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Novel electrolyte for the analysis of cations in low explosive residue by capillary electrophoresis

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Abstract

A novel electrolyte has been developed for the effective separation by capillary electrophoresis of cations detected in low explosive residue. This electrolyte, with a pH of 4.4, employs 17.5 m*M* α-hydroxyisobutyric acid (HIBA) as the complexing agent, 6 m*M* imidazole as the ultraviolet visualization agent, 4 m*M* 18-crown-6 ether as a modifier to enhance the selectivity of the inorganic cations, and 5% (v/v) acetonitrile as an organic additive. Studies which assessed the value of the addition of 18-crown-6 and acetonitrile demonstrated conclusively that both were required in order to achieve unambiguous baseline separation of ammonium, potassium and monomethylammonium ions. The major advantages of the use of this electrolyte are a total run time of less than 7 min and symmetrical peak shapes. Validation on a series of preblast and postblast explosives materials determined that this procedure is reliable and robust. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Explosive residue; Cations

1. Introduction

The increase in terrorist bombings in recent years has heightened awareness of the characterization of the ionic components present in explosive residue. It has been demonstrated that the original composition of some explosive devices may be inferred from the components of the postblast residue [1–5]. The determination of specific cations, such as ammonium (NH_4^+), monomethylammonium (MMA) and potassium (K^+), are critical for the proper identification of explosives and their residues located at a crime scene. The water-soluble cations of interest in explosives materials include the salts of potassium (K^+), ammonium (NH_4^+), monomethylamine (MMA), strontium (Sr^{2+}) and calcium (Ca^{2+}). These materials are common constituents in commercial explosives, such as ammonium nitrate–fuel oil mixtures (ANFO) [5], improvised explosives, flash compositions [6] and black powder. While a number of different capillary electrophoresis (CE) methods have been developed to analyze low levels of inorganic cations [7–11], until recently, only ion chromatography (IC) was useful for the analysis of organic cations such as MMA [12,13]. Beck and Englehart [14] demonstrated the simultaneous separation of organic and inorganic cations, however, this method is ineffective for explosives analysis, since NH_4^+ and K^+ could not be separated.

CE has proven to be an effective technique in forensics for the separation of anions extracted from explosives and explosives residue [13]. However, cations present in explosives residue pose a challenge for separation by CE because of their similar

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electrophoretic mobilities. In addition, proper mobility matching of the cations with the electrolyte is necessary to avoid asymmetrical peak shapes. Consequently, the formulation of the separation electrolyte must be optimized to resolve the cations of interest unequivocally in order for CE to be useful as a technique for the forensic identification of cations in explosives materials.

The electrolyte system in this study is novel because it employs a combination of additives that is effective in separating monovalent and divalent, organic and inorganic cations in explosives materials. Additionally, significant improvement in peak shape of all of the cations that were examined has been accomplished relative to other reported systems [5,15–17].

2. Experimental

2.1. Reagents and standards

All reagents and standards were prepared using 18 MΩ deionized water generated by an EGA Maxima SC water system obtained from EGA (Bucks, UK). The final electrolyte consisted of 17.5 m*M* α-hydroxyisobutyric (HIBA) (Sigma, St. Louis, MO, USA), 6 m*M* imidazole (Sigma), 4 m*M* 18-crown-6 ether (Sigma) and 5% ACS- or HPLC-grade acetonitrile (Fisher, Fair Lawn, NJ, USA). The pH was adjusted to 4.4 using 0.5 *M* tetramethylammonium hydroxide (Sigma).

Standards, at a concentration of 1000 ppm each, were prepared from calcium nitrate, cobalt sulfate and the chloride salts of potassium, ammonium, iron and aluminum (Fisher); copper sulfate, methylamine and the chloride salts of barium, sodium and cesium from Sigma; strontium nitrate and zinc sulfate from Mallinckrodt (St. Louis, MO, USA) and magnesium chloride from Baker (Phillipsburg, NJ, USA).

2.2. Equipment

Analyses were conducted on a Spectrophoresis 500 capillary electrophoresis instrument (Thermo Separation Products, Piscataway, NJ, USA) equipped with a 37 cm×50 μm I.D. (effective length), uncoated, fused-silica capillary (J&W Scientific, Folsom, CA, USA). Samples were introduced into the capillary by hydrodynamic injection for 2 s. A cation standard was run every five samples for comparison of retention time and peak shape. Baseline separations were achieved at a field strength of 568 V/cm at 20°C in under 7 min. Indirect UV absorbance detection was performed in the single wavelength mode at 215 nm with a bandwidth of 6 nm.

