**Inorganic oxidizer detection from propellants, pyrotechnics, and homemade explosive powders using gradient elution moving boundary electrophoresis**

Shannon T. Krauss1,\*,§, Thomas P. Forbes1,\*, and Dillon Jobes2

1National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA.

2Tulane University, Department of Physics and Engineering Physics, New Orleans, Louisiana 70118, USA.

\*Correspondence: Dr. Shannon T. Krauss, 100 Bureau Drive, Mail Stop 8371, Gaithersburg, MD 20899, USA, Email: [skrauss@rti.org](mailto:skrauss@rti.org), ORCID: 0000-0002-6018-7335. Dr. Thomas P. Forbes, 100 Bureau Drive, Mail Stop 8371, Gaithersburg, MD 20899, USA, Email: [thomas.forbes@nist.gov](mailto:thomas.forbes@nist.gov), ORCID: 0000-0002-7594-5514.

§ Present Address: RTI International, Research Triangle Park, NC 27709, USA, Email: skrauss@rti.org

**Non-standard abbreviations:** DART – direct analysis in real time,GEMBE - gradient elution moving boundary electrophoresis, HME – homemade explosive, IC – ion chromatography, IED – improvised explosive device

**Keywords:** capillary electrophoresis, conductivity detection, explosives, inorganic oxidizers, screening

**Abstract**

Advancements in rapid targeted chemical analysis of homemade and improvised explosive devices is critical for the identification of explosives-based hazards and threats. Gradient elution moving boundary electrophoresis (GEMBE), a robust electrokinetic separation technique, was employed for the separation and detection of common inorganic oxidizers from frequently encountered fuel-oxidizer mixtures. The GEMBE system incorporated sample and run buffer reservoirs, a short capillary (5 cm), an applied electric field, and a pressure driven counterflow. GEMBE provided a separation format that allowed for continuous injection of sample, selectivity of analytes, and no sample cleanup or filtration prior to analysis. Nitrate, chlorate, and perchlorate oxidizers were successfully detected from low explosive propellants (*e.g.,* black powders and black powder substitutes), pyrotechnics (*e.g.,* flash powder), and tertiary explosive mixtures (*e.g.*, ammonium nitrate- and potassium chlorate-based fuel-oxidizer mixtures). Separation of these mixtures exhibited detection without interference from a plethora of additional organic and inorganic fuels, enabled single particle analysis, and demonstrated semi-quantitative capabilities. The bulk counterflow successfully excluded difficult components from fouling the capillary, yielding estimated limits of detection down to approximately 10 μmol/L. Finally, nitrate was separated and detected from post-blast debris collected and directly analyzed from two nitrate-based charges.

1. Introduction

The advancement of analytical techniques for the separation and detection of target species from complex samples remains critical for the identification of homemade explosive (HME) and improvised explosive device (IED) components. Though substantial research has focused on military-grade explosives, complex low-order and tertiary explosive mixtures based predominantly on inorganic oxidizers continue to top the U.S. Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF) annual review of explosive device main charges [1]. These fuel-oxidizer mixtures include black and smokeless powders, flash powders, pyrotechnics, propellants, and tertiary explosive mixtures, most commonly comprised of nitrate-, chlorate-, or perchlorate-salt oxidizers. The nature of these mixtures, precursors, post-blast products, and potential sample matrices necessitates robust analytical platforms for the separation of target anions from confounding organic and inorganic components, as well as sample matrix contaminants, interferents, and other particulate, fiber, or biological species. The analysis of anions from complex samples is critical not only for the defense sector, homeland security, and the forensic science community, but also for environmental monitoring and food safety applications [2-8].

A wide array of conventional and novel analytical methods have been employed for the detection and chemical analysis of inorganic oxidizers and related explosive mixtures, including ion chromatography (IC) [5,9,10], infrared and Raman spectroscopies [11-14], colorimetry [15], ion mobility spectrometry [16,17], mass spectrometry [18-27], and capillary electrophoresis [2,8,28,29]. These techniques offer a range of sensitivity, specificity, analysis time, instrumentation cost, and sample cleanup requirements. Depending on the application, guidelines may be available for identifying the most appropriate technique or group of techniques, as well as target compounds. For example, the Technical/Scientific Working Group for Fire and Explosive Analysis (T/SWGFEX) has published guidelines for the identification of both intact and post-blast explosives and residues [30,31]. These guides support the implementation of multiple analytical techniques for the analysis of complex mixtures.

Capillary electrophoresis (CE) has emerged as a selective orthogonal method to analytical techniques that provide structural or elemental characterization, enabling rapid and efficient separation of inorganic anions from complex mixtures. Both laboratory and portable CE systems have demonstrated separation of anions and cations relevant to explosive-based applications, most commonly using capacitively coupled contactless conductivity detection (C4D) [2,18,28,32-37]. The simultaneous separation of both anions and cations using CE presents a challenge due to the opposing charges, requiring reversal of the electroosmotic flow (EOF) and applied voltage polarity for separation from a single sample injection [38,39]. Some groups have addressed this challenge by sample injection from both ends of the capillary, dual-opposite end injection [40-42], or integration of two separate capillaries with simultaneous injections and differing polarities for either cations or anions, sequential injection-capillary electrophoresis [2,35]. Utilizing either EOF reversal or additional hardware for sequential injection into multiple capillaries increases the complexity of the separations and instrumentation. Detection of inorganic oxidizer ions from explosive fuel-oxidizer mixtures can be focused on the characteristic oxidizer anions. Nitrate, chlorate, or perchlorate anions in common salt oxidizers are suitable for use as tracer ions for targeted analysis due to the commonalities between cations in several organic oxidizers and related non-explosive compounds. Although targeted oxidizer anion detection using CE has demonstrated powerful utility, the complexity of explosive mixtures and corresponding sample matrices often leads to adverse effects on system performance, capillary (or microfluidic channel) clogging or fouling, and requires extensive sample cleanup (e.g., filtration or centrifugation) or consumable replacement (e.g., inline filters).

