



A Forensic Workshop Report Concerning (1) The Measurement and Analysis of Energetic Materials and (2) Databasing

by Joseph M. Heimerl

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ARL-SR-77

January 1999

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Weapons and Materials Research Directorate, ARL

Abstract

On Thursday, 20 June 1996, this workshop was convened at BRL Hall (Bldg. 330), located at the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground (APG), MD. The purposes of this workshop were: (1) to define the critical problems that cut across forensic agencies; (2) to provide an open, multidisciplinary forum in which these problems could be addressed and better defined; and (3) to lay the foundation for practical, timely, and cost-effective solutions.

The technical focus of the workshop pivoted on two questions: (1) What is required for a sample to be traceable to a unique compound (or unique class of compounds)? (2) How can the present databases be made into user-friendly, complete, and current databases, accessible by all forensic laboratories?

This report documents the background leading up to the calling for a workshop, the manuscripts of the talks given, and the discussion held.

Acknowledgments

The fact that this workshop took place was due to a large number of people who saw its potential worth and were willing to put forth the effort to make it happen. At the risk of omitting the names of some folks, who have my apologies in advance, I would like to thank each agency's point of contact (POC): Dr. Frank Fox at the Federal Aviation Administration (FAA), Mr. Raymond Voorhees at the Postal Inspection Service, Dr. Steve Burmeister at the Federal Bureau of Investigation (FBI), and Mr. Charlie Midkiff at the Bureau of Alcohol, Tobacco, and Firearms (BATF).

Kudos to Dr. Rose A. Pesce-Rodriguez of the U.S. Army Research Laboratory (ARL) for her roles as technical reviewer, sounding board for ideas, and moderator of the afternoon session. Dr. Kevin McNesby, also of ARL, is thanked for his roles as technical reviewer and presenter. Mr. Ed Simmons of the Aberdeen Proving Ground (APG) Audio/Visual Section is thanked for his audio recordings of the presentations and discussions; the discussion section owes its existence to those audio tapes. (Next time, we will avoid placing a live microphone in the vicinity of the viewgraph's exhaust fan.)

Thanks are also due to Ms. Rhonda Cumpton of ARL for a variety of logistical services and to the Chemical Propulsion Information Agency (CPIA) for permission to publish Dr. Caulder's earlier work. Finally, I want to express my thanks to Ms. Kathleen Higgins at the National Institute of Justice (NIJ) for partial financial support of this workshop and for reviewing this report.

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1. Background

As the presentation of findings in court have made more and more demands on the forensic scientist, the time to do the science that underpins forensic investigations has diminished. With the idea that the Ignition and Combustion Branch (ICB) Chemistry Laboratory at the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground (APG), MD (see Appendix A) could aid forensic laboratories in keeping up with scientific advances, members of the Bureau of Alcohol, Tobacco, and Firearms (BATF), the Federal Bureau of Investigation (FBI), and the U.S. Postal Inspection Service were invited to tour the ICB physical chemistry facilities on 31 January 1996. Eleven forensic scientists from these agencies and one researcher each from the National Institute of Standards and Technology (NIST) and the U.S. Army Edgewood Research, Development, and Engineering Center (ERDEC) participated in this tour. ARL's detection and characterization capabilities and three current problems from each of the forensic agencies were briefed. During the wrap-up session, there was a consensus that a workshop ought to be held to bring problems concerning energetic materials into sharper focus. Later, the Federal Aviation Administration (FAA), at their request, also toured the ICB/ARL facilities and expressed a desire to participate in the planned workshop.

On Thursday, 20 June 1996, a workshop entitled "Forensics: Energetic Materials Measurement, Analysis, and Databasing" was convened at BRL Hall (Bldg. 330), located at ARL, APG, MD. The purposes of this workshop were:

- (1) to define the critical problems that cut across forensic agencies;
- (2) to provide an open, multidisciplinary forum in which these problems could be addressed and better defined; and
- (3) to lay the foundation for practical, timely, and cost-effective solutions.

The technical focus of the workshop pivoted on two questions.

- (1) What is required for a sample to be traceable to a unique compound (or unique class of compounds)?
- (2) How can the present databases be made into user-friendly, complete, and current databases, accessible by all forensic laboratories?

These two focus questions had been formulated in conjunction with the forensic community (see Appendix B). Subsequently, an agenda was established and is given in section 2. Next, a letter of invitation was extended to approximately 30 forensic scientists and researchers. A copy of this letter, the response fax form, and a list of the workshop attendees are given in Appendix C.

As can be seen from the agenda, the format for the workshop consisted of six topical speakers followed by an extensive discussion session. In anticipation of this report, the entire set of talks was audiotaped, transcribed, and returned to the respective authors, who then reviewed the transcription to produce the written manuscripts contained herein. The discussion session was prepared by this author. Because of the rather poor quality of the audiorecordings, each author was free to substitute work already in progress or published elsewhere, provided that the manuscript covered in essence what was presented at the workshop. The body of this report (six manuscripts of the presentations and a discussion section) follows the agenda. Because of a demanding court schedule, Dr. Bermeister could not provide his manuscript; therefore, only his abstract has been included. In addition, for a variety of cumulative reasons, Dr. Caulder was not able to supply a manuscript of his talk. In its stead, by mutual consent of all parties, we have chosen to substitute an earlier version of the talk given, which covers the same kind of material and may be found on pp. 53–67 in the Chemical Propulsion Information Agency (CPIA) Publication No. 588 of August 1992. At the end of the workshop, an evaluation was made, and these results are presented in Appendix D.

2. Agenda

Forensics: Energetic Materials Measurement, Analysis, and Databasing Workshop
Held at the U.S. Army Research Laboratory
BRL Hall (Bldg. 330)
20 June 1996

0830–0855 **Parking** (See Directions)

 Badging (Bldg. 328)

 Walk to BRL Hall (Bldg. 330)

0900–0915 **Welcome**, by Al W. Horst, Chief, Propulsion and Flight Division (PFD)

0915–0920 **Administrative Remarks**, by Joseph M. Heimerl, Workshop Coordinator

Chair of Morning Sessions: Rose A. Pesce-Rodriguez

0920–0940 “Analytical Methods Used in Identifying Trace Constituents in Energetic Materials,”
 by Steve Burmeister, Federal Bureau of Investigation (FBI)

0940–1000 “Characterization and Identification of Explosive and Propellant Formulations Using
 Raman Spectroscopy,” by Kevin L. McNesby, Nicholas F. Fell, Jeffrey M. Widder,
 Jeffrey B. Morris, and Rose A. Pesce-Rodriguez, U.S. Army Research Laboratory
 (ARL), Ignition and Combustion Branch (ICB)

1000–1020 **Break**

1020–1040 “Trace Detection Activities,” by Frank T. Fox, Federal Aviation Administration
 (FAA) Technology Center

1040–1100 “The Explosive Standard Analytical Reference Material (SARM) Program,” by Stan M. Caulder, H. E. Turner, and W. F. Bryant, Naval Surface Weapons Center (NSWC), Indian Head (IH) Division

1100–1120 **Break**

1120–1140 “Problems in Characterizing Smokeless Gunpowders,” by Allan N. Walters, Postal Inspection Service

1140–1200 “Simplifying Access to Complex Databases,” by Ralph D. Semmel and E. A. Immer, The Johns Hopkins University (JHU), Applied Physics Laboratory (APL)

1200–1300 **Lunch** at *Top O’ the Bay*

Chair of Afternoon Sessions: Joseph M. Heimerl

1300–1400 **Open Discussion** (Bldg. 330)

1400–1420 **Break**

1420–1530 **Wrap Up**

Tour Director: Rose A. Pesce-Rodriguez

1530–1630 **Minitour** of Laboratory Facilities (Optional)

3. “Analytical Methods Used in Identifying Trace Constituents in Energetic Materials”

Steve Burmeister
Federal Bureau of Investigation
(Abstract Only Available)

The talk addresses techniques in use today for the analysis of certain explosives and how these results are applied to the sourcing of materials. It includes a discussion of database information currently available.

4. "Characterization and Identification of Explosive and Propellant Formulations Using Raman Spectroscopy"

Kevin L. McNesby, Nicholas F. Fell, Jeffrey M. Widder,
Jeffrey B. Morris, and Rose A. Pesce-Rodriguez
U.S. Army Research Laboratory, Ignition and Combustion Branch
Aberdeen Proving Ground, MD 21005-5066

Abstract

Fourier transform Raman (FTR) spectroscopy employing near-infrared (NIR) laser radiation at 9394.5 cm^{-1} is used to characterize neat energetic materials and several propellant formulations. Raman spectra are reported over the region from 100 cm^{-1} to $3,000\text{ cm}^{-1}$, relative to the Rayleigh line. The technique is extended to the study of crystalline components of propellant formulations during heating. The utility of the technique in determining the principal crystalline ingredient in a propellant formulation is demonstrated.

Introduction

Fourier transform Raman (FTR) spectroscopy using near-infrared (NIR) laser light as the scattering source has been shown to be useful in the identification of crystalline components of propellant formulations [1]. The ease with which many principle components of propellant formulations may be identified is due to the generally good scattering characteristics of crystalline energetic materials combined with the poor scattering characteristics of most plasticizers and binders. Although using NIR laser light as the scattering source limits the signal intensity compared to that obtained using visible laser light scattering, the lack of fluorescence interference when working in the NIR spectral region outweighs this disadvantage. If a disadvantage exists in trying to measure Raman spectra of propellant formulations using NIR laser scattering, it is that most

colored formulations will absorb the laser light and combust. Fortunately, most crystalline neat energetic materials are not colored; so, the technique can often yield excellent results.

Recently, we published a short paper consisting of Raman spectra of several neat energetic materials and several propellant formulations [2]. It was our goal at the time to have that paper be the first in a series to aid in the assembly of Raman spectral database of energetic materials and propellant formulations. Since that time, modifications to our instrument have enabled coverage of a broader spectral range; so, we have remeasured the spectra of neat energetic materials not measured in the first paper and have also included some new energetic formulations and techniques. We hope most readers find this paper a useful continuation of our initial effort toward the characterization of energetic materials by FTR spectroscopy.

Experimental

The experimental apparatus has been described previously [2]. Briefly, the experimental apparatus consists of a Bomem DA-8.02 Fourier transform spectrometer to which a Raman accessory has been added. Incident radiation is provided by a Quantronix Series 100 Nd:YAG laser. A simple sketch of the experimental apparatus is shown in Figure 4-1. Raman-shifted radiation is collected using a back-scattering geometry and detected after filtering and interferometer modulation using a liquid-nitrogen-cooled InGaAs detector. Recently, the interference filters used to exclude the Rayleigh line at 1.06μ (9394.5 cm^{-1}) were replaced by holographic notch filters (Kaiser Optical). This enabled measurement of Raman transitions that shifted from 100 cm^{-1} to $3,000 \text{ cm}^{-1}$ with respect to the Rayleigh line (the previous spectral range of the instrument was from 400 cm^{-1} to $3,000 \text{ cm}^{-1}$). Also, we are able to observe anti-Stokes lines that shifted from the Rayleigh line from 150 cm^{-1} to 600 cm^{-1} .

All spectra reported here were measured at 4-cm^{-1} resolution using coaddition of 256 scans. Incident laser power was 200 mW. Scan time to collect each spectrum was 11 min. Neat samples of energetic materials were placed in 1-mm inside diameter (ID) glass capillary tubes, and the

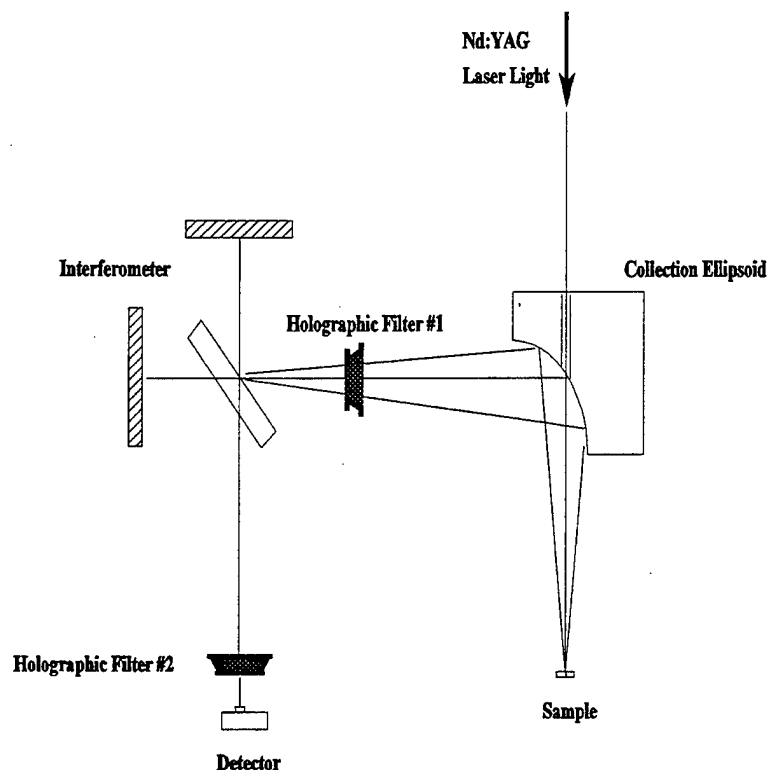


Figure 4-1. Simple Diagram of the Experimental Apparatus Used in These Experiments.

Nd:YAG laser focused on the front surface of the tube. Propellant formulations, when in the form of cylindrical grains, were placed in a temperature-variable holder whose position could be maintained from run to run. Powdered propellant formulations were placed in a sample spinner operated at 2,400 rpm to minimize heating effects. No correction was made to any of the spectra to account for responsivity of the detector, interferometer, or filters used in the experiments. Samples of hexanitrostilbene (HNS) and of a Chinese propellant formulation were provided by Atlas Wireline Services Incorporated. All other propellant samples used in these experiments were obtained from in-house sources.

Results and Discussion

Neat Energetic Materials. Table 4-1 shows a summary of the energetic materials whose FTR spectra are reported herein.

Table 4-1. Energetic Materials Used in These Experiments

Energetic Material	Laser Power (mW)	Composition
RDX	400	neat
HMX	400	neat
PETN	400	neat
NQ	400	neat
ADN	400	neat
TNT	400	neat
b-HNIW	400	neat
TNAZ	400	neat
HNS	400	neat
PDNPA	400	neat
NC	400	neat
DMNA	400	neat
XM39	400	76% RDX, 4% NC, 20% binder and plasticizer

Figure 4-2 shows the FTR spectra of the most common nitramine energetic material, cyclotrimethylenetrinitramine (RDX), and of the eight-membered ring homolog, cyclotetramethylenetetranitramine (HMX). There are several interesting features in these spectra. First, unlike our previously published spectra, we are now able to observe in each spectrum vibrational transitions to within 100 cm^{-1} of the Rayleigh line. Vibrational transitions due to ring deformations in RDX and HMX, occurring at Raman shifts of from 100 cm^{-1} to 400 cm^{-1} , were not measurable in our laboratory prior to installation of the new holographic rejection filters. Crystal lattice modes [3] in nitramine crystals, which occur below 100 cm^{-1} , fall within the “notch” of the holographic filters and are therefore not observable. An interesting result from the FTR spectrum of HMX is that an intense peak is observed centered at a Raman shift of 150 cm^{-1} . This peak is close to the intensity of the most intense ring stretch features occurring in HMX from 800 cm^{-1} to $1,000\text{ cm}^{-1}$.

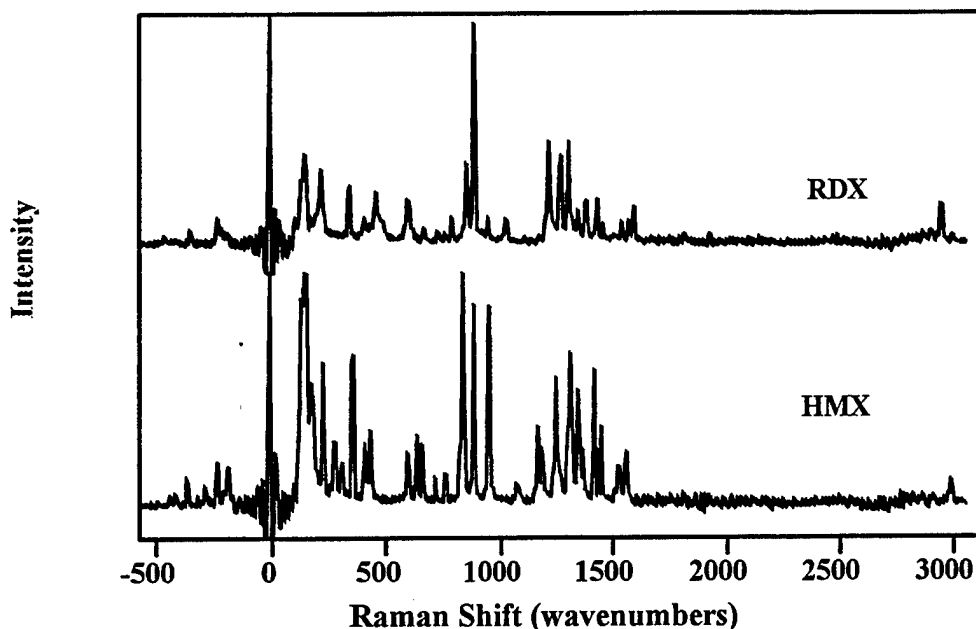


Figure 4-2. The FTR Spectra of RDX and HMX.

Figure 4-3 shows the spectrum of the nitrate ester pentaerythritol tetranitrate (PETN), a common ingredient in some commercial explosives. Also shown is the FTR spectrum of nitroguanidine (NQ). The N-H stretch in NQ at a Raman shift of approximately $3,200\text{ cm}^{-1}$ is not observed, since it occurs beyond the range of the InGaAs detector. Figure 4-4 shows the spectrum of ammonium dinitramide (ADN) and of trinitrotoluene (TNT). In both of these spectra, features below 400 cm^{-1} are among the most intense in each spectrum. For the spectrum of TNT, sample heating is manifested by a slightly elevated baseline. Neat TNT is light yellow in color and absorbs some of the incident Nd:YAG laser radiation.

Figure 4-5 shows the spectra of beta-hexanitroisowurtzitane (b-HNIW), an energetic-caged nitramine, and 1,3,3-trinitroazetidine (TNAZ), an energetic nitramine containing a geminal dinitro group. Figure 4-6 shows the spectrum of HNS, an industrial explosive used in high-temperature applications, and polydinitropropyladipate (PDNPA), an energetic polymeric binder used in some propellant formulations. Both spectra were measured using incident radiation at a power of 400 mW, although the signal-to-noise ratio in the spectrum of HNS is superior to that of the spectrum of PDNPA. These spectra illustrate the general observation that crystalline energetic materials are better Raman scatterers than polymeric energetic materials.

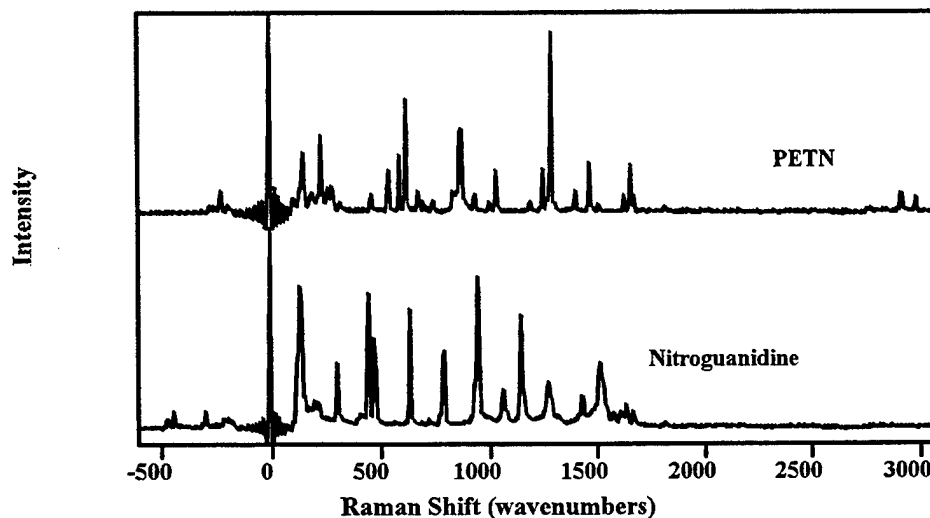


Figure 4-3. The FTR Spectra of PETN and NQ.

