

CHROMSYMP. 2500

# Explosive residue analysis by capillary electrophoresis and ion chromatography<sup>☆</sup>

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## ABSTRACT

Capillary electrophoresis is investigated for application as a complementary technique to ion chromatography in the analysis of low-explosive residues. Detection limits, interference problems, and matrix effects are examined by comparing the use of ion chromatography and capillary electrophoresis in parallel analyses. The residue from several different types of explosive devices are examined, and the results show capillary electrophoresis to be a useful new technique in explosive analysis yielding good sensitivity, high resolution and short analysis times.

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## INTRODUCTION

During the blast of a low explosive, a complex series of chemical reactions takes place. The goal of the forensic chemist is to piece together clues from the residue left behind which can point to the type of explosive material used. For many years, the most powerful tool in these investigations has been ion chromatography (IC) [1]. Parts per million levels of the anions and cations left behind from the blast are easily detected and quantitated using this technique. For example, black powder which consists of charcoal, sulfur and potassium nitrate may produce nitrite, nitrate, sulfate, sulfide, thiocyanate and carbonate anions on analysis of an aqueous extract of its residue. The presence of anions, such as these, is among the most important evidence used to determine the nature and source of the explosive.

Ion chromatographic (IC) analysis suffers from the lack of a good complementary technique for peak confirmation. While X-ray and infrared techniques can be used for residue analysis, these techniques lack the sensitivity and specificity required to verify chromatographic peaks. Instead, the presence of specific anions is commonly confirmed by using a combination of two different IC columns and detection schemes. At the FBI Laboratory two separate systems for this analysis are used: (1) a traditional dual-column ion analysis with suppressed conductivity detection, and (2) a single-column ion analysis with inverse photometric detection [2,3]. Problems with the traditional dual-column IC system include the inability to determine carbonate due to the fact that the eluent is hydrogencarbonate, and the inability to elute certain strongly retained anions, such as perchlorate.

The recent development of capillary electrophoresis (CE) for ion analysis has provided an opportunity to resolve these problems [4,5]. While still providing information in a format similar to IC, the CE system operates using a completely different sep-

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\* This is publication number 92-01 of the Laboratory Division of the Federal Bureau of Investigation. Names of commercial manufacturers are provided for identification purposes only, and inclusion does not imply endorsement by the Federal Bureau of Investigation (FBI).

aration mechanism. The result is a nearly orthogonal separation that is an ideal complement to IC. Analyses reported in the literature have revealed rapid and highly efficient separations of both anions and cations [6].

For our method, we have selected an indirect photometric procedure which requires a borate buffer system with a dichromate chromophore and a diethylenetriamine (DETA) electroosmotic flow modifier [7]. In this system the polarity is set to allow detection at the positive electrode. Electroosmotic flow inside the capillary moves the buffer and analyte ions toward the detector, and separation occurs as a result of differences in electromigration of the anions. For our purposes, questions concerning detection limits, system suitability, and potential interferences had to be answered. In this paper we address these concerns and apply the CE system to various explosive residue problems. In order to better illustrate the use of this technique as a complement to our existing IC analyses, we compare results acquired with a single-column IC to those from the CE system.

## EXPERIMENTAL

### Capillary electrophoresis

The CE system used was a Dionex CES I (Sunnyvale, CA, USA) equipped with an 65 cm  $\times$  75  $\mu$ m I.D. fused-silica capillary and an ultraviolet detector. In addition, a Spectra-Physics 1000 CE (San Jose, CA, USA) equipped with a similar column and a scanning ultraviolet detector was used to determine the most appropriate wavelength for analysis. The detector was positioned at the positive end of the capillary (reversed polarity), and was operated in the UV mode at a wavelength of 280 nm and a potential of 20 000 V. Some analyses were also carried out at 265 nm or 205 nm. Analyses of results was performed using Laboratory Data Systems (Pittsburgh, PA, USA) LabData 200 software. Potassium dichromate, sodium tetraborate, boric acid, DETA, and sodium hydroxide were used as received. The buffer system was prepared by adding 0.53 g of potassium dichromate, 0.76 g of sodium tetraborate and 2.47 g of boric acid to 1 l of deionized water [7]. The pH was adjusted to 7.8 with DETA, and the solution filtered through a 0.45- $\mu$ m nylon 66 filter. The resultant buffer solution was 2 mM

in borate, 40 mM in boric acid, 1.8 mM in dichromate and 1 mM in DETA. The 75- $\mu$ m fused-silica column was prepared for use by first flushing for 2 min with 100 mM NaOH. Approximately 50 nl of sample were injected onto the column using a gravity injection technique.