Gradient elution moving boundary electrophoresis (GEMBE) is an electrokinetic separation technique that eliminates or minimizes sample cleanup requirements, capillary blockages, and fouling by employing a counterflow arrangement to exclude particulates, fibers, and problematic components of complex sample matrices from the microfluidic capillary [43-50]. The elegant GEMBE arrangement simply consists of two fluid reservoirs separated by a short capillary (around 5 cm) or microfluidic channel and the application of an electric field. GEMBE achieves separation of continuously injected analytes through a pressure driven counterflow, from the run buffer reservoir toward the sample reservoir, that decays as a function of time. Electrically charged analytes sequentially enter and migrate through the capillary as their respective electrophoretic velocities overcome the decaying counterflow (combined pressure driven and electroosmotic flows). Simple manipulation of the ramped pressure driven counterflow provides selectivity and separation resolution of analytes, yielding stepwise changes in C4D signal [46,49,50] or similar detection scheme (e.g., fluorescence [43] or channel current [51]). This mode of separation also removes the need for precisely defined injections, enabling simple multiplexing for high-throughput formatting. GEMBE has demonstrated the separation of organic acids [50,52], enzymes [51], proteins [53], and of direct interest here, inorganic salts [45,46].

We present the applicability of GEMBE for the separation and detection of inorganic oxidizers from explosive fuel-oxidizer mixtures of intact and post-blast sample matrices. In this work, we take full advantage of the prominent GEMBE feature, a pressure-driven counterflow that excludes sample components and matrix particulates from clogging the capillary or diminishing performance. Additionally, the pressure-driven counterflow allowed for selectivity of the high mobility anions with similar electrophoretic mobilities towards the cathode without the use of modifiers, such as polymeric or surfactant additives. Nitrate, chlorate, and perchlorate oxidizers were successfully detected from low explosive propellants, pyrotechnics, and tertiary explosive mixtures that contained a variety of common organic and inorganic fuels. The bulk counterflow and chosen buffer successfully excluded these difficult components from fouling or clogging the capillary and provided selectivity of the targeted inorganic anions. Finally, chemical analysis was performed on post-blast debris collected and directly analyzed from two nitrate-based charges.

1. Materials and methods
   1. Chemicals

A stock solution of the run buffer used for inorganic oxidizer separations was diluted to 100 mmol/L acetic acid, 10 mmol/L L-histidine pH 3.69 (Sigma-Aldrich, St. Louis, MO, USA)† in ultrapure water (Millipore Milli-Q, 18.0 MΩ.cm) as needed [45]. Standards of potassium chlorate, potassium perchlorate, potassium nitrate, sodium sulfate, sodium benzoate, and dicyandiamide (Sigma-Aldrich, St. Louis, MO, USA) were used for separation optimization and peak identification. However, sodium benzoate and dicyandiamide were not observed during GEMBE analysis (outside of the target run window) using these separation conditions. Each standard or sample was prepared with 200 µmol/L calcium chloride as an internal standard for migration time normalization.

* 1. Sample collection and preparation

Propellant samples were provided by the U.S. Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF) forensic science laboratory (Ammendale, MD, USA), including black powders: Goex Black Powder FFFg, Elephant Supreme Black Powder FFFg, and Swiss Black Powder FFFg; and black powder substitutes: Pyrodex RS, Triple Seven FFFg, Blackhorn 209, and Jim Shockey’s Gold. Samples were gravimetrically prepared in deionized water to concentrations of 1 mg/mL prior to further dilution in sample buffer. Due to solubility, individual Blackhorn 209 particles were dissolved in acetone prior to further dilution in run buffer.

Pyrotechnic samples were collected from three different firecrackers that contained either a potassium perchlorate/aluminum powder mixture (flash powder) or a mixture of both flash powder and black powder primer. The inside of each carboard tubing that once held the explosive material was scraped, added to run buffer, and vortexed. Then, an aliquot was used for GEMBE analysis.

Homemade explosive fuel-oxidizer mixtures, displayed in Table S1, included either potassium chlorate- (Barium & Chemicals, Inc., Steubenville, OH, USA) or ammonium nitrate-based (Wampum Hardware Company, New Galilee, PA, USA) oxidizers mixed with a range of fuels, including, icing sugar (Giant Confectioners’ Powdered Sugar 10×), flour (Great Value All-Purpose Flour), petroleum jelly (Vaseline: Safeway Petroleum Jelly), kerosene (Fisher K-10), aluminum (Skylighter Aluminum, Spherical 9 micron), or fuel oil (diesel fuel). Fuel-oxidizer mixtures were also gravimetrically prepared in deionized water to concentrations of 5 mg/mL prior to further dilution in sample buffer.

