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A Comparison of Smokeless Powders and Mixtures by Capillary Zone Electrophoresis*

ABSTRACT: The analysis of inorganic ions present in smokeless and muzzleloading powders has been performed using capillary zone electrophoresis (CZE). Previous publications have examined inorganic low explosives using CZE, but have not looked at the ion profiles from smokeless powders. In this report, seven commercially available smokeless powders were analyzed as unburned powder and burned residue. The results demonstrate that ionic profiles can be used to characterize smokeless powders. Our analysis also included a smokeless powder/Pyrodex[®] combination to determine if smokeless powder ions are distinguishable in a mixture; however, the high concentration of ions present in Pyrodex[®]RS prevented its detection. In addition, five different smokeless powder samples as well as Pyrodex[®]RS were collected for analysis subsequent to deflagration in fifteen plastic pipe bombs. The relative ion concentrations between these powders can be used to illustrate the differences between open burning and pipe bomb deflagration.

KEYWORDS: forensic science, explosives, smokeless powders, Pyrodex[®], capillary electrophoresis, ions

During the past 10 years, there have been numerous explosive incidents involving the use of improvised explosive devices (IEDs) that contained inorganic explosives. The inorganic ion analysis of the residue from such incidents can provide investigators with key evidence against the perpetrators (1). Following the explosion, the residues resulting from unburned and burned powder will include many different ion products important for characterization. Some unburned powder will remain, as not all of the explosive will be consumed during the reaction. Examples of fuel sources in improvised explosives include carbon, sugar, and sulfur. Oxidizers include nitrate, perchlorate, and chlorate salts. These reactions also produce many by-products that can be detected upon ion analysis (1,2).

Commercially available propellant powders are low explosives that deflagrate or burn at a propagation speed slower than the speed of sound (2). These powders can be chemically divided into two classes: smokeless powders, typically used for pistols and rifles, and muzzleloading powders such as black powder and Pyrodex[®] (3). Muzzleloading powders, as well as flash powders and other homemade inorganic mixtures can leave as much as 60% of their original weight as residue upon deflagration (4). Smokeless powders consist of a variety of organic constituents, and the focus of analysis in most publications involves the identification of these compounds (5–11). However, these compounds also produce small amounts of inorganic salts on deflagration.

Inorganic salts result from the additives and decomposition products of various components in smokeless powders and may be significant in characterization. These ions can originate from flash suppressants added as alkaline earth salts such as potassium sulfate to preclude secondary flash (12). Another source of ions is the decomposition of nitrocellulose due to moisture, which can yield nitric and nitrous acids (2). Variations in composition arise from the different ways in which the smokeless powders are manufactured (13). Thus, it should be possible to perform inorganic analysis on these propellants to obtain a more complete powder profile.

Capillary electrophoresis (CE) and ion chromatography (IC) have been used in the analysis of inorganic explosive residue in a variety of studies (14–19). McCord et al., used these orthogonal techniques to determine ions in pre- and post-blast residue of a variety of explosives (14). IC was used for anion detection in these residue types. Cations were analyzed using conductivity detection for many of the explosives of interest, including two different smokeless powders (15,17). IC has also been used to determine ions from pipe bomb residue of black powder and Pyrodex[®]RS (14). In one study, smokeless powder particles were analyzed from ammunition cartridges using scanning electron microscopy/energy dispersive X-ray microanalysis (SEM/EDX). This study was performed in order to correlate gun shot residue (GSR) with the cartridge or bullet type used at the crime scene (18). Numerous other studies involving the analysis of organics and inorganics in smokeless powders have been performed. However, despite the success of demonstrating inorganic ion detection, there has been no extensive study performed with respect to the inorganic components of smokeless powder by CE or IC.

In this paper, a variety of smokeless powders were analyzed to determine differences in ionic composition. The components analyzed include ions formed during powder production and those formed following deflagration. Experiments were performed to assess the difference between residue from unburned and burned powders, to evaluate the composition of the residue produced when a smokeless powder is combined with a muzzleloading powder, and to evaluate the different ion products and concentrations between laboratory and field deflagrated samples.

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* Portions of this paper were orally presented by Kristy Hopper at the following conferences: 1) 54th annual meeting of the American Academy of Forensic Sciences in Atlanta, GA. 2) The 2003 Mid-Atlantic Association of Forensic Science annual meeting in Annapolis, MD.

Financial support was provided by Technical Support Working Group (TSWG).

Received 8 Feb. 2004; and in revised form 18 Sept. 2004; accepted 19 Sept. 2004; published 2 Feb. 2005.

Materials and Methods

Chemicals

Capillary Zone Electrophoresis (CZE)—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) (20). 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) (16).

Ion Chromatography (IC)—The anion eluent for IC contained 0.75 g of isophthalic acid (Aldrich) and was added to 3 L of boiling water and 2 mL of 2 M potassium hydroxide to dissolve (2,14). All buffers and ion standards used milli-Q ultrapure 18.2 M Ω deionized water.

Standards—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), and 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), and magnesium.

