

TECHNICAL NOTE

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A Gradient Reversed Phase HPLC Procedure for Smokeless Powder Comparison*

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ABSTRACT: Smokeless powder comparisons are commonly carried out by extracting additives and stabilizer degradation products from the powder using methylene chloride, and analyzing the results by gas chromatography/mass spectrometry. Some of these components are thermally unstable, making comparison of similar powders or of powders originating from different manufacturing lots difficult when GC is used. Isocratic HPLC analysis using C-18 stationary columns can be unsatisfactory due to a wide range of polarities of the additives and stabilizer degradation products and the presence of geometrical isomers. In this paper, a gradient procedure using a C-8 column is described for the analysis of smokeless powders. The procedure provides separation of a wide range of components present in smokeless powders. In this work, analytical figures of merit are provided, UV spectra of each of the components are presented, and the procedure is evaluated by comparing four different lots of smokeless powder from the same manufacturer.

KEYWORDS: forensic science, smokeless powders, explosives, high-performance liquid chromatography, gradient HPLC

In recent years there has been an increasing awareness of the problem of easy access to the materials needed to produce improvised explosive devices. A number of high-profile incidents have involved such devices, from the Unabomber case to the bombing in Atlanta during the Olympics. The United States Bureau of Alcohol, Tobacco and Firearms has reported that fully half of the pipe-bombing incidents they investigate contain smokeless powder fillers (1). Smokeless powders are composed predominantly of nitrocellulose. Double-base powders, which combine nitrocellulose with nitroglycerine, are also common. In addition to these major components, a variety of additives are also included in the mixture to promote stability, aid in processing, and to affect burn rate. The detection of these additives and their breakdown products provides an opportunity for the analyst to produce distinct profiles for different varieties of powders.

There have been a variety of different procedures proposed for the analysis and detection of the additives and stabilizer degrada-

tion products in these materials. Most commonly, smokeless powders are analyzed using gas chromatography/mass spectrometry, as such systems are ubiquitous in forensic laboratories (2–5). Typically the NG and other additives present in the powder are extracted into methylene chloride and injected into the system. The inherent instability of these reactive mixtures can be a problem when powder extracts are subjected to the elevated temperatures utilized in GC injector ports. This is particularly true if quantitative results are required. To solve this problem, cold, on-column injection can be utilized (2), however active sites on the capillary can still pose problems.

To provide quantitative analysis of these materials, alternative techniques such as liquid chromatography and capillary electrophoresis have been proposed (6–10).

Quantitative techniques can be particularly important in the determination of the stability of these powders, a concern when large quantities are placed in storage (6). The ultimate goal of the forensic analyst is a similar one—the detection of components in the powder that give it a unique profile. For example, the buildup of byproducts due to the decomposition of these powders can also be utilized in the detection of lot-to-lot variations between similar propellants. An additional source of variation between similar powders is the introduction of components from reprocessed or outdated powders. It should be noted that smokeless powders are manufactured and sold based on their characteristics as a propellant. Minor variations in product composition can occur as manufacturers adjust various components to achieve a particular burn rate.

In this report we detail a procedure for the detection of components in smokeless powders by gradient HPLC. Previous reports have emphasized the difficulty of separating geometrical isomers such as nitrotoluenes and nitrodiphenyl amines. Bender has recommended a normal phase gradient HPLC system to alleviate these problems (7). We have developed an alternative procedure using gradient reversed phase HPLC. Through careful optimization, this technique provides exceptional separation of the additives and stabilizer degradation products present in smokeless powder and permits the comparison of lot-to-lot variations in composition.

Materials and Methods

Preparation of Samples

The explosive samples were extracted using the following procedure: 5 mg of the powder was placed into a small vial and dissolved in 250 μ L of methylene chloride. The mixture was then al-

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lowed to sit overnight in the absence of light. 20 μL of the mixture was then decanted into a small, clean, and dry vial. The decanted mixture was blown dry by using a light stream of nitrogen gas and diluted with 40 μL of HPLC grade methanol, and 20 μL of sample was then injected into the HPLC system.