Thermoplastic polymer devices were constructed with a number of different charges, including military dynamite (nominally 75/15/5/5 %weight RDX/TNT/cornstarch/engine oil), Schuetzen black powder (potassium nitrate/sulfur/carbon), and Dyno AP (packaged emulsion explosive). The Dyno AP charge consisted of primarily ammonium nitrate, sodium nitrate, and aluminum with additional minor mineral oil, sorbitan monooleate, and polymeric emulsifier components. Post-blast samples were collected in evidence bags from an explosives ordnance disposal range following detonation. Debris from the detonations were collected and returned to the laboratory for direct analysis. Individual pieces were vortexed in 100 µL of run buffer and then an aliquot was used for GEMBE analysis.

* 1. GEMBE apparatus

The details of the GEMBE apparatus (Fig. 1) have been described previously [44]. Briefly, a 2 mL run buffer reservoir and a 0.2 mL sample reservoir were separated by a 5 cm fused silica capillary (360 µm od, 15 µm id) that was threaded through a TraceDec C4D detector (Innovative Sensor Technologies GmbH, Strasshof, Austria), approximately 2 cm effective length. The TraceDec C4D detector settings, as defined by the system signal processing menus, were frequency: 2× high; voltage: 0 dB; gain: 200%, and data acquisition rate: 19.8 Hz. A Mensor 600 Series (San Marcos, TX, USA) pressure controller was directly connected to the sealed run buffer reservoir. Using a house nitrogen supply, the unit manipulated the pressure of the run buffer reservoir to drive the bulk counterflow towards the sample reservoir. A high voltage dc power supply (PS350, Stanford Research Systems, Sunnyvale, CA, USA) applied voltage through platinum wires for electrophoretic migration from the sample reservoir towards the run buffer reservoir. The acetate run buffer was replaced each day and was used to flush the capillary at the start of an experiment. The sample reservoir was rinsed with 0.2 mL water or run buffer after each sample. A process blank of run buffer was analyzed to assess carryover between sample analyses (found to be below detectable limits).

* 1. Experimental procedure

Constant pressure was applied at +30 kPa for 5 s (voltage off) as a prescan step to condition the capillary with run buffer and hold all sample in the sample reservoir until the start of the separation. The initial counterflow pressure was then set between +25.5 kPa and +23.5 kPa and held constant for approximately 10 s while a −3000 V (-600 V/cm field strength) voltage was applied. This was followed by the initiation of a −100 Pa/s pressure ramp. The pressure ramp lasted approximately 150 s, or until all analytes of interest had eluted. Subsequently, the pressure was reset to the initial counterflow pressure value and held for 10 s. Finally, a postscan step was applied for 30 s with the pressure held constant at +30 kPa (voltage off) to flush and condition the capillary for subsequent runs. Analysis times were approximately 2.5 min for each run. The run control and C4D data-logging were performed using a custom-written LabVIEW (National Instruments, Austin, TX, USA) program.

* 1. Evaluation of uncertainty

The uncertainty in quantification of oxidizer components from homemade fuel-oxidizer mixtures was determined from linear least squares calibration, employing standard guidelines [54,55]. Calibration curves were developed from neat oxidizer materials (Table S1), comprised of *n* unweighted values (*ci*, *Ii*) from concentrations (*c*) ranging from 0 μmol/L to 500 μmol/L and the corresponding normalized signal intensity (*I*, target step half-height/internal standard step half-height). A linear calibration curve, specified by *I* = *mc* + *b*, with *m* and *b* representing the slope and intercept, was employed. Oxidizer levels from assorted fuel-oxidizer mixtures (Table S1) were determined from *p* unknown sample measurements of each. The standard uncertainty in oxidizer concentration measurements resulting from variability in response was determined from the calibration function for *p* measurements by . Here, *S* was defined as the root mean square error, *m* was the slope of the calibration curve, *c­­o* was the concentration of the unknown oxidizer, was the average concentration from the *n* calibration concentration values, , and *ci* was the oxidizer concentration of the *ith* calibration point. Signal intensities were derived from an error function fit of the conductivity steps. This curve fitting protocol also introduced uncertainty into the measurement.

Similarly, the uncertainty in each calibration reference value (*ci*) propagated to the unknown oxidizer concentration and was approximated as . In addition, other sources of measurement uncertainty were evaluated, including those from preparation of standard solutions, solute purity, balance calibration, and variations in room temperature. Expanded uncertainties for each were assessed and combined in quadrature, yielding a total relative uncertainty in the calibration concentrations of on the order of a single percent. As discussed below, the variability in the homogeneity of the fuel-oxidizer mixtures and the associated uncertainty from sampled aliquots significantly outweighed the above evaluated uncertainties.

* 1. Safety considerations

Homemade fuel-oxidizer mixtures were stored and prepared in accordance with best practices for the handling of energetic materials. Individual mixtures (1 g each) were not at risk of detonation and stored in anti-static plastic bags within a flammable storage cabinet, minimizing opportunity for static discharge. Regular inspection of the materials was completed, monitoring for changes in color or morphology, or gas evolution. Analyzed fuel-oxidizer mixture, propellant, and pyrotechnic samples were diluted in water and disposed of as trace inorganic waste.

