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PREPARATION AND USE OF LATEX-COATED RESINS FOR ANION CHROMATOGRAPHY*

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SUMMARY

A procedure is described for the preparation of low-capacity anion-exchange resins for use in single-column ion chromatography. The resins are prepared by hydrophobically coating an anion-exchanging latex onto unfunctionalized resins made by Rohm & Haas. The resin exchange capacities are varied by changing the concentration of the sodium chloride or latex in the coating solution. Various resin matrices can be coated and capacities from 5 to over 400 $\mu\text{equiv./g}$ are obtained. The mechanism of latex adsorption is discussed and several highly efficient anion separations are presented.

INTRODUCTION

Since the introduction of suppressed ion chromatography in 1975¹ and single-column ion chromatography (SCIC) in 1979², many improvements have been made in stationary phase technology. Agglomerated resins were originally used in suppressed anion chromatography¹. Polystyrene beads of low cross-linking are lightly sulfonated and made into anion-exchange resins by agglomerating anion-exchanging microparticles onto the surface³. The microparticles are held on the resin surface by electrostatic attractions between the fixed ions of opposite charge. Later, more efficient resins were obtained by agglomerating quaternized latexes onto surface-sulfonated resins of small, uniform size⁴. Although further improvements have been made, anion-exchange resins of this general type are still used and sold commercially.

Resins with chemically bonded quaternary ammonium functional groups have been used with considerable success in single-column anion chromatography. Barron and Fritz⁵ developed reproducible methods for introducing quaternary ammonium groups to produce resins of almost any desired exchange capacity. However, the

* A U.S.A. Patent Application was been filed covering the subject of this contribution.

particle size of their resins was larger and less uniform than desired for highly efficient chromatography.

Recently, many researchers have favored using statically or dynamically coated resins for anion separations in SCIC. In most cases, a long-chain quaternary ammonium compound is added to a coating solution or to the eluent. This hydrophobic compound then coats the resin and allows anion exchange to occur. For example, Cassidy and Elchuk⁶ used dynamic and permanent coating procedures to coat quaternary ammonium halides on a resin surface and separate inorganic ions. DuVal and Fritz⁷ demonstrated the successful use of dynamically and statically-coated polymeric and reversed-phase columns for anion chromatography using long-chain quaternary compounds as coating agents. All of these studies showed that coated resins could be prepared very quickly and easily using a variety of coating agents and resin matrices. Largely because of the easy preparation of coated anion-exchange resins, several other works have been published⁸⁻¹⁰, where these coated resins have been used.

In the present work it is shown that highly efficient resins for anion chromatography can be produced by a simple method of coating quaternized latex particles onto the surface of unsulfonated polymeric resins. A non-porous polystyrene resin of very uniform particle size is described that serves as an excellent substrate for the coated resins. These latex-coated resins are used to obtain highly efficient anion separations.

EXPERIMENTAL

Materials and equipment

All latexes and resins were made by and obtained from Rohm & Haas (Spring House, PA, U.S.A.). All solvents and salts used were reagent grade and were obtained from a number of sources.

The latexes used in this study were strong- or weak-base anion exchangers composed of either polystyrene or acrylic. The latexes vary between 0.08 and 0.60 μm in size and were made by emulsion polymerization followed by chemical functionalization to obtain the appropriate anion-exchange functionality¹¹.

Four different anion-exchanging latexes were used in this study: strong-base exchanger acrylate latex (AL) with quaternary ammonium groups on 60% of the monomer units and 0.09 μm in size; weak-base exchanger acrylate latex which is 0.08 μm in size (AL-WB); strong-base exchanger polystyrene latex which is 100% functionalized and 0.2 μm in size (PL-100); strong-base exchanger polystyrene latex which is 76% functionalized and 0.6 μm in size (PL-76).

The XAD-1 used chromatographically was 20–26 μm or 30–37 μm in size. Preliminary experiments were carried out using 38–44- μm XAD-1. The polystyrene used in this study was prepared by Rohm & Haas, and is 4.2 μm in size, essentially monodisperse and totally nonporous.

Scanning electron microscopy (SEM) of the uncoated polystyrene was performed by F. Laabs of Ames Laboratory (Ames, IA, U.S.A.) using a JEOL 100CX analytical microscope. The samples were prepared in water, dropped onto a slide and air-dried before SEM examination. SEM of the uncoated polystyrene was performed by Rohm & Haas using an AMRAY 1200C analytical microscope. Samples were prepared by dropping dilute solutions of each onto aluminum SEM support stubs. The samples were allowed to air-dry and were then gold-coated before SEM examination.

All size estimations were performed by a Coulter counter (by Rohm & Haas) except for the sizes of the PL-76 latex and XAD-1 resin, which were determined by estimations from electron micrographs.

