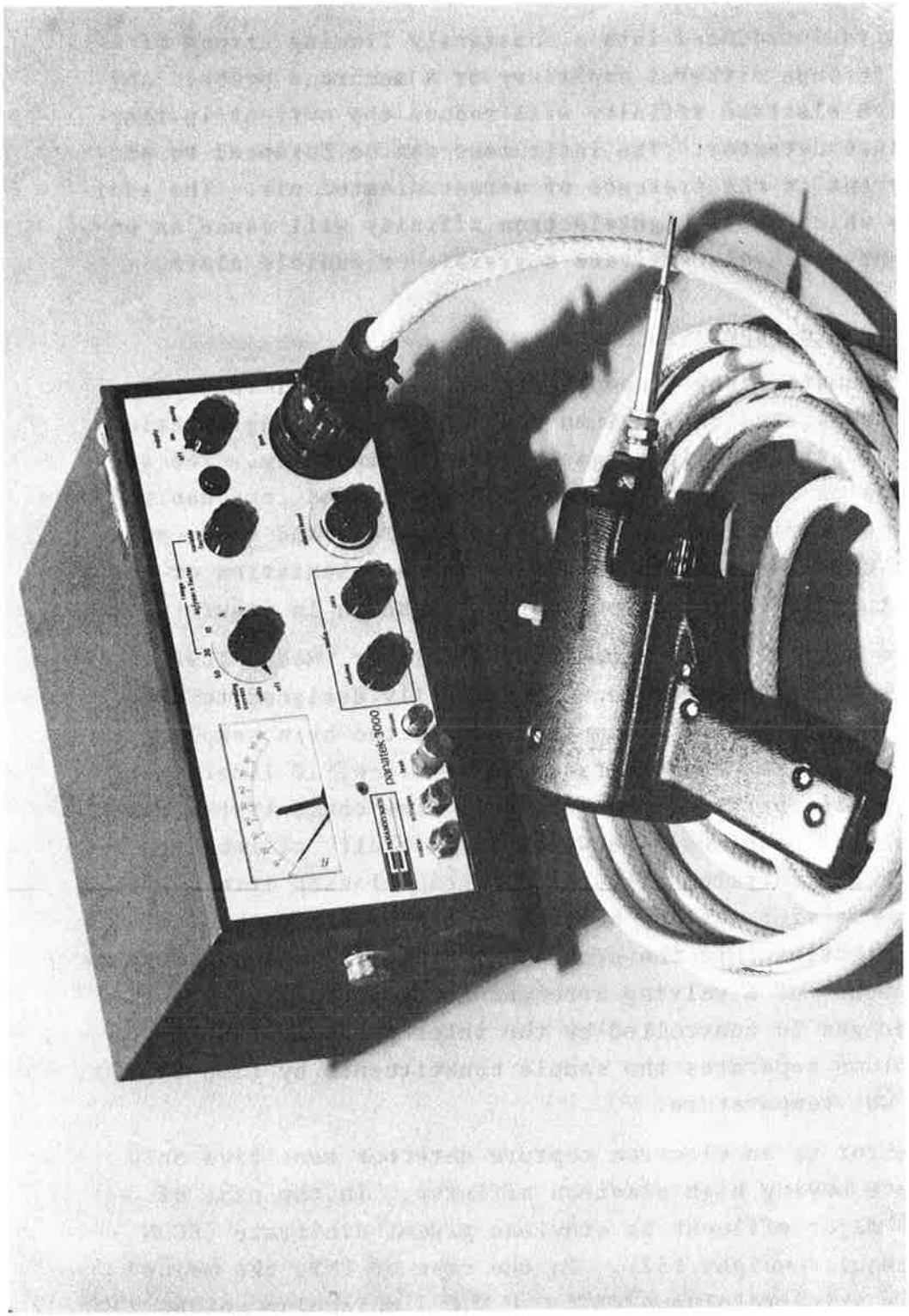


Figure 9 Panatek 3000 Leak Detector

sample of air is introduced into a constantly flowing stream of dry nitrogen through either a capillary or a membrane probe. Any gas having high electron affinity will reduce the current in the electron capture detector. The instrument can be balanced to produce zero current in the presence of uncontaminated air. The addition of a gas which has a high electron affinity will cause an unbalance current which can activate a visible or audible alarm.

2.2.2 Gas Chromatography

In gas chromatography[4], components of mixtures of volatile compounds are separated in a column containing adsorbing material through which a stream of inert gas passes continuously. The separation depends on the retention time of the various components, which depends on their respective vapor pressures, and their solubility in the column material. A schematic representation of the principal features of a gas chromatograph is shown in Figure 10.

The Hydronautics-Israel Vapor Trace Analyzer, Model 103A, (Figure 11) is a gas chromatograph specifically designed to detect explosives effluents. An air sample is collected by a sampling pump and injected into a concentrator at a rate of 10 liters per minute for a preset period (five seconds). The concentrator consists of a coil of platinum wire which is initially at room temperature. The concentrated effluent is then released into a stream of helium (the carrier gas) by heating of the wire. Sample collection and injection into the separator column are sequenced automatically by means of a valving arrangement (Figure 12). The flow of the carrier gas is controlled by the inlet pressure (25 to 40 psi). The column separates the sample constituents by time of passage at a set temperature.

The detector is an electron capture detector sensitive only to constituents having high electron affinity. In the case of dynamite, the major effluent is ethylene glycol dinitrate (EGDN - $C_2H_4N_2O_6$, molecular weight 152). In the case of TNT, the major constituent is trinitrotoluene (TNT-$C_7H_5N_3O_6$, molecular weight 227),

