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A novel method for analysis of explosives residue by simultaneous detection of anions and cations via capillary zone electrophoresis

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Abstract

A novel electrolyte has been developed for the simultaneous separation of cations and anions in low explosive residue by capillary electrophoresis. This electrolyte contains 15 mM α-hydroxyisobutyric acid (HIBA) as the buffer, 6 mM imidazole as the cation chromophore, 3 mM 1,3,6-naphthalenetrisulfonic acid (NTS) as the anion chromophore, 4 mM 18-crown-6 ether as a cation selectivity modifier, and 5% (v/v) acetonitrile as an organic modifier. The pH was adjusted to 6.5 using tetramethylammonium hydroxide (TMAOH), an electroosmotic flow modifier. The method was optimized by varying the concentrations of α-HIBA, imidazole, and 1,3,6-NTS at three different pH values. The results provided a simultaneous indirect photometric analysis of both anions and cations with detection limits ranging from 0.5 to 5 ppm for anions and from 10 to 15 ppm for cations with a total run time of under 7 min. The method was then applied to the analysis of Pyrodex® RS and black powder, as well as several smokeless powders. The results obtained were consistent with previously reported results for separate anion and cation analysis and provide a faster, more complete analysis of each sample in a single chromatographic run.

Keywords: Anions; Cations; Simultaneous detection; Explosive residue

1. Introduction

In low explosive residue analysis, anion and cation determinations by capillary zone electrophoresis (CZE) are normally performed using a separate buffer for each analysis. When only a single CE system is available, the capillary and buffer system must be changed and re-equilibrated in order to switch between anion and cation analysis. This process can be time consuming and laborious. One way to eliminate this problem is to perform a simultaneous analysis, however, to perform such an assay usually requires extensive instrument modification [1–6]. A review of the different simultaneous ion analysis techniques can be found in a paper by Johns et al. [7]. In one report, Kubans utilized an anion buffer with ethylenediaminetetracetic acid (EDTA) to simultaneously run anions and chelated cations. The problem with this method of analysis is that the primary cations of importance in the detection of explosives residue, potassium, ammonium, and sodium, do not form stable complexes with EDTA [8]. Yet another approach using a high magnitude electroosmotic flow (EOF) involved detection of three anions and six cations from the same injection end. However, this method did not use an anionic probe, which limits the detection of many anions [9]. An alternative to this technique is to simultaneously inject into both sides of a single capillary with the detector placed in the center [1–5,10]. This technique is known as dual-opposite injection. Unfortunately, most standard CE instruments are not configured in this manner [6]. However, through careful consideration of osmotic flow parameters, Haumann et al. showed that simultaneous injection into both capillary sides without instrument modification is possible for analysis of alcoholic beverages and drinking water [11]. In this paper we follow a similar approach, requiring no instrumental modification for the simultaneous analysis of cations and anions in low explosives. The detector, located only 10.2 cm from the anode, is fixed. Careful choice of buffer probes and pH permits sequential injection from both capillary ends and the

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results are determined using indirect UV detection. Using this technique, a wide variety of anions and cations of importance in low explosives analysis, including chloride, nitrite, nitrate, sulfate, perchlorate, thiocyanate, chlorate, and cyanate as well as ammonium, potassium, sodium, calcium, and magnesium can all be measured in a single run. This procedure has been used to analyze a variety of low explosives in post-blast residue. The analysis is efficient and rapid with a total run time of less than 7 min.

2. Experimental

2.1. Apparatus

Analyses were conducted on a Beckman Coulter P/ACE MDQ Capillary Electrophoresis System (Fullerton, CA) equipped with a photodiode array (PDA) detector. Fused-silica capillaries (Polymicro Technology, Phoenix, AZ) of 40.2 cm × 50 μm i.d. (effective length) were used. Capillary length to the detector from the cathode is 30 and 10.2 cm from the anode.

2.1.1. Single injection

Samples were introduced into the capillary via a hydrodynamic injection for 5 s. Cations were injected into the anodic end, while the polarity was reversed for anion analysis with injection at the cathodic end. Indirect UV absorbance detection was then performed with cation detection at 215 nm and anion detection at 280 nm. Baseline separation of most species was obtained at a field strength of 248 V/cm at ambient temperature.

2.1.2. Simultaneous injection

Samples were introduced into the capillary via two hydrodynamic injections, one on each end of the capillary. Samples on the cathodic end were injected for 7 s and samples on the anodic end were injected for 5 s. Indirect UV absorbance detection was performed with dual wavelength detection. Cations were detected at 208 nm; while anions were detected at 235 nm. Baseline separation of all species was attained using a field strength of 248 V/cm at ambient temperature.

2.2. Chemicals

All electrolytes and standards were prepared using 18.2 MΩ deionized water. The powders used for analysis include: H335 (Hodgdon, Shawnee Mission, KS, USA), HiSkor 700X (IMR, Plattsburgh, NY, USA), Pyrodex® RS (Hodgdon, Shawnee Mission, KS, USA), black rifle powder (GOEX Inc., Minden, LA, USA), and flash powder obtained from a Ninja firecracker, company unknown.

