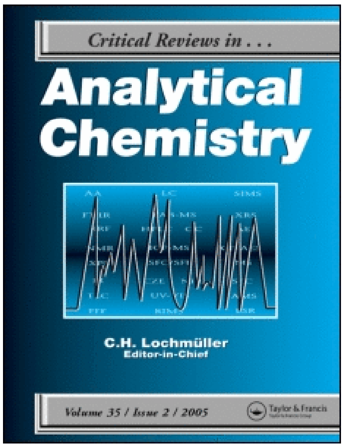

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ANALYSIS OF EXPLOSIVES

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I. INTRODUCTION

The analysis of explosives is of major importance in several analytical fields:

1. Forensic identification of explosives is a major problem in the criminalistic investigation of a bombing which involves connecting the type of explosive used with the suspect. The detection and identification of explosive residues in debris material constitutes a highly difficult task. The thermal instability of most explosives, along with the requirements of high sensitivity of the analysis, limit the number of analytical techniques which can be used in such determinations.
2. The detection of explosives concealed in airline baggage or in mail is an extremely relevant analytical problem which requires a highly sensitive as well as a specific method for its solution. Highly specific monitors are expected to identify and detect the presence of molecules of explosive material in the sampled air environment in the suspected baggage or mail.
3. The accurate determination of the composition of explosives is very important because variation in composition affects the stability, sensitivity, ignitability, and efficiency of performance of these materials. Analysis of explosives in storage is important for assessing the purity of their components, the uniformity of composition, and the various decomposition products.
4. In trace element analysis, the search for contamination from explosives in sea water and in the ocean floor sediment and fauna as a result of obsolete munitions dump in deep water, as well as surveillance and control of explosives pollutants that may find their way into ground and surface water supplies is important.
5. Another important area is biomedical analysis. Because many explosives are toxic, inhalation of their vapor presents a major health hazard. Quantitative monitoring of the vapor of explosives in the environment of industrial plants where explosives are manufactured is, therefore, a necessity. Periodical analyses of body fluids of personnel working in these plants have to be made for the detection of traces of explosives in blood and urine.

Simultaneously, with the increase of fields in which explosives are involved and the development of new types of explosives, the techniques used for their analysis have become more sophisticated. The most widely used techniques for the analysis of explosives are the chromatographic techniques, thin-layer chromatography, gas chromatography, and, recently, high-pressure liquid chromatography. During the last few years, mass spectrometry, especially chemical ionization mass spectrometry, has been developed into a useful technique for the analysis of explosives. This article will review the state of development of the chromatographic and mass spectrometric techniques for the analysis of explosives and estimate their usefulness for this purpose. This article will also consider more limited techniques such as microscopic examination, chemical tests, spectroscopic methods (infrared, ultraviolet, and nuclear magnetic resonance) polarography, and differential thermal analysis.

II. CLASSIFICATION OF EXPLOSIVES

In order to be able to evaluate the methods and techniques used for the analysis of explosives, it is necessary to classify the types of explosives in use and to determine those which this article will include. The classification has been done according to the chemical composition of the explosive rather than its use.

Explosives can be divided into the following groups:[1]

1. Nitro compounds
2. Nitric esters
3. Nitramines
4. Salts of nitric, chloric, and perchloric acids
5. Azides and other compounds capable of producing an explosion
6. Mixtures

This list of explosives does not include all explosive compounds but is intended to give a list of the most widely used explosives and related compounds in context with the various analytical methods of their analysis (Table 1).

III. ANALYTICAL METHODS

A. Microscopic Examination

Microscopic examination is useful in the

TABLE 1

List of Explosives

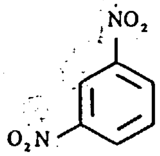
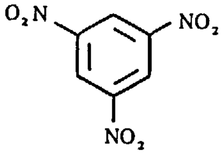
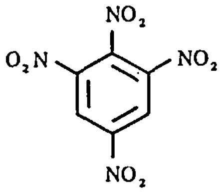
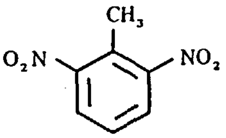
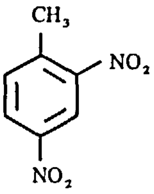
Name	Structure	Comments
Nitro compounds		Characterized by the carbon-nitrogen bond C–NO_2
Aromatic		Mainly those compounds which have three or more nitro groups for one benzene ring and some of those which have two nitro groups (dinitrobenzenes and dinitrotoluenes) exhibit characteristic explosive properties
Nitro derivatives of benzene Dinitrobenzene (DNB)		
Trinitrobenzene (TNB)		
Tetranitrobenzene		
Nitro derivatives of toluene Dinitrotoluene (DNT)	 2,6-DNT  2,4-DNT	

TABLE 1 (continued)

List of Explosives

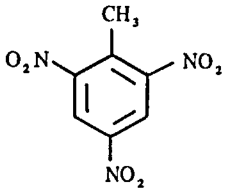
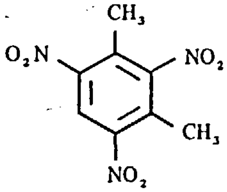
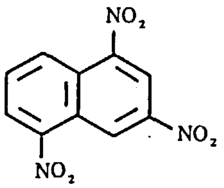
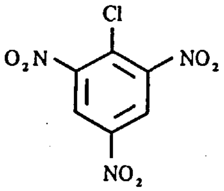
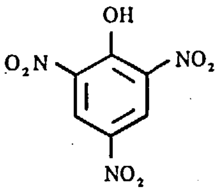
Name	Structure	Comments
Trinitrotoluene (TNT)	 2,4,6-TNT	
Nitro derivatives of xylenes Trinitro-*m*-xylene (TNX)		
Nitro derivatives of naphthalene Trinitronaphthalene (TNN)	 1,3,5-TNN	
Nitro derivatives of chlorobenzene 2,4,6-Trinitrochlorobenzene (picryl chloride)		
Nitro derivatives of phenol 2,4,6-Trinitrophenol (picric acid)		

TABLE 1 (continued)

List of Explosives

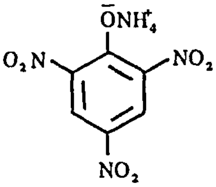
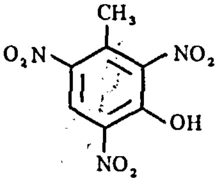
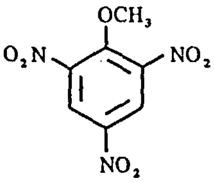
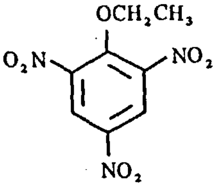
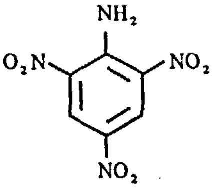
Name	Structure	Comments
Picric acid salts such as ammonium picrate		
Nitro derivatives of cresols Trinitro-*m*-cresol (TNC)		
Picric acid ethers		Formed by substituting the acid hydrogen in picric acid by an aliphatic or aromatic radical in order to eliminate the acidic character of picric acid
Trinitroanisole (TNA)		
Trinitrophenetole (TNP)		
Nitro derivatives of aniline Trinitroaniline (picramide)		

TABLE 1 (continued)

List of Explosives

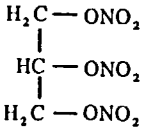
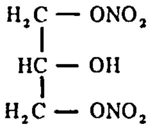
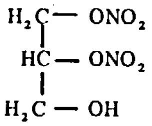
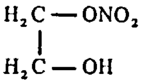
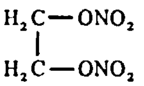
Name	Structure	Comments
Aliphatic		
Nitromethane	CH_3NO_2	
Dinitromethane	$CH_2(NO_2)_2$	
Trinitromethane (nitroform)	$CH(NO_2)_3$	
Tetranitromethane	$C(NO_2)_4$	
Nitric esters		Characterized by the atomic grouping $-C-O-NO_2$, that is, by the presence of a nitroxy group; the nitro group in nitric esters is attached to a carbon atom by means of an oxygen atom; some esters of nitric acid are very powerful explosives because they possess as many nitro ester groups as carbon atoms
Glycerine esters		
Nitroglycerin (NG) or glycerol trinitrate	 $\begin{array}{l} H_2C-ONO_2 \\ \vert \\ HC-ONO_2 \\ \vert \\ H_2C-ONO_2 \end{array}$	One of the most widely used explosives; main component of high explosives such as dynamite, as well as an ingredient in most mining explosives and an essential ingredient of smokeless double-base propellants[2]
Dinitroglycerin or glycerol dinitrate	 $\begin{array}{l} H_2C-ONO_2 \\ \vert \\ HC-OH \\ \vert \\ H_2C-ONO_2 \end{array}$  $\begin{array}{l} H_2C-ONO_2 \\ \vert \\ HC-ONO_2 \\ \vert \\ H_2C-OH \end{array}$	After nitroglycerin, the most powerful explosive among glycerin esters; two isomeric glycerol dinitrates are known
Glycol esters		
Ethylene glycol mononitrate (mononitroglycol or glycerol mononitrate)	 $\begin{array}{l} H_2C-ONO_2 \\ \vert \\ H_2C-OH \end{array}$	
Ethylene glycol dinitrate (EGDN) (nitroglycol) or glycol dinitrate (GDN)	 $\begin{array}{l} H_2C-ONO_2 \\ \vert \\ H_2C-ONO_2 \end{array}$	

TABLE 1 (continued)

List of Explosives

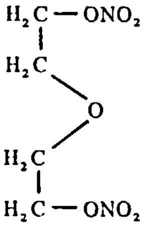
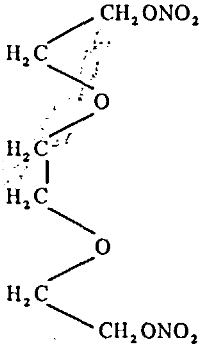
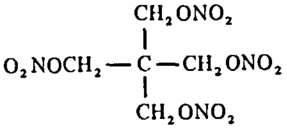
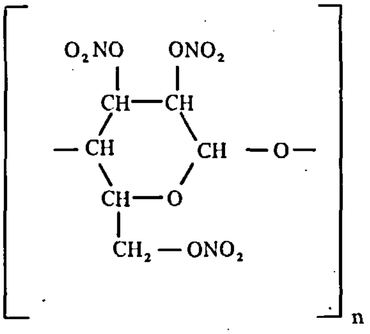
Name	Structure	Comments
Diethylene glycol dinitrate (DEGDN or DEGN)		
Triethylene glycol dinitrate (TEGN)		
Polyhyhydroxylic branched-chain esters Pentaerythritol tetranitrate (PETN)	 $O_2NOCH_2{-}\overset{\overset{CH_2ONO_2}{\vert}}{\underset{\underset{CH_2ONO_2}{\vert}}{C}}{-}CH_2ONO_2$	
Carbohydrate esters Cellulose nitrate or nitrocellulose (NC)	 or $[C_6H_7N_3O_{11}]_n$	The most important explosives of the carbohydrate esters of nitric acid are the polysaccharide nitrates, particularly cellulose nitrate

TABLE 1 (continued)

List of Explosives

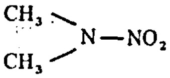
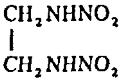
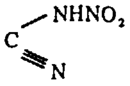
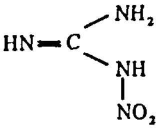
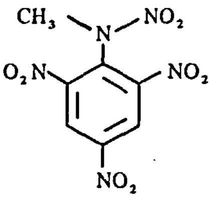
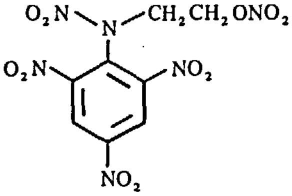
Name	Structure	Comments
Nitramines		Characterized by the band of a nitro group to the nitrogen atom: $N{-}NO_2$; are basically derivatives of the simplest inorganic nitramine,[3] NH_2NO_2
Aliphatic		
Nitramine	NH_2NO_2	
Methylnitramine	CH_3NHNO_2	
Dimethylnitramine		
Ethylenedinitramine (EDNA) (Haleite)	 $\begin{array}{l} CH_2NHNO_2 \\ \vert \\ CH_2NHNO_2 \end{array}$	
Nitrocyanamide		
Nitroguanidine		
Aromatic		
2,4,6-*N*-Tetranitro-*N*-methylaniline (tetryl)		
Nitramino esters of nitric acid, such as trinitrophenyl-β-hydroxy-nitraminoethyl nitrate (pentryl, pentyl)		

TABLE 1 (continued)

