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Bibliographic citation

Hutchinson, J; Evenhuis, CJ; Johns, CA; Kazarian, A; Breadmore, Michael; Macka, Miroslav; et al. (2007). Identification of Inorganic Improvised Explosive Devices by Analysis of Postblast Residues Using Portable Capillary Electrophoresis Instrumentation and Indirect Photometric Detection with a Light-Emitting Diode. University Of Tasmania. Journal contribution.
https://figshare.utas.edu.au/articles/journal_contribution/Identification_of_Inorganic_Improvised_Explosive_Dev_Emitting_Diode/22866449

Is published in: [10.1021/ac0708792](https://doi.org/10.1021/ac0708792)

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Identification of Inorganic Improvised Explosive Devices by Analysis of Postblast Residues Using Portable Capillary Electrophoresis Instrumentation and Indirect Photometric Detection with a Light-Emitting Diode

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A commercial portable capillary electrophoresis (CE) instrument has been used to separate inorganic anions and cations found in postblast residues from improvised explosive devices (IEDs) of the type used frequently in terrorism attacks. The purpose of this analysis was to identify the type of explosive used. The CE instrument was modified for use with an in-house miniaturized light-emitting diode (LED) detector to enable sensitive indirect photometric detection to be employed for the detection of 15 anions (acetate, benzoate, carbonate, chlorate, chloride, chlorite, cyanate, fluoride, nitrate, nitrite, perchlorate, phosphate, sulfate, thiocyanate, thiosulfate) and 12 cations (ammonium, monomethylammonium, ethylammonium, potassium, sodium, barium, strontium, magnesium, manganese, calcium, zinc, lead) as the target analytes. These ions are known to be present in postblast residues from inorganic IEDs constructed from ammonium nitrate/fuel oil mixtures, black powder, and chlorate/perchlorate/sugar mixtures. For the analysis of cations, a blue LED (470 nm) was used in conjunction with the highly absorbing cationic dye, chrysoidine (absorption maximum at 453 nm). A nonaqueous background electrolyte comprising 10 mM chrysoidine in methanol was found to give greatly improved baseline stability in comparison to aqueous electrolytes due to the increased solubility of chrysoidine and its decreased adsorption onto the capillary wall. Glacial acetic acid (0.7% v/v) was added to ensure chrysoidine was protonated and to enhance separation selectivity by means of complexation with transition metal ions. The 12 target cations were separated in less than 9.5 min with detection limits of 0.11–2.30 mg/L (calculated at a signal-to-noise ratio of 3). The anions separation system utilized a UV LED (370 nm) in conjunction with an aqueous chromate

electrolyte (absorption maximum at 371 nm) consisting of 10 mM chromium(VI) oxide and 10 mM sodium chromate, buffered with 40 mM tris(hydroxymethyl)-aminomethane at pH 8.05. All 15 target anions were baseline separated in less than 9 min with limits of detection ranging from 0.24 to 1.15 mg/L (calculated at a signal-to-noise ratio of 3). Use of the portable instrumentation in the field was demonstrated by analyzing postblast residues in a mobile laboratory immediately after detonation of the explosive devices. Profiling the ionic composition of the inorganic IEDs allowed identification of the chemicals used in their construction.

Improvised explosive devices (IEDs) constructed by terrorists often contain “homemade” explosives rather than high explosives, such as nitrated organic compounds (e.g., 2,4,6-trinitrotoluene, TNT), because of the relative ease with which the components used in their manufacture can be procured. Typically, IEDs comprise an explosive created from unrestricted materials and an initiation system involving an electrical charge and a detonator. Inorganic homemade explosives employ vigorous oxidation/reduction chemical reactions using strong inorganic oxidizers such as nitrate, perchlorate, or chlorate.¹

An important facet of counterterrorism procedures is the rapid collection of evidence to determine the type, quantity, and composition of the explosive, preferably using two complimentary analytical techniques in order to provide confirmatory analyses.² Ion chromatography (IC) has been utilized for determining the main components of inorganic IEDs,³ with other techniques such as scanning electron microscopy-energy dispersion X-ray,^{2,4} X-ray diffraction,⁵ infrared,⁶ and atomic absorption spectroscopy,⁷ as well

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(1) Pumera, M. *Electrophoresis* 2006, 27, 244–256.

(2) Royds, D.; Lewis, S. W.; Taylor, A. M. *Talanta* 2005, 67, 262–268.

(3) Dicinoski, G. W.; Shellie, R. A.; Haddad, P. R. *Anal. Lett.* 2006, 39, 639–657.

(4) Kuila, D. K.; Chakraborty, A.; Sharma, S. P.; Lahiri, S. C. *Forensic Sci. Int.* 2006, 159, 127–131.

(5) Green, M. C.; Partain, L. D. *Proc. SPIE—Int. Soc. Opt. Eng.* 2003, 5048, 63–72.

as wet chemical color tests,² also being applied. Capillary electrophoresis (CE) is also a viable alternative analytical technique, and several reviews have appeared recently describing the role of CE in forensic investigations using both capillary^{8,9} and microfluidic chip formats.^{1,10} CE and chip-based methods have been used for the screening of nitroaromatic explosives and inorganic species from explosives and explosives postblast residues, including, separations performed by micellar electrokinetic chromatography,^{11,12} electrokinetic chromatography,¹³ capillary electrochromatography,^{14–16} and mixed-mode methods.¹⁷ Detection has generally involved ultraviolet absorbance,¹¹ electrochemical detection methods,^{16,18–20} indirect and direct laser-induced fluorescence,²¹ and immunoassay.²²

Postblast residues from inorganic IEDs can contain up to 15 different inorganic anions and 12 cations (see later discussion), so a high-efficiency separation tool such as CE is necessary if these ions are to be used to identify the homemade explosive. Moreover, universal detection techniques such as indirect spectrophotometric detection or conductivity detection are required since many of the target analytes show low absorptivities in the UV–visible spectrum. Separating inorganic cations poses a particular challenge because many of these species exhibit similar electrophoretic mobilities and their separation can be accomplished only by addition to the electrolyte of a weak complexant, such as α -hydroxyisobutyric acid (HIBA) or crown ethers.²³