2.3. Sample preparation

For preblast samples, approximately 0.1 g each of black powder (Goex, Moosic, PA, USA), Pyrodex CTG (Hodgdon Powder, Shawnee Mission, KS, USA), IMR 4350 (IMR Powder, Plattsburgh, NY, USA), and Power Max, Power Ditch, Trench Rite, Tovex 210 and Tovex 800 (origins unknown) was placed in a 15-ml conical centrifuge tube (Fisher) and extracted in 2 ml of deionized water overnight at 4°C. Additional quantities of Tovex 210 and Tovex 800 were extracted in 10% ultragrade nitric acid (Sigma), as recommended by Barsotti et al. [18]. The extracts were briefly shaken by hand and filtered through a 0.22-μm nylon disc filter (Gelman Sciences, Ann Arbor, MI, USA) attached to a 5-ml plastic syringe (Becton Dickinson, Franklin Lakes, NJ, USA). A portion of each filtrate of the known explosives was diluted 1:100 (v/v) with deionized water prior to performing the separations.

Sections of previously detonated pipe bombs containing black powder, Pyrodex CTG and IMR 4350, approximately 10 cm^2 in dimension, were swabbed with a piece of clean, white cotton that had been moistened with deionized water. These samples were extracted in 2 ml of deionized water as outlined above. The resultant filtrates were analyzed undiluted.

3. Results and discussion

The results of a forensic examination must be unambiguous and reproducible. In this study, we have taken a methodical approach to develop an electrolyte that effectively separates NH_4^+, K^+ and monomethylammonium cations.

The separation of fifteen alkali, alkaline earth, and transition metal cations using 5 m*M* Waters UVCat-

1, a proprietary detection agent, and 6.5 m*M* HIBA as a complexing agent was demonstrated in 1992 [19]. In this study, it was found that peak shape and resolution were influenced by the concentration of HIBA and visualization agent. A lack of symmetry in peak shape is the result of a mismatch in mobility between the analyte cations and the electrolyte cations, which are termed co-ions [20]. During electrophoresis, the analyte ions displace the co-ions. If the analyte ion elutes faster than the co-ion, fronting of the early eluting peaks will occur. Conversely, if the analyte elutes slower than the co-ion, tailing of the late-eluting peaks will occur [21]. Therefore, mobility matching of analyte and electrolyte is essential for symmetrical peak shape.

In 1996, Billiet et al. [11] demonstrated good separation of cations using an electrolyte system containing 17.5 m*M* HIBA as the complexing agent for alkaline earth and transition metal cations and 6 m*M* imidazole as the visualization agent. However, NH_4^+ could not be separated using this buffer due to the fact that HIBA does not complex with alkali metals. Bächmann et al. [22] were the first to employ the use of a crown ether to separate NH_4^+ and K^+. Results obtained by Yang et al. [15] suggested that the addition of 18-crown-6 ether to the buffer forms an inclusion complex with K^+, enabling it to be separated from the NH_4^+. This result was also demonstrated by Beck and Engelhardt [16] in an electrolyte consisting of *p*-aminopyridine and by Rivello and Harrold [23] in a copper sulfate electrolyte.

A 17.5 m*M* HIBA and 6 m*M* imidazole formulation at pH 4.4 was chosen as the starting point of the electrolyte developed in this laboratory to examine the separation of twelve cations. The NH_4^+ and K^+ ions are not separated (Fig. 1) because they are not complexed by the HIBA and have the same limiting equivalent ionic conductance of 73.5 mho-cm^2/equivalent in aqueous solutions, where mobility is equal to the Faraday constant multiplied by the limiting equivalent ionic conductance [24].