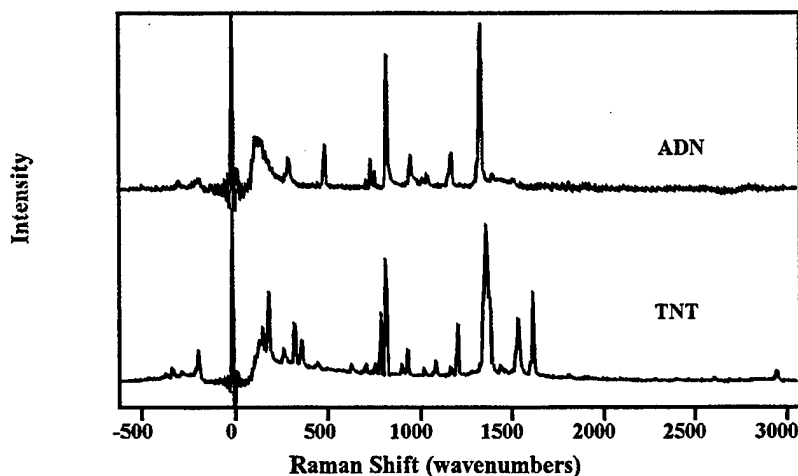


Figure 4-4. The FTR Spectra of ADN and TNT.

Figure 4-7 shows the FTR spectra of dimethylnitramine (DMNA), a simple energetic nitramine, and nitrocellulose (NC). While both spectra were measured using the same incident laser power and sampling technique (1-mm-ID capillary tube), the signal-to-noise ratio in the spectrum of crystalline DMNA is superior to that of polymeric NC. Both samples were in the form of white powders.

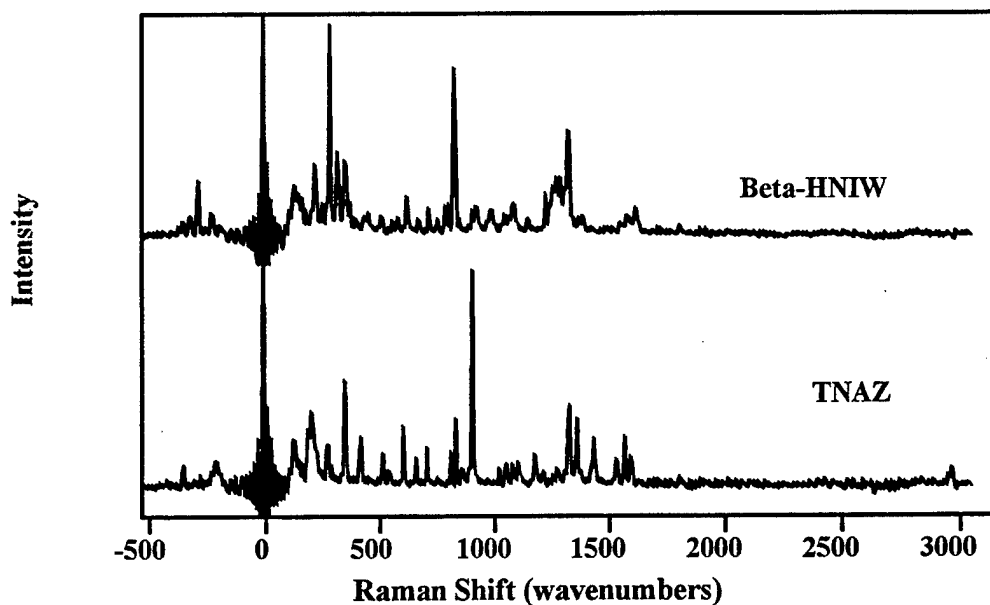


Figure 4-5. The FTR Spectra of b-HNIW and TNAZ.

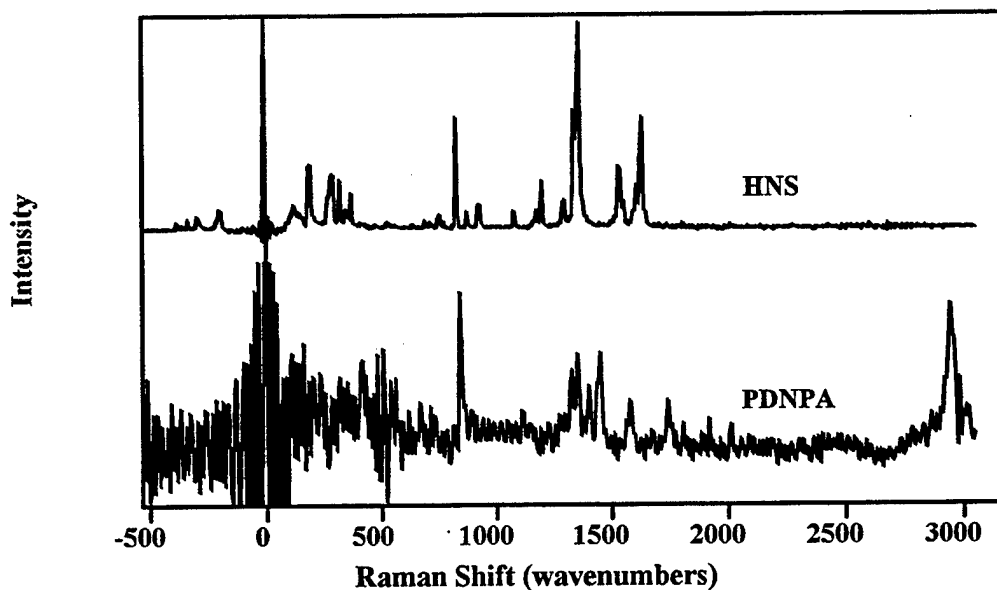


Figure 4-6. The FTR Spectra of HNS and PDNPA.

Applications to Propellant Analysis. Figure 4-8 shows the FTR spectra of RDX, HMX, and XM39 (a propellant formulation whose principal ingredient is RDX). The spectrum of XM39 is a “best case” illustration of the utility of FTR spectroscopy for energetic material characterization. While the spectra of RDX and HMX were measured using neat-powdered samples in capillary tubes, the spectrum of XM39 was measured by scattering off the interior surface of cleaved propellant

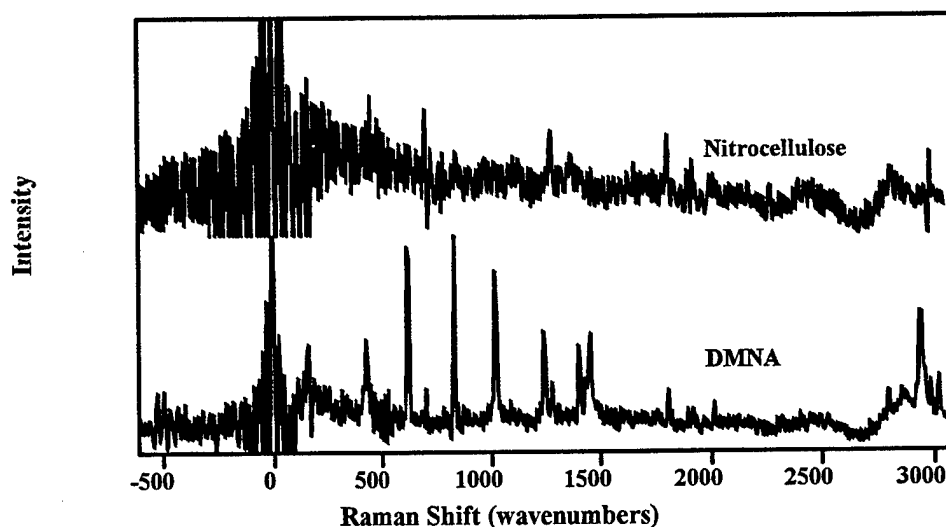


Figure 4-7. The FTR Spectra of NC and DMNA.

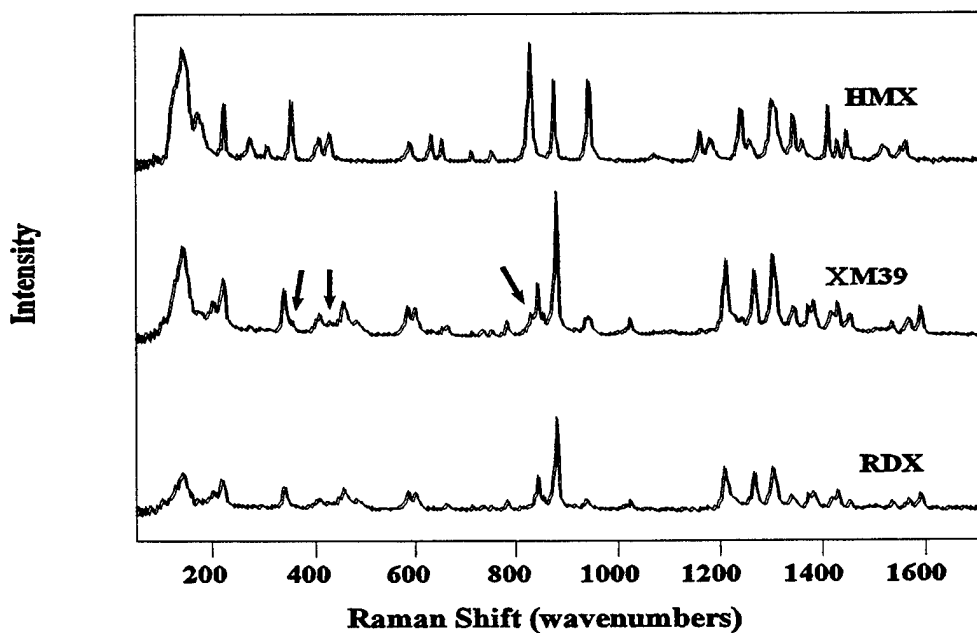


Figure 4-8. The FTR Spectra of RDX, HMX, and XM39. Arrows Indicate HMX Present in Domestically Produced RDX.

grains. Even with this simple sampling technique, assignment of RDX as the principal crystalline energetic ingredient in XM39 is unambiguous. Shown in the spectrum of XM39 is evidence of HMX “impurity” in the formulation. HMX is normal by-product of RDX synthesis in most domestically produced RDX. Also shown in the spectrum of XM39 is the increased intensity

(relative to neat RDX) of the feature near 150 cm^{-1} . This increased intensity (see Figure 4-2) may be due to the small HMX “impurity” in domestically manufactured RDX.

Figure 4-9 shows the FTR spectra of RDX, XM39, and a commercially available propellant formulation believed to be from China (PRC). Since the Chinese propellant formulation had a thin graphite coating that would cause the sample to absorb some of the incident laser radiation, the spectrum was measured by scattering the incident Nd:YAG laser radiation off the front surface of a spinning (2,400 rpm) 5-mm-ID glass tube containing the propellant formulation. From Figure 4-9, it is apparent that the principal crystalline energetic material in the Chinese propellant formulation is RDX. Also, the spectrum of the Chinese propellant formulation shows no trace evidence of HMX, supporting the likelihood that the RDX present in the Chinese propellant formulation is manufactured by a different process than domestically produced RDX.

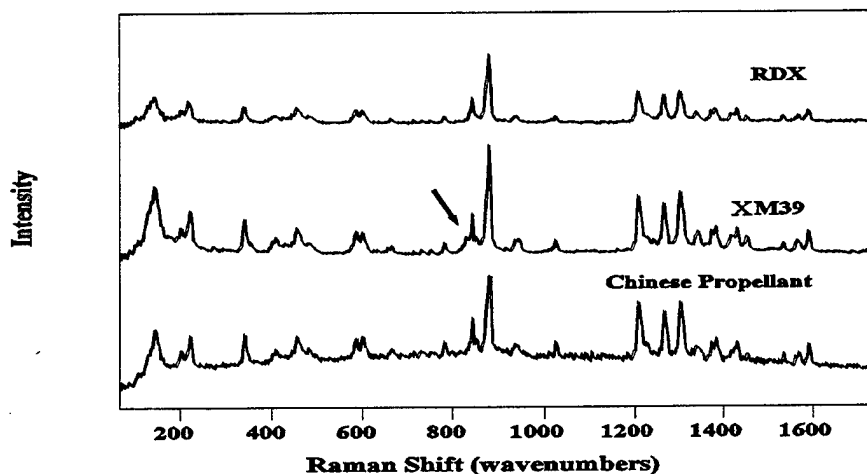


Figure 4-9. The FTR Spectra of RDX, XM39, and a Chinese Propellant Formulation. Note the Absence of HMX Impurities in the RDX Contained in the Chinese Propellant. Arrows Indicate HMX Present in Domestically Produced RDX.

Figure 4-10 shows a portion of the FTR spectrum of XM39 as it is heated from room temperature to the onset of decomposition at 458 K (185°C). This spectrum was measured by scattering the Nd:YAG laser light off the front surface of a slice of XM39 taken from the interior of a propellant grain. As shown previously, the principal crystalline energetic ingredient in XM39 is RDX. The

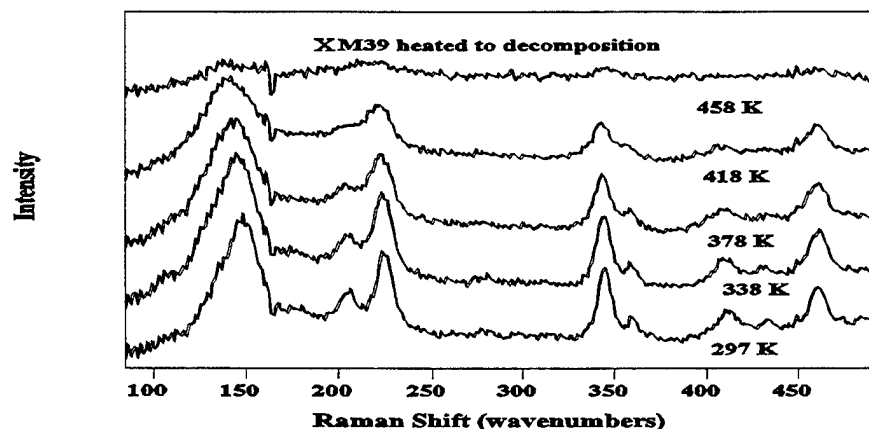


Figure 4-10. The FTR Spectra of XM39 During Heating.

propellant slice was contained in a heatable holder designed for the purpose of investigating changes resulting from heating in energetic materials in propellant formulations. For XM39, as temperature is increased, the scattering intensity decreases (as shown by the increased signal-to-noise ratio in the spectra) and there is a slight red shift of the feature near 150 cm^{-1} . This red shift was most notable for features at low Raman frequencies and was negligible at Raman frequencies above 500 cm^{-1} . As the sample temperature approaches the melting point of RDX (477 K), the Raman intensity rapidly diminishes, reflecting a loss of crystallinity in the principle energetic ingredient in the formulation.

Conclusion

It has been shown that FTR spectroscopy using NIR laser radiation as the scattering source can be a useful tool in characterizing many neat samples of energetic materials and of some propellant formulations. Raman spectra of most common energetic materials, as well as some new energetic materials, have been measured from 100 cm^{-1} to $3,000\text{ cm}^{-1}$. To our knowledge, Raman spectra measured to within 100 cm^{-1} of the Rayleigh line have not been reported previously for most energetic materials. Perhaps the most interesting result of our ability to measure Raman spectra over a wider spectral range is the observation that the strongest peak in the HMX spectrum occurs near

150 cm⁻¹. Finally, we believe that, for many samples of energetic materials containing crystalline principle ingredients, FTR spectroscopy using NIR laser scattering should be the first choice of investigators for forensic analysis. We are presently extending the technique to the investigation of energetic materials at elevated temperatures, in formulations, and in solutions in high-pressure fluids.

Acknowledgments

Support is acknowledged from the National Research Council (NRC) Postdoctoral Associateship Program and the Strategic Environmental Research and Development Program (SERDP) of the Department of Defense (DOD). Many thanks are expressed to Dr. Monte Chawla of Atlas Wireline Services Incorporated for providing the samples of hexanitrostilbene (HNS) and of the Chinese propellant formulation.

References

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2. McNesby, K. L., J. E. Wolfe, J. B. Morris, and R. A. Pesce-Rodriguez. *Journal of Raman Spectroscopy*. Vol. 25, p. 75, 1994.
3. Goetz, F., and T. B. Brill. *Journal of Physical Chemistry*. Vol. 83, p. 340, 1979.

5. "Trace Detection Activities"

Frank T. Fox
Federal Aviation Administration Technology Center

I am Frank Fox with the Federal Aviation Administration (FAA). There are several headquarter locations of the FAA in downtown Washington, DC, and a training facility in the Aerospace Medicine facility in Oklahoma City, OK. In addition, there is a technical center located at the William J. Hughes Technical Center in Atlantic City, NJ. That is where the portion of the research is performed in which I am engaged. The overall mission of aviation security research is to get commercially available explosives-detection instruments into use at airports. These will, of course, have applicability to other transportation modalities as well. I will discuss two of the many ways that the FAA is approaching this problem. One is to detect explosives inside of luggage, typically using penetrating radiation, and the other is to detect explosives on the surfaces of luggage. External contamination occurs due to inadvertent contact or touching by the bomb maker or the dupe delivering the package. Plastic explosives are very sticky, as many of you know. By analogy, imagine that you are working with roofing tar. It is a substance that you cannot avoid getting on you, and it does not wash off very easily either.

Trace detection does not actually detect the explosive or even the presence of a bomb, but, rather, it points a finger of suspicion, and that is the point of it. Congress has mandated that the FAA approve commercially available trace-detection instruments, using a suitable test protocol. There are presently six manufacturers of trace-detection instruments—namely, Barringer, Orion, Graseby, Ion Track, Scintrex, and Thermedics. In order to be approved, it was first necessary to develop the instruments. The FAA funded development of many of these instruments through grants and contracts. It took nearly 10 years to develop trace-detection instruments. There are a number of them currently available now, and they are purchased by other countries and used in many airports around the world. The approval process in this country was a different story entirely because extensive testing procedures for approval for use were mandated. A problem was that the FAA did not have an accurate and repeatable standard to fairly assess the limits of detection or consistency

of detection. Many attempts had been made to produce a "standard" fingerprint, but it has been found that there is quite a bit of variation in the amount of explosive from one fingerprint to another. With my research group, I have developed a technique to accurately deposit nanogram amounts of plastic explosives. The deposited material has the same characteristic-coated crystals that exist in the bulk material. This procedure is described in the attached excerpt of a book chapter "Detection of Hidden Explosives."*

The tragedy of PAN AM 103 led to the start of this program approximately 10 years ago. Subsequently, the Aviation Security Laboratory was built in New Jersey and this whole program became active. Early on, the FAA went with thermal neutron analysis (TNA). The TNA instrument is a bulky and heavy machine, which costs millions of dollars. The TNA instrument gave too many false positives. Six of them were built, but none of them are in use at this time. For some years, the development and evaluation of trace-explosives-detection technologies were done by the manufacturers. The FAA has now reached the point where it has improved its testing procedures for x-ray and other bulk-detection instruments, as well as trace instruments. It is now possible to give feedback to the manufacturers, but it has taken a while to get to this stage.

As far as trace detection is concerned, there are two ways to go at it. You can sample either particulate material or vapors; particulates are the solid particles on the outer surface of luggage left by dust, lint, or inadvertent contamination. Another approach is to detect trace amounts of vapors from volatilized explosives. For detection, the vapors need to emanate from a bulk explosive either hidden inside the suitcase or deposited near the inner or outer surface. In this way, a vacuum inlet to a detector could suck up the vapors. When the trace-work first started out some years ago, analysis of vapors was the approach everyone was taking. The program was even called "Vapor Detection" because everyone assumed that there was a high enough vapor pressure from the explosives that could be detected. As time went by, workers in the field delved more deeply into this research, and it turned out that the military explosives, particularly the ones that are available around

* Beveridge, Alexander (editor). "Detection of Hidden Explosives." *Forensic Investigation of Explosions*, chap. 3, ISBN No. 0748405658, Taylor and Francis Publisher, London, 1998. This excerpt appears as section 6 of this report.

the world, have extremely low vapor pressures. So, nothing detectable would come through the suitcase wall. Emphasis then turned to detecting particles on the surfaces of luggage.

If a person has his/her outer clothing contaminated (not just the suitcase), there is a possibility that, in the normal evolution of body heat, lint will be carried off as tiny dust particles from the clothing. You have to envision a person embedded in a cloud of particles all the time. You cannot see the particles or the plume, but it is possible to take a Schlieren photograph of the heat plume. In that case, you see heat plumes emanating all over a person with a much greater volume than you might expect. If particles are swept off your clothing, such as lint and skin flakes, and, if those are piggybacking little tiny pieces of explosives, then these particles present a detection capability. It may be possible to have a person walk through a portal, just like you walk through a gun-detection portal now, and collect those particles by inducing an air flow over the body, or by having some kind of suction tubes pass over your clothing. Then you collect this particulate on a filter and have concentrators that absorb and concentrate the particles. Heat desorption can release the explosives into an air stream and into an analyzer. It will soon be possible to use these techniques in a walk-through portal to analyze explosives on a person's clothing. You would be amazed at how millions of dollars have been spent on the development of a suitable portal.