CE was first demonstrated as a complementary technique to ion chromatography for inorganic explosive residue analysis by Hargadon and McCord in 1992²⁴ using a chromate background electrolyte (BGE) and indirect photometric detection at 280 nm. They obtained baseline separation in 16 min of eight inorganic anions typically found in residues from black powder and chlorate pipe bombs. In 1994, McCord et al.²⁵ compared their CE method with IC for determining anions present in a Pyrodex pipe bomb residue, but cation analysis was not undertaken. Kishi et al.²⁶ developed two individual CE methods for the analysis of inorganic cations and anions in IEDs. Chloride and chlorate were detected on pipe bomb fragments originally containing an improvised

potassium chlorate/fuel mixture explosive. An emulsion explosive was electrically initiated sitting on a steel plate, which was swabbed with a wet cloth and a water extract taken for CE analysis. The ammonium, sodium, and nitrate were easily detected from the extract, and a differing proportion of analytes could be determined between pre- and postblast extracts. A third sample obtained by water extraction of cotton gloves worn while preparing perchlorate explosives was analyzed for its anion content and chloride, nitrate, and perchlorate were detected. The type of explosive used (ammonium perchlorate) was determined using these data in combination with X-ray diffraction performed on the surface of the cotton gloves. Doyle and McCord²³ developed a similar BGE system for the indirect detection of five cations commonly found in commercial and improvised explosives. The BGE comprised imidazole as the UV-absorbing probe cation for indirect detection, HIBA as the complexant, with 18-crown-6 ether and acetonitrile being added to achieve baseline separation between potassium, ammonium, and monomethylammonium ions. McCord and co-workers²⁷ also developed a CE method for the simultaneous separation of anions and cations in low-explosive residue. This required use of a complex BGE containing anionic and cationic indirect detection probes, cation complexation agents, organic modifier, and an EOF modifier to provide a semipermanent surface coating of the capillary. Cations and anions were injected at opposite ends of the capillary, allowing them to simultaneously migrate electrophoretically in opposite directions past the detector. Six cations and eight anions could be detected in less than 5.5 min, and this method was applied to black and smokeless powder residues.

In recent years, the focus in forensic science applications has shifted toward portable and fast CE methods that can be performed at a crime scene rather than in an analytical laboratory. Microfluidic systems offer a small footprint amenable to on-site analysis, low sample consumption, and also provide fast separation times in the order of tens of seconds. Wang and co-workers have investigated microchip electrophoresis for explosive residue analysis and have used a poly(methyl methacrylate) (PMMA) chip for the determination of seven explosive-related anions and cations in less than 1 min.²⁸ Anions and cations were detected by contactless conductivity detection using the same electrolyte buffer without reversal of the electroosmotic flow (EOF), although separate analyses were required for anions and cations. A moveable contactless conductivity detector was also developed to provide a simple means of experimentally optimizing channel length and separation voltage for the separation of low explosives.²⁹ Wang and co-workers³⁰ have also employed dual-opposite injection of anions and cations in PMMA chips and have achieved simultaneous separation of three inorganic anions, three inorganic cations, and two nerve agent degradation products. The six inorganic ions typically present in low explosives could also be separated in less than 1 min. The disadvantages of chip-based methods in comparison to benchtop CE methods may include the following: a reduced number of analytes that can be separated,

- (6) Sharma, S. P.; Lahiri, S. C. *J. Energ Mater.* **2005**, *23*, 239–264.
- (7) Beveridge, A. D.; Payton, S. F.; Audette, R. J.; Lambertus, A. J.; Shaddick, R. C. *J. Forensic Sci.* **1975**, *20*, 431–454.
- (8) Thormann, W.; Lurie, I. S.; McCord, B.; Marti, U.; Cenni, B.; Malik, N. *Electrophoresis* **2001**, *22*, 4216–4243.
- (9) Tagliaro, F.; Bortolotti, F. *Electrophoresis* **2006**, *27*, 231–243.
- (10) Verpoorte, E. *Electrophoresis* **2002**, *23*, 677–712.
- (11) Oehrle, S. A. *J. Chromatogr., A* **1996**, *745*, 233–237.
- (12) Northrop, D. M.; Martire, D. E.; MacCrehan, W. A. *Anal. Chem.* **1991**, *63*, 1038–1042.
- (13) Groom, C. A.; Halasz, A.; Paquet, L.; D'Cruz, P.; Hawari, J. J. *Chromatogr., A* **2003**, *999*, 17–22.
- (14) Bailey, C. G.; Yan, C. *Anal. Chem.* **1998**, *70*, 3275–3279.
- (15) Giordano, B. C.; Copper, C. L.; Collins, G. E. *Electrophoresis* **2006**, *27*, 778–786.
- (16) Hilmi, A.; Luong, J. H. T. *Electrophoresis* **2000**, *21*, 1395–1404.
- (17) Luong, J. H. T.; Guo, Y. J. *Chromatogr., A* **1998**, *811*, 225–232.
- (18) Wang, J.; Pumera, M. *Anal. Chem.* **2002**, *74*, 5919–5923.
- (19) Wang, J.; Chen, G.; Chatrathi, M. P.; Fujishima, A.; Tryk, D. A.; Shin, D. *Anal. Chem.* **2003**, *75*, 935–939.
- (20) Hilmi, A.; Luong, J. H. T. *Environ. Sci. Technol.* **2000**, *34*, 3046–3050.
- (21) Bailey, C. G.; Wallenborg, S. R. *Electrophoresis* **2000**, *21*, 3081–3087.
- (22) Bromberg, A.; Mathies, R. A. *Electrophoresis* **2004**, *25*, 1895–1900.
- (23) Doyle, J. M.; McCord, B. R. *J. Chromatogr., B* **1998**, *714*, 105–111.
- (24) Hargadon, K. A.; McCord, B. R. *J. Chromatogr.* **1992**, *602*, 241–247.
- (25) McCord, B. R.; Hargadon, K. A.; Hall, K. E.; Burmeister, S. G. *Anal. Chim. Acta* **1994**, *288*, 43–56.
- (26) Kishi, T.; Nakamura, J.; Arai, H. *Electrophoresis* **1998**, *19*, 3–5.

- (27) Hopper, K. G.; LeClair, H.; McCord, B. R. *Talanta* **2005**, *67*, 304–312.
- (28) Wang, J.; Pumera, M.; Collins, G.; Opekar, F.; Jelinek, I. *Analyst* **2002**, *127*, 719–723.
- (29) Wang, J.; Chen, G.; Alexander Muck, J. *Anal. Chem.* **2003**, *75*, 4475–4479.
- (30) Wang, J.; Chen, G.; Alexander Muck, J.; Collins, G. E. *Electrophoresis* **2003**, *24*, 3728–3734.

carryover problems between runs resulting from the “world-to-chip” interface, and a lack of method robustness.