1. Results and discussion

GEMBE provided a separation format for continuous injection of sample, selectivity of analytes, and no sample cleanup or filtration prior to analysis for samples that contained undissolved particulates or common fuel mixtures. A schematic representation of the GEMBE setup and separation mechanism is shown in Figure 1. A constant voltage and positive pressure greater than the critical starting pressure [48] were initially applied, allowing the pressure-driven flow to dominate fluid movement. Due to the applied pressure, analytes remained in the sample reservoir prior to separation and particulate in the sample was excluded from entering the capillary. Then, the pressure was decreased at a constant rate resulting in each sample analyte sequentially entering the separation capillary as the electrophoretic mobilities of the analytes began to offset the counterflow pressure. Analytes migrated down the capillary as moving boundaries due to the continuous injection format at an acceleration equal to the counterflow acceleration. The spacing between the detected analyte moving boundaries, or stepwise changes in signal, were equal to the time each analyte initially entered the capillary.

Optimization of the separation conditions was performed by varying the applied pressure gradient, starting pressure, and electric field strength to balance resolution of the targeted inorganic anions and separation time. All GEMBE separation parameters were controlled by LabView software allowing for rapid method development. Calcium chloride was utilized as an internal standard for normalization of the target anion migration times, and the migration order of the internal standard and target analytes was chloride, nitrate, perchlorate, and chlorate. Additionally, normalization using the internal standard was performed with the leading edge of each analyte step, instead of at the step half height or derivative full width half maximum, to account for changes in the step width correlating to variations in analyte concentrations.

* 1. Black powder and black powder substitute propellants

Black powder is a classical fuel-oxidizer mixture made up of potassium nitrate, sulfur, and charcoal, and is used as a propellant in firearms and pyrotechnics. Alternatively, black powder substitutes were introduced as a replacement to classical black powder for improved performance and to reduce associated storage and handling hazards. These substitute formulations often incorporate potassium perchlorate as an inorganic oxidizer component and utilize alternative organic fuels.

Provided propellant samples of various black powder and black powder substitutes were analyzed without sample cleanup. Representative data are shown in Figure 2 including raw GEMBE stepwise data, derivative electropherograms, and bright field microscopy insets showing the analyzed propellant particle characteristics for relative size, shape, color, and finish. Generally, each type of particle was nonuniform in shape with Triple Seven FFFg and Jim Shockey’s Gold as the smallest and largest in size, respectively. Additionally, the sheen finish on the Swiss Black Powder FFFg and Elephant Supreme Black Powder FFFg could be indicative of a surface coating. Goex Black Powder FFFg and Pyrodex RS were similar in size, however, the Pyrodex RS particles appeared to have increased surface roughness. No detrimental effects were observed for the identification of the target analytes, nitrate and perchlorate, for all black powder and black powder substitutes analyzed. No interfering peaks from the organic components of black powder substitutes were detected. These components included dicyandiamide, 3-nitrobenzoic acid, sodium benzoate, and ascorbic acid. The black powder sample solutions of Goex Black Powder FFFg, Swiss Black Powder FFFg, and Elephant Supreme Black Powder FFFg all contained undissolved particulate suspensions. All black powder samples contained the expected nitrate component, while the black powder substitutes all exhibited peaks for both nitrate- and perchlorate-based inorganic oxidizers.

Interestingly, propellant samples of Blackhorn 209 were expected to contain both nitrate and perchlorate based on the literature [23,56,57], however, initial analyses did not detect both anions. Bright field microscopy was used to visually confirm two different surface roughness characteristics of the tubular-shaped particles [57]. The impact of the particle morphology on the target anions detection was validated by using one Blackhorn 209 particle, approximately 1.0 mg, for each analysis while classifying the particle surface as smooth or rough, relatively. Figure 3A shows the results from 21 individual Blackhorn 209 particles (n = 2 for each particle) analyzed with 9 containing both nitrate and perchlorate and 12 containing only nitrate. Results comprising of both target anions correlated with the Blackhorn 209 particles classified as rough, while the smooth only contained nitrate. Exemplary data for a smooth and rough Blackhorn 209 particle is shown in Figure 3B with bright field image inset. Further mass spectrometry analysis using high temperature thermal desorption direct analysis in real time (DART) [22] confirmed the differences in the rough and smooth particle chemical compositions (Figure 3C). In addition to the targeted anions, nitrate and perchlorate, mass spectrometry characterization also identified further discrimination between the rough and smooth Blackhorn 209 particles.

Sulfur and potassium nitrate, commonly found in black powder, were identified in the smooth particles and guanidine nitrate was identified in the rough particles as an additional nitrate source. These additional ions, sulfur and guanidine, were not detectable using the applied GEMBE separation parameters and analysis time.

