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Detection of Smokeless Powder Residue on Pipe Bombs by Micellar Electrokinetic Capillary Electrophoresis*

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ABSTRACT: Improvised explosive devices are an increasing concern among law enforcement agencies within the United States because of their destructive capability. Capillary electrophoresis has been used previously for the forensic analysis of inorganic constituents in explosives. Micellar electrokinetic capillary electrophoresis (MECE), also known as micellar electrokinetic chromatography (MEKC), is well suited for the forensic analysis of organic constituents of these materials because of its high sensitivity and small sample requirements.

In the present study, pipe bombs filled with known types of smokeless gun powder were detonated under controlled conditions. Samples of explosive residue were collected from the post-blast fragments and analyzed using MECE. The results were compared to the known types and analyzed to investigate the feasibility of matching post-blast residue to a specific powder used as explosive charge.

KEYWORDS: forensic science, smokeless powder, capillary electrophoresis

The production and use of improvised explosive devices is a significant problem in the United States with over 2000 separate incidents occurring in 1994 (1). The explosive materials used in im-

proved devices include both organic and inorganic compounds, making it necessary for the forensic analyst to perform a wide variety of chemical tests to identify components present in the residue. Presently, such tests include a number of chromatographic techniques. The recent development of capillary electrophoresis (CE) provides a new approach that improves speed, resolution and specificity when compared with ion chromatography and thin-layer chromatography (TLC) (2). An additional advantage of CE is its ability to successfully analyze minute samples of forensic evidence.

Micellar electrokinetic capillary electrophoresis (MECE), a derivative form of CE also known as micellar electrokinetic capillary chromatography (MEKC), may be used for the separation and analysis of uncharged molecules such as organic explosives (3). MECE permits a wide variety of compounds to be separated with high efficiency and does not require the extensive setup or equilibration times that are necessary when organic compounds are separated via gradient HPLC. In addition, MECE permits thermally labile materials to be separated without degradation, which is an advantage over previous GC techniques.

In MECE, the capillary is filled with a buffer containing a detergent such as sodium dodecyl sulfate at a concentration sufficient to form micellar aggregates (4). The structure of the detergent micelles provides a hydrophobic interior with a charged hydrophilic surface. MECE uses the micelles' surface charge to induce movement against the electroosmotic flow. Unionized organic analytes present in the capillary partition between the hydrophilic buffer solution and the hydrophobic interior of the micelles. Separation occurs as a function of the hydrophobicity of the analytes; hydrophilic molecules elute first, followed by the more hydrophobic molecules which have been partially retained by the migrating micelles.

Application of MECE to the separation and analysis of organic explosives was originally developed by Northrop et al. for the analysis of organic gunshot residue (5–7). It has also been used to separate and analyze explosive compounds extracted from contaminated soils (8,9). MacCrehan et al. recently completed an evaluation and refinement of sampling protocols for the collection of smokeless powder residue in the presence of external contaminants (10). Results from this study were used to establish experimental conditions for the present study.

In the present study, pipe bombs were prepared with known types of smokeless powder as the explosive charge and detonated under controlled conditions. The collection and analysis of smokeless powder residue from the post-blast fragments demonstrated

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Certain commercial equipment, instruments, or materials are identified to adequately specify experimental protocol. Such identification does not imply recommendation or endorsement by either the Federal Bureau of Investigation or the National Institute of Standards and Technology, nor does it imply that the identified materials and equipment are necessarily the best available for the purpose of forensic residue analysis.

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the potential effectiveness of MECE for forensic explosive detection.

Experimental

The pipe bomb fragments used in the study were generated from improvised explosive devices prepared by the Explosives Unit of the Federal Bureau of Investigation at the FBI Academy in Quantico, Virginia (11,12). Metal pipes eight inches in length with diameters of 2 1/2 in. were used to contain and deflagrate the smokeless powder. The pipe bombs were initiated under controlled conditions and the fragments contained by wrapping the explosive devices in chain link fence. Only those fragments contained by the fencing were collected to ensure that no external contamination occurred. Four smokeless powders from IMR Powder Company (700-X, 4350, 5831, and 7828) were used as explosive charge. Four groups of pipe bombs were prepared. Each group consisted of at least four bombs, and each group was charged with one of the four smokeless powders.

