

GRADIENT ELUTION MOVING BOUNDARY ELECTROPHORESIS OF HOMEMADE FUEL-OXIDIZER EXPLOSIVES

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ABSTRACT

The analysis of complex samples without extensive preparation steps (*e.g.*, filtration or centrifugation) is a persistent challenge for applications ranging from forensic identification to high-throughput security screening. Here, a capillary-based microfluidic electrophoresis platform incorporating a hydrodynamic counterflow and capacitively coupled contactless conductivity detection is employed for the detection of inorganic components from propellants, pyrotechnics, and homemade fuel-oxidizer explosives. The bulk counterflow prohibits capillary clogging by particulate or fiber debris, as well as system fouling from fuels, *e.g.*, petroleum jelly or kerosene.

KEYWORDS: Capillary Electrophoresis, Gradient Elution Moving Boundary Electrophoresis, Capacitively Coupled Contactless Conductivity Detection, Propellants, Pyrotechnics, Fuel-Oxidizer Mixtures, Explosives

INTRODUCTION

Capillary electrophoresis (CE) is a selective analytical technique that has found extensive use for separations in biological applications [1]. As CE-based techniques have evolved, these systems have also found utility in applications ranging from separation of narcotic samples to analysis of post-blast debris. An array of configurations, modalities, and platforms have sought to take advantage of the benefits afforded by microfluidics, *e.g.*, automation, reduced sample sizes, multiplexing capabilities, and high-throughput analysis. One such method, gradient elution moving boundary electrophoresis (GEMBE), is a simple technique consisting of a relatively short capillary (5 cm) connecting two reservoirs and the application of an electric field (Figure 1(a)) [2]. Microfluidic electrophoresis platforms employing GEMBE separation modality have demonstrated the analysis of analytes ranging from amino acids to inorganics to opioids [2-4].

EXPERIMENTAL

GEMBE separation is achieved by gradually reducing a pressure-driven hydrodynamic counterflow (Figure 1(a)). As the hydrodynamic counterflow decreases, each analyte sequentially enters the capillary under electrophoretic transport. Each analyte is detected by coupled contactless conductivity detection (C⁴D) as a moving boundary or step in conductivity (Figure 1(b)).

A 100 mmol/L acetic acid, 10 mmol/L L-histidine, pH 3.69 buffer and 200 μ mol/L calcium chloride internal standard were used for separation under a -600 V/cm (-3000 V voltage) electric field. Following an elevated applied pressure (+30 kPa), the pressure was reduced at -100 Pa/s until all analytes were detected.

RESULTS AND DISCUSSION

The capabilities enabled by GEMBE provide unique utility for the direct analysis of inorganic components from homemade and improvised explosives and post-blast debris. GEMBE has the potential to separate and detect common inorganic oxidizers,