CZE Analysis—Cation and anion analysis was performed using a ThermoSeparations CE500 and CE1000 capillary electrophoresis system (Thermo Separation Products, Piscataway, NJ). An uncoated fused-silica capillary of 43 cm \times 75 μ m internal diameter (I.D.) was used. For these analyses, samples were introduced into the capillary via hydrodynamic injection at 3 and 5 s for cation analysis and 10 s for anion analysis. A field strength of -349 V/cm and 349 V/cm for anions and cations, respectively, was used to obtain peak separation. Indirect absorbance detection was used for anions at a wavelength of 280 nm (Fig. 1) and absorbance detection at a wavelength of 215 nm for cations. Ion mobilities were compared to a 10-ppm standard. Certain anionic samples were analyzed at 214 nm to confirm the identity of nitrite, nitrate, and thiocyanate (Figs. 2 and 3). At this wavelength a shift in peak height and direction occurs for these anions when compared to 280 nm (21). Results were integrated using CE 1000 software. A pipe bomb study was performed using another CZE system, a ThermoSeparations CE Ultra (Thermo Separation Products, Piscataway, NJ) and the ThermoSeparations CE1000. The CE Ultra utilized an uncoated fused-silica capillary of 39 cm \times 75 μ m I.D. for anions. Samples were introduced into the capillary via hydrodynamic injection at a range of 0.5 s to 20 s depending on sample concentration and 5 s for cation analysis. Other conditions for cation analysis are as listed above. Baseline separation was obtained with a field strength of -256 V/cm. Certain samples were analyzed using a reduced field strength.

IC Analysis—Confirmation of specific anions was performed using ion chromatography with a Spectra-Physics SP8800 ternary HPLC system (Spectra-Physics, Inc., Mountain View, CA) coupled to a Gilson UV detector (Model 116). Two different Vydac ion chromatography columns were utilized; a 3021C4.6 column and a 3001C405 column (3,14).

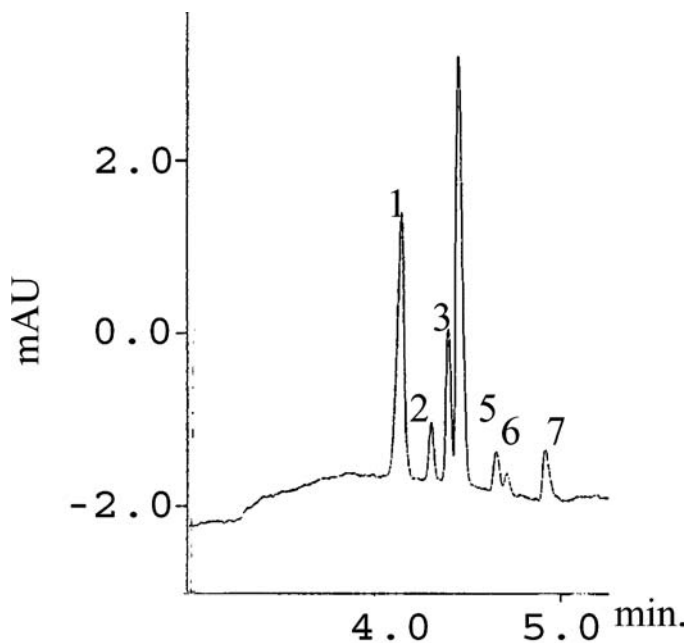


FIG. 1—Residue from pipe bomb containing Pyrodex[®] RS at 280 nm. Peak Identities: 1. Chloride, 2. Nitrite, 3. Nitrate, 4. Sulfate, 5. Perchlorate, 6. Thiocyanate, 7. Cyanate. The anion buffer consisted of 2 mM sodium tetraborate, 1.8 mM potassium dichromate, 40 mM boric acid, pH adjusted to 7.8 with diethylenetriamine with analysis performed on the ThermoSeparations Ultra CE system at a range of 0.5 to 20 s hydrodynamic injection time on a 39 cm \times 75 μ m internal diameter (I.D.) capillary with a field strength of -205 V/cm with indirect detection at 280 nm.

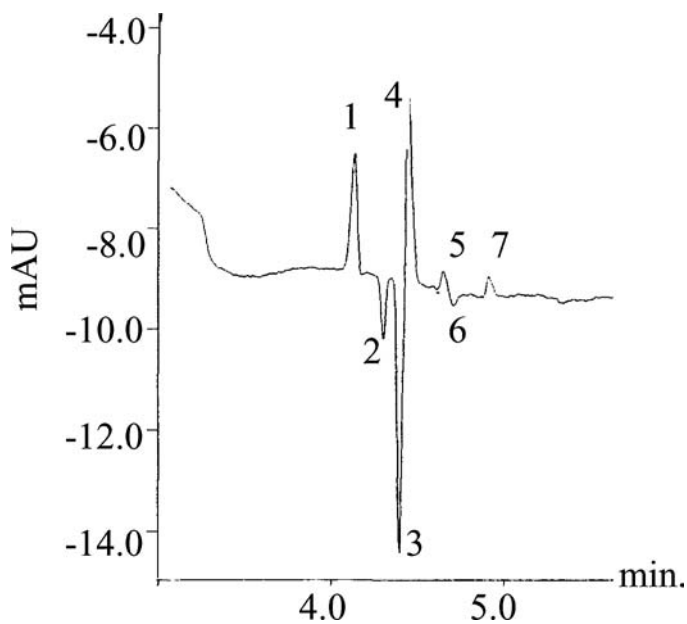


FIG. 2—Residue from pipe bomb containing Pyrodex[®] RS at 214 nm. Peak Identification: 1. Chloride, 2. Nitrite, 3. Nitrate, 4. Sulfate, 5. Perchlorate, 6. Thiocyanate, 7. Cyanate. Analysis conditions are given in Fig. 1.