Masking tape lifts (1 cm²) and cotton swabbings, premoistened with ethanol, were taken from bare pipe fragments as well as from the threaded portions of the pipes. The extraction and analytical

protocols for both the tape lifts and the cotton swabbings were based on previous work, as was the preparation of samples from the unfired powders (10).

The tape lifts were extracted in 1-mL ethanol for 20 min. Following the addition of 10 μ L internal standard (β -naphthol) and 100 μ L system buffer, the ethanol was removed through controlled evaporation under reduced pressure (SpeedVac Concentrator, Savant Instruments, Inc., Farmingdale, NY). The cotton swabbings were extracted with methanol-modified, supercritical carbon dioxide ($\rho = 0.74$ g/mL, $T = 90^\circ\text{C}$, $P = 35$ MPa) using a Hewlett Packard 7680T Supercritical Fluid Extraction System. A 30 min extraction onto stainless steel beads in an on-line trap was followed with acetone elution (2×1.0 mL) into glass vials. Following the addition of 10 μ L internal standard and 100 μ L buffer, the acetone was removed as described above.

Samples of the unburned IMR powders (27 ± 2 mg) were dissolved with 1 mL acetone. The nitrocellulose matrix of smokeless powder, although soluble in acetone, is insoluble in the MECE system buffer. The nitrocellulose was selectively precipitated upon addition of system buffer. Following decantation of the supernatant to a new sample vial, 10 μ L internal standard was added and the re-

