



Review

Preparation and chromatographic performance of polymer-based anion exchangers for ion chromatography: A review



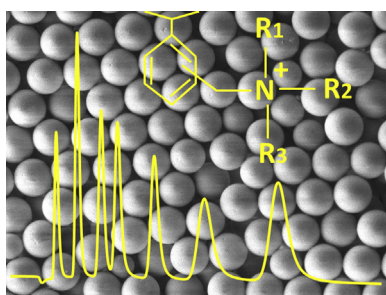
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HIGHLIGHTS

- Methods of the preparation of anion exchangers based on aromatic polymers are considered.
- Application of anion exchangers for separating anions in single-column and suppressed IC is shown.
- Advantages and disadvantages of each type of stationary phase architecture are discussed.
- Examples and applications of commercial columns for IC based on the main 4 architectures are given.

GRAPHICAL ABSTRACT



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ABSTRACT

In the last decade the developments in the field of ion chromatography (IC) were aimed at increasing the efficiency, sensitivity and rapidity of analysis, as well as on improving separation selectivity. Since selectivity and efficiency to the large extent depend on the surface chemistry of the stationary phase, the development of novel anion exchangers remains one of the priority tasks in modern IC. The exact chemistry of commercially available resins is not known and not many literature data devoted to the procedures of preparing anion exchangers for IC have become available in the last 10–15 years. However, the knowledge about the surface chemistry of anion exchangers can provide understanding of the trends in selectivity and efficiency changes, as well as help with the choice of the stationary phase type suitable for solving a particular analytical task. The current review is devoted to the methods of preparing anion exchangers based on polystyrene-divinylbenzene (PS-DVB) and ethylvinylbenzene-divinylbenzene (EVB-DVB) for IC of inorganic and small organic anions and is aimed at demonstrating the improvement of their performance over the years, which was brought by the development of the new types of stationary phase architecture.

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Abbreviations: IC, ion chromatography; PS, polystyrene; EVB, ethylvinylbenzene; PS-DVB, polystyrene-divinylbenzene; EVB-DVB, ethylvinylbenzene-divinylbenzene; VBC, vinylbenzylchloride; TMA, trimethylamine; DMEA, dimethylethanolamine; THA, trihexylamine; MDEA, methyldiethanolamine; TEA, triethanolamine; UDMH, unsymmetrical dimethylhydrazine; MA, methylamine; DMA, dimethylamine; 1,4-BDDGE, 1,4-butanediol diglycidyl ether; RDGE, resorcinol diglycidyl ether; GTMA, glycidyl trimethylammonium chloride; CTMA, (3-chloro-2-propyl)trimethylammonium chloride; ATRP, atom transfer radical polymerization; GMA, glycidyl methacrylate; PGMA, poly(glycidyl methacrylate).

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Contents

1. Introduction	34
2. Substrates for anion exchangers	35
3. Covalently-bonded anion exchange phases based on PS-DVB and EVB-DVB	35
3.1. Chemically derivatized anion exchangers	35
3.1.1. Chloromethylation	35
3.1.2. Friedel–Crafts alkylation and acylation	39
3.1.3. Nitration	41
3.2. Polymer-grafted anion exchangers	41
4. Non-covalently modified anion exchange phases	42
4.1. Anion exchangers dynamically or statically coated with bulky hydrophobic ions	42
4.2. Latex-agglomerated anion exchangers	43
4.3. Polyelectrolyte anion exchangers	44
4.4. Hyperbranched anion exchangers	45
5. Conclusions	46
References	47

1. Introduction

Since the introduction of ion chromatography (IC) by Small et al. in 1975 [1], it has become a preferred method for the determination of inorganic and small organic ions. In the last decade numerous new technologies have been introduced in the field of IC, which were focused on increasing the rapidity of analysis, sensitivity and resolution of separations [2–5].

The recent achievements in IC are associated with the design of new separation media, namely, capillary [6–8] and monolithic columns [3,9], columns packed with particulate ion exchangers having smaller diameter of particles [2] or advanced core shell structure [10]. But the development of novel anion exchangers with improved selectivity and efficiency remains one of the most significant and challenging tasks of modern IC. The column efficiency in IC has a predictable dependence on the parameters common for LC such as the type of substrate [11], particles size and their size distribution [2,12], packing procedure [13] etc., but morphology and surface chemistry of the stationary phase also plays a significant role. Most of the modern anion exchangers have pellicular structure, where anion exchange layer is located on the surface of the substrate and the diffusion of exchanging ions into the pores of the particle is limited [5]. It results in faster mass transfer and thus provides higher column efficiencies.

Anion exchange selectivity mostly depends on complex surface chemistry [14–16] and to some extent on the eluent composition and column temperature [17]. One of the major trends in IC is wide use of on-line generation of potassium hydroxide eluents, which are compatible with suppressed conductivity detection [18] and provide superior convenience in operation and day-to-day reproducibility. The possibility of using electro-dialytic devices for programmable generation of carbonate/bicarbonate and other buffers of different concentration and pH has also been shown [19–21], but the use of hydroxide eluents remains the most popular for the majority of IC applications for analysis of various anionic species [22]. However, the development of this new technology has determined the need in novel selective anion exchange stationary phases compatible with weak hydroxide eluent, which became one of the priority tasks in stationary phase design. In recent years a new type of hydroxide-selective anion exchangers has been developed [5,23].

Another parameter determining the applicability of the anion exchange column for solving the particular analytical task is ion-

exchange capacity. Since the very beginning of IC low capacity anion exchangers were predominantly used because of the limitations of the suppressor systems used for reducing background conductivity. The main drawback of using low capacity columns is the difficulty of analyzing complex samples with concentrated matrices. However, with the development of modern suppressors having much higher suppression capacity and compatible with higher eluent concentrations the novel trend aimed at the gradual increase of anion exchange capacity has appeared [2], which required the use of novel substrates, such as ultra-wide pore polymeric particles [5], the construction of new surface chemistry providing high number of ion-exchange sites in the functional layers [23], and the development of new approaches for the synthesis of anion exchangers with the possibility of controlling their capacity.

According to Pohl [5], typical stationary phases for IC are based on nine basic architectures: (1) – silane-based modification of porous silica substrates, (2) – electrostatic-agglomerated films on nonporous substrates, (3) – electrostatic-agglomerated films on ultrawide-pore substrates, (4) – polymer-grafted films on porous substrates, (5) – chemically derivatized polymeric substrates, (6) – polymer-encapsulated substrates, (7) – ionic molecules adsorbed onto chromatographic substrates, (8) – step-growth polymers on polymeric substrates, (9) – hybrid materials based on the combination of a silane-modified silica-substrate with polymeric exterior coating. Both types of agglomerated phases as well as polymer-grafted, polymer-encapsulated, chemically derivatized substrates, and substrates with step-growth polymers also known as “hyperbranched” phases [23] are predominantly used in modern commercially available columns, moreover, all of them except chemically derivatized ones have pellicular structure with thin ion-exchange layer on the surface of the substrate. As to chemically derivatized phases, it is rather complicated to limit the modification process only to the surface of the substrate, which usually makes it difficult to achieve high column efficiencies.

For preparing the column possessing high selectivity and efficiency complicated multi-step synthesis is usually required. Nowadays almost every developed anion exchanger having good chromatographic performance and exploiting characteristics is turned into a commercial product, therefore, most of the preparation techniques are covered by patents and the information about the production is very limited. Unfortunately, there are not many literature data available describing particular procedure of

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