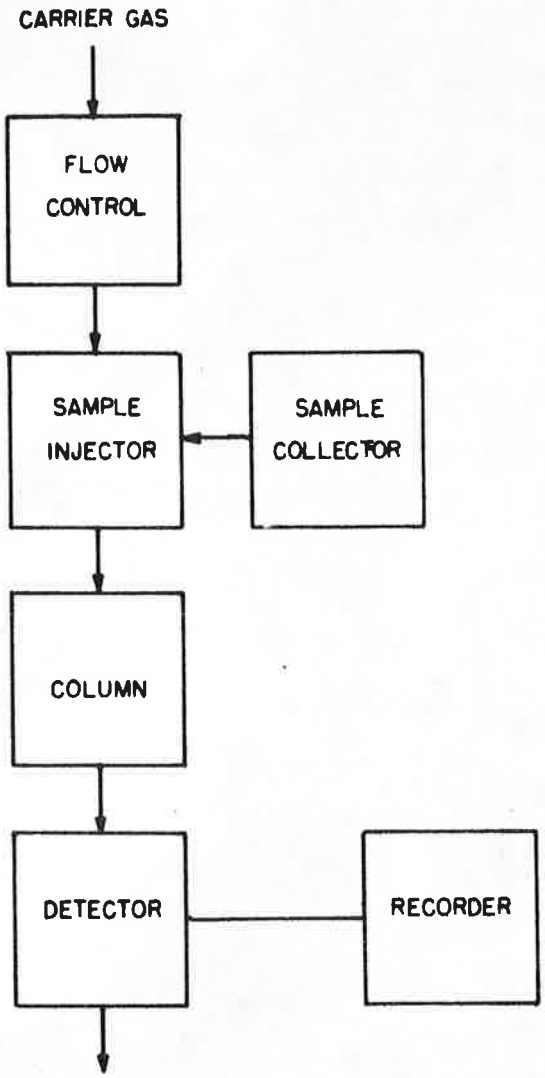


Figure 10 Principal Components of a Gas Chromatograph

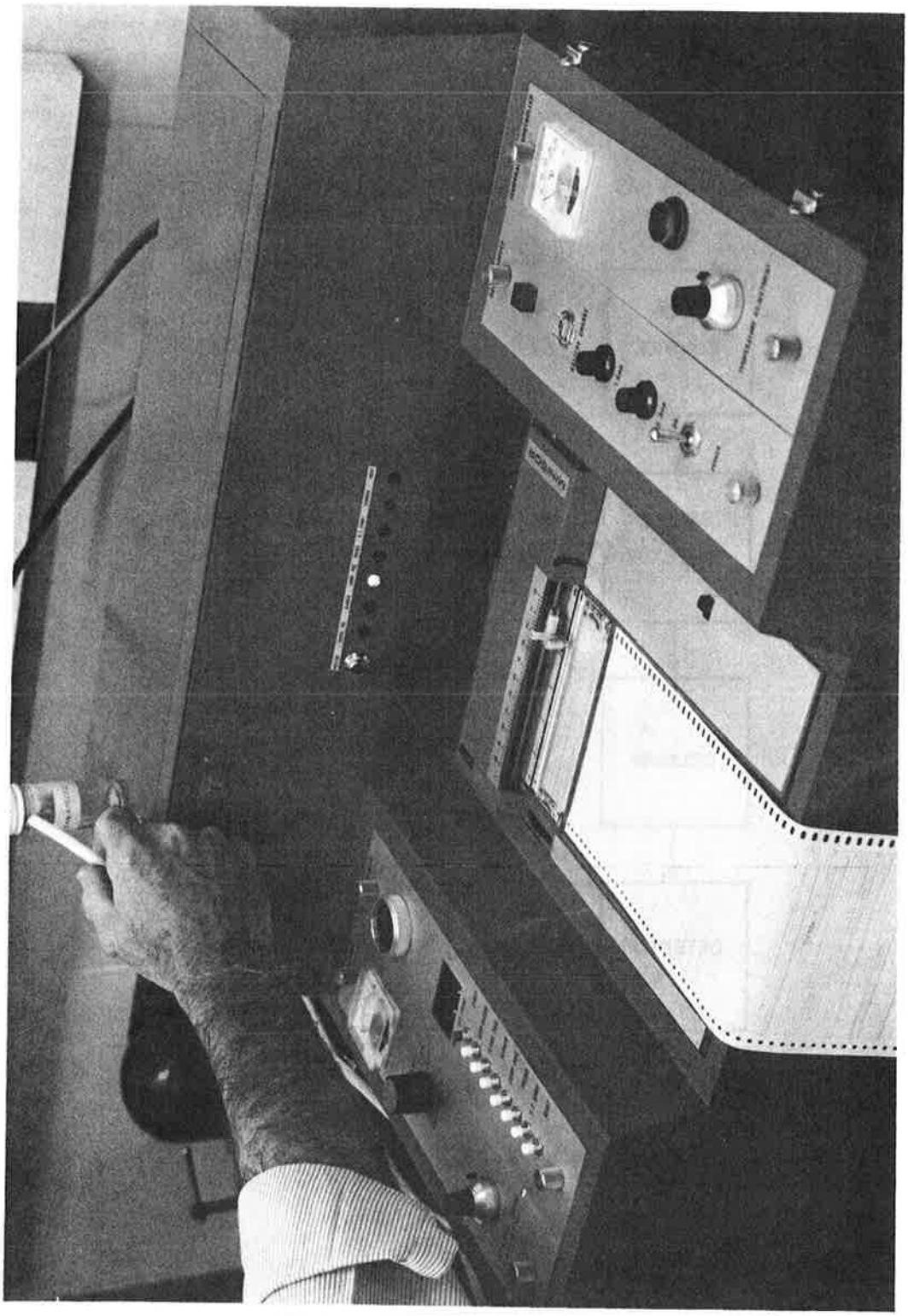


Figure 11 Hydronautics Vapor Trace Analyzer

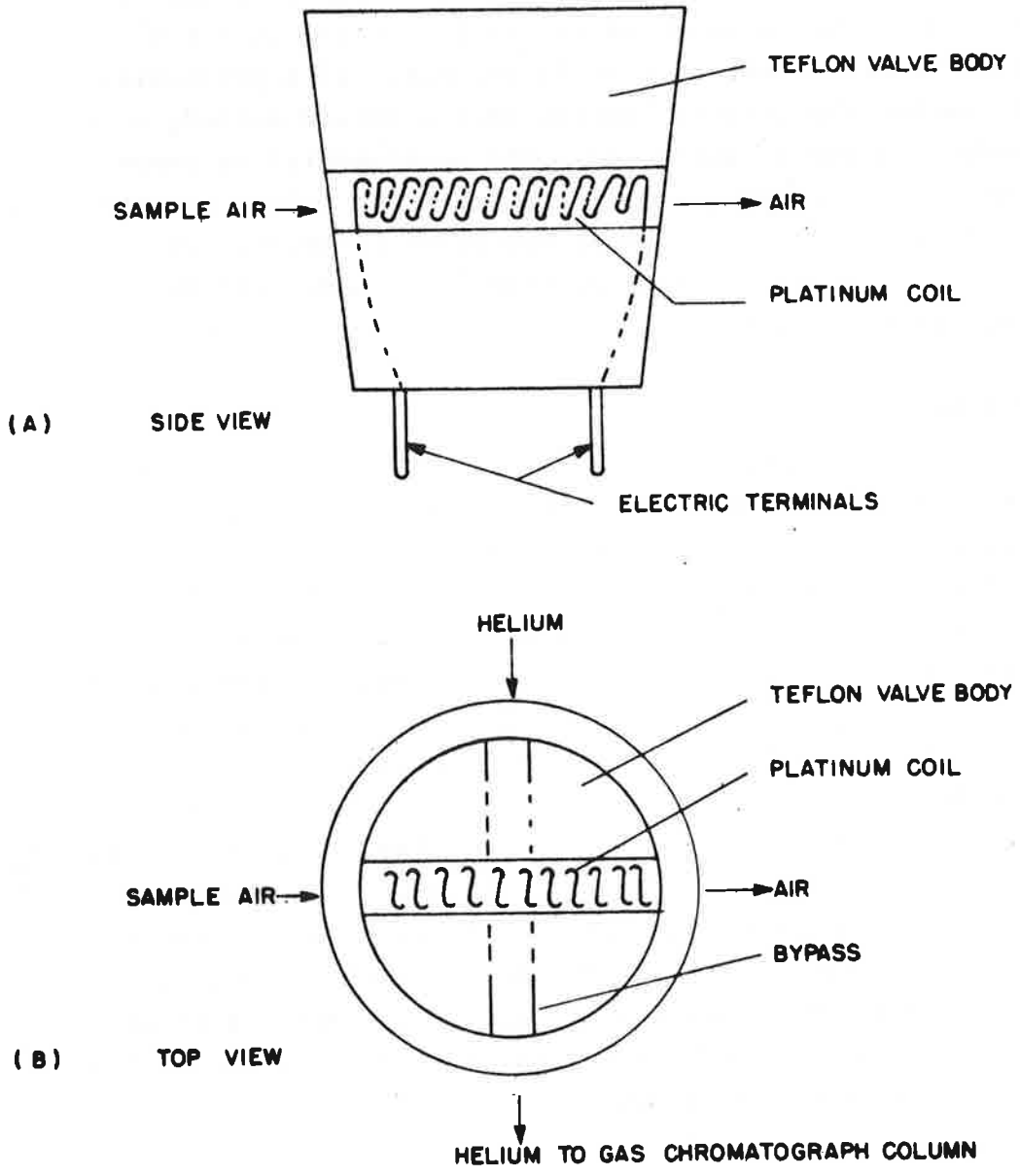


Figure 12 Sequencing Valve with Concentration Coil

but mononitrotoluene and dinitrotoluene are also present in the effluent. The instrumental signature is obtained by recording the detector current as a function of time on a strip-chart recorder. A more practical mode of operation permits automatic programming by providing a 5-second "window" which can be located within a retention time interval from zero to 99 seconds. If a particular constituent reaches the detector during this 5-second period, a visual or audible alarm is activated. The instrumental response can be optimized by varying the temperature of the column and the pressure of the carrier gas. Typical operating parameters are: for dynamite, 75°C, 25 psi, retention time 15 seconds; for TNT, 138°C, 30 psi, 18 seconds.

2.3 BIOLUMINESCENCE DETECTION

In the RPC Vapor Detection System (Figure 13), dynamite effluent can be detected by its effect on the level of light produced by luminescent bacteria. An air sample of 38 cc which contains the effluent is collected by a sampling pump and injected over a layer of these bacteria located on a special nutrient solution. Daily replacement of the bacteria is required for optimum performance. Prior to injection of the air sample, the light level produced by the bacteria is constant. It is measured by a photocell and recorded on a strip-chart recorder. If the bacteria are sensitive to a constituent of the air sample, the light level undergoes a characteristic change (signature) which is also recorded. Alternatively, the characteristic rate of change of electrical signal can also be observed and recorded. The system is provided with a circuit which can automatically balance out the signal when full scale reading is exceeded. A typical recording of the instrumental signature is shown in Figure 14.