2.2.1. Single injection method

The cation electrolyte consisted of 17.5 mM α-hydroxyisobutyric acid (HIBA), 16 mM imidazole, and 4 mM 18-crown-6 ether obtained from Acros (NJ), 6% (v/v) acetonitrile (Fisher Scientific) where the pH was adjusted to 4.4 using 0.5 M tetramethylammonium hydroxide (TMAOH) (Sigma, St. Louis, MO) [12]. Whereas, the anion electrolyte consisted of 40 mM boric acid and 1.8 mM potassium dichromate both obtained from Fisher Scientific (Pittsburgh, PA), and 2 mM sodium tetraborate (Acros, Morris Plains, NJ). The pH was adjusted to 7.8 using diethylene triamine (DETA) (Aldrich, Milwaukee, WI) [13].

2.2.2. Simultaneous injection method

The final electrolyte contained 15 mM α-hydroxyisobutyric acid (HIBA), 6 mM imidazole, and 4 mM 18-crown-6 ether obtained from Acros (NJ), 3 mM 1,3,6-naphthalenetrisulfonic acid (1,3,6-NTS) (Aldrich, Milwaukee, WI), and 5% (v/v) acetonitrile (Fisher Scientific, Pittsburgh, PA) where the pH was adjusted to 6.5 using 0.5 M tetramethylammonium hydroxide (TMAOH) (Sigma, St. Louis, MO).

2.3. Preparation of standards and samples

All standards were initially prepared at a concentration of 1800 ppm and diluted to a working concentration of 10 ppm. The standards were prepared from analytical reagent grade potassium salts of chloride (Spectrum, Gardena, CA), nitrite (Aldrich), nitrate (Aldrich), perchlorate, chlorate (Aldrich), thiocyanate (Acros), and cyanate; analytical reagent grade sodium salt of sulfate (Aldrich); and analytical reagent grade chloride salts of potassium (Spectrum), ammonium (Fisher Scientific), sodium (Spectrum), magnesium and strontium.

2.4. Measurement of electroosmotic mobility of buffer and electrophoretic mobility of analyte

The apparent electrophoretic mobility (μ_{ep}) for each ion was calculated by dividing the field strength, E (V/cm) by the electrophoretic velocity, ν_{ep} (cm/s). These values are given in Table 1. The electroosmotic flow mobility (μ_{eo}) of 26×10^{-9} m^2/V s was determined by injecting a neutral marker, acetone.

3. Results and discussion

3.1. Introduction

The goal of this study was to develop a method to detect the cations and anions, inherent in low explosive residue, in one run by CZE. In a typical analysis of cations by capillary electrophoresis, sample ions are injected at the anode and travel to the detector at the cathodic end. Negatively charged $-SiO^-$ groups on the capillary walls attract the positive ions in the solution creating an electric double layer and inducing a net electroosmotic flow (EOF) towards the cathode. The electrophoretic flow is coelectroosmotic, since the cation mi-

Table 1
Absorptivity, wavelength, pH, and apparent mobility from the literature of possible anion and cation probes to be used in the buffer [11,12]

Probe	Absorptivity (10^3 L/mol cm)	λ (nm)	pH	μ ($\times 10^{-9}$ m^2/V s)
1,3,6-Naphthalenetrisulfonate	31.600	214	8.0	−62.0
2,6-Pyridinedicarboxylate	43.680	192	6.5	−41.5
2-Sulfobenzoic acid	40.000	228	6.5	
Benzoate	44.480	194	6.5	−29.0
Chlorophenol red	28.000	578	6.5	−22.1
Phthalate	37.160	196	6.5	−41.2
Pyromellitate	23.900	214	6.5	−55.1
1-Naphthylamine	50.000	214	3.9	17.0
Imidazole				52.0

gration occurs in the same direction as the EOF. However, anions are not detected in this mode. Instead, to detect anions, polarity is reversed [14,15]. In addition, a quaternary ammonium ion is added to the buffer to produce a coelectrosmotic flow [2,16]. The surfactant ion blocks the silanol groups and produces a positively charged capillary wall. The anions within the solution are attracted to the positively charged wall causing the bulk solution to flow toward the anode.

The above techniques provide useful separation of anions or cations via CE. However, in order to produce a simultaneous analysis of both anions and cations, it is necessary to have either the anions or the cations move counter to the EOF. For such an analysis to be successful, the direction and velocity of the electrophoretic and electroosmotic flows must be carefully considered.

3.2. Development of the simultaneous buffer

In this paper, the capillary was first set up for anion analysis in the forward direction. Tetramethyl ammonium hydroxide (TMAOH) was added to reverse the EOF. The sample is then injected at both ends of the capillary, and the EOF moves toward the anode carrying the anions along toward the detector. The cations migrate against the EOF with a mobility sufficiently high enough to migrate against the EOF (Fig. 1).

