Kelly E. Hall[1] *and Bruce R. McCord,*[2] *Ph.D.*

The Analysis of Mono- and Divalent Cations Present in Explosive Residues Using Ion Chromatography with Conductivity Detection

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ABSTRACT: The separation of nine mono- and divalent cations of interest in explosives residue analysis was achieved using a Waters IC Pak-C Cation M/D column with a 3 mN HNO_3 eluent and conductivity detection. The apparatus was then used to collect data on the types of cations found in a variety of explosive residues including black powder, smokeless powder, and ammonium nitrate based explosives.

KEYWORDS: forensic science, explosive residue, cations, forensic, conductivity, ion chromatography

The ability to precisely ascertain cation composition in explosive residue is an important aid in the determination of the chemical composition of the explosive device [*1–5*]. While the number and variety of cations present in explosive residue is more limited when compared to anionic residue, certain cations such as monomethylamine, ammonium, and magnesium are specific to certain types of explosive formulations [*6*]. Even the ratio of the common ions sodium and potassium in residue has value, as manufacturers of improvised explosives may use the more hygroscopic sodium containing oxidizers rather than the preferred potassium formulations [*7*].

Current procedures for the complete separation of mono- and divalent cations present in post-blast explosive residues require complex gradient techniques or are prone to interferences [*8,9*]. For example, both mono- and divalent cations elute and can be separated in a single isocratic run using the Interaction ION 210 column and a cerium III sulfate eluent [*8*]. Unfortunately coelution of certain ions such as potassium and monomethylamine, and ammonium and ethanolamine can occur. While we have been satisfied with the reliability of this procedure for our general applications, there were problems with the above interferences, and we needed a second analytical procedure to confirm the presence of ammonium and other organic cations. Unlike metal ions, these organic cations cannot be detected by the instrumental techniques used for elemental

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[1] 1991 FBI Honors Intern, Lafayette College, Easton, PA; residence, Newark, DE.

[2] FBI Laboratory, Forensic Science Research Unit, FBI Academy, Quantico, VA.

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analysis. Thus we began a search for a second ion chromatographic method that allows detection of all important organic and inorganic cations with minimal interferences.

This new method uses conductivity detection and a Waters IC-Pak C M/D column to allow complete resolution of nine important cations: lithium, sodium, ammonium, ethanolamine, monomethylamine, potassium, magnesium, calcium and strontium. The column uses a stationary phase similar to that developed by Shomberg et al., and a similar column has recently been described for quality control applications in the explosives industry [*10,11*]. The method has a total run time of under twenty minutes, and the sensitivity of the apparatus is effective to the 150 ppb range.

Experimental

Reagents

Standards and eluents were made from laboratory grade chemicals supplied by a number of manufacturers. The nitric acid used as the eluent was HPLC grade. Aqueous standards and eluents were prepared with 18 megohm water and all eluents were degassed prior to use.

Chromatographic Equipment

A Waters 431 Conductivity Detector was used with a Waters 840 Chromatography Data System was used to control the initiation of each run and to collect and process the results. An Alcott 728 Autosampler and a Waters 501 HPLC pump regulated the injection size of the sample and the flow rate of the system respectively. The IC Pak-C M/D column was from Waters. The flow rate of the pump was set at 1.0 mL/min.

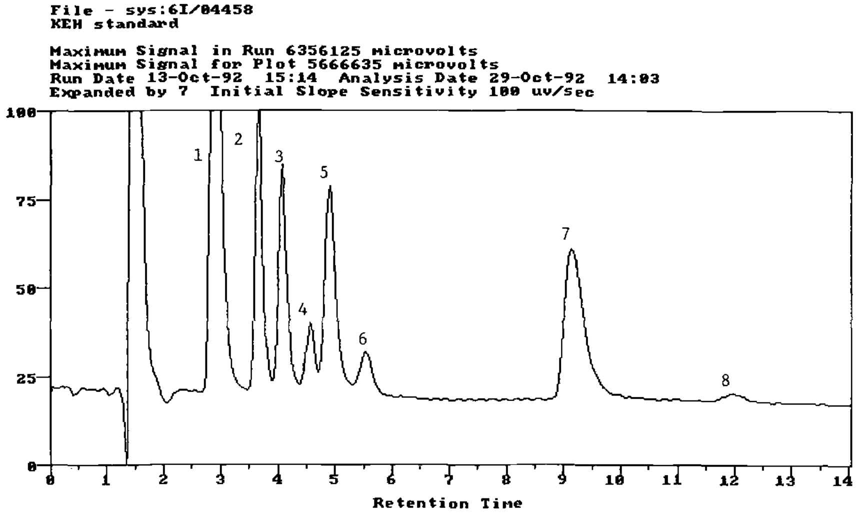
The eluent was prepared by adding 0.0292g EDTA to 850 mL of 18 megohm water and sonicating for 10 min. (The EDTA must be sodium free.) Next, 150 mL of 0.02 N nitric acid (Malinckrodt Volumetric Solution) were added, and the solution filtered through a 0.45 micron nylon 66 filter [*12*]. The resulting solution was 3 mN in nitric acid and 0.1 mN in EDTA. Standards of containing 5 ppm of Li^+, Na^+, NH_4^+, $CH_3HN_3^+$, Mg^{+2}, Ca^{+2}, and Sr^{+2} were prepared by measuring out the calculated amount of their respective salts and diluting to 250 mL with 18 megohm water. The potassium and ethanolamine standards were 3 ppm and 10 ppm respectively.

