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# IV.2

# Identification of unknown solid waste

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## IV.2.1. Introduction

In the wake of the terrorist incidents of the World Trade Center Towers and the Pentagon on September 11, 2001 and the recent world-wide anthrax attacks, no place in the entire world is immune to the terrorist attack using chemical, biological, nuclear and other unconventional weapons. This is supported by the newspaper report that the materials left in a compound used by Osama bin Laden's group may have been trying to develop chemical arms and other unconventional weapons. Foul-smelling liquids and charred papers covered with chemical formulas littered a makeshift laboratory in one building used by Al Qaeda (Anonymous, 2001).

The methodologies discussed in this chapter should be directly applicable to the identification of unknown chemical weapons and their residues, both from past wars and armament production, and from the present and future, potentially even more dangerous terrorist activities we have to deal with.

The most important step in the management of unknown solid wastes is the identification of the unknowns. In the course of our solid waste management in recent years, we have encountered numerous unknowns in various containers with illegible labels or without labels in various buildings at US Army Tank-automotive and Armaments Command Armament Research, Development and Engineering Center (TACOM-ARDEC). These unknowns need to be identified prior to their reuse or disposal.

Careful execution of various phases of the analyses of unknowns, which include sampling, sample preparation, identification, confirmation and quantification, is essential to avoid injuries to laboratory personnel and equipment damage. Furthermore, various analytical methodologies need to be carefully selected and applied in a proper sequence to achieve the analysis in an efficient manner. We have therefore developed an analytical scheme that has been utilized in the last decade (Chen et al., 1990a,b, 1991) in the identification of various unknown wastes (Fig. IV.2.1). The key to this performance-based scheme is the categorization of unknowns into energetic and non-energetic materials followed by volatility categorization, which enables proper choice and sequence of instrumentations to be used in the identification. The objective of this chapter is to describe this scheme and present examples of the applications of the scheme developed to the identification and quantification of militarily unique wastes.

Briefly, the scheme consists of initially identifying liquid and solid unknowns as energetic or non-energetic compounds using spot tests. If the tests for energetic materials are positive, their presence is confirmed by infrared spectrometry (IR) or mass spectrometry (MS) or other techniques as needed. Electron spectroscopy for chemical analysis (ESCA) experiments

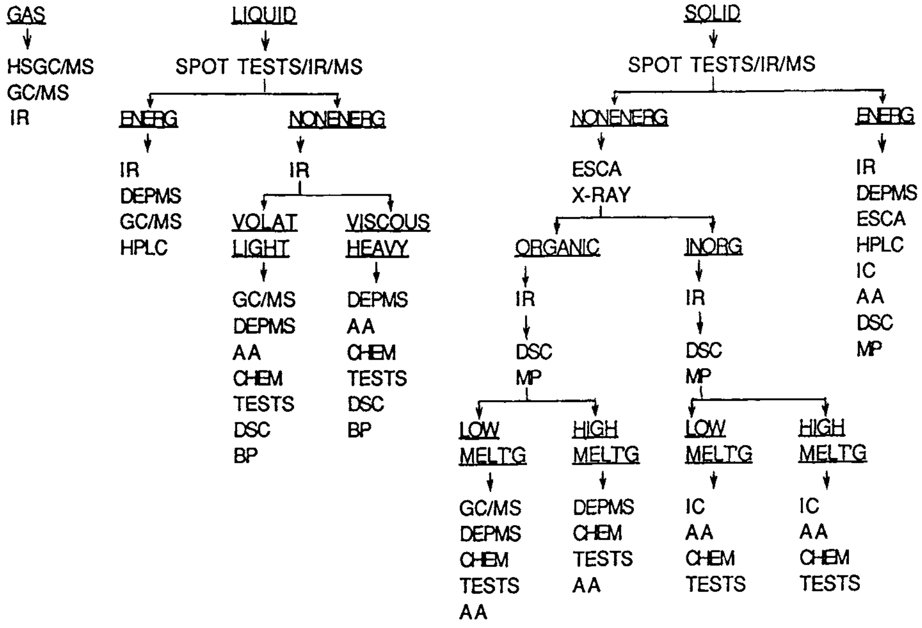


*Figure IV.2.1.* Analytical scheme for the identification of unknown wastes.

is performed on non-hygroscopic, non-volatile solids for their qualitative elemental composition determination. This is usually followed by X-ray diffraction analysis (XRD) to identify the molecular moieties. XRD is then followed by IR. Very often, the unknown could be identified at this stage. The melting point and boiling point are used as supporting evidence for sample identification as well as for sample selection in gas chromatography/mass spectrometry (GC/MS) and MS analyses. Viscous liquids, high boiling and high melting solids are analyzed by direct exposure mass spectrometry (DEPMS), an excellent technique for the analysis of thermally labile, non-volatile compounds. Headspace gas chromatography/mass spectrometry (HSGC/MS) is used for identifying gaseous specimens and gases liberated from solid samples as will be discussed later.

## IV.2.2. Experimental

### *IV.2.2.1. DEPMS experiment*

The specimen was dissolved in acetone or, in other solvent as required, at approximately 1 μg/μl concentration level. About 3–4 μl solutions were deposited, in 1 μl aliquots, on the loop of the direct exposure probe (DEP) heating wire.

The solvent was then allowed to evaporate and the DEP was inserted into the ion source of a Finnigan OWA 1020B Mass Spectrometer. The sample was heated at 10 mA/s to 1 A in the presence of about 3–5 Torr methane gas. The DEPMS experiment, in the positive ion chemical ionization (PICI) mode using methane as the reagent gas, was completed in approximately 100 s.

In the case of the Unknown 854, labeled as "green pigment" which does not dissolve in any suitable solvent, a small amount of specimen was shaken with a few drops of deionized water to form a suspension. A micro-syringe needle is then inserted into the suspension and with careful manipulation, a small particle of the suspended specimen could be placed on the needle utilizing the surface tension of water. The sample is next carefully transferred to the loop of the DEP heating wire. Upon evaporation of water, the sample is very carefully introduced into the interlock section of the probe and pumped very slowly, especially at the beginning to avoid loss of sample prior to introducing the specimen into the ion source of the mass spectrometer. This technique does not work particularly well and several tries may be needed. The problem is loss of sample during transfer to the heating wire and pumping in the sample interlock section.

#### *IV.2.2.2. Other instruments*

These were operated in the usual manner.

### IV.2.3. Results and discussion

In the following, the identification of some unknowns selected from our recent work will be described to demonstrate the usefulness of the analytical scheme developed. It should be noted that the background information and knowledge on the possible identity of the specimen could be utilized to choose appropriate analytical strategy for rapid identification of the unknown. It may be further noted that other techniques not listed in the general scheme are utilized as needed. Flexibility in choosing analytical strategies and use of proper methodologies are essential to successful unknown identification.