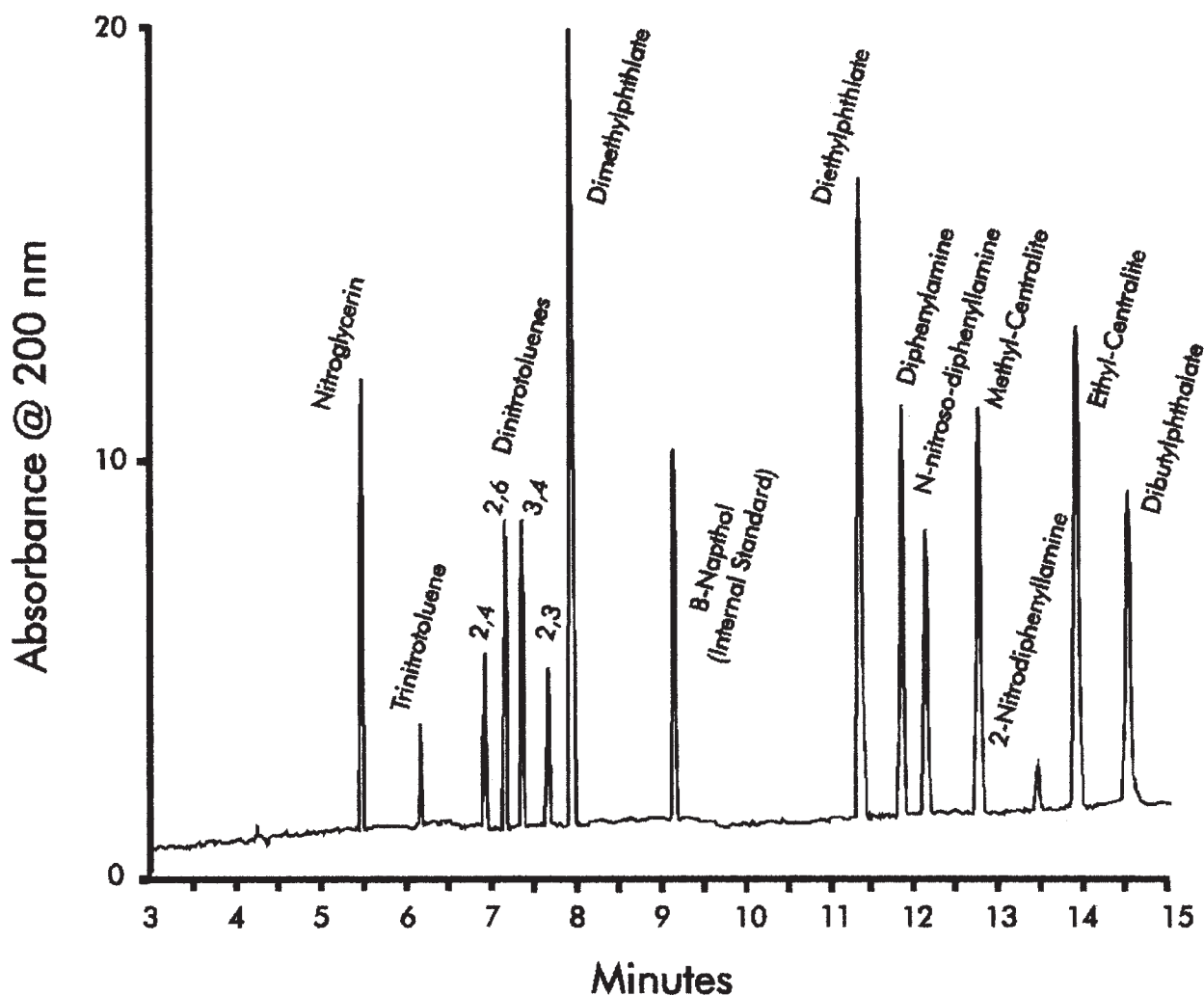


FIG. 1—Electropherogram of the standard mixture of analytical targets under study conditions: 75 μ m bare silica column, 55 cm separation length, 15 mmol/L phosphate buffer (pH of 7.0), 25 mmol/L sodium dodecyl sulfate, electrokinetic injection (5 s, 2 kV), 25 kV applied for 15 min, UV detection at 200 nm wavelength.

maining acetone was removed as described above. The additives present in each powder had already been identified through previous work (10).

A standard solution of known smokeless powder additives was used for the identification of residue components. An initial solution of each additive was prepared in ethanol, limited by solubility to about 10 mmol/L. The individual solutions were combined to obtain a standard mixture whose concentration was approximately 8 mmol/L. Electropherograms of the residues were compared to electropherograms of the standard solution to identify residue components.

Capillary electrophoresis was carried out on an Applied Biosystems 270-HT Capillary Electrophoresis System. The buffer system 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, used for micellar separation, was added to the buffer at a concentration of 25 mmol/L. The capillary was a 75 μm (ID) fused silica column with a separation length of 55 cm. A 5 s electrokinetic injection was performed at 2 kV followed by separation at a voltage of 25 kV for 15 min with UV detection at a wavelength of 200 nm.

Results and Discussion

Previous work had already established the applicability of CE to explosives analysis (2,6) as well as its application to the analysis of

smokeless powders present in organic gunshot residue (5,7,10). An obvious extension of previous studies was the analysis of smokeless powder residue from pipe bombs. It is important to note that this type of analysis is presently carried out by the FBI Laboratory using GC/MS (13).

The object of the present study is to provide a supplementary technique which is capable of analyzing nonvolatile and thermally unstable components of organic residue. Additives are normally introduced in the manufacture of smokeless powder to enhance processing and deflagration characteristics. The presence and quantity of specific additives are class specific and potentially unique for a particular powder. Figure 1 gives an example of the analysis of a standard mixture of explosives and smokeless powder additives by MECE.

When presented with pipe bomb evidence, a forensic chemist initially performs a visual search for unburned explosive particles. The morphology and chemical composition of the particles provide important information used to narrow the search for the specific powder used in the explosive device (14). Unfortunately, unburned particles cannot always be recovered from crime scene evidence. For this reason, samples were not only taken from pipe bomb fragments containing unburned particles, but also from pipe bomb fragments which did not contain unburned particles.