Liquid Chromatography

The liquid chromatographs used were a Hewlett Packard 1050 with a photodiode array detector (Agilent Technologies, Palo Alto, CA) and a Spectraphysics 8875 autosampler and 8850 pump (Thermo Separation Products, Schaumburg, IL) with a Kratos Spectraflow 773 detector. The Hewlett Packard system was connected to a computer for data storage and retrieval and used ChemStation software (Agilent Technologies, Palo Alto, CA), which contained UV spectral library and search routines. Optimization of the HPLC gradient was performed utilizing DryLab Software (LC resources, Lafayette, CA). The software utilized two separate isocratic runs to calculate the final gradient mixture. The mobile phase program consisted of a gradient from 36% methanol at 0 min to 80% methanol at 25 min. The flow rate used was 1.0 mL/min, and the column was a Restek Pinnacle C-8, 150 \times 4.6 mm with a 5 μm particle size. Sample detection was carried out using the photodiode array detector with a wavelength range of 210 to 600 nm and a nominal wavelength of 230 nm.

Data Reduction

The data obtained from each run consisted of a chromatogram of the powder and UV spectra from each peak in the chromatogram. The UV spectra obtained from individually run standards were stored in a software library file for later retrieval and peak matching. Individual powder samples were then run and component peaks were identified by comparison with retention times and stored peak apex spectra in the UV spectral library.

Results and Discussion

The goal of this research was to produce a reversed phase, gradient HPLC procedure for analyzing smokeless powders. In this method we describe a gradient procedure utilizing a C-8 column that allows for the separation of geometric isomers and is compatible with LC/MS. The procedure permits the analysis of lot-to-lot variations and can be used to obtain specific information on powder samples recovered from pipe bombs.

Methods Development and Powder Identification

The initial phase of the study involved the identification of some of the most common organic components in smokeless powders. To aid in these efforts, a standard was prepared consisting of 16 different compounds found in smokeless powder. While not all-inclusive, this standard consisted of a mixture of components of varying polarity and structure for use in optimizing and characterizing the HPLC procedure. The mixture contained 1 mg/mL of each component in 25 mL of acetonitrile and was kept stored at 4°C. All standards were prepared in acetonitrile to improve solubility. A working standard containing a $1/20$ dilution of the standard in methanol was then prepared, and 2 different isocratic HPLC runs were made. The data from these two runs were fed into Drylab HPLC simulation software, and an optimized gradient of 36 to 80% methanol at 1 mL/min was developed. The standards were then run with the given procedure and the chromatogram and spectra obtained. Figure 1 shows the chromatogram of the standard, and Fig. 2 shows the individual spectra for common components in smokeless powders. The spectra for the individual standards were stored within the built-in library function of the ChemStation software. Common components not present in the initial standard, such as *N*-nitrosodiphenylamine and additional nitrodiphenyl amines, were added to the library as well. The separation of the structurally similar dinitrotoluenes and nitrotoluenes proved to be possible with this method, as shown in Fig. 1.