#### ***IV.2.3.1. Unlabeled glass reagent bottles filled with brown fumes and white solid mass***

The stoppers of the bottles were frozen and could not be loosened by the usual laboratory techniques for opening such bottles. They had to be broken very carefully behind a barricade and inside a plastic bucket containing crushed ice to quench any possible acetone and a few drops of the solution were deposited on the sodium chloride IR window. The solvent was allowed to evaporate to form a thin layer of the specimen. This technique will prevent any possible incident that may occur during any laboratory operations involving impact or grinding such as the preparation of KBr pellets for IR studies. From the IR spectra of the prepared specimens, the samples in question were identified to be pure 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (Chen et al., 1991).

#### *IV.2.3.3.* ***Unknown explosive compositions involved in the suspected fraud investigation***

This case was important on two accounts: (1) the fraud will affect the performance of a military item that is in extensive use today and (2) the fraud could affect the sensitivity of the item adversely. Due to possible safety hazards involved in handling the unknowns, this operation was conducted in a room with its relative humidity controlled at 50%. KBr pellets were prepared very carefully for IR analysis of suspected specimens.

Again, the IR proved that most suspected specimens consisted of a mixture of pentaerythritol teranitrate (PETN) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), rather than the pure HMX as specified (Chen et al., 1991).

PETN exhibits five absorption bands distinct from HMX, which enables direct identification of PETN in the mixture of HMX and PETN. The doublet at 1001 and 1034 $cm^{-1}$ is particularly useful in this regard.

#### *IV.2.3.4.* ***Unknown odor from a new composition***

The workers processing a new explosive composition at an ammunition plant noticed an odor and became concerned about the possible occupational safety hazards involved in the processing of this new composition.

For rapid identification of this unknown, the method of choice was *in situ* generation of this odor and subsequent analysis of the sample by HSGC/MS (see Figure IV.2.1 – the analytical scheme). This seemingly straightforward experiment turned out to be fairly difficult as the amount of gaseous sample generated was found to be too small for its positive identification. This problem was solved by generating the gas sample at a higher temperature, i.e. 100°C.

The mass spectrum was identified to be that of ethyl acetate, the solvent used in the manufacture of the composition. Ethyl acetate is a relatively safe compound with an oral LD50 for rats of 11 g/kg. Furthermore, the new composition contained only a very small amount of ethyl acetate. Therefore, it was concluded that the odor in question does not constitute any occupational safety hazards at the ammunition plant (Chen et al., 1991).

#### *IV.2.3.5.* ***Unknown residues from diatomaceous earth and granular carbon columns***

TACOM-ARDEC has a small-scale facility for demilitarization of obsolete munitions. This facility uses diatomaceous earth and granular carbon columns for removing energetic and related materials from the explosive contaminated wastewater generated at this site.

As part of this program, the unknown energetic materials adsorbed on these columns were analyzed (Chen et al., 1994).

The initial spot tests for screening the presence of explosives and propellants on the acetone extracts of the diatomaceous earth and granular carbon were negative. It is to be noted that in the demilitarization plant, the wastewater passes through the diatomaceous earth column first, then the granular carbon column before being discharged. The degree of the contamination of the adsorption material is, therefore, expected to be greater in the first than in the second column. Indeed, this has been found to be the case as will be shown later.

Subsequent to the initial spot tests, which established that the adsorption materials were not contaminated to any significant degree, the extractions were repeated using a larger amount of sample and a more thorough extraction procedure. In this case, only the diatomaceous earth column material exhibited a positive reaction for nitramine.

Since the spot tests are not very reliable due to lack of adequate selectivity, the positive response needs to be confirmed by fingerprinting techniques, most commonly MS and IR. Our method of choice is DEPMS, which enabled us to identify or confirm a large number of labile and non-volatile unknown compounds in the past (Chen and Campbell, 1989, 1993; Chen et al., 1990a; Chen and White, 1994).

Figures IV.2.2 and IV.2.3 show the DEPMS spectra of the adsorption materials from the diatomaceous earth and granular carbon columns, respectively. The former established

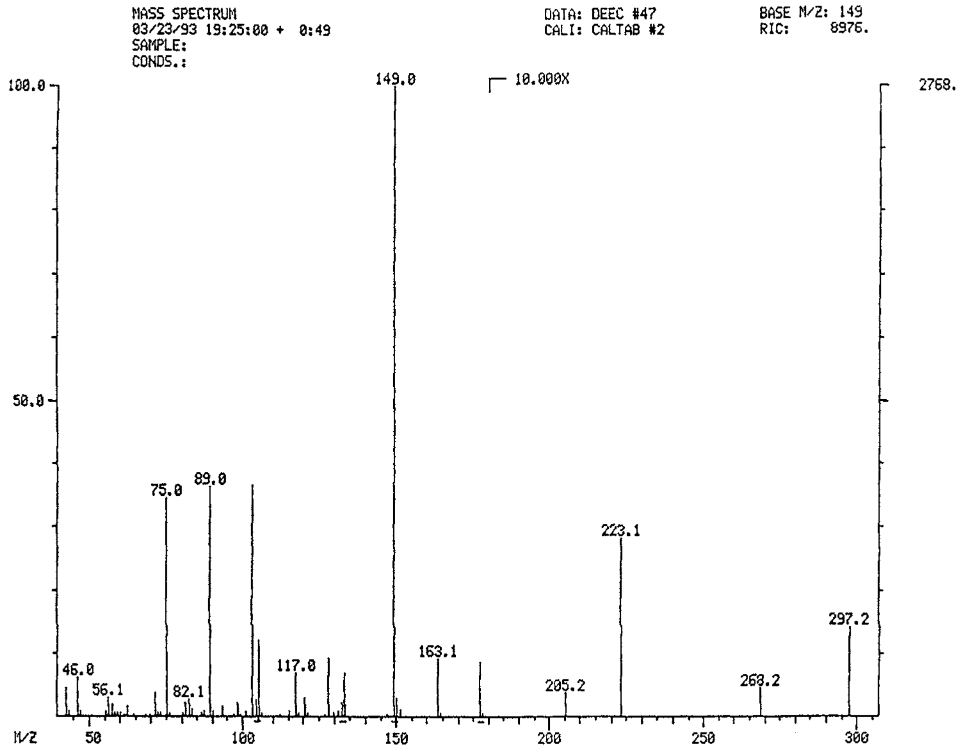


*Figure IV.2.2.* DEMPS spectrum of the unknown from the diatomaceous earth sample.

