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Sampling Protocols for the Detection of Smokeless Powder Residues Using Capillary Electrophoresis

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ABSTRACT: Present techniques for the detection of gunshot residue rely primarily metallic primer components such as lead, barium and antimony. With the advent of reformulated primers that reduce or eliminate these elements, new methods for the detection of organic residue compounds will be needed. Micellar electrokinetic capillary electrophoresis (MECE) is one technique that has been successfully applied to the analysis of these smokeless powder residue compounds.

Protocols for the recovery of the organic residue components under a variety of sampling conditions were evaluated and improved for MECE analysis. The collection of residue samples where external contaminants such as grease or blood were present on the residue substrate were investigated using both tape lifts and solvent swab protocols. In addition, residue component recovery using supercritical fluid extraction techniques was preliminarily evaluated for samples contaminated with blood.

KEYWORDS: forensic science, criminalistics, gunshot residue, sample preparation, capillary electrophoresis, supercritical fluid extraction

TABLE 1—*Common organic additives found in smokeless powders. The abbreviations used in the study and the purpose(s) of the additives are also noted in the table.*

Constituent	Abbreviation	Propellant	Stabilizer	Plasticizer
Dinitrotoluene Isomers	DNT	√		
2,4,6 Trinitrotoluene	2,4,6 TNT	√		
Nitroglycerine	NG	√		
Akardite I			√	
Akardite II			√	
Akardite III			√	
Diphenylamine	DPA		√	
Methyl Centralite (I)	MC		√	√
Ethyl Centralite (II)	EC		√	√
Centralite III			√	√
Dimethylphthalate	DMP			√
Diethylphthalate	DEP			√
Dibutylphthalate	DBP			√
Diamylphthalate				√
Diotyphthalate				√
Camphor				√
Triacetin				√

Within the past decade, ammunition manufacturers around the world have begun to reformulate their firing primers in an effort to decrease or ultimately eliminate the presence of lead, antimony, and barium compounds (1–3). Commonly used gunshot residue tests which are presently available, such as flameless atomic absorption spectrometry (FAAS) and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM/EDX), focus directly on detecting the combined presence of two or more of these characteristic metals in the residue samples (4–6). Examination of the new generation of primer composition will consequently lead to false negatives if residues are analyzed by the currently-available technology.

Smokeless powder, while predominantly composed of nitrocellulose, contains a variety of other organic compounds added to increase the stability and longevity of the powder, improve workability, or enhance the power output during firing (7) (Table 1). These organic additives constitute anywhere from trace amounts up to 50% of the powder mixture (8). The occurrence of a suite of target organic gunpowder additives on the hands of 100 subjects from all walks of life were recently studied (8). With the exception of the ubiquitous phthalate ester plasticizers, no gunpowder additives were found.

The analysis of organic residue components provides a compositional pattern that can be used to illustrate that a residue extracted from an item of evidence is consistent with having originated from a particular source. To analyze the organic constituents in either unfired powder or powder residues, it is necessary to extract the additive compounds from the nitrocellulose matrix. This has often been done with liquid organic solvents, but may also be done with supercritical fluids.

Supercritical fluid extraction (SFE) using carbon dioxide has been investigated for the analysis of propellants and other forensic evidence (9–12). Supercritical fluids combine penetrating power similar to that of a gas with solvating power similar to that of a liquid. In addition, the ability to fine-tune the extraction power of a supercritical fluid by manipulating the pressure or temperature makes SFE a powerful technique for the selective recovery of analytes while excluding coextracted interferences (13). Small amounts of a polar modifier can be added to the carbon dioxide to increase the recovery of polar analytes (14).

Following extraction, the organic constituents are generally separated and detected using a variety of chromatographic and/or spectroscopic techniques. Northrop and MacCrehan first applied micellar electrokinetic capillary electrophoresis to the separation and analysis of smokeless powder additives in the early 1990s (15,16).

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Through the application of a high electric field (250 V/cm) to a buffer solution in a capillary containing charged detergent molecules, the baseline separation of a mixture of 10–15 components of explosives and gunshot residue was achieved in less than 15 min. In these preliminary studies, similar compositional patterns were noted for ethanol extracts of unfired smokeless powder particles and fired residue from the same type of powder. Prior to MECE analysis, solvent-resistant masking tape was utilized to collect gunshot residue particles off shooter's hands.