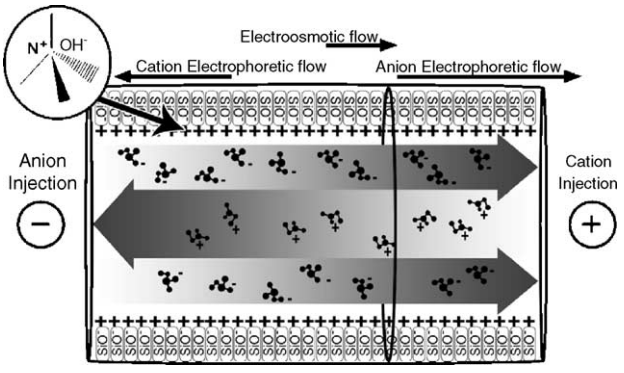

Fig. 1. Schematic of simultaneous separation following addition of cation modifier, TMAOH. Anions are injected at the cathodic end for 7 s followed sequentially by cation injection at the anodic end for 5 s. The electroosmotic flow (EOF) allows the anions to travel towards the anode and is low enough that the cations can traverse the short distance to the detector against the EOF.

Since there is a much shorter distance (10.2 cm) to the detector window, the cations arrive at the detector prior to the anions, and there is no interference between cation and anion detection. The direction and velocity of the EOF is controlled through the choice of TMAOH and the buffer pH.

3.3. Selection of cation and anion probe

Many of the ions utilized in the detection of low explosives do not absorb UV light, thus indirect photometric detection (IPD) must be used. In order to perform simultaneous analysis of cations and anions using IPD, the electrolyte must contain a cationic and anionic visualization agent, known as a probe, to make the electrolyte absorbent [2,5,6,11]. To design a reproducible method for dual analysis of anions and cations, not only it is important to optimize the individual separation systems, but there must also be synergy between the two probes when the methods are combined. For example, the two probes must be selected such that they match both in mobility and pH. As most probes are weak acids or bases, the pH of an electrolyte must be within a range of values such that the chromophoric probe remains charged and retains a high molar absorptivity [16]. Unfortunately, a pH value between 3 and 5 is used for most cation methods and anion separations are rarely performed below a pH of 7.5. This is because low pH values are required to keep the cation probes protonated. Concomitantly, to deprotonate anion probes that are weak acids, the pH must be high [5]. In addition, it is important to match electrophoretic mobility of the probe and the analyte. If the mobility of the probe is less than the analyte, peak fronting will occur; if it is greater than the analyte, peak tailing will occur [16,17]. As the ions pass the detector, a decrease in absorbance is detected as the analyte ions displace the probe ions [15]. However, there will be one system peak observed for every additional probe added. Thus with two probes, one system peak is present [16].

The probes used in this study were selected based on molar absorptivity, wavelength, apparent mobility, and pH. Listed in Table 1 are examples of probes that exhibit high absorptivity values at a particular pH values [17]. If the listed pK_a values for any anionic probe was not within the range of pHs compatible with its complementary cation probe, that chromophore was not considered. In addition, the apparent

Table 2
Apparent mobility from the literature of several ions at specific pH values [11]

Ions	pH	μ ($\times 10^{-9}$ m^2/V s)
Ammonium	ID[a]	76.2
Potassium	ID	76.2
Calcium	ID	61.7
Bromide	ID	−81.0
Chloride	8.1	−74.1
Nitrate	6.5	−64.3
Sulfate	8.0	−70.8
Chlorate	ID	−67.0

[a] Means infinite dilution.

mobility of any probe must be close to that of common ions in explosives residue. Otherwise peak shape and sensitivity will suffer. For example, the apparent mobility value for 1-naphthylamine of 17.0 is too low to match the mobility of the cations most commonly found in explosive residue. However, imidazole has an apparent mobility value that is within the range of apparent mobility values of cations important for low explosive residue detection (Tables 1 and 2) [17,18]. Benzoate, 2,6-pyridinedicarboxylate, chlorophenol red, and phthalate were not selected as anion probes because their optimum wavelengths were either below 200 nm or above 280 nm. Any probe not in the range of 200–280 nm was not considered because imidazole, the only cation probe found to fit the requirements, would not work in that range and the original goal of the study was to perform the analysis at a single wavelength. Pyromellitate was not selected, even though it has a high absorptivity value at a desirable wavelength, because the pH value was too low and the mobility value was lower than many of the anions important for low explosive residue analysis (Tables 1 and 2) [17]. Due to its high absorptivity value, a pH range within that of imidazole, a desirable wavelength, and a mobility value within the range of the anions of interest, 1,3,6-NTS was selected as the anion probe for the buffer. The apparent mobility values with the optimized buffer are given in Table 3. Mobility, pH, and concentration are important factors as they determine peak symmetry and method efficiency.