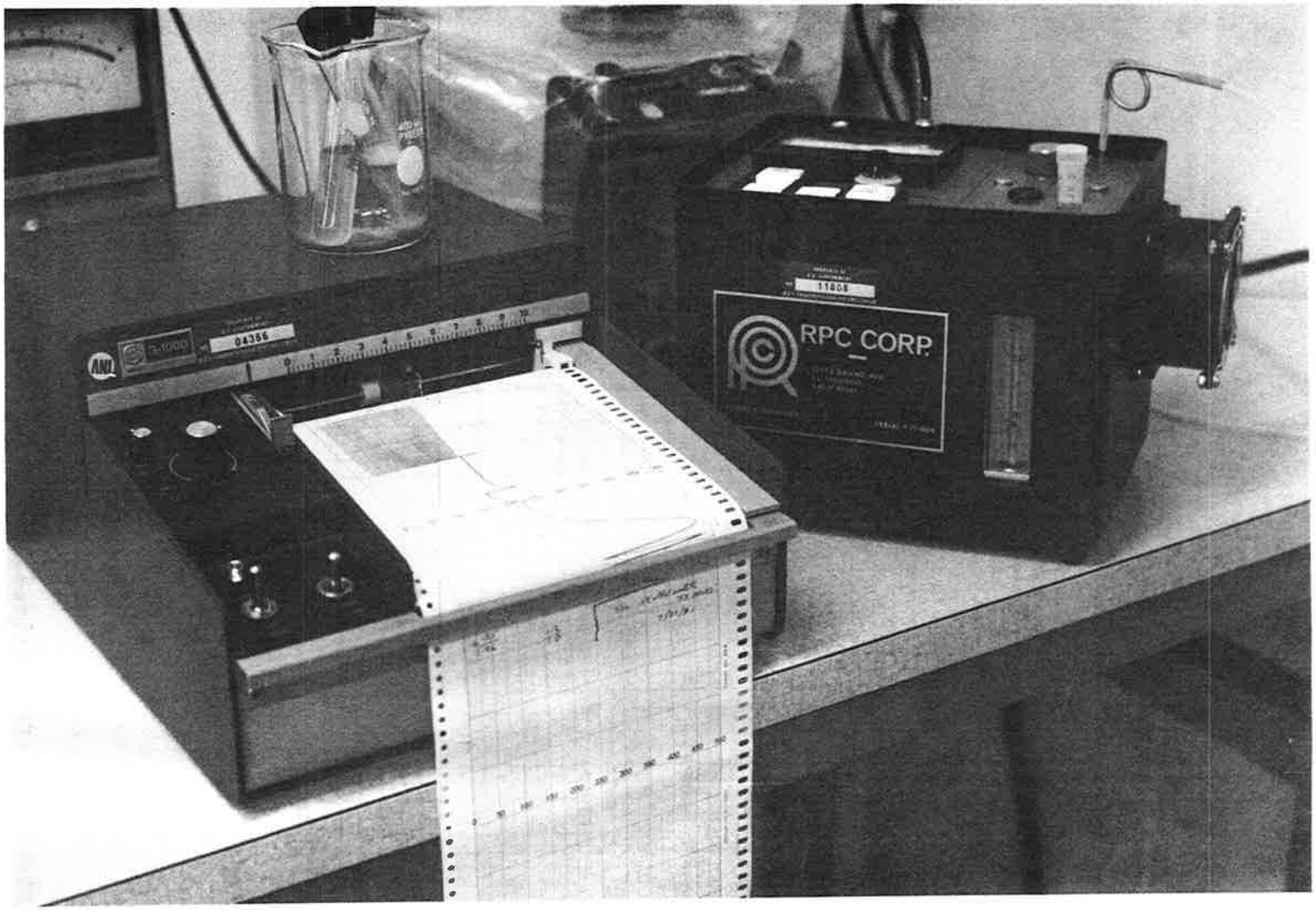


Figure 13 RPC Vapor Detection System (Model 10402-002)

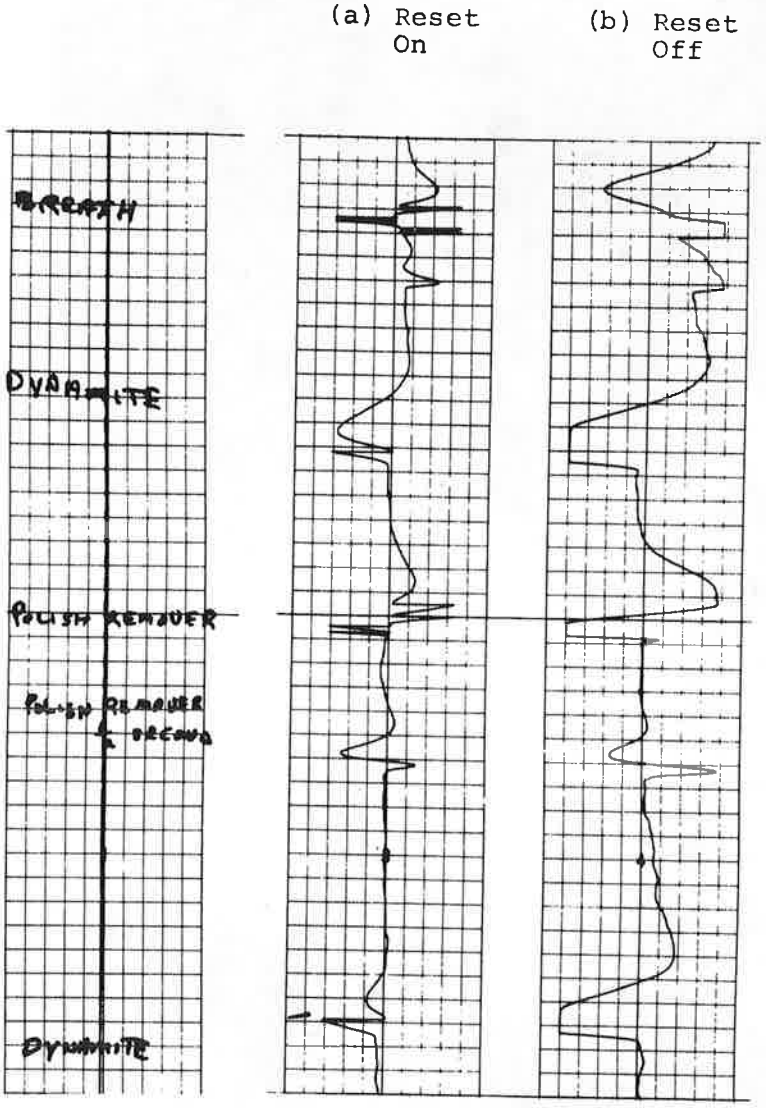


Figure 14 Characteristic Instrumental Signatures of the RPC Detector

3.0 Evaluation of Detectors of Explosives Effluents

The applicability of a sensor of explosives effluents to a practical security system depends on the following instrument characteristics:

1. Sensitivity - the minimum detectable concentration of a trace gas in air;
2. Response Time - the period of time between sample injection and measurable instrument response;
3. Specificity - the uniqueness of the instrumental signature, i.e., the absence of false alarms due to innocuous constituents in air, such as perfumes, shaving lotions, and the various typical containments present in the airport environment;
4. Convenience - this factor includes portability, warm-up time, power consumption, operator training and frequency of adjustment;
5. Cost - capital investment, operational and maintenance expenditures.

The above characteristics were determined at TSC under laboratory conditions for four of the five instruments listed in Figure 1 (Varian, Panametrics, Hydronautics and RPC); only limited tests were made of the plasma chromatograph at another government facilty. The results are discussed in detail in the following pages, and for quick reference, they are summarized in Table 1 and in Appendix A.

3.1 SENSITIVITY

Sensitivity was determined by injecting measured quantities of air saturated with explosives effluent into the airstream which was sampled by the instruments in normal operation. From the magnitude of the instrumental response and a separate determination

of the instrumental background (signal to noise ratio), the minimum detectable concentration was estimated by extrapolation. The estimated sensitivity is based on published values of the saturated vapor pressure at 21°C of pure EGDN (4×10^{-2} torr)[5] and of pure TNT (1.6×10^{-6} torr)[6]. It is recognized that this estimate is likely to err on the pessimistic side since the vapor pressures of these effluents from actual commercial explosives are likely to be lower[7]. The estimated sensitivities are tabulated in Table 1. The only instrument capable of detecting both dynamite and TNT was the Hydronautics VTA. However, as noted in Section 2.2.2, optimum carrier gas pressure and column temperature are not the same for the two explosives. If gas pressure and column temperature are adjusted to detect both, the response time for TNT will be in excess of one minute (probably unacceptably long under operational conditions). The preliminary sensitivity estimate of the plasma chromatograph is based on a limited field test. Further tests are planned at TSC pending the purchase of this instrument.

3.2 RESPONSE TIME

As shown in Table 1, the response time of the instruments listed ranges from between five to 30 seconds. The response time clearly is an important operational characteristic since it would govern the flow of passengers and luggage. Generally, the higher the concentration of the effluent, the shorter the response time. However, a word of caution is in order: once an instrument has been exposed to an unduly high concentration of effluent, it may require a recovery time of several minutes or even longer before regaining its ultimate sensitivity.