Any new analytical technique developed for residue examination must not only be sensitive enough to detect small quantities of residue but must also be capable of dealing with samples contaminated with potential interferences such as blood or grease. In this study, test firings of handguns into cloth targets were used to provide residue samples which were deliberately contaminated with blood, grease, hand lotion, motor oil, gun oil, and sweat. The efficacies of several sampling protocols were evaluated for the recovery of the residue compounds from these contaminated samples for detection using MECE. In addition, a database of determined compositional patterns of smokeless powders was compared to a database maintained by the Bureau of Alcohol, Tobacco, and Firearms (BATF).

Experimental

Two capillary electrophoresis systems were used in the studies: a Dionex Capillary Electrophoresis System I[4] and an Applied Biosystems 270A-HT Capillary Electrophoresis system. Separations were carried out in fused-silica columns (75 μm ID, 55 cm separation length) which had no coating on the interior walls. Experimental conditions were based on previous work in this laboratory (15,16). The columns were rinsed with running buffer for 90 s prior to injection. An electrokinetic injection of 5 s at 2 kV was used. Separation occurred within 15 min in an applied electric field of 25 kV. The total time of analysis for one sample, from initial column rinse to final separation, was less than 20 min. A single wavelength absorbance detector using a deuterium lamp set at 200 nm was used for analyte detection. The buffer was composed of a combination of monosodium and disodium phosphate, adjusted with sodium hydroxide to maintain a pH of 7.0 at 15 mmol/L phosphate concentration. Sodium dodecyl sulfate, the detergent used for the micellar separation, was added to the phosphate buffer at a concentration of 25 mmol/L.

Standard solutions of each target compound were prepared in ethanol, limited to about 10 mmol/L to maintain solubility. Individual solutions were combined to obtain a standard mixture whose concentration was approximately 0.8 mmol/L. Both the individual and standard solutions were refrigerated. Figure 1 illustrates the baseline separation of the standard mixture under experimental conditions.

Test residue samples were prepared by firing a handgun into samples of clean cotton/polyester blend fabric (Style #13/327RN15187, Hav-a-Hank). The following weapons (ammunitions) were used: Sentinal 22 caliber revolver (PMC Zapper .22, Pan Metal Corp.); Ruger Security Six 357 caliber revolver (PMC 158 grain JSP, El Dorado Cartridge Co.); M-S Safari Arms 45 caliber autoloader (PMC 230 grain FMJ); Glock 9 mm autoloader (115 grain FMJ, Winchester/Olin Corp.) Subsamples for contamination experiments were prepared by cutting the impacted cloth into sections of approximately 15 by 15 cm. Prior to test firing, the cloth subsections were contaminated by direct coating with the following materials: motor oil (Superflo 10W40, Exxon Corp.), grease (Lubrimatic lithium grease, Witco Corp.), gun cleaning oil (Breakfree Gun Cleaner, San/Bar Corp.), hand lotion (Swiss Formula Skin Lotion, St. Ives Laboratories), human blood (expired virus-screened blood from the blood bank of the Walter Reed Army Medical Center, Washington, DC). Using a muzzle to target distance of 150 cm, two contaminated sample targets and one uncontaminated positive control target were prepared with each weapon and contaminant. After firing, each target was folded and placed in a sealed white envelope and stored at room temperature until analysis.

Smokeless powder residue from the target cloth samples was collected with ethanol-moistened cotton swabs or on 1 cm^2 pieces of adhesive tape. Except for the study involving soluble-adhesive tapes, conventional solvent-resistant masking tape (National Tape) was used for all tape lifts. The tapes were applied to the residue surface with forceps until the tape lost its initial adhesive properties. The tapes were extracted in 1.0 mL ethanol for 20 min using ultrasonic agitation. Following the addition of 10 μL of an internal standard (β-naphthol) and 100 μL or 500 μL buffer, the ethanol was removed by controlled evaporation under reduced pressure in a heated centrifuge system (SpeedVac Concentrator, Savant Instruments, Inc., Farmingdale, NY) over a period of 45 min. Final sample volume was 100 μL or 500 μL, according to the requirements of the study. Evaporated samples were capped and refrigerated until analysis.