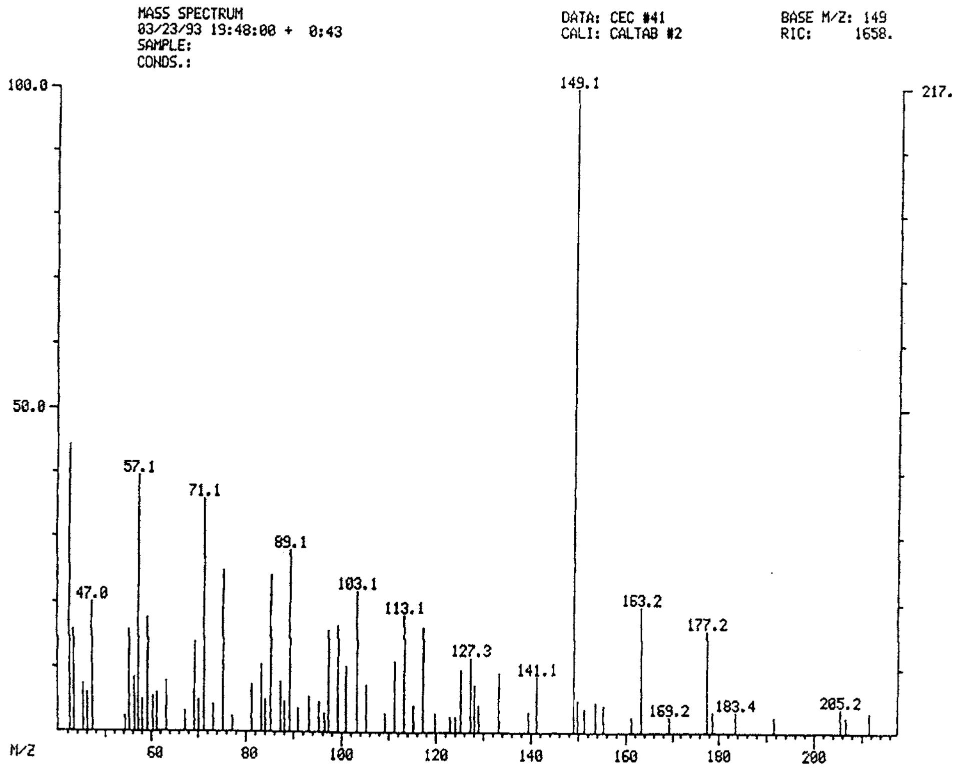


*Figure IV.2.3.* DEMPS spectrum of the unknown from the granular carbon sample.

the presence of RDX or HMX or both from the diagnostic ions and fragmentation ions discussed in our past work (Chen and Campbell, 1989, 1993) while the latter exhibits the presence of possibly a trace of RDX based on the presence of $[(CH_2NNO_2)_2 + H]^+$, $m/z = 149$ and $[(CH_2NNO_2) + H]^+$, $m/z = 75$. The spectrum in Figure IV.2.3 has low ion intensities and it appears to be contaminated with hydrocarbon(s) as indicated by peaks showing repeated $(CH_2)$ loss patterns in the whole spectrum range.

Figures IV.2.4 and IV.2.5 show the DEPMS spectra of RDX and HMX, respectively. The spectra are quite similar. However, there is one striking difference between the two, i.e. the intensity ratio of the $m/z = 103$ and 105 ions, the ratios being about 3.5 for RDX and about 0.5 for HMX. Based on this, it is concluded that the diatomaceous earth sample is contaminated with mostly RDX and possibly with a small amount of HMX. This is in line with the fact that the RDX manufactured in the US contains some HMX.

Figure IV.2.6 exhibits the HPLC chromatogram of the acetonitrile extract of the diatomaceous earth sample. HMX and RDX appear at the retention times of about 2.02 and 2.49 min, respectively. The unidentified peaks include those with retention times at about 1.02, 4.89 and 5.95 min. The HPLC chromatogram of the acetonitrile extract of the granular carbon sample indicates the presence of trace quantities of HMX and RDX. The amounts of RDX and HMX, in wt%, were determined by HPLC to be 0.65 ± 0.03

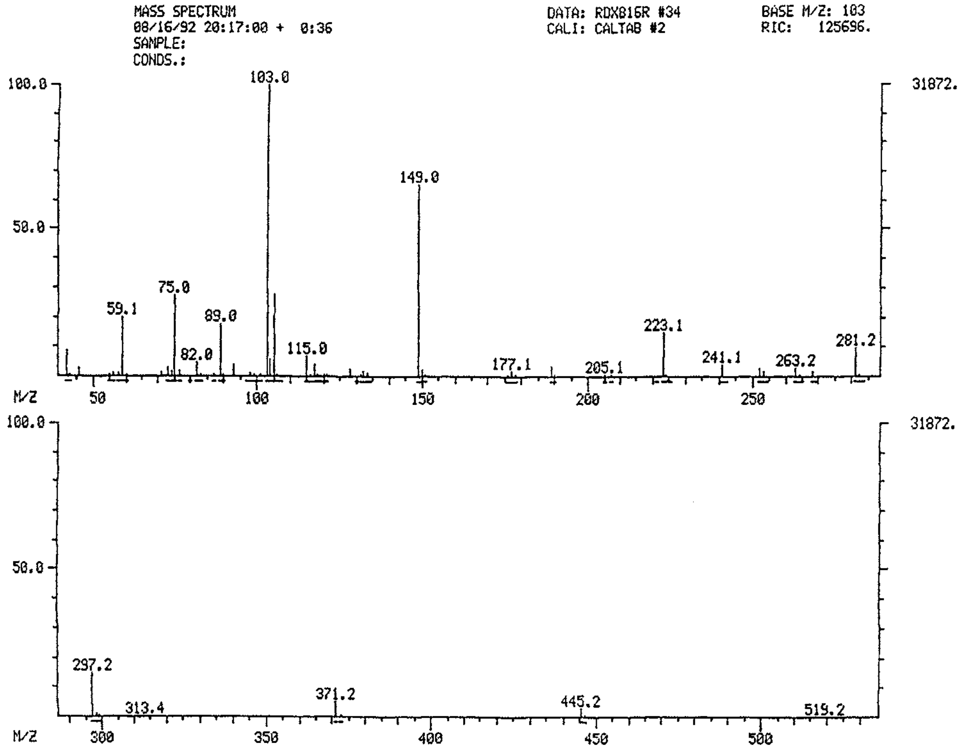


*Figure IV.2.4.* DEMPS spectrum of RDX.

and 0.08 ± 0.02 for the diatomaceous earth sample and 0.03 ± 0.01 and 0.01 ± 0.00 for the granular carbon sample, respectively. Thus, the adsorption column materials were found to be contaminated with less than 1% energetic materials.

### *IV.2.3.6. Unknown desert storm sample*

The slightly brownish sample was collected after the Persian Gulf War and sent to a location where suspected chemical and biological warfare agents can be safely handled.

In the initial screening for the energetic materials, the spot tests were conducted with great care inside a glove box under a slight vacuum to insure safe testing environment. The results tentatively identified the unknown to be trinitrotoluene. The sample was then shipped to ARDEC for confirmation. IR and DEPMS showed the unknown to be 2,4,6-TNT. Supporting evidences were obtained by HPLC and DSC by matching of the retention time and matching of the melting and decomposition temperatures of the sample with those of the standard 2,4,6-TNT. HPLC also showed the sample to be quite pure (Chen, 1992).