### Ion chromatography

The IC system used was a Waters (Milford, MA, USA) 600E multisolvent delivery system attached to a Kratos Spectra flow 783 variable-wavelength UV detector set at 280 nm and a Waters WISP 710B autosampler. The column used was a Vydac 302IC4.6 (Hesperia, CA, USA) with a flow-rate of 2.5 ml/min and an injection volume of 25  $\mu$ l [2]. Detector signals sent to the Laboratory Data Systems LabData 200 system. Isophthalic acid (Aldrich) was used as received. The isophthalic acid eluent had to be prepared in a special manner due to the low solubility of the free acid in water. To prepare this eluent, 0.75 g of the isophthalic acid was added to 3 l of boiling water along with approximately 2 ml of 2 M KOH. Following dissolution of

TABLE I  
RETENTION TIMES OF IONS RELATIVE TO BROMIDE

Results compiled from a series of individual chromatographic runs.

Ion	Relative retention time	
	IC	CE
Iodate	0.65	2.17
Acetate	0.65	2.17
Fluoride	0.77	1.62
Chloride	0.85	1.05
Nitrite	0.92	1.10
Phosphate	0.97	2.04
Bromide	1.00	1.00
Chlorate	1.04	1.27
Nitrate	1.18	1.08
Formate	1.20	1.47
Azide	1.25	1.19
Sulfate	1.41	1.12
Sulfite	1.41	1.12
Maleate	1.48	1.46
Tartrate	1.59	1.57
Sulfide	1.76	—
Iodate	2.39	1.04
Thiocyanate	3.78	1.40
Perchlorate	5.00	1.21
Carbonate	6.87	1.79

the acid, the solution was cooled and the pH adjusted to 4.6 using additional 2 M KOH.

#### Sample preparation

Standards were made up by preparing 100 ppm solutions of the desired components and diluting them as necessary. The materials tested for a response on the two analytical systems are listed in Table I. All solutions and extracts were prepared using 18 M $\Omega$  deionized water. Pipe bombs containing a variety of explosive materials were deflagrated by the FBI Explosives Unit in holes dug at the demolition range at the Marine Corps base in Quantico, VA, USA. Fragments of these bombs were collected and brought back to the laboratory for analysis. The residue from the blast was collected by washing the fragments with deionized water and filtering through a prerinsed Gelman (Ann Arbor, MI, USA) 0.2- $\mu$ m nylon syringe filter. These solutions were spiked with a small amount of KBr standard for use as a retention time marker.

#### RESULTS AND DISCUSSION

The requirements for a good chromatographic analysis of explosive residues include reproducible

retention times, minimal interferences, and the ability to clearly separate the specific ions present in the blast residue. Among the most important of these ions are nitrite, nitrate, sulfate, chlorate, carbonate and perchlorate. Such ions result from the reaction of oxidizers such as potassium nitrate, potassium chlorate and potassium perchlorate with fuels such as carbon, sulfur and sugar. The ability to clearly distinguish the presence of these major ions as well as other associated ions is the major criterion for an acceptable method. Quantitative analysis of the ions is not generally a practical concern. This is because it is not possible to determine the conditions present during the blast. Varying amounts of burned and unburned material are always present, and reaction conditions will vary based on the type of containment, initiator, and condition of the powder used in the device. Instead, the explosives examiner looks for the presence or absence of certain characteristic ions. Thus an ideal method will clearly show all relevant ions in a single chromatographic run with as good a separation as possible in order to avoid any ambiguities.