Residue sampling with two new types of tape was also studied. A "water soluble" adhesive tape, Mask Plus II Ware Solder and a preproduction tape (#90253298-003) with an "alcohol-soluble" adhesive were kindly provided by the 3M Industrial Tape Division. The same sample collection and preparation protocols as for the conventional masking tape were used.

A Hewlett Packard 7680T Supercritical Fluid Extraction System was used for the extraction of residue from bloodstains. Since several groups have utilized supercritical fluids for the extraction of organic constituents from smokeless powder, experimental conditions were obtained through a literature review (9–12,17). Samples were placed in stainless steel thimbles and 100 μL methanol was added to each sample as a modifier. Supercritical carbon dioxide at a density of 0.74 g/mL (T = 90°C, P = 35 MPa) was used as the extraction fluid. The extraction program consisted of a 15 min static equilibration period followed by dynamic extraction for 15 min. During the dynamic extraction, the analytes were cryogenically deposited by decompression on stainless steel beads in an on-line column, controlled by a variable restrictor valve. The trap was maintained at 40°C and the restrictor at 45°C. The trap was eluted with two sequential 1.0 mL volumes of acetone into glass vials, which were then capped. Following the addition of buffer and internal standard, the acetone was removed by controlled evaporation in a SpeedVac using the same protocol as the tape lifts.

Results and Discussion

Database

Approximately 50 smokeless powders were obtained from the BATF laboratory, of which 28 of the powders had constituents

[4]Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

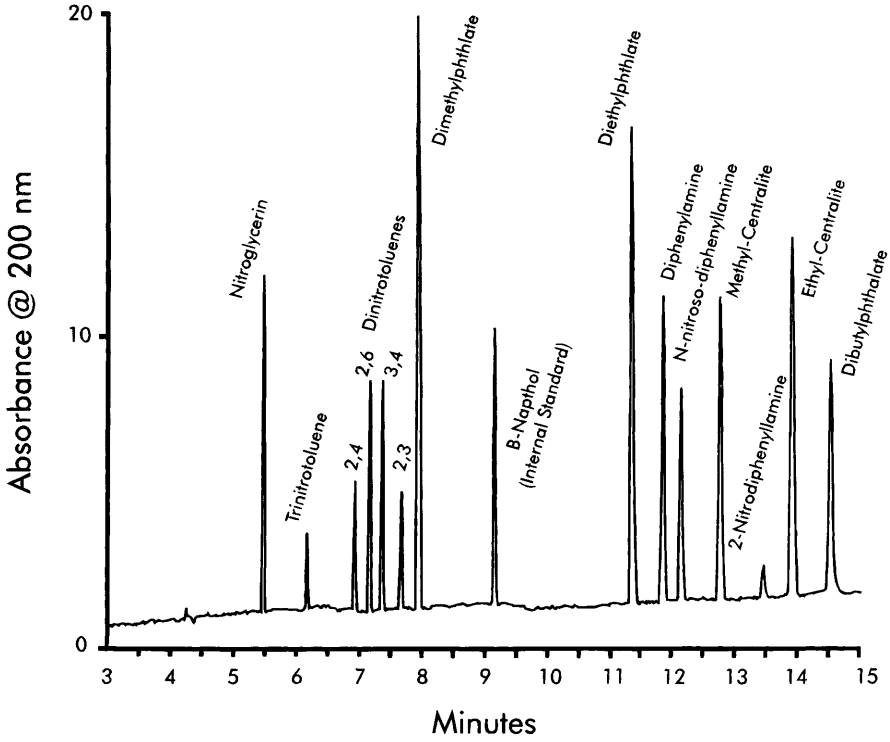

FIG. 1—*Electropherogram of the standard mixture of analytical targets under study conditions: 75 μm bare silica column, 15 mmol/L phosphate buffer (pH of 7.0), 25 mmol/L sodium dodecyl sulfate, electrokinetic injection (5 s, 2 kV), 25 kV applied for 15 min, absorbance detection with a deuterium lamp set at 200 nm.*

reported voluntarily by the manufacturers. The powders were supplied by five different companies. There were 10 disc powders, five ball, and 13 tube powders. Based on information supplied by BATF, 14 of the powders contained nitroglycerin and would be classified as double-base powders (18). Dinitrotoluene and diphenylamine were the next most commonly occurring additives.