Although the above approaches provide valuable analytical information, a minority are applicable to the identification of a wide range of explosives because of the relatively high number of anions and cations required for a universal “fingerprinting” separation addressing all commonly used inorganic homemade explosives. For example, the method described by Knops et al.³¹ was able to identify 16 inorganic anions in the space of ~9 min using a commercial electrolyte, but the method was not appropriate for the detection of inorganic cations, and the limits of detection (LODs) for anions (10–30 ppm) are likely to be too high for the low analyte concentrations usually associated with postblast residues. In this study, we have developed such universal fingerprinting separations of anions and cations and have implemented these separations on a commercially available portable CE instrument, which can be operated in the field. This goal was achieved by modifying the commercial instrument to operate in the indirect spectrophotometric detection mode using a sensitive, miniature light-emitting diode (LED) photometric detector constructed in-house. BGEs containing highly absorbing indirect detection probes were developed, and the emission of the LED was matched spectrally with the absorption maximum of the probe. The developed methods were utilized for field and laboratory testing of residues obtained from inorganic IEDs detonated under controlled conditions.

EXPERIMENTAL SECTION

Apparatus. A portable CE-P2 instrument from CE Resources (Ayer Rajah, Singapore) was used for all analyses. The portable instrument was housed in an attaché case, weighed ~8 kg, drew a maximum power of 50 W, and was equipped with a battery supply capable of 3 h of use when fully charged. Alternatively, the instrumentation could be operated from the mains power supply using the transformer provided. The CE instrument was operated either under standard laboratory conditions or in the field. In the latter case, the instrument was used inside a purpose-built mobile laboratory housed in a standard small delivery van.

An LED photometric detector designed, constructed, and evaluated in-house³² was used for detection purposes. In brief, this detector comprised a LED light source and an extended UV photodiode used in conjunction with a built-in amplifier. These components were encased in a black nylon housing, which excluded stray light. The LED light source could be easily interchanged. In this work, a 470-nm blue LED (part no. 3324515) purchased from (Farnell InOne, NSW, Australia) was used for the indirect detection of cations using the highly absorbing cationic dye, chrysoidine, as the probe cation, and a 370-nm UV LED (part no. 1003156) purchased from the same company was used for the indirect detection of anions using chromate as the probe anion. A commercial alignment interface (Agilent Technologies, Victoria, Australia) was used to position the window of the fused-silica separation capillary in the detection housing.

Reagents. All reagents used were of analytical reagent grade unless otherwise stated. The cationic dye chrysoidine (4-phenyl-azo-*m*-phenylenediamine hydrochloride) was obtained from Fluka

and was further purified according to the method outlined by Johns et al.³³ Other components of the BGE used for the analysis of cations included HPLC grade methanol (BDH, Victoria, Australia) and glacial acetic acid (Biolab, Victoria, Australia). The final composition of the BGE for cation separations was 10 mM purified chrysoidine and 0.7% (v/v) glacial acetic acid in HPLC grade methanol. The BGE for anion separations consisted of a mixture of chromium(VI) oxide (Fluka), sodium chromate (BDH), and tris(hydroxymethyl)aminomethane (TRIS; Sigma-Aldrich, Milwaukee, WI). The final composition of the electrolyte was 10 mM CrO₃, 10 mM Na₂CrO₄, and 40 mM TRIS in Milli-Q water.

The EOF reversal reagent hexadimethrine bromide (HDMB) was purchased from Sigma-Aldrich. Analytical grade sodium hydroxide and hydrochloric acid were obtained from BDH and Ajax (Sydney, NSW, Australia), respectively.

The 1000 mg/L anion standard solutions were prepared individually by volumetric dissolution in Milli-Q water of sodium or potassium salts obtained from Sigma-Aldrich unless otherwise stated. A 5 mg/L standard mixture of the following 15 anions was prepared daily: acetate (May and Baker, Victoria, Australia), benzoate, carbonate (BDH), chlorate, chloride (BDH), chlorite (technical grade 80%), cyanate, nitrate, nitrite, fluoride, perchlorate, phosphate, sulfate, thiocyanate, and thiosulfate. 1-Hexanesulfonic acid, sodium salt was dissolved in Milli-Q water for use as an internal standard in the anion separation.

The following 1000 mg/L atomic absorption standard solutions of cations (as nitrates) were purchased from Sigma-Aldrich: barium, calcium, lead, manganese, magnesium, sodium, strontium, and zinc. The 1000 mg/L ammonium, methylammonium, and ethylammonium individual cation standard solutions were prepared by volumetric dissolution of ammonium nitrate (BDH, 98%), methylammonium chloride (Sigma, laboratory grade), and ethylammonium chloride (Fluka, Puriss grade) salts using Milli-Q water. An aqueous mixed working standard of cations was prepared daily containing 0.61 mg/L ammonium, 1.23 mg/L methylammonium, ethylammonium, potassium, sodium, magnesium, and calcium, 2.44 mg/L strontium, manganese, and zinc, 4.89 mg/L barium, and 9.80 mg/L lead. Measurement of the EOF was used as an internal marker for the cation separation system.

Electrophoretic Procedures. Separation of Anions. Separations were performed using 50- and 75- μ m-i.d. fused-silica capillary purchased from Polymicro Technologies Inc. (Phoenix, AZ). An 88.0-cm length of 50- μ m-i.d. capillary was used with a window burned 9.5 cm from the cathode. The wall of the capillary was coated with HDMB, which resulted in both anions and the EOF migrating toward the anode. The capillary was preconditioned prior to use by flushing at 17 psi 0.1 M NaOH for 10 min, water for 5 min, a 1% aqueous solution of HDMB for 10 min, and then BGE for 2 min. Prior to each run, the capillary was conditioned by flushing the BGE at 17 psi for 2 min. Injection was performed hydrodynamically at 0.4 psi for 30 s. Separation was performed by applying -25 kV across the capillary. During the separation, 0.4 psi was also applied at the inlet end of the capillary. This has been shown to provide more stable baselines³³ when the BGE can potentially interact with the capillary surface and also had the added benefit of shortening the time of analysis by several

(31) Knops, L. A.; Northrop, D. M.; Person, E. C. *J. Forensic Sc.* **2006**, *51*, 82–86.

(32) Johns, C.; Macka, M.; Haddad, P. R. *Electrophoresis* **2004**, *25*, 3145–3152.

(33) Johns, C.; Macka, M.; Haddad, P. R. *J. Chromatogr., A* **2003**, *997*, 87–94.

minutes without detrimentally compromising the separation efficiency.