Upon the addition of 4 m*M* 18-crown-6 ether to the previous electrolyte formulation, the K^+ was

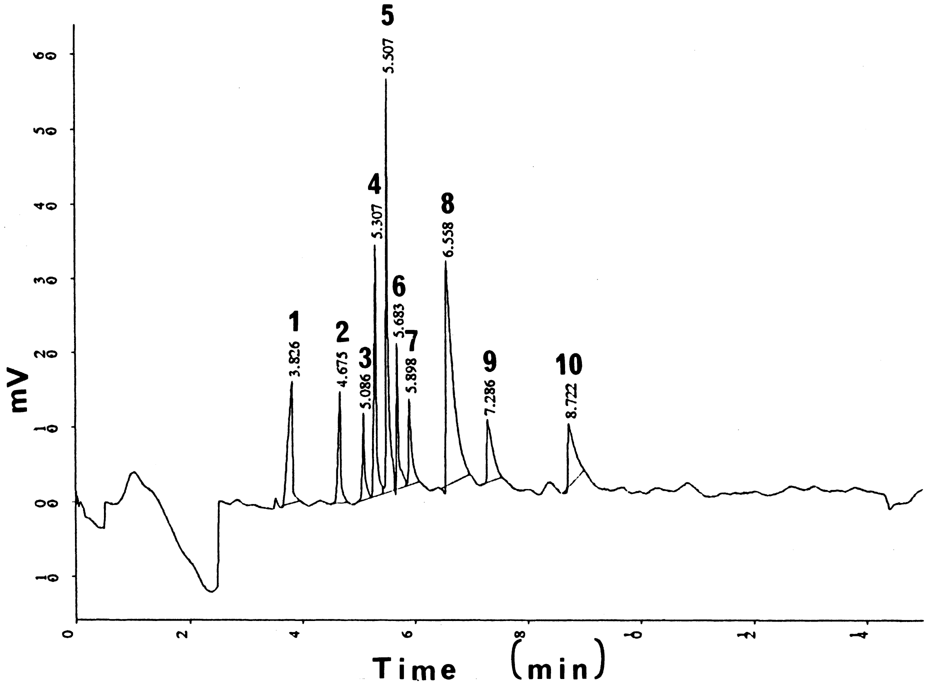

Fig. 1. Cation standard separation using buffer consisting of 17.5 m*M* HIBA and 6 m*M* imidazole, pH 4.4. Capillary, 37 cm×50 μm I.D. uncoated, fused-silica. Applied voltage, 25 kV. Temperature, 20°C. Hydrodynamic injection, 2 s. UV absorbance detection was at 215 nm. Peaks: (1) K^+ and NH_4^+, (2) Ba^{2+} and MMA, (3) Sr^{2+}, (4) Na^+, (5) Ca^{2+}, (6) Al^{3+}, (7) Mg^{2+}, (8) Li^+, (9) Co^{2+} and (10) Zn^{2+}.

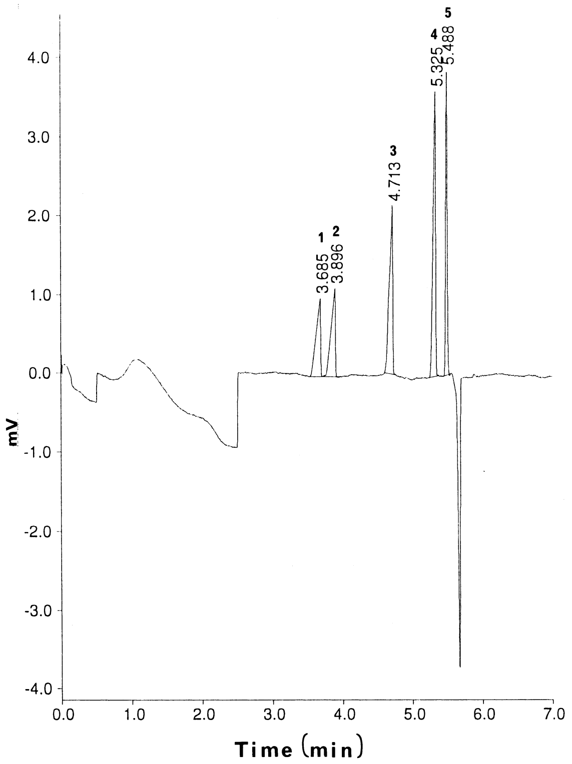

Fig. 2. Cation standard upon addition of 4 m*M* 18-crown-6 ether. Other experimental conditions as in Fig. 1. Peaks: (1) Cs^+, (2) NH_4^+, (3) MMA and K^+, (4) Na^+ and (5) Ca^{2+}. The negative peak is a system peak that occurs at the same position for each run.