To minimize compositional variance that might result from particle-to-particle variation, at least ten particles were taken from each powder as a sample. To prepare liquid samples, acetone was added to a sample of each powder (27 ± 2 mg) for dissolution of the nitrocellulose-based matrix. Nitrocellulose, although soluble in acetone, is insoluble in the aqueous solutions used for MECE. The nitrocellulose was selectively precipitated upon addition of the detergent-containing running buffer. The acetone/aqueous supernatant was decanted into a new sample vial, and internal standard was added before the acetone was removed by controlled evaporation, leaving the additive compounds dissolved in the detergent solution. Analysis of duplicate samples showed no inconsistencies between electropherograms. An additional aliquot of acetone added to redissolve the precipitate did not recover additional, measurable additive components.

The powder compositional information determined by MECE was generally in good agreement with the powder database maintained by BATF, with the exception that additional additives were also detected in several cases. Differences between the BATF database composition and the MECE results were likely to be the result of two factors. Some manufacturers control the burn rate of each lot of powder by the addition of supplementary material, resulting in lot-to-lot variation in composition. In addition, some European powder manufacturers do not consider their powder to be double-base unless nitroglycerin is added above a certain weight percentage, and would not report nitroglycerin as an additive unless it was present above that defined percentage (personal communication, CR Midkiff, BATF).

Different approaches to pattern matching were evaluated to determine the feasibility of uniquely identifying a gunpowder based on the compositional analysis using the MECE technique. Powder matches based on the combination of additive identity and powder morphology were insufficient to unequivocally distinguish closely-related powders. For instance, three disc-shaped powders each contained diphenylamine, N-nitroso-diphenylamine, and methyl centralite.

A second approach to distinguish powders focused on the presence of dinitrotoluene isomers as a discriminatory technique. Our current standard mixture contains four common isomers of dinitrotoluene: (1) 2,4 (2) 2,6 (3) 3,4 and (4) 2,3 dinitrotoluene. Of the powders sampled, only one manufacturer had the 2,3 and 3,4 isomers in addition to the 2,4 and 2,6 dinitrotoluenes in all their powders. Other manufacturers occasionally had the 2,6 isomer in addition to the most common 2,4 dinitrotoluene. Based on the NIST MECE database, detection of more than the 2,4 and 2,6 dinitrotoluene isomers would indicate that the questioned sample could be isolated to one manufacturer. The isomer composition of powder from a given manufacturer may not always be constant, therefore, periodic checks of recently produced ammunition would be necessary to establish the reliability of this indicator.

In a third approach, an analysis of the ratio of the amount of dinitrotoluene to diphenylamine (the most common combination of additives) was investigated in an attempt to distinguish closely related powders. Unique powder identification could not be reliably achieved using this approach or the other two approaches. At this point, it appears that the solvent-dissolution/MECE can only provide evidence that a sample powder composition is consistent with a known powder. Table 2 provides a condensed version of

TABLE 2—*Database of constituent information from 38 smokeless powders based on micellar electrokinetic capillary electrophoresis results.*