Ion chromatography was carried out on a laboratory-built HPLC system previously described¹².

Procedures

The XAD resin was prepared according to a previously published method¹².

To prepare a resin sample for coating, a portion of resin is wetted with acetonitrile, filtered and then rinsed with water to displace the acetonitrile. The resin is then filtered to remove excess water.

To coat the resin, a 25-ml volume of latex/sodium chloride solution is added to the wetted resin. The mixture is stirred and sonicated to remove resin clumps. After allowing time for the latex/resin solution to reach equilibrium conditions (less than 1 h), the samples are filtered and rinsed with deionized, distilled water. The strong-base ion-exchange capacities were determined by a method previously published¹².

All solutions were made up in distilled, deionized water and were prepared from reagent grade salts. Eluents were prepared by dissolving the acid in distilled, deionized water and sodium hydroxide was added, where necessary, to adjust the pH. The eluents were then filtered through a 0.2- μ m membrane filter and a vacuum was applied while stirring to remove dissolved gases.

Columns were packed using an upward packed, stirred slurry technique with either a water or an ethylene glycol-sodium chloride-water (40:1:59) packing solvent. The packing pressure was approximately 2000 p.s.i. for the XAD and 3000 to 5000 p.s.i. for the 4.2- μ m polystyrene resins. The coated XAD and polystyrene resins were packed in glass-lined stainless steel columns (Scientific Glass Engineering, Austin, TX, U.S.A.). Typical operating pressures for the packed columns using a 0.5 ml/min flow-rate were 100 p.s.i. for the XAD columns and 2000 p.s.i. for the 4.2 μ m polystyrene columns.

RESULTS AND DISCUSSION

Resin preparation

A series of experiments were performed in order to determine how well the quaternized latexes coated onto various resins, how to vary the exchange capacity of the coated resins and which coated resins are the most suitable for anion separations by SCIC.

Initial experiments were performed to determine what type of unfunctionalized resins could be coated with the highly charged latexes. Table I shows the exchange capacities obtained after coating several different Rohm & Haas resins with the strong-base anion-exchanging polystyrene and acrylic latexes. All resins were coated using identical coating conditions. After coating, the polystyrene-divinylbenzene, acrylic and amide XAD resins shown in Table I had low capacities which would allow the resins to be used in SCIC. (A typical working capacity range in our laboratories is 5 to 100 μ equiv./g.) It is interesting to note that the latex particles are too large to fit into the pores of any of the resins listed in Table I. It is also important to recognize that unlike the electrostatically-coated latex resins^{3,4}, this procedure does not require

TABLE I
CAPACITY OBTAINED ON VARIOUS LATEX-COATED RESINS

Conditions (except *): 0.25 g of 30–37 μm resin, 1 ml acetonitrile, 1 ml latex solution, diluted to 30 ml with 0.1 *M* sodium chloride; AL = strong-base anion-exchanging acrylic latex (60% functionalized); PL-100 = strong-base anion-exchanging polystyrene latex (100% functionalized); PL-76 = strong-base anion-exchanging polystyrene latex (76% functionalized); DVB = divinylbenzene.

Resin	Functionality	Surface area (m^2/g)	Av. pore diameter (\AA)	Capacity ($\mu\text{equiv./g}$)		
				AL	PL-100	PL-76
XAD-1	Styrene-DVB	100	205	31 \pm 2	46 \pm 6	—
XAD-2	Styrene-DVB	300	90	29 \pm 3	85 \pm 7	—
XAD-4	Styrene-DVB	784	50	16 \pm 2	26 \pm 4	—
XAD-7	Acrylic ester	450	90	25 \pm 2	62 \pm 9	—
XAD-8	Acrylic ester	140	235	14 \pm 2	31 \pm 6	—
XAD-11	Amide	69	352	15 \pm 2	45 \pm 2	—
XAD-1	Styrene-DVB	100	205	—	36 \pm 2*	457 \pm 2*

* Conditions: 0.15 g of 30–37 μm resin, 0.6 ml acetonitrile, 0.31 ml PL-100 or 0.6 ml PL-76 (to add identical grams of latex), diluted to 10 ml with 0.05 *M* sodium chloride.

the use of a sulfonated resin. Virtually any resin which is sufficiently hydrophobic to allow latex adsorption can be coated and used for SCIC.

Latex-coated resins of varying capacities were prepared by altering the concentration of the inert electrolyte (sodium chloride) or the concentration of the latex slurry used to coat the resin. Fig. 1 shows adsorption isotherms for coating latexes onto XAD-1. An increase in the salt or latex concentration resulted in an increase in exchange capacity. Using various resins and latexes, a capacity range of approximately 5 to 400 $\mu\text{equiv./g}$ was possible. This broad capacity range is ideal for use in SCIC and makes available a wide range of anion separations and sensitivities.