The first part of this study involved a comparison of the results obtained from a protocol using tape lifts extracted in ethanol with

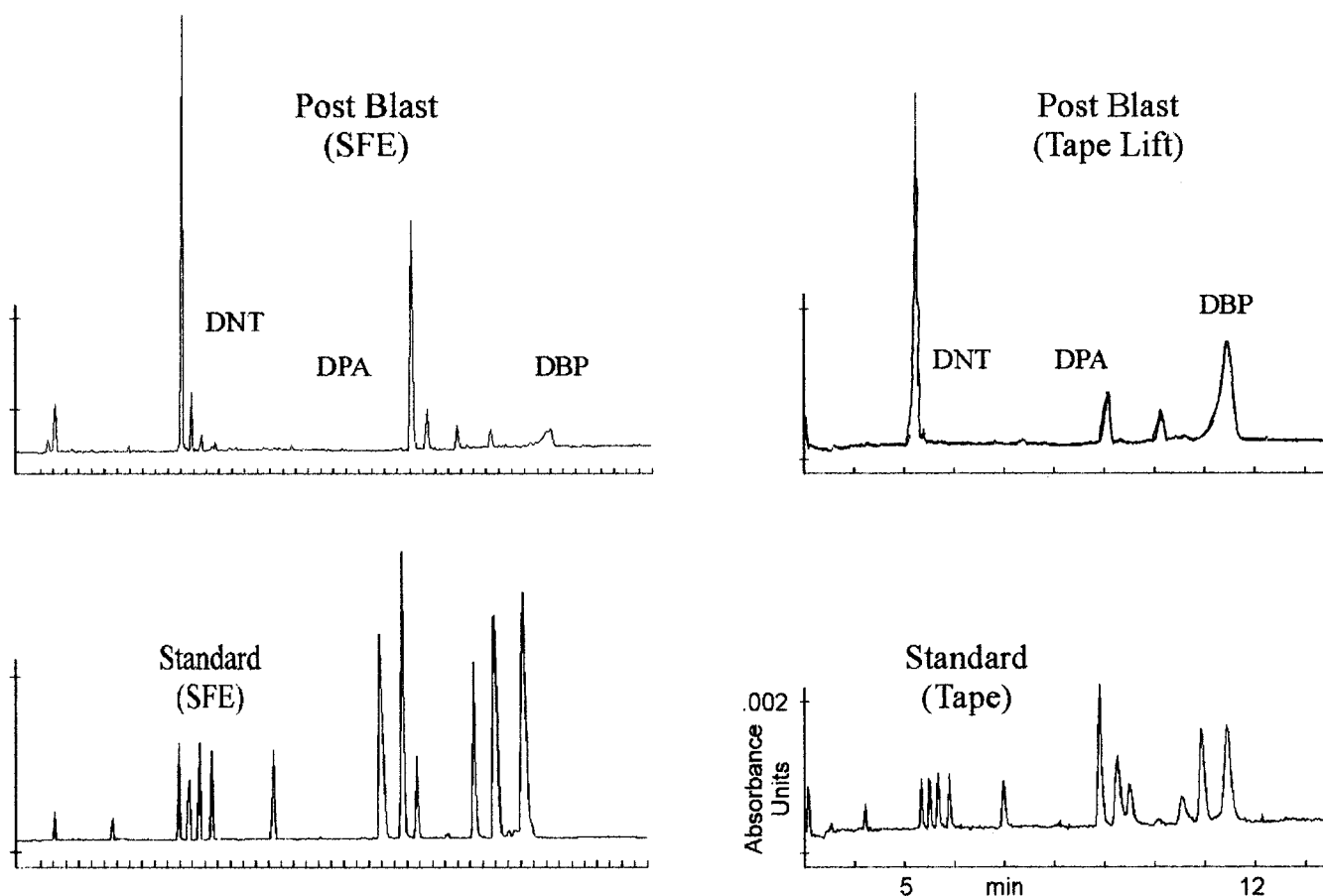


FIG. 2—Comparison of residue samples prepared with solvent extraction of tape lift and supercritical fluid extraction of cotton swabbings. Abbreviations: supercritical fluid extraction (SFE), dinitrotoluene (DNT), diphenylamine (DPA). Conditions as for standard mixture.