Ammunition	NG	TNT	DNT	DPA	MC	EC	DMP	DEP	DBP
ACC ARMS 1680[1]	√			√					√
ACC ARMS 2460[1]	√			√					
IMR 700-X (old)[2]	√		√						
IMR 700-X (new)[2]	√					√			
IMR 800-X[2]	√					√			
IMR 3031[2]			√	√					
IMR 4064[2]			√	√					
IMR 4227[2]			√	√					
IMR 4320[2]			√	√					
IMR 4350[2]			√	√					
IMR 4831[2]			√	√					
IMR 4895[2]			√	√					
IMR 7828[2]			√	√					
IMR SR4756[2]			√	√					
IMR SR4759[2]			√	√					
IMR SR7625[2]			√	√					
Hercules Bullseye[3]	√			√		√			
Hercules Green Dot[3]	√			√					
Hercules 2400[3]	√			√					
Hercules Reloader 12[3]	√			√		√			
Hodgdon BL-C[4]	√			√					√
Hodgdon Clays[4]	√			√					
Hodgdon H110[4]	√			√					√
Hodgdon H380[4]	√			√					
Hodgdon H322[4]	√		√	√					
Hodgdon H870[4]	√		√	√					√
Hodgdon HS-6[4]	√			√					
Scot Brigadier[5]				√	√				
Scot 453[5]	√								√
Scot Pearl[5]	√		√		√				√
Brig 3032[5]				√	√				
Brig 4065[5]				√	√				
Brig 4197[5]				√	√				
WWest 231[4]	√			√		√			√
WWest 296[4]	√			√		√			√
WWest 452AA[4]	√			√		√			√
WWest 473AA[4]	√			√		√			√

[1]Accurate Arms.
[2]IMR Powder Company.
[3]Hercules.
[4]Olin.
[5]Scot.

the MECE-derived database information on powder compositions. A comprehensive database of gunpowder composition has also recently been published by Northrop et al. (8).

Sampling Protocols

Solvent-resistant masking tape has been used for tape lifts of gunshot residue in previous work (15,16). In this protocol, collected samples are subsequently extracted with ethanol to obtain samples appropriate for MECE analysis. One drawback to this approach is the presence of dibutylphthalate from the tape adhesive as an interference. In this study, two new types of tape, with water- and alcohol-soluble adhesives, were evaluated for use as lifting tapes to remove residue from shooters' hands.

A three-step process was used to evaluate the two new tapes for residue collection. The first step was to investigate the solubility of each tape. Next, the background absorbance of the dissolved tapes was evaluated with MECE. Finally, the tapes were used to collect gunshot residue under controlled conditions, and the samples were examined to determine if the composition of the tape might interfere in the MECE analysis of the residue components.

The "alcohol-soluble" tape was found to be insoluble in tetrahydrofuran, acetone, water, or phosphate buffer. Only the adhesive of the "alcohol-soluble" tape was found to be ethanol soluble. This tape showed background absorbances which were too intense for residue detection under the conditions of the MECE measurements, with peaks of 10 mAU to 20 mAU height noted.

Both the adhesive and backing of the water-soluble tape dissolved within 30 s of water immersion, collapsing into a fragile gelatinous mass which was not easily separated from solution. Electropherograms of the tape sample were very noisy, suggesting that microscopic particles of the dissolved tape were being injected into the capillary. Tape samples spiked with a standard mixture, further demonstrated the unsuitability of the tape. Residue component peaks were deformed and showed extended retention times. Thus, neither of the water-soluble and alcohol-soluble tapes was found to be suitable for the collection of gunshot residue for analysis by MECE.

Environmental Contaminants

Evidentiary samples submitted for gunshot residue analysis might be expected to be contaminated by a variety of common substances. To evaluate the capability of the sampling and MECE detection protocols, polyester/cotton blend handkerchiefs were contaminated with the following substances: hand lotion, grease, motor oil, gun oil, and sweat. Masking tape lifts of residue-free handkerchiefs which had been contaminated showed clean electropherograms except for a small dibutylphthalate peak, which is commonly seen with tape lifts. As a preliminary test of analyte recovery, contaminated targets were spiked with a standard mixture of residue components. Analysis of tape lifts from these targets had baseline-resolved electropherograms for all analytes. Residue samples were deposited on other sets of contaminated handkerchiefs by firing handguns of four different caliber into 25 by 25 cm sections of cotton cloth. In all cases, the smokeless powder in the cartridges contained nitroglycerine and diphenylamine.

Nitroglycerine (NG) and diphenylamine (DPA) were detected in each contaminated sample, regardless of the caliber of the weapon used to produce residue (Fig. 2). Diphenylamine was known to be present at a lower concentration than nitroglycerine in each ammunition, but was still readily detectable despite the presence of contaminants. The presence of these common environmental contaminants does not appear to effect residue component detection by MECE using the tape lift sampling protocol.