* 1. Pyrotechnics

The utility of pyrotechnic detection applies directly to the forensic analysis of confiscated packages by law enforcement presumed to contain illicit fireworks based on composition or weight regulations [18], and the environmental monitoring and remediation challenge of large soil areas and bodies of water polluted by firework displays [58]. Samples were collected for analysis from the cardboard tubing of three firecrackers that once contained the explosive pyrotechnic material. These fireworks were known to contain either a mixture of black powder and flash powder or flash powder only (potassium perchlorate and aluminum) [18]. Figure 4 shows the presence of nitrate and perchlorate leading to the detection of both the black powder and flash powder inorganic components. Although two formulations contained black powder and flash powder, one sample contained substantial visible particulate fragments from the cardboard tubing (Figure 4A inset), whereas the other resulted in visual observation of the fuel components, likely aluminum powder and charcoal (Figure 4C inset).

The remaining sample resulted in the largest amount of visible fuel present, likely aluminum powder due to the detection of perchlorate and minimal nitrate signal indicating a flash powder formulation (Figure 4B). No additional steps were taken to reduce the amount of fuel present prior to analysis and no unfavorable results were observed. However, the concentrated perchlorate oxidizer resulted in wider peaks (Figure 4B). This could be minimized by further dilution of the collected sample. The minimal presence of nitrate in this sample with a signal approximately 15× lower than perchlorate likely a result of nitrate background from the cardboard firecracker tubing, as described previously [18].

* 1. Homemade explosives: tertiary explosive fuel-oxidizer mixtures

The analysis of a wide assortment of black powder and black powder substitute propellants and pyrotechnics provided a strong foundation for the detection of inorganic oxidizers from complex mixtures with various organic and inorganic fuels by GEMBE. Next, we considered additional capabilities through the analysis of homemade tertiary explosive fuel-oxidizer mixtures and relative standard solutions of either nitrate or chlorate. Oxidizer compounds containing the target anions were mixed with common fuels including icing sugar, flour, aluminum powder, kerosene, diesel, and petroleum jelly. The potential for bulk quantitative analysis by GEMBE was investigated for these tertiary explosives. Calibration curves were developed from the neat oxidizer components (samples #1 and #6, Table S1) of samples ranging from 0 μmol/L to 500 μmol/L, taking nominally ten replicates at each concentration. Target oxidizer step heights were normalized by a chloride internal standard, and the linear calibration curves (red solid lines) for nitrate (ammonium nitrate) and chlorate (potassium chlorate), along with the 95% confidence intervals (black dashed lines), can be found in supporting information (Figure S1).

Calibration curves were used to quantitatively measure the level of nitrate or chlorate in each of the explosive mixtures from Table S1. Milligram aliquots of each mixture was extracted in deionized water to 5 mg/mL concentrations prior to further dilution to 0.025 mg/mL in run buffer. Table 1 exhibits the amount of oxidizer in each sample per the 200 μL sample reservoir (5 μg total) from triplicate measurements. The linear least squares calibration standard uncertainty was evaluated for each observation (details in Methods section). Several of the samples analyzed varied significantly from the expected fuel-oxidizer ratios. Further investigation identified non-homogeneity in the bulk mixtures as a significant source of uncertainty in the presumed ratios, far outweighing the measurement uncertainty. Although the fuels led to various levels of bulk non-homogeneity in the mixture, they did not have observable detrimental effects on the analysis of target anions. In addition, no interfering peaks from these fuels (*i.e.,* sugar, flour, aluminum, kerosene, diesel fuel, or petroleum jelly) were observed. The internal standard signal remained stable across the analysis of all fuel-oxidizer mixture and the neat oxidizer. The median signal (step height/step width) for each was statistically equivalent within 95% confidence interval (Figure S2), demonstrating minimal effects of the fuel on the overall analysis. In addition to bulk quantitation, the calibration curves were employed to approximate limits of detection based on ASTM E2677 [59] (Standard Test Method for Determining Limits of Detection in Explosive Trace Detectors), yielding 10.5 μmol/L and 9.1 μmol/L for nitrate (ammonium nitrate) and chlorate (potassium chlorate), respectively. In GEMBE, detection of a moving boundary or step change in conductivity can effectively reduce sensitivity of subsequent compounds in mixtures. Similar effects have been shown for binary mixtures of drugs [49]. Reevaluation of sensitivity levels without the inclusion of an internal standard to eliminate this suppression resulted in detection limits of 1.8 μmol/L and 2.0 μmol/L for nitrate and chlorate, in line with previous GEMBE investigations [45]. Other capillary electrophoresis techniques have achieved more sensitive detection, however also required more rigorous and lengthier sample preparation [2, 28, 35].

* 1. Thermoplastic polymer pipe bomb post-blast analysis

Thus far, GEMBE demonstrated the separation and detection of inorganic oxidizers from a range of intact propellants, pyrotechnics, and explosives. Finally, we considered the analysis of post-blast debris. Controlled heated wire detonations of three thermoplastic polymer pipe-based improvised explosive devices were conducted with charges of dynamite, black powder, and Dyno AP (an emulsion explosive comprised mostly of nitrate salts and aluminum fuel). Following detonation, debris was collected, packaged, and returned to the laboratory (Figure 5). IED debris fragments on the order of a couple millimeters in size were selected from each detonation for GEMBE analysis. No sample cleanup, filtering, or centrifugation was completed, simply suspension in buffer (Figure 5 insets). Figure 5 demonstrates the results from the analysis of each IED. A control sample of the pre-blast thermoplastic polymer can be found in supporting information (Figure S3). The military-grade dynamite IED yielded a strong detonation with minimal device debris. GEMBE analysis of a small fragment demonstrated no significant peaks of interest as was expected from its organic nitroaromatic/nitramine composition, TNT/RDX (Figure 5A). Similar to the previous studies, a chloride internal standard was added to each sample. The IED comprised of a black powder propellant produced fragments often still covered in black residue and particulate (Figure 5). The electropherogram resulting from the black powder-based device debris exhibited strong signals for nitrate and sulfate, likely resulting from the potassium nitrate oxidizer and sulfur fuel (Figure 5B). A sodium sulfate standard was spiked into select sample runs to identify the sulfate peak.