a protocol employing cotton swabbings extracted in supercritical carbon dioxide. Both extraction techniques provided samples suitable for analysis; however, the results showed that supercritical fluid extraction provided samples which contained fewer contaminants. In contrast to the clean electropherograms from cotton swabs, extracts from tape lifts showed a higher level of background noise as well as peak deformation. Analysis of blank tape lifts demonstrate similar background noise and deformation of the dibutylphthalate peak. Dibutylphthalate is a component of the adhesive present on the masking tape (10). Figure 2 demonstrates the advantages of using supercritical fluid extraction as a technique for the recovery of organic residue.

The electropherograms from unburned samples of the four smokeless powders used in the study demonstrated baseline separation of all components. IMR 700-X smokeless powder contained dinitrotoluene (DNT), a propellant additive. IMR 4350, IMR 4831,

and IMR 7828 each contained DNT and diphenylamine (DPA), a stabilizing additive (10).

The results obtained from the analysis of the post-blast residue were examined to determine the feasibility of matching post-blast residue back to a specific powder used as an explosive charge. A strong correlation was seen between the unburned and post-blast samples based on a visual comparison of the electropherograms. Figure 3 demonstrates the fact that IMR powder constituents present prior to detonation were easily detectable in post-blast residue. Duplicate analyses were made of fragments from different pipe bombs within a group. Qualitatively, the results were similar. Low level constituents (i.e., DNT and DPA) were present in all residue samples; however, the levels of the individual components appeared to vary widely among samples. Figure 4 compares post-blast electropherograms from the group of pipe bombs charged with IMR 4350.

