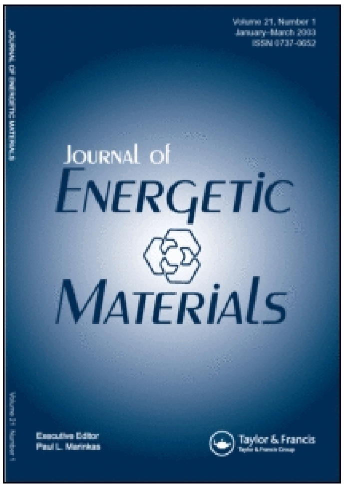

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Vapor characterization of water gel explosives

John R. Hobbs[a]; Edward Conde[a]
[a] Department of Transportation Kendall Square, Transportation Systems Center Research and Special Programs Administration U.S., Cambridge, MA

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VAPOR CHARACTERIZATION OF WATER GEL EXPLOSIVES

John R. Hobbs and Edward Conde
Transportation Systems Center
Research and Special Programs Administration
U.S. Department of Transportation
Kendall Square
Cambridge, MA. 02142

The vapor components of several water gel explosives have been characterized using Pt-wire preconcentration/capillary gas chromatography; concentration of headspace vapors on Tenax-GC with thermal desorption capillary gas chromatography/mass spectrometry; and liquid chromatography with Thermal Energy Analyzer detection. In addition to normal sensitizing agents almost all of the water gel explosives were found to be contaminated with ethylene glycol dinitrate (EGDN) and nitroglycerine (NG) presumed to occur from storage with dynamites in commercial blasting company magazines. Other trace components are presumed to arise from the manufacturing process.

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INTRODUCTION

The Federal Aviation Administration (FAA) of the United States Department of Transportation has a continuing interest in the detection of explosives as part of the effort to prevent airplane hijacking and sabotage. Over the past ten years our laboratory has evaluated many so called explosives vapor detectors for their appliaction to the FAA's problem. Many of these detectors claim to detect a wide variety of explosives, but when tested with military explosives that are uncontaminated, these detectors fail. None of these detectors have been able to detect the plastic explosives or the water gel explosives. A recent trend of explosives manufacturers is to produce less and less nitroglycerine based dynamites and to substitute more and more water gel explosives. It is for these reasons: (1) to obtain an understanding of the contamination problem with commercial explosives, and (2) to determine the volatile species in water gel explosives that could be used for detection, that the work described below was under taken.

Pt-WIRE PRECONCENTRATION/CAPILLARY GAS CHROMATOGRAPHY

An example of a preconcentration gas chromatographic type explosives detector is the XonTech GC-710 shown in FIGURE 1. In the hand held unit is a sampling valve which is connected to a short, packed Teflon GC column and an electron capture detector. FIGURE 2. shows the sampling valve containing the platinium wire preconcentrator. FIGURE 3. shows the sampling head and control unit as connected to the Hewlett Packard 5756A gas chromatograph used to collect the data described below. The sampling head was connected directly to the injection port via a needle septum nut with a 1/8-inch swagelock fitting. The capillry column used was a Supelco 30 meter, 0.75mm ID. glass column with a 1.0 um thick Carbowax 20M coating. The detector used was a tritium foil electron capture detector operated in the pulsed mode. The gas chromatograph was operated in the isothermal mode with runs made at 70, 100, 160, and 200 °C. The 200 °C runs were not successful in that the explosives samples decomposed in the injector and column. The

FIGURE 1. XonTech GC-710 Explosives Detector.

FIGURE 2. Platinum Wire Preconcentrator and Sampling Head.

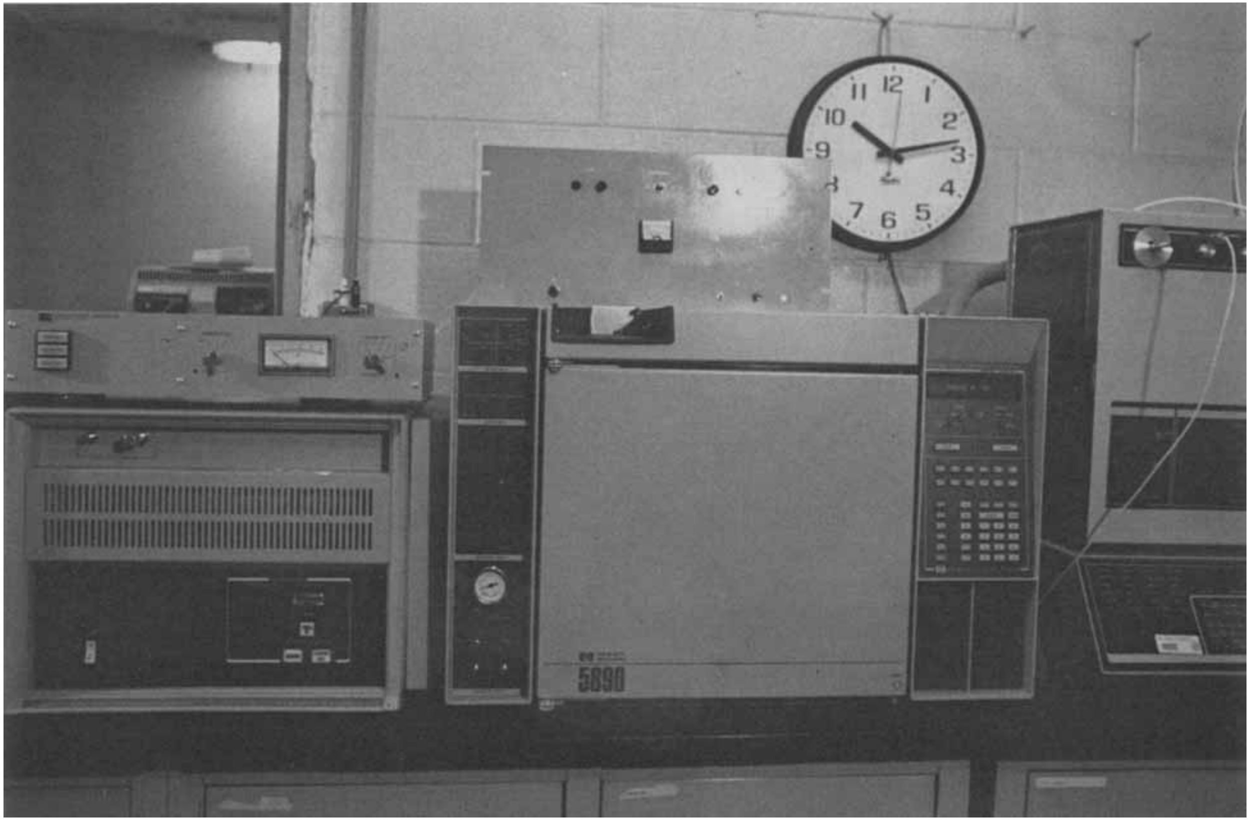
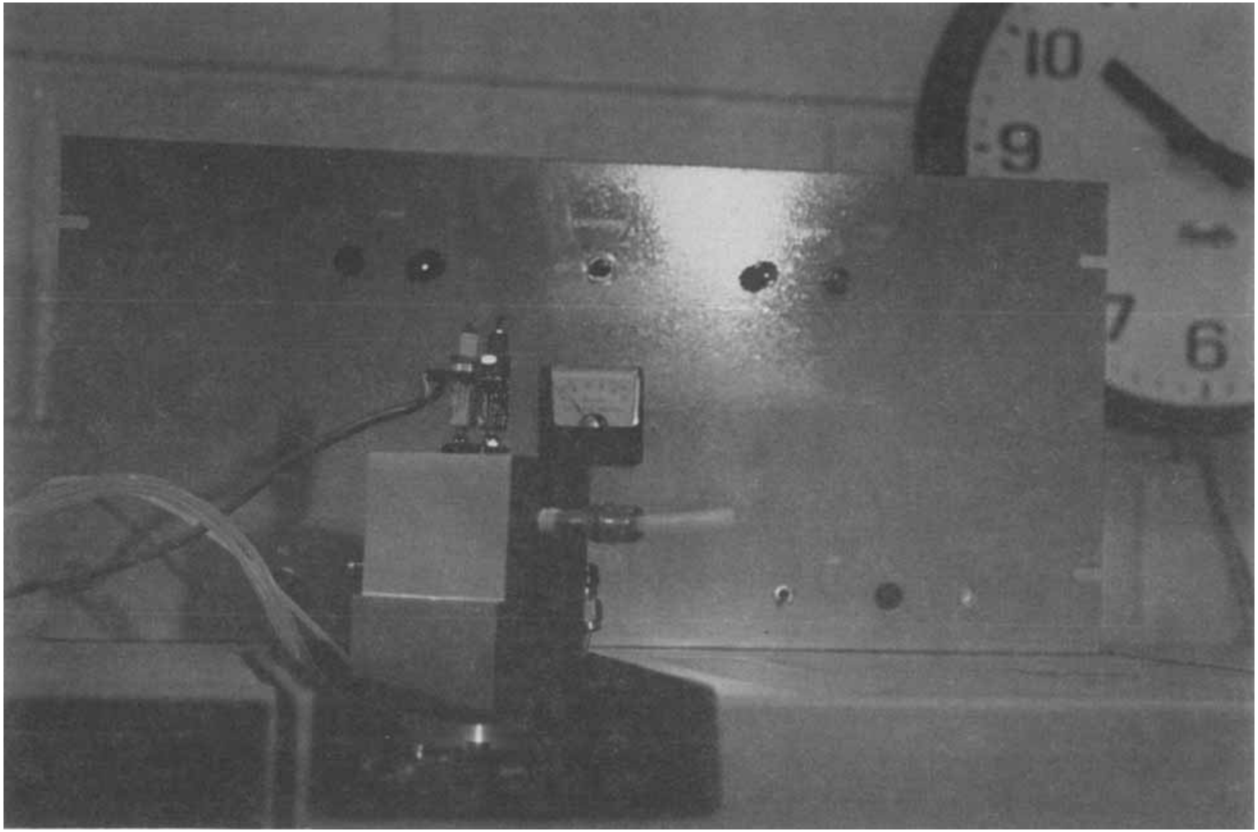