With these requirements in mind, we have investigated the CE separation. The ability of this technique to isolate a wide variety of anions offers a

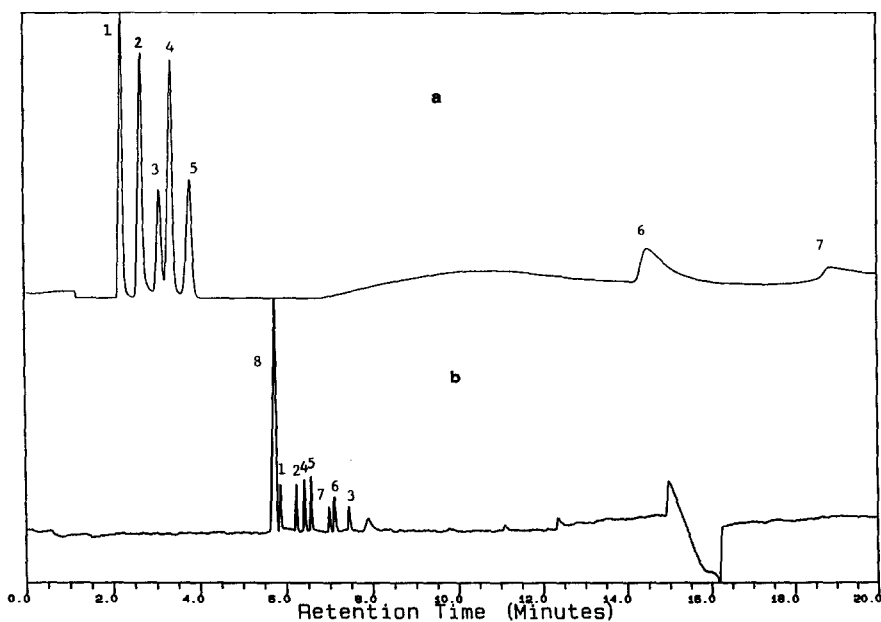


Fig. 1. Analysis of an anion standard using (a) IC and (b) CE. Peaks: 1 = chloride; 2 = nitrate; 3 = chlorate; 4 = nitrate; 5 = sulfate; 6 = thiocyanate, 7 = perchlorate; 8 = bromide.

clear advantage in its favor [8]. Apart from our IC analysis using the Vydac column, most other separations using IC require several different procedures or a complex gradient technique to achieve these results. CE offers the potential of giving an excellent separation using a simple and rapid analytical procedure [9,10]. To compare the results run using CE, we have used an IC method developed in this laboratory specifically for explosive residue analysis [2]. This is the method using the Vydac 302IC4.6 column with 1.5 mM isophthalic acid as the eluent. The low ion-exchange capacity of this column permits a good separation of rapidly eluting ions such as chloride, nitrite and nitrate, as well as late eluting anions such as thiocyanate, perchlorate and carbonate [11].

#### *Comparison of the elution of standards*

A variety of solutions of ion standards were prepared and analyzed using both CE and IC. Fig. 1

shows an analysis of a 10 ppm standard of anions commonly encountered in explosive residue using both CE and IC. The figure clearly shows the extensive differences between the two techniques. The elution order and the retention times are drastically different. Note that the peaks for the CE separation are sharp but not well separated, while those peaks in the IC are better separated but not as sharp. This observation summarizes the practical difference between the two techniques. The CE separation is achieved by the use of high theoretical plate counts (70 000 or more) at the expense of capacity while the IC separation has greater capacity but is not as efficient.

Part of the reason for these differences in elution order lies in the dissimilar separation modes of the two techniques. The CE separation is based on differences in electrolytic conductivity, allowing the elution order to be accurately predicted by using a table of electrolytic conductivity values [8,12]. This