List of Explosives

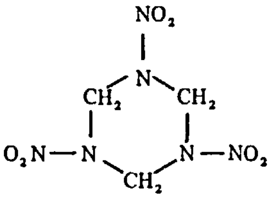
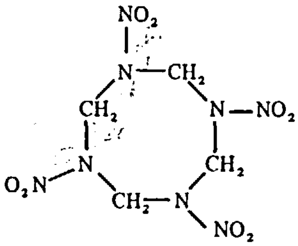
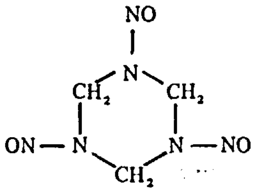
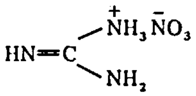
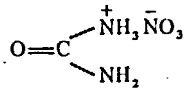
Name	Structure	Comments
Heterocyclic		
1,3,5-Trinitro-1,3,5-triazacyclohexane (hexogen, cyclonite, RDX)		
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (octogen, HMX)		
Nitrosamines such as trimethylene trinitrosamine		
Salts of nitric, chloric, and perchloric acid		
Salts of nitric acid		
Ammonium nitrate	NH_4NO_3	
Guanidine nitrate		
Urea nitrate		
Metallic salts such as sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3)		Not explosives themselves but used in many explosive mixtures as oxygen carriers
Salts of chloric and perchloric acids		
Ammonium chlorate	NH_4ClO_3	
Ammonium perchlorate	NH_4ClO_4	

TABLE 1 (continued)

List of Explosives

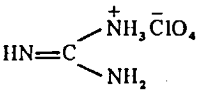
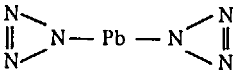
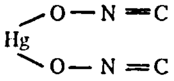
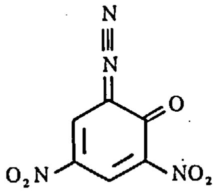
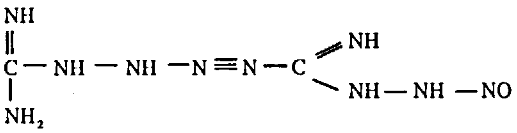
Name	Structure	Comments
Hydrazine perchlorate	$NH_2NH_3ClO_4$	
Nitryl perchlorate	NO_2ClO_4	
Methylamine perchlorate	$CH_3NH_3ClO_4$	
Guanidine perchlorate		
Salts of other acids		
Ammonium bichromate	$(NH_4)_2Cr_2O_7$	
Ammonium permanganate	NH_4MnO_4	
Ammonium nitrite	NH_4NO_2	
Azides and other compounds capable of producing an explosion		
Azides		
Hydrazoic acid	HN_3	
Lead azide	$Pb(N_3)_2$ 	
Silver azide	AgN_3	
Fulminates		
Mercury fulminate		
Silver fulminate	$AgC_2N_2O_2$	
Diazo compounds		
. Diazodinitrophenol		
Derivatives of aminoguanidine		
Tetrazene		
Acetylides		
Cuprous acetylide	CuC_2	
Silver acetylide	Ag_2C_2	

TABLE 1 (continued)

List of Explosives

Name	Structure	Comments
Mixtures		Most modern practical explosives are mixtures of several components in order to obtain the required characteristics; the list of mixtures used is very long; thus, only a limited number of some widely used explosives is given
Amatol	TNT + ammonium nitrate	
Tritonal	TNT + aluminum powder	
Hexolit, composition B	TNT + RDX	
Pentolite	TNT + PETN	
Octol	TNT + HMX	
Torpex	TNT + RDX + aluminum powder	
Tetrytol	Tetryl + TNT	
Dynamites	Nitroglycerin + nitroglycol	
Phlegmatized and plastic explosives		
Black powder, gun powder	Potassium nitrate + sulfur + charcoal	
Smokeless powder	Nitroglycerin + nitrocellulose	

examination of debris collected at an explosion site. Most of the explosive has been consumed upon detonation and usually only a very small amount, if any, of the original material remains. Materials such as wood, masonry, fabric, aluminum, rubber, and other soft materials, which are readily penetrated by flying particles, are most likely to collect explosive residues.

Washington and Midkiff[4] have used a stereomicroscope with variable magnification of 7 to 30 times and a high-intensity light source for the examination of debris from the explosion site for the presence of aggregates or particles of unburned explosive residues. The observed aggregates and particles are then removed and identified by a number of analytical techniques.

Hoffman and Byall[5] have used a stereomicroscope at a magnification of 5 to 15 times. The visual appearance of the explosive residue might give a clue to its identity and suggest the analytical technique to be used. Smokeless powder can be identified solely by the use of microscopic examination because of its characteristic appearance.[5] Beveridge et al.[6] have used microscopic examination as the first stage in a series of techniques for the systematic analysis of explosive residues. Microscopic examination is effective only in the identification of explosive compounds with a specific shape and color, such as granules of unreacted black powder, and should, therefore, be used only as a first qualitative screening technique of debris collected at explosion sites.

B. Chemical Tests

Qualitative chemical analysis of explosives is a long and involved procedure which requires a thorough knowledge of the possible ingredients of the investigated material. General methods of organic analysis are usually based on class tests and physical constants such as the melting points or densities. Such analytical methods can be applied only to pure compounds; therefore, prior separation and purification of the various ingredients of an explosive are needed.

Pristera et al.[7] have prepared a list of melting points and other physical constants of explosives. They have also provided information on the solubility of a series of explosive ingredients in four selected solvents: carbon tetrachloride, benzene, water, and acetone.

Chemical methods for the analysis of mixtures make use of[7] differential solubilities in various solvents, estimation of the organic nitrate content by reduction with a suitable ferrous solution, estimation of the nitroaromatic content by reduction with a suitable titanous solution, and acid-base titrations for acidic ingredients such as picric acid and ethylenedinitramine. These methods, however, are used mainly for qualitative analysis and for the determination of the presence of certain compounds in materials suspected to be explosives, especially for spot tests.

A spot test for dinitro and trinitro aromatic compounds uses the characteristic colors developed in 50/50 acetone-alcohol with 5% potassium hydroxide.[8] This technique has been further developed by Amas and Yallop:[9] the addition of a 5- to 10-mg specimen of one drop of acetone-alcohol and one drop of tetramethylammonium hydroxide produces a blue color with dinitrotoluene, a dark red color with trinitrotoluene and a slightly yellow color with nitroglycerin. The limits of identification are 4 μg for *m*-dinitrobenzene, 2 μg for 2,4-dinitrotoluene, and 1 μg for 2,4,6-trinitrotoluene.

If an excess of iron sulfate is present in concentrated sulfuric acid medium, then when small amounts of nitrates or nitrites are added, a pink to dark red color (depending on the amount present) is obtained.[10] The iron reagent was prepared by a 5:1 (v/v) mixture of concentrated sulfuric acid with a 10% solution of iron sulfate. In mixtures of 2 mg potassium nitrate with 300 mg potassium cyanide, sodium thiosulfate, or ammonium persulfate, nitrate could be detected by the addition of 0.1 g of the mixture to a few milliliters of the reagent. Direct addition to the reagent could not be made to detect nitrate in mixtures containing chlorate, chloride, bromate, bromide iodate, or dichromate because of interference. Amas and Yallop[11] have developed a series of chemical tests to determine the presence or absence of ingredients in industrial blasting gelignite explosives found in explosion debris. The method consists of 16 different chemical tests and visual examination of resulting color. The method is simple and takes no longer than 10 min but requires an amount of 2 to 500 mg of sample, depending on the ingredients of interest.

A spot test developed by Amas and Yallop[12] for the identification of RDX is based on its reaction with thymol and sulfuric acid. This reaction is carried out at 100°C and a violet color is produced. The whole sample is then dissolved in ethanol which results in a blue solution. Under these conditions, sugars and aldehydes give a brown color and HMX gives a pale blue-green color.

Newhouser and Dougherty[13] have developed an explosives-handling detection kit based on a series of tests, which will give visual evidence through chemical reaction if a suspect had direct contact with TNT, RDX, or nitroglycerin-based explosives. Parker et al.[14] have compiled a set of chemical spot tests for a series of explosives. The sensitivity of these tests has not been reported.

Menke[15] has developed chemical spot tests which can be conducted at the scene of an explosion to identify components such as metals and oxidizing salts prior to subsequent confirmatory analysis in the laboratory. The possibility of false positive results must be considered due to contamination of the residue by other materials which are normally within the area of explosion. The chemical spot tests are usually confined to the identification of classes of compounds rather than the identification of a specific material; therefore, they can be used mainly for the screening of explosives and explosive residues.

C. Infrared (IR) Spectroscopy

In the IR region, the NO_2 group produces two characteristic bands of high intensity which characterize symmetric (ν_s) and asymmetric (ν_{as}) vibrations of the $\mathrm{N}\lesssim^{\mathrm{O}}_{\mathrm{O}}$ bonds of the nitro group.

Kornblum et al.[16] have distinguished the vibrations of primary, secondary, and tertiary nitro groups in aliphatic nitro compounds (Table 2). These bands shift under the influence of several factors. Conjugation of the nitro group by attachment to an ethylenic double bond causes a decrease in both types of frequencies.[17] Nitro group frequencies increase under the influence of an α-chlorine atom substitution.[17] The asymmetric frequency is considerably reduced under the influence of a powerful electron donor such as NH_2.[18] Nitro group frequencies can be shifted under the influence of a solvent.[19] They are decreased in polar solvents and their intensity increases.

Asymmetric NO_2 vibrations are shifted toward lower frequencies under the influence of conjugation in aromatic compounds.[20] These examples show the characterization of various nitro compounds according to their nitro group frequencies.

TABLE 2

IR Bands of Aliphatic Nitro Compounds

Nitro compounds	ν_{as} (cm^{-1})	ν_s (cm^{-1})
Primary	1550 ± 2	1379 ± 3
Secondary	1550 ± 2	1357
Tertiary	1536 ± 2	1348 ± 3

The IR spectrum of a compound can, therefore, serve as a "fingerprint" for its positive identification. This can be done by comparing the unknown IR spectrum with a library of IR spectra of standard explosives in order to establish the one to which it is identical.

Pristera et al.[7] have compiled a collection of 68 IR spectra of explosive ingredients and reported qualitative and quantitative methods for their analysis by IR spectroscopy. Table 3 summarizes their compilation. The classification of IR bands according to groups of compounds minimizes the number of standard IR spectra that have to be compared.

Chasan and Norwitz[21] have completed this collection by adding 43 IR spectra of the most common ingredients of primers, tracers, igniters, incendiaries, boosters, and delay compositions. Tompa[22] has determined trace amounts of 0.01 to 0.20% diethylene glycol in nitroglycerin to within 0.005% by IR spectroscopy using the 1122-cm^{-1} absorption band of DEG which is due to the C–O stretching mode of the COH group. These results were obtained by recording IR spectra of both sample and reference compounds.

For solid explosive sample preparation, the infrared pellet technique is used.[21] For liquid samples, one uses cells with two thin sodium chloride or potassium bromide plates. Liquids or solids can be mounted as solutions using solvents which are transparent in certain IR regions.[23]

In using reference libraries of IR spectra, differences in spectra are occasionally obtained, depending on whether the sample is mounted as a solid, a liquid, or in solution. Sometimes the exact position of one or more bands may be shifted in one spectrum relative to another spectrum. In some cases, a band may exist in one type of IR spectrum and not in another. Such an example is given by Pristera et al.[7] for HMX, where the mull spectrum was different than the solution spectrum. To avoid such discrepancies, both unknown and standard must be prepared in the same manner.

The analysis of an unknown complex explosive solely by IR spectroscopy is generally not recommended because of sample mounting difficulties and uncertainty in the interpretation of the recorded spectrum. In such cases, prior chemical separation is recommended.

Beveridge et al.[6] have reported that in a large number of analyses of explosive residues, IR spectroscopy detected explosive components in 50% of the tests, as opposed to 80% for thin layer chromatography, which is a more sensitive and more suitable technique for unknown mixtures, as will be seen later. IR is a good confirmatory tool if sufficient quantity of sample is available.