FIGURE 3. Sampling Head and Control Unit Connected to Gas Chromatograph.



explosives samples used in these studies were obtained from the U.S. Bureau of Mines and from a commercial blasting company. The explosives vapor headspace was sampled for 10 seconds via the sample pump of the sampling head; the sample valve moved to the desorb position into the helium carrier gas stream; and the platinium wire was flash heated and the integrator started.

The results of these experiments at 70 C are shown in FIGURES 4 and 5. FIGURE 4a shows the chromatogram of a 10 second sniff of background air. The two sharp peaks are air peaks due to the movement of the Teflon sampling cartridge into the desorb position and will appear on every chromatogram shown. FIGURE 4b shows a 10 second sniff of the headspace vapor of Thermex water gel. It can be seen that there are two additional peaks, the larger of which has been identified as nitromethane. The chromatograms of Tovex 220 and Atlas water gels are shown in FIGURES 5a and 5b respectively. Note the large peak at 1.29 min in Tovex 220 and the peak at 2.10 min in the Atlas. These peaks have not been identified.

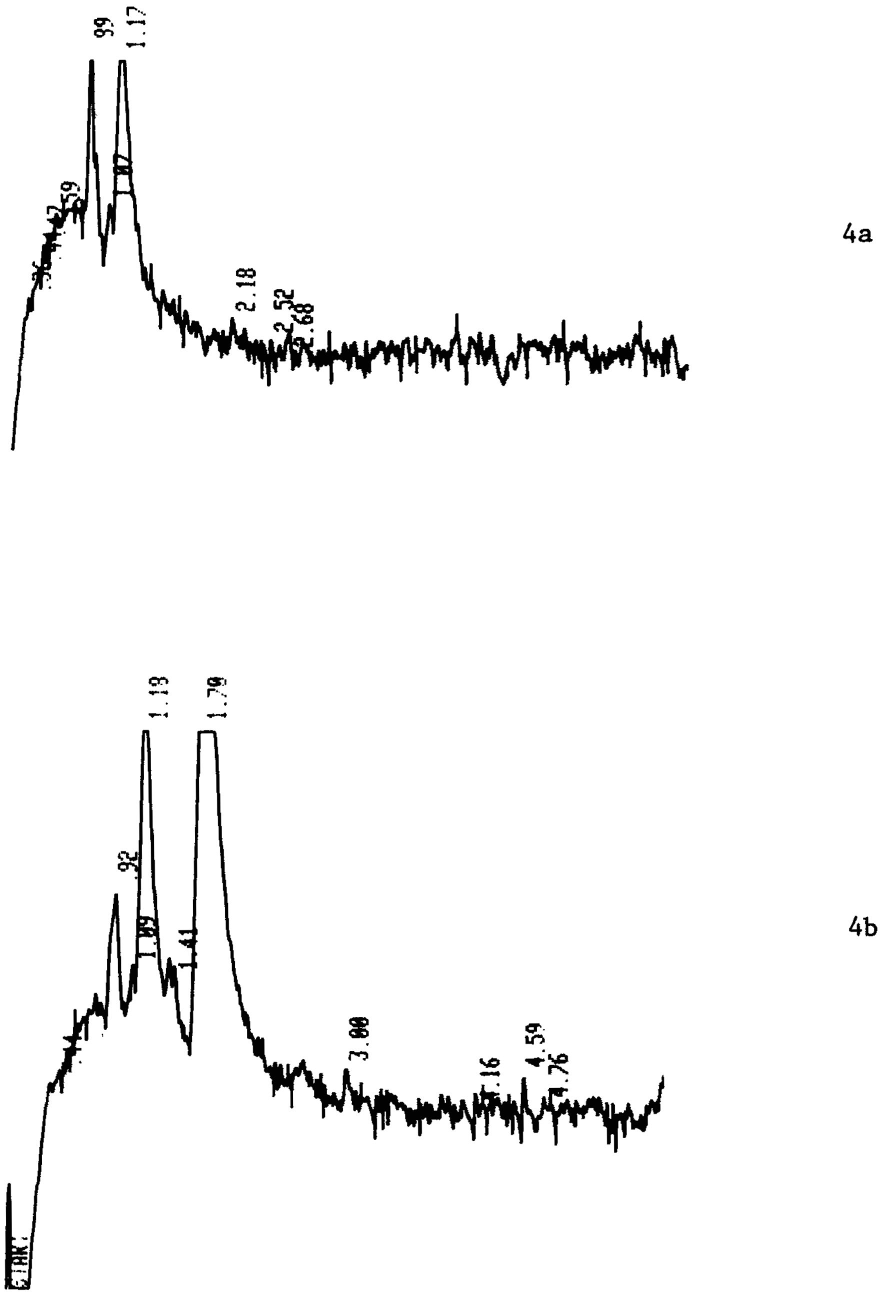


FIGURE 4. Chromatograms of Background Air (4a) and Thermex Water Gel (4b) at 70°C.