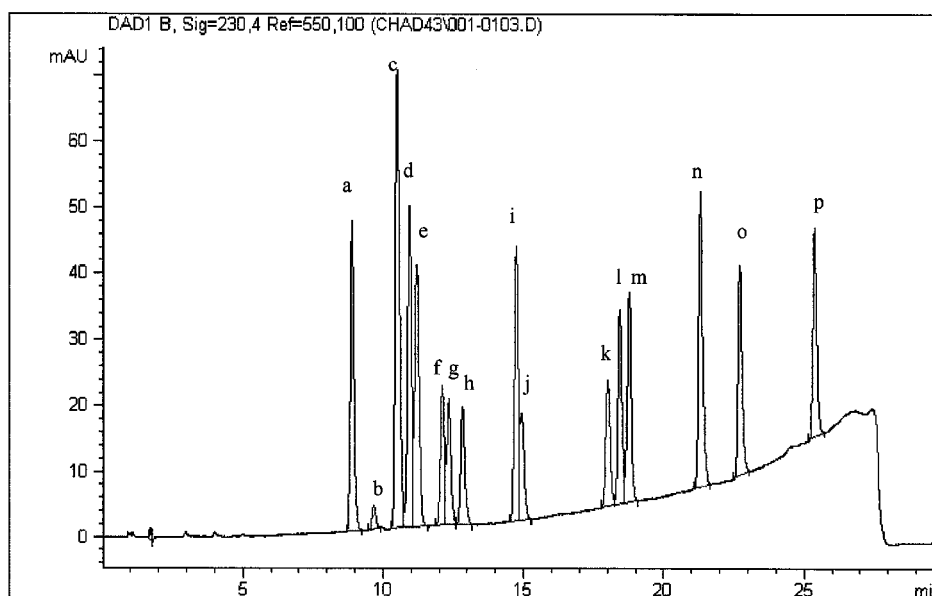


FIG. 1—Chromatogram of standards of common additives in smokeless powders at 230 nm using a Restek Pinnacle C8 column with a methanol/water gradient. Other conditions as reported in the text. Peak identity: (a) dimethyl phthalate, (b) nitroglycerin, (c) 2,4-dinitrotoluene, (d) 2,6-dinitrotoluene, (e) 2,3-dinitrotoluene, (f) 2-nitrotoluene, (g) 4-nitrotoluene, (h) 3-nitrotoluene, (i) diethyl phthalate, (j) 4-nitrosodiphenylamine, (k) methyl centralite, (l) 4-nitrodiphenylamine, (m) diphenylamine, (n) 2-nitrodiphenylamine, (o) ethyl centralite, (p) dibutyl phthalate.