Samples and Preparation

Smokeless Powders

The smokeless powders used include: N130 (Vihta Vuori Oy, Finland), H380 (Hodgdon, Shawnee Mission, KS), H335 (Hodgdon, Shawnee Mission, KS), HiSkor 700X (IMR, Plattsburgh, NY), XMR 2015 (Accurate, McEwen, TN), A 2230

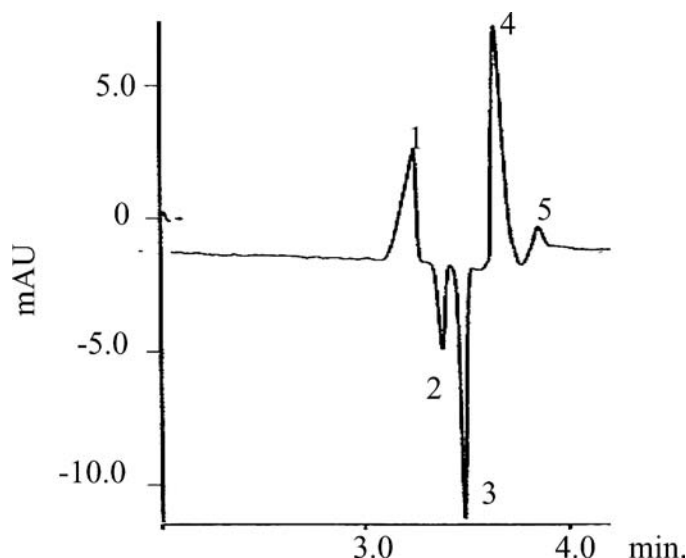


FIG. 3—Residue from pipe bomb containing IMR 4895 at 214 nm. Peak Identification: 1. Chloride, 2. Nitrite, 3. Nitrate, 4. Sulfate, 5. Unknown. Conditions as in Fig. 1 with the exception that the field strength was -256 V/cm.

(Accurate, McEwen, TN), A 2400 (Alliant, Kenil, NJ), IMR 4895 (IMR, Plattsburgh, NY), IMR 4064 (IMR, Plattsburgh, NY USA), AL-8 (Alcan, Sweden), W 296 (Winchester, New Haven, CT), and Alliant Red Dot (Alliant, Kenil, NJ). The muzzleloading powder used for analysis was Pyrodex[®] RS (Hodgdon, Shawnee Mission, KS).

Smokeless Powder Preparation

Two hundred milligrams of powder was used for each sample. Samples containing mixtures of 2 types of powder contained 0.1 g of each powder. To extract the ions each powder was placed in a centrifuge tube with 1 mL of 18.2 M Ω deionized water at room temperature and sonicated for one hour. For the individual muzzleloading powder and for the combination of two powders, 10 μ L of the original solution was diluted to 1 mL in 18.2 M Ω deionized water. Burned samples were prepared by weighing the powder on to a clean, dry watch glass using 0.1 g for each sample; for combined samples, 0.05 g of each individual powder was used. A Bunsen burner was used to deflagrate the sample on the watch glass. The burned residue was dissolved in 2 mL of 18.2 M Ω deionized water and let sit for 5 min. The unburned and burned samples were filtered for removal of particulates using 0.2 μ m ion chromatography Acrodisc[®] syringe filters. The burned powder filtrate was added to 13 mL of 18.2 M Ω deionized water.

Pipe Bomb Study

A pipe bomb study was conducted to compare differences between the deflagration of individual powders within a device and those powders that were openly burned within the laboratory. Fifteen polyvinyl chloride (PVC) pipe bombs were deflagrated by the Ohio State Fire Marshal's Office. The pipe bombs were placed in cardboard boxes secured with duct tape, with the electric squib attached vertically on the pipe, extending from the box, to allow for ignition. Each cardboard box was placed within a tractor tire and covered with a steel plate to contain the pipe to minimize blast residue contamination by environmental interferences. Residue samples from the bottom panels of each cardboard box were collected by

swabbing with dry cotton balls. Each cotton ball was placed in a 15 mL conical vial with addition of 1 mL of 18.2 M Ω deionized water and centrifuged for 8 minutes at 1000 rpm. The ensuing filtrates were diluted with 18.2 M Ω deionized water as necessary. Blanks of 18.2 M Ω deionized water were analyzed with the samples at room temperature and proved to be clean of any interfering ions. Three repetitions of a control were also run using a blank cotton ball. Ions present in the cotton ball included sodium, chloride, and sulfate at concentrations of 10, 15, and 12 ppm, respectively. A trace amount of nitrate was also present. These concentrations were not subtracted from the results.

Results and Discussion

Method Validation on the ThermoSeparations CE500

Cation Method Validation—To determine migration reproducibility and detection limits, three replicate injections were performed using a standard mixture containing ammonium, potassium, sodium, and magnesium (NH_4^+ , K^+ , Na^+ , and Mg^{2+}) with a range of concentrations between 1 and 30 $\mu\text{g}/\text{mL}$. Analyses were performed using a ThermoSeparations Product (TSP) CE 500 with a 3 s pressure injection. The standard deviation for the migration time repeatability of the method for the cation standard at 30 ppm ranged from 0.0058–0.017 (Table 1). Linear regression data for the peak area of each cation over the concentration range of 1–20 $\mu\text{g}/\text{mL}$ was used to determine the detection limits for each cation using $S/N = 3$ (Table 2).

TABLE 1—Average Migration Times and Standard Deviations of three replicate injections of 30 $\mu\text{g}/\text{mL}$ cation and anion standards. Cation analysis was performed on the ThermoSeparations CE500 with a 3 s hydrodynamic injection time on a 43 cm \times 75 μm internal diameter (I.D.) capillary using a field strength of 349 V/cm with absorbance detection at 215 nm. Anion analysis was performed on the ThermoSeparations CE Ultra with a 2.5 s hydrodynamic injection time on a 39 cm \times 75 μm internal diameter (I.D.) capillary using a field strength of -256 V/cm with indirect detection at 280 nm.