3.3 FALSE ALARM RATE (SPECIFICITY).

In the absence of extensive field tests the false alarm rate can only be estimated from tests involving various common laboratory chemicals and substances, such as perfumes, lotions, deodorants, etc.

TABLE 1 EVALUATION OF EXPLOSIVES' EFFLUENT DETECTORS

Detector	Sensitivity (ppb)		Volume Sampled cc	Response Time (Seconds)	False Alarms	Convenience	Unit Cost
	TNT	Dynamite					
Varian CVA	-	1.7	10	10	A	E	$24,000
Franklin GNO Plasma Chromatograph	Not determined	Preliminary .1-1	Not determined	(Estimate 5)	Not determined	Not determined	$32,540
Panametrics Panatek 3000	-	0.8	300	5	B	F	$ 1,850
Hydronautics VTA	0.01 (138°C, 30 psi)	0.03 (75°C, 25 psi)	833	30 18	C	G	$18,750
RPC Vapor Detection System	-	98	38	10	D	H	$ 3,415

A. false alarms by perfumes, alcohol, oxides of nitrogen, nitrobenzine at m/e 30, 46

B. false alarms by perfumes, bath lotions, trichlorethylene, nitrobenzine (shoe polish)

C. no false alarm for dynamite; for TNT only one false alarm (Mennen Skin Bracer)

D. false alarms by nitric acid, ammonia

E. 150 lbs; requires cart for mobility; requires alarm accessory; few adjustments

F. 8 lbs; portable, lightweight; requires carrier gas supply; few adjustments

G. 70 lbs; requires carrier gas supply; few adjustments

H. 6 lbs; requires frequent recharging with microorganisms

The Varian CVA is potentially capable of producing a unique signature for dynamite (see Appendix B). The instrument, as presently configured, does not utilize this capability. Consequently false alarms are possible due to substances such as alcohol and oxides of nitrogen. With a relatively simple data processing accessory, such false alarms could be eliminated.

The Hydronautics VTA did not produce any false alarms on the dynamite setting. On the TNT setting, only one substance - Mennen Skin Bracer - produced a false alarm. When tested in the baggage room of the Northeast Terminal at Logan Airport, where no attempt was made to maintain a clean environment, not a single false alarm was observed.

The Panatek 3000, in addition to explosives, produced alarms with substances such as nitrobenzine (in shoe polish), trichlorethylene, perfumes and bath lotions.

The RPC instrument produced a signature for dynamite which was similar to those for nitric acid and ammonia, substances unlikely to be found on passengers or in luggage.

The Franklin GNO insturment has not yet been tested at TSC for false alarms.

3.4 CONVENIENCE

The Varian CVA is mobile, samples air continuously, and has run in the TSC laboratory continuously for over one year without any maintenance. However, the instrument is heavy (about 150 pounds) and requires an auxiliary power supply, mechanical pumps, a reserve storage battery for use in case of a power failure or during transportation, and a data readout accessory (recorder, oscilloscope, or computerized readout).

The Hydronautics VTA is mobile (weight about 70 lbs.) and can operate with a small portable helium lecture bottle for about four hours. To achieve maximum sensitivity, it requires a "warm-up" time of up to two hours. To maintain this sensitivity on stand-by, a continuous flow of helium is necessary. It has an audio-alarm.

The Panatek 3000 is compact and lightweight; a minor drawback is the need for a bottled supply of nitrogen. The warm-up time is only two minutes. It has an audio-alarm.

The RPC instrument requires daily prepareation of the luminescent bacteria. This procedure is difficult outside the laboratory. However, the instrument is light and portable. It requires a recorder accessory.

3.5 COST

As pointed out in the previous section (3.4) the cost figures shown in Table 1 (at unit rates) are not strictly comparable since additional equipment may have to be added to the basic instrument. In quantity production, costs are likely to be lowered appreciably.

4.0 Conclusions

Based on the laboratory tests the highest sensitivity to dynamite and the lowest false alarm rate was demonstrated by the Hydronautics VTA. Its weaknesses are in its slow response time and relatively high cost.

The Panametrics Panatek 3000 has moderately good sensitivity, low cost and excellent convenience in handling. Its major weakness is its high false alarm rate.

Only these two instruments are currently manufactured as explosives detectors on a production basis. The other three are developmental prototypes and require further engineering and packaging.

Appendix A

Details of Commercial Detectors of Explosives Effluents

EFFLUENT DETECTOR

Manufacturer:	Varian Analytical Instrument Division 611 Hansen Way Palo Alto, Calif. 94303
Type and Model No:	Chemical Vapor Analyzer Model A1
Mode of Application:	Continuous air sampling
Physical Description:	Compact unit, about 150 pounds
Cost:	$24,000 (Prototype)
Delivery:	about 3 months
Operating Principle:	Quadrupole mass spectrometer with membrane separator
Technical Evaluation:	(based on laboratory tests at TSC)
Sensitivity:	Very good for dynamite (1.7 ppb); poor for TNT
False alarms:	Very good; nitrobenzene or nitric acid may interfere
Convenience:	Good. Auxiliary mechanical pumps and dc power supply needed for long-time operation
Need for adjustment:	Very stable
Portability:	Requires cart
Operator's skill required:	Medium to high
Set-up time:	About 10 minutes with instrument on stand-by
Power required:	115v, 60 Hz, 15 amps. Emergency storage battery (12v) needed to maintain ion-pump operation during transportation or power failure

EFFLUENT DETECTOR

Manufacturer:	Franklin GNO Corporation P.O. Box 3250 West Palm Beach, Fla. 33402
Type and Model No.:	Plasma Chromatograph Model Beta VI
Mode of Application:	Continuous air sampling
Physical Description:	Module mounted on wheels
Cost:	$32,540 (1)
Delivery:	60 days
Operating Principle:	Plasma chromatograph separates molecules according to drift velocities at atmospheric pressure in an electric field
Technical Evaluation:	(based on limited field tests)
Sensitivity:	Very good for dynamite (est .1 to 1 ppb), unknown for TNT
False alarms:	Not determined
Convenience:	Not determined. Gas supply required
Need for adjustment:	Not determined
Portability:	Requires cart
Operator's skill required:	Medium to high
Set-up time:	Not determined
Power required:	Not determined

EFFLUENT DETECTOR

Manufacturer:	Analytical Instruments, Ltd. Fowlmere, Royston Hertfordshire, U. K.
American Distributor:	Panametrics 221 Crescent Street Waltham, Ma. 02154
Type and Model No.:	Panatek Model 3000
Mode of Application:	Continuous air sampling
Physical Description:	Small, compact unit, about 8 pounds
Cost:	$1,850 (1-9); $1,665 (10-25)
Delivery:	60 days
Operating Principle:	Electron capture detector with nitrogen carrier gas. Vapor from air passes through a membrane into carrier gas.
Technical Evaluation:	(based on laboratory tests at TSC)
Sensitivity:	Very good for dynamite (0.8 ppb); poor for TNT.
False alarms:	Poor. Sensitive to all compounds with high electron affinity, (nitrobenzene and chlorinated organics).
Convenience:	Excellent. Gas supply required.
Need for adjustment:	Often during operation
Portability:	Excellent
Operator's skill required:	Medium to high
Set-up time:	About 10 minutes
Power required:	115v, 60 Hz, less than 15 amps

EFFLUENT DETECTOR

Manufacturer:	Hydronautics-Israel Ltd. Rehovot, Israel
American Distributor:	Hydronautics, Inc. Pindell School Road Laurel, MD. 20810
Type and Model No:	Vapor Trace Analyzer, Model 103A
Mode of Application:	Discontinuous air sampling up to 2 per minute
Physical Description:	Compact unit, about 70 pounds
Cost:	$18,750 (1); $17,780 (2-5); $16,810 (6 or more)
Delivery:	4 mon. (1); 5 mon. (2-5); 6 mon. (6 or more)
Operating Principle:	Gas chromatograph with electron capture detector and helium carrier gas. Sample injection by desorption of vapor from heated metallic adsorber. Alarm set for retention time of explosive effluent.
Technical Evaluation:	(based on laboratory tests at TSC)
Sensitivity:	Excellent for dynamite (0.03 ppb); good for TNT (0.01 ppb)
False alarms:	Excellent; none found for dynamite, one for TNT (Mennen Skin Bracer)
Convenience:	Good; gas supply required.
Need for adjustment:	Very stable
Portability:	Perferably carried by two men
Operator's skill required:	Medium to high
Set-up time:	With stand-by gas flow, 1 hour
Power required:	115 volts, 60 Hz, less than 15 amps