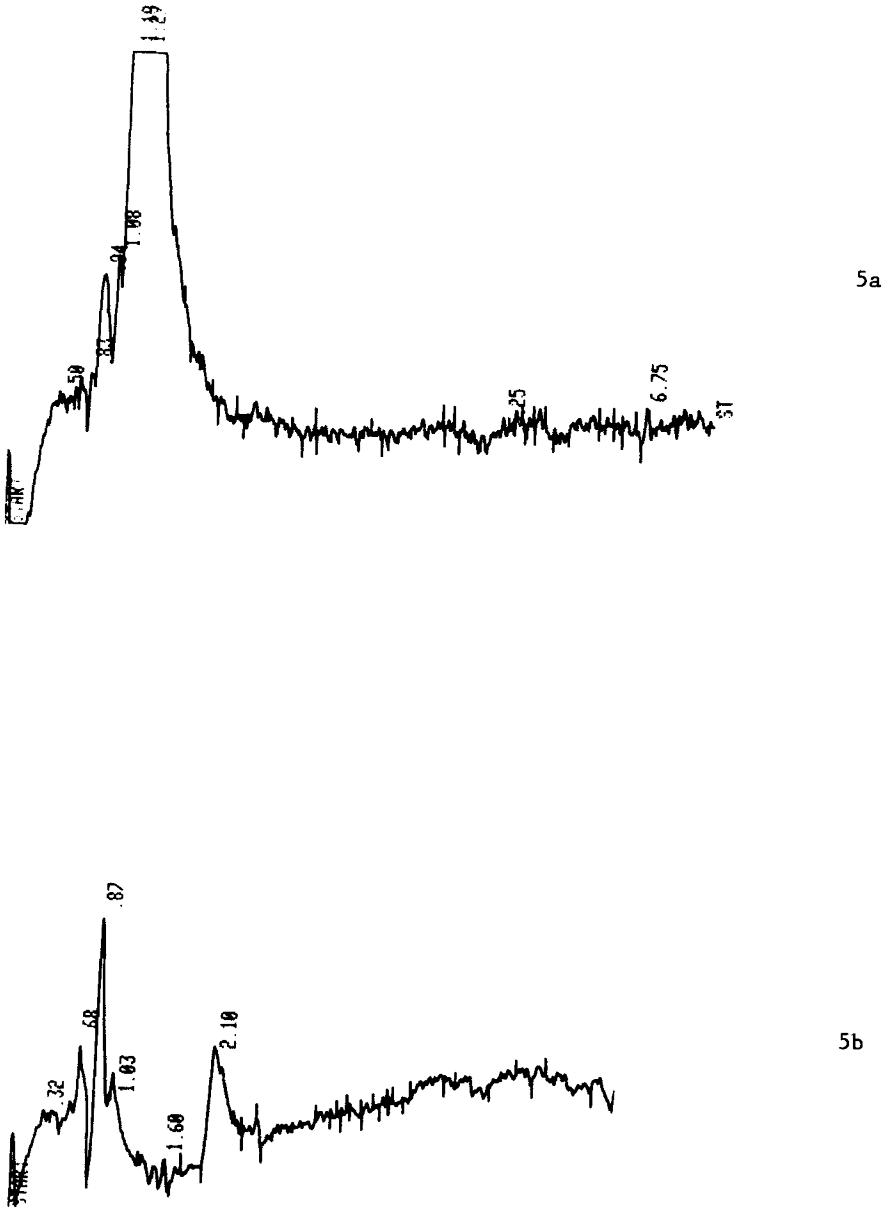


FIGURE 5. Chromatograms of Tovex 220 (5a) and Atlas (5b) Water Gels at 70° C.

TABLE 1 lists the results of the gas chromatographic analysis at 70°C of the headspace vapors from water gel explosives. The Tovex water gels contain a peak about 1.27 min and the other water gels show various peaks at different times. The effluents from dynamite are very slow eluting and produced a very small broad peak at times longer than 25 minutes and are not listed in TABLE 1.

The 100°C data are shown in FIGURES 6, 7, and 8. FIGURE 6a shows the background air sample while FIGURE 6b shows the chromatogram for the Thermex water gel. Note the large peak around 1.00 min and the very large tailing peak at about 10.50 min. FIGURE 7a shows the chromatogram of Tovex 220 water gel and FIGURE 7b shows that for the Atlas water gel. Again, note the large peak at about 0.93 min for the Tovex 220 and a somewhat smaller peak at about 3.4 min for the Atlas. The tailing paek around 10.5 min is present in both samples. This large peak has been identified as coming from dynamite and is presumed to be from ethylene glycol

TABLE 1. GC Retention Times of Water Gels at 70°C.

	Retention Times (min.)							
EXPLOSIVE	0.92	1.09	1.17	1.27	1.47	1.70	2.64	15.424
AIR BACKGROUND	X	X						
TOVEX 100	X	X	X	X				
TOVEX 220	X	X	X	X				
TOVEX 700	X	X	X	X				
TOVEX TR	X	X		X				
THERMEX	X	X	X		X	X		
ATLAS	X	X		X	X		X	X
HERCULES	X	X			X			
TROJAN	X	X	X					
DUPONT TOVEX	X	X						
DYNAMITE	X							
NITROMETHANE	X	X	X			X		

FIGURE 6. Chromatograms of Background Air (6a) and Thermex Water Gel(6b) at 100° C.

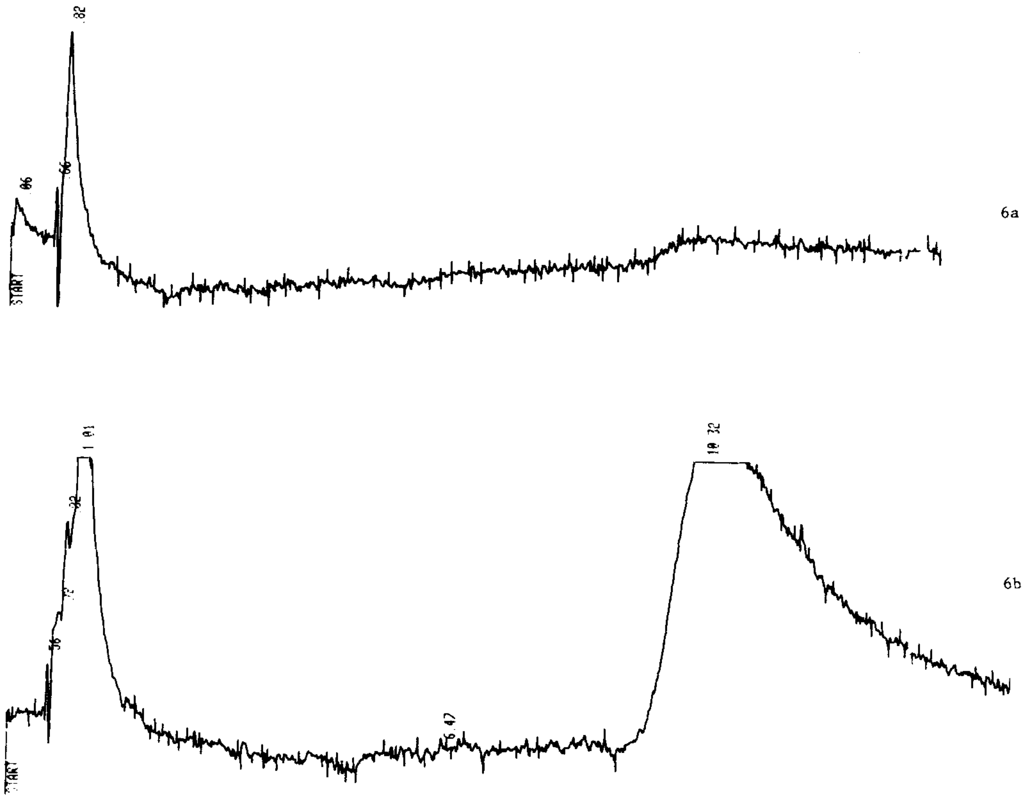
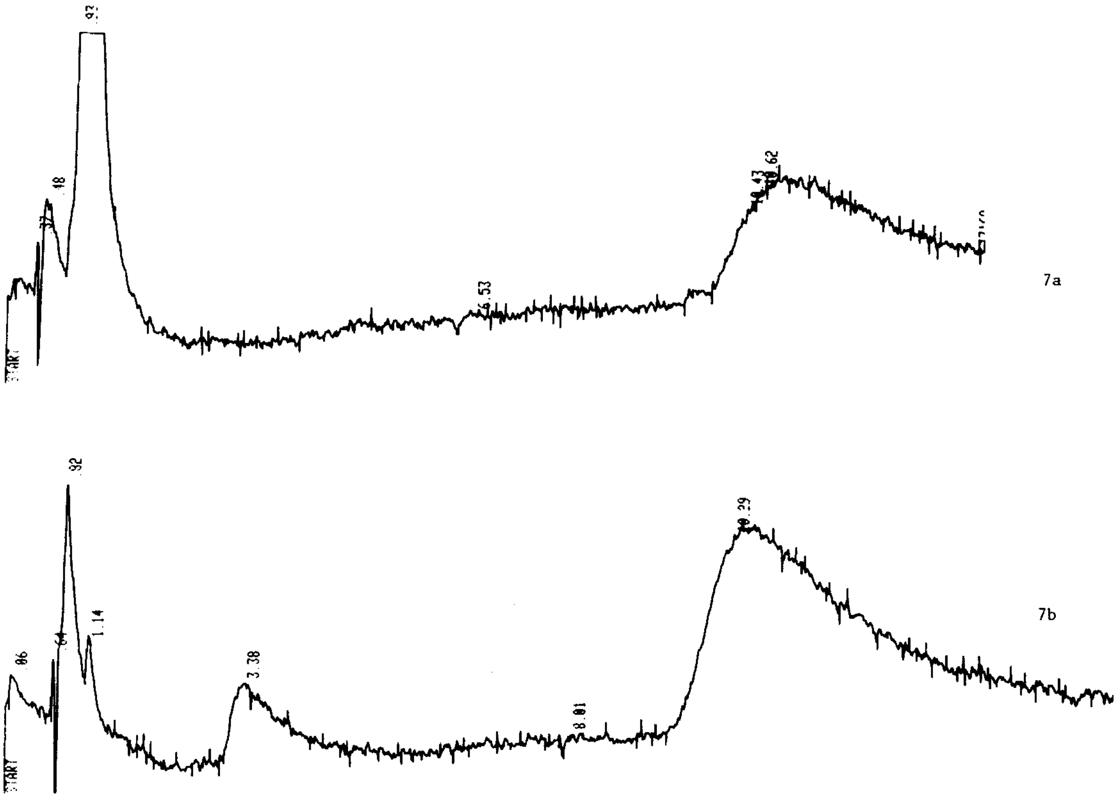


