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Capillary electrochromatography of inorganic cations in open tubular columns with a controllable capacity multilayered stationary phase architecture

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ABSTRACT

In this paper capillary electrochromatography of alkali and alkaline-earth metal cations in open tubular capillary columns is described. Capillary columns are prepared by coating fused silica capillaries of 75 μm I.D. with poly(butadiene-maleic acid) copolymer (PBMA) in multiple layers. Thermally initiated radical polymerization is used to crosslink the stationary phase. Capillary columns with different number of stationary phase layers can be prepared and allow for the adjustment of separation selectivity in the electrochromatographic mode. Fast and sensitive separations of common inorganic cations are achieved in less than 6 min in a 60 cm capillary column with on-column capacitively coupled contactless conductivity detector. Limits of detection (S/N = 3) for the determination of alkali and alkaline-earth metal cations range from 0.3 to 2.5 μM and repeatability is better than 0.5, 4.5 and 6.1% for migration times, peak heights and peak areas, respectively.

1. Introduction

The interest in the use of capillary scale analysis in general and in the use of open tubular format in particular dates back to the 1960s and 1970s when open tubular gas chromatography (OT-GC) [1,2] and open tubular liquid chromatography (OT-LC) [3–7] was explored by several research groups. In gas chromatography, open tubular columns with relatively large inner diameter (I.D.) can be used because the diffusion coefficients of analytes in the gaseous phase are relatively large. This is not true for liquid chromatography; the diffusion coefficients in the liquid phase are several orders of magnitude lower than in the gaseous phase [8] and the I.D. of capillary columns used in OT-LC is more important. Knox and Gilbert [9,10] have outlined some general considerations for an optimum operation of capillary columns and calculated that the optimum I.D. of OT columns in LC is 0.26 μm [10]. Regardless of the availability of tubes of such bore, the time has not come when separation in such columns would be routine or practical. It has been shown that capillary columns may still provide excellent performance even when operated at conditions far from the theoretical optima. Following the first publication by Manz and Simon [11], open tubular ion chromatography (OT-IC) was used for the analysis of inorganic cations [12,13] and anions [13,14] in columns having an I.D. between 2.3 and 9.5 μm. A potentiometric detector was used. Excellent separations were shown attaining nearly the theoretically calculated separation efficiencies. Pyo et al. [15,16] have adopted a different approach to improve the efficiency of OT-IC separations in large bore capillary columns. They have used capillary columns of 50 μm I.D. for the separation of inorganic anions at high temperatures; the diffusive transport of the analytes to the stationary phase attached to the capillary wall is increased at higher temperatures as the diffusion coefficients increase with temperature. They demonstrated that up to a six-fold increase in the number of theoretical plates was achieved in anion separations when the temperature was elevated from room temperature to 120–150 °C. Kubáň et al. [17] have recently demonstrated a novel approach for the preparation of capillary columns for open tubular ion chromatography. They have developed a coating procedure based on a layered architecture of stationary phases, sequentially deposited on the capillary wall. A fused silica (FS) capillary of 75 μm I.D. was coated with up to 25 successive porous layers of stationary phase producing a branched polymeric structure with anion exchange sites. Even in such a large bore capillary column, baseline separation of several inorganic anions was demonstrated with efficiencies comparable to those achieved in conventional size IC. In a subsequent publication, the concept of multilayered stationary phase was extended to OT-IC of cations and separations of alkali metal cations in gravity-flow OT-IC system have been demonstrated [18].

In capillary electrochromatography (CEC) of small ions, high separation efficiency of capillary electrophoresis and ion exchange

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selectivity are combined. Coated capillary columns of diameters from 25 to 75 μm have been frequently used in CEC; several recent reviews are available [19–22] including an overview on OT-CEC of inorganic ions [23].

First CEC separation of inorganic ions in OT columns was shown by Nutku and Erim [24] and was followed by several research articles [25–30] using UV detection. UV detection of small ions suffers from low sensitivity; sample enrichment is frequently applied. Breadmore et al. [27,31,32], have used direct and indirect UV detection modes in combination with on-line isotachophoretic sample preconcentration. Up to 100-fold enrichment was achieved without a significant loss of resolution and separation efficiency. However, the total analysis time increased significantly due to the preconcentration step [32].

Time consuming preconcentration procedures can be circumvented by using more sensitive detection methods. For instance, sensitive determination of inorganic selenium species was achieved in OT-CEC with inductively coupled plasma mass spectrometry [33]. Electrochemical detection is also a viable alternative, because unlike the optical detection methods it can be miniaturized without significant loss in sensitivity. Conductometry, often used in conventional IC, has been made available for capillary format separation methods due to the recent developments in capacitively coupled contactless conductometric detection (C^4D) [34–36]. In C^4D, the measuring electrodes are placed on the outside of the separation capillary and the conductivity of the solution inside the capillary is measured. C^4D is well suited for detection in OT columns regardless of the optical properties of the stationary phase that may otherwise cause difficulties in UV detection. It has been shown that C^4D is suitable for on-column detection of ionic species in packed capillary CEC [37], packed [38,39] and open tubular [17] capillary IC and monolithic capillary HPLC [40] columns and also in non-transparent polymeric materials such as in PEEK capillaries [41,42]. The applications of C^4D in CE, microchip electrophoresis and various separation methods including OT-IC were reviewed recently [43] and other review articles on applications of C^4D in inorganic ion analysis are available [44–47].