Effect of Blood on Residue Recovery

Bloodstained residues were prepared on polyester-cotton handkerchiefs in a manner similar to that used for the environmental contamination study. Three sets of conditions were tested: one set of targets was sampled while the bloodstain was fresh, a second set was sampled following four weeks of storage in a warm, humid environment (to induce decomposition), while a third set was subjected to proteinase K as a means of hydrolyzing the bloodstain prior to sampling.

To evaluate any interfering background absorbance in the MECE analysis from blood residue, masking tape lifts from fresh, decomposed, and proteinase K-digested bloodstains were taken from handkerchiefs which did not contain residue. All the sample electropherograms showed no major peak except for dibutylphthalate. Although no peaks other than DBP were seen, the baseline on most electropherograms was relatively noisy, indicating that the tape adhesive may have been picking up some particulate material

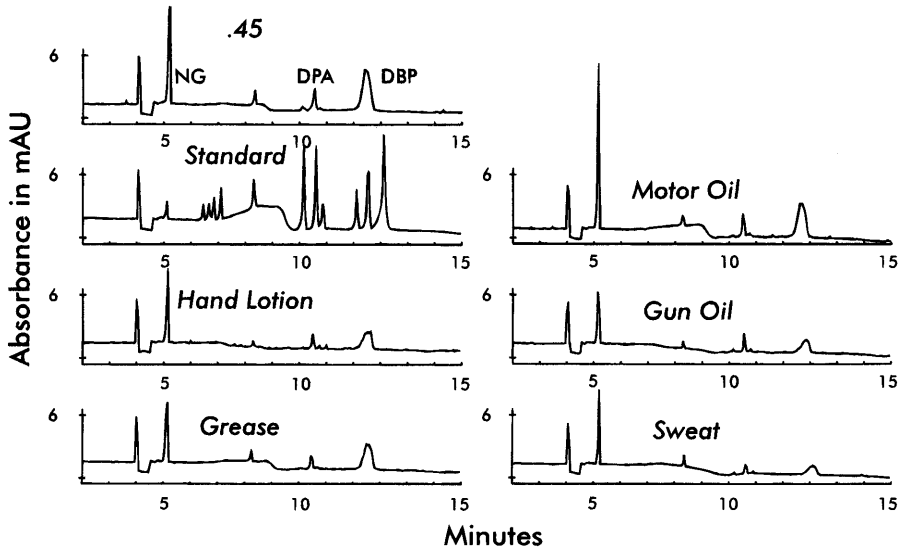

FIG. 2—*Electropherograms of tape lift extracts from contaminated cloths used as targets for a 45 semi-automatic pistol. CE detection at 200 nm.*

from the bloodstained area. These particles can produce very narrow peaks in the MECE analysis.

When freshly-bloodstained handkerchiefs that contained residue were examined, positive identification of nitroglycerin and diphenylamine were obtained in approximately half of the samples. In all cases, either both nitroglycerine and diphenylamine was detected or neither additive was detected. The positive results showed no obvious correlation with any particular type of ammunition. An even lower success rate was found for decomposed bloodstained residues, which yielded positive results in less than one-third of the analyses. Conditions known to be detrimental to bloodstains are also likely to enhance the degradation of residue components: changes in pH, humidity, and temperature. The presence of microbes may also contribute to bloodstain and residue decomposition, and therefore, to a lowered successful rate of NG and DPA detection by MECE.

The removal of the bloodstain prior to residue sampling by detergent washes or proteinase K digestion did not improve the success rate of detection of NG and DPA. If a washed or digested sample was not fully rinsed, the coating formed over the residue hindered its removal with masking tape. Fully rinsing the sample, however, usually resulted in the loss of some portion of the particulate residue, reducing the possibility of obtaining positive detection of NG and DPA.