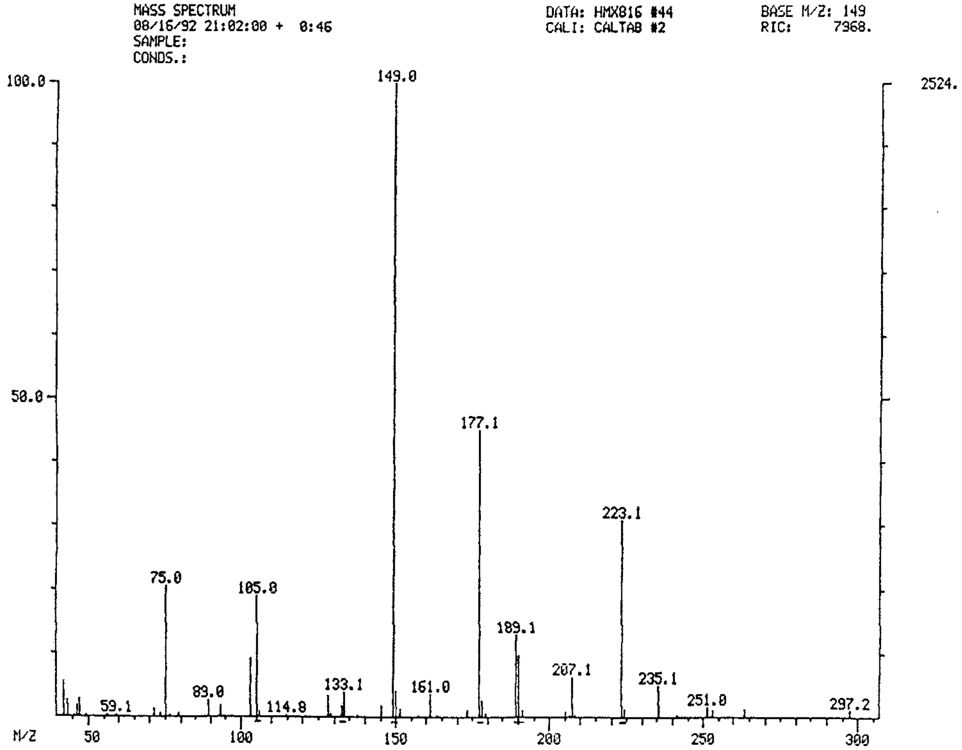


*Figure IV.2.5.* DEMPS spectrum of HMX.

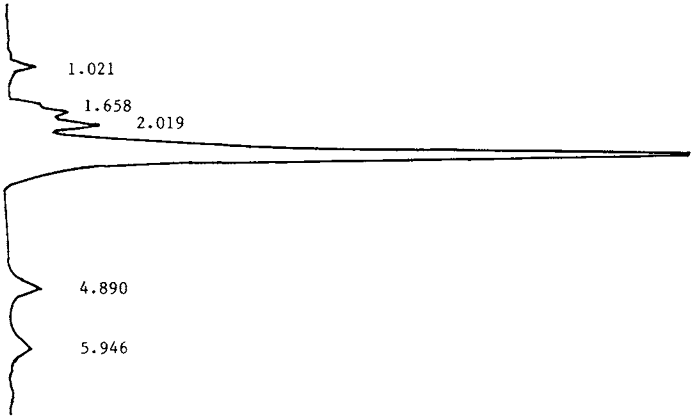


*Figure IV.2.6.* HPLC spectrum of the unknown from the diatomaceous earth sample.

### *IV.2.3.7. Explosive residues from explosive-contaminated wastewater filters*

Samples of the explosive-contaminated granulated carbon filters and the fiber filters were sent to TACOM-ARDEC from a depot activity that was treating the wastewaters generated by the Army Ammunition Plants. In order to meet the regulations and the deadlines of the environmental regulatory agencies, the depot had to dispose of the accumulated waste filters in a short period. This required the identification and quantification of residues in the shortest time possible. Since the identities of major explosive contaminants in the wastewaters were known, the initial screening tests and other fingerprinting techniques shown in the analytical scheme were not needed in this particular case. Instead, a reversed-phase HPLC was used to quantify the explosive contents of the fibers following the sample extraction with acetonitrile.

The granulated carbon filters were found to contain about 9 wt% each of RDX and 2,4,6-TNT and 1 wt% of HMX apparently derived from the Military Grade RDX. The carbon filters also contained two unidentified unknowns in small quantities amounting to a total integrated area of about 4%. The fiber filters contained essentially only 2,4,6-TNT. They were heavily contaminated with 2,4,6,-TNT in the central areas amounting to as much as 50 wt% in one case. Thus, both carbon and fiber filters were heavily contaminated with explosives. On the average, the carbon filters contained a total of about 22 wt% of RDX and 2,4,6-TNT, while the fiber filters contained about 17 wt% 2,4,6-TNT (Chen, 1992).

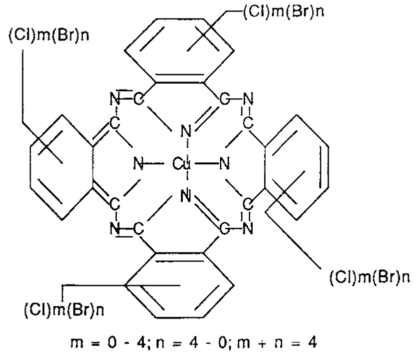
### *IV.2.3.8. Unknown 854*

In contrast to previous examples, this unknown, labeled as "green pigment", required considerably more efforts in its identification (Chen et al., 1990a,b) and confirmation.

The spot tests indicated the specimen to be non-energetic and ESCA showed the presence of chlorine and bromine. However, the XRD of the sample powder did not reveal the identity of the sample. The IR spectrum exhibited no absorptions associated with hydrogens, either alkyl or aromatic. But IR enabled tentative identification of the specimen as copper phthalocyanine complex. The atomic absorption spectrophotometry (AA) confirmed the presence of copper (about 3.5 wt%). It should be pointed out that the sample could not be completely brought into solution during the sample preparation for the AA work by an acid digestion procedure. In fact, the specimen did not dissolve in any solvents we tried to a sufficient degree for use in other analyses requiring the sample in solution. Thus, lack of appropriate solvent prevented the use of nuclear magnetic resonance (NMR) technique.

The initial DEPMS, which has a mass range of only up to 800 Da, provided the structural information of the sample establishing that all hydrogens on all four benzene rings are substituted by chlorine or bromine atoms, in agreement with IR studies. This work enabled the formulation of the structure shown in Figure IV.2.7. This structure was essentially confirmed by the near perfect matching of the IR spectra of the unknown and the commercial Pigment Green 36, 3Y-type with a possible formula of $C_{32}H_4N_8Br_6Cl_6Cu$ (Chen et al., 1990a).