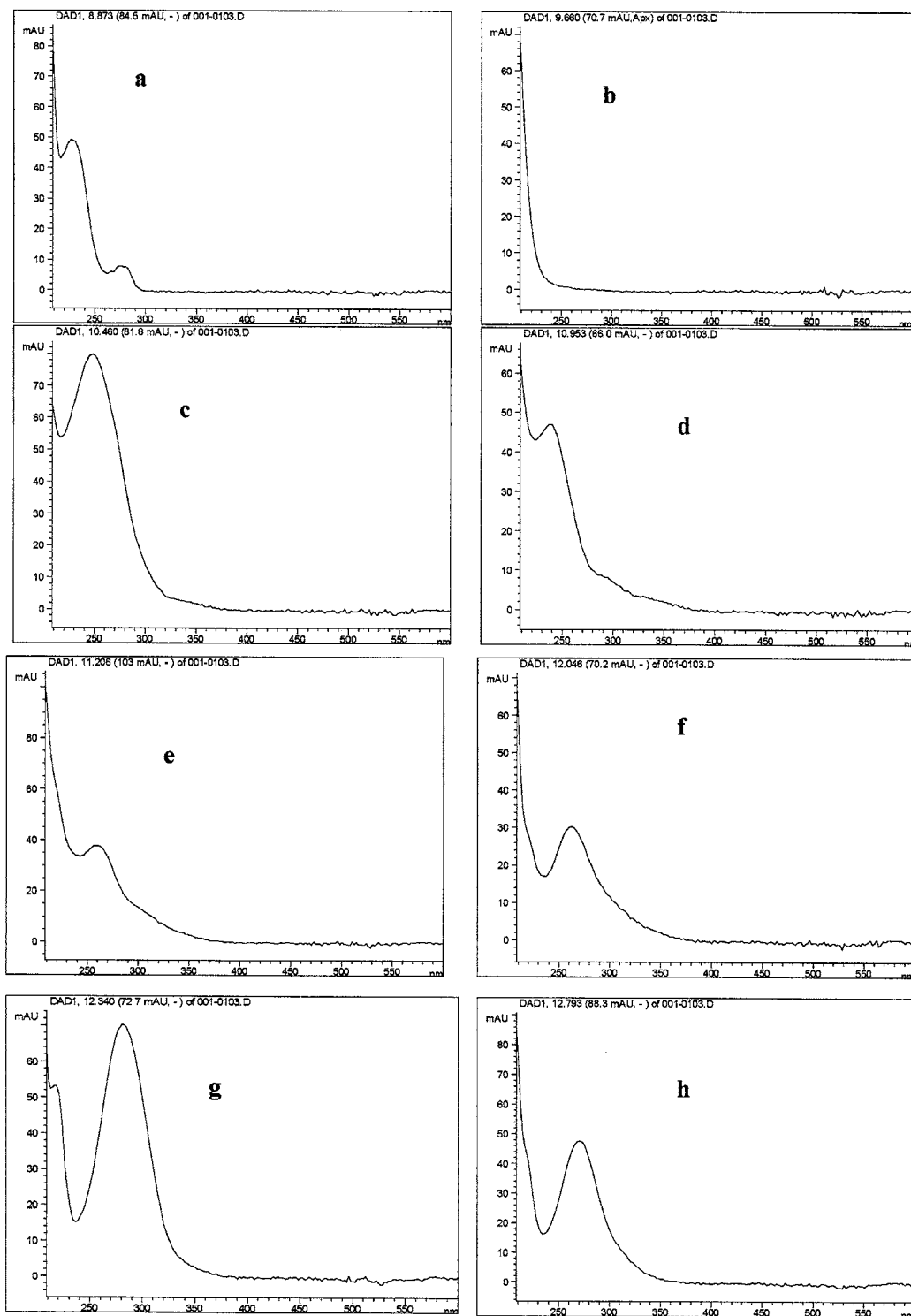


FIG. 2—UV spectra of peaks a-p from the standard. Conditions as in Fig. 1. Peak identity: (a) dimethyl phthalate, (b) nitroglycerin, (c) 2,4-dinitrotoluene, (d) 2,6-dinitrotoluene, (e) 2,3-dinitrotoluene, (f) 2-nitrotoluene, (g) 4-nitrotoluene, (h) 3-nitrotoluene, (i) diethyl phthalate, (j) 4-nitrosodiphenylamine, (k) methyl centralite, (l) 4-nitrodiphenylamine, (m) diphenylamine, (n) 2-nitrodiphenylamine, (o) ethyl centralite, (p) dibutyl phthalate.

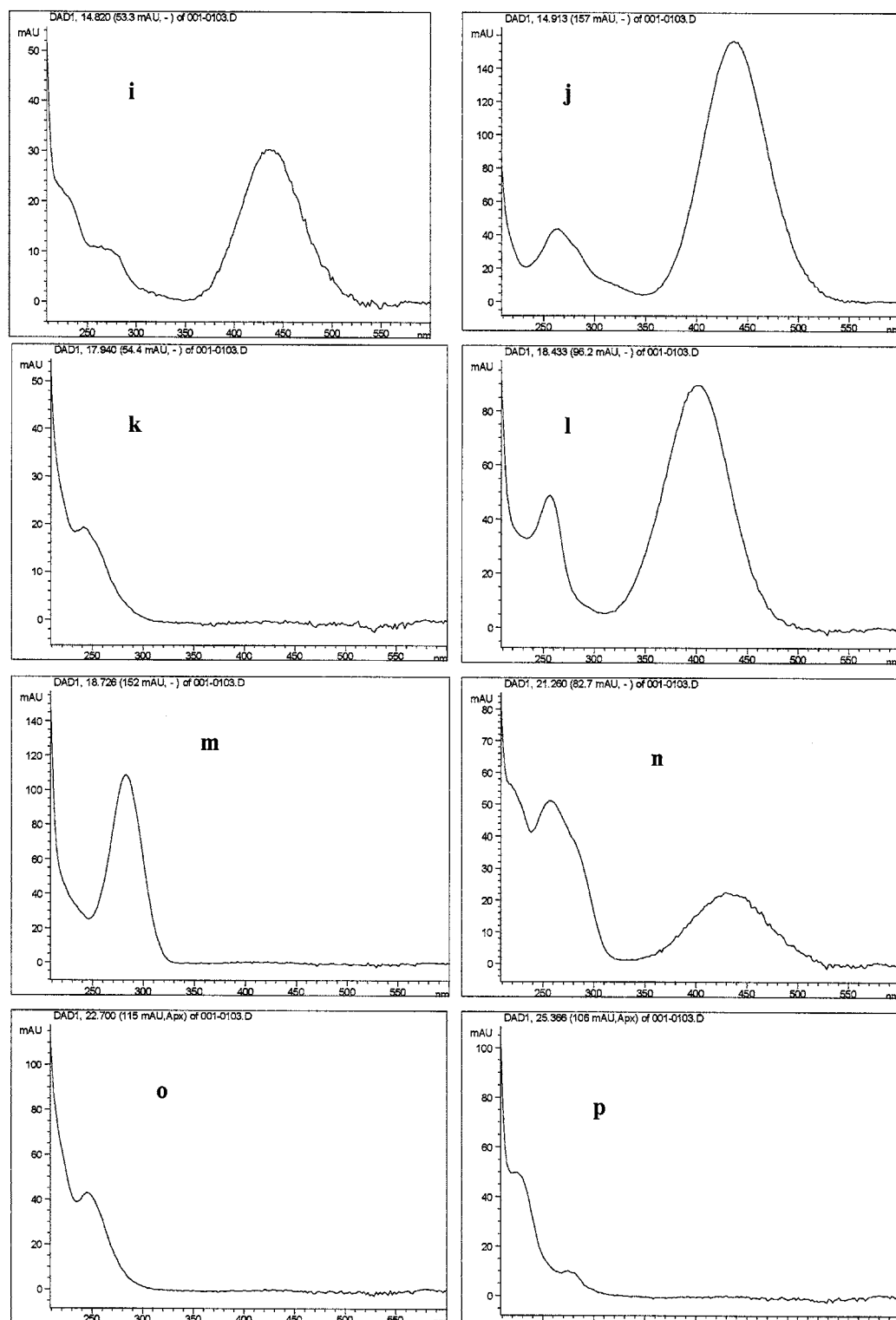


FIG. 2 (continued)