Ions	M.T. (min.)	SD	Ions	M.T. (min.)	SD
NH_4^+	2.34	0.0058	Cl^-	3.85	0.015
K^+	2.72	0.010	NO_2^-	3.99	0.011
Na^+	3.14	0.017	NO_3^-	4.06	0.0095
Mg^{2+}	3.43	0.012	SO_4^{2-}	4.09	0.0058
			ClO_4^-	4.23	0.0049
			SCN^-	4.27	0.0055
			ClO_3^-	4.39	0.0044
			OCN^-	4.46	0.0064

TABLE 2—Cation and Anion Detection Limits (DL) in $\mu\text{g}/\text{mL}$. Cation detection limits were calculated using Microsoft Excel for 3 replicates each of 1, 5, 10, and 20 ppm standards. Anion detection limits were calculated using Microsoft Excel for 3 replicates each of 1, 5, 10, 15, and 20 ppm standards. Analysis conditions are given in Table 1.

Ions	DL ($\mu\text{g}/\text{mL}$)	Ions	DL ($\mu\text{g}/\text{mL}$)
NH_4^+	1.3	Cl^-	0.73
K^+	2.0	NO_2^-	2.5
Na^+	4.0	NO_3^-	8.5
Mg^{2+}	11	SO_4^{2-}	4.4
		ClO_4^-	2.4
		SCN^-	1.4
		ClO_3^-	3.4
		OCN^-	0.74

Anion Method Validation—Three replicates of two standard mixtures, one containing chloride, sulfate, perchlorate, and chlorate (Cl^- , SO_4^{2-} , ClO_4^- , and ClO_3^-) and the second standard containing nitrite, nitrate, thiocyanate, and cyanate (NO_2^- , NO_3^- , SCN^- , and OCN^-) were analyzed using a TSP Ultra CE System with a 10 second pressure injection. Samples were analyzed over a range of 1 to 30 $\mu\text{g/mL}$. Standard deviation values for migration reproducibility of the anion standard at 30 ppm ranged from 0.0044 to 0.015 (Table 1). It should be noted that large changes in sample concentration can cause peak shifts in CE. Therefore, it is good practice to verify migration times by standard addition or the use of internal standards (20). For the instruments used, the calibration was linear. The detection limits are listed in Table 2.

Smokeless Powder Analysis—The quantitative analysis of eight different unburned and burned smokeless powders was performed using the methods discussed above. Figures 4 and 5 show ion concentrations relative to sulfate concentration for burned and unburned powders. In Fig. 4, burned powders XMR 2015, AL-8, 2230,

and N130 contain the ammonium ion whereas the other burned smokeless powders do not. XMR 2015 can be distinguished from the other powders since the relative ratio of potassium to sulfate is approximately the same as the ratio of sodium to sulfate, where in the other powders the ratio is quite different. AL-8 and 2400 can be distinguished from each other due to the presence of the ammonium ion in AL-8 but not in 2400, and the nitrate concentration relative to sulfate is higher in AL-8, but lower in 2400. IMR 4064 differs from 2400 due to the very low nitrate concentration relative to sulfate and the relative potassium concentration present is much greater than the relative sodium concentration present. Burned powders H335 and 2230 are distinguishable due to the large sodium to potassium ratio relative to sulfate. Since environmental interferences were minimal, the concentration levels of these analyzed powders suggest that differences in ionic content among burned smokeless powders may assist in characterization of the type of powder used in an IED.

Unburned powder, often remaining upon bomb deflagration, provided another source for smokeless powder discrimination upon ion

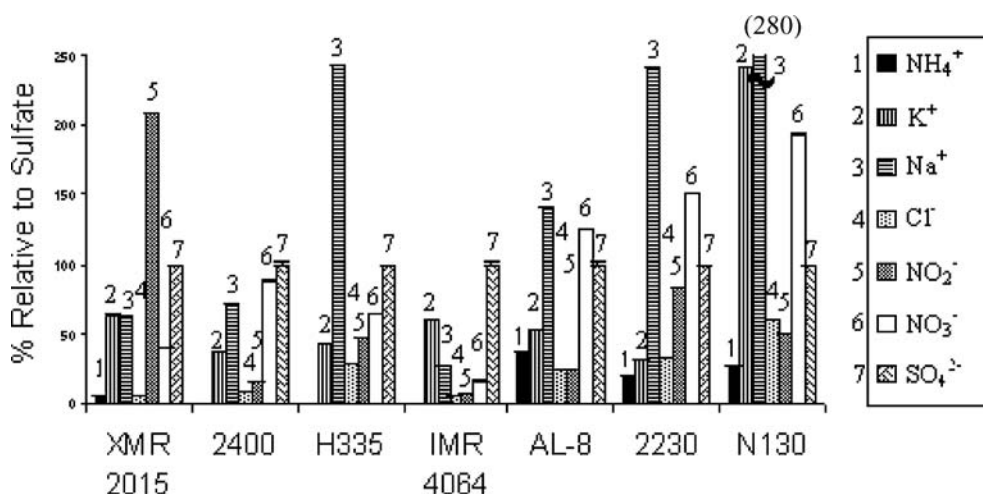


FIG. 4—Relative peak areas of anions and cations produced from burned smokeless powders calculated with reference to the sulfate ion (100%). The result for each powder is the pooled standard deviation of 3 samples of each powder analyzed 3 times. Identification of powders is given in the text. Cation analysis was performed on the ThermoSeparations CE500 at a 3 s hydrodynamic injection time on a 43 cm \times 75 μm internal diameter (I.D.) capillary across a field strength of 349 V/cm with absorbance detection at 215 nm. Anion analysis was performed on the ThermoSeparations CE1000 with a 10 s hydrodynamic injection time on a 43 cm \times 75 μm internal diameter (I.D.) capillary using a field strength of -349 V/cm with indirect detection at 280 nm.