FIGURE 7. Chromatograms of Tovex 220 (7a) and Atlas (7b) Water Gels at 100°C.



dinitrate (EGDN). FIGURE 8a shows a 4 second sniff of headspace above 40% dynamite and the large peak is clearly seen at about 10.6 min.

To illustrate that the water gel explosives are not the only explosives that suffer from the contamination problem, FIGURE 8b shows the chromatogram of the headspace above a sample of 2,4,6-trinitrotoluene supplied by the manufacturer of an explosives detector. The peak at 6.78 min has not been identified and the peak at 10.6 min has been identified as coming from EGDN.

The results of the gas chromatography studies at 100°C are shown in TABLE 2. It can be seen that all the water gel explosives with the exception of the Atlas, show the presence of the EGDN contamination. The Atlas water gel also exhibited the EGDN contamination when the gas chromatograph was run at 125° and 160°C. This data clearly shows that explosives can be contaminated with EGDN from dynamite in the normal course of storage and distribution in the commercial marketplace. Therefore, it is not improbable that those who

FIGURE 8. Chromatograms of 40% Dynamite (8a) and 2,4,6-Trinitrotoluene (8b) at 100°C.

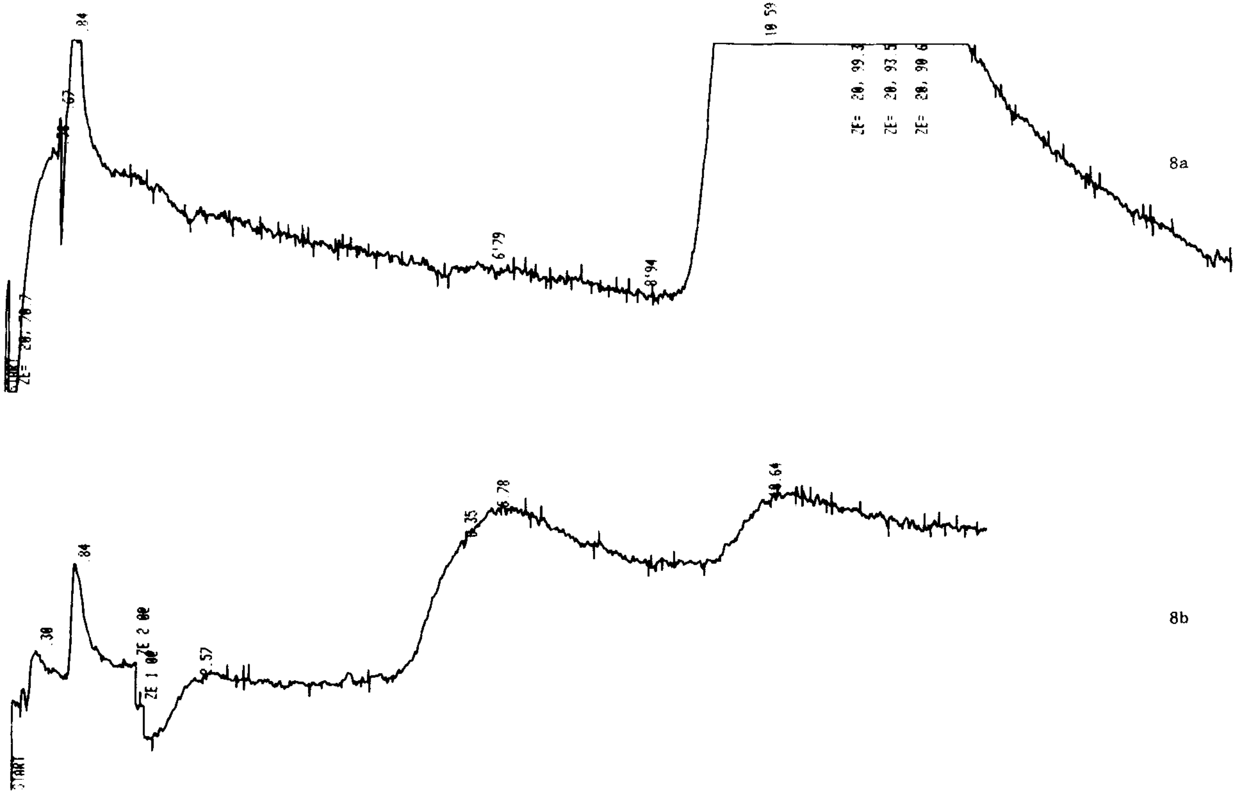


TABLE 2. GC Retention Times of Water Gels at 100°C.

	Retention Time (min.)					
EXPLOSIVE	0.40	0.52	0.90	1.14	3.38	10.59
AIR BACKGROUND	X	X				
TOVEX 100		X	X			X
TOVEX 220	X	X	X			X
TOVEX 700		X	X			X
TOVEX TR	X		X			X
THERMEX		X	X	X		X
ATLAS		X	X	X	X	X
HERCULES	X		X			X
TROJAN	X	X	X			
DUPONT TOVEX	X	X	X			X
DYNAMITE	X	X	X			X
NITROMETHANE		X				

store their plastic explosives in the same location with commercial dynamite will find them contaminated with EGDN.

To further identify some of the unknown peaks, the sampling head was connected to the Hewlett Packard 5890 capillary gas chromatograph equipped with a Hewlett Packard 5970B mass selective detector. However, the flow conditions for the injector and the mass spectrometer could not be arranged properly to permit data taking. This was probably caused by the internal plumbing of the split/splitless injector and the lack of good flow control from the XonTech sampling head.

