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Concurrent determination of anions and cations in consumer fireworks with a portable dual-capillary electrophoresis system

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ABSTRACT

A new automated portable dual-channel capillary electrophoresis instrument was built and applied to the concurrent determination of cations and anions. The system uses a single buffer and hydrodynamic injection of the sample is performed autonomously. A novel engraved flow-cell interface is used at the injection ends of the capillaries allowing the autonomous operation of the system. The engraved flow-cell replaces traditionally used split injectors in purpose made capillary electrophoresis systems and makes the system design easier. A new software package with graphical user interface was employed to control the system, making its operation simple and increasing its versatility. The electrophoretic method was optimized to allow the baseline separation of 12 cations and anions commonly found in fireworks. The system was proven to be useful for the analysis of consumer fireworks, saving time and expenses compared to separate analyses for anions and cations. This is the first time that cationic and anionic compositions of fireworks are investigated together. The analysis of samples revealed several inaccuracies between the declared compositions for the fireworks and the obtained results, which could be attributed to cross-contamination during their manufacture or to a transfer between other components of the pyrotechnic item. The presence of certain unexpected peaks, however, had no apparent reason and might represent an irregularity in the manufacture of some devices.

1. Introduction

Professional and consumer fireworks are two groups of pyrotechnic devices of high interest due to their wide use and required quality control [1]. They are defined as explosive materials and therefore come under the general explosive regulations regarding importation, manufacture, sale, storage and transport [2]. This normative try to guarantee a high level of protection to users, the general public and the environment [3]. Fireworks are subjected to quality controls in order to adjust to these normative, trying to avoid accidents caused by malfunctions and to inhibit illegal and dangerous mixtures of reagents. Quality assurance procedures include examination, determination of chemical content and performance testings. For example, it is possible to know the pyrotechnic charge of fireworks by studying their composition using several analytical techniques. These tools have been gathered in a recent review article [1]. Among potentially portable techniques, spectroscopy techniques such as Raman and Fourier-transform infrared (FTIR) have been proposed to detect the molecular composition of this type of pyrotechnic devices, although conventional non-portable apparatus were used. The use of portable spectroscopy techniques also shows advantages in terms of sample preservation, since they are non-destructive techniques. Another suitable technique for the *in-situ* analysis of fireworks is capillary electrophoresis (CE), since it allows the determination of cationic and anionic compositions in a given sample with the same instrument. A recent paper has focused on the determination of anions in consumer fireworks by CE with photometric detection in which certain inaccuracies were found between the declared compositions and the determined anions [4].

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The electrophoretic determination of both cationic and anionic compositions in samples can be tedious since usually separate analyses have to be performed for cations and anions. This is also cost and time consuming. On the other hand, the concurrent determination of cations and anions in CE saves both time and expenses of separated analyses. Over the last three decades, several and very different strategies for the concurrent electrophoretic separation of both classes of species have been proposed. They have recently been reviewed showing their advantages and disadvantages, and pointing out the system requirements for each of them [5]. Some methods force analytes to move against their electrophoretic mobility towards the detector. These methods involve the modification of the sample or BGE with complexing agents to form anionic complexes with metal cations [6,7], the use of micelles in electrokinetic chromatography [8], the modification of the electroosmotic flow (EOF) magnitude [9–13] or the use of assisting pressure during the electrophoretic separation [14–16]. Other methods that are based on (physical) manipulation of sample plugs are dual opposite-end injection [17–22] and "dual single-end injection" [15], in which sample plugs are placed into both ends of the capillary and the detector is located somewhere near the middle of the capillary. A similar approach, referred to as "single injection with positioning of the sample plug" uses a single sample plug, which is pumped and positioned around the middle of the capillary between two detectors [15,23].

A completely different approach is *dual-channel CE*. Dual CE uses two different and independent capillaries, which are grounded at one end while the opposite ends are connected to the positive and the negative high voltage (HV) supplies, respectively. Therefore, each capillary is devoted for the separation of only one type of ions. Two detectors are also needed, one for anions and the other for cations, but if contactless conductivity detection is employed this is not a significant extra expense. Similarly, the additional HV power supply does not add significantly to the cost and this is outweighed by the significant advantages of the approach compared to the methods mentioned above. These are chiefly the possibility of independent optimization of the separation and analysis time, as well as freedom from peak overlaps between cations and anions.

