Trends in Analytical Chemistry 62 (2014) 162–172

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Simultaneous separation of cations and anions in capillary electrophoresis

Jorge Sáiz [a,b], Israel Joel Koenka [c], Thanh Duc Mai [c,d], Peter C. Hauser [c,*], Carmen García-Ruiz [a,b]

[a] Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, University of Alcalá, Ctra. Madrid-Barcelona Km 33.6, 28871 Alcalá de Henares (Madrid), Spain
[b] University Institute of Research in Police Sciences (IUICP), University of Alcalá, Ctra. Madrid-Barcelona Km 33.6, 28871 Alcalá de Henares (Madrid), Spain
[c] Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland
[d] Centre for Environmental Technology and Sustainable Development (CETASD), Hanoi University of Science, Nguyen Trai Street 334, Hanoi, Viet Nam

ARTICLE INFO

Keywords:
Anion
Capillary electrophoresis (CE)
Cation
Complexing agent
Concurrent separation
Dual capillary
Dual opposite-end injection (DOEI)
Micelle
Simultaneous determination
Simultaneous separation

ABSTRACT

With capillary electrophoresis, it is desirable to have simultaneous determination of cations and anions, which avoids costs and time spent on separate analyses, so concurrent approaches to separation gained popularity in recent years. We review the different strategies employed for the simultaneous separation and determination of cations and anions, including the use of complexing agents, micelles, two injectors, dual detectors, or two capillaries. We give an overview of the methods reported to date, and their benefits and drawbacks, and we evaluate the instrumental requirements of the different approaches.

Contents

1. Introduction

Capillary electrophoresis (CE) is an electrokinetic analytical technique for the separation of ionic species by their relative electrophoretic mobilities. The capillaries, with sub-millimeter inner diameter and a length of typically 50 cm, are filled with a background electrolyte (BGE) and a high voltage (HV) of up to 30 kV

Abbreviations: BGE, Background electrolyte; C^4D, Capacitively coupled contactless conductivity detection; CDTA, 1,2-cyclohexanediaminetetraacetic acid; CE, Capillary electrophoresis; DOEI, Dual opposite-end injection; DTPA, Diethylenetriaminepentaacetic acid; EDTA, Ethylenediaminetetracetic acid; EOF, Electroosmotic flow; HV, High voltage; PDCA, 2,6-pyridinedicarboxylic acid.

* Corresponding author. Tel.: ++41 61 267 1003; fax: ++41 61 267 1013.
E-mail address: Peter.Hauser@unibas.ch (P. C. Hauser).

http://dx.doi.org/10.1016/j.trac.2014.07.015
0165-9936/

is applied. Samples are injected into one end of the capillary and a detector is normally placed at the other end. Usually, only cations or anions can be determined, depending on the polarity of the applied electric field. The capillaries commonly used in CE are made of fused silica, for which an electroosmotic flow (EOF) in the direction of the cathode occurs. The EOF will cause loss of cation resolution due to accelerated migration (co-EOF migration). In contrast, the EOF equally slows down all anions as they move towards the anode (counter-EOF migration) and anions with low mobility may be carried towards the cathode by the EOF.

If cations and anions have to be determined in the same sample, two separate analysis runs with changed polarity are usually required. If different separation buffers are needed for the two groups of ions, then the capillary also needs to be rinsed and re-conditioned when changing over.

Concurrent determination of cations and anions in CE is therefore a very desirable feature as it saves both time and the expense of separate analyses. For this reason, a considerable effort has been devoted by research groups over the past three decades to the development of such methods. A number of very different strategies have been proposed. Some methods involve modification of the sample or the BGE with additional reagents; others change the magnitude and the direction of the EOF. Certain strategies require modification of conventional commercial CE systems, while some require purpose-made instruments.

We survey the state-of-the-art of simultaneous separations of anions and cations in this review. We discuss the principles of operation, types of injection, specific options and the technology required for each method. We critically compare different approaches and note their advantages and disadvantages. Table 1 shows the advantages, the disadvantages and the system requirements for each of the methods compared in this review. Our aim is to provide a contemporary guide reviewing all the approaches used to date for the simultaneous separation of differently charged analytes.

2. Complexing agents

The employment of complexing agents for simultaneous separation of cations and anions is well known from ion chromatography. The procedure consists of a reaction between a metal cation and a ligand or complexing agent to form an anionic complex, which can be separated together with the native anions in the sample. The resulting complexes must be stable, soluble and have good detectability. Cation complexation is a relatively simple technique, which does not require special instrumentation. There are two approaches for this procedure: pre-capillary and on-capillary complexation.