D. Ultraviolet (UV) Spectroscopy

The nitro group produces an absorption band in the UV region of the spectrum whose position and

TABLE 3

IR Bands of Explosives

	Bands	
Type of explosive	cm^{-1}	µm
Sym-trinitro compounds which have the following additional groups: CH_3, C_2H_5, OCH_3, OC_2H_5, COOH, OH, NH_2	1081	9.25
m-Dinitro compounds which have the following additional groups: CH_3, C_2H_5, OCH_3, CHO, COOH, OH, $N{=}NH_2$, CH_3NH, C_2H_5NH	930–922	10.85–10.95
In trinitro compounds (addition of NO_2)	939–909	10.75–11.0
o-Mononitro compounds which have one of the following groups ortho to the nitro: CH_3, C_2H_5, CHO, COOH, NH_2	787–781	12.7–12.8
p-Mononitro compounds which have one of the following groups para to the nitro: CH_3, C_2H_5, CHO, COOH, NH_2	1111	9.0
Nitramines	1282	7.8
Organic nitrates	1667, 1282, 833	6.0, 7.8, 12.0
Inorganic nitrates	833	12.0

intensity depend on several factors. Aliphatic nitro compounds have absorption bands in the 260- to 270-nm region at very low intensities.[1] A systematic study of the UV absorption spectra of polynitro compounds was carried out by Conduit.[18] Aromatic nitro compounds have sharp and intense absorption bands in the 210- to 280-nm region. The absorption maximum of a nitro compound can be shifted and its intensity changed under the influence of a larger number of nitro groups on the aromatic ring. In nitric esters, the nitroxy group gives an extremely low intensity absorption band of about 265 nm.[24]

The UV absorption spectra of nearly 60 nitramines were recorded by Jones and Thorn.[24] Nitramines dissolved in water, alcohol, or dioxane gave a broad UV absorption band, the maximum of which was between 225 and 240 nm. The influence of the solvent on the UV absorption spectra of nitro compounds is as follows. Changing the polarity of the solvent from polar to nonpolar causes a shift toward longer wavelengths for aliphatic nitro compounds[25] and a shift toward shorter wavelengths for aromatic nitro compounds.[26]

The use of UV spectroscopy as a technique for the analysis of explosives is, therefore, limited. It can, however, be used for nitroaromatic compounds for which it is a sensitive and rapid method of analysis.

E. Nuclear Magnetic Resonance (NMR)

NMR has long been recognized as an analytical tool for structural identification. In the NMR process, radio frequency (RF) energy is absorbed by the proton placed in a magnetic field which causes it to flip over to a less stable alignment. The amount of energy required to cause the proton to realign depends upon factors such as field strength of the magnet, electronic configuration of the molecule, type of molecule, intermolecular interaction such as hydrogen bonding, and upon the applied RF energy. The locations of the absorption bands (chemical shifts) indicate the chemical nature of the hydrogens. The band multiplicities (splitting patterns) give the spatial positions of the hydrogens and the band intensities or peak areas are proportional to the number of hydrogens.

Gehring and Reddy[27] have used NMR for the determination of low concentrations of di- and trinitrotoluene (TNT) isomers in crude and refined 2,4,6-TNT. NMR chemical shifts and long-range $H-CH_3$ coupling constants were used to identify the individual components in mixtures of di- and trinitrotoluenes. Richter et al.[28] have used NMR for the analysis of aromatic polynitro compounds

Hogan and Richter[29] have used NMR for the identification of composite explosives. They have compiled a collection of 94 NMR spectra of 58 explosive materials. Sample identification is based on matching of NMR signals with this file of spectra. Samples were analyzed in 5-mm O.D. NMR tubes as dilute solutions. The required sample volume was 0.3 to 0.6 ml. The solvents used were deuteroacetone, deuterodimethylsulfoxide (DMSO) and deuterium oxide. The internal reference standards were tetramethylsilane for acetone and DMSO and sodium-2,2-dimethyl-2-silapentane-5-sulfonate for deuterium oxide.

NMR for the identification of explosive mixtures should be used carefully because of the following influences on spectra:

1. The sample concentration effect
2. The solvent/solute interaction which may cause formation of new molecular species
3. The isotope exchange between solvent deuteriums and solute hydrogens which occurs in explosives containing active hydrogens

NMR cannot be used for the detection and identification of explosive residues in after-explosion debris material because of the large amount of sample required for analysis. According to Hogan and Richter,[29] 60 mg of sample per analysis is required. However, NMR can be used for industrial analysis of explosives. The NMR method is not applicable to nonhydrogenous initiators such as lead azide and mercury fulminate.

F. Differential Thermal Analysis (DTA)

Thermal analysis can be defined as an analytica technique in which some physical property of the analyzed sample is measured as a dynamic function of temperature. In DTA the temperature of the sample under study is compared continuously to the temperature of an inert reference sample as both samples are heated together in a furnace at a controlled rate. As the sample undergoes a reaction, additional heat is absorbed or evolved. This causes the temperature to lag behind or go ahead of the reference material. A record of the temperature difference provides an indication of the reactions which occur and which characterize the analyzed sample. In the resulting DTA thermo gram, the area under the curve is related to the energy absorbed or given off. This system must be calibrated with materials of known heat content because the absolute value of the temperature change is dependent on instrument design and on the material's enthalpy.

Reich[30] has used DTA to study the decomposition behavior of various RDX-HMX mixtures. Consequently, DTA traces of several of these mixtures are given. Reich[31,32] has also used DTA to study the decomposition behavior of mixtures of various polymers with explosives. DTA thermograms and decomposition temperatures of mixtures of RDX and cellulose nitrate with various polymers[31] and of mixtures of PETN and nitroguanidine with various polymers[32] are reported.

DTA has been used to study thermal decomposition behavior of lead azide[33-35] and mercury fulminate.[34] Using DTA, Maycock[36] determined the thermal properties of TNT, tetryl, RDX, HMX, PETN, nitroguanidine, ammonium picrate, and ammonium nitrate. DeHaan[37] has used DTA for quantitative analysis of nitrocellulose firearm propellants. Parker [38] has used DTA analysis for monomethylamine nitrate and obtained a DTA thermogram.

The amount of sample necessary for a DTA analysis varies according to the type of sample and the thermal analyzer being used. DeHaan[37] has reported DTA analysis with sample sizes in the range of 20 to 600 μg. DTA results are instrument dependent: they depend on the degree of sample containment and the heat capacity of the sample chamber.

DTA analysis of explosives is best suited for pure compounds rather than mixtures. It should be used for comparative analysis between sample and reference materials while using the same instrumentation. DTA is also a valuable tool for the determination of dynamic thermal properties of explosives and can serve as a complementary method for the analysis of these materials.

G. Polarography

Polarography is based on the principle that the current flowing between a counter electrode and a dropping mercury electrode, at a particular potential, is related to the type and concentration of the species present in the solution through which the current is flowing. Various types of polarography are being used, including differential pulse, alternating current (AC), and linear sweep polarography.

Hetman[39] has used linear sweep polarography for the determination of PETN and RDX during the various stages of technological process of solid propellants manufacturing. His method gives the possibility of determining both PETN and RDX in the presence of a large excess of perchlorates, nitrates, nitrocellulose, and nitroglycerin. The method is based on the use of pyridine as a solvent and as a component of the base electrolyte.

Whitnack[40] has used linear sweep polarography to determine microgram quantities of TNT in milligram samples of warhead exudates. The method is based on the use of a 25% acetone and 75% 0.1 *M* lithium chloride solution. 2,4-Dinitrotoluene, HMX, and RDX in concentrations up to a 50-50 mixture with TNT did not interfere with the measurement.

Hetman[41] has summarized the use of polarography for the analysis of 20 different types of explosives: nitric esters, aromatic and self-linking nitrogen compounds, and nitramines. He has used both linear sweep and AC polarography. He has specified the solvents used for each type of explosive, polarographic peaks obtained, noninterferring explosives, and detection limits which are in the micrograms per milliliter range for most explosives.

Whitnack[42] has used single-sweep polarography for the analysis of traces of explosives such as nitroglycerin, TNT, RDX, 1,2-propylene glycol dinitrate, and 2,4-DNT in water supplies. Extractions of the organic substances from the water with organic solvents were necessary to establish positive identity.

Brandone et al.[43] have determined the composition of some explosive mixtures with polarography: commercial mine explosives containing RDX, TNT, ammonium nitrate, and fuel oil; and compound B containing TNT and RDX. This has been done by comparing the samples to standard solutions.

Polarography as an analytical method for explosives should be used with great care due to the strong dependence of polarographic peaks on the type of electrolyte. For pure compounds and with suitable standards, polarography can be used for quantitative determinations; however, it cannot be used for the direct analysis of unknown multicomponent explosives.

H. Chromatography

Chromatography is a technique for separating a sample into various fractions and then identifying those fractions. The heart of the chromatograph is the substrate or stationary phase, which is either a solid or a liquid. The substrate is mounted on a support, and the sample, in vapor form or dissolved in a solvent, is then moved across or through the substrate by a liquid or gas carrier.

In thin-layer chromatography, usually silica gel is spread along a glass plate and the sample crosses it by capillary action. The separation of components occurs through adsorption, and the silica gel surface competes with the carrier for the solute.

In gas chromatography, the sample passing through the chromatograph is in the form of gas. Gas chromatography is applicable to any substance which can undergo conversion to a stable, nonreactive vapor and then pass through a column. The interaction between the stationary phase and the components of the mixture is based on the difference of boiling points, electronegativity, solubility, and molecular structure which causes the various components to pass through the stationary phase at different rates (the principle of separation).

In liquid chromatography or high-pressure liquid chromatography, the sample passing through the chromatograph is in liquid form. The liquid sample is injected into a chromatographic column through which a suitable solvent is being pumped. The separated components emerge from the end of the column at different times and pass through a suitable detector.

1. Thin-layer Chromatography (TLC)

TLC has been widely used for many years for the analysis of explosives. The method consists of the following steps:

1. The preparation of the thin-layer plate, that is coating of the glass plates with the appropriate support (silica gel or aluminum oxide)
2. Extraction of the explosive ingredients from the crude samples by means of various solvents (acetone, ether, water, etc.)
3. Application of a spot of the solution near the edge of the TLC plate
4. After the spot has dried, the plate edge below the spot is placed in an appropriate solvent or developer. By capillary action, the solvent moves into the thin layer, and the components of the mixture separate from each other as they move (development). After the solvent has substantially crossed the thin layer, the plate is removed and dried.
5. After spraying the plates with visualization reagents, the separate spots and hence the various components can be identified.

The rate of advance of each compound in a given solvent is expressed as the R_f value, which is the single-development ratio of spot velocity to solvent velocity, and is usually measured as the ratio of two distances:

$$R_f = \frac{\text{distance of the compound from the origin}}{\text{distance of the solvent from the origin}}$$

The efficient use of TLC for the analysis of explosives is based on the preparation of appropriate TLC plates and development solvents as well as visualization reagents. Table 4 gives the results of several works on TLC of explosives and shows the differences in results obtained by the use of different plates and developers.

TLC has been used by Yasuda[50] for the identification of impurities in TNT. He has used a two-dimensional TLC method to identify dinitro and trinitrotoluenes in α-TNT. The developing method consists of incorporation of a zinc reductor directly in the thin layer. After development, the impurities are located by spraying *p*-diethylaminobenzaldehyde on the plate. Impurities in the microgram range could be detected with this method. Yasuda[51] has also used the same method to separate and identify *N*-nitroso- and nitrodiphenylamines. Evendyk[52] has used two-dimensional TLC for qualitative analysis of the components of smokeless powder.

Kohlbeck et al.[53] have used two-dimensional TLC for the analysis of impurities in TNT in order to improve the continuous TNT manufacturing process. They have used benzene-cyclohexane-ethyl acetate (50:45:5) for initial development and benzene-cyclohexane (75:25) as a second solvent. No single-solvent system was found which could separate all nitration products in one separation.

TLC has also been widely used in the detection and identification of explosive residues in trace quantities after an explosion has occurred. Jenkins and Yallop[45] have described the use of TLC for the analysis of explosive residues as well as for the identification of traces of explosive on the hands and clothing of persons suspected of using them. Lloyd[54] has used TLC for the detection of microgram amounts of nitroglycerin in air and biological materials.