The UV spectrum of the buffer containing the two probes is shown in Fig. 2. Several absorbance maxima are seen, and

Table 3
Apparent mobility of ions calculated using an optimized buffer composition of 15 mM α-HIBA, 6 mM imidazole, 3 mM 1,3,6-naphthalenetrisulfonic acid, 4 mM 18-crown-6 ether, and 5% acetonitrile with the buffer adjusted to 6.5 using TMAOH

Ions	μ ($\times 10^{-9}$ m^2/V s)
Strontium	53.6
Ammonium	31.0
Potassium	35.4
Sodium	38.8
Calcium	42.2
Magnesium	43.5
Bromide	44.9
Chloride	46.8
Nitrite	50.4
Nitrate	52.1
Sulfate	53.7
Perchlorate	59.4
Thiocyanate	61.5
Chlorate	63.4
Cyanate	66.8

Ion analysis was performed with a Beckman P/ACE MDQ system at a 7 s. Cathodic injection time followed by a 5 s anodic injection time using a 40.2 cm × 50 μm i.d. capillary using a field strength of 248 V/cm with detection at 208 and 235 nm.

the figure clearly illustrates the optimum wavelength for each probe: cations at 208 nm and anions at 235 nm. Fig. 3a and b show an electropherogram where a 10 ppm anion and cation standard were injected at the respective ends and analyzed using a wavelength of 235 and 208 nm. A photodiode array (PDA) detector can be used to permit detection at multiple wavelengths during one run. These two different wavelengths can also be used for anion confirmation [15]. At 208 nm, bromide, hydrogen sulfide, and nitrate absorb and produce peaks in the negative direction. The anions can be superimposed at the two wavelengths, helping to confirm peak identity and increase specificity.

3.4. Developing an optimized electrolyte

Interactions between the concentration of the cation and anion probe, electrolyte, and α-HIBA affected the asymmetry, resolution, and peak height responses. A set of 12 different buffers was created due to the significant effect the various

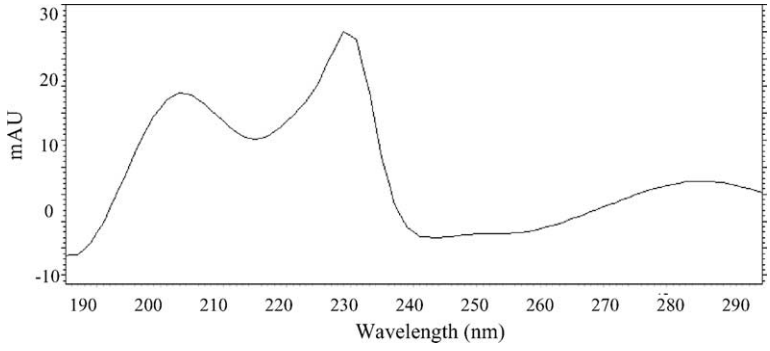

Fig. 2. UV absorbance spectrum for the simultaneous buffer system. Peak maxima occur at three different wavelengths: 208, 235, and 295 nm.