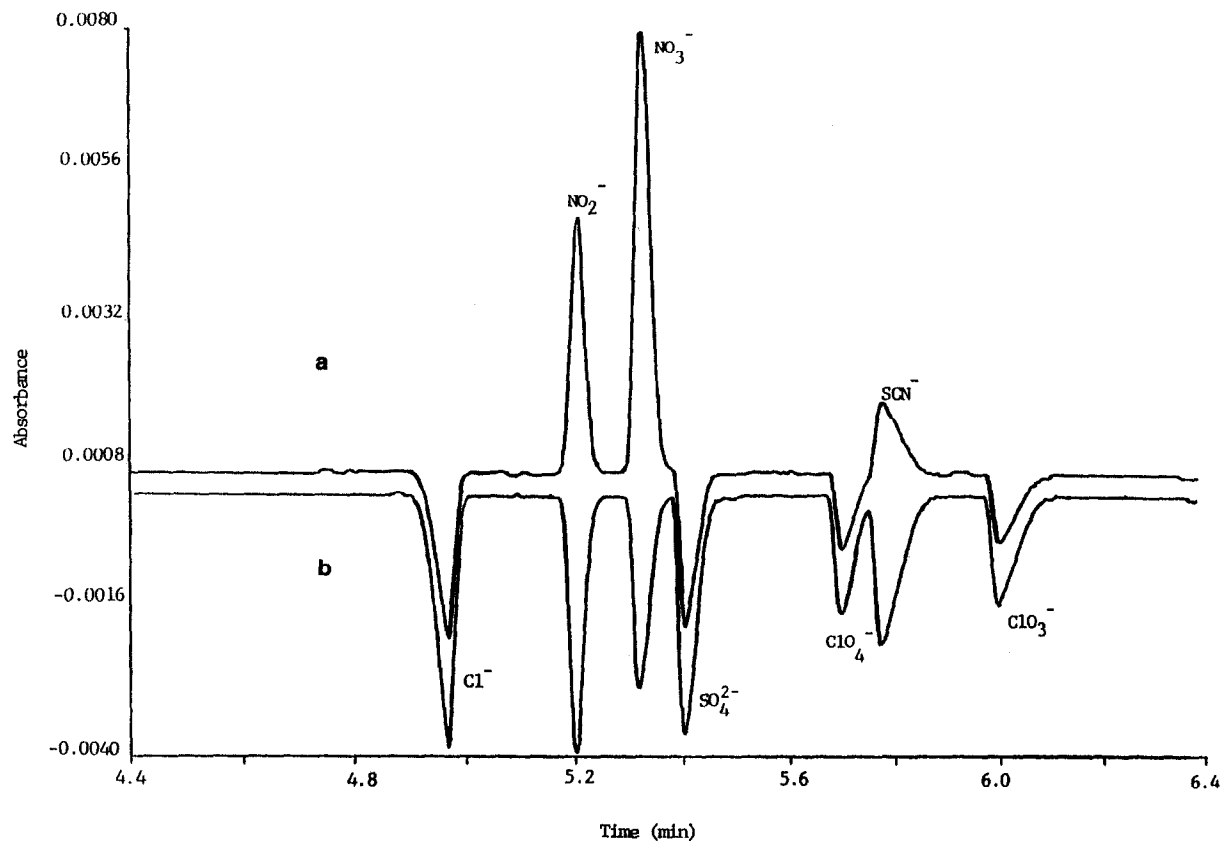


Fig. 2. Analysis of an anion standard at (a) 205 nm and (b) 280 nm.

property can be extremely useful in instances where unknown peaks appear. More subtle forces are at work in the IC separation including equilibria, concentration, and size and density effects [13]. As one would expect, there is little association between the retention times of the two different techniques. This observation is the key to understanding the use of CE as a confirmation technique. Since there is so little relationship between the separation mechanisms, it is highly unlikely that two ions could co-elute undiscovered in one technique without being separated using the other. Actual retention times for a variety of anions are given in Table I.

The reproducibility of retention times was checked by running the 10 ppm standard 12 times over a period of 2 months on the same capillary. A relative standard deviation of less than 1% for the retention times of most ions was observed. In order to compensate partially for these slight variations, we have used bromide as a marker for calculating relative retention times. Bromide was selected because it was the earliest eluting ion tested, and because it is not usually found in explosive compositions [14].

It was also found that a useful technique for determining peak identity in CE is to do a second analysis with detection at a lower wavelength. We have determined that at a wavelength of 205 nm, nitrite, nitrate and thiocyanate produce peaks in a positive direction due to their UV absorbance. Anions that do not absorb at this wavelength produce peaks in the negative direction due to displacement of the absorbent buffer. This yields an electropherogram that, while only slightly less sensitive than that at 280 nm, produces a distinctive pattern of positive and negative peaks allowing easy identification of ions. Fig. 2 shows the results of an analysis of our standard recorded at 205 and 280 nm using a CE system with a scanning UV detector (Spectra-Physics 1000 CE).