There are now several working models, and a commercial version is getting close. The basic elements of a portal walk-through trace-detection instrument consist of four components: (1) the sampler, (2) the concentrator, (3) the discriminator, and (4) the detector. The detector is usually just an ordinary ion mobility spectrometer or a chemiluminescent detector. The Thermedics EGIS system uses the latter and all of the rest use the former. Scintrex uses an electrochemical detector. The discriminator can be a gas chromatograph (EGIS and Orion) or a membrane (Ion Track). A concentrator is usually a filter. The sampler is one of the most difficult parts of the analysis system; it must be designed for high efficiency and without inherent interferences. Typical materials used to wipe the surface are cotton cloth or gloves, synthetic fiber cloth, wire-mesh screen, or paper. The point is to remove a very sticky material that is present in trace amounts at unknown locations off a variety of surfaces. If you wipe too little, the contaminated spot may be missed; if you wipe too

much, you can easily relocate the sample onto uncontaminated areas of the suitcase, since the sample transfer is a two-way process.

The two approaches being taken are: (1) to simply vacuum the surface and hope that the particle explosives come off, possibly piggybacked onto dust, and (2) to take a cloth or paper patch and wipe the surface. Incredibly, that is the degree of sophistication that exists to this day for sampling trace amounts of explosives. That is as far as it has advanced. (Thousands of years ago, people were polishing statuary in ancient Egypt during the time of the Pharaohs. And how did they do it? They probably wiped it down with a cotton cloth or papyrus paper. That is as far as we have gone!) Surprisingly, it is not easy to come up with more sophisticated methods because the sampler has to be low cost, efficient, water resistant, simple to use, and absolutely safe; in addition, it cannot bleed contaminants from its own matrix. So, it needs to be something clever. You cannot use solvents or compressed gases, and you cannot use soaps because they will interfere with the analysis. As improved samplers are developed, it is certain that they will be adopted.

Sampling by collecting particles in the air stream or by wiping the surface also picks up other materials. For example, if a person has some material, perfume, mothballs, dry-cleaning fluid, you name it, the question comes, "Will those compounds be analyzed and be detected as false positives or false negatives?" So, to approve the machine, you have to determine interferents experimentally. The FAA has a big project going on now to determine interferences, and it is almost complete. So far, the results indicate that, under approximately realistic conditions, there is little or no false-positive or false-negative interferences from common substances.

6. "Detection of Hidden Explosives"

Frank T. Fox
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The preparation of the type of bomb that involves the secretion of explosives into the cavities of a portable item (such as a suitcase, laptop computer, radio boom box, or telephone) very frequently leads to inadvertent contamination of the outer surfaces. This contamination can result from the activity of the original bomb maker or intermediaries in the process of delivery to the final destination. Consideration given by aviation security has been focused, to a large degree, on detection of hidden-explosive devices in portable items, as these are most easily placed onto the aircraft or in other locations. In addition to surface contamination, explosives vapors can be detected. Many explosives have sufficient volatility inherent to the primary explosive or a component of the mixture comprising the explosive to allow detection. This process is enhanced by the use of taggants [1].

Over the past approximately 10 years, a variety of commercial instruments has become available for the detection of trace amounts of explosives. These devices have a spectrum of capabilities, features, and prices. Sampling time of 5–15 s is a feature that is common to virtually all of the instruments. Total analysis time is approximately 5–20 s for most of the instruments. This speed is crucial to keep up with passenger flow in a busy airport concourse, for example. The detectors in most of the instruments consist of enhanced versions of classical techniques. They are robust and highly sensitive to extremely low levels of explosive. One of the reasons for the high sensitivity is the low efficiency of wipe or suction sampling to remove plastic and other particulate explosives from surfaces. Eventually, a dramatic improvement in this area may lead to less-sensitive detector requirements and subsequent lower instrument costs. All of the instruments are designed to be portable, by use of built-in wheels for the heavier instruments. Nearly all require a 110-V alternating current (AC) outlet.

Detection of trace contamination on the surfaces involves four steps: (1) sampling, (2) concentration, (3) analysis, and (4) discrimination. The first step in the detection process, sampling, is the transfer to the preconcentrator of the trace analyte from the suspect object presumably containing a bomb. The analyte may be particulate matter from a wipe or vapor emanating from the object. Development of efficient sampling methods has been elusive. The sampling technique typically consists of the operator simply wiping the test object with a cotton glove, followed by vacuuming the glove to collect particles from it onto a collector or preconcentrator. This is often a metal or fiber filter that is subsequently heated to desorb the explosives into the analyzer. Sampling in this way typically has removal efficiencies from less than 1% up to as much as 10% of the plastic explosives contaminating the surface.

Research efforts to develop an improved sampling method have previously been limited to deposits made from solutions of explosives dissolved in organic solvents or particles of siliceous material that has been coated with explosive crystals by evaporation of a solution [2, 3]. Unfortunately, dissolution of plastic explosives followed by recrystallization yields a material without the particle size or adhesion character of the original plastic. Use of actual fingerprints as a test standard also presents difficulties because of the inconsistent nature of the deposit due to differences in finger size, pressure used, nature of the bulk explosive touched, and many other factors [4, 5].

Many attempts have been made to achieve a consistent deposit that has the characteristics of the original material, especially for plastic explosives. Attempts to standardize multiple imprints or determine the surface contamination upon bomb manufacture under controlled conditions have been tried [6]. The requirement, when using multiple fingerprints to prepare a standard amount of explosive on a surface, is to extract and quantitate alternate prints. These data allow one to assume that an "average" unassayed alternate print in the imprint series prepared in the same experiment has a known amount deposited. Unfortunately, the error in the amount of explosive analyzed from print to print is greater than the amount of explosive removed by the wipe method of sampling.

This disparity is due to the very small amount of explosive removed using standard/inefficient wipe sampling techniques. An “average” amount of explosive per fingerprint calculated in this way has too much variation to allow determination of sampling efficiency or to use this method to prepare explosive standards. In addition to fingerprints not being reproducible, another drawback is the inability to set the amount deposited at will [7].

This laboratory has recently developed a method for the consistent accurate production of deposits of plastic explosives that have the same sampling characteristics—namely, “stickiness” as the bulk explosive. The method works with the major commercial and military plastics. The technique takes advantage of the fact that plastic explosives are manufactured as crystals of explosive that are stabilized and protected by plastic coating, such as polyisobutylene or styrene-butadiene. The result is encapsulated crystals that are made into the final product by pressing the particles together into bricks or sheets, along with a little oil or other agent to aid flexing. Normal production of a fingerprint occurs by touching the bulk explosive and removing some of the coated particles mechanically from the bulk because they stick to the skin. The particles are then transferred to the next object or surface touched.

Our method takes advantage of the encapsulation resulting from the manufacturing process. The adhesion forces between the coated particle in the compressed bulk are overcome mechanically. A small piece of plastic explosive is agitated with water, causing particles of the coated explosive to be simply shaken loose from the bulk and suspended in the water. By analogy, touching the bulk causes mechanical removal of particles due to pressure and adhesion. The explosive is not dissolved by the water-agitation process, but particles from the bulk are merely suspended by gentle mechanical means. Variations on the agitation include stirring, sonication, and shaking. Once the explosive in its normal form of coated crystals is put into suspension, the actual amount is determined by usual methods including high-performance liquid chromatography (HPLC), gas chromatography (GC), and mass spectroscopy (MS). Dilution is then made to an appropriate level.

In order to prepare a deposit consisting of the desired amount of explosive, an aliquot of the diluted and quantified suspension is pipetted onto the surface of a test object and the water is

evaporated. The dried residue consists of plastic-coated explosive crystals in the original state, as would occur with a natural fingerprint or smear. The amount of dried residue deposited can easily be varied by simply controlling the degree of dilution of the original suspension of explosive particles. Reproducible deposits have been prepared, ranging from high micrograms to low nanograms. The concentration of the deposit is verified by back extraction of a test surface and quantitation of the extract. Particle size of each preparation is verified by scanning electron microscopy (SEM). Consistent particle size range in the deposit was the goal of this laboratory in the preparation of a standard. Comparability of the particle size range of the deposit to actual fingerprints was also considered important. An unusable variation in the amount deposited would be large if large particles appeared. Consistent analysis with relative standard deviation (RSD) of less than 10% was obtained on back extraction and analysis of the deposits. In addition, a close comparison of particle size between a fingerprint and a deposit of the suspension of the explosive (C4) was observed [8, 9].

The controlled deposition of several plastic explosives on some typical carry-on electronic items was used on commercial instruments at the 1995 International Civil Aviation Organization (ICAO) meeting of the Ad Hoc Group of Specialists on the Detection of Explosives, held at the Federal Aviation Administration (FAA) Technology Center in Atlantic City, NJ. Six commercial instruments were tested over several days using the standard sampling technique proposed by the trace-detection instrument manufacturer. Participants in the exercise included manufacturer representatives and an international group of persons experienced in trace-explosives detection [10].

The older technique of simply dissolving the plastic explosive bulk material in an organic solvent for deposit by recrystallization on evaporation removes the plastic coating and inevitably changes the sampling characteristics observed. Coating inert material with a solution of plastic explosive and evaporating the solvent has the same drawback [11].

The deposition technique provides a means to produce an accurate standard—so far limited to plastic explosives—which can be used for testing and evaluating trace-detection instrument systems, including the efficiency of the sampler and the effect of interferents. In addition, deposits onto fabric

may provide a standard for testing walk-through portals designed to detect traces of explosives on passenger clothing. Several portals are in the developmental stage. Explosives removal techniques in these portals are dependent on air flow onto a collector or intimate sampling by means of suction of the surface of passengers' clothing as they pass along tubes with suction holes along their length. In both types of collection, the sample ultimately ends up on a prefilter and is desorbed and analyzed by analytical means similar or identical to those used in commercial stand-alone trace-detection instruments. Some advances in portal development were presented at an FAA-sponsored portal conference in January 1995 [12].

The testing of checked-in and carry-on luggage, as well as passenger garments and hands, is an obvious immediate application of trace-based hidden-explosives detection; however, there are other applications. Trace-detection-based technologies are under development at several centers for cargo inspection. Ultimately, the application may be adapted to postal needs and to other transportation modalities.

Trace detection is, of course, not limited to explosives hidden in bombs, it may be used to detect a wide variety of other chemicals used in hidden devices. Such hidden devices have been used recently in Japan for toxic gases. There is a long list of flammable and toxic substances that may be hidden and yet detected by trace methods, and there is a plethora of available literature on this subject. Interested parties could begin by contacting either Delta Press, El Dorado, AZ, or Paladin Press, Boulder, CO.

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7. "The Explosive Standard Analytical Reference Material (SARM) Program"*

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Abstract

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) has entered into an agreement with the Naval Surface Warfare Center (NSWC), Indian Head (IH) Division, MD, for them to maintain the USATHAMA explosive Standard Analytical Reference Material (SARM) repository, consisting of 19 explosives compounds and 6 degradation products. The explosives and their degradation products are purified and then analyzed using various instrumental techniques such as high-performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR), inductively coupled plasma (ICP) spectroscopy, x-ray diffraction (XRD), atomic absorption (AA), and gel-permeation chromatography (GPC). The standards are packaged in blasting-cap containers and Federal Expressed, only upon USATHAMA approval, to designated laboratories.

The analysis of the following compounds are discussed: trinitrobenzaldehyde, nitrocellulose (NC), nitroglycerine (NG) (acetone and two nitrodiphenylamine [2-NDPA]), pentaerythritol tetranitrate (PETN), normal lead styphnate, and the structural isomers 2-amino-4,6-dinitrotoluene (DNT) and 4-amino-2,6-DNT.

* Financial support of this program is provided by the U.S. Army Toxic and Hazardous Materiel Agency (USATHAMA), Contract no. CC789000.

Introduction

The purpose of the explosive SARM repository is to furnish the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) designated laboratories with reference standards that have a minimum 99.0% purity. The repository presently consists of 19 explosive compounds and 6 degradation products. Four more explosive degradation products are presently being synthesized. The compounds in the repository are shown in Table 7-1. The compounds presently being synthesized are shown in Table 7-2.

Table 7-1. Compounds in the Standard Analytical Reference Material Repository

Compounds	
Cyclotetramethylenetetranitramine (HMX)	Cyclotrimethylenetrianitramine (RDX)
Nitroglycerine (NG)	Nitrocellulose (NC)
2,4,6-Trinitrotoluene (TNT)	1,3,5-Trinitrobenzene (TNB)
2,4,6-Trinitrobenzaldehyde	4-Amino-2,6-Dinitrotoluene (DNT)
2-Amino-4,6-DNT	2,4-DNT
2,6-DNT	2,4-Dinitroaniline
Pentaerythritol Tetranitrate (PETN)	Tetryl
Tetracene	Nitroguanidine (NQ)
Picric Acid	Normal Lead Styphnate
Basic Lead Styphnate	2-Amino-4-Nitrotoluene
4-Amino-2-Nitrotoluene	3,4-DNT
2,4-Diamino-6-Nitrotoluene	2,4-Diaminotoluene
2,6-Diaminotoluene	

Table 7-2. Compounds Being Synthesized

Compounds
2,2',6,6'-Tetranitro-4,4'-Azoxytoluene
4,4',6,6'-Tetranitro-2,2'-Azoxytoluene
2',4,6,6'-Tetranitro-2,4'-Azoxytoluene
Hexahydro-1-Nitroso-3,5-Dinitro-1,3,5-Triazine

Procedure for Obtaining Standard Reference Material

In order to receive the explosive reference material, the government organization requesting the compounds must submit a letter along with the request that the reference explosives are required for government-sponsored contractual laboratory work. This letter must be signed by the government contracting officer and include the following information:

- (1) the name of the laboratory with its full address (no post office box) and a point of contact to receive the standards;
- (2) the telephone and facsimile numbers for the person receiving the samples;
- (3) the government contract number under which the samples are being ordered;
- (4) the list of standards requested; and
- (5) the name, address, and telephone number of the government contracting officer associated with the requested material.

A statement verifying the need and use for the compounds must also be included prior to forwarding the material request form to the Naval Surface Warfare Center (NSWC), Indian Head

(IH) Division, MD. All of the aforementioned information in its entirety, must be sent to: Commander, U.S. Army Toxic and Hazardous Materials Agency, ATTN: CETHA-TS-C (Ms. D. Bader), Aberdeen Proving Ground, MD 21010-5401.

USATHAMA forwards an approved request to NSWC-IH, at which time it is filled and shipped. A maximum of 200 mg of each ordered sample is packed in polyethylene bottles. The bottles are then packaged in a blasting-cap container approved by the Department of Transportation for shipping explosive materials. Along with the containers, a package containing the material safety data sheets (MSDS) and the experimental data sheets for each compound is enclosed. The experimental data sheet consists of high-performance liquid chromatography (HPLC) curves and/or nuclear magnetic resonance (NMR) spectra for each compound. The entire package is then Federal Expressed to the designated laboratory. The entire process takes about 3 weeks once NSWC-IH receives the approved request. The laboratories are required to ship the blasting-cap containers back to NSWC-IH within 2 weeks.

Experimental Evaluation of Several Reference Compounds

Each compound is analyzed by various analytical techniques and purified by recrystallization, if found necessary. The analysis results of several of the reference compounds are presented.

2-Amino-4,6-DNT and 4-Amino-2,6-DNT. In the case of structural isomers such as 2-amino-4,6-DNT and 4-amino-2,6-DNT, NMR was used to identify each isomer and to ascertain whether or not it was a pure compound. HPLC was also run on these compounds, as well as on a mixture of them. The NMR curves for these compounds are shown in Figures 7-1 and 7-2. As can be seen, the C^{13} NMR differentiates the two isomers and shows that each of them is a pure compound. Figure 7-3 shows the NMR curve for a mixture of the two structural isomers. The mixture contained 2% 2-amino-4,6-DNT. The HPLC traces of the two compounds are shown in Figures 7-4 and 7-5. The HPLC curves of each of the compounds give almost identical retention times. However, the peak heights are different. HPLC of a mixture of the two compounds (Figure 7-5) produces one peak. A mixture of the two compounds was not resolved into two peaks.

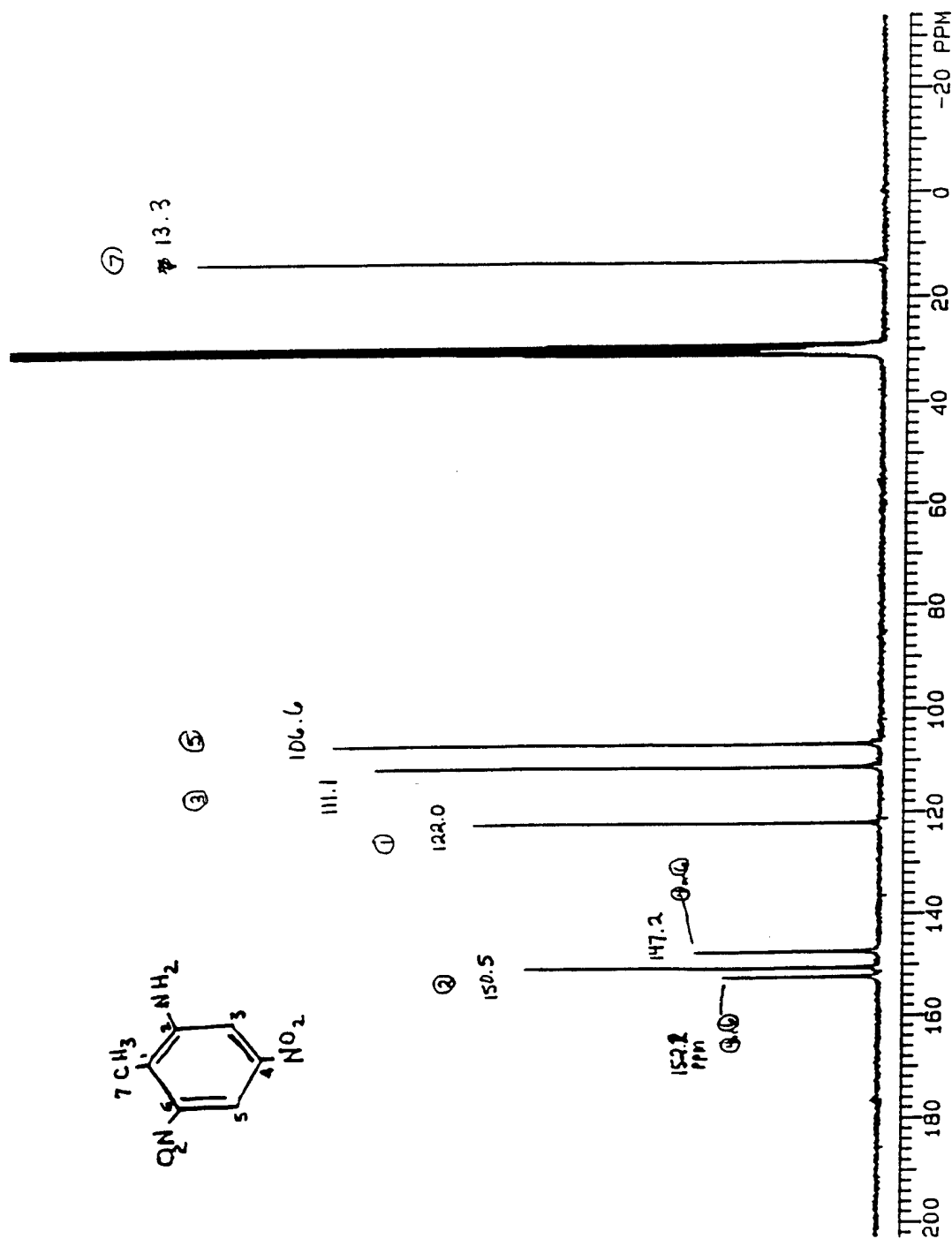


Figure 7-1. ^{13}C NMR Spectrum 2-amino-4,6-dinitrotoluene.