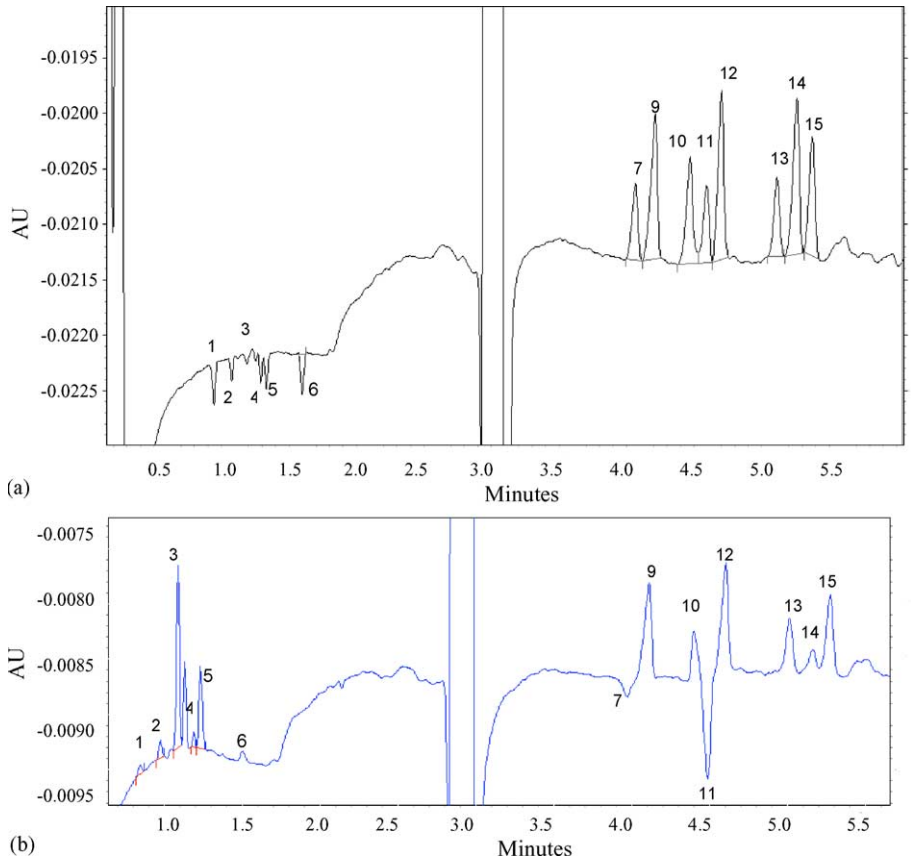

Fig. 3. (a) 10 ppm cation and anion standard at 235 nm. Ions are: 1, ammonium; 2, potassium; 3, sodium; 4, calcium; 5, magnesium; 6, strontium; anions at 10 ppm: 7, bromide; 9, chloride; 10, nitrite; 11, nitrate; 12, sulfate; 13, perchlorate; 14, thiocyanate; 15, chlorate. Buffer parameters: 4 mM 18-crown-6 ether, 5% (v/v) ACN, 15 mM α-HIBA, 3 mM 1,3,6 or 7-naphthalene trisulfonic acid, and 6 mM imidazole with pH = 6.5 adjusted using TMAOH. Instrument parameters: long end injection, 7 s; short end injection, 5 s; and 10 kV separation and (b) 10 ppm cation and anion standard at 208 nm. Ions are: 1, ammonium; 2, potassium; 3, sodium; 4, calcium; 5, magnesium; 6, strontium; anions at 10 ppm: 7, bromide; 9, chloride; 10, nitrite; 11, nitrate; 12, sulfate; 13, perchlorate; 14, thiocyanate; 15, chlorate. Conditions are given in (a).

concentrations had on these responses (Table 4). The optimal buffer concentrations were determined by examining resolution, peak height, and pH. Acetonitrile was tested at values of 0, 5, and 10% (v/v) while 18-crown-6 ether was tested at 2, 4, and 6 mM concentration values. The nitrate peak disappeared with the use of 0% ACN, while 10% ACN, as well as 2 and 6 mM 18-crown-6 ether concentrations gave greatly reduced peak height values. Thus, the optimum concentrations were set at fixed values of 5% (v/v) and 4 mM, respectively. Resolution between the ions was compared using α-HIBA concentrations of 10 and 15 mM. The best resolution was obtained using 10 mM α-HIBA. In addition, the optimization of anion and cation probe concentrations was based on peak height (Table 5), peak asymmetry (Table 6) and resolution. It is important to note that while the internal standards were added for quantitative calculations, they were not utilized in the optimization studies and thus the variation reported here is higher than in the final method. Buffer #2, with a pH value of 5.25 and buffer #10, with a pH value of 6.5, both contained a 6 mM imidazole probe and a 3 mM 1,3,6-NTS probe. Buffer #2 had the highest overall peak heights, with buffer #10, second. However, the resolution between nitrite and nitrate and between thiocyanate and chlorate was below the accepted value of 1.0 at 0.47 and 0.70, respectively. The resolution values for buffer #10 were all above 1.0 and most are above 1.5. Buffers #4 and #6 had more symmetrical peaks

Table 4
Component variations within buffers used to obtain the optimized buffer composition of 15 mM α-HIBA, 6 mM imidazole, 3 mM 1,3,6-naphthalenetrisulfonic acid, 4 mM 18-crown-6 ether, and 5% acetonitrile with the buffer adjusted to 6.5 using TMAOH

Buffer #	α-HIBA (mM)	1,3,6-Naphthalenetrisulfonate: imidazole (mM)
1	10	3:6
2	15	3:6
3	10	5:10
4	15	5:10
5	10	3:6
6	15	3:6
7	10	5:10
8	15	5:10
9	10	3:6
10	15	3:6
11	10	5:10
12	15	5:10

Conditions are given in Table 3.

Table 5
Peak height of several cations and anions where buffers #1, #2, #5, #6, #9, #10 contain 6 mM imidazole and 3 mM 1,3,6-NTS; buffers #3, #4, #7, #8, #11 and #12 contain 10 mM imidazole and 5 mM 1,3,6-NTS

Buffer #	pH	NH_4^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	ClO_4^-
1	5.25	627 ± 28.8	417 ± 14.6	1980 ± 236	1670 ± 118	3270 ± 439	1360 ± 212
2	5.25	1230 ± 86.3	912 ± 77.7	4150 ± 121	3370 ± 446	7390 ± 478	3350 ± 341
3	5.25	272 ± 28.3	194 ± 23.1	932 ± 96.8	731 ± 72.5	1560 ± 212	607 ± 70.5
4	5.25	411 ± 120	293 ± 96.0	617 ± 181	455 ± 159	1030 ± 299	385 ± 142
5	5.90	224 ± 8.54	183 ± 47.1	1030 ± 136	691 ± 162	1830 ± 257	681 ± 144
6	5.90	301 ± 21.5	248 ± 19.4	548 ± 57.6	356 ± 35.9	947 ± 70.4	327 ± 40.7
7	5.90	450 ± 63.6	239 ± 35.2	687 ± 108	478 ± 108	1140 ± 190	460 ± 93.8
8	5.90	503 ± 89.8	253 ± 57.1	1060 ± 164	806 ± 147	1630 ± 313	759 ± 156
9	6.50	324 ± 37.3	191 ± 15.6	1450 ± 197	869 ± 63.4	2310 ± 173	913 ± 56.8
10	6.50	666 ± 59.2	275 ± 21.1	2390 ± 248	1240 ± 207	4060 ± 493	1690 ± 195
11	6.50	910 ± 68.2	226 ± 29.0	1170 ± 50.7	823 ± 24.3	1810 ± 63.3	842 ± 33.8
12	6.50	1070 ± 47.1	341 ± 25.5	895 ± 185	642 ± 96.7	1410 ± 234	546 ± 86.6