EFFLUENT DETECTOR

Manufacturer:	RPC Corporation 1222 E. Grand Ave. El Segundo, Calif. 90245
Type and Model No.:	Vapor Detection System Model No. 10402-002
Mode of Application:	Continuous air sampling
Physical Description:	Small, compact unit, about 6 pounds
Cost:	$3,415
Delivery:	60 days
Operating Principle:	Bioluminescence detector. Change of light output from microorganisms is caused by vapor in air sample and is read on meter or recorder.
Technical Evaluation:	(based on laboratory testing at TSC)
Sensitivity:	Fair for dynamite (98 ppb); poor for TNT
False alarms:	Good; nitric acid or ammonia may interfere
Convenience:	Fair; daily innoculation of microorganisms is required for optimum response
Need for adjustment:	Often during operation
Portability:	Excellent
Operator's skill required:	Medium to high
Set-up time:	About 10 minutes
Power required:	115v, 60 Hz, less than 15 amps

Appendix B

Mass Spectrometer Signature of Dynamite

INTRODUCTION

In order to determine the performance characteristics of explosives detectors, it is necessary to have an understanding of the nature of the effluent as well as of the instrumental signatures by which the effluents may be identified. The present study was undertaken since a survey of the literature offered no adequate explanation of the signature of the Varian CVA for dynamite.

As discussed in Section 2.1.1 the interface between the ambient atmosphere and the mass analyzer of this instrument is a three-stage Llewellyn-Arnold membrane separator[8] utilizing semipermeable membranes of dimethyl silicone, heated to 65°C. Air is sampled at a rate of 60 cc/min through a 1/8-inch diameter stainless steel tube heated electrically to about 70°C. The two chambers of the separator are differentially pumped to maintain the required pressure differentials. The mass spectrometer is maintained at 10^{-6} torr by an integral sputter-ion pump. According to the manufacturer, highest sensitivity of the instrument for dynamite had been observed at the ionic mass peak of 30 AMU. The mass spectrum of the instrument for dynamite effluent near 30 AMU, as obtained by TSC, is demonstrated in Figure 15. The lower trace is the spectrum of the ambient background, the upper trace is that of dynamite effluent in air. In the upper trace, the amplitude of the peak at 30 AMU is increased about four times, that of the peak at 29 AMU about one and one-half times; the peak at 32 AMU is unchanged. The complete mass spectrum (not shown here) also contained additional peaks at 46 and 76 AMU; their amplitude was smaller than the peak at 30 AMU. There is considerable evidence from other investigations[9] that the principal effluent from dynamite is ethylene glycol dinitrate [EGDN, $(CH_2NO_3)_2$, molecular weight 152.07] . The characteristics of this compound are listed in Figure 16 and its vapor pressure as a function of reciprocal temperature is plotted in Figure 17[5]. At room temperature the saturated vapor pressure is 4×10^{-2} torr; this pressure corresponds to a concentration of 52 ppm in air at atmospheric pressure. When sampled by the CVA, however, only the mass peaks re-

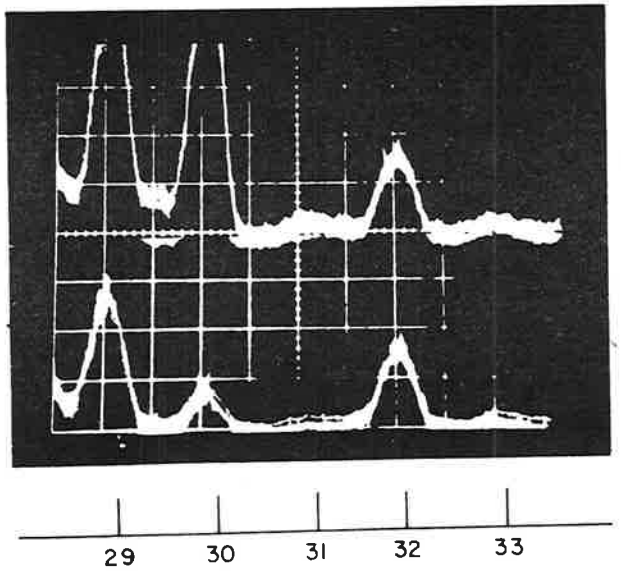


Figure 15 CVA Spectral Peaks from Dynamite (low resolution)

ported above were observed; there was no peak near 152 AMU. In view of the reported instability of explosive compounds[10] it seemed most likely that there was complete fragmentation of EGDN in the ionization region of the mass spectrometer. Before proceding on this assumption, a few simple tests were performed with instrumentation already available at TSC, to obtain more tangible confirmation. From published work on other explosives[10] the most likely compounds to appear at 30, 46, and 76 AMU in the mass spectrum were thought to be ions of oxides of nitrogen (NO^+ - 30 AMU, NO_2^+ - 46 AMU), and also the compound ions CH_2O^+ (30 AMU) and $CH_2NO_3^+$ (76 AMU). Therefore, the following questions had to be addressed: (1) whether some of these observed compounds were present in the natural effluent of dynamite; (2) how easily they could pass through the membranes; (3) whether there was any fragmentation of EGDN in passing through the membranes. In addition to the CVA, two other instruments were used for these tests: a chemiluminescent detector for NO, constructed at TSC, (limiting sensitivity of 0.001 ppm) and a commercial electrochemical detector for oxides of nitrogen, (limiting sensitivity 1 ppm, Environmetrics Model NS-220S, with transducers type N46H2A for NO_2 and type N76H2 for total NO_x). The results of the tests were as follows: (1) the amount of NO in natural dynamite effluent was typically on the order of 0.05 ppm and the amount of NO_2 less than 1 ppm; (2) after passing through a single membrane, the concentration of NO was only about 20% of the initial concentration; (3) The concentration of NO in an air sample saturated with dynamite effluent (approximately 50 ppm EGDN and 0.05 ppm NO) after passing through a single membrane was only about 0.02 ppm NO; this measurement showed that there was no significant fragmentation of EGDN into NO in passing through the membrane. It should be noted that the separator of the CVA consisted of three membrane stages with intermediate differential pumping; in each of the three stages, the concentration of NO could be expected to fall to less than 20% of the concentration at entry. Thus, the concentration of NO in the dynamite effluent sample which finally passed into the ion source of the CVA was probably less than one percent of the initial amount, namely 0.0005 ppm. The three tests thus conclu-

sively demonstrated that the amount of NO in the effluent sample which produced the observed peak at 30 AMU in Figure 15 was insignificant. The case for a source other than natural oxides of nitrogen to explain the magnitude of the peak at 30 AMU was further demonstrated when the sensitivity (lowest detectable concentration) of the CVA was measured for NO and NO_2. The measurement established the lowest detectable concentrations from calibrated samples of NO and NO_2 as 20 ppm and 3 ppm, respectively. From this calibration, the signal at 30 AMU from an air sample which contained 5 ppm dynamite effluent was measured to be 300 times larger than the signal obtained for 20 ppm of NO. Since the amount of NO in the sample was now only about 0.005 ppm, and further attenuation took place in its passage through the separator, the measured signal at 30 AMU was more than one million times too large for this quantity of NO. There is, however a simple explanation of this observation, namely, that EGDN readily passes through the membranes and is then fragmented by ionization, the peak at 30 AMU being that of the most abundant fragmentation product.

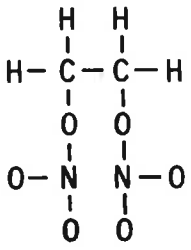
PROPERTY	EGDN
FORMULA	$C_2H_4N_2O_6$
STRUCTURE	
MOLECULAR WEIGHT, G/MOLE	152.07
DENSITY AT 20°C, G/CC	1.483
MELTING POINT, °C	-20
BOILING POINT, °C	(169)