In this paper, open tubular capillary chromatography of inorganic anions with contactless conductometric detection is described. The capillary columns are prepared using a concept of multilayer stationary phase deposition and thermally initiated radical polymerization. Several capillary columns are evaluated in OT-CEC mode and the advantage of selectivity changes is demonstrated by fast and sensitive determinations of alkali and alkaline-earth metal cations.

2. Materials and methods

2.1. Chemicals

All chemicals used were of reagent grade. Poly(butadiene-maleic acid) prepolymer (PBMA, 42% solids in aq. solution) was received from Polysciences Europe (Eppelheim, Germany). Azobis(isobutyronitrile) (AIBN) was from Acros Chemicals (Geel, Belgium) and methanol was from Sigma (Schnelldorf, Germany). All stock solutions for the preparation of background electrolytes (BGE), eluents in OT-IC (tartaric acid) and those of inorganic cations were prepared from analytical grade reagents (Pliva-Lachema, Brno, Czech Republic). The stock solutions of inorganic cations (100 mM) were prepared from their corresponding chloride salts except for the magnesium stock solution, which was prepared from magnesium sulfate. Reagent grade acetic acid (99.8%, Riedel de Haen, Seelze, Germany) was used for the preparation of optimized BGE solutions for cation separations. All stock, standard and BGE solutions were prepared in and diluted with DI water with resistivity higher than 18 MΩ.

2.2. Instrumentation

2.2.1. Preparation of columns

Before coating, the inner surface of a 75 μm FS capillary (75 μm I.D., 375 μm O.D., 1.2 m long, Microquartz GmbH, Munich, Germany) was sequentially treated with a mixture of HF and HNO_3 (2.5%, v/v, each, Penta, Chrudim, Czech Republic) and a 1% solution (v/v) of HCl at 0.5 μl/min for 30 min. A peristaltic pump (Gilson, Villiers le Bel, France) equipped with Viton® pump tubing was used. DI water was then pumped at the same flow rate until neutrality and the capillary was dried by a flow of nitrogen. The capillary was filled with a 10 mM PBMA solution in methanol containing 5% AIBN (w/w, relative to the prepolymer). The solution was then removed by a gentle flow of nitrogen, leaving a thin film of prepolymer on the capillary surface. The capillary was placed in an oven at 160 °C for 15 min to crosslink the prepolymer. This procedure was performed *n* times to prepare a column with *n* layers of stationary phase. Further details on optimization of the column preparation can be found elsewhere [18].

2.2.2. CEC system

A purpose-built capillary electrophoresis instrument consisting of a box made from Perspex with two compartments for injection and detection was employed for all electrochromatographic runs. A potential of +15 kV was applied to the injection side of the separation capillary using a high voltage supply unit (Spellman CZE2000R, Start Spellman, Pulborough, UK). All BGE solutions were filtered through 0.45 μm nylon syringe filter (BGB Analytik, Anwil, Switzerland) and degassed in an ultrasonic bath for 5 min. Typically capillary columns having total and effective lengths of 60 and 46 cm, respectively, were used. They were preconditioned with BGE solution for 10 min prior each analysis. The injection of standard solutions was carried out hydrodynamically by elevating the sample vial to a height of 5–15 cm for 5–20 s. The temperature during the experiments was 25 ± 1 °C.

2.2.3. Chromatographic system

The chromatographic system consisted of a syringe pump (Type V6, Kloehn Ltd., Las Vegas, NV, USA), capable of pumping at flow rates of 100 nl/min to 10 μl/min. The pump was operated with an in-house written software. A 200 nl injection valve (Vici Valco, Houston, TX, USA) was used for sample injection.

2.2.4. Detection system

A capacitively coupled contactless conductivity detector used was a modified version of an earlier design [36] and was described in a recent publication [48]. It consists of a detector cell, an external ac voltage source for excitation and a detector circuitry for processing the cell current. The excitation voltage is provided by a circuitry based on a MAX038 oscillator (Maxim Integrated Products, Sunnyvale, CA, USA). The oscillator operates at various frequencies between 100 and 400 kHz and a voltage booster with a high voltage operational amplifier (PA91, Apex Microtechnology, Tucson, AZ, USA), produces a peak-to-peak output of up to 360 V. The detector cell contains a current-to-voltage converter (OPA655, Texas Instruments, Dallas, TX, USA) as a preamplifier. The excitation and output voltages of the C^4D cell were monitored using a dual-channel oscilloscope (TDS 1002, Tektronix Inc., Beaverton, OR, USA). The data was collected using an in-house written software and a 20-bit sigma-delta data acquisition card (Lawson Labs Inc., Malvern, PA, USA) connected to a personal computer.