TABLE 4

TLC of Explosives

Explosive	TLC plate	Developer	Visualizer	Color of spot	R_f	Ref.
Picric acid	Silica gel	Benzene/ethyl acetate (85/15%)	$TiCl_3$/butyl nitrite/*N*-naphthylethylene diamine	Pale green-violet	0.03	44
DNT	Silica gel	Benzene/ethyl acetate (85/15%)	$TiCl_3$/butyl nitrite/*N*-naphthylethylene diamine	Pink-violet	0.78	44
TNT	Silica gel	Benzene/ethyl acetate (85/15%)	$TiCl_3$/butyl nitrite/*N*-naphthylethylene diamine	Violet-pink	0.85	44
Trinitroanisole (TNA)	Silica gel	Benzene/ethyl acetate (85/15%)	$TiCl_3$/butyl nitrite/*N*-naphthylethylene diamine	Pink-violet	0.80	44
Tetryl	Silica gel	Benzene/ethyl acetate (85/15%)	$TiCl_3$/butyl nitrite/*N*-naphthylethylene diamine	Yellow-pink	0.56	44
		Trichloroethylene/acetone (80/20%)	KOH/Griess	Yellow-orange	0.38	44
Nitroglycerin	Silica gel	Trichloroethylene/acetone (80/20%)	KOH/Griess	Pink	0.46	44
Nitrocellulose	Silica gel	Trichloroethylene/acetone (80/20%)	KOH/Griess	Pink	0	44
RDX	Silica gel	Trichloroethylene/acetone (80/20%)	KOH/Griess	Pink	0.11	44
Diphenylamine	Silica gel	Benzene/ethyl acetate (85/15%)	Butyl nitrite	Blue	0.91	44
DNT	Silica gel	Benzene	$TiCl_3$/dimethylaminobenzaldehyde	Yellow	0.40	45
TNT	Silica gel	Benzene	$TiCl_3$/dimethylaminobenzaldehyde	Brown	0.44	45
Ammonium nitrate	Silica gel	Ethanol	Thymol/H_2SO_4	Purple spots on pink	0.58	45
Nitroguanidine	Silica gel	Ethanol	NaOH/Griess	Red	0.58	45
Nitrocellulose	Silica gel	Ethanol	NaOH/Griess	Red	0	45
RDX	Silica gel	Chloroform/acetone (1:1)	Thymol/H_2SO_4	Purple spots on pink	0.47	45
HMX	Silica gel	Chloroform/acetone (1:1)	NaOH/Griess	Red	0.40	45
PETN	Silica gel	Chloroform/acetone (1:1)	NaOH/Griess	Red	0.69	45
Tetryl	Silica gel	Chloroform/acetone (1:1)	NaOH/Griess	Red	0.66	45
Diphenylamine	Silica gel	Chloroform	$NaNO_2/H_2SO_4$	Blue-green	0.86	46
		Benzene	$NaNO_2/H_2SO_4$	Blue-green	0.62	46
		Toluene	$NaNO_2/H_2SO_4$	Blue-green	0.61	46
Ammonium nitrate	Silica gel	Petrol-ether/acetone (5:3)	Diphenylamine	Colorless	0	47
Picric acid	Silica gel	Petrol-ether/acetone (5:3)	Diphenylamine	Yellow	0.09	47
HMX	Silica gel	Petrol-ether/acetone (5:3)	Diphenylamine	Colorless	0.23	47
RDX	Silica gel	Petrol-ether/acetone (5:3)	Diphenylamine	Colorless	0.39	47
Tetryl	Silica gel	Petrol-ether/acetone (5:3)	Diphenylamine	Yellow-olive	0.62	47
TNT	Silica gel	Petrol-ether/acetone (5:3)	Diphenylamine	Brown-red	0.71	47
PETN	Alumina, neutral	Toluene	Diphenylamine		0.27	48
Ethylene glycol dinitrate	Alumina, neutral	Toluene	Diphenylamine		0.82	48
Nitroglycerin	Alumina, neutral	Toluene	Diphenylamine		0.68	48
Diethylene glycol dinitrate	Alumina, neutral	Toluene	Diphenylamine		0.64	48

TABLE 4 (continued)

TLC of Explosives

Explosive	TLC plate	Developer	Visualizer	Color of spot	R_f	Ref.
Dinitrobenzene (DNB)	Silica gel	Trichloroethylene/acetone (80/20%)	KOH/Griess	Yellow	0.45	49
Trinitrobenzene (TNB)	Silica gel	Trichloroethylene/acetone (80/20%)	KOH/Griess	Orange-pink	0.57	49
Trinitro-*m*-xylene (TNX)	Silica gel	Trichloroethylene/acetone (80/20%)	KOH/Griess	Blue-gray turning to orange after oven-drying	0.60	49

Kempe and Tannert[55] have described a TLC method for the identification of nitrate esters such as nitroglycerin, ethylene glycol dinitrate, and PETN on hand swabs from subjects suspected to have handled explosives. Hoffman and Byall[56] have used TLC to analyze explosive residues on hand swabs and explosive debris.

Monomethylamine nitrate can be detected by TLC to a limit of 0.5 μg.[38] Beveridge et al.[6] have developed a systemic analysis of explosive residues based on a series of techniques including TLC. In order to cover all probable explosives, they used a system of five developers: benzene, benzene/hexane, xylene/hexane, ethanol, and chloroform/acetone and four visualizers: NaOH/Griess reagent, titanium trichloride/dimethylaminobenzaldehyde ($TiCl_3$/DMAB), diphenylamine/H_2SO_4, and ethanol/Nessler reagent. According to Beveridge et al.,[6] in order to characterize dynamite by TLC, a minimum of three systems had to be employed. Fisco[57] has developed a portable TLC kit for identification of explosives in debris material at the site of the explosion.

The majority of spray reagents is destructive in that they destroy or modify the materials which they visualize. In preparative thin-layer work or in quantitative work where the sample is to be eluted before assay, such destructive methods cannot be used. Visualization techniques are being used involving the presence of phosphorescent or fluorescent substances in thin-layer adsorbents. When the developed plates are irradiated with UV light, colored spots will show up due to fluorescence excitation. The use of different UV wavelengths will result in spots of different colors.[58] When analyzing explosive residues in acetone extractions with TLC, many impurities carried with the sample will appear in the chromatogram as a long streak.[59] This streak is highly fluorescent under UV light and appears in many colors when sprayed with reagents. Because this might decrease the sensitivity of analysis of explosives by TLC, other solvents should be used.

Quantitative analysis of explosives using TLC can be done by several methods. Kohlbeck[60] has measured nitroglycerin quantitatively in micro samples of propellant by using a weight-area relationship on thin-layer chromatograms. Reproducibility was about 4% for nitroglycerin amounts in the range of 4 to 60 μg.

Glover and Hoffsommer[61] have determined HMX traces in water by measuring the areas of the HMX spots on the TLC plates and calculating the appropriate weights. They have been able to determine 0.05 to 1 ppm quantities of HMX with a 15% accuracy.

Quantitative analysis is also possible by using direct spot densitometry[47] or by removing the material from the spots and using a spectroscopic technique. Hoffsommer and McCullough[62] have used a combination of TLC and visible spectrometry for quantitative analysis of polynitroaromatic compounds in complex mixtures. They have obtained a reproducibility of 2 to 5% for a three-component mixture, each component consisting of more than 20 μg.

Macke[63] has used a combination of TLC and spectrophotometry for the measurement of plasticizers and stabilizers in aged double-base propellants. 2-Nitrodiphenylamine and resorcinol were measured in the UV, while nitroglycerin and triacetin were measured in the IR region of the spectrum. The reproducibility was between 0.6 and 2.0% for milligram quantities of materials. Parihar et al.[64] have used TLC combined with UV spectroscopy for the determination of amounts up to 1.5 μg of nitroaromatic explosive mixtures.

TLC is a relatively simple and sensitive method for the analysis of explosives. However, it has some limitations:

1. In the analysis of unknown explosives, a set of several developers and visualizers has to be used in order to cover all probable explosives, which is time consuming.
2. No developing mixture giving satisfactory migrations for nitrostarch or nitrocellulose has yet been found.
3. Reproducibility of R_f values and spot colors depends on the thickness of the thin layer and on the exact composition of developer and spray mixtures. Samples should be analyzed relative to standards.
4. Quantitation is difficult.

2. *Gas Chromatography (GC)*

Although some explosives are thermally unstable, GC has been found to be a good method for separation and analysis of explosives. The samples must first be converted into vapor state. Then, they are swept by a constantly flowing carrier gas stream through a long narrow column which is packed with a stationary phase. This column has to be maintained at a sufficiently high temperature to keep the samples in the vapor state. The eluted components can be detected by various devices (thermal conductivity detector, flame ionization detector, electron capture detector, and mass spectrometer) and are then recorded on a strip-chart recorder or a digital data-acquisition system. The obtained chromatogram consists of a series of peaks, usually one for each component. The peak retention time (R_t) is the time required for elution of the component and is used for qualitative identification. The peak area relative to the peak area of appropriate standards is used for quantitative measurement. The efficient use of GC for the analysis of explosives is based on the right choice of column, stationary phase, and temperature program.

GC is especially well suited for nitroaromatic compounds due to their higher decomposition temperatures. Parsons et al.[65] have used GC for the separation and determination of mono- and dinitrotoluene isomers. They have used a 12-ft stainless steel column with a mixture of Chromosorb® W with Apiezon® L grease as stationary phase. Helium at 112 cc/min has been used as carrier gas. The inlet temperature was 260°C and the column temperature was 213°C. Figure 1 shows their chromatogram of mono- and dinitrotoluene isomers.

Courtier et al.[66] have used GC to separate and determine quantitatively dinitrotoluene isomers. They have compared results from three different laboratories using different equipment but the same stationary phase (XE-60) and have obtained good reproducibility. Gehring and Shirk[67] have used GC to separate and determine isomers of trinitrotoluene. They have used two 9-ft X 0.25-in. stainless steel columns, one serving as reference, packed with 10% DC-LSX-3-0295 silicone copolymer on 80 to 90 mesh Anakrom®-ABS support. Helium was used as carrier gas at a rate of 200 cc/min. The thermal conductivity filament detector and the injection port were both held at 225°C. Gas chromatograms were obtained by injecting 15 μl of acetone solution and programming from 100 to 225°C at 8°C/min, then maintaining isothermal operation at 225°C until all components were eluted.

Figure 2 shows a gas chromatogram of a

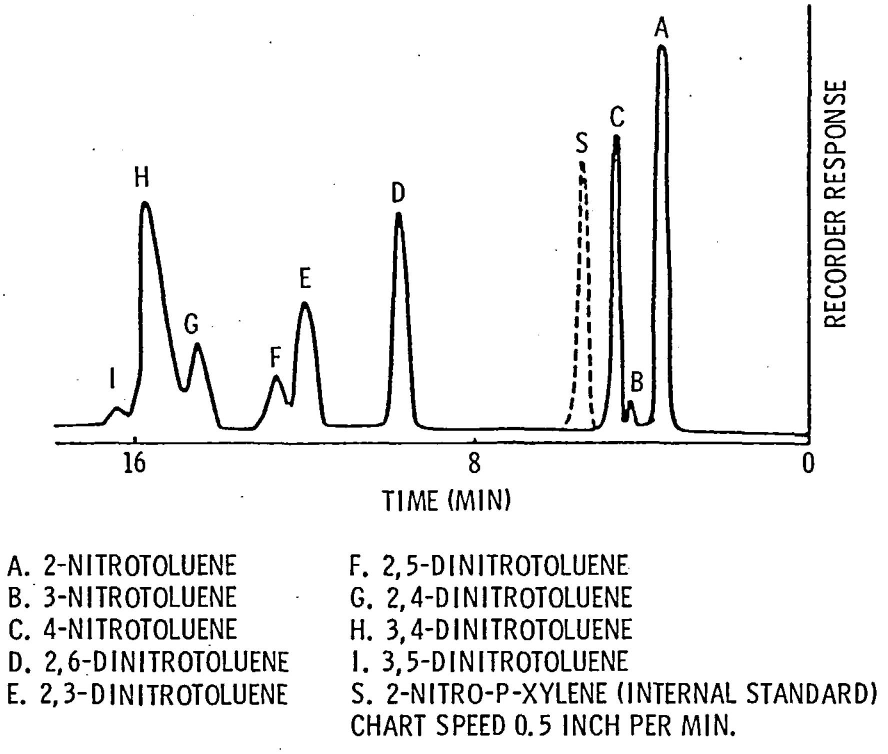


FIGURE 1. Gas chromatogram of mono- and dinitrotoluene isomers. (Reprinted with permission from Parsons, J. S., Tsang, S. M., DiGiaimo, M. P., Feinland, R., and Paylor, R. A. L., *Anal. Chem.*, 33, 1858, 1961. Copyright by the American Chemical Society.)

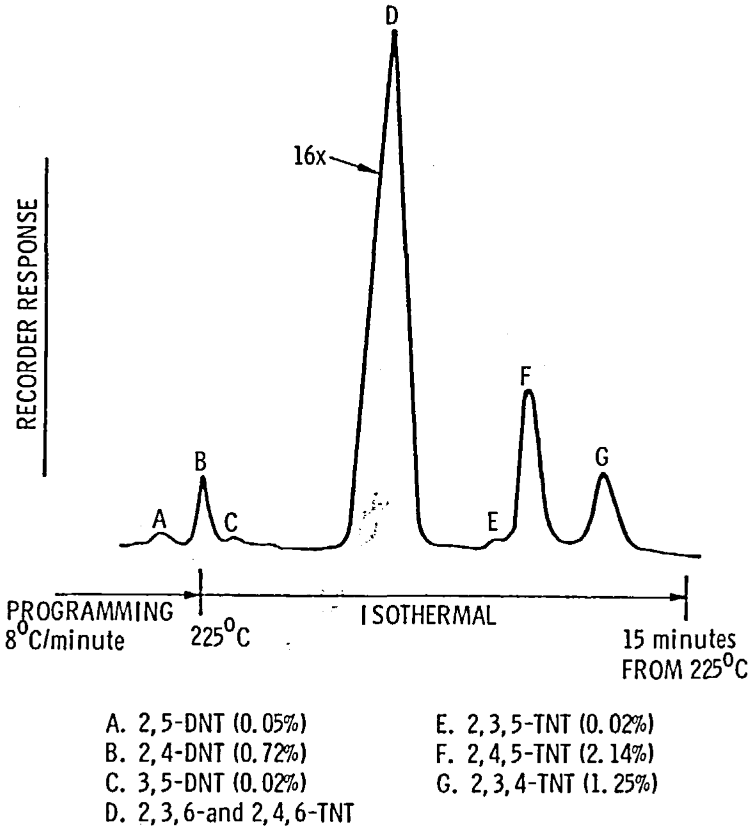


FIGURE 2. Gas chromatogram of production sample of crude TNT. (Reprinted with permission from Gehring, D. G. and Shirk, J. E., *Anal. Chem.*, 39, 1315, 1967. Copyright by the American Chemical Society.)

production sample of crude TNT. Standard deviations for the 2,4-DNT and 2,4,5-TNT impurities were found to be ±0.03% within the 0.05 to 1.00% range. The lowest detectable impurity concentration was about 0.02%.