Results and Discussion

Standards

Nine standards of the individual cations were tested to determine their retention times. A standard containing all of the ions showed complete resolution in less than 20 min (Fig. 1). Analysis of 20 separate injections over a three day period produced variation in retention times for sodium and ammonium ions of under 2% RSD. Figure 2 shows a 330 ppb standard. An estimate of signal to noise ratio from this figure indicated that the method was sensitive well into the 150 ppb range.

One of the problems resulting from the exceptional sensitivity of the detector was the fact that the blank often showed traces of sodium. This phenomena can result from sodium leaching out of glass test vials or contamination of the distilled water source. In terms of the analysis, trace amounts of sodium are not a concern as sodium is ubiquitous in the environment; however, care must be taken in interpreting very small amounts of the more common cations. Generally if an inorganic low explosive device is used, large amounts of residue are produced, and the major concern is determining an appropriate



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KEH standard

Maximum Signal in Run 6356125 microvolts
Maximum Signal for Plot 5666635 microvolts
Run Date 13-Oct-92  15:14  Analysis Date 29-Oct-92  14:03
Expanded by 7  Initial Slope Sensitivity 100 uv/sec
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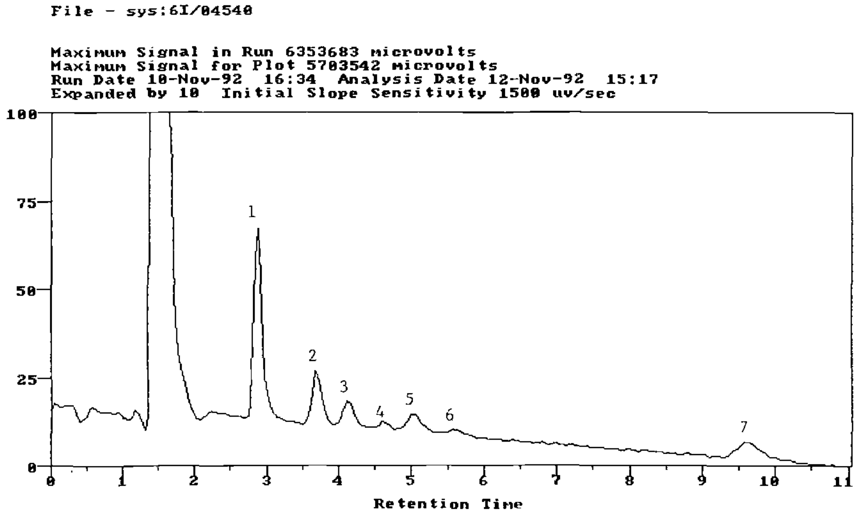
FIG. 1—*Cation standard. Peak identification: 1 = Lithium (5 ppm); 2 = Sodium (5 ppm); 3 = Ammonia (5 ppm); 4 = Ethanolamine (10 ppm); 5 = Methylamine (5 ppm); 6 = Potassium (3 ppm); 7 = Magnesium (5 ppm); 8 = Calcium (5 ppm).* NOTE: *Strontium, if included in this sample would appear at 17.1 min.*



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Maximum Signal in Run 6353683 microvolts
Maximum Signal for Plot 5703542 microvolts
Run Date 10-Nov-92  16:34  Analysis Date 12-Nov-92  15:17
Expanded by 10  Initial Slope Sensitivity 1500 uv/sec
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FIG. 2—*Standard solution at 300 ppb. The elution order is the same as Fig. 1.*

dilution factor in order to avoid overloading the column. In such cases it is the ability to see the trace components in the presence of the major ions that is important.