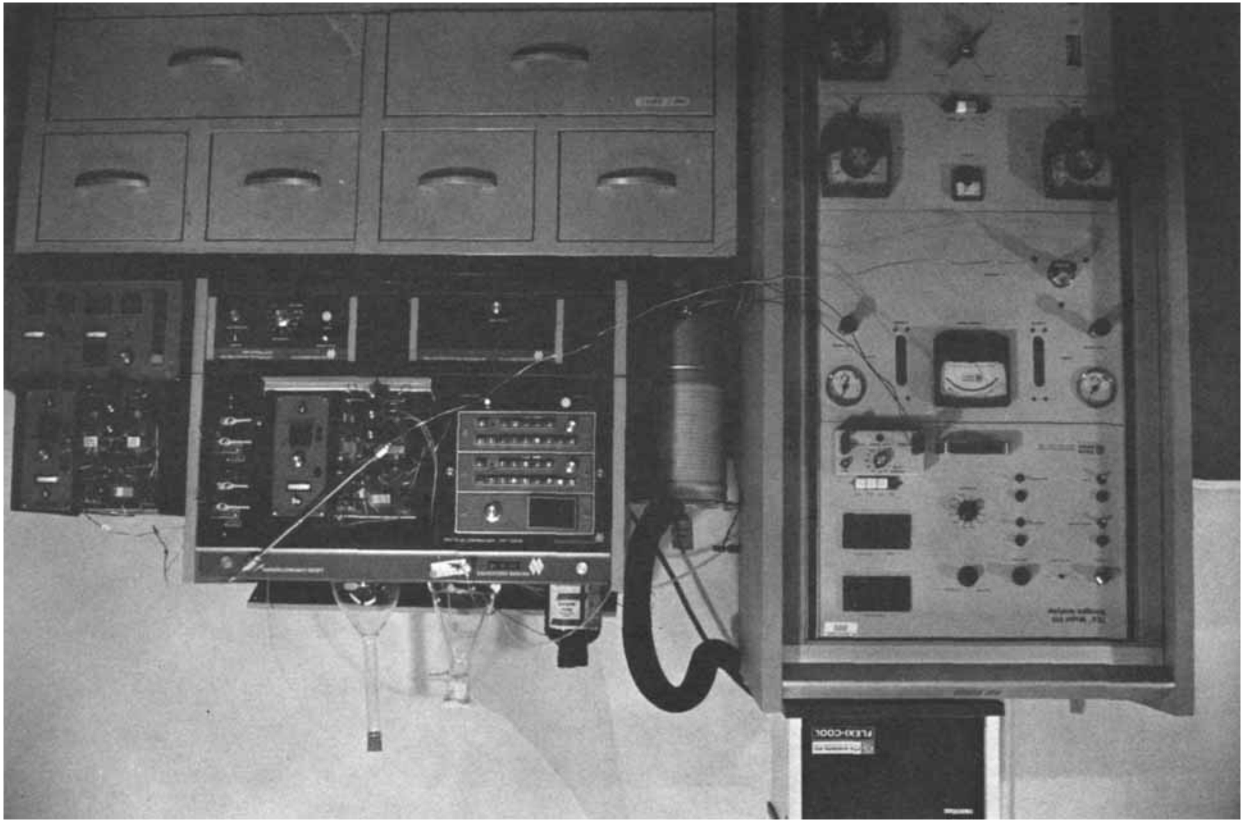
Headspace vapors from the explosives were sampled by Tenax-GC traps using a constant volume sampler. The stainless steel sample tubes containing the Tenax- GC were desorbed in a Chemical Data Systems Model CDS-120 thermal desorption apparatus into the Hewlett Packard 5890 capillary gas chromatograph equipped with the Hewlett Packard 5970B mass selective detector. The capillary column was a 0.20 mm ID, 25 meter long, Ultra-performance column coated with a 0.33 um crosslinked 5% phenyl methyl silicone film. The gas chromatograph was held isothermal at 40°C for 6 min, then temperature programed at 6°C per min to 200°C and then held for 10 min at 200°C. Thermex water gel and 40% Dynamite were the only explosives samples that could be analyzed by this technique. Thermex showed the presence of nitromethane and nitropropane while the dynamite sample contained both EGDN and NG. The other water gel samples did not show the presence of any volatiles trapped by the Tenax-GC.

LIQUID CHROMATOGRAPHY-THERMAL ENERGY ANALYSIS

Beacuse the unknown peaks in the gas chromatograms could not be identified by GC/MS analysis of trapped vapors on Tenax-GC, it was decided to try to analyze the water gels by high pressure liquid chromatography followed by thermal energy analysis (HPLC/TEA). The water gel samples were dissolved in both acetone and the HPLC solvent and allowed to stand over a weekend. The samples were filtered on a sample filtration system and the extracted materials analyzed on a Waters liquid chromatograph connected to a Thermedics Model 510 thermal energy analyzer. A Waters Model 6000A solvent delivery system, a Waters Model U6K injector, and a Waters u-Bondedpak CN column (3.9mm x 30cm) comprised the liquid chromatograph. The HPLC was operated isocratically with a solvent system of iso-octane/methylene chloride/methanol in the ratio 165/35/10. The solvents used were Burdick and Jackson and were filtered on a Waters Durapore 0.22μ solvent filtering system. Solvent flow rates were 1.5 and 2.0 ml/minute. The apparatus is shown in FIGURE 9.

The results of the HPLC/TEA analysis are shown in FIGURES 10, 11, and 12. FIGURE 10 shows the HPLC/TEA chromatogram of Tovex 220 in solvent (10a) and in Acetone (10b). The peaks at 3.2 and 4.3 min are from the EGDN and NG contaminates from dynamite. FIGURE 11a shows the HPLC/TEA chromatogram for Thermex and FIGURE 11b shows the HPLC/TEA chromatogram for Trojan water gels in acetone. Again the peaks are due to the presence of EGDN and NG contamination. FIGURE 12 shows the

FIGURE 9. High Pressure Liquid Chromatograph and Thermal Energy Analyzer.



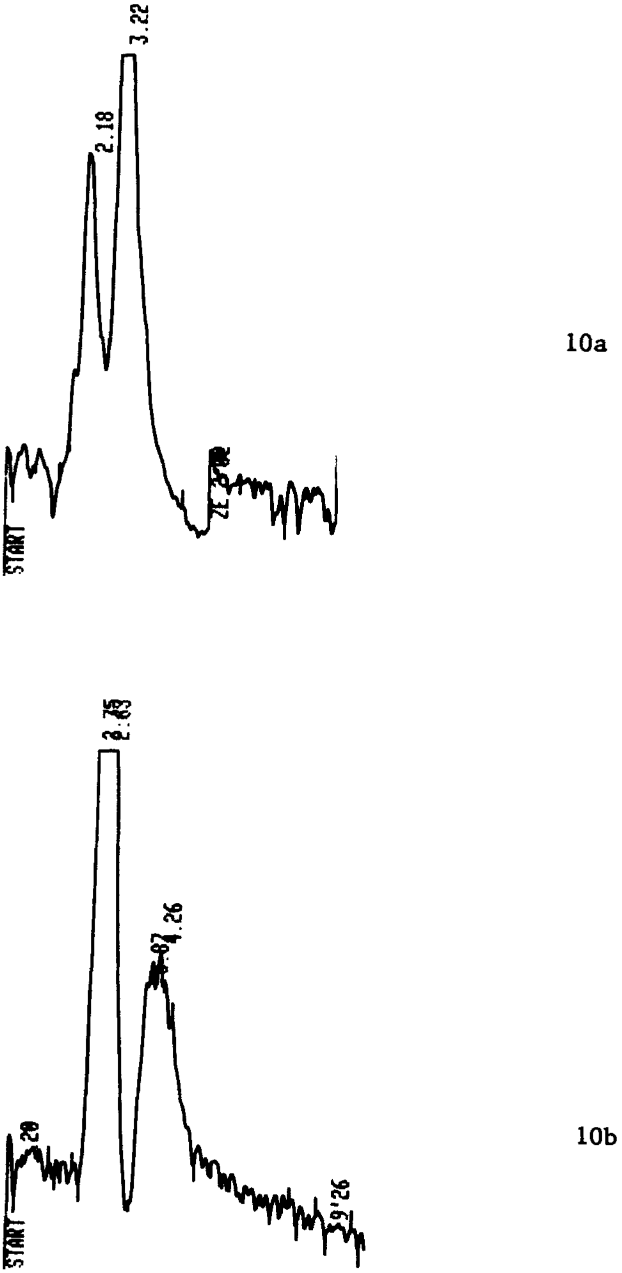


FIGURE 10. HPLC/TEA Chromatograms of Tovex 220 in Solvent (10a) and Acetone (10b).

