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On the use of capillary electrophoresis for the determination of inorganic anions and cations, and carbohydrates in residues collected after a simulated suicide bombing attack

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ABSTRACT

In order to train scientist field investigators after terrorist attacks, the laboratory of the Prefecture de Police of Paris simulated a suicide bombing attack in a bus. After collection of the residues, analyses were carried out to determine the composition of the original explosive charge. This article focuses on the combined use, for the first time, of three new capillary electrophoresis methods for the determination of inorganic anions and cations, and carbohydrates in two representative extracts. Capillary electrophoresis appears as an effective tool to identify and quantify the compounds in real extracts and is fully complementary to chromatographic methods.

1. Introduction

Suicide bombing attacks in public transports (bus, train, subway, etc.) or in public areas are one of the main terrorist threats against western countries. In order to anticipate this kind of event, the Central Laboratory of the Prefecture de Police of Paris organized, in 2010, a practical exercise simulating a suicide bombing attack in a bus. This simulation, carried out in a military field, aimed at training scientist field investigators to better visualize a blast scene and to carry out first investigations and residue samplings more efficiently. The collected samples were next analyzed in laboratory, in order to determine the explosive charge composition.

For the forensic confirmation of the presence or the absence of some compounds in samples, two analytical methods, with orthogonal mechanisms, were required. Thus organic compounds were analyzed by HPLC/MS [1,2], thin layer chromatography (TLC) [3], and GC/MS [4,5]. Inorganic traces were analyzed by ion chromatography (IC) [6,7] and capillary electrophoresis (CE) [8]. New CE methods were recently developed by our group for the analyses of inorganic anions [9], cations [10], and a special formulation of both [11] in order to confirm IC results. A new CE method dedicated to carbohydrate analyses was also recently optimized [12–14]. It replaced the TLC method, and currently represents the new powerful analytical method for carbohydrate analyses in the Central Laboratory of the Prefecture de Police. Three of these new methods were involved all together for the first time for the study of residues collected after simulating a suicide bombing attack.

2. Materials and methods

2.1. Real sample preparation

In order to be as close as possible to a suicide bombing attack in a bus, a scene representing real life was created around a bus with the presence of stalls, pedestrians, and cyclists. Inside the bus, three killed butchery animals played the role of suicide bomber and passengers. The explosive charge, mainly composed of ammonium nitrate and icing sugar, was next activated. Important

Abbreviations: BGE, background electrolyte; 18-C-6, 18-crown-6-ether; DAD, diode array detector; IC, ion chromatography; CE, capillary electrophoresis; EOF, electroosmotic flow; HDMB, hexadimethrine bromide; LOD, limit of detection; PVS, polyvinylsulfonic acid sodium salt; SMIL, successive multiple ionic-polymer layers; TLC, thin layer chromatography; Tris, tris(hydroxymethyl)aminomethane

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damages were observed and investigations and sampling were next carried out.

The sampling method consisted of wiping water-moistened cotton swabs over residues. These cottons were beforehand purified by assisted solvent extraction using an ASE 200 instrument (Dionex, Voisins-le-Bretonneux, France), with one cycle of 5 min at 100 °C and 100 bar with water, and next with acetone. After sampling, they were next extracted in hot water in a sonication bath for 10 min. The obtained solutions were filtered through a 150 μm cellulose filter (Les Filtres Durieux, Marne-La-Vallée, France) and a 0.45 μm nylon syringe filter (Teknokroma, A.I.T. France, Houilles, France) just before analysis. In this report, the analysis of two representative extracts, collected directly in two different places inside the bus, named Extract ♯1 and Extract ♯2, are presented. Blank cotton swab extracts were regularly analyzed in lab and no analytes were detected [9,10].

2.2. Standards

Individual anionic standard solutions were prepared weekly by volumic dilution of sodium salts (Sigma-Aldrich, Saint-Quentin-Fallavier, France) in ultra-pure water delivered by a Direct-Q3 UV system (Millipore, Molsheim, France). A standard mixture of the 11 anions (chloride, nitrite, nitrate, thiosulfate, perchlorate, chlorate, thiocyanate, sulfate, carbonate, phosphate, and formate) was prepared daily (20 mg L^{-1} each in ultra-pure water).

All cationic standard samples were purchased from VWR (Fontenay-sous-Bois, France). Individual cation solutions in 3% HNO_3 were prepared weekly by volumetric dissolution in ultra-pure water. A standard mixture of the cations of interest (ammonium, potassium, monomethylammonium, calcium, sodium, magnesium, strontium, barium, and lithium) was prepared daily (15 mg L^{-1} each in ultra-pure water).

All carbohydrates used as standard samples (fructose, glucose, lactose, and sucrose) were purchased from VWR and naphthalenesulfonic acid used as internal standard was purchased from Sigma-Aldrich.