Separation of Cations. A 55.0-cm length of 75- μ m-i.d. fused-silica capillary was used with a window burned 9.5 cm from the cathode. This capillary was used uncoated, but prior to use it was preconditioned by flushing aqueous 0.1 M NaOH at 17 psi through the capillary for 5 min, water for 5 min, methanol for 5 min, and then BGE for 5 min. Prior to each run, the capillary was conditioned at 17 psi for 0.5 min with an aqueous solution of 1 M HCl, to remove any adsorbed species, 0.5 min with methanol, and 0.7 min with BGE. Introduction of the sample was performed using hydrodynamic injection at 0.1 psi for 1 s. The voltage applied during the separation was 25 kV.

Sample Collection and Preparation. Witness plates were used to collect explosive residues from field tests. These plates were composed of galvanized steel sheets of rectangular dimensions, 34 cm \times 32 cm. For each inorganic IED, a witness plate was placed on the ground and the explosive device was positioned in the center of the plate. Four further witness plates were arranged laterally around the IED at a distance of 1–2 m. The IED was detonated and the witness plates were collected in polyethylene bags, which were subsequently heat-sealed to avoid contamination. Soil samples were also taken directly under the base plate both before and after the detonation.

The sampling of ions deposited onto the witness plates was performed as follows. A sterile MWE102 rayon swab (Imbros, Tasmania, Australia) was moistened in Milli-Q water, wiped over a 50-cm² portion of the witness plate, and then placed in a Dionex polypropylene 10-mL sample vial (Sunnyvale, CA). The vial was filled with 8 mL of Milli-Q water, capped, shaken, and sonicated for 5 min to aid extraction. The aqueous sample was then filtered through a 0.45- μ m nylon filter (Phenomenex, NSW, Australia) to remove any particulate material into a 2-mL snap-top glass sample vial (Agilent Technologies) ready for analysis by CE. The same extraction procedure was performed on an unused witness plate and this formed the sample blank. Blank runs were also conducted for the sterile swabs and for the 0.45- μ m syringe filters.

The EOF marker (water dip) was used as an internal standard for the cation analyses. For the anion analyses, 5 mg/L of the sodium salt of 1-hexanesulfonic acid was added to each sample after filtration for the purpose of internally standardizing the retention time of analytes between runs.

RESULTS AND DISCUSSION

Target Analytes Present in Residues from Inorganic IEDs.

The principal ingredients of IEDs are fuels and oxidizers. Fuels that are used commonly include fuel oil, carbon, zinc, phosphorus, smokeless powder, sugar, charcoal, sulfur, and alkylammonium nitrates. These substances can be mixed with inorganic oxidizers, such as salts containing nitrate, chlorate, or perchlorate. Lighter elements, such as beryllium, aluminum, and magnesium, can also be included to increase the heat of combustion, and the properties of the explosives can be modified using water, gums, thickeners, and cross-linking agents. During the explosion, these chemicals also undergo chemical reaction to produce the ionic species present in postblast residues.

After careful consideration of the components of common homemade explosives, their probable decomposition products, and

Table 1. Inorganic Improvised Explosive Devices and the Target Analytes in Postblast Residues Analyzed in This Study

device	composition	characteristic anions	characteristic cations
ANFO	ammonium nitrate, fuel oil	NO ₃ ⁻	NH ₄ ⁺
black powder	potassium nitrate, sulfur, charcoal	NO ₃ ⁻ SO ₄ ²⁻ S ₂ O ₃ ²⁻	K ⁺
chlorate/sugar	sodium chlorate	ClO ₃ ⁻	Na ⁺
perchlorate/sugar	sugar, potassium perchlorate,	Cl ⁻ ClO ₄ ⁻	K ⁺
chlorate/sulfur/aluminum	sulfur, sodium chlorate,	Cl ⁻ ClO ₃ ⁻	Na ⁺
	sulfur, aluminum	Cl ⁻ SO ₄ ²⁻ S ₂ O ₃ ²⁻	Al ³⁺ ^a

^a Requires sample pretreatment. Present as water-insoluble oxide.

consultation with Australia's national forensic science agencies,³⁴ a set of target analytes comprising 12 cations (ammonium, monomethylammonium, ethylammonium, potassium, sodium, barium, strontium, magnesium, manganese, calcium, zinc, lead) and 15 anions (acetate, benzoate, carbonate, chlorate, chloride, chlorite, cyanate, fluoride, nitrate, nitrite, perchlorate, phosphate, sulfate, thiocyanate, thiosulfate) was selected. Inorganic ions that may be found in IEDs include the following: oxidizers such as the ammonium, sodium, sodium, potassium, strontium, or barium salts of nitrate, chlorate, and perchlorate and their corresponding reduced species; the oxidized species of carbon and sulfur; metal ions added to increase the temperature of the reaction (e.g., aluminum, magnesium); sodium benzoate to provide acoustic effects; and also a number of components that can be found in fireworks (metal ions such as sodium, calcium, barium, or strontium). The set of target analytes was chosen to enable separation of characteristic analytes in postblast residues in the presence of ionic contaminants that are typically present in soil (calcium, magnesium, manganese, potassium, sodium, chloride, nitrate, sulfate), carbonate from the atmosphere, lead from primary explosives, and trace amounts of zinc from galvanized metal surfaces. Aluminum was not included in the set of target cations because previous tests had shown that during the explosion it was converted to a water-insoluble form that was not extracted from the witness plate using the outlined aqueous swabbing procedure.

The above group of target analytes is considerably larger than any used in previous studies, and full separation of these species would permit fingerprinting not only of all of the common inorganic IEDs listed in Table 1 but also for the identification of a wider range of other, less frequently used inorganic IEDs.

Development of Cation Separation. Since most inorganic cations exhibit low absorptivities in the UV region, indirect photometric detection is necessary when a photometric detector is to be employed. This is a well-established universal detection mode in CE and is performed by the addition of an absorbing probe ion of the same charge as the analytes and by monitoring absorbance at a wavelength at which this probe ion absorbs. Light

(34) Paul Kirkbride, N. I. o. F. S. N.; Dicoski, G., Ed., 2006.