Reproducibility and Detection Limits

To determine the reproducibility and detection limits of the method, serial dilutions of individual standards ranging from 1 to 1000 $\mu\text{g/mL}$ of 2,4-dinitrotoluene, ethyl centralite, and diphenylamine were prepared and run. The chromatograms were obtained

and integrated by the software and statistical analysis performed on the data. The detection limit for these three compounds ranged from approximately 1.0 to 0.5 $\mu\text{g/mL}$, and there was a linear relationship between concentration and peak area over the entire range. The reproducibility of retention times was determined to be 0.5% RSD for ten replicate runs of the ethyl centralite peak at 22.68 min.

In the next set of experiments, a series of common smokeless powders were analyzed using the method. These powders included Hercules (Alliant) Green dot, Red dot, Bullseye, IMR HI Skor, IMR 4350, IMR 4381, IMR 7828, and Winchester Super Target. All peaks obtained from each chromatogram were then searched against the library of standards and checked for peak identity. If no match was obtained, the peak and its spectra were saved as an unknown in the built-in library. Samples containing significant unidentified peaks were injected on a Finnigan GCQ (ThermoQuest, Schaumburg, IL), GC/MS system for further analysis. This technique was particularly useful for the identification of various phthalates that are used as plasticizers in these powders. Samples of these and other components were then obtained and added to the spectral library. Figure 3 shows sample chromatograms from some of the smokeless powders used in the study with labeled peaks. These powders all showed a variety of

different additives and stabilizer degradation products, and the chromatograms clearly illustrate variations in the concentrations of these components.

Lot-to-Lot Comparisons

The next phase of the study involved probing the possibility of utilizing this technique to characterize differing manufacturing lots of smokeless powders. We modified the extraction technique reported by Martz (2) in which the powder sample was extracted in a small vial containing methylene chloride. We then removed a small amount of sample, evaporated it to dryness, and reconstituted it in methanol for injection into the HPLC. The advantage of using methylene chloride as an extraction media was that the nitrocellulose remained insoluble. To check that the results of this extraction were not biased by time or by interference from the nitrocellulose,