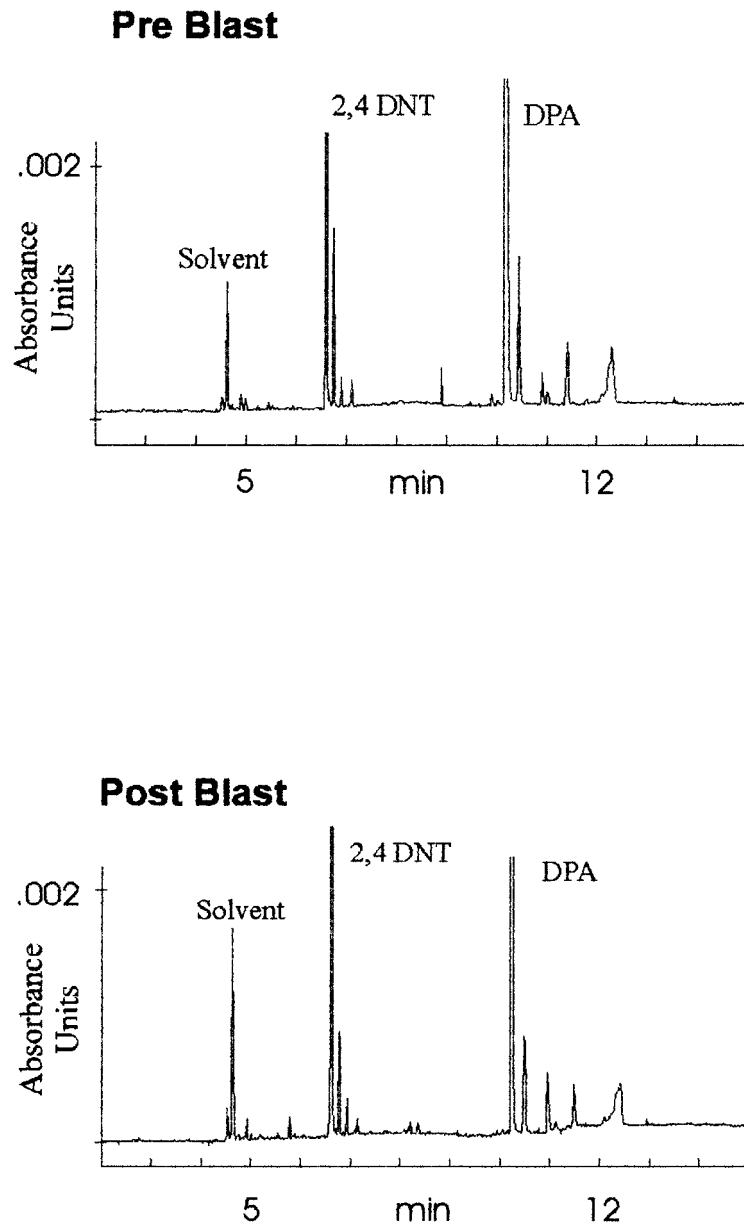


FIG. 3—Analysis of IMR powder before and after detonation. Abbreviations: dinitrotoluene (DNT), diphenylamine (DPA). Conditions as for standard mixture.