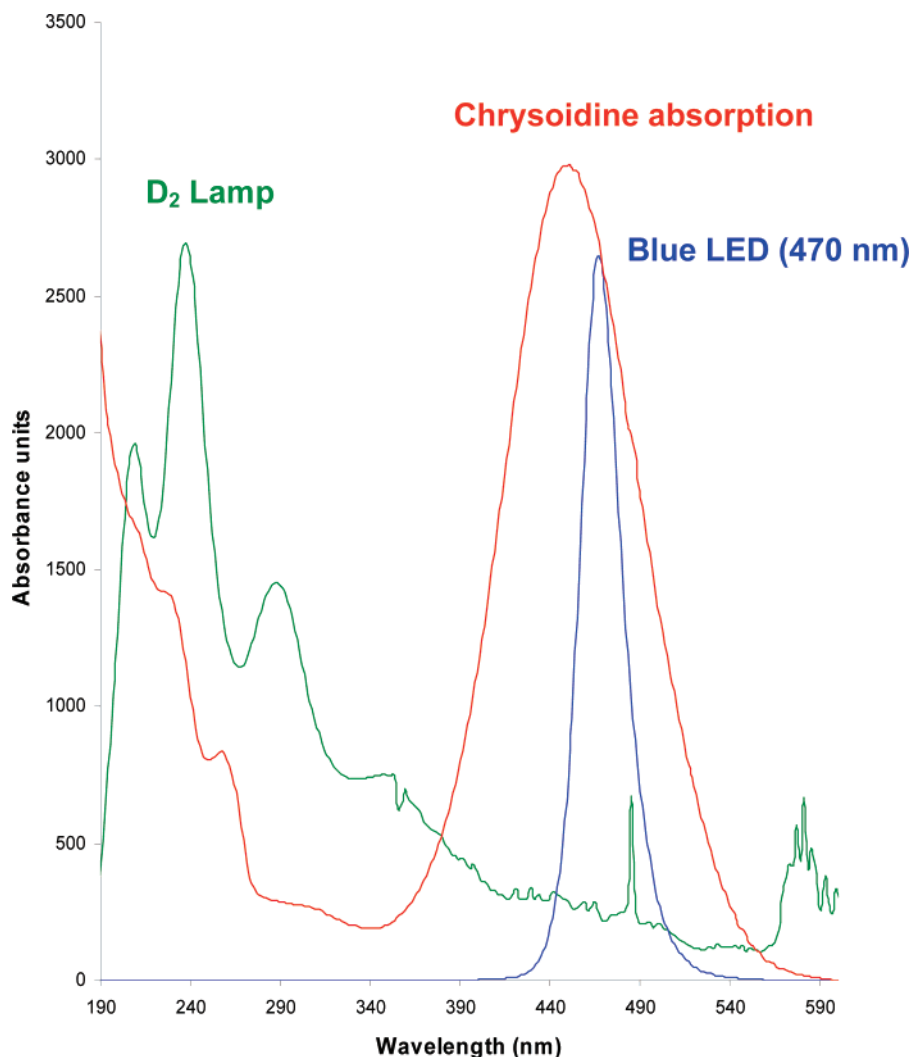


Figure 1. Comparison of the emission spectra of a deuterium lamp, blue LED, and the absorption spectrum of the cationic dye chrysoidine.

sources used typically on CE instruments emit strongly in the UV region but have only weak emission in the visible region³⁵ For this reason, most probes used for indirect photometric detection have been developed to be compatible only with UV light sources.

LEDs, especially those with emission in the visible region, can be used as an alternative light source for indirect photometric detection. LEDs provide a highly stable narrow spectrum low-noise output, have low power requirements, can be purchased quite cheaply, are small in size and have very long lifetimes in comparison to other light sources. A miniature LED detector has been developed previously in this research group³² and can accommodate LEDs of differing wavelengths depending on the absorption maximum of the probe used for indirect photometric detection.

Dyes can often exhibit greater absorptivity than probes typically used for indirect detection in CE, and previous work by Johns et al.^{33,36–38} has demonstrated the benefits of using dyes as

indirect detection probes. Paramount among these benefits are lower detection limits, which arise as a result of the effects of the molar absorptivity of the probe (ϵ) on the concentration limit of detection (C_{LOD}), according to eq 1,

$$C_{\text{LOD}} = \frac{C_p}{RD_r} = \frac{N_{\text{BL}}}{R\epsilon l} \quad (1)$$

where C_p is the probe concentration, R is the transfer ratio (the number of moles of the probe displaced by 1 mol of analyte), D_r is the dynamic reserve (the ratio of background absorbance to noise), N_{BL} is the baseline noise, and l is the detection cell path length. Use of a highly absorbing probe ion, such as the cationic dye, chrysoidine ($\epsilon = 26\,733 \text{ L mol}^{-1} \text{ cm}^{-1}$), is clearly desirable. Moreover, it was possible to closely match the absorption maximum of chrysoidine (454 nm) with a 470-nm blue LED, as shown in Figure 1.

Previous work using chrysoidine as a probe for the indirect detection of cations³³ has involved use of an aqueous BGE containing the probe in base form, together with HIBA, which

(35) Heraeus; Heraeus Noblelight GmbH Data Sheet Long-Life Deuterium Lamp DX Series, http://www.heraeus-noblelight.com/fileadmin/user_upload/PDF/OpticsAnalytics/OA_Product_Brochure.pdf accessed July 9, 2007; Hanau, 2007.

(36) Rodemann, T.; Johns, C.; Yang, W.-S.; Haddad, P. R.; Macka, M. *Anal. Chem.* **2005**, *77*, 120–125.

(37) Johns, C.; Macka, M.; Haddad, P. R. *Electrophoresis* **2000**, *21*, 1313–1319.

(38) Johns, C.; Macka, M.; Haddad, P. R. *Electrophoresis* **2002**, *23*, 43–48.

Table 2. Analytical Figures of Merit for Cation Separation System by CE

analyte	retention time ($n = 10$)		peak area RSD (%)	theoretical plates/m	resolution	LOD (S/N = 3, mg/L)	calibration R^2
	min	RSD (%)					
1 monomethylammonium	2.388	1.03	8.55	89 000	3.16	0.21	0.9925
2 ammonium	2.545	1.08	10.7	97 000	1.04	0.20	0.9906
3 ethylammonium	2.583	1.02	9.02	134 000	3.26	0.19	0.9882
4 potassium	2.724	0.91	16.1	103 000	6.25	0.22	0.9889
5 sodium	3.074	0.96	10.6	84 000	11.8	0.11	0.9867
6 barium	4.123	0.83	17.5	75 000	3.11	1.26	0.9869
7 strontium	4.462	0.72	11.8	100 000	2.76	0.57	0.9834
8 magnesium	4.745	0.93	11.6	71 000	1.38	0.13	0.9858
9 calcium	4.889	0.77	16.5	99 000	5.47	0.23	0.9898
10 manganese	5.432	0.94	13.3	120 000	19.3	0.37	0.9828
11 zinc	8.425	0.70	11.6	93 000	1.30	0.52	0.9823
12 lead	8.669	0.92	12.3	84 000		2.30	0.9847

acted as the counteranion, as a buffer ($pK_a \sim 4.84$ at 20°C), and as a weak complexant to enhance the selectivity of the CE separation of inorganic cations. Problems associated with baseline instability were attributed to adsorption of the dye onto the inner surface of the capillary and were minimized through a combination of coating the capillary with poly(ethyleneimine), addition of a neutral polymer to the BGE, and addition of a small amount of hydrodynamic pressure during the separation. This BGE was

