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On-line simultaneous and rapid separation of anions and cations from a single sample using dual-capillary sequential injection-capillary electrophoresis

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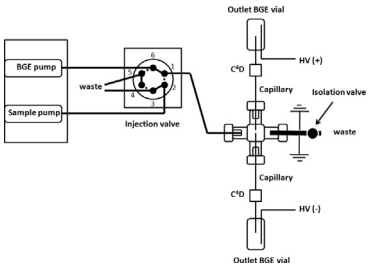
HIGHLIGHTS

- Dual capillary sequential injection-capillary electrophoresis instrumentation.
- Separation of 23 inorganic and organic anions was achieved within 3 min.
- Fully automated analysis of water over a 50 h.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel capillary electrophoresis (CE) approach has been developed for the simultaneous rapid separation and identification of common environmental inorganic anions and cations from a single sample injection. The method utilised a sequential injection-capillary electrophoresis instrument (SI-CE) with capacitively-coupled contactless conductivity detection (C^4D) constructed in-house from commercial-off-the-shelf components. Oppositely charged analytes from a single sample plug were simultaneously injected electrokinetically onto two separate capillaries for independent separation and detection. Injection was automated and may occur from a syringe or be directly coupled to an external source in a continuous manner. Software control enabled high sample throughput (17 runs per hour for the target analyte set) and the inclusion of an isolation valve allowed the separation capillaries to be flushed, increasing throughput by removing slow migrating species as well as improving repeatability. Various environmental and industrial samples (subjected only to filtering) were analysed in the laboratory with a 3 min analysis time which allowed the separation of 23 inorganic and small organic anions and cations. Finally, the system was applied to an extended automated analysis of Hobart Southern Water tap water for a period of 48 h. The overall repeatability of the migration times of a 14 analyte standard sample was less than 0.74% under laboratory conditions. LODs ranged from 5 to 61 $\mu g\,L^{-1}$. The combination of automation, high confidence of peak identification, and low limits of detection make this a useful system for the simultaneous identification of a range of common inorganic anions and cations for discrete or continuous monitoring applications.

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1. Introduction

The benefit of simultaneous analysis of anions and cations is clear; it negates the requirement for two separate analyses, thus reducing sample consumption and decreasing the time required. Technically however, this can be difficult to achieve. It can be done by ion chromatography, through for example, the use of a zwitterionic functionalised surface, called electrostatic ion chromatograph or coupling two columns directly [1–4]. The only other viable chromatographic approach is the use of two separate instruments coupled together in some way. In most instances, separations of less than 10 anions and cations are achieved with separation times from 10 to 30 min.

An alternative approach is to use capillary electrophoresis (CE). In conventional CE, simultaneous analysis of anions and cations is difficult because one of the charged species must migrate against the electroosmotic flow (EOF). It is possible to separate both anions and cations but only when the EOF is greater than the electrophoretic mobility of all of the target analytes having opposite polarity to the separation electrode [5], and the closer in magnitude of the EOF with the analyte of highest mobility, the longer is the total analysis time. The practical drawback of this approach is that it is not suitable for the separation of the complete range of inorganic ions. With a cathodic EOF, this approach can separate the full range of cations, but is only suitable for low mobility anions. With an anodic EOF the reverse is true in that the full range of anions can be separated but only the low mobility cations. The peak capacity of the ions separated in a co-EOF manner is also compromised due to the speed at which they reach the detector.

A clever method designed to overcome this problem was demonstrated in 1998 by Kuban and Karlberg [6] and Padarauskas et al. [7]. This approach, termed "Dual-Opposite end Injection" (DOI-CE), relies upon the injection of positively and negatively charged species from opposite ends of the capillary. This injection may occur simultaneously (electrokinetic injection) or sequentially (electrokinetic or hydrodynamic injection). During electrophoretic analysis which occurs under conditions of reduced EOF, analytes migrate from each end of the capillary, and in opposite directions towards the detector located near the centre of the capillary. A number of papers [8–10] have been published on the successful application of this technique in conjunction with UV or C^4D detection for the simultaneous determination of small anions and cations. Whilst simple, the compromise with this approach is that the separation space is reduced so there must be precise control of the timing to ensure that anions and cations do not reach the detector at the same time.