Figure 16 Characteristics of EGDN

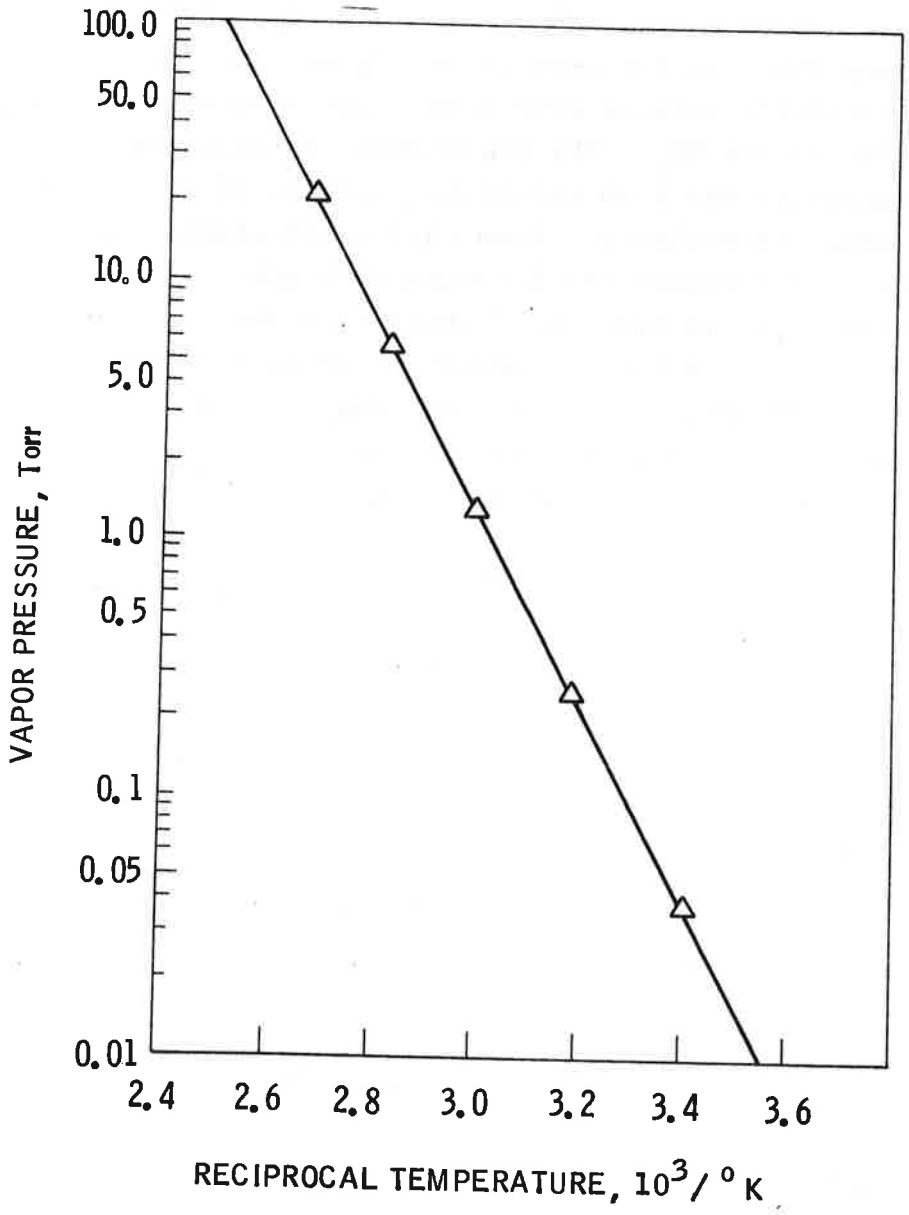


Figure 17 Vapor Pressure vs. Reciprocal Temperature of EGDN

Having established conclusively that fragmentation by ionization is the dominant factor leading to the observed mass spectrum, the investigation was concentrated on further detailed study of the ionization process. For this purpose, the CVA did not have the necessary flexibility and resolution. However, another laboratory instrument was available at TSC, a Hitachi-Perkin Elmer RMU-6E, 90^{o} magnetic sector mass spectrometer (Figure 18). In order to obtain the necessary sensitivity, its inlet system was modified to accommodate a three-stage differentially pumped separator. A series of controlled measurements of the EGDN spectrum was then performed, with the samples admitted through the separator.

An examination of the electron impact spectrum of EGDN demonstrated that characteristic major peaks at 29, 30 and 46 AMU and a minor peak at 76 AMU were present throughout, while the energy of the ionizing electrons was varied from 10 to 80 electron volts. A minor peak 152 AMU was present only below 40 electron volts. Since fragmentation of molecular ions is usually greatly reduced if a field ionization source is employed rather than an electron impact source [11], the laboratory mass spectrometer was next equipped with a field ionization source of TSC design based on previous work by the NASA Electronics Research Center. It consisted of a matrix which contained about 2,000 tips, one micron in diameter. This matrix was obtained by drawing a bundle of platinum wires embedded in a silver matrix. After drawing, about one-half inch of the matrix was cut off and the wire tips were exposed by etching. In the ion source, the tips were kept at 3.6 kV positive and an accelerating electrode at a distance of 3 mm was maintained at 10 kV negative. Under these conditions, the field ionization spectrum was obtained as shown in Figure 19. In addition to the characteristic peaks at 30, 46 and 76 AMU, this spectrum contained an additional peak at 60 AMU, but again there was no peak at 152 AMU. The peak at 18 AMU was due to a background of water vapor. The peaks at 19 and 37 AMU $\left[(H_2O)H^{+}\text{and } (H_2O)_2H^{+}\right]$ were characersitic of the field ion spectrum of water vapor.