As a result of these studies, tape lifts were determined to be unreliable for positive identification of the two residue components (NG and DPA) in the presence of blood contamination. Because of the inconsistent results from these studies, we decided to investigate supercritical fluid extraction (SFE) as a means to more reliably recover residue components. Supercritical extraction of residue-free, bloodstained cellulose thimbles using carbon dioxide with and without methanol modifier yielded extracts which were free of MECE detectable interferences except for a peak at the elution time of dibutylphthalate. Methanol was chosen as a modifier because of its ability to swell the nitrocellulose matrix, which was expected to improve the penetration of the extraction fluid and to improve recovery of the polar residue compounds (12). To demonstrate the possibility of using SFE for the recovery of the residue components from bloodstained samples, a standard mixture of residue components was applied to a cellulose thimble, stained with blood, and then air-dried. Supercritical carbon dioxide, with or without methanol modifier, successfully extracted the mixture components from the bloodstained thimble. The recovery of the standard mixture was enhanced by the application of methanol to the thimble prior to extraction. Figure 3 shows the comparison between electropherograms of uncontaminated standard and standard which had been masked by a bloodstain.

Conclusions

Previous work at NIST had established the success of MECE for the detection of gunshot residue from the hands of a person shooting a handgun. As in the previous studies, tape lifts were shown to offer accurate, positive identification of residue components from hands. Two new soluble tapes were found to be unsuitable for MECE analysis due to their chemical/physical properties. Solvent-resistant masking tape lifts were conducted on cloth samples, extending the applicability of MECE to new sample environments. Most all common environmental contaminants did not prevent the successful detection of residue components by MECE. However, the presence of blood was found to be detrimental to MECE analysis, particularly if decomposition had occurred. The adverse effect of blood was found to result, in part, from the ability of blood to limit residue recovery using tape lifts. Preliminary studies with supercritical fluid extraction demonstrated that residues may be efficiently recovered from such bloodstained samples. In addition, a database of additive information from 38 smokeless powders was established, laying the groundwork for future studies on the ability of MECE to detect and positively identify unknown residue samples.

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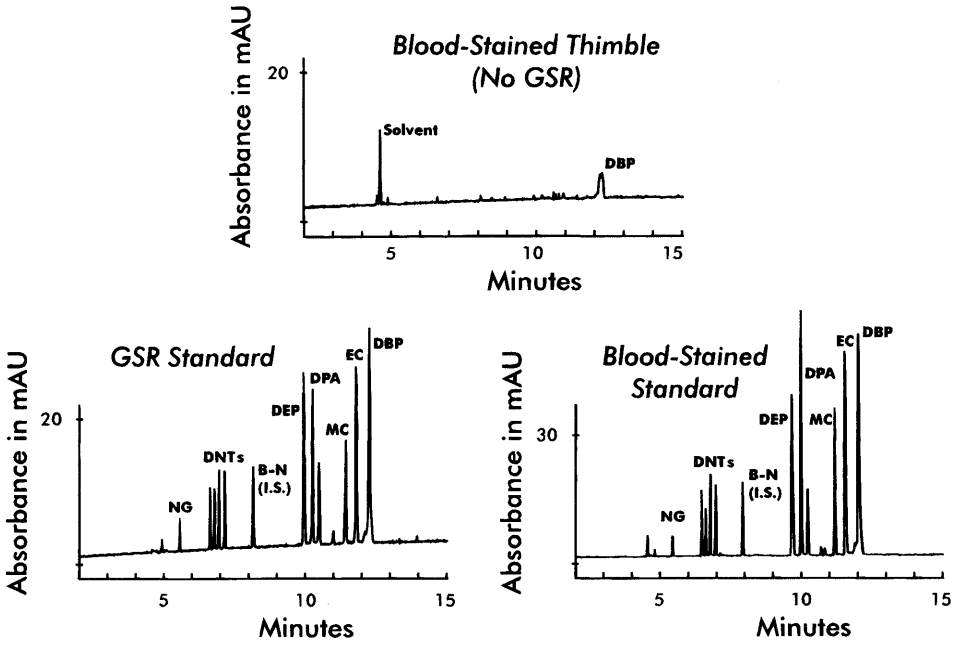

FIG. 3—*Electropherograms from the investigation of supercritical CO_2 extraction in the recovery of residue from bloodstains. CE detection at 200 nm.*

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