Haumann et al. compared both of the above approaches for the simultaneous determination of anionic and cationic species [11]. Initially, a high pH was used to maximise the EOF in an uncoated fused-silica capillary; however, this resulted in the formation of alkaline earth metal hydroxides. This was overcome by separating at pH 6.0, but in order to separate all the anions, the addition of a hydrodynamic pressure was required, which resulted in an increase in zone broadening, especially for high mobility anions, and a loss in resolution of cationic species. A third method studied was a DOI-CE approach using hydrodynamic injection and this was found to be superior to the other methods. During the course of this work, Mai and Hauser examined the use hydrodynamic injection in narrower diameter (10 μm i.d.) capillaries with the result that Taylor dispersion was minimal due to the narrow capillary diameter [12]. They also introduced additional approaches in which the sample was injected and hydrodynamically positioned in the centre of the capillary before application of the voltage and with anions and cations detected at opposite ends of the capillary.

An alternative approach for simultaneous CE separation of anions and cations involves the use of an anionic complexing agent that is also the anionic indirect detection probe [13–15]. Metal ions are converted to their chelated forms with EDTA [13] or 2,6-pyridinedicarboxylate [14,15] and separated from other anionic components under conventional anion separation conditions. Whilst this simplifies the experimental set-up, it is only applicable to metals that can form a strong, anionic complex and is not suitable for alkali and alkaline earth metals.

An entirely different approach was introduced by Bächmann et al. based on a single pressure injection to introduce the sample onto two different capillaries, using the same background electrolyte (BGE) in both capillaries, with detection performed using two fluorescence detectors operated in the indirect mode [12]. Recently, in a very similar method, Reschke et al. [16] demonstrated the simultaneous separation of cations and anions on a microfluidic device with suppressed EOF and a single injection point. In this method, a single pressure-driven sample injection stream was simultaneously siphoned in two directions into separate microchannels for electrophoretic separation. Hydrodynamic restrictors at the entrance to the electrophoretic separation channels allowed the achievement of high separation efficiencies. The methods of Bächmann et al. and Reschke et al. have similarities to the technique presented in the present study. However in our approach, hydrodynamic suppression is achieved solely through the optimisation of channel geometry and flow-rates and is constructed from simple commercially available components, while injection is achieved by simultaneously applying equal and opposite potential differences at the outlet end of each capillary and grounding at the approximate centre of the separation interface. Our method also does not require splitting the sample as was required to generate the hydrodynamic flow in the device proposed by Reschke et al. [16].

The broad aims of this study were threefold. The first was to demonstrate the simultaneous injection concept for later transfer to a microchip application. The second was to assess how the system behaviour deviated from that expected from independent analyses of the anions and cations. Finally, we wished to develop the concept and associated injection system into a simple, robust and repeatable method of detection for real-world samples, which will be subsequently developed for the rapid separation of inorganic explosive tracer ions.

2. Experimental

2.1. Apparatus

A SI-CE system was developed in-house, based upon a modified design of the instrument designed for the rapid separation of inorganic explosive anions by Blanco et al. [17]. A schematic representation of the bench-top system is depicted in Fig. 1(a). A double syringe pump (Harvard Apparatus, Model 33, Holliston, MA, USA) was used to deliver sample and BGE to the system. Two 20 mL plastic syringes (Livingstone, Holliston, MA, USA) or glass syringes (Hamilton, Reno, NV, USA) were used. A two-position injector valve (MXP-7980, Rheodyne, Oak Harbour, WA, USA) enabled the alternate delivery of sample or BGE to the separation interface. A PEEK cross-piece connection (P-729, Upchurch Scientific, Oak Harbour, WA, USA) of 500 μm i.d. was used to interface the two capillaries to the flow system. A 20 mm stainless steel tube cut from a syringe needle (0.51 mm i.d.) served as a waste outlet and ground electrode. An isolation valve (HP225K021, NResearch, West Caldwell, NJ, USA) mounted on the cross-piece outlet line allowed for the on-line flushing of capillaries for equilibration and cleaning.

Two separate fused-silica capillaries of 50 μm i.d. (Polymicro, Phoenix, AR, USA) were utilised for the anion and cation separations. The distance between the two capillary tips within the