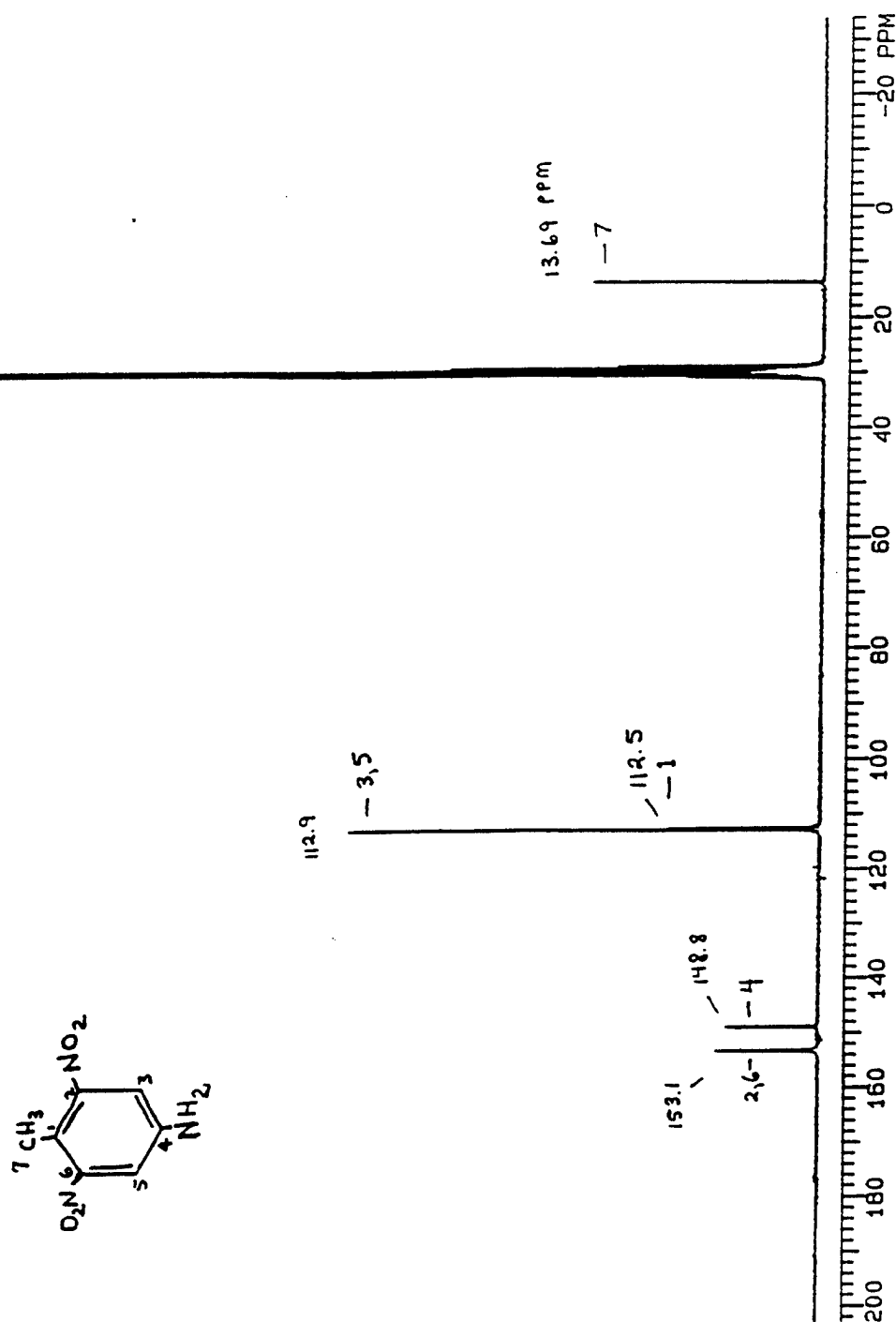


Figure 7-2. ^{13}C NMR Spectrum 4-amino-2,6-dinitrotoluene.

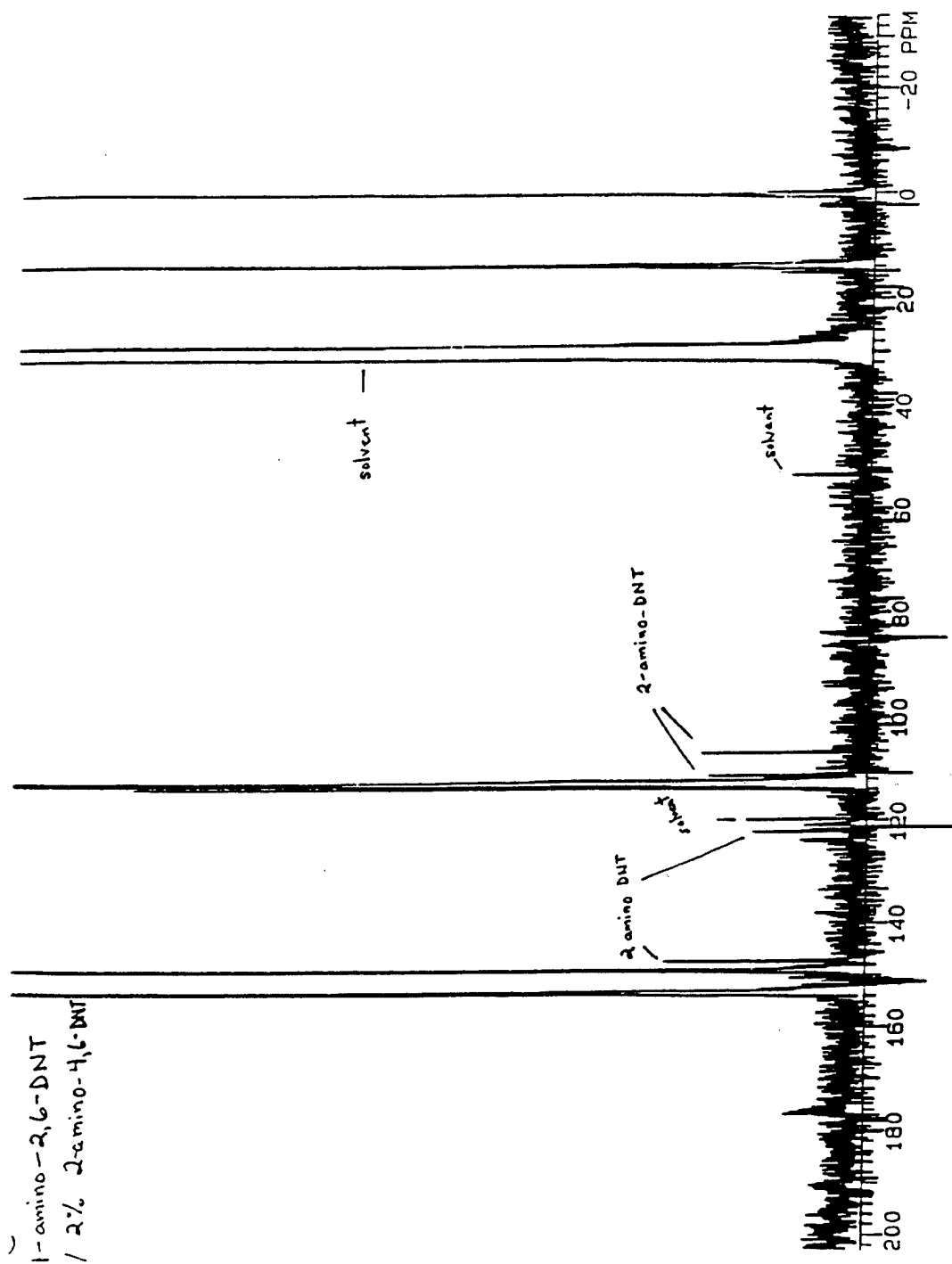
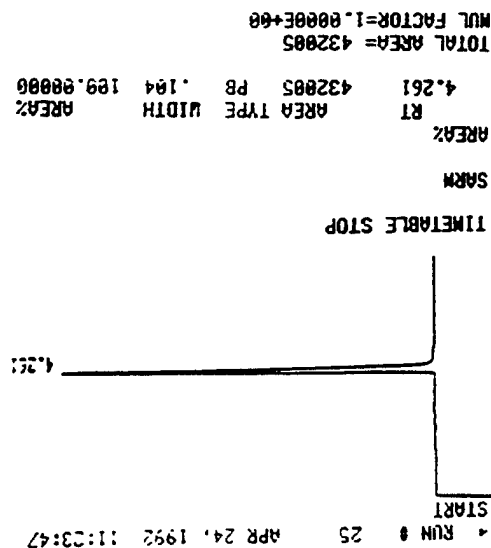


Figure 7-3. C^{13} MNR Spectrum Mixture 2% 2-amino-4,6-DNT/98% 4-amino-2,6-DNT.

HPLC CHROMATOGRAMS OF SARM STANDARDS

HPLC: WATERS MODEL 202
 COLUMNS: ALTECH C18 RP (5 MICRON)
 SOLVENT SYS: 65 / 35 ACN / H₂O
 FLOW RATE: 1.0 ML per min
 DETECTOR: UV(254 NANOMETERS)
 SENSITIVITY: 0.1 AUFS
 INJECT VOL: 50 MICROLITERS
 DATA ACQUI: 3393 HP INTEGRATOR
 TEMPERATURE 28 DEG

2-AMINO-4,6-DNT



4-AMINO-2,6-DNT

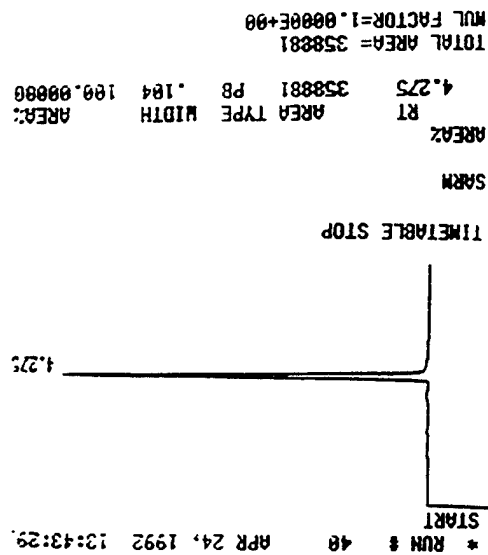


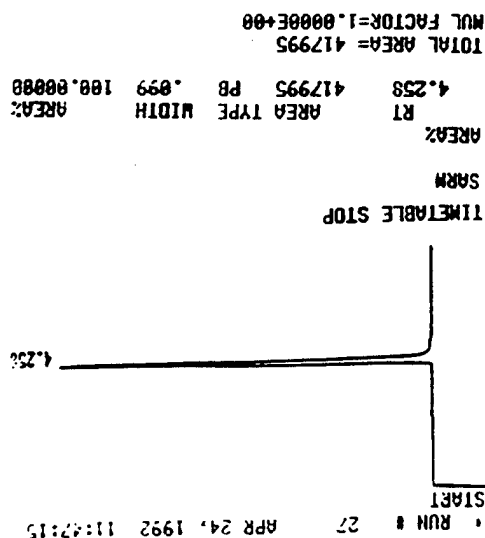
Figure 7-4. HPLC Pure 2-amino-4,6-DNT and 4-amino-2,6-DNT.

HPLC CHROMATOGRAMS OF SARM STANDARDS

HPLC: WATERS MODEL 202
 COLUMNS: ALTECH C18 RP (5 MICRON)
 SOLVENT SYS: 65 / 35 ACN / H₂O
 FLOW RATE: 1.0 ML per min
 DETECTOR: UV(254 NANOMETERS)
 SENSITIVITY: 0.1 AUFS
 INJECT VOL: 50 MICROLITERS
 DATA ACQ: 3393 HP INTEGRATOR
 TEMPERATURE 28 DEG

2- AMINO 4,6-DNT / 4- AMINO 2, 6-DNT

9:1 RATIO



2- AMINO 4,6-DNT / 4- AMINO 2, 6-DNT

1:1 RATIO

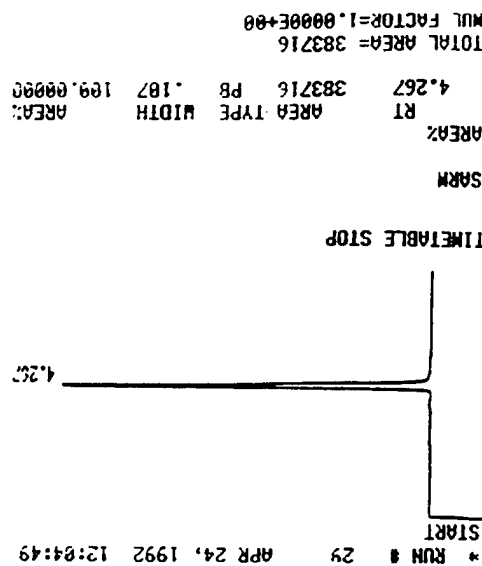


Figure 7-5. HPLC 1:1 Ratio and 9:1 Ratio 2-amino-4,6-DNT/4-amino-2,6-DNT.

However one can analyze the peak heights and gain some insight as to whether one of the structural isomers is contaminated with the other structural isomers.

Trinitrobenzaldehyde. Trinitrobenzaldehyde was analyzed using both proton and C^{13} NMR and HPLC. The NMR curves are shown in Figures 7-6 and 7-7. The HPLC curve is shown in Figure 7-8. In Figure 7-6, the C^{13} NMR curve is labeled to show the seven different carbon atoms. In Figure 7-7, the proton NMR shows the two different hydrogens in the trinitrobenzaldehyde compound.

Nitrocellulose (NC). The repository has two NC standards, one containing 12.6% N and the other 13.15% N. Unless specified, the 12.6% standard is sent. Along with the standard, an HPLC preparation sheet is enclosed, which outlines the precautions that must be taken when preparing standards in acetonitrile for HPLC analysis. They are as follows: (1) the concentration of NC in acetonitrile should be between 10 and 15 mg/ml of acetonitrile, (2) a greater concentration of NC may not go into solution, and (3) it is recommended that the solution be allowed to stand for 48 hr to allow all the NC to dissolve. A representative HPLC curve is shown in Figure 7-9.

NG. The NG sample that is shipped is prepared in the manner described next. One gram of neat NG is weighed into a 10-ml volumetric flask equipped with a stopper. Ten milligrams of two nitrodiphenylamine (2-NDPA) are added to the 10-ml volumetric flask to stabilize the NG. Five milliliters of HPLC grade acetone are added using a 5-ml pipet. Each milliliter of acetone contains 200 mg of NG and 2.0 mg of 2-NDPA. One milliliter of each solution is placed into an amber vial and sealed for shipment. The HPLC curves for NG, 2-NDPA, and acetone are shown in Figure 7-10.

PETN. As received in our laboratory, PETN is coated with polyethylene. The coating is removed using a soxhlet extractor. The solvent is reagent grade acetone. The material is refluxed for 16 hr at 56° C. After 16 hr, the acetone extract is concentrated on a rotoevaporator to dryness. The white solid (PETN) is removed from the flask with a plastic spatula onto a drying dish. The solid is dried in an oven at 50° C until a constant weight is obtained.

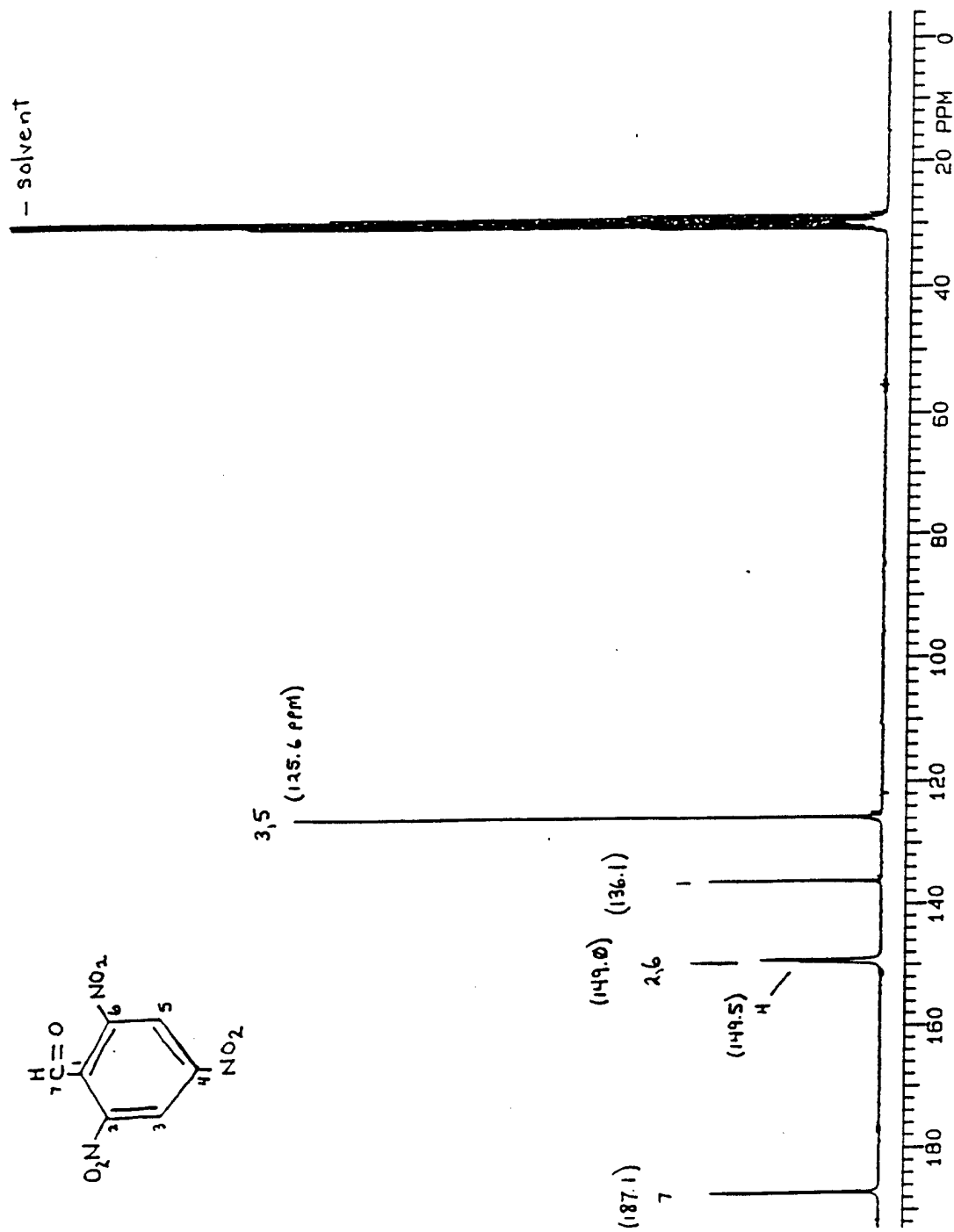


Figure 7-6. ¹³C NMR - 2,4,6-Trinitrobenzaldehyde.

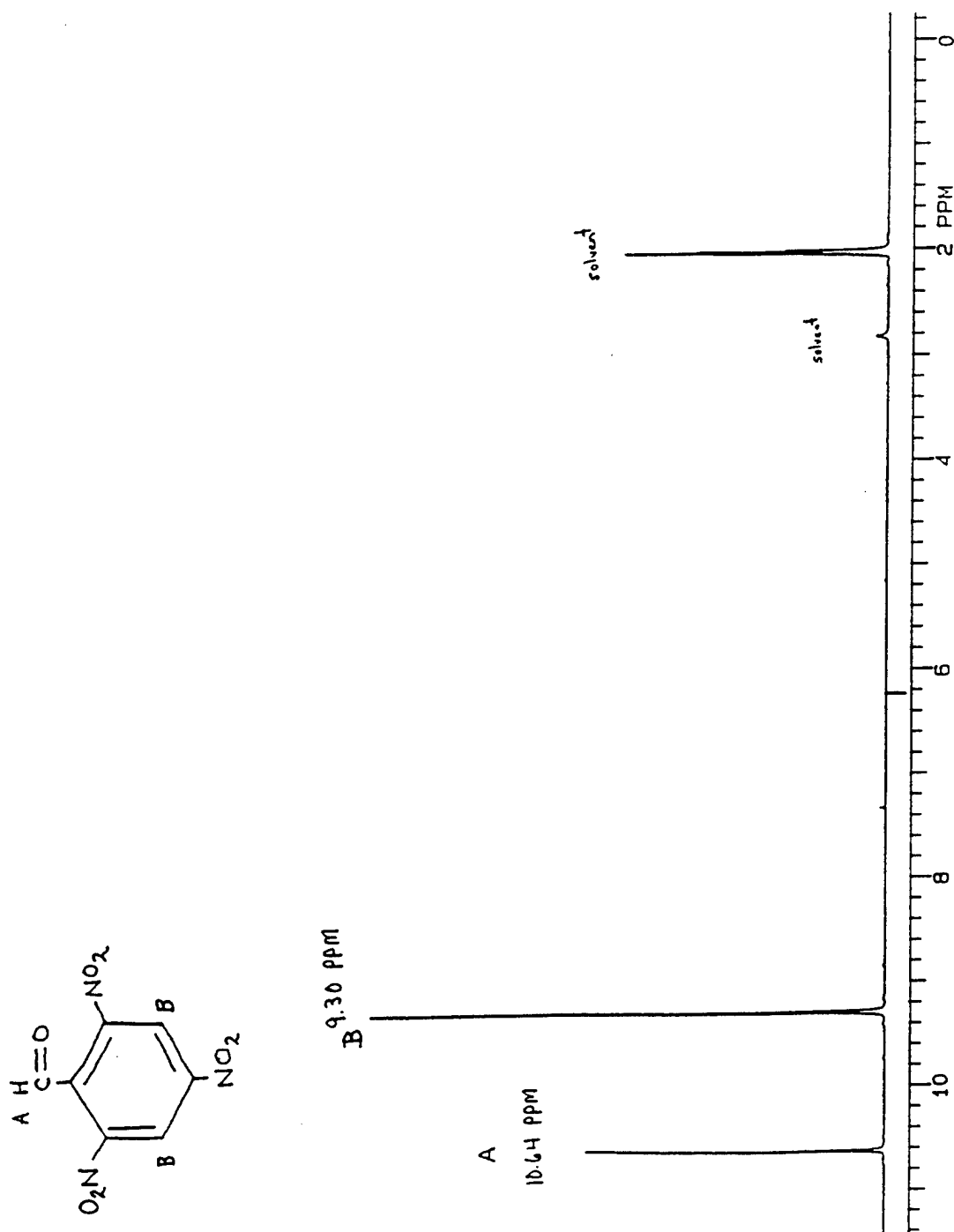


Figure 7-7. Proton NMR 2,4,6-Trinitrobenzaldehyde.