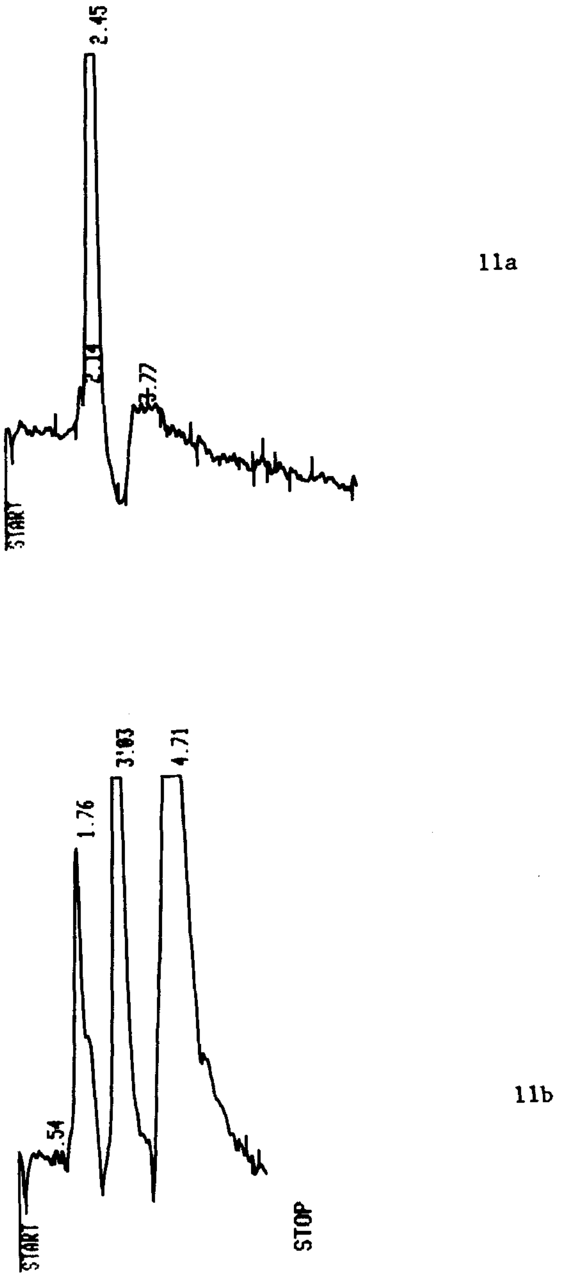


FIGURE 11. HPLC/TEA Chromatograms of Thermex (11a) and Trojan (11b) in Acetone.

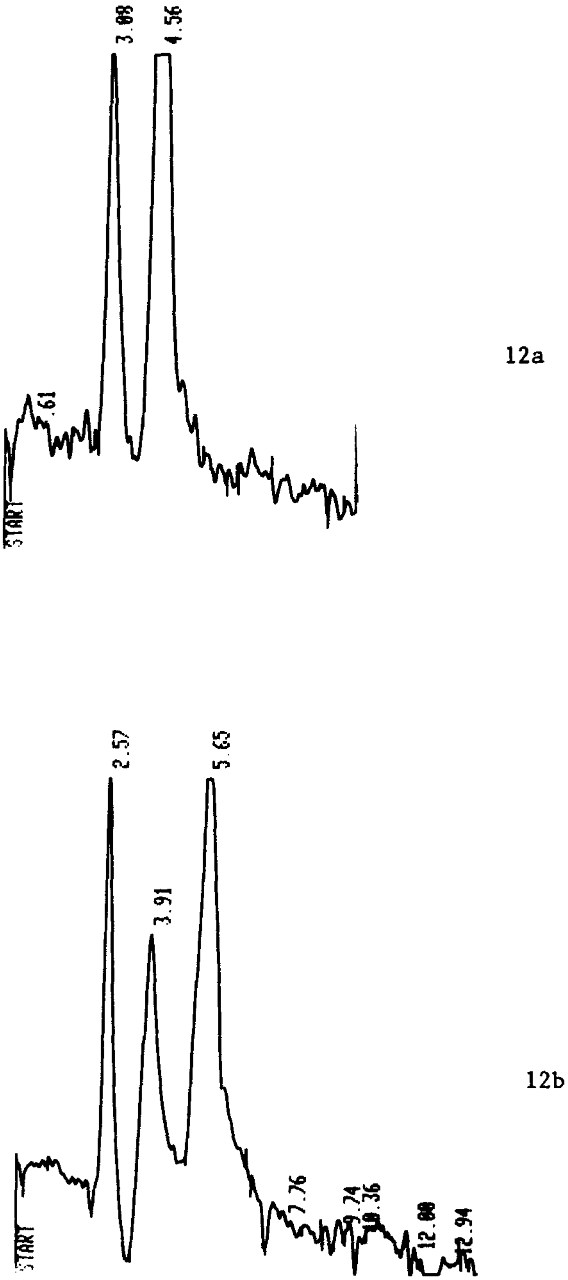


FIGURE 12. HPLC/TEA Chromatograms of 40% Dynamite in Solvent (12a) and Acetone (12b).

HPLC/TEA chromatograms for 40% dynamite in solvent (12a) and in acetone (12b).

The results of the HPLC/TEA analysis are shown tabulated in TABLE 3. It can be seen from the data in the table that every water gel analyzed showed the presence of EGDN and NG contamination from dynamite.

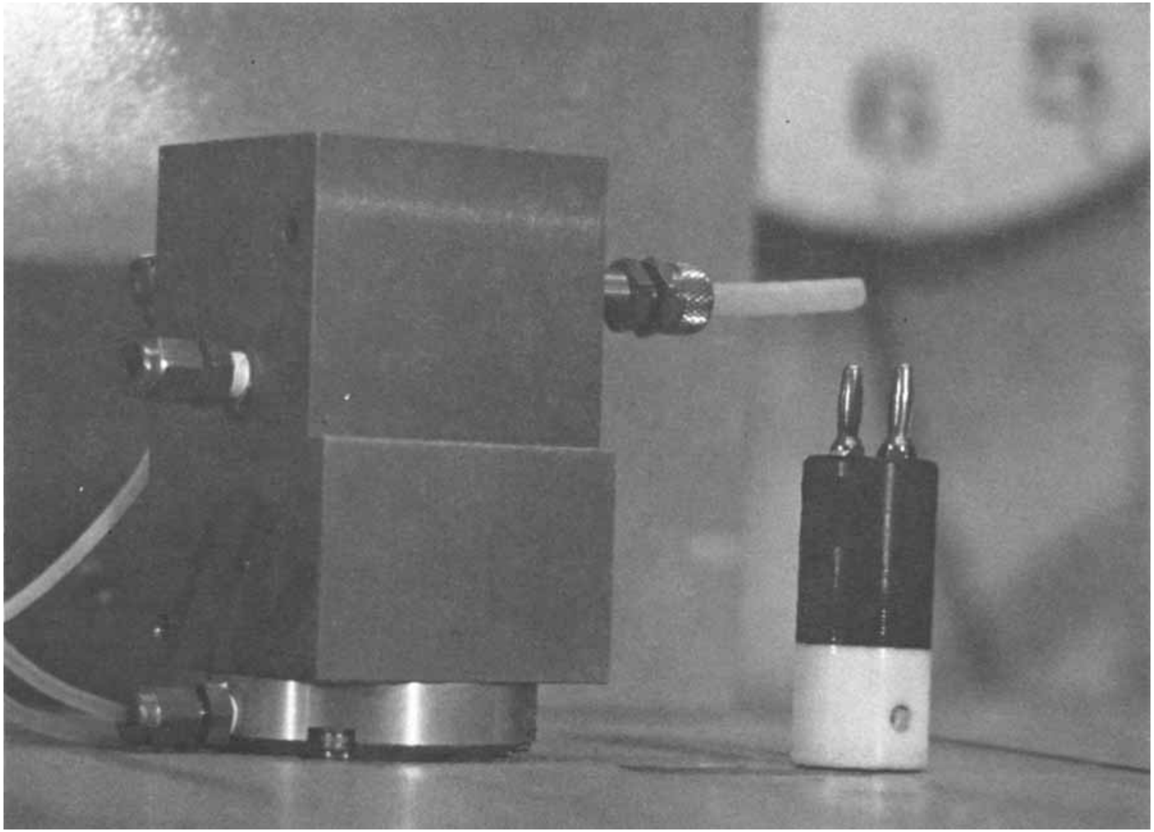
GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Further analysis of the dissolved water gels was carrried out using combined gas chromatography-mass spectrometry. The analytical system used was the Hewlett Packard 5890 gas chromatograph and the Hewlett Packard 5970B mass selective detector described above. Splitless injections were used with the septum purge vent opened 0.45 sec after injection. The oven was held at 36 °C for 2.75 min and then temperature programmed to 200 °C at the rate of 6 °C/min and held at 200 °C for 10 min. The apparatus is shown in FIGURE 13.

TABLE 3. HPLC/TEA Retention Times of Water Gels.