Conditions are given in Table 3.

than buffer #10, however, buffers #4 and #6 had smaller peak height values than #10. Thus, buffer #10 with a composition of 15 mM α-HIBA, 3 mM 1,3,6-NTS, 6 mM imidazole, 4 mM 18-crown-6 ether, 5% acetonitrile, pH adjusted to 6.5 with 0.5 M TMAOH, was utilized for all further testing.

3.5. Sample introduction

The method was optimized using reversed polarity. The cathode is located on the left side of the instrument, the anode on the right side. The same sample is injected on both sides of the instrument, 7 s on the long end of the capillary (anions) and 5 s on the short end (cations). Since the same sample is used, both will contain anions and cations. However, anions will migrate from the cathodic end and cations will migrate from the anodic end. The EOF must be adjusted such that the migration velocity of the slowest cation is faster than the migration of the fastest anion in order to avoid peak overlap. In addition, a larger sample plug must be injected at the cathode since the subsequent injection at the anode will push some sample out at the cathode [11]. Reversed polarity was used, meaning that the anions were separated using the longer distance to the detector because in explosives residue analysis, a wide variety of anions are utilized as oxidizers and all of these ions must be separated. There are only three major cations of interest in the detection of low explosives, ammonium, potassium, and sodium, thus the shorter distance to the capillary window (10.2 cm) was used for these ions as high resolution was not necessary due to the wide range of mobilities exhibited by these ions.

Sample injection introduces another problem encountered with the simultaneous method. A lack of peak area reproducibility was initially observed. This variation was believed to be due to the unique injection process. Because the second injection (5 s) pushes sample in the opposite direction to the first injection (7 s) variation in the total amount of sample placed on the capillary can occur. To solve this problem, a cation and anion internal standard must be used with this method. The cation internal standard, strontium, shows poor sensitivity at 208 nm, but produces a distinct peak at 235 nm with the peak direction reversed. The anion internal standard is bromide.

Table 6
Peak asymmetries of several cations and anions where buffers #1, #2, #5, #6, #9, #10 contain 6 mM imidazole and 3 mM 1,3,6-NTS; buffers #3, #4, #7, #8, #11, and #12 contain 10 mM imidazole and 5 mM 1,3,6-NTS

Buffer #	pH	NH_4^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	ClO_4^-
1	5.25	1.1 ± 0.079	1.2 ± 0.092	0.24 ± 0.031	2.7 ± 0.55	0.19 ± 0.023	0.47 ± 0.038
2	5.25	0.65 ± 0.065	1.2 ± 0.047	0.14 ± 0.010	0.60 ± 0.056	0.15 ± 0.012	0.25 ± 0.025
3	5.25	0.91 ± 0.058	0.88 ± 0.053	0.35 ± 0.017	2.0 ± 0.31	0.32 ± 0.040	0.58 ± 0.031
4	5.25	1.1 ± 0.18	1.2 ± 0.049	0.52 ± 0.10	0.89 ± 0.080	0.59 ± 0.23	0.79 ± 0.11
5	5.90	1.0 ± 0.12	0.90 ± 0.056	0.43 ± 0.065	0.63 ± 0.11	0.34 ± 0.056	0.74 ± 0.15
6	5.90	0.91 ± 0.047	1.1 ± 0.064	0.57 ± 0.010	0.67 ± 0.081	0.53 ± 0.036	0.77 ± 0.021
7	5.90	0.89 ± 0.035	1.1 ± 0.092	0.42 ± 0.035	0.59 ± 0.055	0.49 ± 0.040	0.52 ± 0.017
8	5.90	0.93 ± 0.079	1.2 ± 0.11	0.37 ± 0.091	0.42 ± 0.045	0.32 ± 0.050	0.62 ± 0.021
9	6.50	0.98 ± 0.036	1.1 ± 0.0058	0.28 ± 0.030	0.49 ± 0.061	0.24 ± 0.015	0.55 ± 0.020
10	6.50	0.62 ± 0.095	1.1 ± 0.083	0.39 ± 0.025	0.63 ± 0.099	0.88 ± 0.15	0.48 ± 0.021
11	6.50	0.89 ± 0.093	1.0 ± 0.12	0.26 ± 0.010	0.29 ± 0.0058	0.20 ± 0.0058	0.45 ± 0.027
12	6.50	0.60 ± 0.025	1.1 ± 0.015	0.36 ± 0.029	0.49 ± 0.095	0.31 ± 0.025	0.57 ± 0.017

Conditions are given in Table 3.