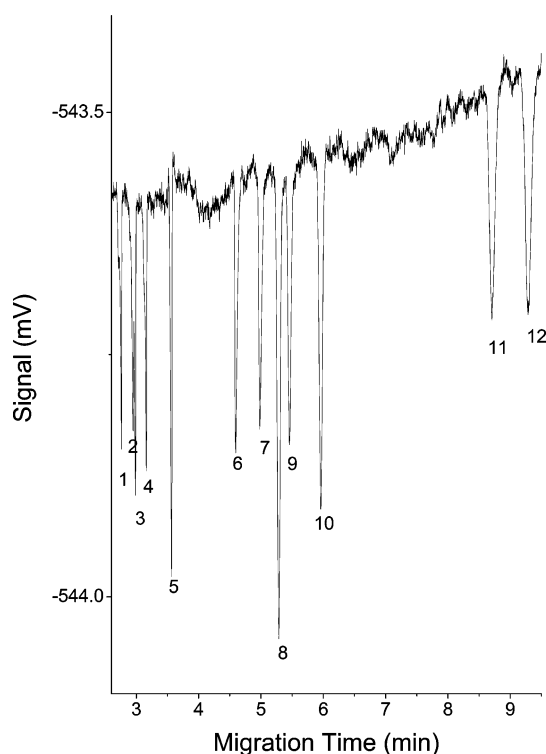


Figure 2. CE separation of target cation mixture using the portable CE-P2 equipped with a miniaturized indirect photometric LED detector. Conditions: 75- μm -i.d. fused-silica capillary, $L_{\text{total}} = 55.5$ cm. BGE was 10 mM chrysoidine in MeOH, with 0.7% glacial acetic acid added. Separation voltage, 25 kV. Detection performed using a 470-nm LED source, operating current 40 mA, 9.5 cm from cathode ($L_{\text{detector}} = 46.0$ cm). An extended UV photodiode detector collected the signal obtained. Samples injected using a pressure of 0.1 psi for 1 s. Sample concentrations: 20.5 mg/L ammonium, 41 mg/L methylammonium, ethylammonium, potassium, sodium, magnesium, and calcium, 81.5 mg/L strontium, manganese, and zinc, 163 mg/L barium, and 326.5 mg/L lead. Cations are numbered throughout all figures in correspondence with Table 2.

applied in the present study, but baseline stability continued to be a problem. However, stable baselines were observed using a nonaqueous BGE in which chrysoidine purified as the free base was dissolved in methanol and glacial acetic acid was added to protonate the dye. This BGE provided unique separation selectivity as a result of the effects of methanol on the electrophoretic mobilities of the metal ions³⁹ and also as a result of the weak complexation effects provided by acetate. Furthermore, chrysoidine was much more soluble in methanol than in aqueous solution, and this prevented the dye from adsorbing onto the capillary wall, thereby providing a relatively stable baseline during electrophoresis. A separation of the 12 target cations in less than 10 min is shown in Figure 2. No internal standard was required since the position of the EOF could be determined easily (EOF peak not shown in Figure 2), and this peak was used to normalize migration times. Table 2. provides the analytical figures of merit calculated from 10 replicate injections. Resolution was greater than 1 in all cases, the number of theoretical plates per meter ranged between 71 000 and 134 000, and the limits of detection ranged between 0.11 and 2.3 mg/L based on injecting 0.05% of the capillary. For larger injections, resolution between all analytes was not maintained.

In comparison to previous studies,^{23,27} the separation shown in Figure 2 includes a much wider range of cations, gives superior baseline stability, and does not suffer from difficulties in resolving potassium from ammonium and barium from monomethylammonium. The improved separation characteristics were the result of altered separation selectivity due to solvation effects by methanol, leading to a migration order in methanol which was quite different from that observed using an aqueous electrolyte. Other solvents, such as DMSO, ethanol, and acetonitrile were also investigated, but complete separation of all target cations could not be achieved.

Development of Anion Separation. As was the case for cations, indirect photometric detection was again the preferred detection method for the target group of inorganic anions. BGEs based on chromate as the probe have been used extensively for this purpose,^{40–42} although optimal detection sensitivity can be achieved only when the composition of the BGE is designed such

(39) Qu, F.; Lin, J.-M. *J. Chromatogr. A* **2005**, *1068*, 169–174.

(40) Macka, M.; Haddad, P. R. In *Encyclopaedia of Separation Science*; Wilson, I., Ed.; Academic Press: London, 2000; pp 3128–3140.

(41) Doble, P.; Macka, M.; Haddad, P. R. *TrAC, Trends Anal. Chem.* **2000**, *19*, 10–17.

(42) Macka, M.; Johns, C.; Doble, P.; Haddad, P. R. *LC-GC* **2001**, *19*, 38–47.

Table 3. Analytical Figures of Merit for Anion Separation System by CE

analyte	retention time ($n = 10$)		peak area RSD (%)	theoretical plates/m	resolution	LOD (S/N = 3, mg/L)	calibration R^2
	min	RSD (%)					
1 chloride	5.139	0.42	4.25	162 000	1.32	0.30	0.9998
2 thiosulfate	5.216	0.46	5.51	130 000	1.79	0.65	0.9944
3 nitrite	5.306	0.42	3.54	163 000	1.51	0.43	0.9978
4 nitrate	5.382	0.43	5.75	187 000	3.00	0.57	0.992
5 sulfate	5.547	0.48	5.24	153 000	1.35	0.49	0.9989
6 perchlorate	5.616	0.44	4.80	241 000	1.29	0.90	0.9968
7 thiocyanate	5.677	0.44	6.99	232 000	2.09	0.63	0.9938
8 chlorate	5.787	0.45	7.14	167 000	1.33	0.72	0.999
9 cyanate	5.865	0.45	5.71	143 000	4.67	0.44	0.9978
10 fluoride	6.370	0.49	6.40	38 000	2.47	0.30	0.9882
11 chlorite	6.664	0.51	5.62	157 000	3.15	0.63	0.9969
12 phosphate	6.947	0.66	7.26	100 000	1.88	0.71	0.9943
13 carbonate	7.184	0.64	10.35	83 000	3.62	0.24	0.9967
14 acetate	7.668	0.56	7.64	115 000	8.08	0.79	0.9914
15 benzoate	8.690	0.60	7.73	115 000		1.15	0.9938

that there are no competing anions present.⁴³ For this reason, a BGE containing chromium(VI) oxide, chromate, and TRIS was used. With this BGE, the separation selectivity for divalent anions can be manipulated by varying the concentration of TRIS due to its interactions with these ions. The composition of the BGE that yielded the best separation of the target anions was optimized using a single variable design, and it was found that the best resolution was achieved using a 1:2 ratio of CrO_3 /TRIS. The ionic strength of the electrolyte was adjusted to optimize the peak shape without producing excessive Joule heating at the maximum field strength ($2.84 \times 10^4 \text{ V m}^{-1}$). It was also found that baseline stability was improved considerably by applying a low pressure at the inlet end of the capillary, and this also reduced the time taken for the separation. The effects of the added pressure on band broadening were not investigated as the resolution for each of the target analytes was more than satisfactory.