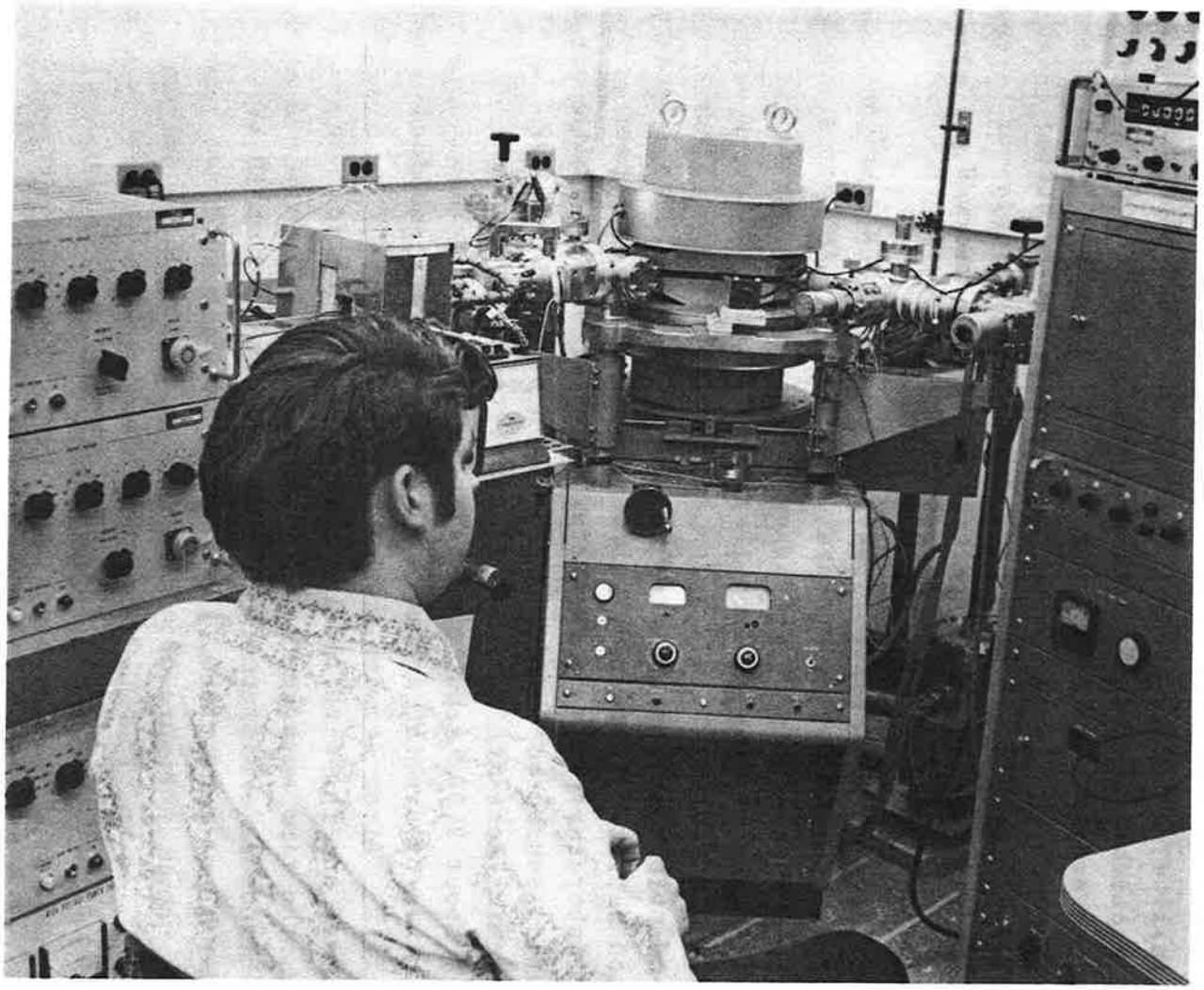


Figure 18 Hitachi-Perkin Elmer Mass Spectrometer

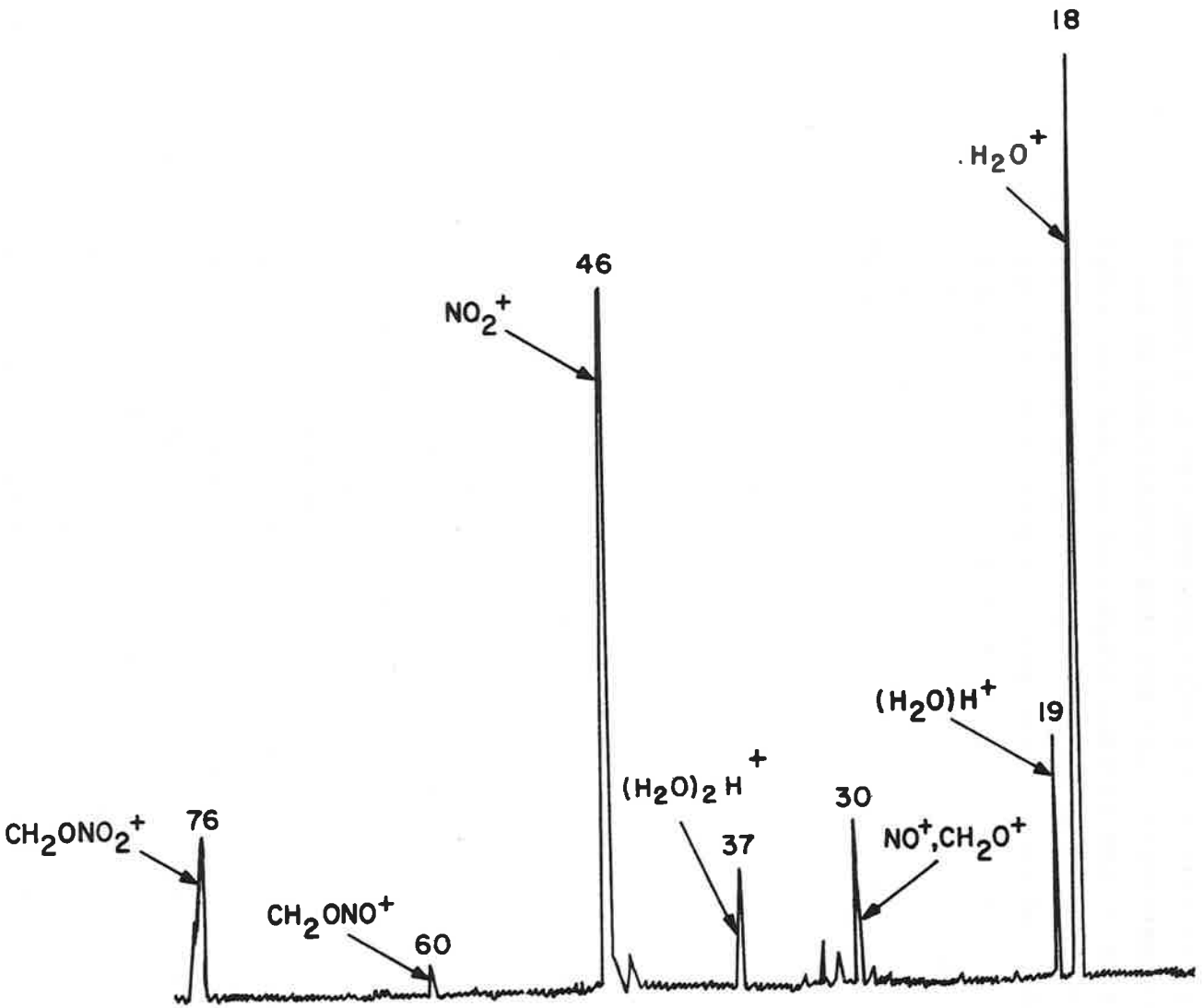


Figure 19 Field Ionization Spectrum of EGDN

IDENTIFICATION OF FRAGMENTATION PRODUCTS

In order to identify the various mass peaks and, in particular, to ensure that small mass differences were resolved adequately, it was necessary to perform an accurate calibration of the mass spectrometer at maximum resolution. For this purpose, both the source slit and the multiplier slit of the mass spectrometer were reduced to 0.0125 mm. The atomic mass scale was then established by determining the position of the various fragmentation peaks of ethyl alcohol (parent peak, $C_2H_6O^+$ at 46 AMU). This compound readily passes through the membranes and the various spectral peaks are well documented in the literature.[12] The calibration procedure is exemplified by the following determination of the mass peaks at 29 and 30 AMU. These peaks of the ethyl alcohol spectrum are shown in Figure 20: the doublet CHO^+ and $C_2H_5^+$ at 29 AMU and the peak CH_2O^+ at 30 AMU. The molecular masses and peak heights relative to the major peak of the spectrum, CH_3O^+ at 31 AMU (not shown in Figure 20), as published,[12] are listed in Table B-1. Based on the table, the peaks are labeled as shown. It should be noted that the minor peak, $C^{12}C^{13}H_5^+$, listed in the table at 30 AMU, which would be located to the left of the CH^2O^+ peak, is not seen in the spectrum. There is, however, a small peak to the right of CH_2O^+ in the position of NO^+. This peak is also present in the instrumental background (Figure 21), which contains the two peaks CHO^+ and NO^+. The CHO^+ background peak is not unexpected. Both the Varian CVA and the Hitachi mass spectrometer are pumped by ion pumps which produce a high background of hydrogen and carbon monoxide[13]. These two gases may readily form CHO^+ in the ion source. Based on this observation, the background spectrum or the Varian CVA in Figure 15 (lower trace) can be identified as follows: CHO^+ - 29 AMU, NO^+ - 30 AMU, O_2^+ - 32 AMU.

From the calibration with ethyl alcohol, the spectrum of EGDN was determined in two steps. First, both ethyl alcohol and EGDN were admitted simultaneously in the instrument, which produced the spectrum shown in Figure 22. Next, EGDN was admitted alone, which produced the spectrum shown in Figure 23. The significant features of the spectrum in Figure 22 are the greatly increased peak height of CHO^+ in the doublet at 29 AMU, and the appearance of the doublet

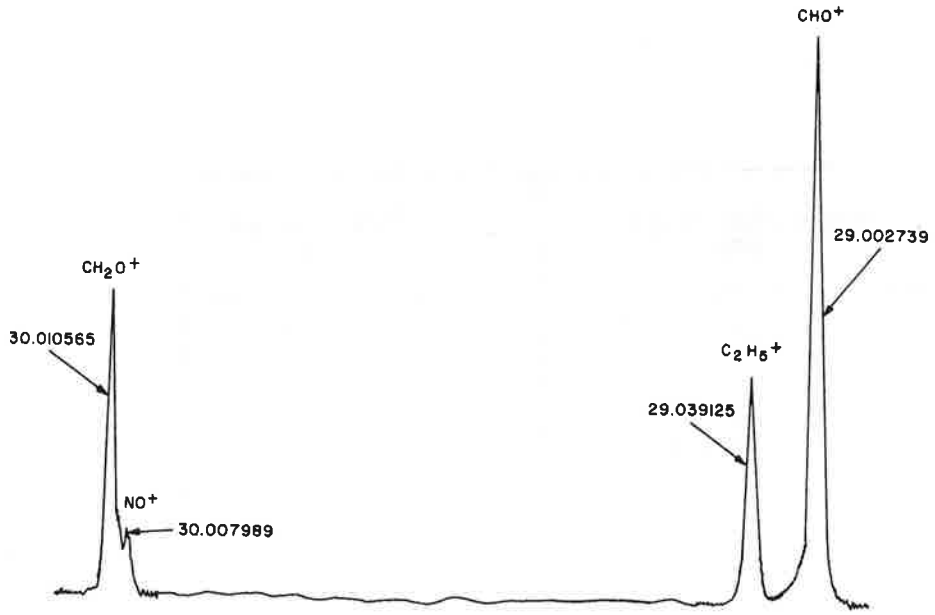


Figure 20 Spectral Peaks of Ethyl Alcohol (electron impact)