separated from the NH_4^+ (Fig. 2). Fig. 3 demonstrates that the selectivity of the method may be manipulated by varying the concentration of the 18-crown-6. The mobility of the K^+ shifts with the concentration of this compound because 18-crown-6 ether forms an inclusion complex with K^+ [25]. At 4 m*M* 18-crown-6, the migration of the K^+ is retarded to the extent that the K^+ comigrates with the MMA. It is interesting to observe the magnitude of this phenomenon as the uncomplexed ionic conductances of K^+ (73.5 mho-cm^2/equivalent) and MMA (58.3 mho-cm^2/equivalent) are considerably different [23,24]. However, the resultant comigration of the K^+ with MMA was undesirable for explosives analysis because both are cations of interest in explosives residue. It is true that, by increasing the concentration of the 18-crown-6 ether to 5 mM, the K^+ will be retarded to the extent that it will be separated from the MMA. However, the pH of the electrolyte will be lowered and will require additional adjustment.

It is known that decreasing the electrolyte's polarity increases the affinity of crown ethers for metal ions [15,25]. This can be performed through the addition of an organic additive. Acetonitrile was used because it is less polar and less viscous than methanol, thereby producing a smaller change in electroosmotic flow (EOF) [17]. Figs. 4 and 5 illustrate that, by adding 5% acetonitrile (ACN) to

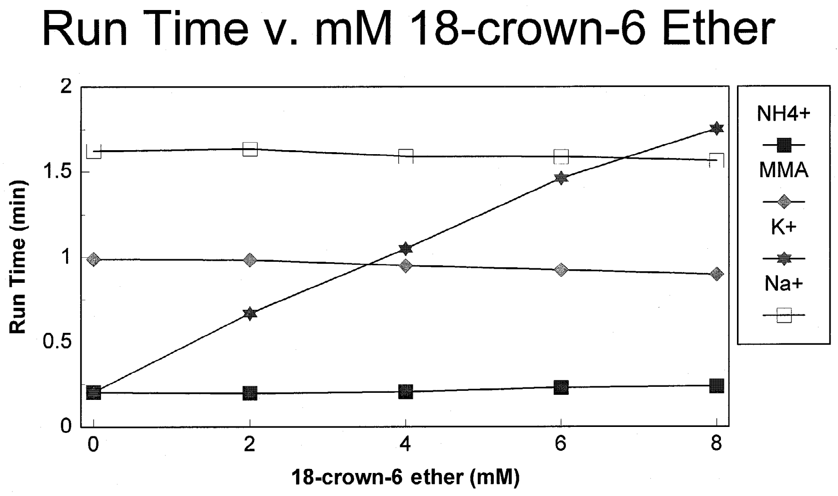

Fig. 3. Run time (min) vs. 18-crown-6 ether (m*M*).

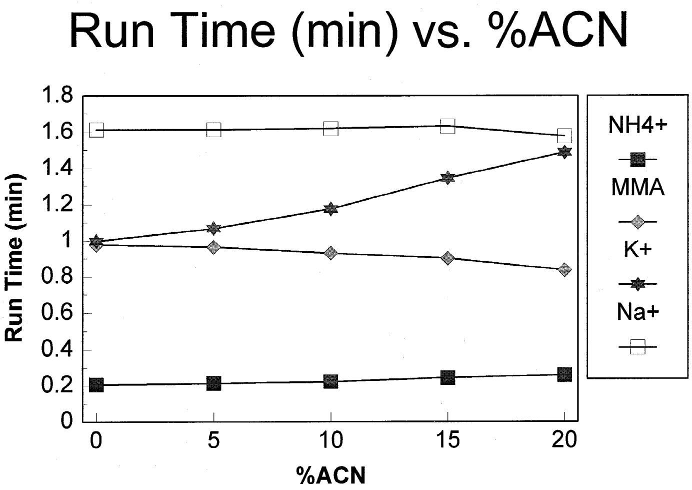

Fig. 4. Run time (min) vs. %ACN.