2.1. Pre-capillary complexation

In pre-capillary complexation, the complexing agent is added to the sample before injection into the capillary. This process is usually time consuming and often requires heating of the sample, which is not always feasible. Moreover, the addition of a complexing agent in excess will result in an additional peak in the electropherogram, which might overlap with other peaks of interest.

The use of pre-capillary complexations of metal cations in CE was reported several times in the 1990s and several complexing agents have been used. Krokhin et al. [1] simultaneously determined the anionic 4-(2-pyridylazo)resorcinol chelates of Co(II), Ni(II) and Fe(II) alongside Br^-, Cl^-, I^-, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-, F^-, HPO_4^{2-}, HCO_3^- and acetate. Pozdniakova and Padarauskas [2] compared the use of 1,2-cyclohexanediaminetetraacetic acid (CDTA), ethylenediaminetetracetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) as complexing agents for the speciation of Cr(VI/III) and V(V/IV), in different water samples. Cr(VI) is normally present as the CrO_4^{2-} anion, and Cr(III) as the cationic Cr^{3+} ion. Complexation with DTPA allowed the determination of both species as anions, together with other anionic complexed metal cations and native inorganic anions. V(IV) in solution is present as the cationic vanadyl (VO^{2+}) ion and V(V) as an anionic vanadate ion. To enable concurrent determination, these were separated as the $VOEDTA^{2-}$ and VO_2EDTA^{3-} complexes. The simultaneous separation of Cr(III) and Cr(VI) alongside other metal cations and anions has also been achieved by treating the sample with CDTA [3,4]. EDTA has been used for the simultaneous determination of Ba^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, lactate, butyrate, salicylate, propionate, acetate, phosphate, formate and citrate [5].

2.2. On-capillary complexation

The addition of the complexing agent to the BGE is known as on-capillary complexation, since the complexation reaction occurs inside the capillary, while the compounds are being separated. Besides saving time compared to the pre-capillary approach, a further advantage is prevention of in-capillary dissociation of unstable transition-metal complexes.

EDTA has also been used for on-capillary complexation of several metal cations and their simultaneous determination with a variety of anions [6]. However currently, 2,6-pyridinedicarboxylic acid (PDCA) is the most popular complexing agent for creating anionic metal chelates. The main reason for this preference is that it also allows the indirect detection of anions having little or no UV absorbance alongside the direct detection of chelated cations. PDCA was first used by Soga and Ross [7] for the determination of Cu^{2+}, Ni^{2+} and Fe^{2+}, and several inorganic anions and organic acids. Recently, it was used by Wharton and Stokes [8] for the separation of Cu^{2+}, Ni^{2+} and Fe^{3+} in an NaCl solution, by Sarazin et al. [9] for aluminum and other metal cations and anions, and by Wang et al. [10] for the separation of phosphate and calcium in river water.

3. Micelles

Wei et al. [11] recently demonstrated the use of micelles for concurrent determination of basic and acidic drugs. The procedure consisted of an injection sequence, in which the acidic drugs were electrokinetically injected first, followed by a hydrodynamic plug of BGE and finally the electrokinetic injection of the basic drugs. The plug of BGE was necessary, probably because the anions were attracted to the inlet end during cationic injection because of the direction of their electrophoretic mobilities. The acidic drugs (in their anionic form in the sample matrix) turned to neutral after their introduction due to the low pH of 3.0 in the BGE. The separation was then carried out via micellar electrokinetic chromatography. The fast-moving anionic micellar phase carried both neutral and cationic analytes toward the detector in a reverse migration mode for cations. In this work, electrokinetic injection was used and the acidic analytes were determined in their neutral form. Although it has not been performed to date, it should also be possible to use hydrodynamic instead of electrokinetic injection. As is the case for complexing agents, this separation method can be implemented on an unmodified conventional CE system.

4. Capillary electrophoresis driven by electroosmotic flow

As can be seen in Fig. 1, this approach uses traditional single-end injection with detection near the opposite end. In conventional capillary-zone electrophoresis (CZE), a cathodic EOF is created when the electric field is established. Anions with electrophoretic mobilities of lower magnitudes than the EOF will be carried toward the cathode, their effective mobilities being opposite to their electrophoretic mobilities. Certainly, an EOF of high magnitude will be