Monolithic chromatography for elemental and speciation analysis

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Monolithic supports are increasingly used in the field of chromatography. They are appropriate for different applications (e.g., separation of biomolecules, organic acids and inorganic anions). However, only a few research groups are investigating the potential of using monolithic phases for rapid separation of metal cations and elemental speciation analysis.

Monolithic supports based on porous monolithic silica have been successfully applied in separation of alkaline-earth and transition-metal cations in environmental waters and high ionic-strength samples.

The present review covers applications of monolithic supports for chromatographic separation of metal cations and the potential for using monolithic chromatography in elemental speciation analysis. We critically evaluate the performances and the advantages of monolithic supports and compare them to conventional particle-packed chromatographic supports.

Keywords: Alkaline earth; Chromatography; Determination; Elemental speciation analysis; Metal cation; Monolithic chromatography; Monolithic support; Particle-packed support; Rapid separation; Transition metal

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1. Introduction

Monolithic supports are progressively used in the field of chromatography as an alternative to conventional particle-packed columns in high-performance liquid chromatography (HPLC), ion-exchange chromatography (IEC) and fast-protein LC (FPLC) separations. The advantages of monolith-based supports relate to very efficient mass transport at low back pressures, good separation efficiencies and operation of chromatographic separations at higher than usual flow rates. The separation medium in monolithic supports is a single piece of rigid, porous material comprising micro-pores, meso-pores, and macro-pores. This material is hermetically sealed into the wall of a tube, forcing the stream of the mobile phase to flow through the pores of the separation medium. Monoliths represent a single body and are based on organic or inorganic polymers that possess low shrinkage rates [1,2].

Monoliths are formed from synthetic polymethacrylate [3], polyacrylamide [4] and polystyrene polymers [5], natural agarose polymers [6] or from inorganic silica [7], zirconium and hafnium [8] and carbon-based supports [9]. Monolithic supports are available in disk, column and tube packings. They allow very fast chromatographic separations in different applications. Monoliths are used for preparative and industrial separation of biomolecules (e.g., proteins, protein aggregates, plasmid DNA and viruses) [3]. They are frequently applied in purification of proteins and DNA [10]. Monolithic supports are widely used in separation of biomolecules (e.g., serum-plasma proteins [11], nucleosides, nucleic bases and sugar derivates [12], single-stranded and double-stranded nucleic acids [13] and peptides [14]). They were also applied in analysis of impurities in immunoglobulin concentrates [15], analysis of organic acids [16] and isolation of tomato pectin methylesterase and polygalacturonase [17]. Ion chromatography (IC) using porous monolithic stationary-phase media offered new possibilities in ion analysis [18].

Recently, the concept of monolithic columns has been transferred to the fast separation of inorganic anions (e.g., chloride, chlorate, iodide, iodate, bromide, bromate, nitrite, nitrate, sulfate and phosphate) [19–25] and to separation of hydroxide anion [21] and thiocyanate and chromate from some other anions [23].

However, only a few research groups are investigating the use of monolithic phases for rapid separation of metal cations and the possibilities for their implementation in elemental speciation analysis. We review the use of monolithic supports for chromatographic separation of metal cations. In addition, we present the potential of the use of monolithic chromatography in elemental speciation analysis. We critically evaluate the performance and the

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advantages of monolithic supports, which we compared to the conventional particle-packed chromatographic supports.

2. Separation of metal ions in complex matrices

In past decade, monolithic chromatography has been used as an advanced tool for metal-ion analysis in a variety of complex sample matrices. Regarding the sample matrix and characteristics of the detection techniques, different materials have been used as monolithic chromatographic supports (e.g., silica, methacrylate and styrene-divinylbenzene). We critically evaluate the advantages and the drawbacks of using monolithic chromatography for separation of metal ions in the following sub-sections.