Lastly, debris from the IED containing Dyno AP, a packaged emulsion explosion typically used for quarry, construction, and other blasting applications, was analyzed. Dyno AP is comprised of both ammonium nitrate and sodium nitrate oxidizers and left a whitish residue on some of the device debris. The GEMBE response for a small fragment from the Dyno AP detonation yielded a strong nitrate signal (Figure 5C). It is important to note that low levels for nitrate and other anions are commonly observed as background in soil, other environmental samples, and may also be a contaminant from previous detonations at the site. Similar to the concentrated pyrotechnic sample, highly concentrated debris samples yielded wider peaks. However, the analysis of device debris resulted in clear differentiation of the main charges investigated here based on their composition, with no observable interference from background ions (*e.g.,* environmental arsenic, carbonate, phosphate, or fluoride). The counterflow nature of the GEMBE technique allowed for direct analysis of the sample without lengthy sample clean-up and no observable clogging or other detrimental effects from the large amounts of particulate and residue on the analyzed fragments. Similar electrophoretic techniques often require extraction, ultrasonication, and filtration prior to analysis.

1. Concluding remarks

Target inorganic oxidizer components – nitrate, chlorate, and perchlorate – were successfully detected from low explosive propellants, pyrotechnics, and tertiary explosive mixtures and with characteristic limits of detection on the order of 10 μmol/L levels. GEMBE demonstrated quantitative capabilities, exhibiting linearity over approximately two orders of magnitude in concentration. The GEMBE bulk counterflow and prudent buffer selection provided exclusion of all other difficult fuel components in the mixtures from fouling the capillary or impacting the detection of the target analytes. The selective separation of target anions from complex pre- and post-blast explosive mixtures could provide utility to forensic and criminal investigations as a Category 3 analytical tool (T/SWGFEX recommendations). The simple GEMBE design allows for easy multiplexing and high-throughput simultaneous screening of many samples. The utility of the GEMBE platform for rapid analysis was demonstrated here with run times < 2 min. Further reduction in analysis times and resolution improvements could be achieved through background electrolyte manipulation, additive inclusion [46], and advanced peak processing protocols [60]. Similarly, as interest in instrumentation for the screening of inorganic-based explosives advances [61], GEMBE enables a simple platform and analysis in a potentially field deployable package. The direct sample-in/answer-out nature of GEMBE, without the need for sample cleanup or significant consumable filtration, provides a powerful alternative to conventional injection capillary electrophoresis.

1. Acknowledgments

The authors would like to thank Cindy Wallace at the Bureau of Alcohol, Tobacco, Firearms, and Explosives for providing the black powders and black powder substitutes; Karlijn Bezemer and Arian van Asten at the Netherland Forensic Institute for providing the firecracker samples; and Matthew Staymates, Jessica Staymates, and Greg Gillen at NIST for providing post-blast samples. This research was performed while S.T.K. held a National Institute of Standards and Technology (NIST) National Research Council (NRC) Research Postdoctoral Associateship Award. The U.S. Department of Homeland Security Science and Technology Directorate sponsored a portion of the production of this material under Interagency Agreement IAA FTEN-18-00014 with the National Institute of Standards and Technology.

† Certain commercial equipment, instruments, or materials are identified in this article in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

‡ Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.

*The authors have declared no conflict of interest*.

**References**

[1] United States Bomb Data Center (USBDC) 2018 Explosives Incident Report (EIR). https://www.atf.gov/explosives/docs/report/2018-explosives-incident-report-eir (accessed September 2019).

[2] Blanco, G. A., Nai, Y. H., Hilder, E. F., Shellie, R. A., Dicinoski, G. W., Haddad, P. R., Breadmore, M. C., *Anal. Chem.* 2011, *83*, 9068-9075.

[3] Butt, S. B., Riaz, M., *J Liq. Chromatogr. Relat. Technol.* 2009, *32*, 1045-1064.

[4] Crevillen, A. G., Hervas, M., Lopez, M. A., Gonzalez, M. C., Escarpa, A., *Talanta* 2007, *74*, 342-357.

[5] Dicinoski, G. W., Shellie, R. A., Haddad, P. R., *Anal. Lett.* 2006, *39*, 639-657.

[6] Pinheiro, K. M. P., Moreira, R. C., Rezende, K. C. A., Talhavini, M., Logrado, L. P. L., Baio, J. A. F., Lanza, M. R. V., Coltro, W. K. T., *Electrophoresis* 2019, *40*, 462-468.

[7] Rubio, S., Perez-Bendito, D., *Anal. Chem.* 2009, *81*, 4601-4622.