#### *Sensitivity and dynamic range*

When analyzing the residues from explosive devices, sensitivity is usually not a problem if a significant portion of the device is recovered. Generally more than adequate amounts of residue can be found in an aqueous extract of the fragments. Situations to arise, however, when samples are either limited in size, or have been washed during efforts

to extinguish a subsequent fire. Such problems make it important to determine the minimal detectable concentrations for ions of interest. There are also practical concerns with sensitivity when a comparison is made between two techniques. Injection overload and dynamic range are problems in CE due to the low capacity of the capillary column. Sample concentrations which are ideal for column chromatography may require significant dilution in order to be analyzed by CE. For these reasons detection limits and dynamic range for both the IC and CE techniques were determined. A stock solution containing 1000 ppm each of nitrite, nitrate, chlorate and perchlorate was prepared and serial dilutions were made. These solutions were injected on both systems and limits of detectability were calculated. For the CE system, the minimum detectable concentration calculated as three times the background signal was 0.5 ppm, while that for the IC column was 2 ppm. It should also be noted that the sample volume used in the CE system was 1000 times less than that of the IC.

The dynamic range of the CE system was found to be similar to that suggested in earlier literature or approximately 2–3 orders of magnitude [7,8]. This range was limited however by the requirement that adequate resolution be maintained between the peaks of interest. A more reasonable range of concentrations would be between 1 and 50 ppm. This can be compared to the 5 to 200 ppm range of concentrations applicable to our IC system which utilized a 25- $\mu$ l injection loop. The practical result of these studies was that effective analysis of residue by both systems requires that the residue solution analyzed by the IC system had to be diluted 5- to 10-fold in order to achieve the most effective CE separation. Such dilutions become necessary in situations in which there is an abundance of residue found on the bomb fragments at the crime scene. In such circumstances, the maximum effective concentration should be used in both instruments to be certain that important minor components are not missed.

#### *Analysis of pipe bomb fragments*

To test the applicability of this analysis scheme, four pipe bombs were prepared by the FBI's Explosive Unit, and detonated on the explosives demolition range at the Marine Corps Base in Quantico,

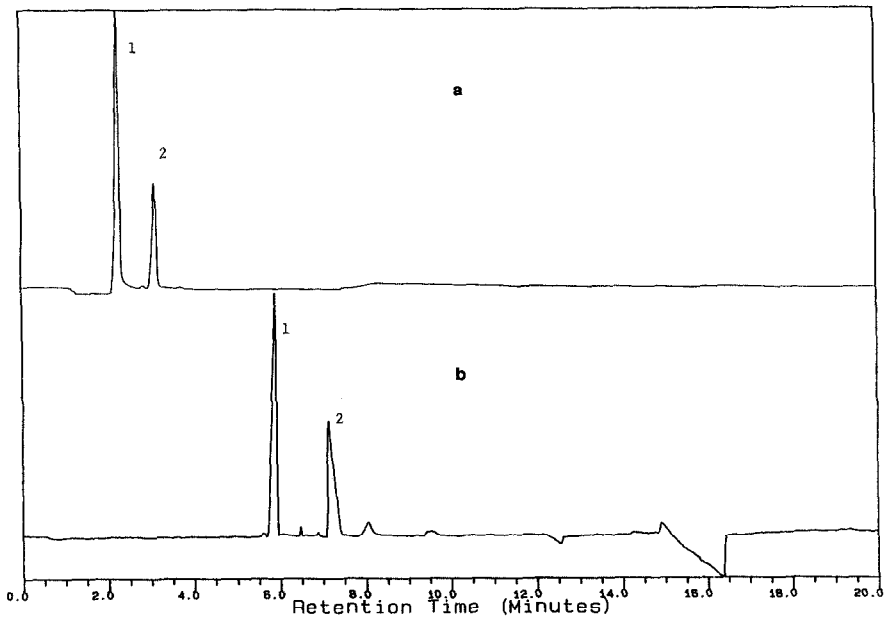


Fig. 3. The analysis of residue taken from a pipe bomb containing a mixture of potassium chlorate and vaseline using (a) IC and (b) CE. Peaks: 1 = chloride; 2 = chlorate.

