A71 Separation and Identification of Anions Using A Porous Graphitic Carbon Column and Electrospray Ionization Mass Spectrometry: Application to Inorganic Explosives and Their Post-Blast Residues

Joshua N. Cummins, BS, Indiana University Purdue University Indianapolis, 402 North Blackford Street, LD 326, Indianapolis, IN 46202; Jason Hull, BS, Indiana University Purdue University Indianapolis, 402 North Blackford Street, Indianapolis, IN 46202; and John V. Goodpaster, PhD, Indiana University Purdue University Indianapolis, Forensic and Investigative Sciences Program, 402 North Blackford Street, LD 326, Indianapolis, IN 46202*

After attending this presentation, attendees will learn the benefits of utilizing a Porous Graphitic Carbon (PGC) HPLC column coupled with Electrospray Ionization Mass Spectrometry to analyze inorganic low explosives.

This presentation will impact the forensic science community by introducing an efficient method for detection of inorganic low explosive constituent anions using readily available instrumentation.

Identification of the anions in inorganic explosives and their post- blast residues using ion chromatography (IC) and/or capillary electrophoresis (CE) is well established. However, IC and CE instrumentation are not as common in forensic science laboratories. Furthermore, coupling IC and CE to a mass spectrometer can be challenging as volatile buffers are required or ion suppressors must be used. Porous Graphitic Carbon (PGC) stationary phases are a relatively recent column type that is available for High Performance Liquid Chromatography (HPLC). This stationary phase is known for its high retention of polar species and separation of anions using PGC has been demonstrated.

In this presentation, the application of a PGC column (100 x 2.1 mm, 5 µm particles, 250 Å pores) to the separation of anions in low explosives will be discussed. The chromatographic method used a mobile phase of 0.5% formic acid in HPLC-grade water at 0.4 mL/min, a sample run time of 10 minutes, an injection volume of 1 µL, and a column temperature of 30˚ C. The mass spectrometer cone temperature and voltage were set to 550˚ C and 75 V respectively.

The inorganic low explosive propellants analyzed were milligram quantities of American Pioneer Powder, GOEX Black Powder, Triple Seven, and Pyrodex. All powders were dissolved in 2 mL of HPLC grade

water until completely dissolved. Burnt residues of the same powders were then analyzed by rinsing the residue several times with 2 mL of HPLC water from the watch glasses on which they were burned. A used piece of fire clay from a pyrotechnic device was also analyzed by rinsing with 5 mL of HPLC water. The samples were then filtered into 2 mL LC vials using a nylon syringe filter with a 0.2 µm pore size. All samples were then analyzed at full concentration.

An HPLC water blank was run between each sample and selective ion monitoring was utilized to detect both isotopic forms of chloride $^{35}Cl^-$ and $^{37}Cl^-$ (m/z = 35 and 37 respectively); nitrate NO^- (m/z = 62); both

linear dynamic range for the quantification of ammonium nitrate. Method validation will require the preparation of an ammonium nitrate solution gravimetrically and quantifying the solution by UV/VIS. The goal was to obtain measurement agreement between the two techniques of ≤ 5 % relative standard uncertainty. In addition, the use of inkjet printing systems for precision deposition of known quantities of the ammonium nitrate on a variety of surfaces will be evaluated.

Prior to analysis, the spectrophotometer was calibrated using standards in both the UV and Vis range to ensure wavelength accuracy. Preliminary results showed that UV/VIS spectroscopy can be used to

isotopic forms of chlorate $^{35}ClO^-$

and $^{37}ClO^-$ -(m/z = 83 and 85 2-detect and quantify ammonium nitrate from 275-196 nanometer (nm). respectively); dichlorodiamide (DCDA) (m/z = 83); sulfate SO_4 (m/z = Maximum absorbance was measured at a wavelength of 201 ± 3 nm. 97); and both isotopic forms of perchlorate $^{35}ClO^-$ and and 101 respectively). $^{37}ClO^-$ (m/z = 99 Stability studies indicate that a sample remains stable for a period of at least nine days and that instrument drift is negligible (0.042% relative

The major ions present in the propellants analyzed were consistent with their formulation. The results for black powder revealed the presence of nitrate. The results for American Pioneer Powder revealed the presence of nitrate and perchlorate. Analysis of Pyrodex and Triple Seven powders revealed the presence of nitrate, DCDA, and perchlorate. The water extract from the fire clay contained chloride, nitrate, sulfate, and perchlorate.

Inorganic Explosives, Porous Graphitic Carbon, HPLC

 ** Presenting Author*