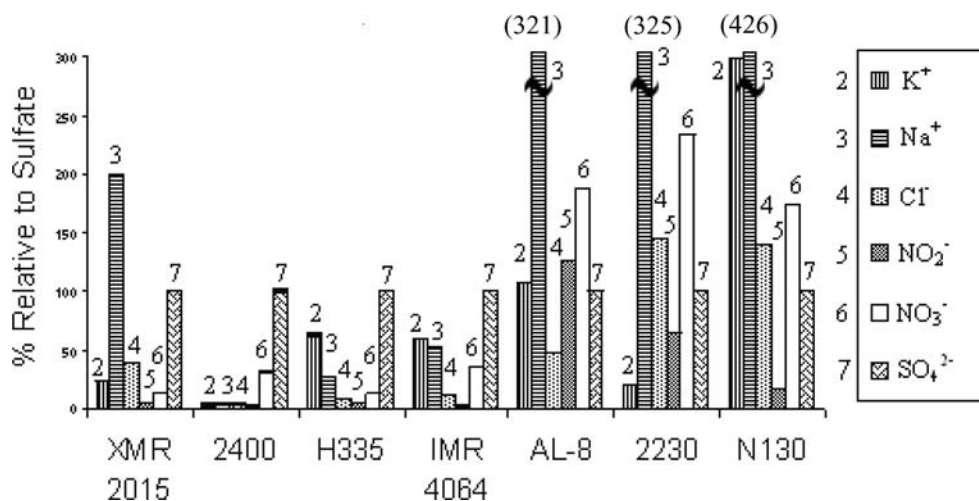


FIG. 5—Relative peak areas of anions and cations produced from unburned smokeless powders calculated with reference to the sulfate ion (100%). The result for each powder is the pooled standard deviation of 3 samples of each powder analyzed 3 times. Identification of powders is given in the text. Analysis conditions are given in Fig. 4.

analysis as the differences in various powders allowed for distinction from one another (Fig. 5). For example, 2400 can be distinguished from the other unburned powders as K^+ , Na^+ , Cl^- , and NO_2^- exist only in trace quantities in this powder. Unburned H335 and IMR 4064 have similar profiles, however, the ratio of potassium to sodium relative to sulfate in H335 is much more pronounced than in IMR 4064. Unburned XMR 2015 is similar to IMR 4064, but is distinguishable due to its elevated sodium concentration. Unburned AL-8, 2230, and N130 also have similar profiles, yet can still be differentiated. AL-8 is distinguishable from 2230 by a larger concentration of potassium relative to sulfate. Also, the chloride concentration is lower than the nitrite concentration relative to sulfate. A large concentration of potassium as well as sodium relative to sulfate distinguishes unburned N130.

A large amount of unburned powder was found among the burned residue from the deflagrated pipe bomb study discussed later in the paper. The likelihood of both burned and unburned powder being present at a scene may permit determination of the ionic profile of both burned and unburned powder. It is also instructive to compare the results of both the burned and unburned powders. The profile of relative ion concentrations change from unburned to burned powders (Figs. 4, 5). Burned XMR 2015 contains ammonium and exhibits a ratio of potassium to sodium close to one. However in the unburned powder no ammonium ion is detected and the ratio of sodium to potassium is large. The nitrite to chloride ratio is high in the burned powder whereas the ratio of chloride to nitrite is high in the unburned powder. The ion ratios to sulfate are low in unburned 2400 compared to the burned powder. In burned H335, the ratio of sodium to potassium and nitrite to chloride is high, whereas in the unburned H335 the potassium to sodium and the chloride to nitrite ratio is high. In burned IMR 4064, the nitrite to chloride level is high, but in unburned IMR 4064, the chloride to nitrite level is high. Burned AL-8, 2230, and N130 contain ammonium ion, but the unburned powders do not. The chloride and nitrite concentrations are approximately the same in burned AL-8, but the nitrite to chloride ratio is high in unburned AL-8. In burned 2230, the nitrite to chloride ratio is high, but in the unburned powder the chloride to nitrite ratio is high.

General observations from the comparisons show that in most burned powders, there is a reduction in the sodium concentration

compared to the unburned powders. Since the sodium concentration should be approximately the same, either sodium is not being extracted from the bulk powder or it becomes ejected as smoke during the burning process. With the exception of AL-8, the ratio of chloride to nitrite is high relative to sulfate in the unburned powders. In the burned powders analyzed, the ratio of nitrite to chloride is high relative to sulfate suggesting that upon deflagration, the nitrogen present from the powder components forms inorganic nitrites. Thus the ions detected provide a characteristic profile for each unburned and burned powder analyzed.

Smokeless Powder and Pyrodex[®] RS Combination Comparisons—A single IED may contain a mixture of black and smokeless powder. If these powders are present together, the possibility that the ionic components will be distinct enough to allow for mixture discrimination of post blast residue needs to be examined. Pyrodex[®], a muzzleloading powder, consists of potassium nitrate, potassium perchlorate, sodium benzoate, sulfur, charcoal, and dicyandiamide (14). Burned Pyrodex[®] RS was compared to burned XMR 2015. The level of ions detected are calculated in microgram per gram of sample used ($\mu\text{g/g}$). The ion concentrations in burned XMR 2015 range from below 800 $\mu\text{g/g}$ for sulfate, 500 $\mu\text{g/g}$ for potassium and sodium, and 300 $\mu\text{g/g}$ for nitrate to below 50 $\mu\text{g/g}$ for the other ions present in burned XMR 2015. These levels are substantially lower than the level of ions detected in Pyrodex[®] RS with most ions exhibiting concentrations greater than 1,000 $\mu\text{g/g}$ (Fig. 6). Therefore, it is not surprising that a distinction between the components of the mixtures cannot be determined. Ammonium is detected in Pyrodex[®] RS, but not in the combination. Unburned Pyrodex[®] RS yields nitrate and perchlorate upon anion analysis and sodium and potassium upon cation analysis (Fig. 7). Unburned smokeless powder XMR 2015 contains chloride, nitrite, nitrate, and sulfate upon anion analysis and sodium and potassium upon cation analysis (Fig. 5). When unburned Pyrodex[®] RS was combined with unburned XMR 2015, the ions detected are nitrate, perchlorate, sodium, and potassium (Fig. 7). Chloride, nitrite, and sulfate are not detected within the mixture due to the fact that ions from unburned Pyrodex[®] RS overwhelm the detection of the other ions present, which are all below 50 $\mu\text{g/g}$, in XMR 2015. Thus, in situations where a mixture