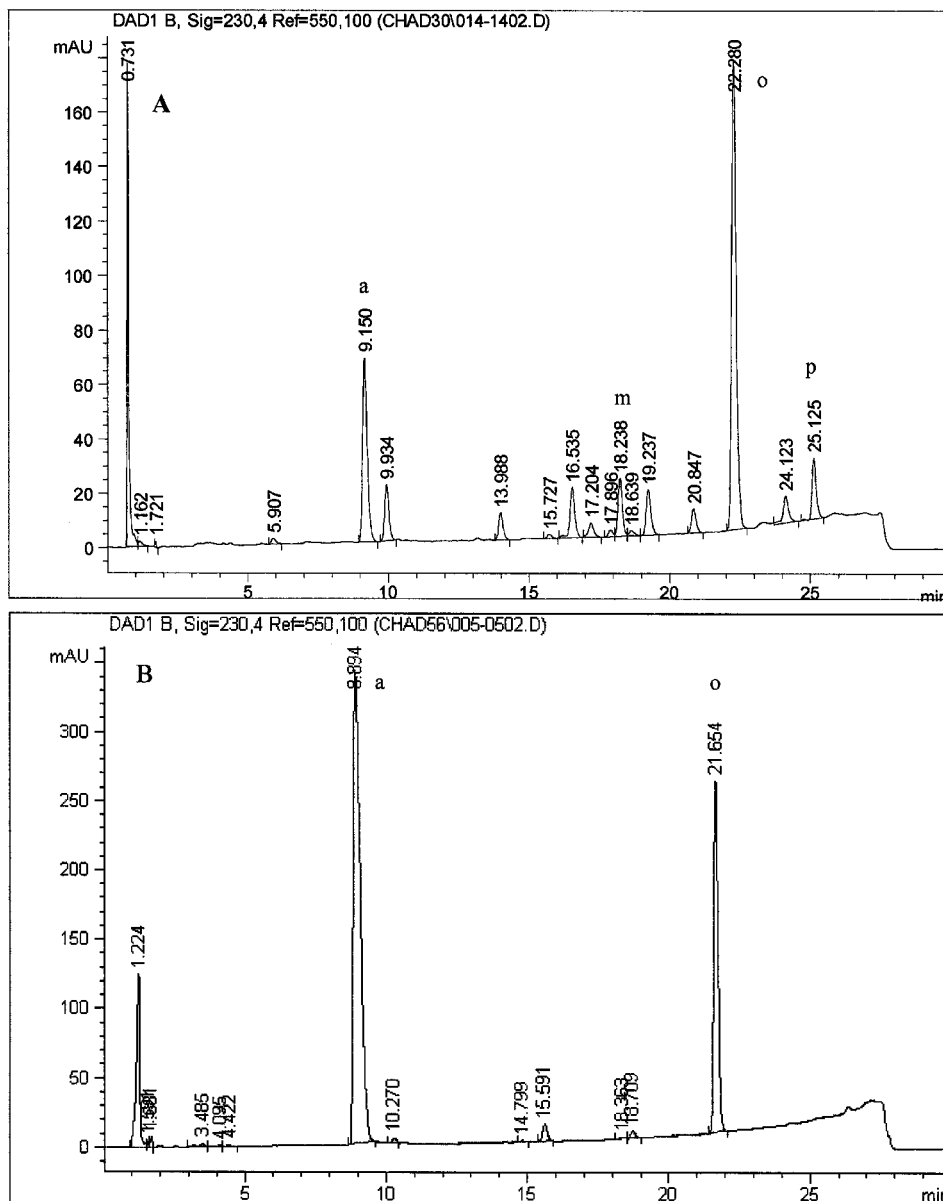


FIG. 3—Chromatograms of (A) Winchester Ball Powder and (B) IMR 700-X; peak identity: (a) nitroglycerin, (m) diphenyl amine, (o) ethyl centralite, (p) dibutyl phthalate. Analysis conditions as in Fig. 1.