3.6. Validation

3.6.1. Method

To determine migration reproducibility and detection limits, three replicate injections were performed using a standard mixture containing the cations: NH_4^+, K^+, Na^+, Ca^{2+} and Mg^{2+} and anions: Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-, SCN^-, ClO_3^- and OCN^-. The cation and anion internal standards strontium (Sr^{2+}) and bromide (Br^-) were present at a concentration of 10 ppm in each standard. Concentrations ranged between 5 and 30 μg/mL. Analyses were performed using a Beckman P/ACE system MDQ. Linear regression data was collected from the peak areas of each anion and cation over a limited concentration range. The linear regression equation for perchlorate, for example, was $y = 0.121x - 0.0229$ with an r^2 value of 0.9995. The r^2 values for the cations ranged from 0.8323 for calcium to 0.9170 for magnesium and the anions ranged from 0.9741 for cyanate to 0.9998 for chloride. Detection limits were then estimated using three times the standard deviation of the y estimate obtained from the regression line. Results for sodium were not included as a system peak interfered with the quantitation of this ion, and thus it was mainly used for qualitative analysis. The pooled standard deviation for the migration time reproducibility of the method for the standard ranged from 0.007 to 0.013 min for cations and form 0.013 to 0.035 min for anions (Table 7).

Table 7
Detection limits and migration times of ions in the standard with % relative standard deviation (% R.S.D.)

Ions	DL (μg/mL)	MT (min)	R.S.D. (%)
NH_4^+	14	0.79	0.51
K^+	11	0.91	0.44
Na^+	–	0.99	0.32
Ca^{2+}	15	1.09	0.51
Mg^{2+}	9.5	1.12	0.49
Cl^-	0.5	4.70	0.14
NO_2^-	1.0	5.05	0.16
NO_3^-	1.7	5.21	0.17
SO_4^{2-}	5.0	5.37	0.16
ClO_4^-	0.8	5.93	0.22
SCN^-	0.8	6.15	0.21
ClO_3^-	1.2	6.33	0.23
OCN^-	5.4	6.67	0.25

Conditions are given in Table 3.

3.6.2. Sample analysis

Pyrodex® RS, flash powder, and black powder as well as the smokeless powders, H335 and HiSkor 700X were analyzed using the optimized buffer. Ions in Pyrodex® RS, black powder, and flash powder were compared to those produced in literature. Pyrodex® has been shown to produce the following ions: sodium, potassium, chloride, hydrogen sulfide, nitrite, nitrate, sulfate, perchlorate, thiocyanate, cyanate, and hydrogen carbonate. Black powder has been shown to produce ammonium using IC, potassium, sodium, hydrogen sulfide, chloride, nitrite, nitrate, sulfate, thiocyanate, cyanate, hydrogen carbonate, and an unknown ion [12,19]. Flash powder has been shown to produce chloride, nitrate, sulfate, chlorate, and hydrogen carbonate [19]. The same ions were detected when comparing the novel simultaneous method used for analysis with the individual methods used in literature (Table 8). Hydrogen carbonate was not analyzed since it can appear following exposure to air.

The powders analyzed by the simultaneous method were compared to analysis of anions and cations performed using individual methods in Table 8 [12,19]. The individual and simultaneous methods give comparable ion concentrations for the powders tested. In the table, higher variations for calcium and sodium are likely the result of coelution with a system peaks in the individual and simultaneous methods, respectively. In addition, nitrate and hydrogen sulfide are not detected in the individual methods for flash powder and HiSkor

Table 8
The analysis of anions and cations in a variety of deflagrated explosives using single and dual analysis methods

Ions	Pyrodex RS		Black powder		Flash powder		H380		HiSkor 700X	
	Single	Dual	Single	Dual	Single	Dual	Single	Dual	Single	Dual
NH_4^+							1.0 ± 0.1		–	
K^+	255 ± 12	197 ± 14	561 ± 8	515 ± 8	119 ± 2	94 ± 7	33 ± 2	32 ± 2	2.0 ± 0.1	–
Na^+	12 ± 1	50 ± 10	2.0 ± 0.2	–	3.0 ± 0.1	50 ± 3	–	–	–	
Ca^{2+}				112 ± 64		16 ± 6				
Mg^{2+}				3 ± 1	2.0 ± 0.1	3 ± 1				
HS^-	18 ± 2	8.0 ± 0.6	40 ± 5	38 ± 3						3.0 ± 0.4
Cl^-	59 ± 5	67 ± 3		6 ± 3	88 ± 14	82 ± 33	1.0 ± 0.3	2 ± 1		
NO_2^-	34 ± 3	7.0 ± 0.9	4 ± 2	3 ± 1						
NO_3^-	10 ± 1	3.0 ± 0.4	6 ± 1	–	7 ± 3	23 ± 2	25 ± 1	7 ± 4	10.0 ± 0.1	
SO_4^{2-}	148 ± 14	134 ± 12	522 ± 16	421 ± 21	16 ± 1	41 ± 20	–	2110.0 ± 0.1 2	–	9 ± 1
ClO_4^-	6 ± 1	3 ± 1								
SCN^-	27 ± 3	10 ± 1	6 ± 1	5 ± 2						
ClO_3^-					29 ± 4	18 ± 8			3 ± 1	3.0 ± 0.1
OCN^-	122 ± 14	66 ± 2	33 ± 3	30 ± 4						

Pyrodex, black powder and flash powder are inorganic explosives. H380 and HiSkor are smokeless powders. Concentrations are provided in ppm ± pooled standard deviations. The same powder samples were used between methods. Conditions for the dual injections are given in Table 3. The conditions for single injections of cations and anions are given in Refs. [12,13]. Dashed lines indicate trace levels detected.