Dalton et al.[68] have used GC for the analysis of isomers of mono-, di-, and trinitrotoluenes in samples from a continuous TNT purification process. The GC column was stainless steel, 1/8 in. O.D. X 12 ft long packed with 10% UC-W98 silicone gum rubber on 80-100 mesh Diatoport®-S. Injection port temperature was 230°C and column temperature was programmed from 150 to 240°C at 6° per minute. Helium carrier flow was 60 cc/min.

Camera and Pravisani[69] have used GC to separate monoethylene glycol dinitrate (EGDN), nitroglycerin (NG), diethylene glycol dinitrate (DEGN), and triethylene glycol dinitrate (TEGN). They used two stainless steel columns, 35 and 50 cm long, packed with 40- to 60-mesh Celite® C22 ak which had been coated with 10% ethylene glycol succinate. The 35-cm column was operated at 145°C and the 50-cm column was operated at 150°C. They obtained good resolution with minimum NG decomposition.

Rowe[70] has used GC for the determination of TNT in cyclotol (RDX + TNT). The column was a 1/8-in. O.D. X 33-in. long stainless steel tube packed with 5% Apiezon L on Chromosorb W (100 to 120 mesh). The GC was equipped with a flame ionization detector and a disc integrator for peak areas measurement. Temperatures for the injection port, column, and detector were 225, 150, and 155°C, respectively. Helium carrier flow rate was 50 ml/min. Benzene was used as solvent in order to eliminate the RDX decomposition peak because RDX is only slightly soluble in benzene. 1-Chloro-2,4-dinitrobenzene was used as internal standard for quantitative measurement of the amount of TNT. For an average amount of 22.29% TNT, standard deviation was ±0.21%.

Rowe[71] has also used GC to determine RDX in HMX. The column was 10% Dow-Corning 550 silicone fluid on firebrick (60 to 80 mesh) packed in a 1/8-in. O.D. X 36-in. long stainless steel tube. Injection and column temperatures were, respectively, 240 and 180°C. Helium carrier flow rate was 75 ml/min. HMX was not eluted while the decomposition of RDX (at 180°C) was minimal and reproducible. Trinitrobenzene was used as an internal standard. The minimum detectable amount of RDX in HMX was less than 0.05%.

Trowell[72] has used GC to determine the dinitroglycerin and nitroglycerin levels in double-base type propellants. He has used a 6-ft X 1/8-in. stainless steel column packed with 2.5% OV-17 silicone and 2.5% QF-1 (a trifluoropropyl-substituted silicone) on 60 to 80 mesh Gas Chrom® Q. Injection port temperature was 70°C and column temperature was 70 to 230°C programmed at a rate of 10°C/min. Helium carrier flow was 65 cc/min. Sample size was 0.004 cc.

Camera et al.[73] have developed a GC method for mixtures of nitric esters with nitro compounds. They have studied the GC of 28 compounds using two columns alternately. The use of two different columns was necessary because the optimal separation conditions of the numerous groups of these compounds are different. Both columns were packed with 10% silicone grease E301 added to Celite C22 ak. The first column consisted of a 6-mm O.D. X 70-cm long stainless steel tube. Column and evaporator temperatures were 150 and 160°C, respectively. The second column consisted of a 6-mm O.D. X 200-cm long stainless steel tube. Column and evaporator temperatures were 180 and 200°C, respectively. The short column is suitable for materials with very short retention time while the longer column is for materials having a longer retention time.

GC has also been used for the determination of plasticizers and stabilizers in propellant compositions. Trowell and Philpot[74] have used GC to determine resorcinol, triacetin, dimethyl sebacate, and 2-nitrodiphenylamine in composite modified double-base propellants using dimethyl phthalate as internal standard. They used a 1/8-in. O.D. X 4-ft stainless steel column packed with 5% OV-17 on 60 to 80 mesh Gas Chrom Q. Injection port temperature was 70°C and column temperature was 70 to 250°C programmed to increase at a rate of 15°C/min. Helium carrier flow was 15 cc/min. They eliminated interference from nitroglycerin by a technique of programmed temperature on-column injection of the sample. This was achieved by placing an additional injection port inside the oven which was then programmed simultaneously with the column temperature, thus allowing low temperature injection and avoiding decomposition of the NG.

Using GC, Tunstall[75] has determined triacetin, diacetin, dimethyl phthalate, and dimethyl sebacate in propellant compositions using diethyl phthalate as internal standard. He used a 1/8-in. O.D. X 2-m stainless steel column packed with 5% Antarox® CO-990 on 80 to 100 mesh AW-DMCS Chromosorb G. Injector and column temperatures were 275 and 185°C, respectively. Nitrogen carrier flow was 25 ml/min. Norwitz and Apatoff[76] have used GC to determine dimethyl, diethyl, and dibuthyl phthalates in small arms double-base propellants. They used a 1/4-in. O.D. X 6-ft stainless steel column packed with 20% silicone rubber SE-30 on 60 to 80 mesh Chromosorb W. Column temperature was 200°C for dimethyl and diethyl phthalates, with triacetin as internal standard, and 230°C for dibutyl phthalate, with dimethyl sebacate as internal standard. Injector temperature was 275°C and helium carrier flow 35 ml/min. Diphenylamine interference was eliminated by the presence of nitroglycerin which decomposed and nitrated the diphenylamine.

Alley and Dykes[77] have further developed the Trowell and Philpot[74] method for the determination of nitrate esters, as well as plasticizers and stabilizers, in all types of nitrocellulose-based propellants. They used 1/8-in. O.D. X 2-ft stainless steel columns packed with the following three types of stationary phases and supports: OV-101 with 80 to 100 mesh Gas Chrom Q, OV-210 with 80 to 100 mesh Chromosorb W-HP, and OV-225 with 80 to 100 mesh Gas Chrom Q. Digital integration was used to enhance the detection sensitivity of the nitrate ester and the measurement precision of its peak area.

Hoffsommer[78] has developed a method for quantitative analysis of nitro compounds in the micro- to picogram range by a combination of TLC and GC, using the nickel-63 electron capture detector. He used a 1/4-in. X 4-ft glass column packed with 2.53% Apiezon M on 60-80 mesh Diataport-S. Column, injector, and detector temperatures were, respectively, 150, 160, and 275°C. Carrier gas was Ar-CH_4 (95:5) at flow rates between 67 and 250 ml/min. Because of the high sensitivity of the nickel-63 detector, it can be easily contaminated and overloaded; 1.6 X 10^{-8} g of TNB was the upper limit for linear detector response. Hoffsommer and Glover[79] used the same GC set-up for quantitative analysis of nanogram amounts of α-TNT with 1,2-dinitrobenzene as internal standard.

Washington and Midkiff[80] have used a vapor trace analyzer for scanning bomb debris and hand swabs for traces of certain types of explosives. The device consists of an air sampling valve, a diethylene glycol succinate-packed GC column with helium as carrier gas and a tritium electron capture detector. Dynamite was analyzed in the presence of interference materials such as nitrobenzene and diazodinitrophenol. Hoffman and Byall[56] have successfully used the same instrument in testing air samples taken from the scene of an explosion or from a closed compartment which had contained explosive compounds with relatively high vapor pressures, such as nitroglycerin-based dynamites.

GC has also been used for the analysis of explosives in water. Hoffsommer and Rosen[81-83] have developed a method for the detection of TNT, RDX, and tetryl in the part per billion to part per trillion range. The GC column was a 1/4-in. O.D. X 4-ft glass column packed with 2.92% Dexsil® 300 GC on 80 to 100 mesh Chromosorb W AW-DMCS, with Ar-CH_4 (95:5) carrier gas at a flow rate of 217 ml/min. The detector was a nickel-63 electron capture detector. Column, injector, and detector temperatures were, respectively, 165, 200, and 295°C. 1,2-Dinitrobenzene was used as internal standard.

Pies et al.[84] have used GC for the determination of EG, DEG, and TEG in water. They used a 5-mm I.D. X 1-m long column packed with 20% Carbowax® 20M on 60 to 80 mesh Chromosorb W AW-DMCS with a flame ionization detector. Column, injector, and detector temperatures were, respectively, 170, 190, and 190°C. The internal standard for quantitative measurements was dimethyl sulfolane. Lower limits of detection were 3 ppm EG, 6 ppm DEG, and 50 ppm TEG.

GC is a very good analytical method for separation and identification of nitroaromatic explosives. It can also be used for the analysis of nitrates and nitramines which are thermally unstable, but special attention should be taken in order to prevent catalytic or thermal decomposition. This can be done by using short glass columns at optimal temperatures (high enough for evaporation and low enough to prevent thermal decomposition).

For maximum sensitivity, an electron capture detector can be used, which, on the other hand, can be easily overloaded and contaminated. Because the electron capture detector is linear only in a limited concentration range, quantitative measurements should be done with appropriate reference samples. This detector is very useful in the detection of traces of explosives, in the search for water contamination, or in after-explosion debris. GC has also been used in conjunction with a mass spectrometer. This technique is then called GC-MS and will be reviewed in the section on mass sprectrometry.

3. Liquid Chromatography (LC)

LC has been used only during the last few years for the analysis of explosives, but seems to be a very promising future analytical technique. In LC, the sample is injected into a chromatographic column and packed with spheres 10 to 50 μm in diameter, through which a suitable solvent is being pumped at flow rates of 0.5 to 5 ml/min. As the sample size is in the order of 10 to 20 μl, the dilution of the sample is great. The output of the LC detector appears as a recorder peak where the area gives an indication of the concentration of the sample component being measured.

Doali and Juhasz[85] have used LC for qualitative analysis of nitroaromatic compounds, nitrate esters, and nitramines. The LC columns used were glass, 3 mm I.D. X 6.5 O.D. X 1 m long, packed with Corasil® II (a solid core glass bead with a silica gel layer and a particle range of 37 to 50 μm). They used as detectors a refractive index and a UV detector. The refractive index detector measures differences in the optical refractive index of the solvent and the solvent plus sample. The UV detector measures the absorbance of the solvent and that of solvent plus sample. With a mobile phase of 10% dioxane and 90% cyclohexane, they separated TNT and tetryl in tetrytol; with 35% dioxane and 65% cyclohexane, they separated RDX and HMX; with 30% dioxane and 70% cyclohexane, they separated TNT, tetryl, and RDX which are the components of the explosive PTX-1.

They also used LC to separate and analyze nitroglycerin and ethyl centralite (using a mobile phase of 16% chloroform in cyclohexane) and nitroglycerin, diphenylamine, and dibutylphthalate (using 10% chloroform in cyclohexane) in double-base propellants. It seems that the separation depends strongly on the composition of the mobile phase. Therefore, an isocratic system is not recommended.

Dalton et al.[86] have used LC for quantitative determination of nitroglycerin, diethyl phthalate and ethyl centralite. The column used was a precision-bore stainless steel 2.1-mm I.D. X 1-m long tube containing 30 to 40 μm Vydac® adsorbent. The flow rate of the mobile phase, 1,1-dichloroethane, was 0.8 ml/min at a pressure of 450 psig. A UV detector was used. Quantitative measurements were made using acetanilide as internal standard. The coefficients of variation in ten runs for NG, diethyl phthalate, and ethyl centralite were 0.53, 0.89, and 0.48%, respectively.

Poyet et al.[87] have used LC for the quantitative analysis of a stabilizer of nitrate esters, 2-nitrodiphenylamine, and its nitro derivatives. They used a 1/4-in. X 30-cm column packed with Microbondapack® C18 with a mobile phase of 67.5% methanol and 32.5% distilled water. The flow rate was 1 ml/min at a pressure of 2000 psi. A UV detector was used in conjunction with an integrator for the measurement of peak areas. Precision obtained was between 2 and 5%.

They have also used LC for the detection of trace amounts as low as 0.01% of RDX in HMX. They used two different types of columns: 1/4 in. X 20 cm packed with Lichrosorb® Si 60 and 1/4 in. X 30 cm packed with Microporasil®. For both columns, the mobile phase was 55% cyclohexane and 45% dioxane at a flow rate of 1.5 ml/min. HMX samples were introduced as acetone solutions (1% HMX), 2 μl per sample.