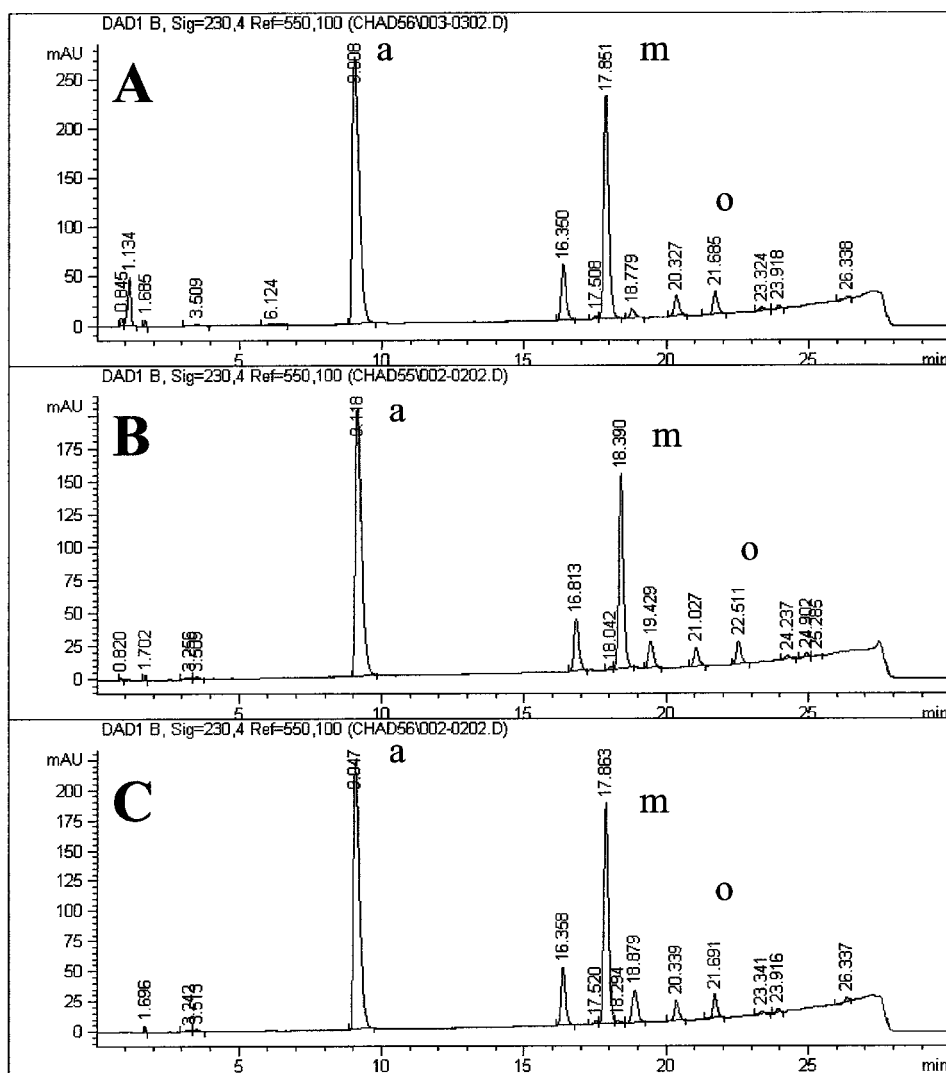


FIG. 4—Results of the extraction of Red Dot Powder using different extraction procedures. HPLC conditions as in Fig. 1. (A) Extraction in MeCl_2 overnight, (B) extraction in MeCl_2 at 1 week, and (C) extraction in acetone for 6 h followed by precipitation of dissolved nitrocellulose. Peak identity: (a) nitroglycerin, (m) diphenylamine, (o) ethyl centralite.

an experiment was performed in which a sample as examined using the standard overnight extraction as well as with a 1 week extraction period. Relative peak heights were consistent between the two samples, Fig. 4A and 4B, although a minor peak appeared in the 1 week extraction at 26.337 min. A third comparison sample (Fig. 4C) of the same powder was prepared by completely dissolving the sample including the nitrocellulose in acetone. The nitrocellulose was then precipitated through the addition of water, and the sample was centrifuged. The supernatant was then injected on the HPLC and compared with the previous two results. As shown in the figure, with the exception of a difference in intensity for an unknown peak at 18.779 min, and a not unexpected increase in extraction efficiency from A–C, the results from the acetone extractions and the methylene chloride extraction are nearly identical.

Samples of four different lots of Hercules Red Dot powder (presently manufactured by Alliant Powder) were next examined and chromatograms and spectra obtained, Fig. 5. The chromatograms illustrated the utility of the technique in identifying lot-to-lot variations among the powder samples. The results show that

each lot can be defined by the presence of different minor components and through peak ratios of common additives and stabilizer degradation products that were specific to that lot. Though the presence of minor components varied between lots, the main constituents were present in all the powders.

Conclusions

This paper presents a method for the comparison of smokeless powders using reversed phase gradient HPLC. This method can be used to separate geometric isomers of nitrotoluenes and nitrodiphenyl amines present in the additives and stabilizer degradation products of these powders. The technique can also be used to ascertain lot-to-lot variations among different samples of smokeless powders. The combination of retention time and UV spectra of each component can be used to quickly determine the composition of the powder, and the ability to distinguish between lot samples makes this technique a powerful tool for the forensic laboratory.