HPLC CHROMATOGRAMS OF SARM STANDARDS

HPLC: Waters Model 440
Column: Walters P/N 27477 NP 30 cm
Solvent Sys: 75/25 Heptane/Ethyl Acetate
Flow Rate: 2.0 ml/min
Detector: UV (280 NANOMETERS)
Sensitivity: 2.0 AUFS
Inject Vol: 90 microliters
Data Acqui: Chart Recorder
Temperature: 28° C

TRINITROBENZALDEHYDE



Figure 7-8. HPLC - 2,4,6-Trinitrobenzaldehyde.

HPLC CHROMATOGRAMS OF SARM STANDARDS

HPLC: WATERS MODEL 202
 COLUMNS: ALL/TECH C18 RP (5 MICRON)
 SOLVENT SYS: 65 / 35 ACN / H₂O
 FLOW RATE: 1.0 ML PER MIN
 DETECTOR: UV (254 NANOMETERS)
 SENSITIVITY: 0.1 AUFS
 INJECT VOL: 20, 3.0, 5.0 MICROLITERS
 DATA ACQUI: 3393 HP INTEGRATOR
 TEMPERATURE: 28 DEGREES C

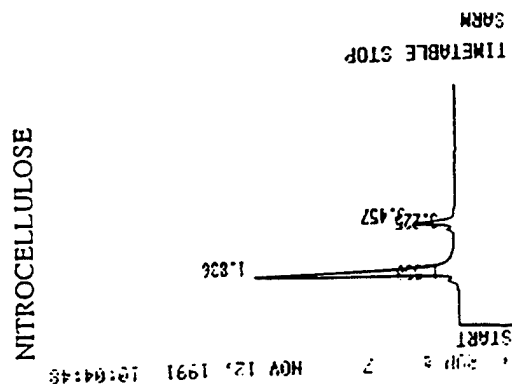


Figure 7-9. HPLC - 12.6% Nitrocellulose.

HPLC CHROMATOGRAMS OF SARM STANDARDS

HPLC: WATERS MODEL 202
 COLUMNS: ALL-TECH C18 RP (5 MICRON)
 SOLVENT SYS: 65/35 ACN / H2O
 FLOW RATE: 1.0 ML PER MIN
 DETECTOR: UV (254 NANOMETERS)
 SENSITIVITY: 0.1 AUFS
 INJECT VOL: 2.0, 3.0, 5.0 MICROLITERS
 DATA ACQ: 3393 HP INTEGRATOR
 TEMPERATURE: 28 DEGREES C

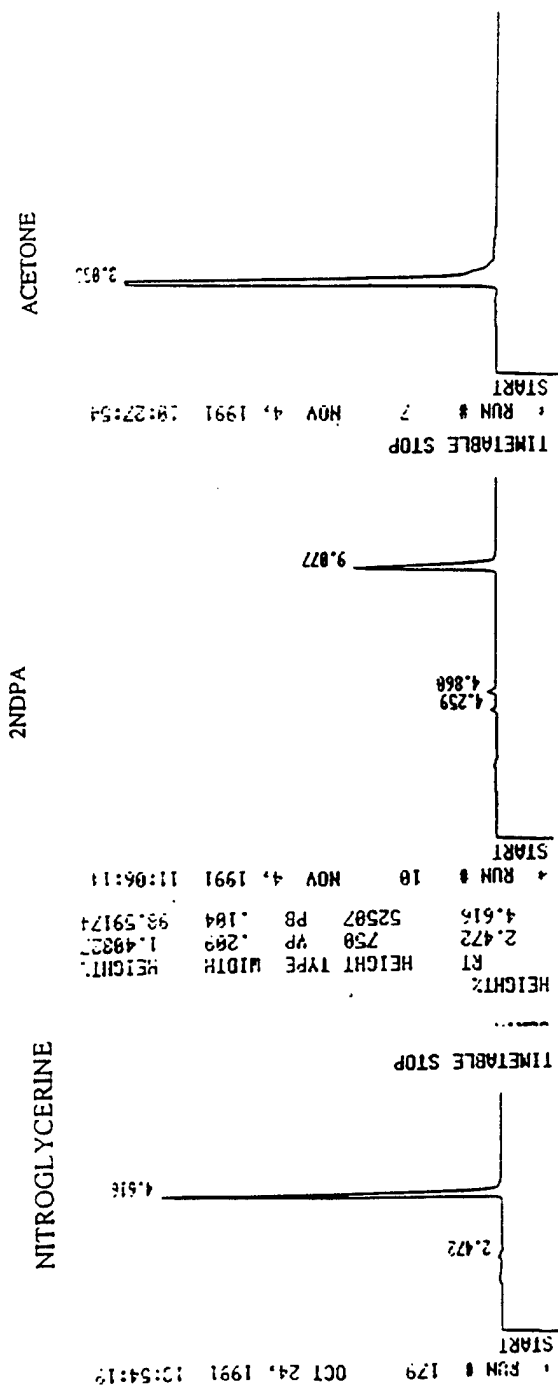


Figure 7-10. HPLC - Nitroglycerine (NG) With 2NDPA in Acetone.

This PETN is then triple-recrystallized from acetone and thoroughly dried to generate an analytical standard. The HPLC curve of PETN is shown in Figure 7-11.

Normal Lead Styphnate. The lead styphnate is analyzed using HPLC and atomic absorption (AA). The AA gives the percent of lead. The lead styphnate is dissolved in a 10% ammonium acetate solution and filtered if necessary. A 2-ml aliquot of a solution containing 5 mg of lead styphnate in the ammonium acetate solution is placed in a 10-ml volumetric flask and brought up to volume with acetonitrile. The sample is filtered if necessary and analyzed by HPLC. The HPLC curve is shown in Figure 7-12.

Discussion and Conclusions

The previous analysis of some representative Standard Analytical Reference Material (SARM) Program compounds illustrates how our laboratory prepares and qualifies explosive samples for the SARM repository. The compounds in the repository are reanalyzed every 3 months, except for the NG, which is freshly prepared each time a request is received. Over the period September 1991 to September 1992, more than 375 compounds were shipped throughout the United States.

HPLC CHROMATOGRAMS OF SARM STANDARDS

HPLC: WATERS MODEL 202
 COLUMNS: ALLTECH C18 RP (5 MICRON)
 SOLVENT SYS: 65 / 35 ACN / H2O
 FLOW RATE: 1.0 ML PER MIN
 DETECTOR: UV (254 NANOMETERS)
 SENSITIVITY: 0.1 AUFS
 INJECT VOL: 2.0, 3.0, 5.0 MICROLITERS
 DATA ACQUI: 3393 HP INTEGRATOR
 TEMPERATURE: 28 DEGREES C

PETN

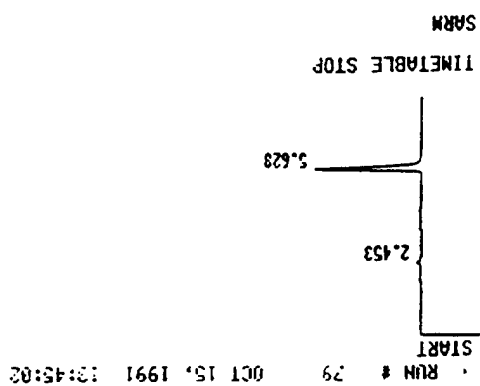


Figure 7-11. HPLC - PETN

HPLC CHROMATOGRAMS OF SARM STANDARDS

HPLC: WATERS MODEL 202
 COLUMNS: ALTECH C18 RP (5 MICRON)
 SOLVENT SYS: 65 / 35 ACN / H₂O
 FLOW RATE: 1.0 ML per min
 DETECTOR: UV(254 NANOMETERS)
 SENSITIVITY: 0.1 AUFS
 INJECT VOL: 10 MICROLITERS
 DATA ACQUI: 3393 HP INTEGRATOR
 TEMPERATURE 28 DEG

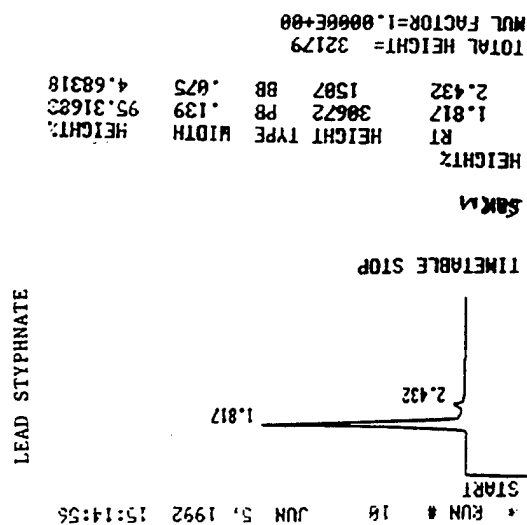
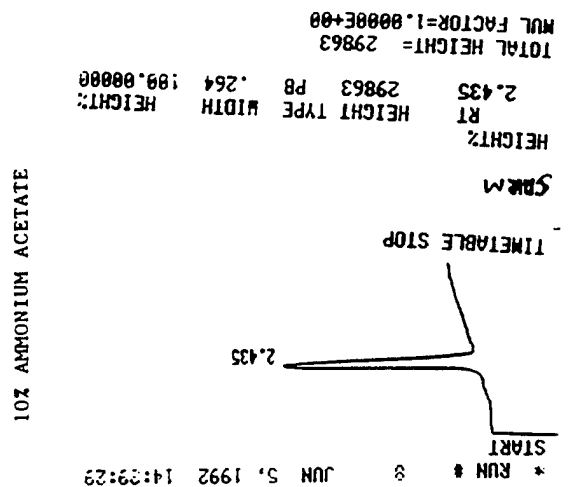


Figure 7-12. HPLC - Normal Lead Styphate.

8. "Problems in Characterizing Smokeless Gunpowders"

Allan N. Walters
Postal Inspection Service

I am Allan Walters, a forensic chemist for the U.S. Postal Inspection Service Forensic Laboratory. We are located near Dulles Airport. Most of the work that I do involves the analysis of explosives from improvised explosive devices, pipe bombs, and other types of devices that are placed in or around postal property, mailboxes, or sent through the mail. Probably 99% of the types of explosives that we see are low explosives, such as black powder; smokeless powder; Pyrodex; flash powder; and, once in a while, improvised mixtures or pyrotechnic powders that have been emptied from commercial fireworks or Class C fireworks, which you can buy at roadside stands. Of particular interest to us is the use of smokeless powders in these improvised devices. We get quite a bit of that, and it is easy material to obtain. Most people who make these sorts of bombs are somewhat familiar with it. So, basically, we try to identify these. Our inspectors ask, "What was the explosive material? Can you give me any leads based on the identity of the powder?" If there are intact particles, we try to identify those. We try to give the inspectors as much information as we can because they may conduct a search and obtain samples of powder for later comparison.

I am going to borrow some materials that were supplied by Hercules Corporation and were used by Steve Burmeister in his course at the Federal Bureau of Investigation (FBI) Academy on explosive residue analysis (Table 8-1). What we see are single- and double-base powders. I have never seen a triple-base powder, but, maybe someday, I will. Basically, we go about this sort of identification based on size and shape and whether it is extruded or ball powder and so forth. This is all pretty basic stuff, and what we see are the shot shell, rifle, and pistol powders. Some come from reloading components, and others from ammunition that has been emptied. Shot shells contain a little bit more powder than most rifle cartridges; so, they seem to be popular with bombers. Propellants that are supplied to domestic manufacturers for factory-loaded ammunition are more difficult to identify than the canister powders used by reloaders. There are over 100 types, and, occasionally, if you get lucky, you might see a blue or red dot Hercules or something with an

Table 8-1. Physical and Chemical Data of Hercules Canister Powders

Powder Type	Bullseye	Red Dot	Green Dot	Unique	Herco	Blue Dot	Hercules 2400	Reloder 7	Reloder 12	Reloder 15	Reloder 19	Reloder 22
Impetus (kft-lb/lb) ^a	384.5	366.7	368.2	367.7	372.2	364.5	359.8	338.4	346.0	345.3	353.1	344.0
Heat of explosion at 25° C (cal/g) ^b	1,232	1,084	1,035	1,088	1,065	1,047	1,008	934	914	952	951	939
Relative quickness (%) ^c	100.0	94.1	77.9	61.6	56.1	37.8	27.0	19.4	14.4	13.7	11.3	11.1
Tv (K) ^a	3,740	3,433	3,391	3,379	3,486	3,312	3,214	2,859	3,001	3,015	3,113	2,964
Molecular weight of gases ^a	27.1	26.0	25.6	25.6	26.1	25.3	24.9	23.5	24.1	24.3	24.5	24.0
Gas (mol/g) ^a	0.0370	0.0384	0.0390	0.0391	0.0384	0.0396	0.0402	0.0426	0.0414	0.0412	0.0408	0.0417
Specific heat at constant volume (cal/g-°C) ^a	0.3398	0.3393	0.3416	0.3417	0.3410	0.3428	0.3450	0.3456	0.3446	0.3475	0.3461	0.3471
Ratio of specific heats ^a	1.209	1.219	1.222	1.222	1.218	1.225	1.228	1.244	1.237	1.233	1.231	1.237
Covolume (cm ³ /g) ^a	0.862	0.885	0.890	0.890	0.881	0.895	0.902	0.930	0.919	0.915	0.907	0.919
Solid density (g/cm ³) ^c	1.63	1.64	1.63	1.63	1.64	1.63	1.62	1.61	1.62	1.62	1.62	1.61
Bulk density (gr/in ³) ^b	156.79	121.38	130.23	154.26	144.14	197.25	220.01	225.86	252.36	233.7	224.9	224.9
Nominal Physical Dimensions (thousands of an inch)												
Outside diameter	34	62	62	62	62	62	30	32	37	31	43	43
Inside diameter	0	0	0	0	0	0	0	6	6	4	6	6
Length	3	3	3	7	6	10	9	22	40	47	59	59
Gas Composition (mole %) ^a												
CO	30.7	37.6	38.9	39.1	36.8	40.0	41.3	46.4	44.5	42.9	42.4	44.3
H ₂ O	27.3	25.0	24.7	24.5	25.6	24.1	23.6	18.7	20.8	22.5	22.9	21.2
CO ₂	19.9	15.4	14.3	14.1	16.0	13.1	12.2	8.2	9.8	10.7	11.3	9.7
N ₂	14.3	12.9	12.6	12.6	13.0	12.4	11.9	11.0	11.3	11.1	11.5	11.0
H ₂	5.1	7.7	8.5	8.6	7.4	9.4	10.5	15.3	13.0	12.3	11.5	13.4
Other	2.7	1.4	1.0	1.1	1.2	1.0	0.5	0.4	0.6	0.5	0.4	0.4

^a Data obtained from theoretical calculations of nominal compositions.

^b Data obtained from experimental measurements of reference lot.

^c Data obtained from close bomb testing of reference lot at 0.170 g/cm³ loading density.

identifier. Using powder from ammunition is pretty tedious. Imagine 300 little 0.22-cal. bullets to make a pipe bomb, especially if you are using 0.22 "shorts!"

To understand the way these powders are manufactured, consider this diagram (Figure 8-1) of the manufacturing process provided by Hercules Alliant. They make smokeless powder and then add nitroglycerin (NG) and a couple of additives, which I would like to talk a little bit more about later. One of the interesting things is, down here, we get to the extrusion part that provides our shape and size and so forth. Then it is coated and dried. The particles are not all the same size. The lots can be as large as 10,000 lb, which are then sorted into sublots. There is a room in a warehouse full of barrels that are then blended for the ballistic characteristics rather than chemical composition. It is sort of like brand identification of gasoline, which is blended for octane rating. Powders are blended to optimize pressure, probably burn time and maybe accuracy and velocity of certain loads, and packaged up and sent out. I have noticed that there have been a lot of differences among the same ABC brand of powder from one lot to another. From 1 year to another, the differences could be shape, color, and so forth. Some of the basic analyses (i.e., looking for the methylethyl centralites and the diphenylamine, nitrotoluenes, and NG) have been well documented. Some of the other classes of the ingredients that I am wondering about are the stabilizers, plasticizers, flash suppressants, deterrents, and dyes. Is there any way we could do an analysis of these to further characterize the powder with a little bit more accuracy?

Previously, Stan Caulder (see section 7) alluded to the nitrogen content of the various nitrocelluloses (NC), NG, and nitroguanidine (NQ). Since these materials react over time, there is a problem of not knowing the storage history of a propellant that we find in our bomb. This bomb maker may have had the powder around in his/her house or shed for 20 years before it is used in a bomb. With respect to the plasticizers, deterrents, and so forth, I do not know to what extent some of these are used. The deterrents control the burning rate of the powder. Again, they are present in small amounts, but, if you have intact particles, it might be a way to further analyze the powder. There are two types that Hercules uses: (1) the penetrating type, which penetrates the actual grain, and (2) the inhibiting type, which is a coating. They have dyes added for identification, opacifiers, and graphite glazing. We have a relatively modest collection of smokeless powders in our

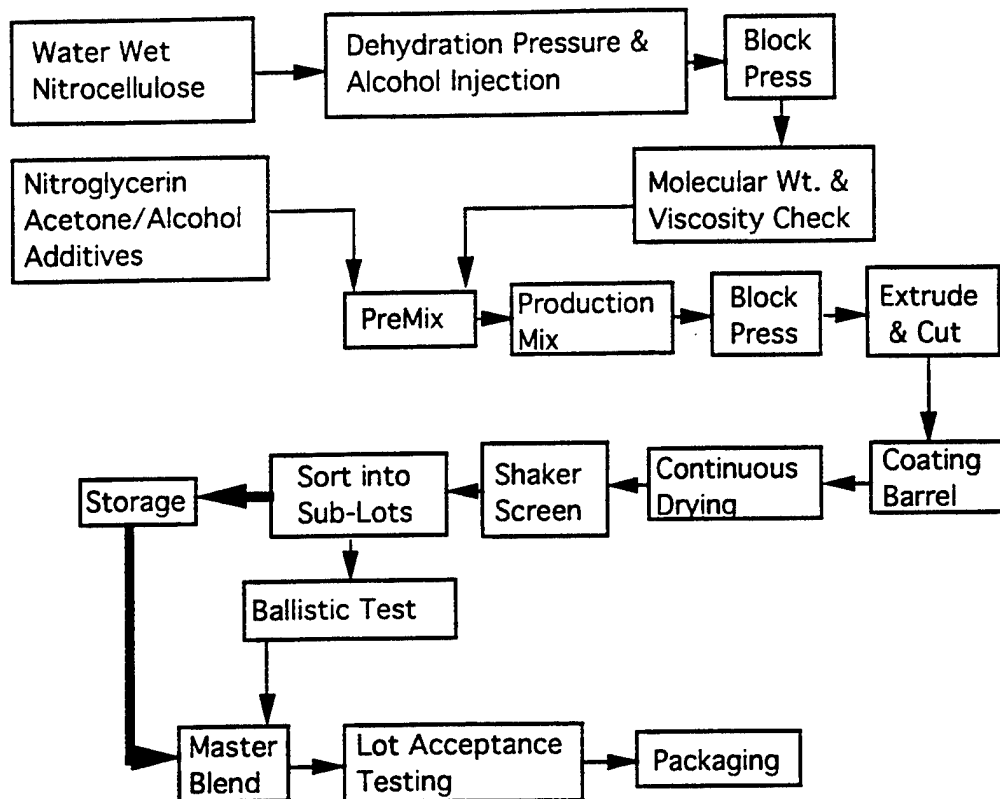


Figure 8-1. Schematic of Alliant Double-Base Smokeless-Propellant Manufacturing Process.

laboratory. Cindy Wallace at the Bureau of Alcohol, Tobacco, and Firearms (BATF) laboratory maintains a large collection of commercial powders used in reloading. This chart (Table 8-2) shows the relative burning rates of various powders. Number 1 is a real fast burner, and no. 94 is very slow. I think by now (i.e., 1993), there are a lot more powders available at a local sporting goods store.

How do you determine the difference between Bullseye and 2400? Well, the NG level is 40% in the Bullseye, but you need to do a chemical analysis. The thickness of the Bullseye is a lot less than the 2400, but, as I said, these grain sizes are nominal; so, you could get different-sized grains of the same powder.