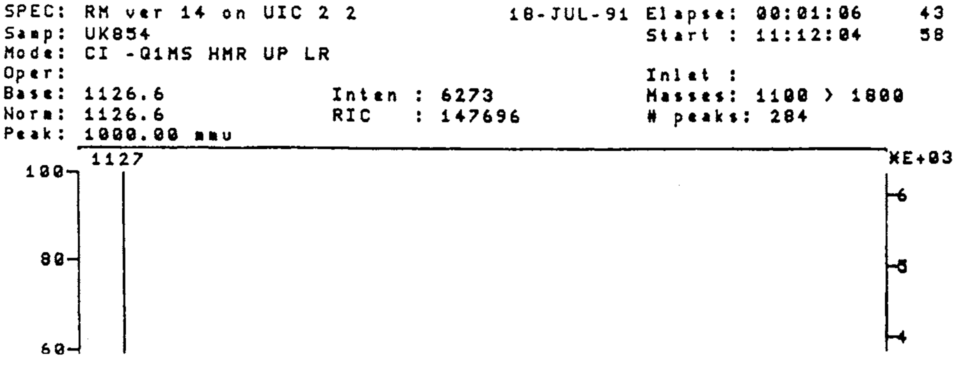
The differences in the spectra can be attributed to the halogen contents, i.e. the unknown contains more bromine atoms than the commercial product.



m = 0 - 4; n = 4 - 0; m + n = 4
Maximum no. of Cl in a molecule = 16
Maximum no. of Br in a molecule = 13

*Figure IV.2.7.* Structure of Unknown 854.

Subsequently, the DEPMS experiment using an instrument with a mass range of up to 2000 Da confirmed the previous conclusions. Furthermore, as can be seen from the 14 cluster ions in Figure IV.2.8, the specimen was shown to be a mixture of 14 copper phthalocyanine complexes consisting of a completely chlorinated {$C_{32}N_8(Cl^{35})_{16}Cu^{63}$–$C_{32}N_8(Cl^{37})_{16}Cu^{63}$; M.W. = 1119–1151} complex and 13 complexes with formulas, ranging from $C_{32}N_8(Cl^{35})_{15}Br^{79}Cu^{63}$–$C_{32}N_8(Cl^{37})_{15}Br^{81}Cu^{63}$ (M.W. = 1163–1195) to



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Norm: 1126.6         RIC   : 147696           # peaks: 284
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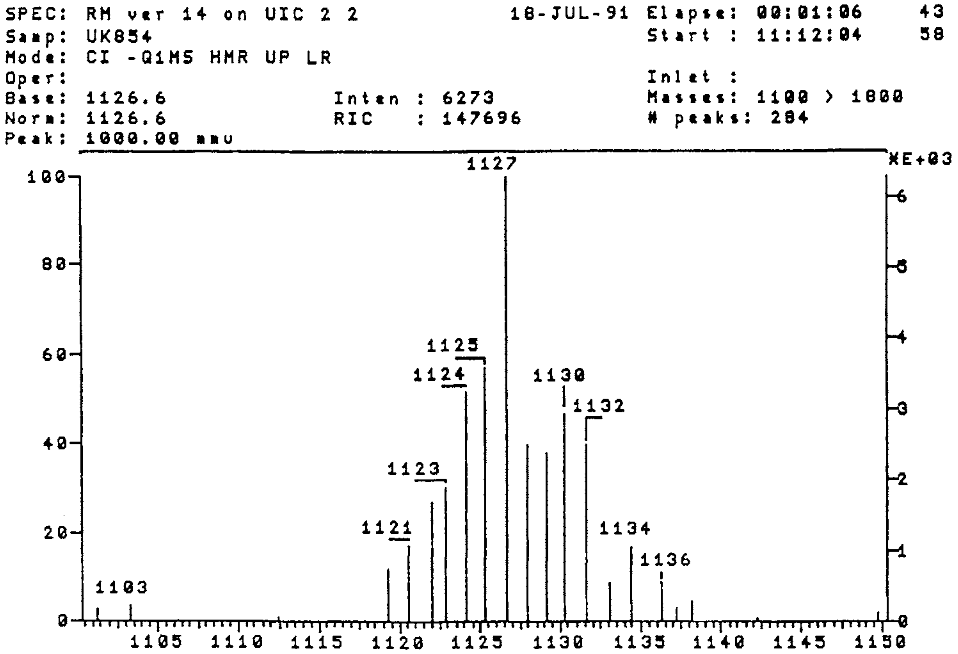

*Figure IV.2.9.* The expanded DEMPS spectrum of the first cluster ions of Unknown 854.

$C_{32}N_8(Cl^{35})_3(Br^{79})_{13}Cu^{63}$–$C_{32}N_8(Cl^{37})_3(Br^{81})_{13}Cu^{63}$ (M.W. = 1691–1723). The sum of chlorine and bromine atoms in the 13 complexes is 16 and the maximum number of bromine atoms is 13. The only structural feature that still needs to be elucidated is the distribution pattern of halogens in the 13 complexes. Figure IV.2.9 shows the expanded spectrum of the first cluster ions with a computed $(M + H)^+$ ranging from 1120 to 1152 Da (Chen, 1992).

### *IV.2.3.9. Unknown liquid*

This sample is brownish viscous oil with potential application for use as a high temperature lubricant for weapon systems such as guns. We spent considerable effort in the identification, quantification and environmental impact of this material for its potential application (Chen et al., 1998).

The DEPMS spectrum of the unknown (Fig. IV.2.10) exhibited complicated chlorine cluster ion patterns. It may be noted that these ions are protonated ions. This was interpreted to consist of two homologous series of polychlorinated compounds. The overlapping of some chlorine clusters not only made it difficult to interpret the major series but also made it quite difficult to infer the presence of the second less abundant series.

The Fourier transform infrared (FTIR) spectrum of the unknown (Fig. IV.2.11) exhibited the presence of the alkyl group at about 2931 and 2860 $cm^{-1}$, the ester group at about 1743 $cm^{-1}$ and the dichloro and trichloro carbon radicals at about 1459 and 732 $cm^{-1}$. Further, the spectrum appears to have a close resemblance to that of the alkyl oxalate ester.