The separation also underwent some degradation after approximately 2 months of use when samples containing actual bomb debris were analyzed. Degradation of peak resolution could be a result of organic compounds in the sample solution or charged species irreversibly binding to the column. To help alleviate this problem, the manufacturer suggests prefiltering contaminated samples through a C-18 Sep-Pak (Waters Inc.) prior to analysis and storing the column in 10% acetonitrile/water when not in use [*12*]. Such treatment helped to lengthen the useable lifetime of the column.

Samples

The development of a cation detection system with high sensitivity and improved resolution is one step toward the ultimate objective of creating an explosive residue data base for swift determination of unknown samples in the crime laboratory. By testing the composition of samples collected from a series of bombs made with the same explosive, progress towards identification of the explosive used based on a semiquantitative determination of ions in the residue can be explored.

To develop applications of this technique, small samples of a variety of burned explosives were prepared. Other samples analyzed include shrapnel of bombs containing the residues of black powder, smokeless powder, and uninitiated ammonium nitrate based explosives. Samples were prepared by aqueous extraction of the residue or unburned material and filtration of the extract through a prerinsed 0.45 micron teflon syringe filter (Alltech Associates, Inc.) or C-18 Sep-Pak (Waters Inc.). Figure 3 shows an example of the analysis of the cations present on shrapnel resulting from a black powder pipe bomb.

The overall results, shown in Table 1, reveal the types of cations present in the analyzed samples. One interesting result is the presence of significant quantities of ammonium (11% by area) in the residue of the burned smokeless powder, Fig. 4. This ion had not been detected with our other analytical systems. This is presumably due to our practice of drying the extracts prior to analysis or to the time lag that often occurs between the bombing incident and receipt of the evidence. Either of these situations could lead to loss of volatile ammonia from the residue [*13*].

The amounts of ammonium found in shrapnel resulting from smokeless powder must be interpreted carefully as these materials leave relatively small amounts of residue. It is possible that the ammonium results from the pyrolysis of amine stabilizers present in the powder. Amplification of these low quantities of ammonium through the extraction process could distort their significance and might incorrectly lead the investigator to suspect that an ammonium nitrate based explosive was also present. These results underscore the importance of a thorough investigation of the evidence with evaluation of both inorganic and organic extracts before the final determination of the nature of the questioned sample is made.

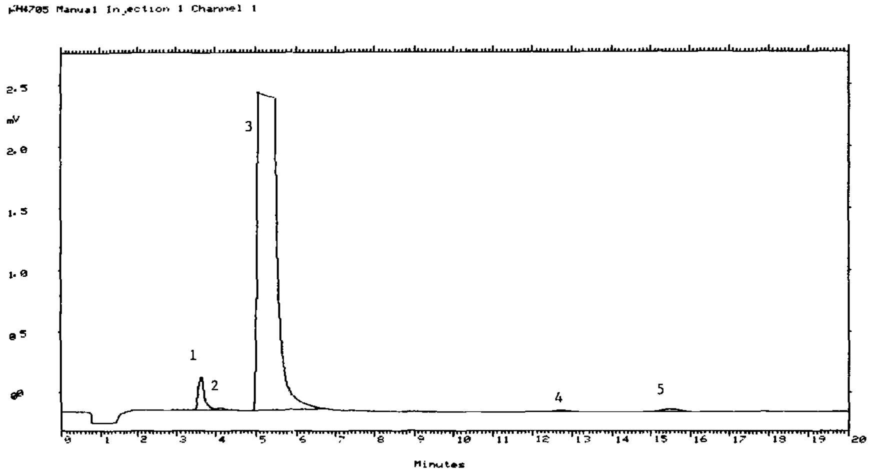

FIG. 3—*Cations in black powder residue. Peak identification: 1 = Sodium; 2 = Ammonium; 3 = Potassium; 4 = Magnesium; 5 = Calcium.*

TABLE 1—*Ions found in explosive extracts.*

Explosive	Cations found
Burned black powder	Na$^+$, K$^+$, NH$_4^{+a}$
Burned golden powder	Na^{+a}, K$^+$, NH$_4^{+a}$
Burned Pyrodex	Na$^+$, K$^+$
Burned Red Dot Smokeless Powder	Na$^+$, NH$_4^+$, K$^+$, Mg^{++}, Ca^{++}
Burned IMR 4895 Smokeless Powder	Na$^+$, NH$_4^+$, K$^+$, Mg^{++}, Ca^{++}
Trenchrite (DuPont)	Na$^+$, NH$_4^+$, MMA$^+$, Ca^{++}
Powdermax 140 (Atlas)	Na$^+$, NH$_4^+$
Powerditch 750 (Atlas)	Na$^+$, NH$_4^+$
Tovex (DuPont)	Na$^+$, NH$_4^+$, MMA$^+$

[a] Trace levels.