Table 8-2. Relative Burning Rates of Various Powders

No.	Powder	No.	Powder	No.	Powder
1	R-1, Norma	33	HS-7, Hodgdon	65	IMR-4895, IMR Co.
2	N310, VihtaVuori	34	Blue Dot, Hercules	66	N135, VihtaVuori
3	Bullseye, Hercules	35	No. 9, Accurate Arms	67	IMR-4064, IMR Co.
4	Solo 1000, Scot	36	2400, Hercules	68	Brigadier 4065, Scot
5	No. 2, Accurate Arms	37	N110, Vihta Vuori	69	2520, Accurate Arms
6	Red Dot, Hercules	38	R-123, Norma	70	IMR-4320, IMR Co.
7	N320, VihtaVuori	39	H110, Hodgdon	71	N-202, Norma
8	Royal Scot, Scot	40	296, Olin	72	N140, VihtaVuori
9	HP-38, Hodgdon	41	SR-4759, IMR Co.	73	Reloder 15, Hercules
10	231, Olin	42	N120, VihtaVuori	74	H380, Hodgdon
11	Trap 100, Hodgdon	43	5744, Accurate Arms	75	760, Olin
12	453, Scot	44	IMR-4227, IMR Co.	76	N150, VihtaVuori
13	Hi-Skor 700-X, IMR Co.	45	H4227, Hodgdon	77	H414, Hodgdon
14	452AA, Olin	46	1680, Accurate Arms	78	IMR-4350, IMR Co.
15	Green Dot, Hercules	47	680, Olin	79	H4350, Hodgdon
16	N330, VihtaVuori	48	N-200, Norma	80	N-204, Norma
17	PB, IMR Co.	49	N133, VihtaVuori	81	Brigadier 4351, Scot
18	No. 5, Accurate Arms	50	Brigadier 4197, Scot	82	Reloder 19, Hercules
19	Unique, Hercules	51	H4198, Hodgdon	83	N160 VihtaVuroi
20	SR-7625, IMR Co.	52	IMR-4198, IMR Co.	84	IMR-4831, IMR Co.
21	473AA, Olin	53	Reloder 7, Hercules	85	3100, Accurate Arms
22	HS-6, Hodgdon	54	IMR-3031, IMR Co.	86	H450, Hodgdon
23	N340, VihtaVuori	55	N201, Norma	87	H4831, Hodgdon
24	540, Olin	56	H322, Hodgdon	88	MRP, Norma
25	Herco, Hercules	57	2230, Accurate Arms	89	N165, VihtaVuori
26	SR-4756, IMR Co.	58	Brigadier 3032, Scot	90	Reloder 22, Hercules
27	Solo 1250, Scot	59	748, Olin	91	IMR-7828, IMR Co.
28	3N37, VihtaVuori	60	BL-C(2) Hodgdon	92	8700, Accurate Arms
29	Hi-Skor 800-X, IMR Co.	61	2460, Accurate Arms	93	N170, VihtaVuroi
30	No. 7, Accurate Arms	62	H335, Hodgdon	94	H870, Hodgdon
31	Solo 1500, Scot	63	H4895, Hodgdon		
32	N350, Vihta Vuori	64	Reloder 12, Hercules		

Note: These listings are approximate; faster burning powders have lower numbers.

Here is another characteristic: the larger "dot" propellants (red dot, green dot, and blue dot) all physically look the same; the NG level is the same. If you do not have the little dots in your sample (and there are not a lot of dots in these powders), how do you distinguish them? Do you need to

distinguish them? Here are some characteristics: the diameters may be similar and you could have some particles that fit one category, but maybe it is another type. Some were made in this country and some were made in Sweden. Tables 8-3, 8-4, and 8-5 are based on some work done by Cindy Wallace at BATF. I know she found some differences among the various lots of Hercules 2400, blue dot, and Bullseye, based on diameter and thickness. Basically, we keep a collection of smokeless powders that are commercially available; but, when trying to identify powder, we do measurements of the applicable characteristics that I described in those tables. It was difficult to distinguish between the two. Sometimes it is impossible, but we keep trying to do it because we cannot always know or understand the future significance of the forensic comparison we do. Here is a chart on physical data (Table 8-6). Is there anything in the physical data that could help us distinguish among various types of powder? Down on the left side of the chart, we have a lot of other properties of the powders.

To sum up, we have large-sized lots on some of these powders, and there is a lot of variation among lots of the same ABC powder.

We have a case now that has two pipe bombs that are about an inch and a half or so in diameter, 6 in long, full of powder, and rendered safe by an Army Explosive Ordnance Disposal (EOD) squad. They sorted through this debris and recovered 1 gr of tubular smokeless powder. It was a smokeless powder used in the bomb, as they were able to eliminate the powder that was used by the EOD people in the de-arming procedure. There were some further complications: (1) when they hit the pipes with the de-arming cannon, both pipes detonated; (2) the dearming was done in the middle of a road; and (3) there was a rain storm. As you can see, the environment we deal with does not resemble a controlled laboratory environment.

I looked in my cupboard the other day and noted where the powders were manufactured. I found powders made in the United States, Czechoslovakia, Scotland, Israel, and Australia. Since my collection is not complete, I know there are still other countries involved. Hodgdon imports a lot of the powders and repackages them. But, today's Hodgdon ABC may be different in size and shape from tomorrow's Hodgdon ABC. Again, the powders are blended for the ballistic properties.

Table 8-3. BATF Database for Hercules 2400

Inventory No.	Manufactured	Count	Diameter		Thickness		NG	DPA	2,4-DNT	DBP	EC
			(d)	(SD[d])	(T)	(SD[T])					
R-2400.1	TR476	50	0.777	0.060	0.248	0.072	X	X	—	—	X
R-2400.2	Lot 366	50	0.767	0.027	0.281	0.038	X	X	—	—	X
R-2400.4	Shift 2, 2400 655, 20 Feb 92	50	0.719	0.023	0.238	0.042	X	X	X	—	X
R-2400-5	2400 758, Shift 2, 7 Aug 94	50	0.750	0.026	0.331	0.103	X	X	—	—	X
Averages	—	—	0.753	0.034	0.275	0.064	A	A	S	—	A

Notes: d = Diameter. DPA = Diphenylamine. X = Ingredient found in propellant.
SD = Standard deviation. DNT = Dinitrotoluene. A = Always found.
T = Thickness. DBP = Dibutyl phthalate. S = Sometimes found.
EC = Ethyl centralite.

Table 8-4. BATF Database for Hercules Blue Dot

Inventory No.	Manufactured	Count	Diameter		Thickness		NG	DPA	2,4-DNT	DBP	EC
			(d)	(SD[d])	(T)	(SD[T])					
R-BLUE.2 ^a	BD169	50	1.322	0.080	0.260	0.053	X	X	—	X	X
R-BLUE.5 ^a	Shift 2, 276, 9 Jul 94	50	1.488	0.167	0.210	0.071	X	X	—	—	X
Averages	—	—	1.405	0.424	0.235	0.062	A	A	—	S	A
R-BLUE.1 ^b	Lot BD038	50	1.336	0.073	0.246	0.039	X	X	—	X	X

Notes: d = Diameter. DPA = Diphenylamine. X = Ingredient found in propellant.
SD = Standard deviation. DNT = Dinitrotoluene. A = Always found.
T = Thickness. DBP = Dibutyl phthalate. S = Sometimes found.
EC = Ethyl centralite.

^a Newer blue dot with filler in IDs.
^b Older blue dot.

Table 8-5. BATF Database for Hercules Bullseye

Inventory No.	Manufactured	Count	Diameter		Thickness		NG	DPA	2,4-DNT	DBP	EC
			(d)	(SD[d])	(T)	(SD[T])					
R-BULL.1	Lot BE 114	50	0.894	0.050	0.133	0.030	X	(X)	—	—	X
R-BULL.2	Lot BE 170	50	0.885	0.053	0.137	0.042	X	X	X	—	X
R-BULL.3	BE 555	50	0.870	0.044	0.144	0.033	X	—	—	—	X
R-BULL.4	Lot 939	50	0.870	0.050	0.127	0.031	X	—	—	—	X
R-BULL.7	Illegible, purchased 1994	50	0.907	0.046	0.168	0.075	X	(X)	—	—	X
Averages	—	—	0.885	0.049	0.142	0.042	A	S	S	—	A

Notes: d = Diameter. DPA = Diphenylamine. X = Ingredient found in propellant.
SD = Standard deviation. DNT = Dinitrotoluene. A = Always found.
T = Thickness. DBP = Dibutyl phthalate. S = Sometimes found.
EC = Ethyl centralite.

Table 8-6. Hercules Large-Die Smokeless Powders

Characteristics		Red Dot	Green Dot	Unique	Herco	Blue Dot
Diameter ^a (thousandths of inches)		65	65	65	65	65
Thickness ^a (thousandths of inches)		3	4	5	7	10
NG Level ^a (%)		20	20	20	20	20
Appearance of Flakes		black	black	black	black	brown/black
Inside Diameter (ID) Grains		Red	Green	None	None	Blue
Packaging	1-lb cans	Yes	Yes	Yes	Yes	Yes
	4-lb cans	Yes	Yes	Yes	Yes	No
	5-lb cans	No	No	No	No	Yes
	8-lb kegs	Yes	Yes	Yes	Yes	No

^a This information is nominal; actual values may vary.

Sometimes, more than one kind of smokeless powder is used in a pipe bomb. I had one pipe bomb where I found four types of powder. Does it do any good to say the dominant one is double based? Well, if double base were present, NG could migrate to the other particles. So, how then does one distinguish between double base and single base? Were these powders taken from reloading-type powders, or did someone empty ammunition? I had a case recently where a man sent a bomb, I think it was to his wife or ex-wife. She is lucky; it did not go off, and it was rendered safe. During the render-safe procedure, the pipe burned for quite a while and left some black residue, but there was tape on the outside of the pipe. (Bomb makers love tape, and there was black electrical tape wrapped around the pipe.) I looked at it under the microscope and noticed several types of smokeless powder particles, indicating three or four different types of smokeless powder. The conclusion is that this bomber used a mixture of propellants. Some of the smokeless powder particles that survived were in one of the end caps that had a cotton wad in it. But the powder seemed to be from factory ammunition. When the bomb maker eventually confessed to making the device, he said he emptied out the propellant and then threw the rest of the ammunition components

away. So, the ammunition that I had identified in the search warrant had powder that was vastly different in appearance from what the suspect actually used in the device.

9. “Simplifying Access to Complex Databases”

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Abstract

Database query formulation is a difficult task. While a domain expert may have a good understanding of the information stored in a specific database, successful data retrieval requires detailed implementation knowledge. Thus, query formulation typically involves significant effort on the part of a database expert, and decision makers are restricted from immediate access to the information they need. QUICK (Universal Interface With Conceptual Knowledge) is an automated query formulation system that uses database design knowledge to generate SQL (Structured Query Language) queries from high-level user requests. Providing more intuitive access to the database, QUICK facilitates information retrieval by end users and supports the development of query processing systems and knowledge discovery systems over complex databases.

Introduction

Query formulation is a difficult task that requires knowledge of both the information to be retrieved and details about how that information is stored in the database. In SQL (Structured Query Language), the most common database query language, a data request must identify (1) the attributes of interest, (2) the specific constraints on those attributes, (3) the relations that contain them, and (4) the join path through the database relations that connects the requested data. In real-world databases, it is not unusual for a request over a few data items to result in a query that is multiple pages in

length. Thus, significant effort is required to develop correct queries to return the required data. Query formulation is further complicated when the database implementation does not correspond directly to its conceptual design due to ongoing maintenance modifications, performance-driven optimizations, or poor design decisions. These factors make it difficult, even for a domain expert, to understand the database well enough to formulate a correct query in a timely manner. In particular, it is unlikely that anyone who is not intimately familiar with the details of the database implementation will be successful in retrieving the desired data. As a result, direct information requests are typically limited to preformulated queries, and ad hoc queries must be supported by the time-consuming handcrafting of queries by database experts.

Information access is further restricted when data are distributed throughout an organization. Typically, enterprise information that evolves over time is often collected at multiple locations and may be separated into different databases developed using various design models and database management system (DBMS) implementations. Not only is it difficult to locate specific data within such a collection of distributed and possibly heterogeneous databases, but those databases may contain conceptually related information that would be quite valuable to decision makers if they could access it in a consolidated manner. Unfortunately, tools to support wider data access are costly to develop and difficult to maintain because of their tight coupling to the implementation details of the underlying databases.

This paper describes a query formulation approach that facilitates information retrieval from complex database systems. Utilizing conceptual-level database design knowledge, the approach supports the user's intuitive understanding of the problem domain, promotes direct ad hoc querying, permits the conceptual integration of related databases, and supports database integration into larger knowledge discovery systems. The Database Design and Implementation section reviews the fundamentals of database design and implementation. Then, the Conceptual-Level Query Formulation section shows how conceptual-level knowledge can be used to automate query formulation. The QUICK (Universal Interface With Conceptual Knowledge) section describes a system that implements the approach and reviews some of its applications. Finally, the Conclusion and Future Research section discusses areas for future research.

Database Design and Implementation

Database development typically proceeds along the information system life cycle from problem specification to design to implementation to maintenance. Once the problem domain has been analyzed and the system requirements have been discovered, a conceptual-level design is produced. This design provides an abstraction of the real-world problem area and restricts the focus to those aspects of the domain that are critical to the application requirements. An accurate conceptual-level design is vital for successful database implementation, and, upon completion, it provides a detailed and intuitive understanding of the database.

The entity-relationship (ER) model is one of the principal mechanisms for conceptual-level database design [1, 2]. Objects in the real-world problem domain are modeled as entity types and described by a collection of attributes. Relationship types are used to identify associations between entities and provide additional semantic information in the form of cardinality ratio and participation constraints that indicate the number of times an entity may participate in a relationship and whether or not it is required to do so. A number of extensions to the ER model have been developed to support increased descriptive detail and data complexity in database designs [3]. In particular, modeling concepts, such as complex attribute specifications, N-ary relationship types, and subset and generalization hierarchies, provide significant additional support for modeling complex real-world systems.

An ER diagram provides a graphical representation of the database design information, where the entity types are indicated by rectangles, the relationships between entity types are represented by diamonds, and the descriptive attributes of entity (or relationship) types are indicated by ellipses. Figure 9-1 shows the ER diagram for a simple banking database example, where bank branches offer accounts, and loans, which are in turn held by customers. The entity types (branch, customer, account, and loan) contain information about each of these objects in the problem domain as indicated by their associated attributes. Closely related attributes may be conceptually grouped into composite attributes; `customer_address` and `street_address` are examples

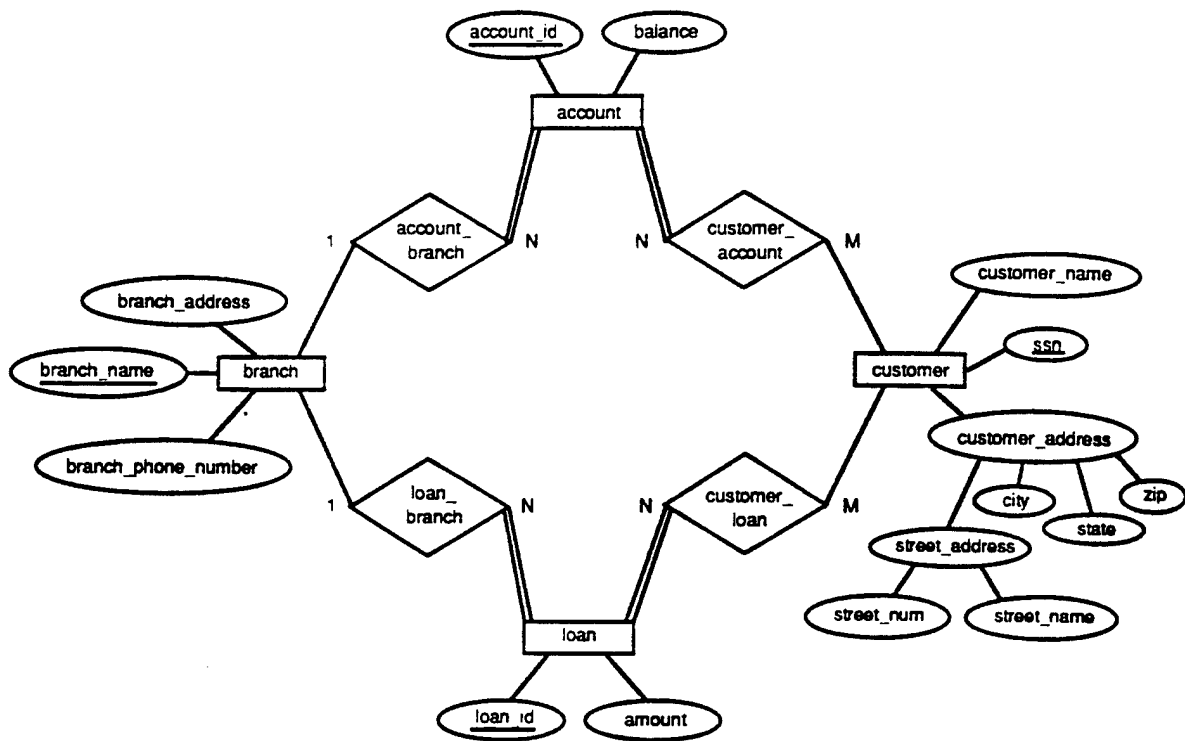


Figure 9-1. A Banking Example ER Diagram.

in Figure 9-1. The set of attributes that uniquely identifies a particular entity is called the identifier; those attributes are underlined in the ER diagram. For example, each account is identified by its `account_id`.

The relationship types (`account_branch`, `customer_account`, `loan_branch`, and `customer_loan`) identify the conceptual associations between the objects in the banking problem domain. The participation constraint for each entity type associated with a particular relationship type is specified by the connection to that relationship type, where a single line denotes partial participation and a double line indicates total (or mandatory) participation. Consider, for example, the `customer_account` relationship type in the banking database. An account must be related to a customer, but each customer need not be related to an account. This design models the real world, where a customer may have a loan but not an account with the bank. The cardinality ratio constraints that indicate the number of times each entity may participate in a

relationship is denoted by the labels on the lines connecting the relationship type to each of its participating entity types. The ER diagram in Figure 9-1 contains N-to-M and N-to-1 relationship types. Again, looking at the `customer_account` relationship type, the N-to-M notation indicates that there is a many-to-many relationship between customers and accounts. Thus, an account must be related to at least one customer but may be related to many, while a customer need not be related to any account, but may be related to many. This corresponds to the real-world notions of joint bank accounts and customers that have more than one account with a particular branch. Similarly, the N-to-1 (i.e., many-to-1) relationship type `account_branch` denotes that, while a branch may be associated with any number of accounts, each account must be associated with a single branch.

There is a straightforward algorithm for converting a database ER diagram to a logical-level implementation in the form of a set of relations (see Elmasri and Navathe [2] for a detailed explanation). These relations define the tables in a relational database, where the columns correspond to the included attributes, and the rows contain specific data entries in the database. Applied to the database design in Figure 9-1, this process results in the following six relations (where the underlined attributes indicate the primary key, which is the set of columns that uniquely identifies each row in the table).

- (1) `branch` (`branch_name`, `branch_address`, `branch_phone_number`)
- (2) `account` (`account_id`, `balance`, `branch_name`)
- (3) `loan` (`loan_id`, `amount`, `branch_name`)
- (4) `customer` (`ssn`, `customer_name`, `street_num`, `street_name`, `city`,
 `state`, `zip`)
- (5) `customer_account` (`ssn`, `account_id`)
- (6) `customer_loan` (`ssn`, `loan_id`)

Once the database is implemented and the data loaded, queries may be submitted. Consider, for example, a request for the names and addresses of all customers with a loan amount greater than \$10,000. The SQL query is as follows.

```

SELECT
    customer.customer_name,
    customer.street_num,
    customer.street_name,
    customer.city,
    customer.state,
    customer.zip
FROM
    customer,
    customer_loan,
    loan
WHERE
    loan.amount > 10000 AND
    customer.ssn = customer_loan.ssn AND
    customer_loan.loan_id = loan.loan_id

```

The **SELECT** clause identifies the attributes to be returned, the **FROM** clause identifies the relations required to process the query, and the **WHERE** clause specifies the constraints on the requested attributes and the join path through the database tables to connect related data. Notice that the query for this simple request is not trivial to formulate. Not only must each attribute be located within its particular table, but this query requires knowledge of the `customer_loan` relation that connects specific customers to their loans.

Conceptual-Level Query Formulation

Unfortunately, converting a database design to a relational implementation removes a significant amount of conceptual knowledge. For example, in the banking relational database previously defined, the tightly coupled sets of data items that formed composite attributes are no longer distinguished. Similarly, relationships are not necessarily explicit, cardinality ratio constraints can only be inferred from relational schemas, and the participation constraints have been removed. Much of the semantic meaning that is so clearly defined in the design of Figure 9-1 and that so closely corresponds to the user's view of the problem domain has been discarded in the database implementation.

Query formulation is further complicated by the duplication of attributes in the relational schema. In the banking database implementation, for example, the column `branch_name` appears in three

relations: (1) branch, (2) account, and (3) loan. It may not be clear which subset of these relations is required to formulate a query for branch_name information. Notice that there is no ambiguity at the conceptual level; however, the branch_name attribute is associated only with the branch entity type.