2.1. Silica-based monolithic supports

Silica-based monilithic columns, in particular those modified for reversed-phase (RP) separations, are increasingly in use. Recent years saw the first reports on their application in the analysis of metal ions and H^+. Xu et al. [26–28] developed an analytical procedure for the high-speed simultaneous determination of the major cations in rainwater by use of monolithic RP octadecylsilyl (ODS) silica-gel column modified with lithium dodecylsulfate (Li-DS). Under optimized analytical conditions, monovalent cations Na^+, NH_4^+, K^+ and H^+ were separated within 3 min using acidic LiCl. The separated cationic species were detected by conductometry. The limits of detection (LODs) were 6.20 μmol/L for H^+, 20.0 μmol/L for Na^+, 12.0 μmol/L for NH_4^+ and 9.84 μmol/L for K^+.

In the continuation of their research, Xu et al. improved the sensitivity of fast chromatographic determination of acidity [27] by using the ethylene diamine tetraacetic acid (EDTA) dipotassium-salt dihydrate (EDTA-2K) as eluent. H^+ was separated from other monovalent and divalent cations (e.g., Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) within 2 min. Conductometry was used for detection of separated cations. The optimized procedure allowed reproducible determination of H^+ concentration in the presence of Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} in the pH range 2–6. The LOD for H^+ was 0.372 μmol/L. The procedure was successfully applied to the determination of acidity of rainwater and deionized water. Good agreement of the proposed ion-chromatography (IC) method was obtained by conventional determination of the acidity by pH meter.

Further efforts of Xu et al. were oriented to achieving high-speed, simultaneous chromatographic separation of H^+ from Mg^{2+} and Ca^{2+}, the important ionic components in acid rain [28]. The separation was performed on the previously described monolithic stationary phase coated with anionic surfactant Li-DS [26], while, for detection, conductometry was applied. Using 2 mmol/L ethylenediamine and 0.1 mmol/L Li-DS as an eluent, Na^+, NH_4^+, and K^+ were eluted in one peak before H^+, followed by the separation of Mg^{2+} and Ca^{2+} ions. The chromatographic run was completed within 4 min. The LOD was 1 μmol/L for H^+ and 2 μmol/L for Mg^{2+} and Ca^{2+}.

The main advantages of silica-based monolithic columns over the use of conventional particle-packed IC columns were in high speed of determination of acidity (chromatographic runs were completed in 2–4 min). IC columns, which were commonly applied to determination of acidity, enabled determination of H^+ down to 50 μmol/L concentration level [29] or at similar sensitivity as monolithic columns, but required much longer times for separation of monovalent cations from H^+ (12–30 min) [30,31]. However, under optimized analytical conditions, particle-packed IC columns offered more selective determination of cations. Seven cations (H^+, Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were separated within 22 min in rainwater samples, using a C_{30} column dynamically coated with dodecylsulfate [32].

Chromatographic supports based on porous monolithic silica have also been successfully applied in separating alkaline-earth and transition-metal cations in high ionic strength samples [33,34]. Sugrue et al. [33] developed high-performance covalently-bonded monolithic silica iminodiacetic acid (IDA)-chelating ion-exchange column for very rapid determination of Mg^{2+} and Ca^{2+} at low-mg/L concentration levels in up to 2 mol/L NaCl and KCl brines. Separated ions were detected by spectrophotometry. Using 1 mol/L KCl as eluent, Mg^{2+} and Ca^{2+} were separated within 40 s. Simultaneous determination of Mg^{2+} and Ca^{2+} and considerably faster determinations are the main advantages in comparison with methods based on spectrophotometry and flow-injection fluorometric analysis [35,36].

In the continuation of their research, Sugrue et al. [34] studied ion-exchange properties of monolithic and particle-type IDA-modified silica columns. This monolithic support enabled separation of alkali cations (Li^+, Na^+, K^+, Cs^+) and NH_4^+, which were detected by conductometry, as well as alkaline-earth cations (Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}) and selected transition-metal cations (Mn^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}), which were detected by spectrophotometry. The results demonstrated better selectivity of the IDA silica-gel particle-packed column for the alkali metal ions. For alkaline-earth and transition-metal ions, the selectivity of IDA silica monolith closely matched that of IDA silica-gel particle-packed column. However, the separation of transition-metal cations was much faster on the IDA monolithic column.

Efforts were also made to prepare stationary zwitterionic-based monolithic phases containing both cation-