Doali and Juhasz[88] have also used LC for the determination of 2-nitrodiphenylamine in a composite modified double-base propellant. They used a 100-cm X 2.1-mm I.D. stainless steel column packed with Corasil II. The mobile phase consisted of 20% methylene chloride and 80% cyclohexane, with a flow rate of 0.5 ml/min. A UV detector was used, the output of which was monitored by an integrating system producing a print-out of retention times and areas of eluted peaks. They used 2,4-dinitrotoluene as internal standard and obtained quantitative results with a standard deviation of less than 1%. This accuracy was determined from statistical evaluation of four samples. The chromatogram showed no interference from reaction products of the stabilizer.

Farey and Wilson[89] have used LC for quantitative determination of tetryl and its degradation products. The determination of tetryl and ten degradation products was done by using a 30-cm X 4.4-mm I.D. stainless steel column packed with μ Bondapak® CN with a mobile phase of cyclohexane-chloroform-redistilled tetrahydrofuran (77:20:3) at a flow rate of 2 ml/min at a pressure of 1750 psi. A UV detector and integrator were used for peak area measurements. Picric acid, however, was very strongly retained in this column. Therefore, another system has been used to separate picric acid from the other compounds. This second system consisted of a 60-cm X 2.2-mm I.D. stainless steel phenyl/Corasil reversed-phase column with a mobile phase of water-methanol (75:25) at a flow rate of 2 ml/min at a pressure of 1700 psi. They obtained reproducibility variations of 0.39% for picric acid and 1.08 to 3.23% for tetryl and ten degradation products.

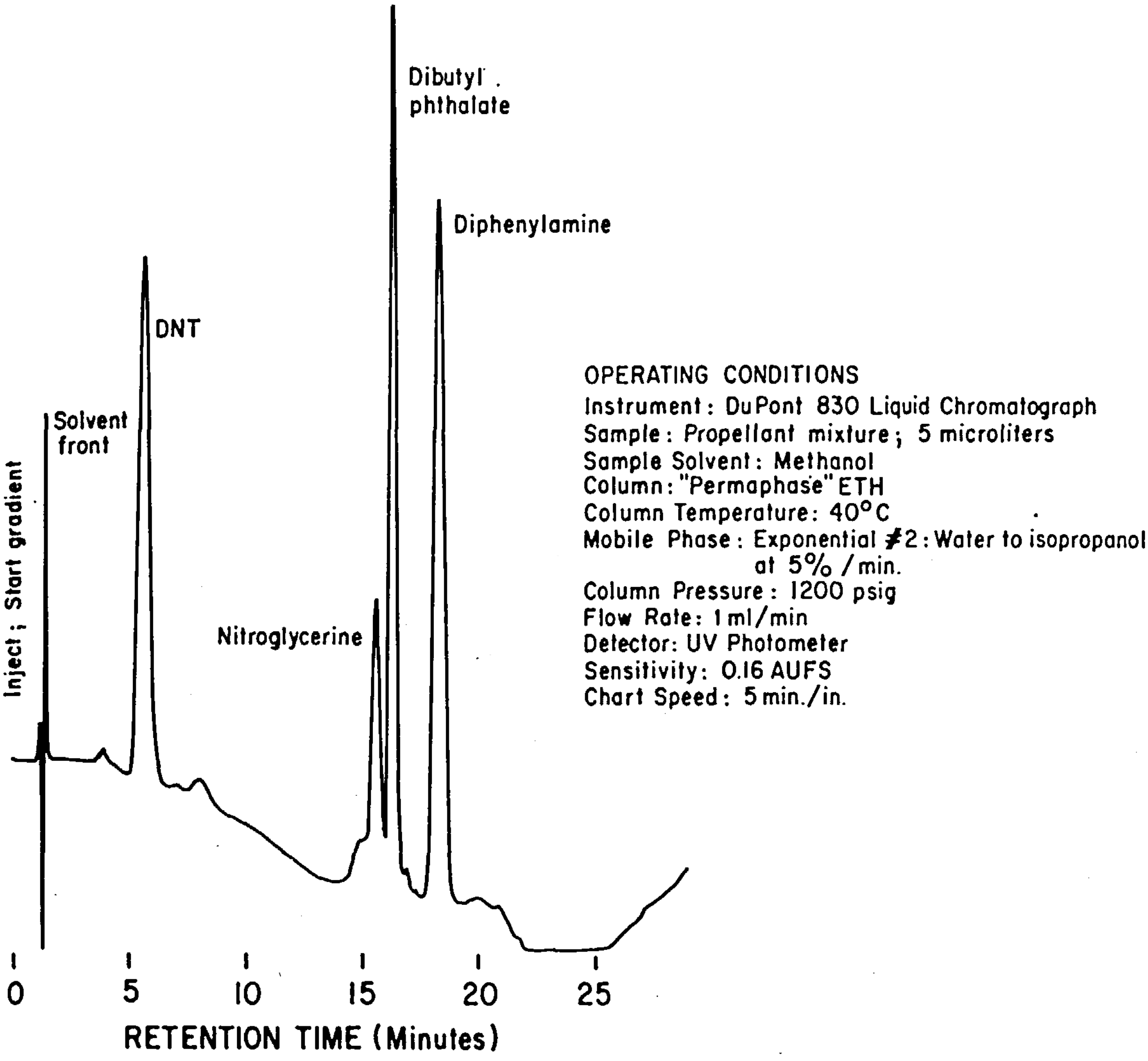
Freeman et al.[90] have investigated the effectiveness of various polymeric adsorbents for the liquid-chromatographic separation of RDX and HMX. Cross-linked poly-*N*-vinylpyrrolidone was found to adsorb HMX twice as strongly as RDX and with a high capacity. Another adsorbent, the ammonium form of sulfonated macroporous copolystyrene-divinylbenzene, gave high selectivity with higher efficiency and higher speed, but with lower capacity. They used a 13.5 X 0.6 cm I.D. and 7 X 0.3 cm I.D. (for the increased speed experiments) glass columns and a refractive index detector. The mobile phase was acetone. Figure 3 shows the LC chromatogram[91] of a propellant mixture.

Liquid chromatography is well suited for quantitative analysis of explosives, especially for thermally unstable compounds since it does not require sample heating. Because of the nondestructive nature of LC, it can be used in combination with other methods such as GC or mass spectrometry.

LC requires little sample preparation and permits nonvolatile compounds to be separated. LC is faster than other chromatographic methods: the average time of analysis is from 10 to 45 min depending on the composition of the sample. In some cases more than one column is necessary to separate all the components of a mixture.

I. Mass Spectrometry (MS)

MS is the field dealing with the separation and analysis of compounds according to their atomi



OPERATING CONDITIONS
Instrument: DuPont 830 Liquid Chromatograph
Sample: Propellant mixture; 5 microliters
Sample Solvent: Methanol
Column: "Permaphase" ETH
Column Temperature: 40°C
Mobile Phase: Exponential #2: Water to isopropanol at 5% /min.
Column Pressure: 1200 psig
Flow Rate: 1 ml/min
Detector: UV Photometer
Sensitivity: 0.16 AUFS
Chart Speed: 5 min./in.

FIGURE 3. Liquid chromatogram of a propellant mixture. (From DuPont Liquid Chromatography Applications Lab Report, No 72-01, E. I. DuPont de Nemours and Company, Instrument Products Division, Wilmington, Del., 1976.)

and molecular masses. As the mass spectrometer is a very sensitive device for the analysis and identification of trace quantities of material, it has become a widely used tool for the analysis of explosives. Several MS techniques are available; therefore, they will be dealt with separately according to their particular usages in the analysis of explosives. In most types of mass spectrometers, the sample has to be analyzed in the vapor state. However, the sample can be introduced into the mass spectrometer through a special inlet device either as a liquid or an organic solid or through a gas chromatograph.

1. Electron-impact (EI) Mass Spectrometry

In EIMS, which is the conventional type of MS, the sample molecules are ionized by impact with electrons usually having an energy of 70 eV. Positive ions thus produced usually decompose to fragmentation products which can be charged or neutral. The positive ions are accelerated into an analyzing field (which can be a magnetic field, an RF quadrupole field, time-of-flight analyzer or some other type of mass separation analyzer) in which they are separated according to their mass to charge ratio (m/e). The mass separated ion beam hits a collector to which an amplifying and recording system is connected. The produced mass spectrum includes a whole series of fragment ions but not always the molecular ion of the investigated compound. The complexity of the EI mass spectrum is an advantage because of its "fingerprint" value, but a disadvantage when mixtures of impure materials are analyzed.

The first works on MS of explosives were done with EIMS. Collin[92] studied the EI mass spectra of several nitroparaffins; nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane, using a CEC 21-103 mass spectrometer. The spectrum of nitromethane has a base peak at m/e 30 due to NO^+ and a major molecular ion peak at m/e 61. However, the base peak of nitroethane is at m/e 29 ($C_2H_5^+$) and that of the nitropropanes is at m/e 43 ($C_3H_7^+$).

Aplin et al.[93] studied the mass spectra of several aliphatic and alicyclic nitro compounds using both low- and high-resolution EIMS. The mass spectra were measured with an AEI MS9 instrument using the heated inlet system. Inlet system and ion source temperatures were 60 and 130°C, respectively. They found that, with the exception of nitromethane, the molecular ion peak in the mass spectrum of nitroalkanes was either very small or nonexistent. An important process in EI of nitroalkanes is the loss of an NO_2 radical and in higher mass nitroalkanes subsequent decomposition of alkyl fragments. Therefore, the probability of obtaining $(M-NO_2)^+$ ions in nitroalkanes decreases with increasing chain length. Hydrocarbon fragments, which can be found in the mass spectra of all functional derivatives of alkanes, can also be observed in the nitroalkane mass spectra. Another feature of EI mass spectra of nitroalkanes is the appearance of oxygen-free CHN and higher homolog fragments. All these characteristic features are of diagnostic use in the MS analysis of nitroalkanes.

The EI mass spectra of polynitroalkanes are characterized by the loss of NO_2 and NO. According to Larkins et al.,[94] the similarity between aliphatic nitro and polynitro compounds is the lack of an appreciable molecular ion peak. With the increase in the number of nitro groups in the molecule (up to six), a decrease in the number and intensity of the NO^+ and NO_2^+ ions is observed.

Although the mass spectra of nitroaromatic compounds have been studied by many workers, only those works which have analytical relevancy will be reviewed here. The EI mass spectrum of nitrobenzene, which is the simplest nitroaromatic compound, has been studied by Fields and Meyerson.[95] Its mass spectrum has a base peak at m/e 77, which corresponds to the phenyl ion, and a major peak at m/e 51 ($C_4H_3^+$), which is a fragmentation ion of $C_6H_5^+$. The molecular ion appears also as a major peak in the spectrum. The mass spectrum contains many more low-intensity fragmentation ion peaks.

Meyerson et al. have also studied the EI mass spectra of the dinitrobenzene isomers[96] and 1,3,5-trinitrobenzene.[97] The base peak in all three dinitrobenzene isomers (ortho, meta, and para) is at m/e 30 (NO^+). The ortho isomer has a smaller parent peak and larger fragmentation peaks than the other two isomers, which can serve as a means of identifying the ortho isomer. The major fragmentation ion peaks of the three isomers are at m/e 50 ($C_4H_2^+$), 63 ($C_5H_3^+$), 64 ($C_5H_4^+$), 74 ($C_6H_2^+$), 75 ($C_6H_3^+$), 76 ($C_6H_4^+$), 92 ($C_6H_4O^+$), and 122 ($C_6H_4NO_2^+$).

The base peak in the trinitrobenzene mass spectrum is at m/e 30 (NO^+). The major fragmentation peaks have been studied by recording the metastable transition peaks and by precise mass measurements. The major fragment ions are, in order of decreasing abundance, m/e 75 ($C_6H_3^+$), 74 ($C_6H_2^+$), 213 [molecular ion, $C_6H_3(NO_2)_3^+$], 120 ($C_6H_2NO_2^+$), 63 ($C_5H_3^+$), 91 ($C_3H_3O^+$ and $C_6H_5N^+$), and 62 ($C_5H_2^+$).

Mass spectra were recorded with a CEC 21-103 mass spectrometer with the inlet system and ionization chamber both at 250°C. Metastable scanning and precise mass measurement were done with a CEC 21-110 double-focusing mass spectrometer.

Mass spectra of 2,4,6-TNT have been recorded by several workers.[98-102] The base peak in the EI mass spectrum of TNT is at m/e 210 and was found by high resolution[102] to be $(M - OH)^+$. This ion results from an ortho effect which occurs in *O*-nitro compounds with a hydrogen-containing substituent such as CH_3, OH, and NH_2 ortho to a nitro group. The $(M - OH)^+$ ion is the base peak also in trinitro-*m*-xylene (TNX) at m/e 224 and a major peak in trinitro-*m*-cresol (TNC) at m/e 226. These results have been obtained by Zitrin and Yinon,[102] who have recorded the EI mass spectra of 11 trinitroaromatic compounds. They used a DuPont 21-490B mass spectrometer for low-resolution and a Varian MAT 711 mass spectrometer for high-resolution spectra. Major ions in TNT and other trinitro compounds are at $(M - 138)^+$, which is due to the loss of three nitro groups, and at m/e 30 (NO^+).