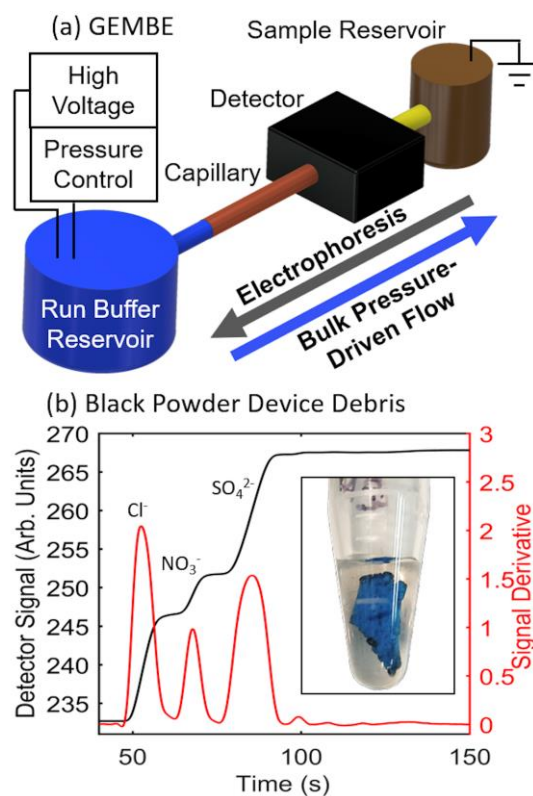


Figure 1: (a) Schematic representation of GEMBE separation. (b) GEMBE analysis of post-blast debris collected from a black powder charge thermoplastic polymer device. Raw signal showing step-wise increases in conductivity (black trace) and raw signal derivative demonstrating traditional peaks (red trace) from signal piece of debris (inset).

including nitrate, chlorate, and perchlorate from low explosives without the need for extensive sample preparation or filtration. Figure 1(b) demonstrates the direct analysis of post-blast debris from the controlled heated wire detonation of a black powder ($\text{KNO}_3/\text{S}/\text{C}$) charge thermoplastic pipe-based improvised explosives device. Individual millimeter sized fragments of the device were analyzed without sample preparation, filtering, or centrifugation to eliminate particulate or other contaminants.

GEMBE separation of pre-blast black powders and black powder substitutes revealed detection of the main nitrate and perchlorate oxidizers without interference from an array of additional organic and inorganic fuels common to these propellants (e.g., sulfur, dicyandiamide, nitro-benzoic acid, or sodium benzoate). Screening of tertiary explosives based on ammonium nitrate or potassium chlorate oxidizers with fuels including aluminum, icing sugar, petroleum jelly, fuel oil, and kerosene was also investigated. The GEMBE configuration excluded these fuels from fouling the capillary, enabled semi-quantitative analysis, and detection down to under $10 \mu\text{mol/L}$.

CONCLUSION

GEMBE has the potential for quantitative forensic analysis and high throughput screening applications targeting the inorganic components of homemade explosives and post-blast debris. The nature of the GEMBE counterflow excludes particles, fibers, and detrimental components of samples from entering the capillary. This significantly reduces sample preparation (e.g., filtration or centrifugation) and capillary fouling. In addition, unlike traditional electrophoretic separations, GEMBE does not require a defined injection. This simplification allows for multiplexed devices, scaling up throughput. Furthermore, separation resolution is simply controlled through the rate of pressure reduction and applied voltage.

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Certain commercial equipment, instruments, or materials are identified 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.

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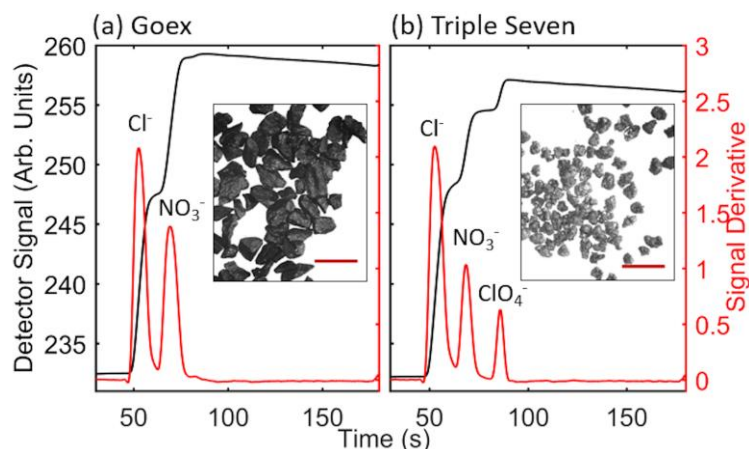


Figure 2: GEMBE separation of (a) Goex black powder and (b) Triple Seven black powder substitute samples containing nitrate and perchlorate. Raw data in black showing stepwise increases in conductivity and derivative representation of the raw data with identified peaks shown in red (internal standard: chloride). Bright field microscopy inset images of each with scale bar: 2 mm.