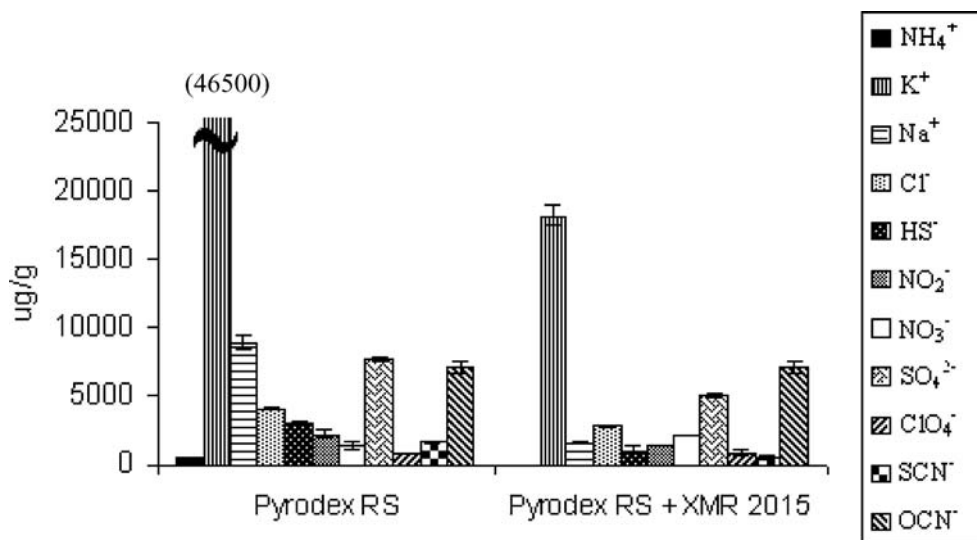


FIG. 6—An analysis of a mixture of deflagrated Pyrodex[®] and XMR 2015 smokeless powder. Concentrations are given in micrograms of ion produced per gram of smokeless powder. The result for each powder is the pooled standard deviation of 3 samples of the mixture analyzed 3 times. Analysis conditions are given in Fig. 4.

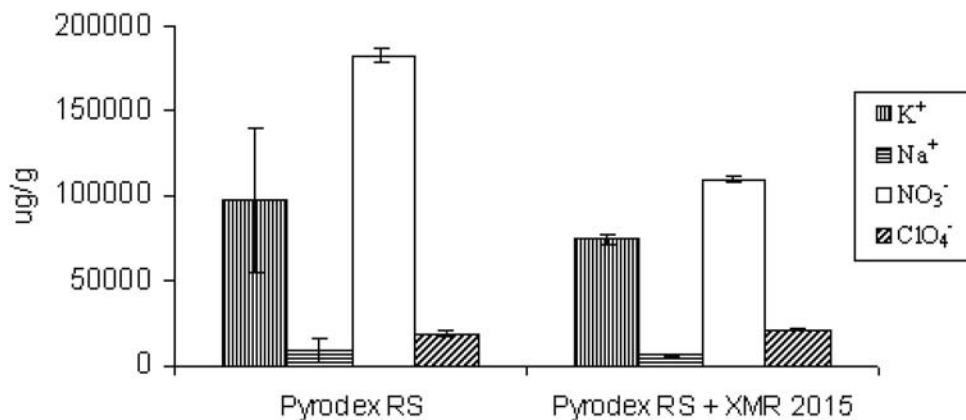


FIG. 7—An analysis of an unburned mixture of Pyrodex[®] and XMR 2015 smokeless powder. Concentrations are given in micrograms of ion produced per gram of smokeless powder. The result for each powder is the pooled standard deviation of 3 samples of the mixture analyzed 3 times. Analysis conditions are given in Fig. 4.

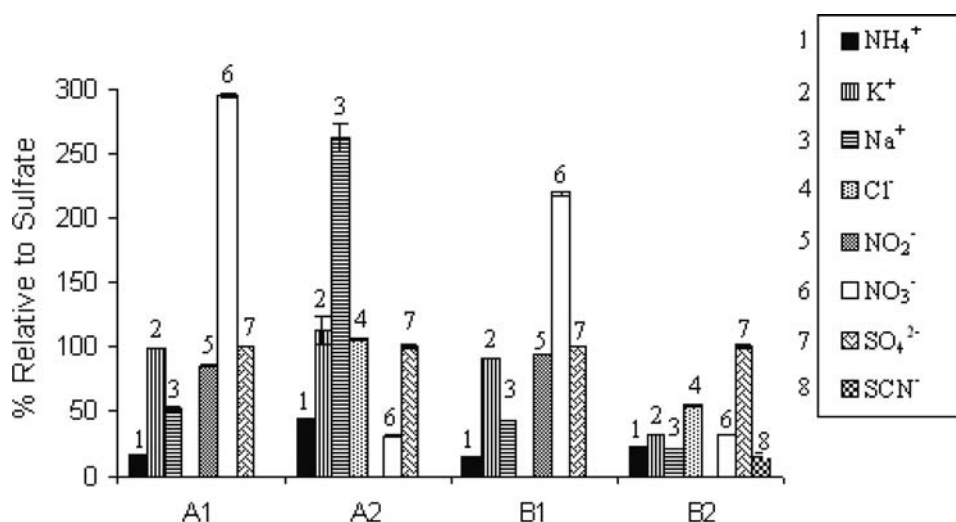


FIG. 8—A comparison of ARD (A) and W296 (B) laboratory deflagrated (1) and field deflagrated (2) powders. The results are the average of three separate analyses of each powder. Pipe bomb results from W296 are from of 2 different lots of the powder while all laboratory results and those of ARD are from a single lot. Peak areas are calculated relative to the sulfate ion (100%). Analysis conditions are given in Table 1.

of smokeless powder and inorganic powder is suspected, it is important to assess both the inorganic and organic content of the residue. Additionally, if unburned powder is present, the morphology of the powder should permit further discrimination.