[8] Calcerrada, M., Gonzalez-Herraez, M., Garcia-Ruiz, C., *Trac-Trend. Anal. Chem.* 2016, *75*, 75-85.

[9] Lang, G. H. L., Boyle, K. M., *J Forensic Sci.* 2009, *54*, 1315-1322.

[10] Johns, C., Shellie, R. A., Potter, O. G., O'Reilly, J. W., Hutchinson, J. P., Guijt, R. M., Breadmore, M. C., Hilder, E. F., Dicinoski, G. W., Haddad, P. R., *J Chromatogr. A* 2008, *1182*, 205-214.

[11] Chen, J., Shi, Y. E., Zhang, M., Zhan, J. H., *Rsc Advances* 2016, *6*, 51823-51829.

[12] Shi, Y. E., Wang, W. S., Zhan, J. H., *Nano Research* 2016, *9*, 2487-2497.

[13] Zapata, F., Garcia-Ruiz, C., *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 2018, *189*, 535-542.

[14] Lopez-Lopez, M., Garcia-Ruiz, C., *Trac-Trend. Anal. Chem.* 2014, *54*, 36-44.

[15] Peters, K. L., Corbin, I., Kaufman, L. M., Zreibe, K., Blanes, L., McCord, B. R., *Anal. Methods* 2015, *7*, 63-70.

[16] Kelley, J. A., Ostrinskaya, A., Geurtsen, G., Kunz, R. R., *Rapid Commun. Mass Spectrom.* 2016, *30*, 191-198.

[17] Peng, L. Y., Hua, L., Wang, W. G., Zhou, Q. H., Li, H. Y., *Scientific Reports* 2014, *4*. 6631.

[18] Bezemer, K. D. B., Forbes, T. P., Hulsbergen, A. W. C., Verkouteren, J., Krauss, S. T., Koeberg, M., Schoenmakers, P. J., Gillen, G., van Asten, A. C., *Forensic Sci. Int.* 2020, *308*, 110160.

[19] Cody, R. B., Dane, A. J., *Rapid Commun. Mass Spectrom.* 2014, *28*, 893-898.

[20] Evans-Nguyen, K. M., Quinto, A., Hargraves, T., Brown, H., Speer, J., Glatter, D., *Anal. Chem.* 2013, *85*, 11826-11834.

[21] Forbes, T. P., Sisco, E., Staymates, M., *Anal. Chem.* 2018, *90*, 6419-6425.

[22] Forbes, T. P., Sisco, E., Staymates, M., Gillen, G., *Anal. Methods* 2017, *9*, 4988-4996.

[23] Forbes, T. P., Verkouteren, J. R., *Anal. Chem.* 2019, *91*, 1089-1097.

[24] Sokol, E., Jackson, A. U., Cooks, R. G., *Cent. Eur. J Chem.* 2011, *9*, 790-797.

[25] Ewing, R. G., Valenzuela, B. R., Atkinson, D. A., Freeburg, E. D. W., *Anal. Chem.* 2018, *90*, 8086-8092.

[26] Flanigan, P. M., Brady, J. J., Judge, E. J., Levis, R. J., *Anal. Chem.* 2011, *83*, 7115-7122.

[27] Forbes, T. P., Sisco, E., *Anal. Chim. Acta* 2015, *892*, 1-9.

[28] Hutchinson, J. P., Johns, C., Breadmore, M. C., Hilder, E. F., Guijt, R. M., Lennard, C., Dicinoski, G., Haddad, P. R., *Electrophoresis* 2008, *29*, 4593-4602.

[29] Tagliaro, F., Pascali, J., Fanigliulo, A., Bortolotti, F., *Electrophoresis* 2010, *31*, 251-259.

[30] Recommended Guidelines for Forensic Identification of Intact Ex-plosives. https://www.swgfex.com/publications, February 21, 2020.

[31] Recommended Guidelines for Forensic Identification of Post-Blast Explosive Residues. https://www.swgfex.com/publications, February 21, 2020.

[32] Kobrin, E. G., Lees, H., Fomitsenko, M., Kuban, P., Kaljurand, M., *Electrophoresis* 2014, *35*, 1165-1172.

[33] Wang, J., Chen, G., Muck, A., *Anal. Chem.* 2003, *75*, 4475-4479.

[34] Wang, J., Chen, G., Muck, A., Collins, G. E., *Electrophoresis* 2003, *24*, 3728-3734.

[35] Gaudry, A. J., Guijt, R. M., Macka, M., Hutchinson, J. P., Johns, C., Hilder, E. F., Dicinoski, G. W., Nesterenko, P. N., Haddad, P. R., Breadmore, M. C., *Anal. Chim. Acta* 2013, *781*, 80-87.

[36] GreyScan ETD-100. https://greyscandetection.com/, February 21, 2020.

[37] Krauss, S. T.; Forbes, T. P.; Lawrence, J.A.; Gillen, G.; Verkouteren, J. R. *Electrophoresis* 2020, *41*, 1482-1490.

[38] Haumann, I., Boden, J., Mainka, A., Jegle, U., *J Chromatogr. A* 2000, *895*, 269-277.

[39] Johns, C., Yang, W. C., Macka, M., Haddad, P. R., *J Chromatogr. A* 2004, *1050*, 217-222.