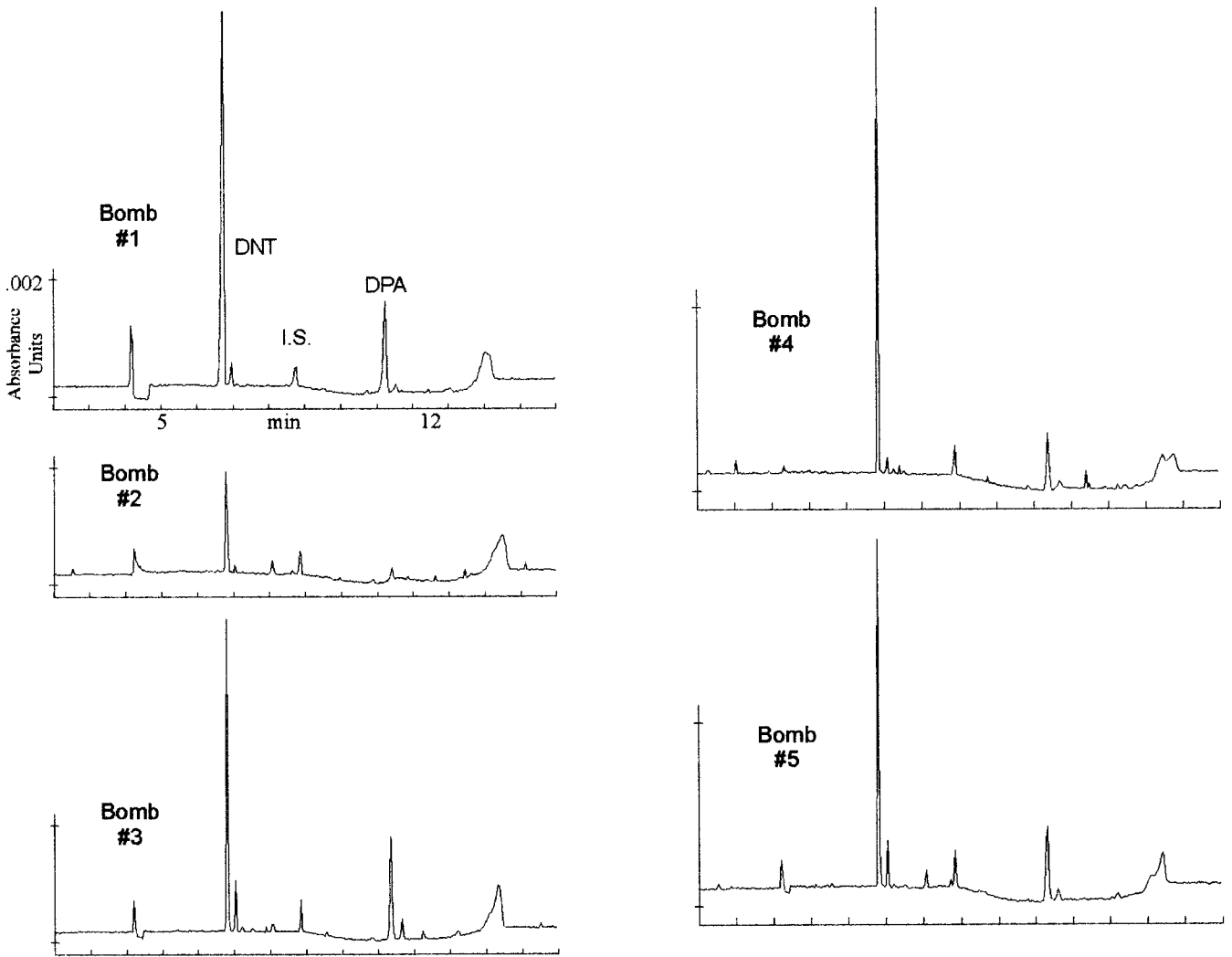


FIG. 4—Analysis of post-blast residue from group of pipe bombs charged with IMR 4350. Duplicate analyses not shown. Abbreviations: dinitrotoluene (DNT), internal standard (IS), diphenylamine (DPA). Conditions as for standard mixture.

IMR 700-X powder, used to charge the first set of pipe bombs, contained DNT as an additive. An analysis of the DNT peak height and area (relative to internal standard) over a series of analyses performed on post-blast residue demonstrated a wide variability. Some variability in results was expected due to the chaotic nature of the explosive process. The question of interest was whether the variability in post-blast analysis would inhibit efforts to match post-blast residue back to a particular smokeless powder used as an explosive filler. In an attempt to distinguish among the three powders that contained DNT and DPA, the ratio of DNT to DPA was examined, using both peak height and area. The ratio of DNT to DPA was calculated using data from post-blast analysis of the powder residues. The preliminary data shown in Table 1 supports the potential of MECE in providing information which is useful to the forensic chemist, although more information is needed than a simple ratio DNT to DPA to identify a smokeless powder (10). Future studies will investigate the utility of combining information from the DNT:DPA ratio with information from other additives commonly present in smokeless powder (i.e., plasticizers/stabilizers such as the Centralites). It is reasonable to surmise that the chaotic nature of the explosive process will require a multi-variable analysis of post-blast residue to unequivocally identify the explosive charge.

TABLE 1—Analysis of DNT variability and DNT: DPA ratio in four groups of pipe bombs. Results shown as average \pm standard deviation. Experimental data based on duplicate analyses of residue from explosive residue. There were at least four pipe bombs in each group.

Powder	Height Ratio DNT:DPA	Area Ratio DNT:DPA
#1	$2.38 \pm 1.39^*$	$2.25 \pm 0.98^*$
#2	8.1 ± 4.5	4.3 ± 2.4
#3	7.6 ± 1.0	3.8 ± 0.8
#4	14 ± 4.3	6.7 ± 2.0

* Powder #1 contained DNT only. Results indicate variability of DNT.

Conclusions

Micellar electrokinetic capillary electrophoresis has shown promise in the analysis of gunshot residue. The use of this technique has been extended to the separation and analysis of pipe bomb residue. MECE has excellent selectivity, and its sensitivity can be enhanced through optimized extraction procedures, such as

supercritical fluid extraction. The MECE technique is useful for situations in which separation of thermally labile samples is required. With MECE, components are not subject to thermal breakdown as they are with gas chromatography. Because MECE does not require the extensive equilibration time necessary for gradient HPLC, evidence can be examined in a time-efficient manner. MECE provides the forensic chemist with useful information about post-blast residue composition and is a useful tool for the characterization of smokeless powder.

Acknowledgments

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