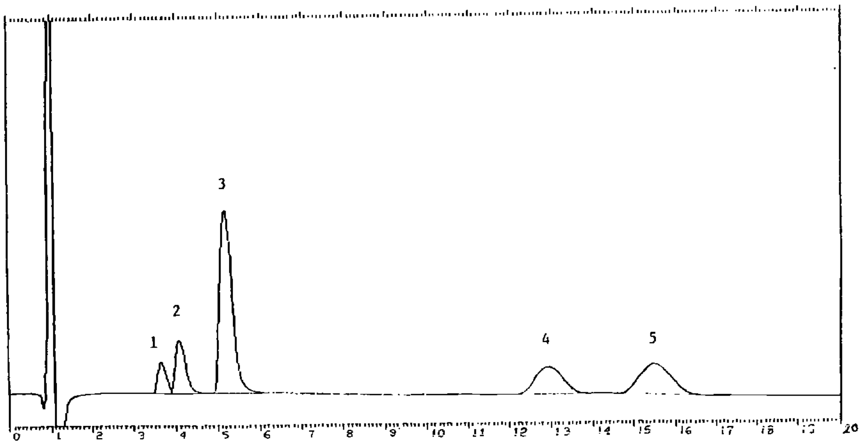

FIG. 4—*Cations in burned Red Dot smokeless powder (Hercules Inc.). Peak identification: 1 = Sodium; 2 = Ammonium; 3 = Potassium; 4 = Magnesium; 5 = Calcium.*

Ammonium and other cations can also appear when the sample has been contaminated by soil from the blast site. In running such analyses, it is desirable to check a soil blank to confirm the lack of any unusual background materials.

Monomethylamine nitrate is used as a sensitizer for ammonium nitrate based explosives from ETI Inc. (formerly DuPont) [*3*]. Therefore, the detection of this compound in a residue points to a strong possibility of this type of explosive in the original bomb. Figure 5 shows the result of the analysis of an aqueous extract of the DuPont explosive Trenchrite. The chromatogram reveals the presence of monomethylamine as well as sodium, ammonium, and calcium. The analysis of other organic amines of interest in explosives analysis also feasible with this column, such as ethanolamine and other positively charged alkyl amines [*14*].

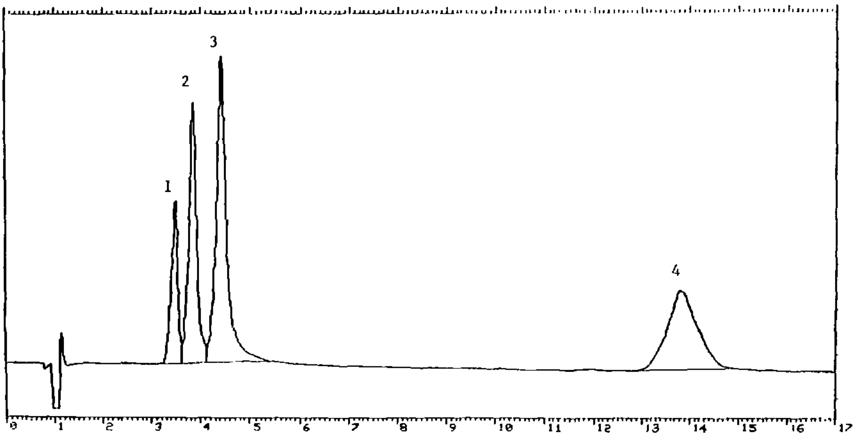

FIG. 5—*Trenchrite extract (DuPont Inc.). Peak identification: 1 = Sodium; 2 = Ammonium; 3 = Monomethylamine; 4 = Calcium.*

Conclusions

The conductivity detector in combination with the IC Pak C M/D column from Waters has allowed the successful resolution at very low concentrations of nine major cations found in post-blast explosive residues. The technique will prove to be useful in developing more extensive libraries of information detailing the post-blast composition of explosives. The improved sensitivity and selectivity will make the apparatus an excellent addition to current methods used in the examination of explosive evidence as a wider range of ions can be detected and analyzed.

Acknowledgments

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Address requests for reprints or additional information to
Bruce R. McCord, Ph.D.
Forensic Science Research Unit, FBI Laboratory
FBI Academy
Quantico, VA 22135