2.3. Electrolytes

All reagents used were of analytical reagent grade. The background electrolyte (BGE) for anion separations consisted of a mixture of chromium (VI) oxide (Fluka, Lyon, France), sodium chromate (Fluka), and tris(hydroxymethyl)aminomethane (Tris) (Sigma-Aldrich), and ethanol (VWR). For the cationic analysis, guanidine acetate used as chromophore was obtained from Sigma-Aldrich. Other components of the BGE were 18-crown-6-ether (18-C-6) (Sigma-Aldrich) and acetic acid (VWR). Finally, the BGE for the analysis of carbohydrates was composed of NaOH (Carlo Erba, Val-de-Reuil, France) and NaCl (Sigma-Aldrich). The reagents for electroosmotic flow (EOF) reversal and double layer coating of the capillary wall, hexadimethrine bromide (HDMB) and polyvinylsulfonic acid sodium salt (PVS), were purchased from Sigma-Aldrich.

2.4. Apparatus

CE analyses were carried out with a Beckman Coulter P/ACE MDQ system (Villepinte, France) equipped with a fixed wavelength UV detector (mercury lamp) at 254 nm for anion analyses, or with a diode array detector (DAD) set at 190 ± 4 nm (analysis wavelength) and 300 ± 40 nm (reference wavelength) for cation analyses, and 270 ± 10 nm (analysis wavelength) and 350 ± 40 nm (reference wavelength) for carbohydrate analyses. Instrument control and data acquisition were performed using the 32 Karat® software. A Dionex ICS-2000 (Voisins-Le-Bretonneux, France) ion chromatograph equipped with a suppressed conductivity detector (Dionex ASRS suppression and conductivity cell) was used for chromatographic anion analyses and a Dionex DX120 ion chromatograph equipped with a suppressed conductivity detector (Dionex CSRS-4 mm suppression and conductivity cell) was used for cation analyses. Instrument control and data acquisition were performed using the Chromeleon 6.8® software. A 25 μL loop was employed for the cation and anion injections.

2.5. Electrophoretic procedures

The three CE methods were previously developed, validated, and described (anions [9], cations [10], and carbohydrates [12–14]). Electrophoretic separations were performed using bare fused-silica capillaries purchased from Polymicro (Photonlines, Marly-Le-Roi, France). A detection window was created at 10 cm from the detection end. Before first use, capillaries were conditioned by successive percolations with 1 M NaOH for 3 min, 0.1 M NaOH for 3 min, and ultra-pure water for 3 min, each under 40 psi.

2.5.1. Anions

Electrophoretic separations were performed using 50 μm I.D. × 87 cm capillaries. After every 10 analysis, capillaries were rinsed with HDMB solution (2.5 g L^{-1} in ultra-pure water) under 40 psi for 3 min in order to keep EOF constant. Between each run, they were rinsed with the BGE, containing 25 mM CrO_3, 25 mM Na_2CrO_4, 100 mM Tris, and 6% (v/v) ethanol in ultra-pure water (aqueous pH 8.2), under 50 psi for 3 min. Injections were performed electrokinetically under −2 kV for 50 s. Separations were run at 15 °C under −30 kV.

2.5.2. Cations

Electrophoretic separations were performed using 75 μm I.D. × 80 cm capillaries. Capillaries were conditioned by successive flushes with HDMB solution (10 g L^{-1} in ultra-pure water), PVS solution (0.01% (w/w) in ultra-pure water), and finally BGE containing 15 mM guanidine acetate adjusted at pH 4.0 with acetic acid, and 3 mM 18-C-6 in ultra-pure water, each under 40 psi for 3 min (12 capillary volumes), except for PVS flushes which were under 20 psi for 5 min (10 capillary volumes) in order to have a better coating. Between each run, PVS layer was renewed, and followed by the percolation of BGE. Injections were performed hydrodynamically under 0.8 psi for 4 s (0.6% of the capillary volume). Separations were run at 20 °C under 30 kV.

2.5.3. Carbohydrates

Electrophoretic separations were performed using 50 μm I.D. × 60 cm capillaries. Capillaries were conditioned by successive flushes with HDMB solution (1 g L^{-1}) and BGE, containing 98 mM NaOH and 120 mM NaCl (pH 12.9) prepared in ultra-pure water, each under 40 psi for 3 min (12 capillary volumes). Between each run, HDMB layer was refreshed. Injections were performed hydrodynamically under 50 mbar for 5 s (0.75% of the capillary volume). Separations were run at 26.5 °C under −14 kV. BGE was changed between each run.

2.6. Chromatographic procedures

Procedures described in this part were previously optimized in the laboratory and conducted routinely (accreditation ISO/IEC 17025).

2.6.1. Anions

Chromatographic anion separations were performed at 30 °C with a Dionex AS19 column (250 × 4 mm) equipped with a