Chromate exhibits absorption maximums at 273 and 371 nm,⁴⁴ and most work has been performed using a UV light source operating at 254 nm. In the present study, a 370-nm UV LED was used as the light source (this was interchangeable with the 470-nm blue LED used in the cation detection system). The LED system provided a more sensitive indirect detection approach than most systems described in the literature⁴⁴ due to the low baseline noise of the LED and its strong emission at the most intense absorption maximum of chromate. An extended UV photodiode was required for collecting the optical signal. Finally, the capillary used for the anion analysis was coated with the cationic polymer HDMB to reverse the direction of the EOF, thereby increasing the speed of the separation.

Figure 3 shows the separation obtained on the portable CE instrument under the chosen conditions. Baseline separation of the 15 target analytes (plus hexanesulfonate as the internal standard) was accomplished in less than 9 min, which compared favorably with the simultaneous detection system developed by Hopper et al.²⁷ on a benchtop CE instrument in which 8 anions were separated in 5.5 min. One initial rinse of HDMB resulted in stable migration times for at least 10 subsequent separations of

the target anions. Table 3 provides the analytical figures of merit calculated from 10 replicates of the anion separation. Resolution was greater than 1.3 in all cases, up to 241 000 theoretical plates/m were achieved, and the limit of detection ranged between 0.24 and 1.2 mg/L based on a sample injection plug, which was 0.94% of the capillary volume. It was found that the resolution deteriorated for larger injection plugs.

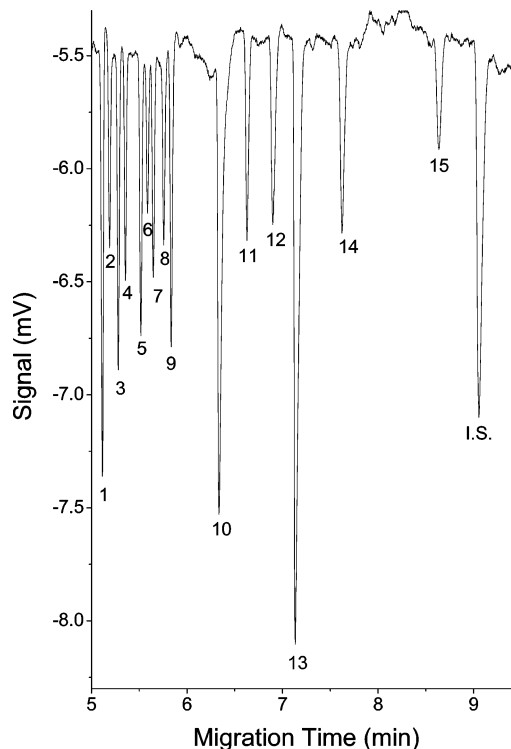


Figure 3. CE separation of target anion mixture using the portable CE-P2 equipped with a miniaturized indirect photometric LED detector. Conditions: 50- μm -i.d. fused-silica capillary, $L_{\text{total}} = 88.0 \text{ cm}$. BGE was 10 mM CrO_3 , 10 mM Na_2CrO_4 , and 40 mM Tris in aqueous solution. Voltage, -25 kV . Detection performed using a 370-nm LED source, operating current 40 mA, 9.5 cm from cathode ($L_{\text{detector}} = 78.5 \text{ cm}$). An extended UV photodiode detector collected the signal obtained. Samples injected using a pressure of 0.4 psi for 30 s. Sample concentrations, 5 mg/L for all species. Anions are numbered throughout all figures in correspondence with Table 3. The internal standard (I.S.) was hexanesulfonate.

(43) Johns, C.; Macka, M.; Haddad, P. R. *Electrophoresis* **2003**, *24*, 2150–2167.

(44) King, M.; Paull, B.; Haddad, P. R.; Macka, M. *Analyst* **2002**, *127*, 1564–1567.

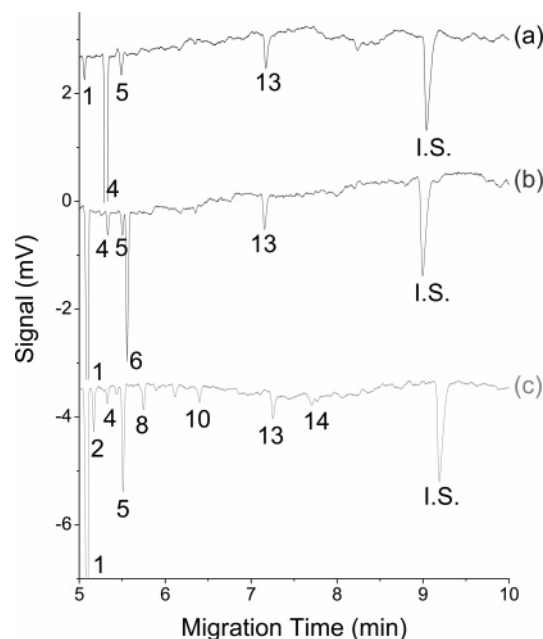


Figure 4. Analysis of anions extracted from postblast residues resulting from improvised (a) ammonium nitrate/fuel oil (ANFO), (b) potassium perchlorate/sugar, and (c) sodium chlorate/sulfur/aluminum explosive devices. Conditions: The postblast residue aqueous samples were injected without dilution. The capillary electrophoresis method used is outlined in Figure 2.

Analysis of Postblast Residues from Inorganic Homemade Explosives. Controlled detonations of IEDs containing the homemade explosives listed in Table 1 were undertaken, and residue samples were collected by swabbing galvanized steel witness plates (see Experimental Section). These samples were analyzed directly for their anion and cation profiles using the CE methods described earlier. A blank swab sample was also analyzed and was found to contain trace amounts of chloride, sulfate, and sodium: these blank levels were therefore taken into account when interpreting the sample data.