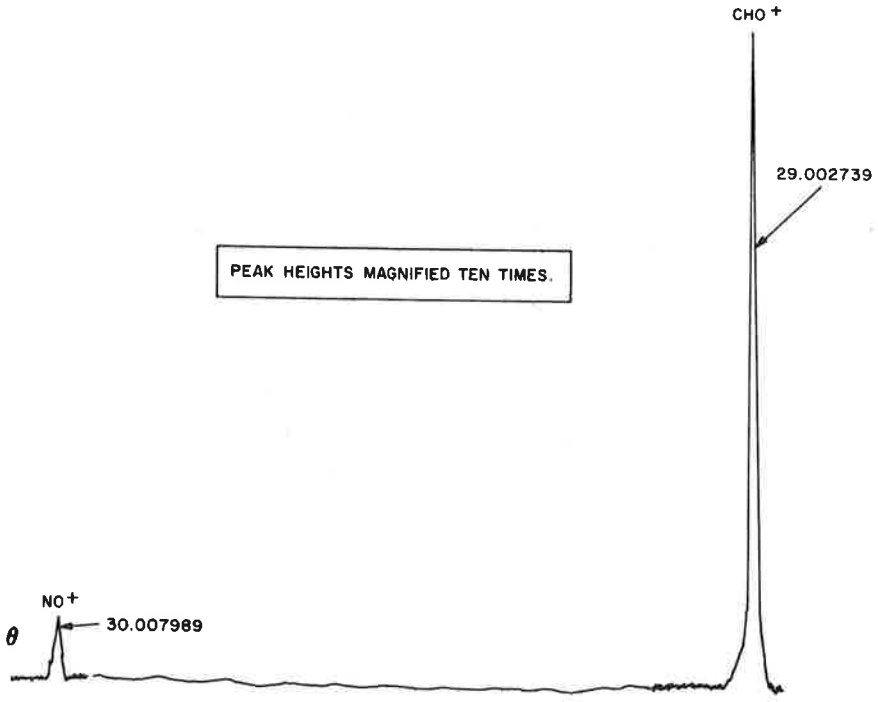


Figure 21 Spectral Peaks of Laboratory Air (electron impact)

TABLE B-1 MASS PEAKS OF ETHYL ALCOHOL

Ion Formula	Molecular Mass AMU	Peak Height %
CHO	29.002739	9.7
C_2H_5	29.039125	3.9
NO*	30.007989	
CH_2O	30.010565	4.6
$C^{12}C^{13}H_5$	30.042480	0.02
CH_3O	31.018389	100

*(NO is included for comparison)

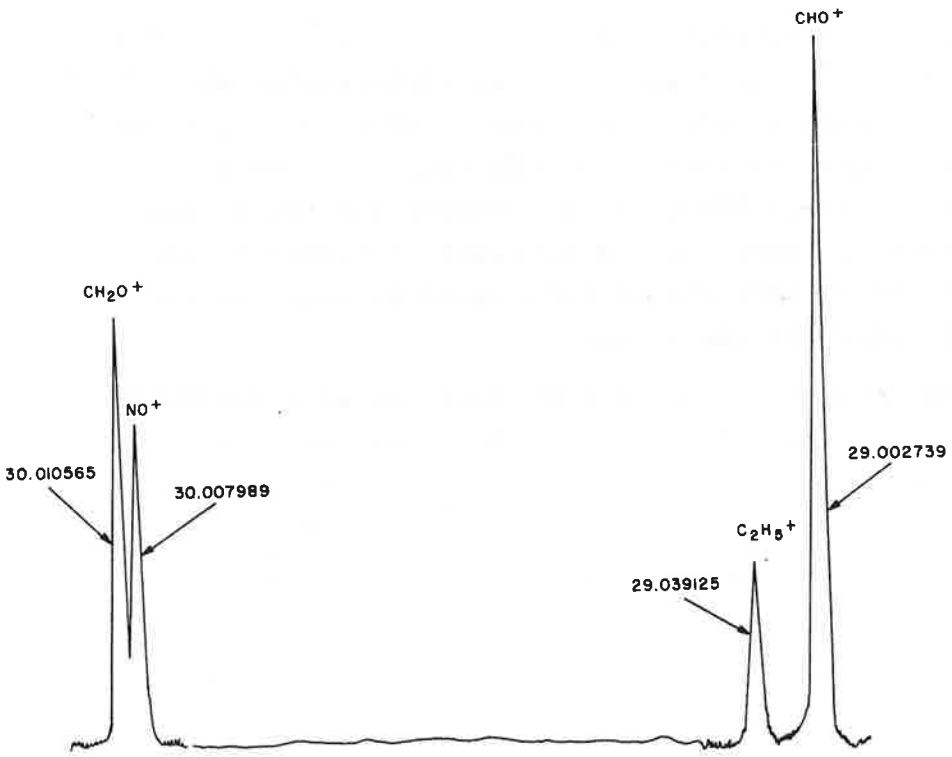


Figure 22 Spectral Peaks of Ethyl Alcohol/EGDN Mixture (electron impact)

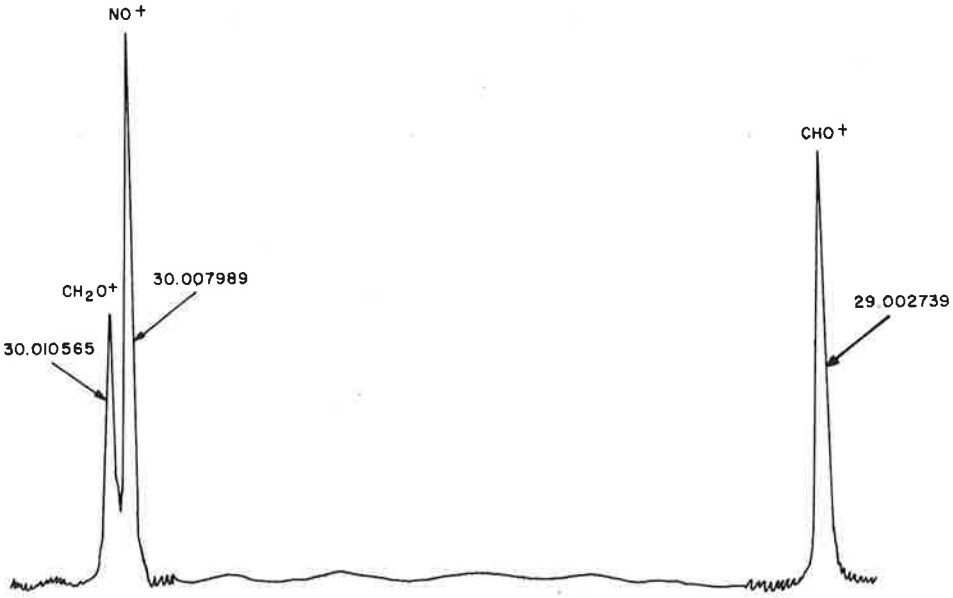


Figure 23 Spectral Peaks of EGDN (electron impact)

at 30 AMU. This spectrum establishes the location of the three EDGN peaks, CHO^+, NO^+ and CH_2O^+. In Figure 23, the high-resolution spectrum of EGDN is reproduced with the identification of the three peaks confirmed. It should be noted that the mass spectrometer, whose specified resolution is 5000, cannot resolve the two peaks, CH_2O^+ and NO^+ completely. Their mass difference is 0.002576 AMU and a resolution of 30/0.002576 (or 11,600) would be required to resolve them with a valley of ten percent.

The peaks at 46, 60 and 76 in the EGDN spectrum were resolved by a similar calibration procedure. No doublet peaks were observed and the three peaks were identified as NO_2^+, $CH_2NO_2^+$ and $CH_2NO_3^+$. The relative intensities of these peaks, as measured both by electron impact and by field ionization are shown in Table B-2. The fragmentation processes which are likely to be similar to those reported in a related study[10], are given in Table B-3.

The present study has demonstrated that the characteristic mass peaks of the EGDN spectrum are at 30, 46 and 76 AMU. A mass spectrometer, equipped with a membrane separator, can be an effective detector of dynamite. As regards the possibility of false alarms, detection of the peaks at 30 AMU or at 46 AMU may be caused not only by EDGN but, for example, by ethyl alcohol. Oxides of nitrogen, because of the low penetration rates through the membranes, are less likely to interfere than was first expected. False alarms could be minimized by simple automatic data processing which would utilize the measurement of relative peak heights at 30, 46 and 76 AMU.

TABLE B-2 EGDN FRAGMENTATION PEAKS

Electron Impact Ionization. Electron Energy 80 eV.

Ion Formula	Molecular Mass AMU	Peak Height %
CHO^+	29.002739	25
NO^+	30.007989	25
CH_2O^+	30.010565	15
NO_2^+	45.992902	100
$CH_2NO_3^+$	76.005466	40

Field Ionization

Ion Formula	Molecular Mass AMU	Peak Height %
NO^+	30.007989	20
CH_2O^+	30.010565	10
NO_2^+	45.992902	100
$CH_2NO_2^+$	60.008542	5
$CH_2NO_3^+$	76.005466	25

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