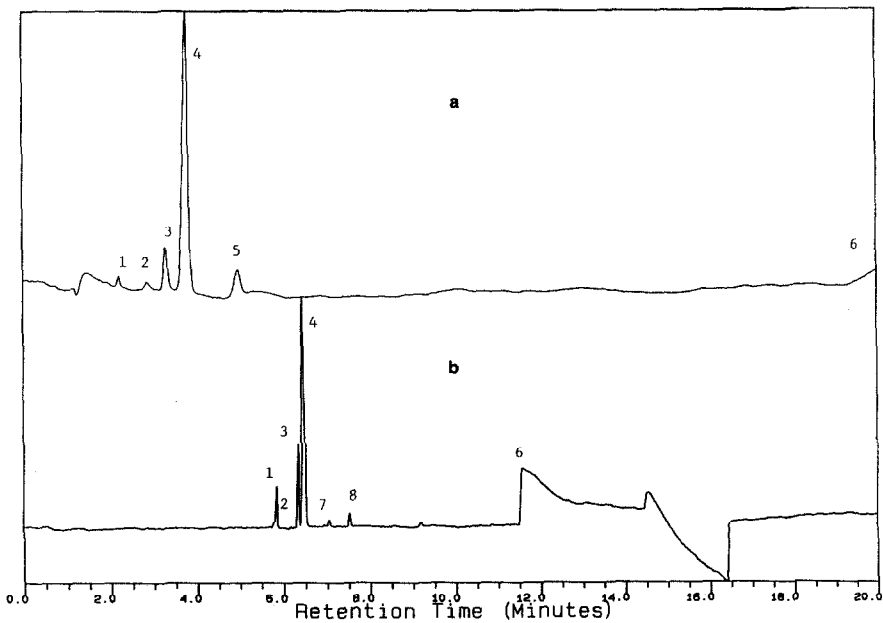
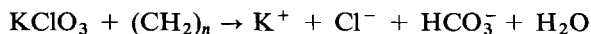


Fig. 4. The analysis of residue taken from a black powder pipe bomb using (a) IC and (b) CE. Peaks: 1 = chloride; 2 = nitrite; 3 = nitrate; 4 = sulfate; 5 = sulfide; 6 = hydrogencarbonate; 7 = thiocyanate; 8 = cyanate.

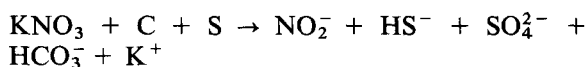
VA, USA. The bombs were filled with the following explosive mixtures: (1) potassium chlorate–vaseline, (2) black powder, (3) smokeless powder and (4) a mixture of black and smokeless powder. Fragments from each of these bombs were extracted with water, filtered, and run on both systems.

The results of the chlorate–vaseline and black powder bombs are shown in Figs. 3 and 4. The sample runs may be overlaid with their respective standards, allowing unambiguous peak assignments. Dual IC and CE runs are made because establishment of peak identity is crucial in the forensic arena where the type of explosive powder used can be critical in determining the guilt of innocence of a suspect. In actual casework each of these peaks would also be individually spiked to further establish peak confirmation.

As can be seen from these results, both product and reactant ions remain in the residue. In Fig. 3, the residue from the potassium perchlorate–vaseline pipe bomb, the chlorate ion peak is seen along with the chloride ion. Hydrogencarbonate was expected but not seen and was perhaps tied up by the residual vaseline left on the bomb. These ions are the products and reactants of the following equation:



The black powder residue (Fig. 4) shows the nitrate ion from the unburned potassium nitrate as well as the ions nitrite, sulfate, sulfide and hydrogencarbonate. These aqueous ions are consistent with the presence of a potassium nitrate oxidizer and a carbon and sulfur fuel, and are the products and reactants of this equation:



The key to a successful analysis of explosive residue evidence is to examine the pattern of amount and type of ion and reconstruct the hypothetical explosive mixture. In the future, a variety of such mixtures will be tested in order to obtain detailed information on the types and distributions of such residue.

## CONCLUSIONS

The large differences in separation mode and action of the two techniques give great assistance to the analyst in determining the nature of the sample. Use of IC and CE in tandem greatly reduces problems caused by interfering ions and allows easy peak confirmation. In addition, the inherent sensitivity advantage of CE works in concert with the greater capacity of the IC system allowing a wide variety of concentrations and types of residue to be screened. For these reasons, we have found that the application of these two techniques greatly expands the capability of our laboratory in undertaking explosive residue analyses.

## ACKNOWLEDGEMENTS

We would like to thank Special Agent Frederic W. Whitehurst, and the FBI Explosives Unit for their assistance in carrying out these experiments, and Pat Williams, formerly of Dionex, Inc., for help in preparing methodology.

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