Pipe Bomb Study—Laboratory deflagration, while providing a basis for powder profiling, must be verified with field samples. Comparisons help to ensure that the controlled environment of laboratory simulated burned powders are representative of actual pipe bomb deflagrations. There are varying factors which effect residue formation. These include the type of containment devices, the initiators, powder composition, as well as temperature and pressure effects. Due to these factors, there can be differing amounts of unburned and burned powder present following the explosion. In addition the types of intermediates formed may vary (20). Results are provided in Figs. 8–11, which compare data produced by open burning of the powders with data obtained from a pipe bomb study performed with help from the Ohio State Fire Marshal's Office using the same powders. The data from open burning of the powders was from one lot of the same powder used in each of the pipe bomb experiments, however, several other lots of each powder were also

used to prepare individual devices. As a result the data from all pipes is averaged. The figures show that analysis of the powder and powder extracts enables individual ions from the deflagrated pipe bombs to be detected.

Cotton swabs were used to collect the residue from the bottom of the boxes used to contain the pipes. The swabs were stored in polyethylene bags until extraction could be performed. The following powders were examined: Alliant Red Dot (ARD), Winchester 296 (W296), Hodgdon H380 (H380), Pyrodex[®] RS, HiSkor 700X, and IMR 4895. When the results of both the laboratory samples and pipe bomb samples were compared, variations in the relative levels of ions did exist. Chloride was present in all of the deflagrated smokeless powder pipe bombs analyzed, but not in the open burns. The PVC pipe could be a source for the presence of the chloride detected in the pipe bombs. This has been reported previously (2). Chloride is present due to the cotton balls, as well. Hydrogen sulfide was detected in H380 and HiSkor 700X pipe bombs, but not in the lab samples. Thiocyanate, another reaction intermediate, was also detected in the pipe bombs H380 and HiSkor 700X, but not in the lab burns. Thus, sulfur produces two specific ions, HS^- and SCN^- , in these powders that do not appear when samples are burned in the

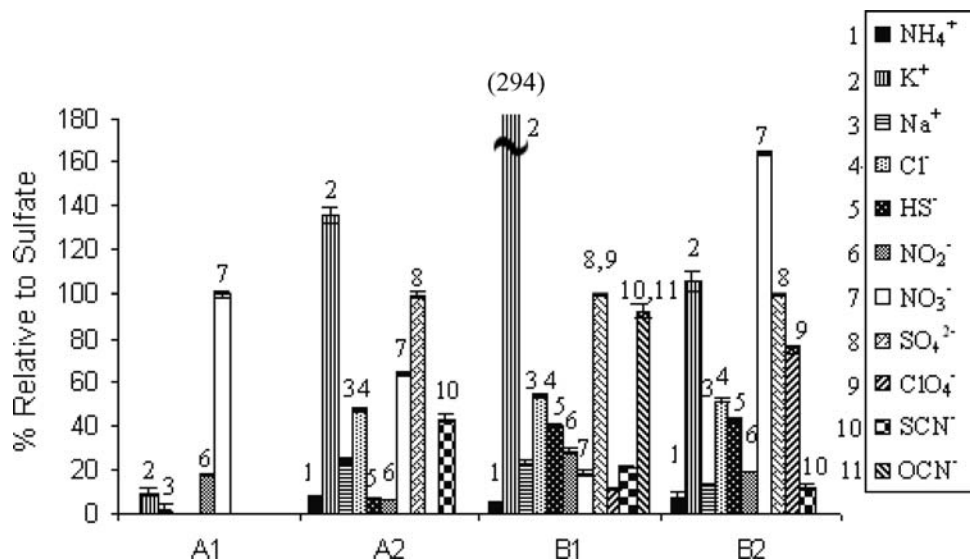


FIG. 9—A comparison of H380 (A) and Pyrodex RS (B) laboratory deflagrated (1) and field deflagrated (2) powders. The results are the average of three separate analyses of each powder. Pipe bomb results from H380 are from 2 different lots of powder while those from Pyrodex are from 3 different lots. All laboratory results are from a single lot of the powder. Peak areas are calculated relative to the sulfate ion (100%). Analysis conditions are given in Table 1.