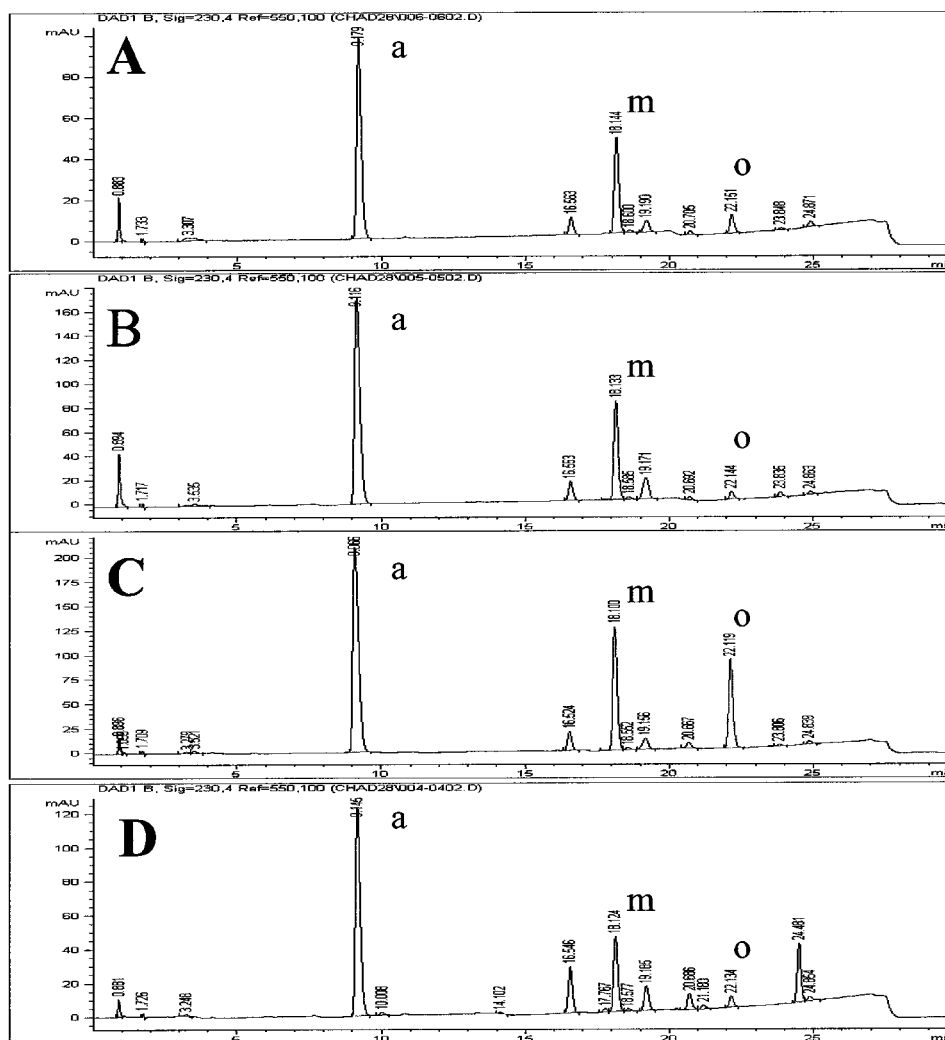


FIG. 5—Analysis of different lot samples of Hercules Red Dot (now Alliant Powder). Powder A—HRD 503, Powder B—HRD 511, Powder C—HRD 532, Powder D—HRD 839. Analysis conditions as in Fig. 1. Peak identity: (a) nitroglycerin, (m) diphenylamine, (o) ethyl centralite.

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References

- Wallace CL, Midkiff CR. Smokeless powder characterization, an investigative tool in pipe bombings. In: Yinon J, editor. *Advances in the analysis and detection of explosives*. Boston, MA: Kluwer Academic Publishers, 1993;29–39.
- Martz RM, Lasswell, LD. Identification of smokeless powders and their residues by capillary column gas chromatography/mass spectrometry. *Proceedings of the international symposium on the analysis and detection of explosives*, Washington, DC: U.S. Government Printing Office, 1983;245–54.
- Trowell JM, Philpot MC. Gas chromatographic determination of plasticizers and stabilizers in composite modified double base propellants. *Anal Chem* 1969;41:166–8.
- Stankovic M, Vujovic B, Filipovic M. Capillary gas chromatography of double-base propellants. *Chromatographia* 1996;42:593–4.
- Kee TG, Holmes DM, Doolan K, et al. The identification of individual propellant particles. *J Forensic Sci Soc* 1990;30:285–92.
- Stine GY. An investigation into propellant stability. *Anal Chem* 1991;63:A475–8.
- McCord BR, Bender EC. Chromatography of explosives. In: Beverage A, editor. *Forensic investigation of explosives*. London: Taylor and Francis, 1998;231–66.
- Bender EC. Analysis of smokeless powders using UV/TEA detection. *Proceedings of the International Symposium on the Analysis and Detection of Explosives*. Washington, DC: U.S. Government Printing Office, 1983;309–20.
- Northrop DM, Martire DE, MacCrehan WA. Separation and identification of organic gunshot and explosive components by micellar electrokinetic capillary electrophoresis. *Anal Chem* 1991;63:1038–42.
- Smith KD, McCord BR, MacCrehan WA, et al. Detection of smokeless powder residue on pipe bombs by micellar electrokinetic capillary electrophoresis. *J Forensic Sci* 1999;44:789–94.

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