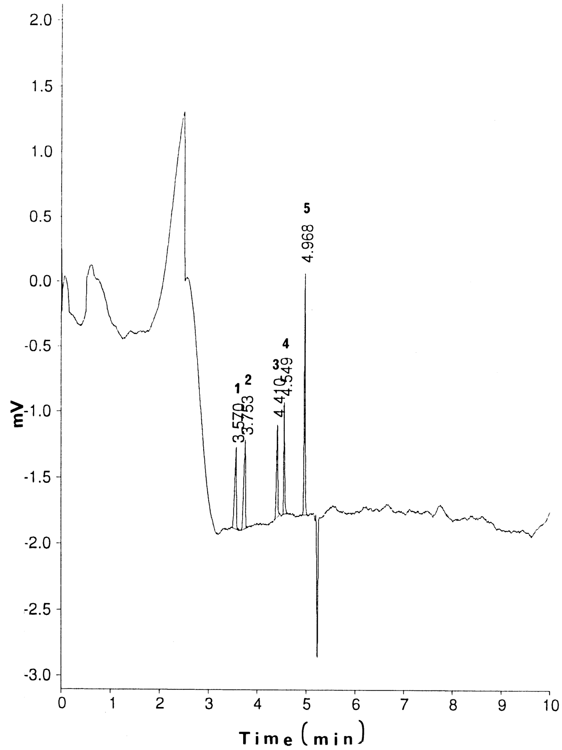

Fig. 5. Effect of the addition of 5% acetonitrile to electrolyte containing 4 m*M* 18-crown-6 ether. Other experimental conditions as in Fig. 1. Peaks: (1) Cs^+, (2) NH_4^+, (3) MMA, (4) K^+ and (5) Na^+.

the existing buffer, the relative migration times of K^+ and MMA were shifted. This is probably due to a change in the equilibrium constant for the inclusion complex of K^+ and 18-crown-6 ether. Fig. 4 shows that greater separation could be achieved with the addition of 10% ACN, but baseline noise increases with the larger concentrations of solvent. Fig. 5 depicts the final result at 5% ACN.

A series of cations, including Al^{3+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Li^+, Mg^{2+}, $Sr^{2+}$and Zn^{2+}, was tested to ascertain the potential of any interference with the cations in the standard used throughout the study. None of the above-listed cations exhibited any comigration with the cations in the standard.

A reproducibility study was conducted on a cation test mix containing NH_4^+, MMA, K^+, Na^+ and Cs^+. These cations were chosen because NH_4^+, MMA and K^+ are important constituents of explosives residue, Na^+ is ubiquitous in nature, and Cs^+ is a good internal standard since it is rarely a component of explosives materials. Five repetitions were performed at concentrations of 5 through 25, in increments of 5 and 50 ppm. The migration times of each cation at the varying concentrations did not exceed 1.1% R.S.D. The areas of the other cations in the test mix were adjusted by assuming the same response as that of the internal standard, Cs^+, which resulted in a R.S.D. of less than 6%. Additional studies determined the minimum detectable quantity to be approximately 0.5 ppm.

Table 1
Qualitative comparison of IC [12] and CE results of explosives and residue

Sample	IC results	CE results
Black powder	Na^+, K^+, NH_4^+	Na^+, K^+
Pyrodex	Na^+, K^+	Na^+, K^+
Trench Rite	Na^+, NH_4^+, MMA, Ca^{2+}	Na^+, NH_4^+, MMA Ca^{2+}
Power Max	Na^+, NH_4^+	Na^+, NH_4^+
Power Ditch	Na^+, NH_4^+	Na^+, NH_4^+
Tovex	Na^+, NH_4^+, MMA Ca^{2+}	Na^+, NH_4^+, MMA Ca^{2+}

Results of analyses conducted on water extracts of known samples of black powder, Pyrodex CTG, IMR 4350, Power Max, Power Ditch and Trench Rite were comparable in terms of the detected cations to those obtained with ion chromatography by Hall and McCord [12] (Table 1). These samples were not compared quantitatively as they were extracted at separate times from two independent sets of explosive residue samples. Fig. 6 illustrates that conclusive results were not obtained from a water extract of Tovex 210 in that NH_4^+ was not detected. When the same material was extracted using an aqueous solution containing 10% HNO_3, as described by Barsotti et al. [18] for IC, all of the cation components present in the sample were resolved unambiguously without degradation of the capillary column.