	Retention Time (min.)				
EXPLOSIVE	2.20	2.55	3.1-3.2	3.90	4.56
ACETONE	X	X			
HPLC SOLVENT					
TOVEX 100		X		X	X
TOVEX 220	X	X	X	X	X
TOVEX 700	X		X		X
TOVEX TR	X		X		X
THERMEX	X		X	X	
ATLAS		X		X	X
HERCULES	X		X	X	X
TROJAN	X		X		X
DUPONT TOVEX	X		X	X	
DYNAMITE		X	X	X	X
NITROMETHANE		X			

FIGURE 13. Hewlett Packard Gas Chromatograph-Mass Spectrometer.



Typical total ion chromatograms are shown in FIGURE 14 for Tovex 220 water gel and in FIGURE 15 for Hercules water gel. FIGURE 16 shows a typical mass spectral library match for the peak at 3.468 min and FIGURE 17 shows similar match for the peak at 4.632 min. The results of the GC-MS analysis of the water gels are tabulated in TABLE 4. where the compounds identified are listed under each water gel. All of the water gels contain 2-butanone, 2,2-dimethyl-1,3-dioxolane, and 1,1-ethanediol diacetate. A variety of other compounds were also found. In only one analysis was nitromethane found and this was due to the fact that the nitromethane was so close to the solvent peak and was not always separated.

CONCLUSIONS

The results of these analysis show that commercially available explosives can become contaminated with EGDN and NG when stored with dynamites. It is also probable that plastic explosives could also become contamined in the same way even when stored near dynamite in the

FIGURE 14. Total Ion Chromatogram of Tovex 220 Water Gel.

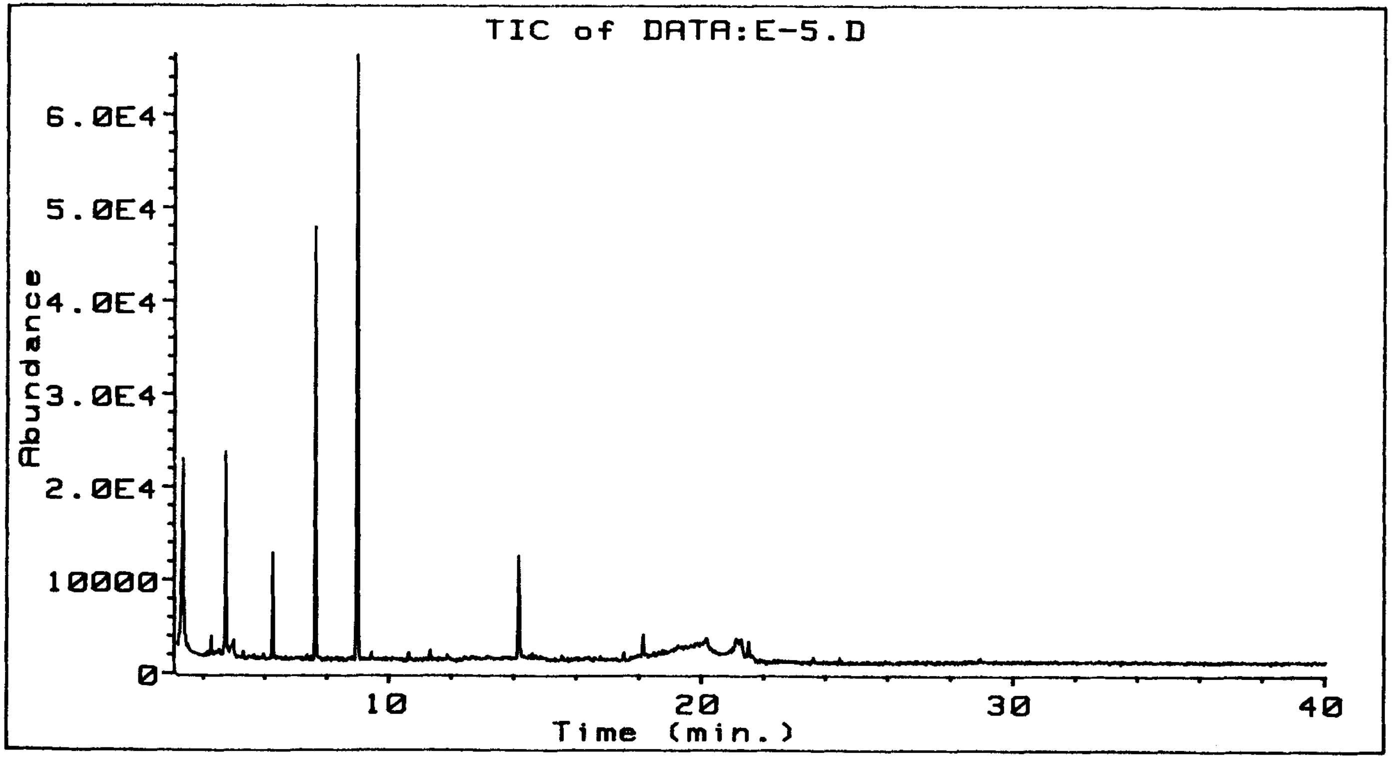


FIGURE 15, Total Ion Chromatogram of Hercules Water Gel.

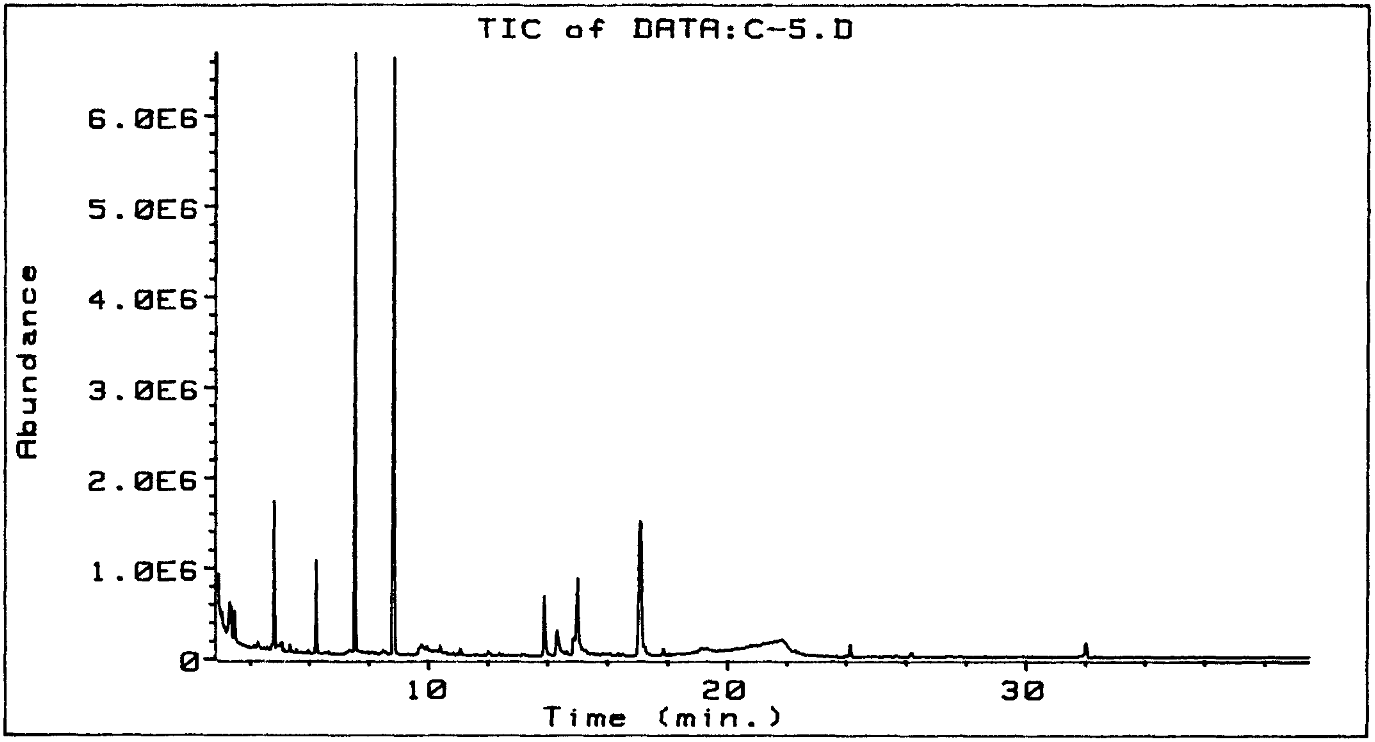


FIGURE 16. Mass Spectral Library Match of Scan 22 (3.468 min).