Murrmann et al.[101] have studied the EI mass spectra of the TNT and DNT isomers. In the DNT isomers with a nitro group at an ortho position to the methyl, the base peak is at m/e 165 due to $(M - OH)^+$. The other isomers do not have this ion peak. The base peak, in 3,4-DNT is at m/e 30 (NO^+) and in 3,5-DNT at m/e 89.

In the mass spectrum of 2,4,6-trinitrophenol (picric acid),[102,103] the base peak is at m/e 229, which is the molecular ion, and a major peak is at m/e 30 (NO^+).

The EI mass spectrum of tetryl[98,100] has its base peak at m/e 241 $(M - NO_2)^+$ and major peaks at m/e 194 $(M - NO_2 - HNO_2)^+$, m/e 181 $(M - 2NO_2 - CH_2)^+$, m/e 149 $(M - 3NO_2)^+$, m/e 46 (NO_2^+), and at m/e 30 (NO^+).

The EI mass spectra of trinitroaromatic compounds can be characterized by several common features:[102] $(M - 3NO_2)^+$ ions, high abundant NO^+ ions, and low abundant NO_2^+ ions (with tetryl as the exception). There are also several characteristic fragmentation patterns: "ortho" effects in TNT, TNX, and TNC lead to abundant $(M - OH)^+$ ions; a triple "ortho" effect in TNX leads to a $(M - 3OH)^+$ ion; loss of CH_2O from TNA, $CH_2{=}CH_2$ from TNP, and $H_2O + OH$ from TNC produce major ions in their respective mass spectra. Figure 4 shows the EI mass spectrum of 2,4,6-trinitro-*m*-cresol (TNC).

Fraser and Paul[104] have recorded the EI mass spectra of 31 nitrate esters using an AEI MS2H mass spectrometer. All nitrate esters have abundant m/e 46 fragment ions but no molecular ion.

The mass spectrum of EGDN contains a base peak at m/e 46 and major ion peaks at m/e 29, 30, and 76; the mass spectrum of DEGN has its base peak at m/e 46 and major ion peaks at m/e 29, 30, 44, 45, and 73; and the mass spectrum of nitroglycerin has a base peak also at m/e 46 and major ion peaks at m/e 29, 30, and 76.

The EI mass spectrum of PETN has been reported by Coates et al.,[100] who used a time-of-flight mass spectrometer, and by Zitrin and Yinon,[105] who used a magnetic sector mass spectrometer. The spectrum consists of a base peak at m/e 46 and two major peaks at m/e 30 and 76.

In the EI mass spectrum of RDX, as published by several groups,[98,100,105-107] differences in ionic peak abundances were found. Volk and Schubert,[98] Coates et al.,[100] and Stals[107] have reported a base peak at m/e 28, while Bulusu et al.[106] and Zitrin and Yinon[105] have reported a base peak at m/e 46. There are also differences in the abundances of other major peaks. These are due[107] to the thermal fragmentation pattern of RDX which is different in the various works due to different probe and ion source temperatures.

These differences in ionic abundances also appear in the EI mass spectra of HMX. Volk and Schubert[98] have reported a base peak at m/e 28, Stals[107] at m/e 42, Bulusu et al.[106] at m/e 46, and Zitrin and Yinon[105] two equal base peaks at m/e 42 and 46. Although the mass spectra of RDX and HMX are very similar, it is possible to differentiate between these two compounds due to

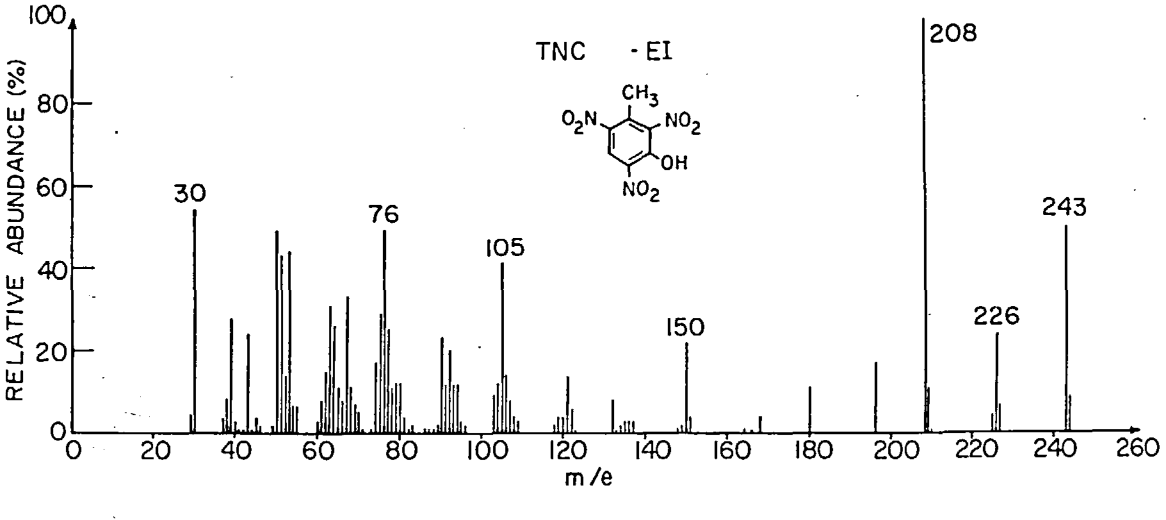


FIGURE 4. EI mass spectrum 2,4,6-trinitro-*m*-cresol (TNC). (From Zitrin, S. and Yinon, J., 7th Int. Mass Spectrometry Conf., Florence, Italy, September 1976.)

the peak at m/e 222: while in RDX, where m/e 222 is the molecular peak, it is very small; in HMX, where m/e 222 is due to $(M - CH_2NNO_2)^+$, it is a much larger peak. However, reproducibility of mass spectra of these two compounds is difficult due to thermal fragmentation which is dependent on working temperatures.

The EI mass spectrum of nitroguanidin has been reported by Volk and Schubert.[98] The spectrum consists of a major molecular ion peak at m/e 104 (87% of the base peak), a base peak at m/e 58 $(M - NO_2)^+$, and major peaks at m/e 74, 46, 43, 42, 41, 31, 30, and 17. Alm[108] has recorded the EI mass spectra of diphenylamine and ten of its nitro and nitroso derivatives using an LKB 9000A mass spectrometer. The EI mass spectra of these compounds have mostly molecular ion base peaks or major molecular ion peaks and can, therefore, be easily identified.

Anderson et al.[99] have reported the EI-mass spectra of several explosive mixtures. The EI spectrum of pentolite 50/50 (TNT + PETN) is similar to the spectrum of TNT with one exception: the peak at m/e 46 is much larger in the spectrum of pentolite than in TNT, because this is the base peak in the spectrum of PETN. The EI mass spectrum of composition A-3 (91% RDX + 9% wax) cannot be recognized as the spectrum of RDX.

The EI mass spectrum of composition B (RDX + TNT + wax) as recorded by Anderson et al.[99] was similar to that of TNT. Coates et al.[100] have recorded the EI mass spectrum of composition B at two different temperatures: at 60°C the spectrum was similar to that of TNT and at 180°C the spectrum was similar to that of RDX.

The EI mass spectrum of composition C-4 [91% RDX, 2.1% polyisobutylene, 1.6% motor oil and 5.3% di(2-ethylhexyl)sebacate] has been recorded by Anderson et al.,[99] who found it to be different from the spectrum of RDX, and by Coates et al.,[100] who found it to be similar to the spectrum of RDX.

Zitrin and Yinon[105] have recorded the EI mass spectrum of an explosive mixture containing RDX, PETN, and a plasticizer, which has been used in letter bombs. The two major peaks in the spectrum are at m/e 46 (base peak) and 30. The EI mass spectrum is in this case insufficient for the identification of the components of this mixture.

EIMS is a very sensitive and fast method for the analysis of organic explosives. However, it is not suited for nonvolatile compounds such as polymers and salts or for mixtures where the large amount of fragmentation ion peaks makes identification difficult. In pure unknown compounds, the EI fragmentation process is advantageous as it gives a lot of structural information which makes identification of these compounds possible.

2. Gas Chromatography-Mass Spectrometry (GC-MS)

In order to solve the problem of analysis of mixtures by MS, a combination of a mass spectrometer with a chromatographic method can be used. This combination can be either off-line or on-line. A widely used method is the on-line GC-MS combination which enables separation and identification of unknown mixtures. Michnowicz[109] has demonstrated the use of GC-MS for explosive mixtures by analyzing a sample containing nitroglycerine, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, methyl centralite, and butyl phthalate esters. A 1-μl sample was injected in a 3-ft column packed with 3% OV-101 on 100-120 mesh Chromosorb W AW-DMCS. Helium was used as a carrier gas at a flow of 40 cc/min. The mass spectrometer, a Hewlett-Packard 5930A, was scanned periodically from m/e 50 to 400. By this method, only three out of the six components of the mixture were identified. Chemical ionization (see next paragraph) had to be used in order to identify all components of the mixture.

GC-MS greatly simplifies identification of explosive mixtures but is not good enough as a sole technique for the identification of all components in complex mixtures. Requirements and limitations applying to GC apply also to GC-MS.

3. Chemical Ionization (CI) Mass Spectrometry

In CIMS, ions are mainly formed by proton transfer from ionic species generated by ion-molecule reactions in a reagent gas at pressures of the order of 1 torr. CI ions may also be formed by addition reactions or hydride abstraction reactions. Reagent gases commonly used are methane, isobutane hydrogen, water, and ammonia. The MH^+ or $(M + 1)^+$ ions formed by proton transfer, as well as the addition ions, have relatively little excess energy, so they are much less likely to decompose than the M^+ ions formed in EIMS. The resulting CI mass spectra are, therefore, quite simple, as they contain only a small number of peaks.

CI mass spectra of 2,4-DNT have been recorded by Saferstein et al.,[110] who used isobutane as reagent, and by Zitrin and Yinon,[105] who used methane as reagent gas. In both works, the base peak, which is almost the only peak in the spectrum, is the $(M + 1)^+$ ion peak at m/e 183. Zitrin and Yinon[111] have recorded the CI mass spectra of ten 2,4,6-trinitroaromatic compounds using methane and isobutane as reagent gases. They have used a DuPont 21-490B mass spectrometer with a dual CI/EI source. The $(M + 1)^+$ ion is the base peak in the CI mass spectra of most compounds recorded: TNB, TNT, TNX, picric acid, TNC, TNA, TNP, picramide, and picryl chloride. Exceptions are the CI methane spectrum of TNP, which has a base peak at m/e 230 due to the $(M + 1 - 28)^+$ ion, and the CI spectrum (with methane or isobutane) of tetryl which has a base peak at m/e 243 due to the $(M + 1 - 45)^+$ ion, a small molecular ion peak, and a few major fragmentation ion peaks.

The mass spectra of RDX, HMX, and PETN have been recorded by Saferstein et al.[110] using isobutane as reagent, by Zitrin and Yinon[105] using methane and isobutane as reagents, by Gillis et al.[112] using hydrogen, and by Yinon[113] using water as reagent gas. In PETN, the base peak depends on the reagent gas: with methane as reagent,[105] the base peak is at m/e 46 $(NO_2)^+$; with isobutane,[110] the base peak is at m/e 359 $(M + C_3H_7)^+$; with hydrogen,[112] the base peak is at m/e 46 $(NO_2)^+$, MH^+ being a major ion in the spectrum; and with water as reagent,[113] the base peak is at m/e 362 $(M + NO_2)^+$, MH^+ being a major ion in the mass spectrum.

The CI mass spectrum of RDX is also different for different reagent gases. With methane as reagent,[105] the base peak in the CI spectrum of RDX is at m/e 149 $(M + 1 - CH_2\ NNO_2)^+$, and the $(M + 1)^+$ ion peak at m/e 223 is only 20% of the base peak. With isobutane, the base peak is at m/e 131 $(CH_2NNO_2 + C_4H_9)^+$. With hydrogen as reagent,[112] the base peak is at m/e 75, and with water,[113] it is at m/e 241 $(M + H_3O)^+$. Similar differences are also observed in the CI mass spectra of HMX.

Although CI mass spectra are much simpler than EI mass spectra, great care has to be taken to keep reagent gas pressure and temperatures constant in order to obtain reproducible CI mass spectra. Figure 5 shows the EI and CI H_2O mass spectra of PETN.[113] In the CI mass spectrum, the M + 1 and adduct ions are the major ions in the spectrum and thus make identification possible.