4. Conclusions

The results of this study demonstrate that both 18-crown-6 ether and acetonitrile are necessary in this electrolyte formulation in order to achieve unambiguous separation of NH_4^+, MMA and K^+ for explosives residue analysis. This technique is robust for the following reasons: (1) the use of 10% HNO_3 as an alternative extraction medium did not produce deleterious effects on the separation of the samples

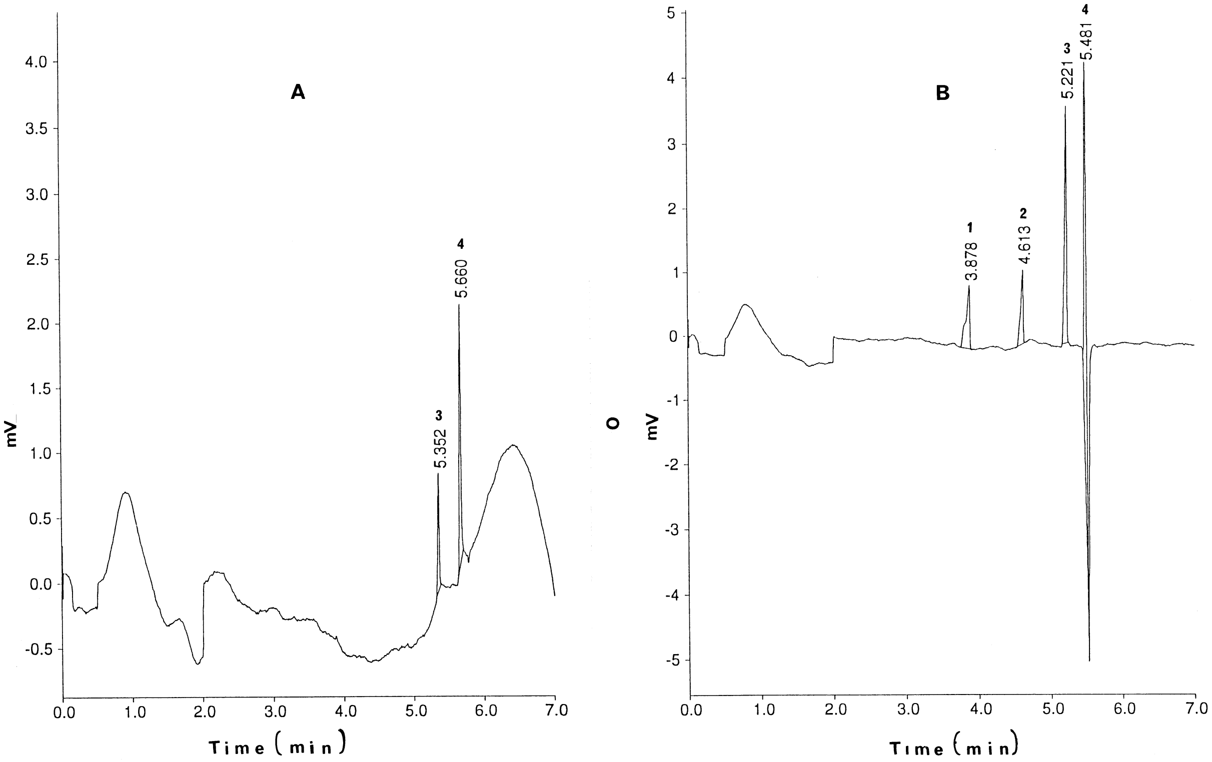

Fig. 6. Contrast of extraction of Tovex 210 in (A) aqueous solution not containing HNO_3 and (B) aqueous solution containing 10% HNO_3. Electrolyte composition as in Fig. 5. Other experimental conditions as in Fig. 1. Peaks: (1) NH_4^+, (2) MMA, (3) Na^+ and (4) Ca^{2+}.

or contribute to column degradation and (2) other cations did not produce interferences with the cations of interest in explosives residue. The reproducibility of separations using this buffer is demonstrated by symmetrical peaks with consistent run times of less than 1.1% R.S.D. Consequently, results obtained using this method may be interpreted with confidence. Capillary electrophoresis of explosive materials using this buffer produces comparable results with those obtained using ion chromatography [12]. The major advantage is that the separations by CE are accomplished in less than half of the time required for IC.

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