The easiest way for injecting the sample in dual-channel CE is to perform an electrokinetic injection [24]. However, it is well known that electrokinetic injection suffers of sampling bias due to the different mobilities of different ions in the sample. Hydrodynamic injection, however, does not suffer of sampling bias. Sample injection by elevating the injection end of the capillary (syphoning) have also been performed in dual-channel CE [22,25], although manual operation of the injection usually deteriorates reproducibility. Recently, a semi-automated dual-channel CE with two capacitively coupled contactless conductivity detector (C^4D) was developed for the determination of NH_4^+, NO_3^- and NO_2^- in water samples [26]. The sample injection was done automatically using a split injector, avoiding reproducibility errors produced by manual operation. These dual-channel CE systems were bench-top instruments with only limited capability for mobile deployment and on-site applications. Microchips have also been adapted to dual-channel separations. The separation of peptides and proteins, which were injected electrokinetically, has been conducted by dividing the differently charged analytes when they passed an intersection, migrating according to their electrophoretic mobility and being extracted into opposite channels [27]. More recently, a novel microchip was used for the determination of inorganic anions and cations using hydrodynamic injection [28].

In this work, we present a new automated portable dual-channel CE. The system uses two capillaries with two C^4D detectors for the concurrent determination of anions and cations using a single BGE. Hydrodynamic injection is performed automatically in a new flow-cell engraved in a plexiglass plate. The system was applied to the concurrent determination of typical cations and anions in consumer fireworks, optimizing a method for their separation with a single BGE. The use of a portable system for the analysis of consumer fireworks is of utility when quality control analyses wants to be performed directly at the manufacturing place and factories, in borders or harbours, and by distributors or importers.

2. Materials and methods

2.1. Reagents and samples

All chemicals were of analytical grade. Sodium hydroxide, L-Histidine (His), 2-(N-morpholino)ethanesulfonic acid (MES), acetic acid 99.7%, 18-Crown-6, potassium perchlorate and sodium chlorate were from Sigma–Aldrich (St. Louis, MO, USA). Magnesium sulfate heptahydrate, barium nitrate, calcium chloride and copper sulfate pentahydrate were from Panreac (Barcelona, Spain). Ammonium chloride and strontium nitrate were purchased from VWR (Darmstadt, Germany). Ultrapure water, purified using a Milli-Q system from Millipore (Bedford, MA, USA), was used for the preparation of all solutions. Consumer fireworks (a complex firecracker, a smoke bomb, a single-charge firecracker and a rocket) were purchased in a local store in Alcalá de Henares (Madrid, Spain).

2.2. Instrumentation

The portable dual-CE system was controlled with an Arduino microcontroller using the Instrumentino software package [29]. Pneumatic pressurization was achieved from a small metal cylinder which is filled with a manual pump (normally used to pressurize shock absorbers of bicycles). The outlet pressure of the cylinder was adjusted to 1 bar with a regulator. This way, polyethylene tubes containing the BGE and the sample were pressurized. The caps of this tubes were modified in order to hold two fittings for tubings, one for the incoming pressure and the other one for the outgoing BGE or sample. The fluidic part is based on a novel flow-cell interface with engraved channel design machined from two polymethylmethacrylate (PMMA) plates (10 cm (w) × 15 cm (l) × 1.5 cm (h)), on which solenoid valves with 30 psi holding pressure purchased from the Lee company (LFVA0030000C-LFVA1230113H and LFRA0030000C-LFRA1230110H, Westbrook, CT, USA) and a miniaturized peristaltic pump (RP-Q1-SP45A, Takasago Fluidic Systems, Westborough, MA, USA) were positioned. The channels were 2 mm wide and 1 mm deep and were machined only in one of the two plates, having a semicircular cross-section. The grounded electrode was separated 15 mm from each capillary inlet being the volume of BGE enclosed around 47 μL, a larger volume than that used in our previous split injector interfaces [30–32]. All fluidic connections were made with 0.02 in. I.D. and 1/16 in. O.D. Teflon tubing and with polyether ether ketone flangeless nuts and ¼-28 ferrules purchased from Upchurch Scientific (Oak Harbor, WA, USA). The HV units were two UM20*4 modules (Spellman, Pulborough, UK), with dimensions of 120 mm (w) × 38 mm (d) × 25 mm (h), an input voltage of 12 V, a maximum output current of 200 μA and a weight of 200 g each. They provide a maximum of 20 kV at positive or negative polarities. Two vials with buffer were positioned on the high voltage sides where the end of the capillaries and the HV electrodes were also placed. The head stage of a commercial detector (eDAQ, Denistone East, NSW, Australia) was used for the determination of cations. The excitation frequency was set to 1200 kHz and the amplitude to 100%. A purpose made detector was built and used for the detection of anions. The resulting signals were recorded with an ER225 C^4D Data System modified to be powered with 12 VDC (eDAQ, Denistone East, NSW, Australia). Although the ER225 C^4D data system has two channels, channel 1 can only be used with