CIMS can be used for the identification of explosive mixtures without prior separation. Yinon[113] has recorded the CI H_2O spectrum of an explosive mixture containing RDX, PETN, and a plasticizer. The mass spectrum consists of the CI H_2O spectra of RDX and PETN and a combination of both. A typical peak of the mixture is at m/e 539 which is due to $(M_{PETN} + M_{RDX} + 1)^+$. CIMS has also been used for forensic identification of explosives in debris at explosion sites. Such a case has been reported by Zitrin and Yinon,[114] who identified TNT in an explosive residue which was introduced directly into the mass spectrometer after acetone extraction.

CIMS is a very good method for qualitative analysis of explosives. However, for quantitation it should be used under controlled parameters. As most commercial mass spectrometers have dual EI/CI sources, an EI mass spectrum should also be recorded for final confirmation. This combination of CIMS and EIMS is a very sensitive and specific technique for the analysis of explosives.

4. *Negative-ion Mass Spectrometry*

Negative ion mass spectra are highly dependent on electron energy because of the variety of processes involved in negative-ion formation, which occurs in the energy range below 15 eV. The main processes are ion pair formation, dissociative attachment, and resonance capture followed by collisional stabilization. Unlike positive-ion MS, the question of sensitivity in the production of negative ions is related to the type of molecules being examined, their electron affinity, and the energy of the colliding electrons.

Brown and Weber[115] have recorded the negative-ion mass spectra of *p*-dinitrobenzene and *m*-dinitrobenzene at 10-eV electron energy, using a Hitachi RMU-6E mass spectrometer. The mass spectrum of both compounds consists of a base peak at m/e 46 $(NO_2)^-$, a molecular ion peak at m/e 168, and a large number of fragmentation peaks.

Bowie[116] has recorded the negative-ion mass spectra of dinitrobenzenes at 70-eV electron energy and has obtained much simpler mass spectra containing less peaks. In the spectra of the para and meta isomers, the molecular ion was the base peak, while in the ortho isomer, the $(M - NO)^-$ ion was the base peak. When using 70-eV electrons, the negative ions result from capture of secondary electrons, which are produced by collisions of primary electrons with metallic surfaces in

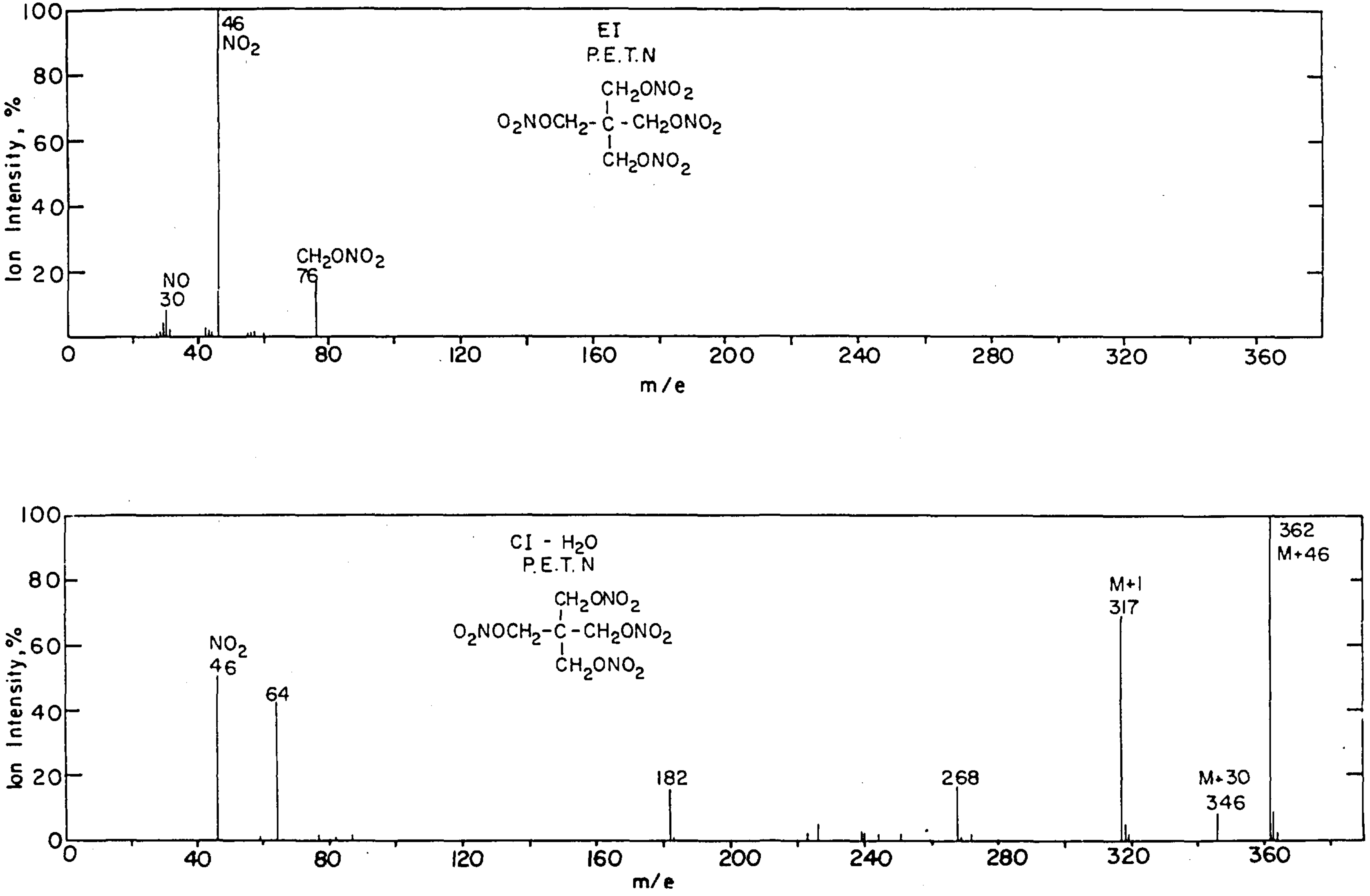


FIGURE 5. EI and CI-H_2O mass spectra of PETN. (From Yinon, J., *Biomed. Mass Spectrom.*, 1, 393, 1974. With permission.)

the ionization chamber as well as by scavenging of electrons produced in the positive-ion production process.

Large variations in negative-ion mass spectra at different electron energies of nitrobenzene and TNT have been reported by Yinon and Boettger.[117] In the negative-ion mass spectrum of nitrobenzene at 3 eV, the base peak is at m/e 46 $(NO_2)^-$ and the molecular ion peak is small, while at 20 eV, the molecular ion is the base peak.

In the negative-ion mass spectrum of TNT at 6 eV,[118] the ion current due to the anion NO_2^- is 57% of the total negative ion current of TNT. This intense peak at m/e 46 has also been found in the negative-ion mass spectra of a series of other nitrated explosives.[119] Therefore, Yinon et al.[118] have suggested the use of negative-ion MS for the detection of explosives concealed in airline baggage.

The use of negative-ion MS for the analysis of explosives is limited due to the large variations in mass spectra at various electron energies. Some workers[116,117] have also reported variations in mass spectra at different source pressures. This technique for the analysis of explosives is recommended as a complementary technique to EIMS and for the screening and detecting of nitrated explosives.

5. Other Mass Spectrometry Techniques

Field Ionization (FI) – St. John et al.[120] have used FIMS to determine the concentrations in air of DNT, TNT, NG, EGDN, PETN, and RDX using isotope dilution. In order to observe a molecular ion, precise adjustment of the ion source temperature and the use of a high ionizing field were required. The high fields, required to remove an electron from the molecule, produce strong polarization forces which contribute to the thermal instability of the explosives. The minimum temperature needed to maintain the explosive samples in the gas phase was very close to the temperature causing thermal decomposition. Although the FI mass spectra of explosives are simple relative to EI mass spectra, the critical adjustment of temperature and electrical field makes this technique too complex for routine analysis of explosives.

Field desorption (FD) – Schulten[121] has used FDMS for the analysis of TNT, TNB, RDX, and tetryl. The FD mass spectrum of TNT consists of a molecular ion base peak and two abundant peaks at $(M + 1)^+$ and $(M + 2)^+$. The FD mass spectrum of TNB consists of two base peaks: the molecular ion and the $(M + 1)^+$ ion peaks, an abundant $(M + 2)^+$ ion, and some major fragment ions. The FD mass spectrum of tetryl consists also of two base peaks: the molecular ion and the $(M + 1)^+$ ion peaks, abundant $(M + 2)^+$ and $(M + 3)^+$ ions, and a series of abundant fragmentation ion peaks. The FD mass spectrum of RDX has a base peak at m/e 223 $(M + 1)^+$, an abundant $(2M + 1)^+$ ion peak, and a large series of abundant fragmentation ion peaks. Although chemical ionization of TNT and TNB produces simpler mass spectra as they contain only an $(M + 1)^+$ ion peak, FDMS seems more appropriate for RDX and tetryl, where M^+ and $(M + 1)^+$ ions are observed. To date, only initial work has been done on the application of FD for the analysis of explosives. Therefore, more studies should be conducted on the dependence of FD mass spectra of these compounds on temperature, field strengh, and sample introduction. Analytical FDMS should be used as a complemtary technique to either EI or CI.

Plasma chromatography (PC) – PC operates at atmospheric pressure and uses a Ni^{63} ionizer followed by an ion-molecule reactor coupled to an ion-mobility spectrometer. Karasek and Denney[122] have detected and identified picogram quantities of the vapors of DNT and TNT in air, using PC. The instrument operates at atmospheric pressure and uses either air or nitrogen carrier gas into which the sample can be injected directly. Compound identification is provided by both positive and negative characteristic mobility spectra. Although this technique could be used as a detector of TNT in air, it has not yet proven itself as a method for the analysis of other explosives as well as explosive mixtures.

Atmospheric pressure ionization (API) – APIMS uses, as in PC, a Ni^{63} ionizer followed by an ion-molecule reactor and is then coupled to a mass analyzer (quadrupole or magnetic sector type). Dzidic[123] has detected an identified TNT in air and nitrogen in the subpicogram range by observing characteristic negative ions of TNT. When using air as carrier gas, the negative ions (at 200°C) are O_2^-, O_4^-, and $O_2^-(H_2O)$. TNT is then ionized by the proton transfer to O_2^- ions:

$$O_2^- + TNT \longrightarrow (TNT - H)^- + O_2H$$

When using pure nitrogen as carrier gas, the negative charge is carried by thermal electrons and

TNT is then ionized by the electron capture reaction

$$e_{\text{thermal}} + \text{TNT} \longrightarrow (\text{TNT})^-$$

Reid et al.[124] have also used APIMS in the negative-ion mode to detect TNT in air in the parts per billion range. According to Reid et al., for TNT, the negative-ion mode is more sensitive than the positive-ion mode, where MH^+ ions are produced, because of the low proton affinity of TNT. More studies must be conducted on the application of APIMS for the analysis of explosives in order to evaluate its usefulness as an analytical method for these compounds.

IV. SUMMARY

Although the various methods reviewed are very different in the amount of instrumentation involved (and consequently in cost), in simplicity or complexity, and in easy availability, a comparative summary is given without taking the above-mentioned factors into account, based solely on performance as analytical techniques for explosives.

Microscopic examination and chemical tests are well suited for qualitative screening of explosives and explosive residues in debris collected at explosion sites. Chemical spot tests can also be used to determine traces of explosives on suspect individuals.

IR, DTA, and polarography are not recommended for the analysis of unknown complex explosives. They should be used after chemical separation as a complementary method. Polarography can be used as a quantitative method for pure compounds. UV is recommended only for nitroaromatic compounds, for which it is a fast and sensitive method.

The limitation of NMR is that a large amount of sample is required. Therefore, this method is recommended for industrial and storage analysis of explosives where the amount of material is not limited. TLC is a simple and sensitive method but is not suited for quantitation unless it is used in combination with other techniques such as GC or UV. LC is well suited for quantitative analysis, especially for thermally unstable compounds. GC is good for separation and identification of nitroaromatic explosives. With an electron capture detector, GC is recommended as a very sensitive method for qualitative analysis of residues in after-explosion debris.

CIMS is well recommended as a fast and sensitive method for qualitative analysis of multicomponent explosives. In combination with EIMS, it is a powerful technique. EIMS should be used as a complementary method for structure determination or as combined GC-MS technique. Negative-ion MS could be used for screening and detecting of explosives but is not recommended as a general analytical technique. Other MS techniques have not yet produced enough published experimental data to determine their usefulness as analytical methods.

A future powerful technique for the analysis of explosives would be the combination of a liquid chromatograph and a mass spectrometer (LC-MS) with both CI and EI capabilities.

Two fields in the analysis of explosives which have so far received only little attention are the analysis of inorganic impurities in explosives and the analysis of explosives in body fluids. With the availability of modern analytical techniques, these fields should be further investigated.

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