Some illustrative examples of the electropherograms obtained from the residue samples are given in Figure 4 (anions) and Figure 5 (cations). In all instances, the dominant peaks could be used to identify the composition of the IED. It is possible that if poorly resolved peaks were overloaded it would not be possible to identify the dominant species unequivocally. In such cases, the sample should be diluted so that the dominant species can be identified with certainty. Electropherograms from all other samples tested are included as Supporting Information. Figure 4 compares the anionic constituents present in the postblast residues of an improvised ANFO emulsion (Figure 4a), a perchlorate/sugar device (Figure 4b), and a chlorate/sulfur/aluminum device (Figure 4c). The electropherogram from the improvised ANFO device was characterized by the dominant peak for nitrate, while chlorate and perchlorate were both clearly evident in the chlorate/sulfur/aluminum and perchlorate/sugar devices, respectively. During the explosion, chlorate and perchlorate are reduced to chloride and this was clearly evident in the postblast samples. Similarly, sulfur is the fuel in the chlorate/sulfur/aluminum device, and its oxidized species (sulfate, thiosulfate) were detected in postblast residues. All samples showed the presence of carbonate as a contaminant of the water used for swabbing and sample

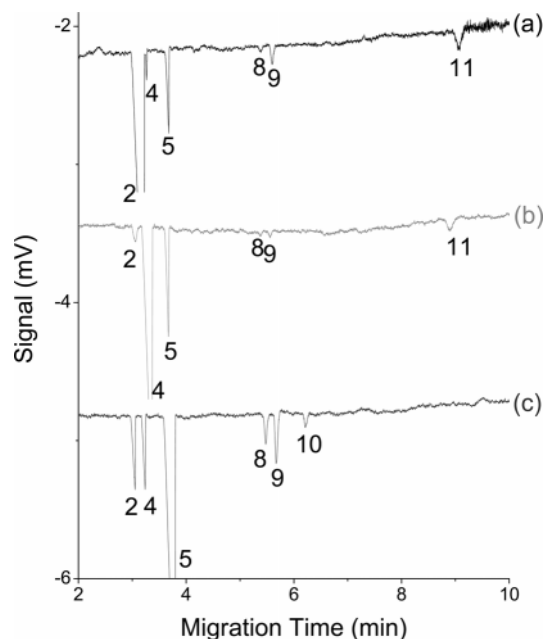


Figure 5. Analysis of cations extracted from postblast residues resulting from improvised (a) ANFO, (b) potassium perchlorate/sugar, and (c) sodium chlorate/sulfur/aluminum explosive devices. Conditions: The postblast residue aqueous samples were injected without dilution. The capillary electrophoresis method used is outlined in Figure 3.

extraction. In view of the possibility that soil particles would be transferred to the witness plates during detonation, preblast soil samples were extracted and analyzed. These were found to contain small amounts of nitrate and sulfate, but the observed levels did not introduce significant uncertainty in the identification of the IEDs. These examples demonstrate that field-based, rapid identification of these three devices could be performed reliably using the separation of anions as a fingerprinting tool.

Confirmatory identification of the inorganic IED could also be obtained from the cation separations (Figure 5). The improvised ANFO device (Figure 5a) showed the expected dominant peak for ammonium, while the perchlorate/sugar device (Figure 5b) and chlorate/sulfur/aluminum device (Figure 5c) showed dominant peaks for the countercation used in their preparation (i.e., potassium and sodium, respectively). Soil analysis showed the presence of trace amounts of ammonium, sodium, potassium, calcium, and magnesium, while zinc was also detected in all samples as a result of deterioration of the galvanized witness plate during the explosion. Again, the examples shown demonstrate the ability to fingerprint the IEDs by the determination of cations in residue samples. Taken together, the anion and cation profiles provide very strong evidence as to the identity of the homemade explosive used.

Portable CE Analysis at Explosion Site. The results shown thus far were obtained on the portable CE instrument housed in an analytical laboratory. Witness plates were transferred to the laboratory, and all sampling and analysis procedures were undertaken under normal laboratory conditions. The utility of the portable CE instrument for field analysis was also evaluated by using the instrument in a small, mobile laboratory, which was driven onto the range where the explosives were detonated. Such conditions would be similar to those encountered if sampling and

analysis were taken at the site of a terrorist attack. The portable CE was set up in a van modified as a mobile laboratory and performed satisfactorily under these conditions except for a significant increase in migration times compared to those observed under standard laboratory conditions (e.g., the migration time for sodium increased from 3.6 min in the laboratory to 6.0 min in the field). This effect was directly attributable to viscosity changes⁴⁵ since the ambient temperature at the time of field testing was 7 °C and the portable CE instrument used did not have any means of regulating temperature. For this reason, frequent calibration and the use of internal standards were essential for field-based analyses.

CONCLUSIONS

CE methods have been developed on a portable commercial instrument modified for use with LED detection for the fingerprinting identification of inorganic homemade explosives through the determination of anions and cations in postblast residues. These methods permit simultaneous separation of all target analytes likely to be present in residues left by all common inorganic homemade explosives, so that the same separation conditions are applicable to all sample types. In most cases, positive identification of the inorganic homemade explosive can be obtained by considering both the anion and cation profiles of the residue sample. Sampling can be conducted by simple aqueous swabbing of hard surfaces in the proximity of the explosion site.

(45) Jandik, P.; Bonn, G. *Capillary electrophoresis of small molecules and ions*; VCH Publishers Inc.: New York, 1993.

The swabbing procedures used in this work could be modified if required to give a smaller final sample volume, leading to enhanced detectability of the analytes. Future studies will involve the use of alternative miniature detection methods, especially contactless conductivity detection, as well as the development of microchip CE techniques. A parallel study involving the fingerprinting of explosive residues using ion chromatographic methods has also been undertaken, and the results will be reported separately.

ACKNOWLEDGMENT

This project is supported by the National Security Science & Technology Unit grant provided by the Australian Government Department of the Prime Minister and Cabinet, the Australian Federal Police, and the National Institute for Forensic Science. The authors acknowledge the assistance of the Australian Bomb Data Centre for the preparation and detonation of the improvised explosive devices used to generate the postblast residues analysed in this study.

SUPPORTING INFORMATION AVAILABLE

Figures S-1–S-9, electropherograms for a number of improvised and commercial inorganic explosives. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Received for review April 30, 2007. Accepted July 13, 2007.

AC0708792