[40] Padarauskas, A., Olsauskaite, V., Schwedt, G., *J Chromatogr. A* 1998, *800*, 369-375.

[41] Kuban, P., Karlberg, B, *Anal. Chem.* 1998, *70*, 360-365.

[42] Kuban, P., Karlberg, B., Kuban, V., *J Chromatogr. A* 2002, *964*, 227-241.

[43] Shackman, J. G., Munson, M. S., Ross, D., *Anal. Chem.* 2007, *79*, 565-571.

[44] Strychalski, E. A., Henry, A. C., Ross, D., *Anal. Chem.* 2009, *81*, 10201-10207.

[45] Flanigan, P. M., Ross, D., Shackman, J. G., *Electrophoresis* 2010, *31*, 3466-3474.

[46] Strychalski, E. A., Henry, A. C., Ross, D., *Anal. Chem.* 2011, *83*, 6316-6322.

[47] Ross, D., *Electrophoresis* 2010, *31*, 3650-3657.

[48] Ross, D., *Electrophoresis* 2010, *31*, 3658-3664.

[49] Krauss, S. T., Ross, D., Forbes, T. P., *Anal. Chem.* 2019, *91*, 13014-13021.

[50] Munson, M. S., Karp, E. M., Nimlos, C. T., Salit, M., Beckham, G. T., *ACS Sustain. Chem. Eng.* 2016, *4*, 7175-7185.

[51] Ross, D., Kralj, J. G., *Anal. Chem.* 2008, *80*, 9467-9474.

[52] Ross, D., Romantseva, E. F., *Anal. Chem.* 2009, *81*, 7326-7335.

[53] Kralj, J. G., Munson, M. S., Ross, D., *Electrophoresis* 2014, *35*, 1887-1892.

[54] Taylor, B. N., Kuyatt, C. E., NIST Technical Note 1297, Guidelines for evaluating and expressing the uncertainty of NIST measurement results 1994, http://www.nist.gov/pml/pubs/tn1297/.

[55] Ellison, S. L. R., Rosslein, M., Williams, A., Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement. Second Ed.; 2000.

[56] Racette, M., Viau, S., Lepage, D., Black powder substitutes for small caliber firearms. US Patent US8257522B2, 2012.

[57] Lang, G. L., Reis, K., In Characterization and Analysis of Blackhorn 209, a New Black Powder Substitute; America Academy of Forensic Sciences Annual Scientific Meeting, Seattle, WA, February 22−27, 2010; Seattle, WA, 2010.

[58] Steinhauser, G., Klapotke, T. M., *Angew. Chem. Int.* 2008, *47*, 3330-3347.

[59] Standard Test Method for Determining Limits of Detection in Ex-plosive Trace Detectors, ASTM International, 2014.

[60] Patel, D. C., Wahab, M. F., O'Haver, T. C., Armstrong, D. W., *Anal. Chem.* 2018, *90*, 3349-3356.

[61] Forbes, T.P., Krauss, S.T., Gillen, G., *Trends Anal. Chem.* 2020, 131, 116023.

**Figure legends and tables**



Figure 1. Schematic of a GEMBE separation for different analytes (denoted yellow and green) from the sample reservoir towards the run buffer reservoir with pressure-driven and electrophoresis-driven flows opposing for separation of analytes within the capillary.



Figure 2. GEMBE separation of black powder, A.-C., and black powder substitute, D.-F., samples containing nitrate and perchlorate. Raw data in black showing stepwise increases in conductivity and derivative representation of the raw data with identified peaks shown in blue (internal standard: chloride). Bright field microscopy inset images of each sample with scale bar in red (2 mm).



Figure 3.Blackhorn 209 particle analysis. A. GEMBE analysis of 21 individual Blackhorn 209 particles, classified as either rough or smooth, for the presence of nitrate- and perchlorate-based inorganic oxidizers. Representative raw (black) and derivative (blue) data from a smooth, B-i., and rough, B-ii., Blackhorn particle. C. Confirmatory analysis of smooth, C-i., and rough, C-ii., particles with high temperature thermal desorption DART mass spectrometry.



Figure 4.Separation of three collected pyrotechnic samples with raw data shown in black and derivative representation of the raw data in blue with inset images of each sample mixture.



Figure 5.GEMBE analysis of post-blast debris collected from thermoplastic polymer devices constructed with different charges including A. military dynamite, B. black powder, and C. Dyno AP packaged emulsion explosive. Raw and derivative data is denoted as black and blue, respectively, and images of the collected post blast fragments (above data - black scale bar: 5 cm) and sample mixtures (insets) are shown.

Table 1. Mass of ammonium nitrate (AN) or potassium chlorate (PC) from homemade fuel-oxidizer mixtures. Standard uncertainty due to variability in system response.

|  |  |  |  |
| --- | --- | --- | --- |
| AN Mixture | AN(μg) | PC Mixture | PC(μg) |
| Icing sugar | 2.9 ± 0.2 | Icing sugar | 3.8 ± 0.2 |
| Aluminum | 2.8 ± 0.2 | Flour | 4.1 ± 0.2 |
| Petroleum jelly | 3.9 ± 0.2 | Petroleum jelly | 3.7 ± 0.2 |
| Fuel oil | 3.3 ± 0.2 | Kerosene | 4.5 ± 0.2 |