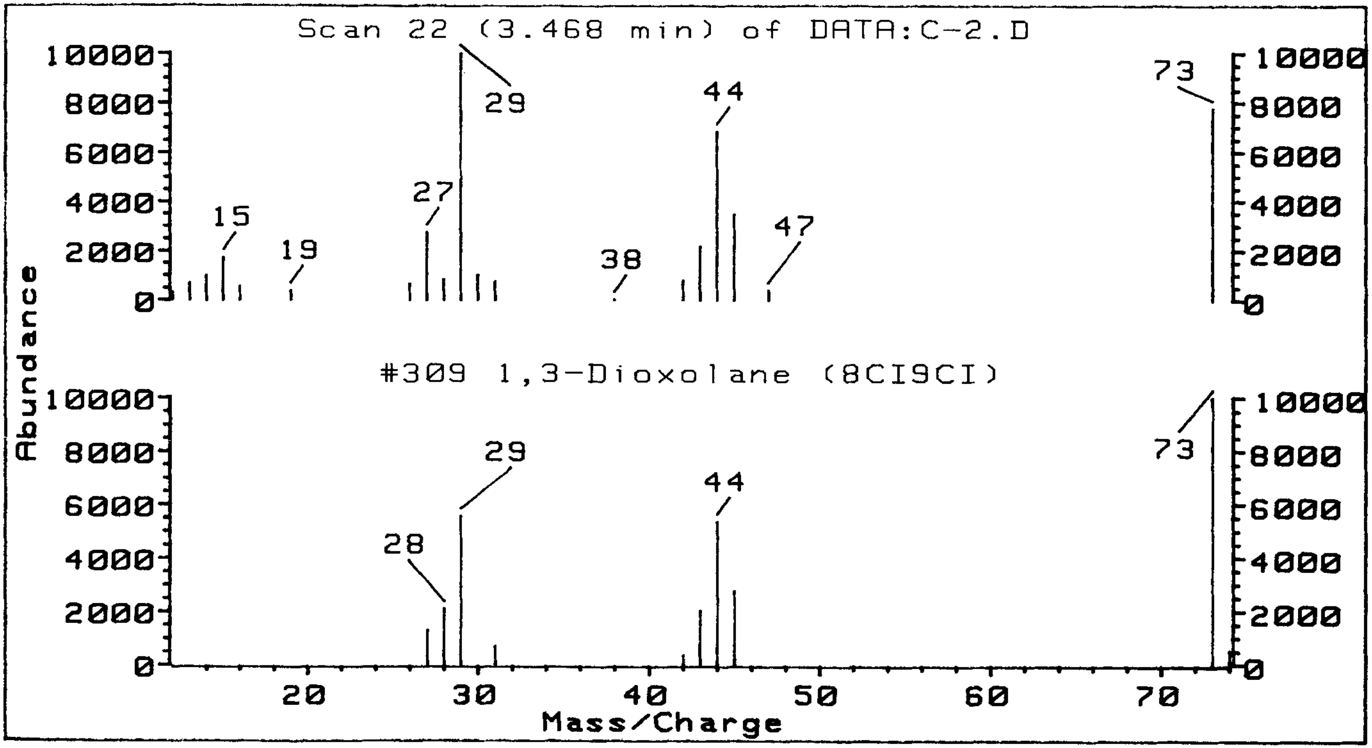


FIGURE 17. Mass Spectral Library Match of Scan 67 (4.632 min).

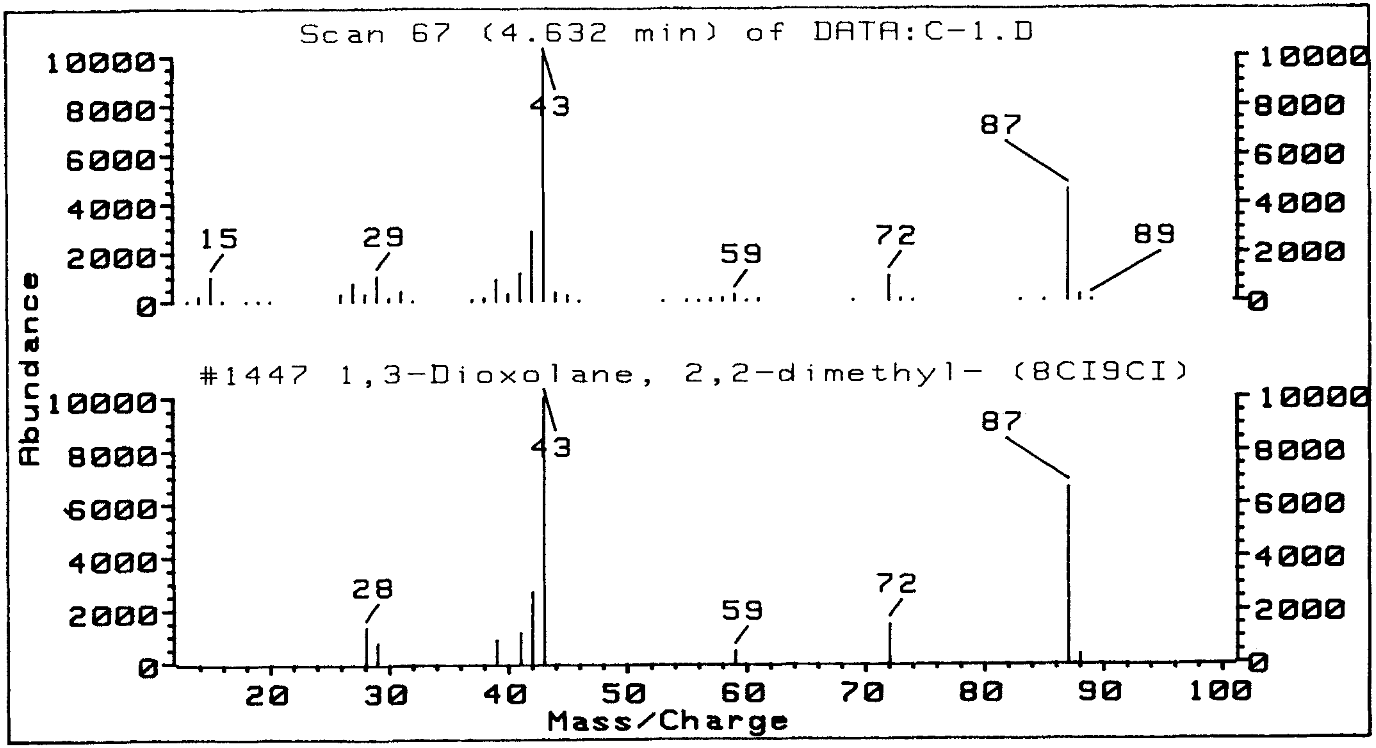


TABLE 4. Compounds Identified in Water Gels by GC/MS.

	Water Gel									
COMPOUND	1	2	3	4	5	6	7	8	9	10
NITROMETHANE	X	X								
2-BUTANONE	X	X	X	X	X	X	X	X	X	
CYCLOPENTANAMINE	X	X		X						
1,3-DIOXOLANE				X	X	X	X	X	X	X
2,2-DIMETHYL-1,3-DIOXOLANE	X	X	X	X	X	X	X	X	X	X
PROPYL ESTER ACETIC ACID			X	X	X		X		X	
4-METHYL-2-PENTEN-2-ONE	X	X	X	X		X	X	X	X	
2-NITROSO-2-PROPANOL ACETATE		X	X	X	X	X	X	X	X	X
CYCLOHEXANONE		X		X	X				X	
3,4-DIMETHYL-3-PENTEN-2-ONE					X				X	
1,1-ETHANEDIOL DIACETATE	X	X	X	X	X	X	X	X	X	X
3,5,5-TRIMETHYL-2-CYCLOHEXAN-2-ONE	X	X		X	X		X		X	

1	TOVEX 100
2	TOVEX 220
3	TOVEX 700
4	TOVEX TR
5	THERMEX
6	ATLAS
7	HERCULES
8	TROJAN
9	DUPONT TOVEX
10	NITROMETHANE

laboratory. These results emphasize that one should be very careful in handling and storing explosives used for the purpose of evaluating explosives detectors since erroneous results could be achieved.