Recall that an SQL query must specify the relations that contain the desired attributes and the join path through the database that connects the requested data. Since this information is specific to the database implementation and is typically not known to an individual with a data request, a mismatch exists between the user's understanding of the database at the conceptual level and the standard method for accessing information contained in that database at the logical level. One approach to bridge this gap is to permit the user to request data in a more intuitive manner. The universal relation (UR) concept [4] refers to a single, virtual relation that contains all of the attributes from all of the tables in the database. Queries over a universal relation would simply specify the attributes of interest and any constraints that must be applied to those attributes; there is no need to identify the implementation-specific details required in an SQL query. As a result, this type of representation provides a more natural mechanism to pose requests.

While a UR-like interface simplifies a user's data request, an additional burden is placed on the supporting query formulation system to identify semantically reasonable join paths for the requested attributes. This can be accomplished by using the semantic knowledge contained in the ER database design to define maximal subgraphs consisting of strongly related conceptual objects [5]. Known as contexts, these overlapping subsets of the database schema provide the knowledge necessary to define associations between requested attributes and to develop the relational join path required for query formulation. In particular, if a context covers the set of attributes in a high-level user request, then it is inferred that the user request corresponds to the join path defined by that context. Conversely, if no context is found, then it is assumed that the requested attributes are not related.

Contexts are developed from a database ER design using an extension of the concept of a lossless join. If a join between two relations is lossless, then a strong association exists between the tables. In particular, a lossless join ensures that all the rows that should be connected are, and that no

extraneous rows are added to the result (see Elmasri and Navathe [2] for more details). Applying this notion to the conceptual-level database design, two ER objects are strongly associated if their corresponding tables can be joined in a lossless manner. Thus, contexts are generated by extending outward from each relationship type in the ER schema to include all strongly associated conceptual objects. Any context that is a subset of another is removed, leaving the set of maximal ER subgraphs.

Applying this procedure to the banking database example of Figure 9-1, two contexts are generated.

Context 1:

(customer, customer_account, account, account_branch, branch)

Context 2:

(customer, customer_loan, loan, loan_branch, branch)

These contexts correspond to the strong semantic associations between customers and bank branches through their accounts (Context 1) and through their loans (Context 2).

QUICK

QUICK is an automated query formulation system developed at The Johns Hopkins University (JHU) Applied Physics Laboratory (APL) [6]. QUICK exploits conceptual-level database design knowledge to generate semantically reasonable SQL queries from high-level requests. Once a text-based representation of the graphical ER database design is entered into the system, the conceptual schema is mapped to the corresponding logical implementation and contexts are generated. Then, requests can be processed.

QUICK allows the user to submit queries in a language known as USQL (a simplified version of SQL that operates over a UR-like interface). Consider again the banking database request for the names and addresses of all customers with a loan amount greater than \$10,000, originally presented in the Database Design and Implementation section. The USQL query, specifying only the attributes and constraints of interest, is simply as follows.

```
SELECT
    customer_name,
    customer_address
WHERE
    amount > 10000
```

Given this query as input, QUICK exploits its conceptual knowledge of the banking database design to convert the composite attribute `customer_address` to its constituent components, to provide the necessary relation names and join path information, and to generate the SQL query previously presented.

Looking at this process in more detail, consider a request for the `customer_name` and `branch_name` corresponding to each account with a balance greater than \$5,000. The USQL version of this query is as follows.

```
SELECT
    customer_name,
    branch_name
WHERE
    balance > 5000
```

The process followed by QUICK to convert this request to SQL for execution on the underlying database is straightforward. First, find the contexts that cover the requested attributes. In this case, Context 1 (the account portion of the schema) is the only candidate. Next, prune the contexts of extraneous ER objects until all leaves in the remaining ER subgraph cover the requested attributes. Since the entity types `branch` and `customer` both account for requested attributes, no pruning is necessary. In general, pruning multiple candidate contexts may yield identical results; in that case, remove the duplicates. Next, map the remaining ER objects in the pruned context to their

logical-level relations and identify the join path. Finally, generate the SQL query. For this example, the result is as follows.

```
SELECT
    customer.customer_name,
    branch.branch_name
FROM
    customer,
    customer_account,
    account,
    branch
WHERE
    account.balance >
5000 AND
    customer.ssn =
customer_account.ssn AND
    customer_account.account_id =
account.account_id AND
    account.branch_name =
branch.branch_name
```

QUICK facilitates meaningful information retrieval and supports an ad hoc querying capability without requiring detailed understanding of the underlying database implementation. In particular, the system provides the relation names for all attributes in the query, the complete SQL FROM clause, and the join path required in the SQL WHERE clause from the conceptual-level knowledge contained in the ER design. Notice that even in this simple example, the resultant SQL query is significantly more complex than the original USQL request. In real-world databases, it is quite common to generate a page or more of SQL from a relatively simple USQL request. Thus, the time required to generate a semantically meaningful and syntactically correct SQL query is greatly reduced through the use of QUICK, regardless of the user's database expertise. In addition, query formulation can be further simplified through the use of high-level user interfaces that assist in the selection of query attributes. By encapsulating the query formulation function, QUICK supports the development of user interfaces that focus on problem domain specifics.

Having demonstrated how QUICK provides decision makers with simplified access to information within databases, we now consider the larger problem of integrating related information across multiple data sources. This has become a critical issue as organizations seek to exploit recent

knowledge discovery advances by applying data-mining approaches to extract previously hidden patterns and relationships from their large and diverse databases [7]. Prior to implementing such efforts, however, a unified view of the disparate data sources and database implementations, as well as uniform methods to access these data, must be made available. Extending the conceptual-level approach across multiple databases, QUICK may be used to support the formation of such an organization-wide data access infrastructure.

In particular, QUICK has been used to demonstrate the retrieval of information across semantically related heterogeneous databases [8] for the U.S. Army Research Laboratory (ARL). Two distinct databases, the ARL Electronic Intelligence (ARL-ELINT) relational database and the Military Intelligence Integrated Data System and Integrated Database (MIIDS/IDB) inverted file database, contain an entity type that corresponds to the same conceptual object in the intelligence domain. By extending the ER model to include a gateway relationship type that describes the association and join specification between the common entity types, a conceptual model of the fused databases was developed. After mapping to the logical database implementations and generating contexts, USQL requests were processed as before. The user's perspective was a single, high-level interface over the fused databases, permitting straightforward access to all the data.

A typical query over these combined intelligence databases might, for example, request the last-known activities, mobility status, and equipment types and quantities of any known enemy unit associated with a site where a pulse repetition frequency of 50 Hz has been detected. In USQL, the query is as follows.

```
SELECT
    site_name,
    unit_name,
    unit_role,
    echelon,
    activity_name,
    mobility_status,
    equip_code,
    equip_quantity
WHERE
    allegiance = 'ENEMY' AND
    prf = 50
```

Applying the query formulation process described earlier, QUICK generates the following SQL query over the MIIDS/IDB and ARL-ELINT databases.

```
SELECT
    miids.site.site_name,
    miids.unit.unit_name,
    miids.unit.unit_role,
    miids.unit.echelon,
    miids.unit.activity_name,
    miids.unit.mobility_status,
    miids.equipment_type.equip_code,
    miids.equipment.equip_quantity
FROM
    miids.equipment,
    miids.unit,
    miids.equipment_type,
    miids.site,
    elint.eob_site,
    elint.eob_component,
    elint.elint_report,
    elint.elint_prf
WHERE
    miids.unit.allegiance =
        'ENEMY' AND
    elint.elint_prf.prf =
        50 AND
    miids.equipment.unit_name =
        miids.unit.unit_name AND
    miids.equipment.unit_role =
        miids.unit.unit_role AND
    miids.equipment.echelon =
        miids.unit.echelon AND
    miids.equipment.equip_code =
        miids.equipment_type.equip_code AND
    miids.equipment.site_name =
        miids.site.site_name AND
    miids.site.site_name =
        elint.eob_site.eob_site_name AND
    elint.eob_component.eob_site_db_id =
        elint.eob_site.eob_site_db_id AND
    elint.elint_report.elnot_id =
        elint.eob_component.elnot_id AND
    elint.elint_prf.elint_report_db_id =
        elint.elint_report.elint_report_db_id
```

This query is particularly interesting in that the requested data attributes (as identified in the SELECT clause) are all contained in the MIIDS/IDB database but the specific data items to be returned are constrained by information located in the ARL-ELINT database (specifically, the restriction that

prf = 50). Thus, by providing a combined access capability, QUICK permits the straightforward exploitation of additional data found in related databases to enhance the quality of information returned to decision makers. Similarly, through this unified view of enterprise data, QUICK can facilitate the development of larger data analysis and decision support systems.

Conclusion and Future Research

Query formulation can be a complicated and time-consuming task. By providing a conceptual-level query interface and utilizing the semantic knowledge contained in the conceptual-level design, query formulation can be greatly simplified. The QUICK system supports a user's intuitive understanding of the data items in the database, facilitates the Ad Hoc group querying to provide information on demand, and provides a mechanism to integrate conceptually related databases into enterprise-wide information systems. Finally, this consistent view of organizational data, unconstrained by DBMS implementation details, provides the underlying support necessary to implement data-mining and data-analysis systems.

Future research is focused on several areas. First, gateway relationship types are being extended to provide a general mechanism to integrate conceptually related database schemas. Next, contexts are being enhanced to help disambiguate queries where multiple contexts cover the requested attributes. Finally, integrating alternative conceptual and logical models into QUICK is being explored.

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10. Discussion Section

Workshop Questions and Responses

What Is Required for a Sample to Be Traceable to a Unique Compound (or Unique Class of Compounds)? A database can be forensically useful, even if it does not uniquely identify the sample in question. For example, suppose the residue from a bomb is examined and adhesive tape is found. Subsequent analysis of the backing thickness shows that the adhesive composition is made by the 3M Company and it is one of their specialty tapes. If the possibilities can be narrowed to just a few and one of these possibilities is found in a suspect's house, there are grounds for a legal case.

For energetic compounds, the sampling question has two facets. First, there is the domestic concern with low-order explosions, mainly based on smokeless powders. Second, there is the international concern, generally with high-order explosives. Because of the different types of energetic materials, these can be thought of as two separate problems.

Smokeless powders are involved in the majority of domestic bombing incidents. There are not many cases involving high explosives. Detonators are interesting, but they are not seen in very many cases either.

How Can the Present Databases Be Made Into User-Friendly, Complete, and Current Databases, Accessible by All Forensic Laboratories? There are two questions here: one is database structure, the other is database entry.

It was concluded that a user-friendly and user-accessible set of databases can be and, in fact, is being constructed. More research is required, and several problems have been identified. How complicated must a database be to serve its intended purpose? How much information is needed? How is this information validated? Apparently, some of these questions, as well as others, are being addressed by the already-established Technical Working Groups for MATerials analysis (TWGMAT).

General Aspects of Databases

The following general aspects of a database were considered: completeness, maintenance, validity, modeling, accession, and security. The first four topics are considered internal aspects of a database; the last two are considered external aspects.

Internal Aspects.

Completeness. It was the consensus of the participants that one never has everything in a database; it is never complete. A constant updating of the database was envisioned.

Proprietary Information. It was recognized that, sometimes, the most important information is proprietary, which can create problems. If proprietary data were put into a database, then anybody accessing the database would have access to the proprietary data.

An irony was noted for the proprietary status of some information. Personal experiences have shown that much that is labeled "proprietary" is really common knowledge throughout the industry or readily accessible in the open literature.

Processing Changes. It had been observed that manufacturers will routinely make slight changes in their manufacturing, either in the processing steps or in the ingredients used. Either the manufacturers themselves do not recognize the changes, or they choose to remain silent to the fact. Such changes usually do not become a part of the audit record.

These changes may be beneficial. They may alter the characteristics of the material so that a previously common material becomes unique. On the other hand, these changes may be confounding when, say, an altered ingredient shows up in analysis when it is not supposed to be there.

Maintenance. One or two people could maintain a sufficiently small or simple database (i.e., sometimes data would be input, and, at other times, data would be deleted). For example, in the Federal Bureau of Investigation (FBI) automotive paint file, paints that are over 25 years old are not typically needed; so, they are deleted. As a counterexample, one probably would not delete entries from the Bureau of Alcohol, Tobacco, and Firearms (BATF) smokeless powder database because very old powders are still encountered in the field.

For sufficiently large or complex databases, a central location or “clearing house” might be required. A central location leads to the question of who bears the cost of maintaining and upgrading the database? If a clearing house were employed, it might be easier to control who has access to the data; so, a security benefit might be gained.

Validity.

Consistency. Two levels of error checking were distinguished. At data input, how certain is the entry? For multilevel bases, how can entry common to several databases be simultaneously changed? The first situation more or less is dependent upon the experimenter or analyst to determine the sensibility of the entry and is commonly encountered by those who maintain their own (private) databases. The second situation is not yet routinely encountered within the forensic community, according to the participants.

There are solutions built into database systems that automatically perform consistency maintenance to some extent. There are commercially available tools that do what is called “data scrubbing.” Turn one of these operations loose on a database, and it will look for and report likely inconsistencies within the data records and data sets.

However, there is a bigger problem. For example, suppose A maintains database a, and B database b, with X as the common column between a and b. If B changes an entry in X, does A know about it? Some sort of data administrator or central clearing house charged with control of the data was recommended. Someone has to know the structure of the entire database if changes are to

be made consistently. If b is changed and the appropriate change in a is not made, consistency will have been lost.

Structure. Some ideas were put forth on advanced databases. The desired database system that combines text, analytical information, and image data was defined.

It was recommended to start with a small, constrained set of databases. The idea was to find out what works at the smaller domain before building up to the larger. This was recommended simply to conserve resources (i.e., if the system fails, let it fail in the smaller domain).

Databases that contain about 50 tables and several thousand attributes have been dealt with. The size, structure, and interrelationships of the databases (i.e., tables) are more important than simple volume of data entries. Terabytes (10^{12} B) of data can be handled with no problem. The numbers of tables in the current smokeless powder and in the paints and coatings databases are 6 and 20, respectively. It was thought that the paints and coatings database might provide an adequate exercise of the database tools discussed, whereas the smokeless powder database would probably be too small to make effective use of these tools.

Modeling. Whether one has a specialized database for one's own data or is meshed with a complex series of interlinking tables of data, one must decide at the outset what the data should look like. In the more complex cases, one normally goes through some conceptual and logical modeling efforts associated with the data. If one has a thousand attributes and a hundred entities that are all related, with many multiple relationships existing among those entities, one will probably have a complicated model, requiring several modeling approaches before it is adequately formulated. This kind of modeling requires a major effort.

Consider this counterexample. The Army has many legacy systems that are not well structured from a data viewpoint. Essentially, they consist of gigantic files that are simply record, after record, after record. Such a database might consist of 10,000 records, but it is just one table. The database tools discussed here are not designed for this kind of database and, so, do not exercise the power of

this tool. If the data have some inherent structure, then it probably makes sense to model them. Most databases that have any relational richness at all should be structured so that one ends up with perhaps 40 or 50 tables. The main point is that such a modeling effort is not necessarily easy or trivial.

External Aspects.

Accession. Consideration was given to question of retrieval design. Specifically, could the receiving format be universal, or would it have to be specialized? At this time, one would build some sort of program that parses the data (e.g., this number of bytes goes here; that number goes there). In other words, this program would be a translator, which is not difficult to construct but has a low priority just now.

A dialog-type access is the ultimate goal. But right now, the reality is more of a Windows-based interface in which much more material is presented on screen to decrease the time spent narrowing down selections.

Security and Release Authority. Concern, based on individual experience, was voiced about the ability to obtain release authority from controlling agencies for specific propellants or explosives. Such authority appears to be a function of the agency and the releasing officer, and, without it, the particular energetic material could not be legally entered into an open database. However, the individual energetic ingredients were thought to be relatively immune to this obstruction to database entry.

The Chemical Propulsion Information Agency (CPIA) based at The Johns Hopkins University (JHU) has been trying to assemble a spectral database of energetic materials. They are attempting to massage their data so that they can meet the release requirements for information to be distributed by wire (e.g., the Internet). (Note added in proof: CPIA now has a web site that requires a password to gain access.)

Particular Database Topics

Energetic Materials.

Smokeless Powders. Some smokeless powders are easy to identify because they are fairly unique: for example, in their size, shape, or coating. Others are difficult to identify by brand. Production lots of smokeless powders are blended together so that the blend meets some ballistic limit (a velocity or a pressure). Thus, there may not be a unique identification because of the random way the smokeless powders are blended. In these cases, one gathers as much information as one can to limit the number of possibilities.

What would be useful is to further characterize smokeless powders beyond that which is done now.

Dynamite. The situation for dynamites in the United States is almost the complete opposite of the smokeless powders. There is one dynamite production facility in the United States, maybe two. But they make all the dynamite sold in the United States and Canada. Thus, identifying a unique brand name like Atlas or Hercules means little or nothing.

Detonators. Some time ago there was an identification guide for detonators, but, now, there are many new types of detonators and no standard classification of these newer types. Such a database is needed because, in a recent case, a fact-finding mission had to be undertaken throughout various parts of the world to find a standard for the newer detonators.

On the one hand, the Federal Aviation Administration (FAA) might have an interest in an updated detonator database; on the other, the BATF has not seen a case with a nonelectric blasting cap in many years. (Note added in proof: The National Institute of Justice [NIJ] has subscribed to the Raman database generated by Dr. K. McNesby, U.S. Army Research Laboratory [ARL].)

Paints. NIJ, through the National Institute of Standards and Technology (NIST), is working on a project that includes the entire forensic community: specifically, the FBI, TWGMAT, the forensic associations, the federal and state forensic laboratories, and the local forensic laboratories. Some countries, such as Canada, are also participating. The basic idea is to create a database of paint for all automobiles manufactured in the last 25 years and, also, all paints or coatings for everything from a building to a utensil or an appliance.

It is a large database that contains pigments, resins, and additives and all the different chemicals and formulations with their spectral analysis, (e.g., Fourier transform infrared [FTIR], ultraviolet [UV], or infrared [IR] spectra). The system operates from a central location where it can be administrated and maintained. All of the laboratories that participate either supply paint samples or collect paint samples. Only the laboratories that participate have access to this database, and in a read-only mode.

Automotive Parts. As another example, another forensic laboratory is cataloging parts and collecting part numbers of all automobiles manufactured, both foreign and domestic. (The idea was originally championed and developed by the Royal Canadian Mounted Police.) In an explosion, the identifying number might be broken into two or more parts. The goal is to be able to access that number, or number fragment, and identify the part and the manufacturer.

In this case, even though one can envision a huge number of records, the number of tables would probably be small. A large number of records is not an issue. Say that one has 5,000 company entries and a couple of million part entries; there are still only two tables, and the structural complexity of this database is relatively minuscule, even though one has millions of records. Database complexity is not obtained when one simply has millions of records, but rather when one has these records spread over many different tables.

Crystal Patterns. There exists a diffraction pattern database whose structure is simple. A crystal structure for a selected material is obtained from an x-ray experiment, and the lattice parameters are submitted to the database manager for incorporation. Here, though, there might be

three or four different submissions for nominally the same material. A record of crystallographic information may be deleted after 20–25 years, or whenever a better recognized structure has been determined. This database is constantly upgraded and published every 2 years; one must purchase a license to access it.

Legal Aspects

Uniqueness of Forensic Samples. By definition, physical evidence is circumstantial evidence. This means that, in court, one tries to provide as much circumstantial evidence as possible to convince a judge and jury. From a forensic point of view, one attempts to identify samples by as many techniques as are practical. This strategy increases the probability that the substance is what one thinks it is. If it is not possible to uniquely identify samples in this manner, then one tries to supply a limited list of possibilities for the forensic sample.

Comments on Courtroom Procedures. In the past, the only questions have been those of sample collection, sample custody, and procedures. It is important how the sample was collected, where the sample has been, whether it was contaminated, and whether it was properly stored. Sample custody procedures and processes are attacked in court; lawyers are not known to attack the validity of forensic analysis.

On the other hand, BATF has recently run into a problem with their firearms database. Error checking and the validity of the database entries have become a significant legal issue. Questions have been asked in court: How well is your error checking done? How is the integrity of your database routinely checked?

The two opposing views may both be correct. The one looks to past events, while the other to possible future courtroom strategies.

TWGMAT - The Next Step

Ultimately, databases, not only from the forensic people in the United States, but also from all over the world, will need to be joined together or otherwise accessed. The concerns will not be limited to the energetic materials discussed here but will encompass a whole host of other topics. There are legal problems and many interesting computer problems (e.g., just getting the data gathered together). A working group ought to be formed to hammer out a proposal that would be submitted to NIJ for funding a technical working group to address these rather massive database problems.

TWGMAT is a collaborative effort among forensic agencies: the FBI, state, local, and several international forensic laboratories. The TWGMAT subcommittees are developing standards (e.g., standards for databases and methods). They have the capability of expanding into other areas such as terrorist applications and improvised explosives. The TWGMAT approach is a systematic way of addressing important forensic issues.