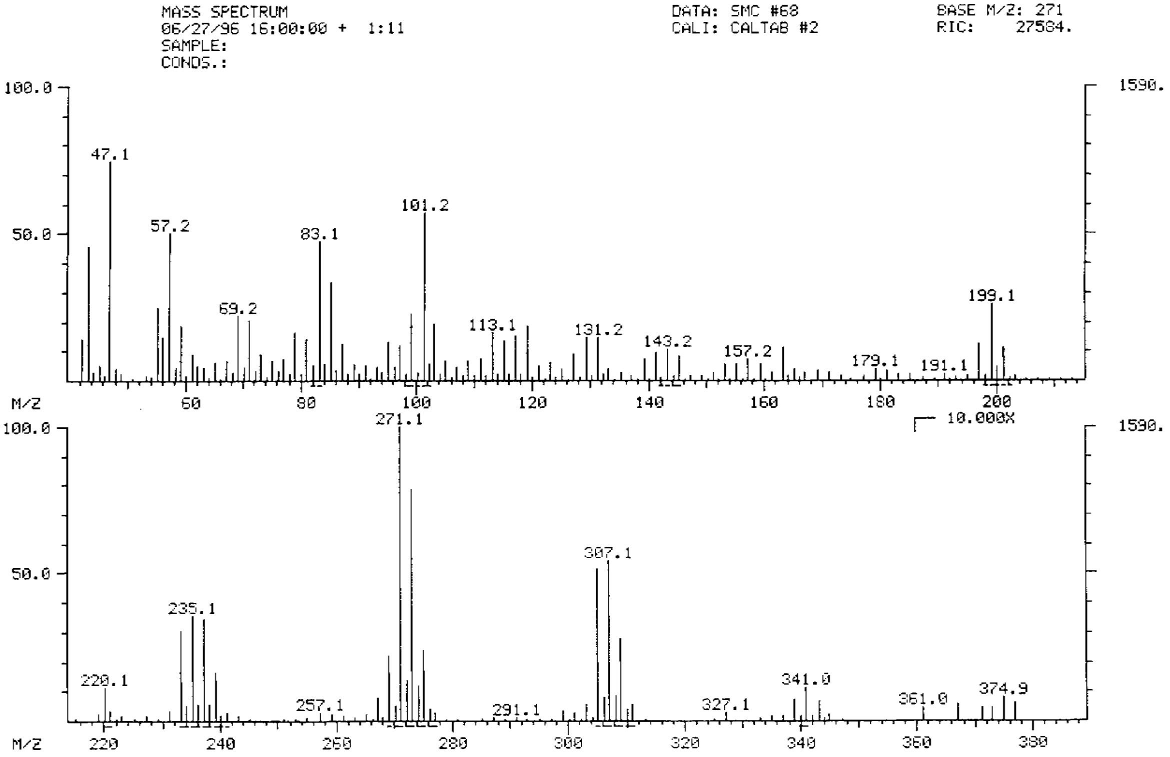

*Figure IV.2.10.* DEPMS spectrum of the unknown liquid.

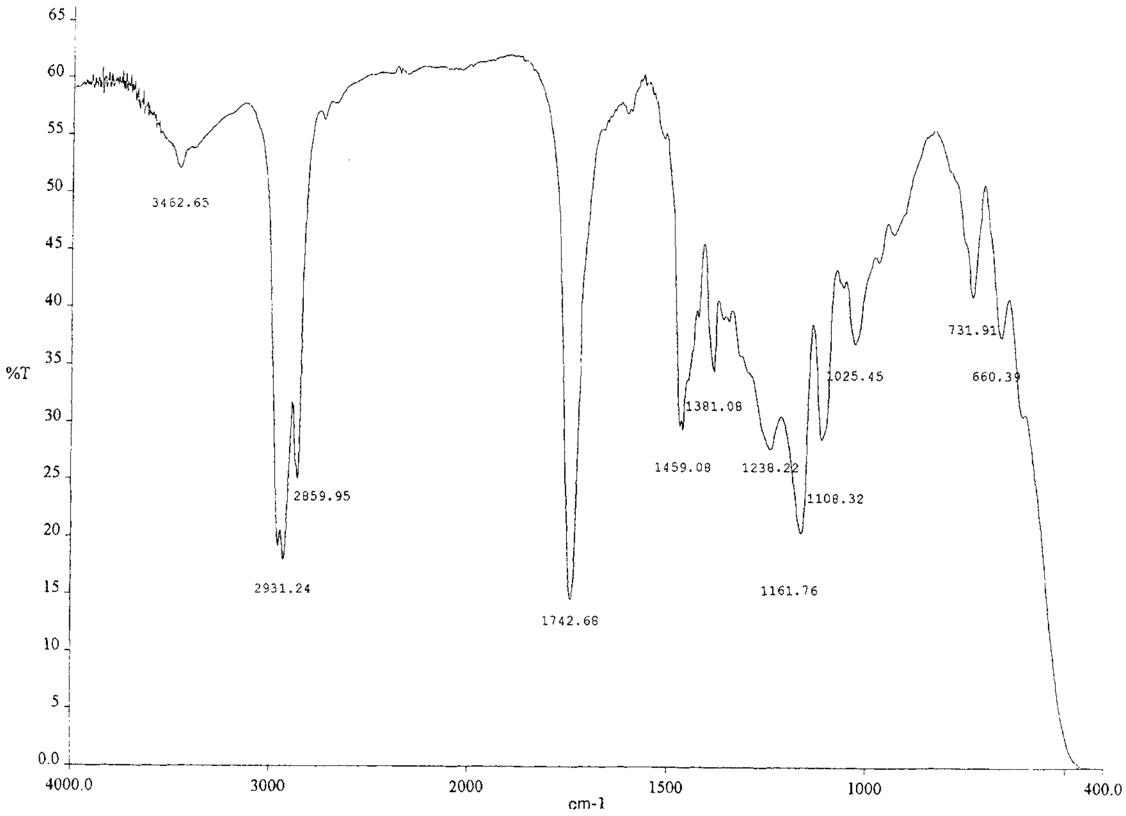

*Figure IV.2.11.* FTIR spectrum of the unknown liquid.

Incorporating the structural features observed by FTIR, the unknown was inferred to consist of primarily two 5 members each homologous series of polychloroalkyl oxalates and polychlorodihydroxyalkyl oxalates. One series has abundance of approximately two and half times of that of the other. The predominant series consists of, in the decreasing order of abundance, $C_8H_{16}Cl_2(COO)_2$, $C_8H_{15}Cl_3(COO)_2$, $C_8H_{17}Cl(COO)_2$, $C_8H_{14}Cl_4(COO)_2$ and $C_8H_{13}Cl_5(COO)_2$ with the molecular weight of $Cl^{35}$ species ranging from 236 to 372 Da. The intensities of the last cluster ions are very weak. The general formula for this series is $C_8H_{17-13}Cl_{1-5}(COO)_2$. The second less abundant series consists of, in the decreasing order of abundance, $C_3H_4Cl_2(OH)_2(COO)_2$, $C_3H_5Cl(OH)_2(COO)_2$, $C_3H_3Cl_3(OH)_2(COO)_2$, $C_3H_2Cl_4(OH)_2(COO)_2$ and $C_3HCl_5(OH)_2(COO)_2$ with the molecular weight of $Cl^{35}$ species ranging from 198 to 334 Da. The general formula for this series is $C_3H_{5-1}Cl_{1-5}(OH)_2(COO)_2$.

The differential scanning calorimetry (DSC) thermogram of the unknown (Fig. IV.2.12) was interpreted to exhibit a boiling range from about 250 to beyond 410°C of a mixture with some decompositions occurring in the vicinity of 320°C. This indicates that GC/MS may not be an appropriate approach for the identification of this unknown due to the indicated non-volatility and the decomposition of some components at high temperatures. Indeed, in our GC/MS experiments with the column temperature programmed up to 300°C failed to yield any information regarding the identity of this specimen.