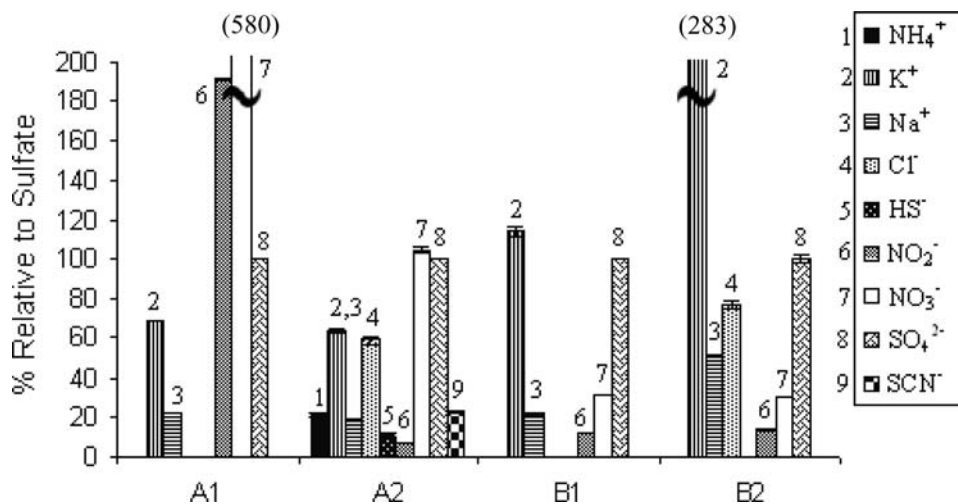


FIG. 10—A comparison of HiSkor 700X (A) and IMR 4895 (B) laboratory deflagrated (1) and field deflagrated (2) powders. The results are the average of separate analyses of each powder. Pipe bomb results from HiSkor 700x are from 4 different lots of the powder while those from IMR4895 are from 3 different lots. All laboratory results are from three samples of a single lot of the powder. Peak areas are calculated relative to the sulfate ion (100%). Analysis conditions are given in Table 1.

lab. Reaction conditions during pipe deflagration are the probable cause.

Another intermediate, nitrite, was produced in the concentration range of 80–180 ppm in the ARD, W296, and HiSkor 700X lab deflagrated powders but if present in the respective pipe bombs, the concentration is under 20 ppm. (Figs. 8, 10). Similar results showing the lack of nitrite, despite the presence of nitrate were shown previously by McCord, et al. (14). A possible explanation is that most or all of the nitrite is oxidized to nitrate upon pipe deflagration. Lower pressures, higher oxygen levels, and temperature effects in the open burns could cause differences in the rate of nitrite formation, producing fewer intermediates. In addition, background levels can vary depending on the sampling technique that was used. Laboratory deflagrated samples were analyzed by direct water extracts while the pipe bomb residue was swabbed with cotton and then

extracted with water. Low levels of ions in the cotton swabs and soil contamination from the explosion may also produce interferences. An interesting feature detected when comparing Pyrodex[®] RS was the presence of cyanate in the open burn but not in the pipe bomb. Thus cyanate provides a potential marker for uncontained Pyrodex[®] reactions.

The profile of one lot of the original powders used in the pipe bomb experiments was also examined (Fig. 11). The ionic concentrations of the smokeless powders are low compared to Pyrodex[®] RS, but Pyrodex[®] RS is expected to have a larger ionic concentration. The smokeless powders ARD, H380, and HiSkor 700X have large ionic concentrations compared to W296 and IMR 4895. ARD can be distinguished from H380 and HiSkor 700X because potassium and nitrate are the only two ions detected with large concentrations. Smokeless powders H380 and HiSkor 700X have

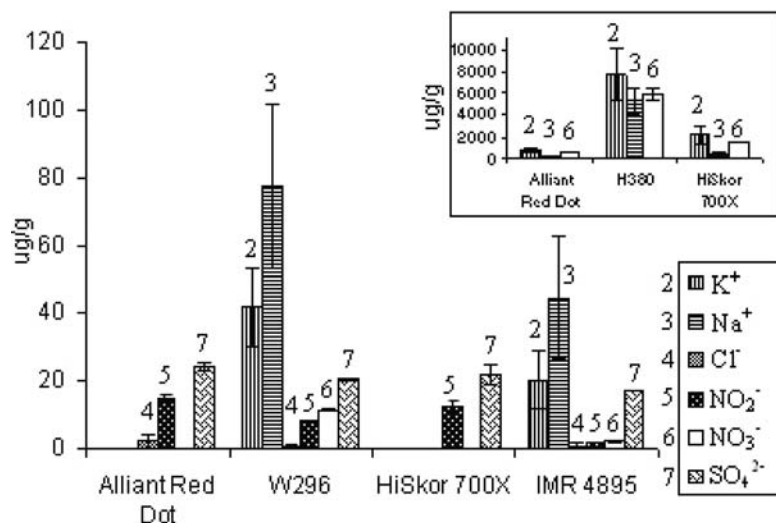


FIG. 11—Quantification of ions present in unburned powders used in the pipe bomb experiments. The graph in the top right corner provides data for potassium, sodium, and nitrate for the powders with high levels of ions. Concentrations are given in micrograms of ion produced per gram of smokeless powder. Analysis conditions are given in Table 1.

large concentrations of sodium detected as well as potassium and nitrate. However, HiSkor 700X can be differentiated from H380 because there are detectable levels of nitrite and sulfate also present.

Conclusions

In this study, the levels of inorganic ions in a variety of smokeless powders were examined. The results show that concentration of inorganic ions in burned and unburned smokeless powders can yield useful information in the characterization of these materials. We have also examined the difference between ions present in deflagrated pipe bombs and those created through open burning in the laboratory. Ions present within the open burned powders were comparable to the ions in the pipe bomb residue; however, relative ion concentrations can vary and various intermediates will appear. The overall results suggest that the analysis of burned powders in the laboratory can be representative of actual field samples. The major ions detected in all of the smokeless powder samples were similar to those found in residues of inorganic propellants. Therefore, the presence of these ions within explosives residue does not necessarily mean an inorganic explosive was used. In general, this study demonstrates that differences in relative and overall ionic concentrations can prove useful in distinguishing between individual smokeless powders and between smokeless powders and inorganic powders.

Acknowledgments

The authors would like to acknowledge the Ohio State Fire Marshal's Office for their expertise, and Janet Doyle as well as Robert Heramb for advice and technical assistance in performing this work. Major support for this work was provided by the Technical Services Working Group.

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