Right now, TWGMAT has three major technical subcommittees operating: (1) the group for fiber analysis; (2) the group for paints and coatings analysis; and (3) the group for glass analysis, the newest group. Each of these groups has a database subcommittee, and the issues that have been discussed here are under consideration by each of the TWGMAT groups. For example: How does one database fiber information? Paint information? Glass information? How does one handle proprietary information?

Some of the participants of this workshop ought to consider becoming part of TWGMAT because the issues discussed today have been and are confronting the other TWGMAT groups. They do not have the level of expertise demonstrated here and could benefit from such expertise. This new group would compliment the other TWGMAT groups.

Summary of Discussions

Energetic materials in the forensic community can be broken down into two major classes: (1) domestic, mainly smokeless powders and (2) international, mainly high-order explosives.

Up to the present time, the smokeless powder database has been sufficient for legal cases. Two situations were distinguished. First, the forensic sample does not have to be uniquely identified. And second, the veracity of the database entries have only recently been questioned in court.

Database complexity is a function of the number of tables and interrelationships, and not sheer volume of records. Specific examples in the areas of energetic materials, paints, automotive parts, and crystal patterns were discussed.

The construction, verification, and modeling of large, complex databases are subjects of ongoing research. To date, databases that contain 50 tables and several thousand attributes have been dealt with.

There was a strong endorsement that a database working group be formed within the TWGMAT organization. The objective of this group is to address database construction, maintenance, verification, and management problems that are currently impeding progress of the three TWGMAT database working groups in fiber analysis, paints and coatings analysis, and glass analysis.

Appendix A:

Details of the Chemical Characterization Research Facilities at the Ignition Combustion Branch (ICB), U.S. Army Research Laboratory (ARL)

Techniques and Facilities

Physical Chemistry, High-Temperature Chemical Kinetics, and Combustion Diagnostics.

Shock-Tube Chemical Kinetics. A gas-driven shock tube (for gas-phase kinetic studies to 4,000 K), including gas handling system; light sources, monochromators, filters, detectors and digital oscilloscopes for microsecond absorption and emission measurements in the ultraviolet (UV), including Lyman alpha vacuum UV; visible (VIS) and infrared (IR), including IR diode laser system; and other laser systems available from other groups.

Low-Pressure Burner Flame Facility. Huntington/Newport low-pressure chamber; McKenna burner with meters-kilograms-seconds (MKS) digital pressure and flow measurement systems; and Laser Photonics IR Diode Laser System, including liquid helium cryogenic refrigerator, mode selection monochromator, etalon, mercury-cadmium-telluride (MCT) detector, lock-in amplifiers (two), and personal computer (PC)-based data-acquisition board and software. Argon ion laser for fluorescence/Raman measurements. Other available flame diagnostics include thermocouples, UV/VIS absorption and emission spectroscopy, using Fourier transform infrared (FTIR) and mass spectroscopy (MS) instrumentation listed in the following sections.

Imaging and Visualization of High-Speed Events. Cordin Image Converter Camera Systems (two each) with streak and framing plug-ins for nanosecond to millisecond visualization, absorption, and emission and Raman spectroscopy in the visible spectral region.

Analytical (Organic/Inorganic/Polymer) Chemistry, Moderate-Temperature Chemical Kinetics, and Ignition (Pyrolysis) Diagnostics.

Thermal Analysis (Differential Scanning Calorimeter [DSC], Thermal Gravimetric Analyzer [TGA]). Mettler 3300 DSC (with cryogenic accessory), Mettler TGA, and Cahn microbalance.

FTIR-Raman Spectroscopy and UV/VIS Spectroscopy.

- (1) Bomem DA8 FTIR, 0.02-cm⁻¹ resolution, with FTIR-Raman accessory and Nd:YAG laser.
- (2) Mattson RS1 FTIR: Includes Polarization Modulated (PM) FTIR spectrometer driven by a Dell Pentium processor. Includes a Harrick refractor reactor for temperature, an ambient atmosphere control, and in situ characterization of surfaces. The Mattson PM-FTIR employs a differential reflectance spectra obtained by the polarization modulation of the FTIR interferograms from measurements of the signal during each modulation cycle. This instrument is valuable in probing the characteristics of thin films and monolayers at reflective surfaces.
- (3) Mattson Sirius 100 FTIR, 0.12-cm⁻¹ resolution, Bullseye MCT, InSb, Deuterated Triglycine Sulfate (DTGS) detectors, and external optics for burner flame diagnostics.
- (4) Mattson Polaris FTIR (0.5-cm⁻¹ Spectra Tech IR-Plan IR microscope system with MCT detector), reflectance, and transmission modes.
- (5) FTIR accessories for photoacoustic spectroscopy (with room-temperature and high-temperature capability), diffuse reflectance, pyrolysis diffuse reflectance, variable angle automatic target recognition (ATR), cylindrical internal reflection (CIR), specular reflectance, long-path (20 m) gas studies (including photolysis), variable temperature (-190 to +200° C) measurements, and high-pressure work (diamond anvil cell). Complete collection of digital Sadtler condensed vapor phase and specialty IR spectral libraries.
- (6) Hewlett Packard (HP) model 8453 diode array UV/VIS (190–820 nm) spectrometer with UV-VIS ChemStation and full-feature Windows-based software control.

High-Pressure Liquid Chromatography (HPLC) and Gel Permeation Chromatography (GPC).

- (1) HPLC: The ISCO Company, model 2350 pumping system with 2360 gradient controller, Thermo Separation Products SpectraFocus (1-, 2-, 3-wavelength or scanning) UV/VIS detector with PC-1000 operating system (OS)/2-based acquisition software (90-mHz Pentium Workstation), ISCO ChemResearch data acquisition software, ISCO V-4 variable wavelength detector, and Gilson 201 programmable fraction collector.
- (2) GPC: ISCO 2350 pumping system, and UV/VIS and refractive index detectors.

High-Performance Liquid Chromatography-Mass Spectroscopy (HPLC-MS). HP 5988A mass quadrupole mass spectrometer with electron impact (EI) and chemical ionization (CI) and negative ion, HPLC-MS interface, HP 1050 isocratic HPLC pump, HP 5980 GC (for gas chromatography [GC]-MS), 1.4-mbyte HP 9000/236 (59970B) computer, 81- and 15-mbyte disk drives (Local-Area Network [LAN], National Institute of Standards and Technology [NIST]) mass spectral library.

Supercritical Fluid Extraction (SFE), Reaction, and Chromatography.

- (1) Computer Chemical Systems (CCS) model 3100, 10,000-psi SFE system.
- (2) CCS model 3100-100, 10,000-psi SFE system with dynamic and static modes and CCS model OM-300 solvent modifier addition module.
- (3) CCS model 5000 supercritical fluid chromatography (SFC) system, (configured for operation up to 10,000 psi and 250° C and can be configured as reactor up to 6,000 psi and 400° C) includes CCS model 301B extractor/accumulator.
- (4) CCS model OM-220 solvent modifier addition and flame ionization detector; specialized (custom built) CCS supercritical fluid equipment includes 3,000-psi 50-ml view cell, gas separator, and variable restrictor/collection modules

- (5) ISCO SFC-500 (with PC interface and software) 50 ml (to 10,000 psi, 0.08 to 600 μ l/min) and ISCO 260D 260 ml (to 7,500 psi, up to 100 ml/min) syringe pumps.
- (6) ISCO heated variable linear flow restrictors.
- (7) Harrick high-pressure (to 5,00 psi) variable path length optical cell for FTIR and FT Raman studies.
- (8) Aabspec high-pressure (to 10,000 psi) back-scattered Raman cell.
- (9) High-pressure equipment manual pressure generators (5,000 and 10,000 psi).
- (10) Heise digital-pressure measurements systems (2,000 and 10,000 psi).
- (11) Water heater/chiller/recirculators (two).
- (12) High-pressure flow cells for ISCO V-4 and TSP SpectraFocus HPLC detectors (can be used with SFC).
- (13) High-pressure extraction vessels (all up to 10,000 psi) including 1-, 6-, 7.5-, 10-, 50-, and 103-ml vessels from CCS, Keystone Scientific, and Autoclave Engineers. This collection of supercritical fluid (SF) handling equipment allows for custom assembly of specialized systems such as a closed-loop CO₂ extractor (for bulk extraction applications) or a spectroscopic solubility measurement system using combinations of high-pressure pumps, flow cells, and extractors.

MS, GC-MS, and Pyrolysis Mass Spectroscopy (PMS). Finnigan Incos 50 quadrupole mass spectrometer with HP 5890 GC, solids probe, chemical ionization, and NIH/EPA mass spectral library. Interface for ionization volume laser photolysis.

Pyrolysis-Gas-Chromatography (PGC)-FTIR-MS (Simultaneous FTIR and MS Data From Single GC Run). Communication Detection System (CDS) 122 Pyroprobe, CDS 330 cryogenic trap concentrator with column cryofocuser, HP 5890 GC with thermal conduction detector (TCD) and flame ionization detector (FID), HP 5965B dedicated IR (FTIR) detector (IRD) with array processor, HP 5980 mass selective (quadrupole) detector (MSD), HP ChemStation Software, EPA vapor phase FTIR and NIST/Wiley MS libraries.

Surface Microscopy and Elemental Analysis. JEOL 820 scanning electron microscope (SEM), and Kevex Delta Class x-ray fluorescence attachment with light element (down to boron) detector.

Visible Laser/Raman System. Lexel Model 95 Argon ion laser, Jarrel-Ash 0.25-m monochromator, EI&G Model 1455 intensified linear diode array, and an EI&G Model 1460/1463 controller.

Novel Optical Chemical Sensors.

Laser-Induced Breakdown Spectroscopy (LIBS) Sensors. LIBS is based on laser induced plasma emission spectroscopy. We are developing LIBS for trace metal and trace explosives detection. LIBS utilizes a compact Nd:YAG laser (up to 200 mJ/pulse, capable of field application), fiber-optic delivery, and photodiode/capacitor-coupled detector (CCD) array detection.

Near Infrared Tunable Diode Laser Sensors (NIR-TDL). Compact NIR-TDLs operating at room temperature can be used for the detection of numerous gases of environmental interest by sensitive frequency modulated vibrational/electronic absorption spectroscopy.

Acoustic Optic Tunable Filter (AOTF)-Based Sensors. AOTFs are inherently compact and rugged with very low power requirements. Their use in fieldable sensors for chemical contamination is being explored utilizing spectroscopic techniques such as LIBS, Raman, and near-infrared (NIR)-absorbance/reflectance. AOTFs cover the wavelength range from 0.2 to 2 μm .

Fast Flow Reactor/Triple Quadrupole Mass Spectrometer (TQMS). A flow reactor is capable of examining radical-radical reactions and their kinetic rate constants. The flow reactor has two microwave discharges to produce the radicals. The temperature of the flow reactor can be varied so that temperature-dependent measurements of kinetic rates can be determined. The output of the flow reactor is sampled by a molecular beam sampler to introduce small portions to a triple quadrupole mass spectrometer to allow for product determination from the reactions studied.

Miscellaneous Equipment Available in the Propulsion and Flight Division (PFD). Mettler-Parr model DMAs ultrasonic calculating density meter, Brinkman 672 autotitrator with computer interface, accelerating rate calorimeter, Parr combustion calorimeter, ISI SEM, dynamic mechanical analyzer, high-rate mechanical properties testers, low- and high-pressure (50 Kpsi) strand burners, closed bombs to 200 Kpsi, and all kinds of lasers and related spectroscopic techniques, etc.

Appendix B:
Development of the Workshop Focus Questions

In order to address the problems actually facing the forensic agencies, it was decided to formulate a set of potential workshop questions and send them to the four forensic agencies for comment. These questions were based on the dialog, comments, and notes from the forensic tour of 31 January 1996.

- (1) It is assumed that the major forensic interest in energetic materials lies with black powder and smokeless powder and that these energetic materials have the highest priority. Are there any other high-priority energetic materials? If so, which ones?
- (2) What specific entries in a database are desired (e.g., spectra, physical parameters, etc.)?
- (3) What items (types of entries) already exist in database format? How do you access them? (i.e., do you think entry and retrieval could be improved? If so, what would you like to see?)
- (4) What do you think is necessary to bring existing or contemplated databases to "courtroom" quality?
- (5) Is ISO-9000 important? If so, how?
- (6) What is the top item(s) on your wish list (i.e., complete this sentence: "We really need...XX...;" where XX = a method, or a type of information, or a device, etc.)?

All four agencies responded, and, from their written comments, we determined that the two focus questions for this workshop should be:

- (1) What is required for a sample to be traceable to a unique compound (or unique class of compounds)?
- (2) How can the present databases be made into user-friendly, complete, and current databases, accessible by all forensic laboratories?

These two questions were then recirculated to the forensic agencies for additional comment. All agreed that the questions as stated were reasonable ones for the workshop. A letter of invitation was then extended to approximately 30 forensic scientists and researchers.

Appendix C:

Workshop Details

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Dear Colleague:

You are invited to attend a 1-day, unclassified workshop, entitled: "Forensics: Energetic Materials Measurement, Analysis, and Databasing," which will be held on Thursday, 20 June 1996 at BRL Hall (Bldg. 330), located at the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground (APG), MD. The workshop focuses on two questions.

- (1) What is required for a sample to be traceable to a unique compound (or unique class of compounds)?
- (2) How can the present databases be made into user-friendly, complete, and current databases, accessible by all forensic laboratories?

The workshop purposes are:

- (1) to define the critical problems that cut across forensic agencies;
- (2) to provide an open, multidisciplinary forum in which these problems can be addressed and better defined; and
- (3) to lay the foundation for practical, timely, and cost-effective solutions.

The workshop agenda is enclosed. The more formal presentations are made in the morning sessions, while the afternoon sessions are reserved for open, intensive, and extensive discussions.

In order to keep the number of participants small (for effective interactions), this 1-day workshop is limited to government agencies and attendance is by invitation. Alternate or additional government employees who would benefit from attending this workshop are welcome. A response form is enclosed; please fill out and fax to the number stated before 28 May 1996. This will greatly ease the logistics planning for 20 June.

For efficiency and accuracy in assembling a proceedings, the audio portion will be taped and transcribed. In order to encourage frank and open discussions, anyone stating his or her opinions has right of "first refusal" with respect to correcting, deleting, or qualifying any of their verbal statements. (No videotape of the workshop sessions has been planned.)

While the workshop is unclassified, you will need an ARL security badge to enter the compound. To improve the efficiency of the badging process, kindly fax the enclose security form, unless you are not planning to attend.

Sincerely,

Joseph M. Heimerl
Ignition and Combustion Branch
U.S. Army Research Laboratory

Encls: Response form, Security form, Directions to ARL/APG, Agenda for workshop, and list of initial invitees.

Forensic Workshop Response Fax

WEAPONS TECHNOLOGY DIRECTORATE *PROPULSION AND FLIGHT DIVISION* Aberdeen Proving Ground, MD

Fax Transmission Cover Sheet

Date (by 28 May 1996):

To: J. M. Heimerl
Organization: AMSRL-WM-PC
Office Phone No.: 410-278-6111
Fax No.: 410-278-6150

From: _____
Organization: _____
Office Phone No.: _____
Fax No.: _____

Subject: Response form for attendance at the Workshop: "Forensics: Energetic Materials Measurement, Analysis, and Databasing," Thursday, 20 June 1996, at BRL Hall, Bldg. 330, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005-5066.

ADDITIONAL NAME(S):

_____ WILL ATTEND

_____ PLAN TO ATTEND

_____ WILL NOT ATTEND

(IF ATTENDING OR PLANNING TO ATTEND, REMEMBER TO FAX SEPARATE SECURITY FORM(S) TO CAROL FIFE, ARL SECURITY, FAX: 410-278-7675.)

Forensic Workshop Participants

20 June 1996

<u>Name</u>	<u>Organization</u>
Todd H. Anderson	Office of Special Technology (OST), Technical Support Working Group (TSWG)
Kenneth Basom	Naval Surface Warfare Center (NSWC), Indian Head (IH) Division
Steve Burmeister	Federal Bureau of Investigation (FBI)
Stan M. Caulder	NSWC-IH
Robert Daniel	Ignition and Combustion Branch (ICB), U.S. Army Research Laboratory (ARL)
Linda Deel	Bureau of Alcohol, Tobacco, and Firearms (BATF)
Pete Dreifuss	BATF
Alim Fatah	National Institute of Standards and Technology (NIST)
Frank T. Fox	Federal Aviation Administration (FAA)
Joseph M. Heimerl	ICB-ARL
Mark Kindl	Information Science and Technology Directorate (ISTD), ARL
Kevin L. McNesby	ICB-ARL
Al Mercado	Federal Aviation Administration (FAA) Technology Center
Charlie Midkiff	BATF
Andrzej Miziolek	ICB-ARL
Rose A. Pesce-Rodriguez	ICB-ARL
Ralph D. Semmel	The Johns Hopkins University (JHU), Applied Physics Laboratory (APL)
Mary Tungol	FBI
Cynthia Wallace	BATF
Allan N. Walters	U.S. Postal Service
Lou Wasserzug	Naval Explosive Ordnance Disposal Technology Division (NAVEODTECH)
Jeffrey M. Widder	ICB-ARL

Appendix D:
Workshop Evaluation

In order to obtain some feedback on the technical and administrative aspects of the workshop, an evaluation form was constructed and distributed to each attendee at the very end of the sessions. (A copy of this form is given at the end of this appendix.) There were seven written responses with the distributions given as follows.

(1) How well were the purposes met relating to SAMPLE UNIQUENESS?

	<u>GOOD</u>	<u>OK</u>	<u>POOR</u>
(a) defined the critical problems	6	1	0
(b) provided an open, multidisciplinary forum	7	0	0
(c) laid the foundation	5	2	0

Comments

- 1) "Did not talk much about finding solutions."
- 2) "Determination of sample uniqueness will only follow compilation and substantial use of databases."

(2) How well were the purposes met relating to CURRENT DATABASES?

	<u>GOOD</u>	<u>OK</u>	<u>POOR</u>
(a) defined the critical problems	4	3	0
(b) provided an open, multidisciplinary forum	5	2	0
(c) laid the foundation	3	4	0

Comments

- 1) "Have attendees who have databases provide an overview of the use and contents of them."
- 2) "Databases flushed out well in discussion."
- 3) "Need to include person more experienced in database warehousing to prevent rediscovering the wheel."

(3) What would you do differently?

Comments

- 1) "More focus on the problem to be solved."
- 2) "Good workshop; do it again!"
- 3) "Less open seating to force people together."
- 4) "Improve focus with each successive meeting."
- 5) "Within the defined goals, would run workshop similarly."

Interpretation

My interpretation of the responses: the workshop did a good job of addressing the SAMPLE UNIQUENESS question, and the CURRENT DATABASES question was less well addressed.

"Forensic" Workshop Evaluation Form

This workshop was to focus on two questions:

- (1) What is required for a sample to be traceable to a unique compound (or unique class of compounds)?
- (2) How can the present databases be made into user-friendly, complete, and current databases, accessible by all forensic laboratories?

The workshop purposes were to:

- (1) define the critical problems that cut across forensic agencies;
- (2) provide an open, multidisciplinary forum in which these problems can be addressed and better defined; and
- (3) lay the foundation for practical, timely, and cost-effective solutions.

(1) How well were the purposes met relating to SAMPLE UNIQUENESS?

- | | | | |
|---|------|----|------|
| (a) defined the critical problems | GOOD | OK | POOR |
| (b) provided an open, multidisciplinary forum | GOOD | OK | POOR |
| (3) laid the foundation | GOOD | OK | POOR |

Comments: _____

(2) How well were the purposes met relating to CURRENT DATABASES?

- | | | | |
|--|------|----|------|
| (a) defined the critical problems | GOOD | OK | POOR |
| (b) provide an open, multidisciplinary forum | GOOD | OK | POOR |
| (c) lay the foundation | GOOD | OK | POOR |

Comments: _____

(3) If you were to host a similar workshop, what would you do differently? _____

(4) Additional Remarks: _____

(5) Optional: (AGENCY): _____ and/or (NAME): _____

THANK YOU!

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13. ABSTRACT (Maximum 200 words) On Thursday, 20 June 1996, this workshop was convened at BRL Hall (Bldg. 330), located at the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground (APG), MD. The purposes of this workshop were: (1) to define the critical problems that cut across forensic agencies; (2) to provide an open, multidisciplinary forum in which these problems could be addressed and better defined; and (3) to lay the foundation for practical, timely, and cost-effective solutions. The technical focus of the workshop pivoted on two questions: (1) What is required for a sample to be traceable to a unique compound (or unique class of compounds)? (2) How can the present databases be made into user-friendly, complete, and current databases, accessible by all forensic laboratories? This report documents the background leading up to the calling for a workshop, the manuscripts of the talks given, and the discussion held.				
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