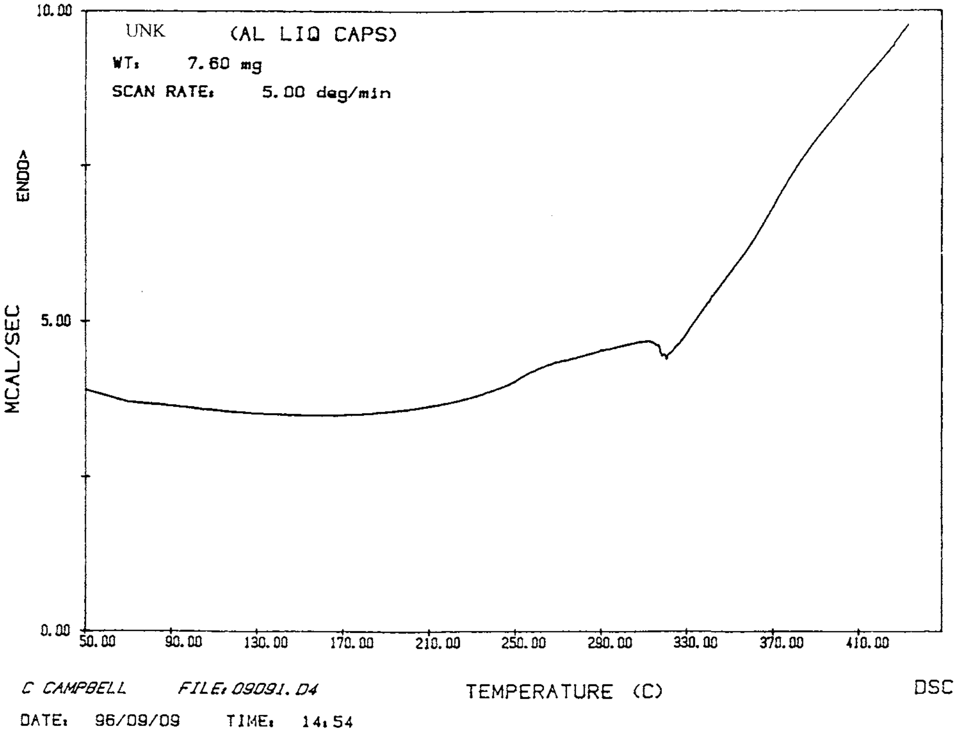

*Figure IV.2.12.* DCS thermogram of the unknown liquid.

In order to confirm the empirical formulas of the two homologous series of polychloroalkyl and polychlorodihydroxyalkyl oxalates discussed earlier, the accurate mass measurement of one of the more abundant cluster ions was attempted by desorption chemical ionization high resolution mass spectrometry (DCIHRMS). Contrary to expectations, Figure IV.2.13 exhibits complex hydrocarbon-like patterns. The entire features of the spectrum were interpreted to consist of essentially two 13 members each homologous series of high molecular weight dialkyl oxalates and dihydroxyalkyl oxalates. One series predominates the other in abundance by approximately 5–1.

The predominant series consists of 13 members of dialkyl oxalates with carbon numbers ranging from 22 to 34 and molecular weight ranging from 370 to 538. The general formula for this series is $C_{(n+m)}H_{2(n+m)+2}(COO)_2$, where $n$ and $m$ are the carbon numbers of the two alkyl groups attached to the oxalate group. The values of the sum of $n$ and $m$ range from 20 to 32. The accurate mass of the most abundant ion in this series, i.e. $m/z = 427$, was determined to be 427.378470 corresponding to the protonated ion of the inferred species, $[C_{26}H_{50}O_4 + H]^+$ or $[C_{24}H_{50}(COO)_2 + H]^+$. This number agrees very well with the theoretical value of 427.378736, the difference being only about $0.2m$ Da.

The less abundant series consist of 13 members of dihydroxyalkyl oxalates with carbon numbers ranging from 27 to 39 and molecular weight ranging from 472 to 640. The general formula for this series is $C_{(n+m)}H_{2(n+m)+2}(OH)_2(COO)_2$ with the values of the sum of $n$ and $m$ ranging from 25 to 37. The accurate mass of the most abundant ion in this series, i.e. $m/z = 571$, was determined to be 571.493837 corresponding to the protonated ion of the inferred species, $[C_{34}H_{66}O_6 + H]^+$ or $[C_{32}H_{64}(OH)_2(COO)_2 + H]^+$. This number agrees very well with the theoretical value of 571.493766, the difference being only about $0.1m$ Da. It should be noted that both sets of homologous series have identical structural types except that in the first set, the alkyl groups are polychlorinated. Thus, HRMS essentially confirmed the empirical formula assignments for the two 13-member homologous series discussed above.

The apparent discrepancy regarding the identity of the unknown in the DEPMS and DCIHRMS studies was attributed to the loss of most of the more volatile, lower molecular weight polychloroalkyl and polychlorohydroxy oxalates during the DCIHRMS experiment prior to the accurate mass measurements. As a result, only the less volatile, higher molecular weight components of the unknown, i.e. the two homologous series of the alkyl and hydroxyalkyl oxalates were observed.

To assess the environmental impact of the use of the unknown as a potential lubricant candidate for guns in the high temperature environment, the chlorine content of the unknown needs to be determined. Initially, the chlorine content determination by gravimetry as silver chloride was attempted. The procedure consisted of the alkaline hydrolysis of the specimen with sodium hydroxide and precipitation of the resulting chloride ions in the aqueous extract with silver nitrate as silver chloride after acidification of the extract with nitric acid. This was not successful because this unknown was found to be highly resistant to the alkaline hydrolysis. Subsequently, the sodium fusion procedure (Pasto and Johnson, 1969) was employed to decompose the unknown for the determination of the chlorine content. All reactions involved in this procedure are very vigorous and extreme care needs to be exercised to avoid the loss of solution by spattering. The resulting chloride ions were then determined by gravimetry as silver chloride. The chlorine content was determined to be 28.0 ± 0.2%.

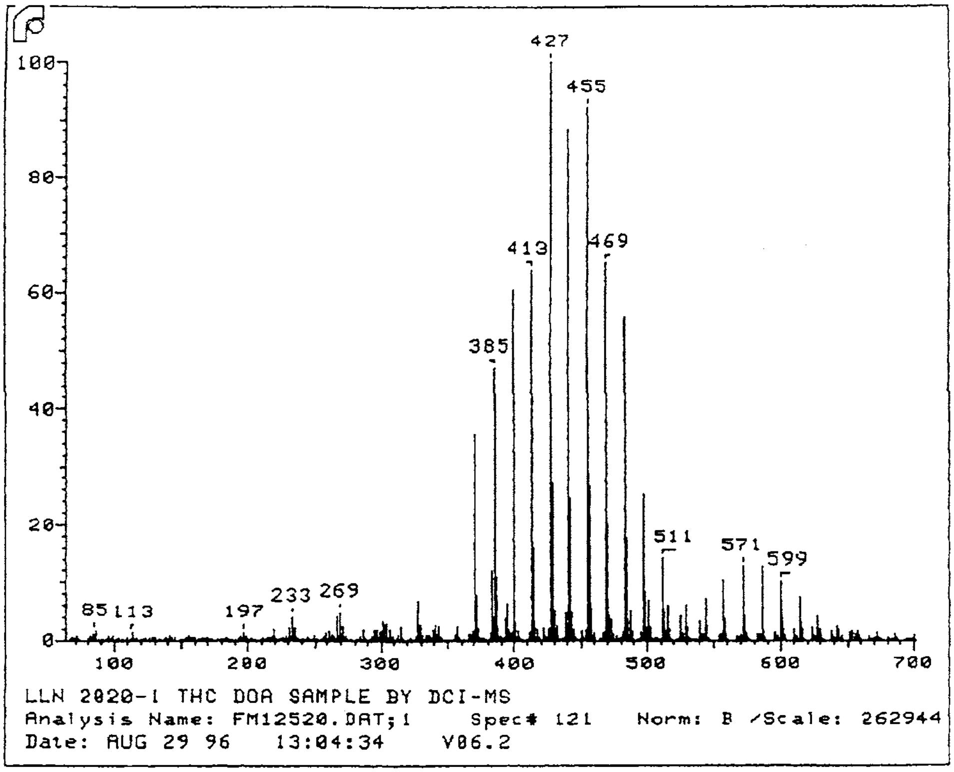

*Figure IV.2.13.* DCIMS spectrum of the unknown liquid.