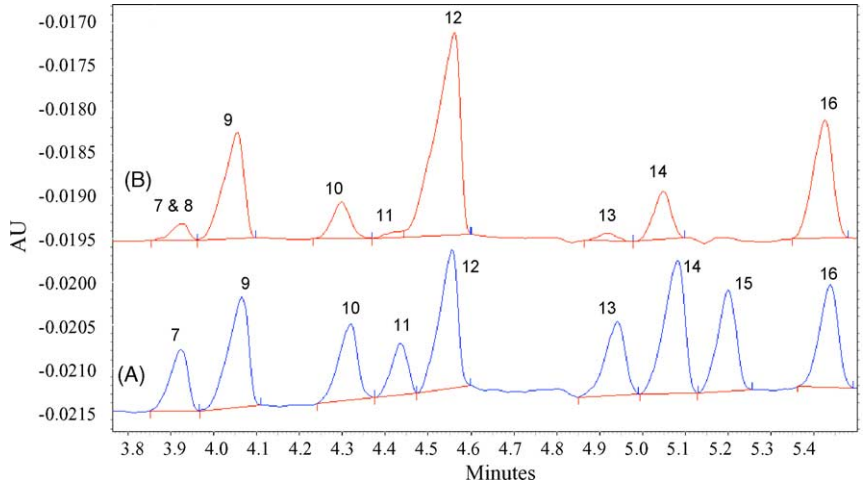

Fig. 4. (A) 10 ppm standard; (B) Pyrodex® RS with Br^- as the IS, 235 nm; ions are identified as: 7, bromide; 8, hydrogen sulfide; 9, chloride; 10, nitrite; 11, nitrate; 12, sulfate; 13, perchlorate; 14, thiocyanate; 15, chlorate; 16, cyanate; conditions are given in Fig. 3a. Bromide coeluted with hydrogen sulfide in (B), therefore, hydrogen sulfide was confirmed in a separate analysis.

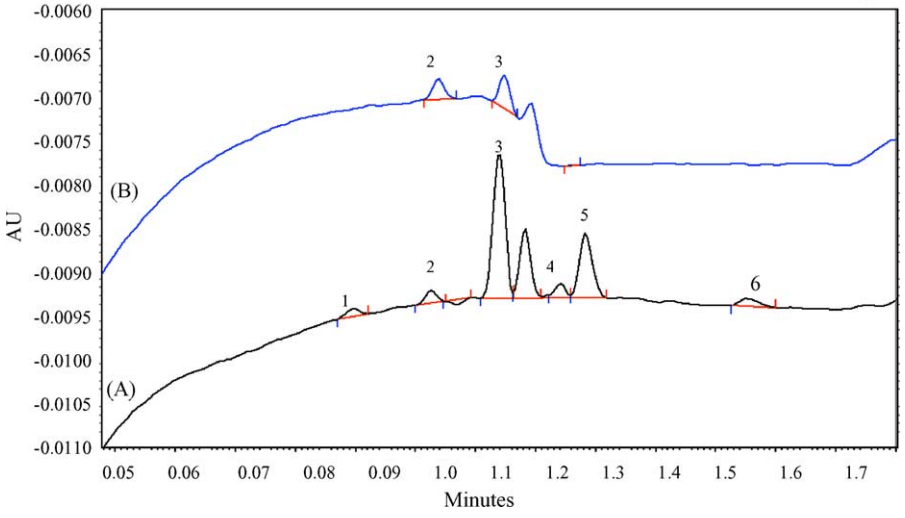

Fig. 5. (A) 10 ppm standard; (B) Pyrodex® RS, 208 nm; ions are identified as: 1, ammonium; 2, potassium; 3, sodium; 4, calcium; 5, magnesium; 6, strontium; conditions are given in Fig. 3a.

700X, probably due to poor method sensitivity. Examples of electropherograms from the analysis of Pyrodex® RS are shown in Figs. 4 and 5.

4. Conclusion

This is the first report on simultaneous detection of anions and cations using CZE for low explosives residue. The electrolyte uses imidazole and 1,3,6-NTS for the probes with indirect UV detection at 208 nm for the cations and 235 nm for the anions. The method was validated by examining the precision of migration time and peak area and defining the overall detection limits. Furthermore, a comparison between individual ion analysis and simultaneous detection was made using residue samples produced by five different explosive powders. The method has also been used for analysis of inorganic ions in approximately 400 environmental samples. This method produces a rapid and reproducible assay of explosive residue and should prove useful in a variety of applications in which a complete ionic profile is needed in a single run.

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