The approximate chlorine content and the average molecular weight of the unknown were also computed from the approximate normalized intensity ratios of the two sets of homologous series of $Cl^{35}$ cluster ions (Fig. IV.2.10) and the chlorine contents and the molecular weights of the 10 chlorine species. This yielded approximate chlorine content and the average molecular weight for the unknown of 27% and 262, respectively.

The agreement of the values for the chlorine content obtained by gravimetry and by computation from DEPMS spectrum indicates that the unknown consists of primarily two 5-member homologous series of polychloroalkyl and polychlorodihydroxyalkyl oxalates ranging in molecular weight for the $Cl^{35}$ species from 198 to 334 and 236 to 372 Da, respectively. The minor components of the unknown consist of the two 13-member homologous series of dialkyl and dihydroxyalkyl oxalates ranging in molecular weight for the $Cl^{35}$ species from 370 to 538 and 472 to 640 Da, respectively.

## IV.2.4. Some comments on analytical scheme

We have optimized the DEPMS conditions for the identification of non-volatile and labile energetic compounds, especially RDX and HMX. As pointed out earlier, DEPMS enabled us to identify and confirm a large number of labile and non-volatile unknown compounds in the past (Chen and Campbell, 1989, 1993; Chen et al., 1990a; Chen and White, 1994).

It should be pointed out that, DEPMS operated under our conditions provides, in most cases, the molecular weight and the structural information in a single experiment very rapidly. This is the primary reason for our preference and reliance on this particular MS technique in the analytical scheme developed. We have also employed HRMS to confirm the identity of diagnostic ions (Chen and Campbell, 1989), and identify unknown mixtures (Chen, 1983; Chen et al., 1998). Proton nuclear magnetic resonance (p-NMR) was also utilized in the structural elucidation as well as the composition analysis of an unknown liquid explosive mixture (Chen, 1983). Optical microscopy was used in aiding the identification of the unknowns.

Liquid chromatography/mass spectrometry (LC/MS) and related techniques such as the bench-top LC/MS/MS have now been widely employed in the analyses of complex mixtures. These powerful and versatile techniques enable the analyses of complex mixture samples with minimum or no sample preparation. Moreover, the MS/MS capability allows the analysis of unknown mixtures at the trace levels with reliable identification of unknown species. However, in the comparative study of RDX and HMX by DEPMS and thermospray liquid chromatography/mass spectrometry (TSLC/MS), the latter operated in the negative ion mode with discharge provides only limited molecular weight and structural information. Such information for RDX and HMX basically could not be obtained under the conditions of particle-beam LC/MS (PBLC/MS) (Chen, 1993). This study was preliminary in nature, and further work is needed to confirm these initial findings.

Although not included in the scheme, capillary electrophoresis techniques such as capillary zone electrophoresis (CZE), micellar electrokinetic chromatography (MEKC) and capillary electrochromatography (CEC) are now widely applied to the analysis of unknowns. These techniques complement IC and HPLC.

### IV.2.5. Further developments

September 11th 2001 terrorist attacks and the subsequent terrorism and bio-terrorism in the USA revealed new monitoring and analytical challenges faced by environmental laboratories around the world. Due to the specific character of the terrorism of the 21st century that uses in full the trumps of extreme mobility, taking by surprise, and unpredictability in choosing the targets of scorching blasts, the laboratories should be no less flexible, mobile and prepared to an instant effective response to the attack, wherever it happens. They have to deal with a new wider range of unknown substances/waste in any compartment of the environment and any place worldwide. The success can be assured by the parallel efforts utilizing the performance-based measurement system (PBMS) approach at the stationary laboratory exemplified above, and further development of field monitoring and field-based analytical methods (FAMs) (see Chapter IV.1). The advantages of these result-oriented approaches in the field of identification of unknown substances/waste are obvious: (i) they address sample- and site specificity, analytical flexibility and freedom in keeping pace with current improvements in analytical chemistry techniques; (ii) they permit on-site identification and preliminary characterization of a hazard, which greatly improve promptness of response, mobility and economic and scientific feasibility in achieving the objectives of public and environmental safety.

Among the variety of FAMs also discussed and referred to in Chapter IV.1, several methods developed recently address directly the objectives of on-site identification of unknown substances/wastes (Davoli et al., 2001), explosives (Carles et al., 2001; Ewing and Miller, 2001; Hewitt et al., 2001), buried objects and landmines (SPIE, 1999) and biological hazards (Denniger and Lee, 2000; Snyder et al., 2000). Besides, the US EPA (2002) provides broad, continuously updated information on currently available FAMs and equipment that can be applied on site for unknown substances/waste identification and sample collection activities. They include methods that can be used outdoors with hand-held equipment, as well as more rigorous methods that require the controlled environments of a mobile laboratory. Some of the most common FAMs addressed in the US EPA document (2002) are fiber optic chemical sensors: rapid optical screening tool (ROST) and laser-induced fluorescence (LIF) coupled with the site characterization and analysis penetrometer system (SCAPS). Other widely used FAMs comprise portable GC, immunoassay test kits (IA), X-ray fluorescence (XRF) and GC/MS.

Besides technical aspects, the principles of analysis are of importance. The American Chemical Society (ACS) Committee on Environmental Improvement is considering an update of the 1983 "Principles of Environmental Analysis". One of the crucial topics this Committee plans to address is establishing criteria for unknown compound identification (Richardson, 2002), which should also provide a valuable assistance in this area.

Many laboratories and their staff – analysts, scientists and managers – were on the front line of response actions to terrorists attacks of September 11, 2001 and of undertaking preventive measures for protection of the next potential targets. The real world analytical challenges faced by these laboratories in responding to these attacks were reflected in the presentations at the Special Session of the 18th Annual Waste Testing and Quality Assurance Symposium (WTQA, 2002).

The awareness of specificity of threat caused by terrorism will undoubtedly give a further strong impulse to the improvement of existing and development of new analytical methods and equipment for faster, more cost-effective and reliable identification and management of hazard posed by terrorism to the public health and environment. Along with these new disasters, the residuals of past, present and future wars and improperly disposed and buried unknown hazardous waste are to be no less adequately identified and managed.

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