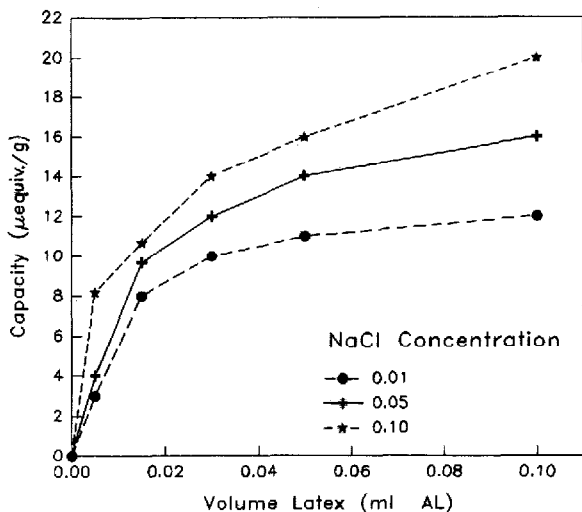


Fig. 1. Adsorption isotherms for AL-XAD-1 (strong-base anion-exchanging latex, AL, coated on 38–44- μm XAD-1).

A new polystyrene resin has been developed¹³ that is greatly superior to the XAD resins for preparing latex-coated anion exchangers for use in anion chromatography. This resin is prepared in stages. The first is an emulsion polymerization performed with water-soluble initiators. The resin particles are $< 1 \mu\text{m}$ in diameter and are used as seed particles for the subsequent expansion stages. Although conditions can be adjusted to vary the particle size, the materials made available to us had a very uniform particle size of around $4.2 \mu\text{m}$ (see optical micrograph in Fig. 2a). The particles are approximately spherical but the method of polymerization gives them a somewhat billowy appearance, as shown in Fig. 2b. These resins, which will be designated as PS in this paper, have no porosity.

Fig. 2c shows some PS resin beads that have been coated with rather large $0.6\text{-}\mu\text{m}$ polystyrene 76% quaternized particles. The exchange capacity of this coated resin is fairly high ($138 \mu\text{equiv./g}$) but the sparseness of the coating (Fig. 2c) and the large size of the quaternized latex particles gave very inefficient separations when a column packed with this material was used for ion chromatography.

Polyacrylate latexes (AL) with 60% of the theoretical amount of quaternary ammonium groups were available in smaller particle sizes: $0.09 \mu\text{m}$ for strong-base acrylate latexes and $0.08 \mu\text{m}$ for the weak-base acrylate latexes. PS resins coated with these latexes produced columns with very high efficiencies for separating anions (see section on chromatographic separations). Stevens and Langhorst⁴ reported that for electrostatically coated latex resins the use of latexes smaller than $0.1 \mu\text{m}$ gave the most efficient anion separations.

Table II lists the resins which were used chromatographically during the course of this study. The coated polystyrene (PS) gave more efficient separations than the coated XAD resins. Therefore, much of the chromatographic work done in this study was performed using the AL-PS columns. The AL-PS columns had linear pressure *versus* flow behavior up to a least 3500 p.s.i. Flow-rates of 0.5 to 1.0 ml/min were typically used, which gave column pressures of 1000 to 1900 p.s.i.

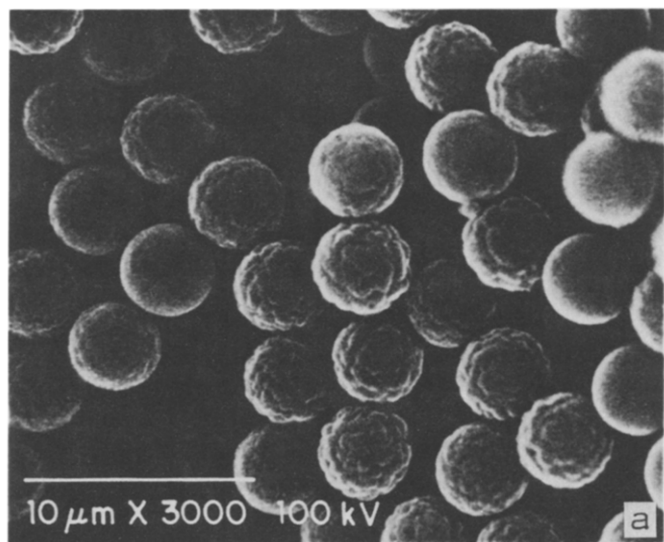


Fig. 2.

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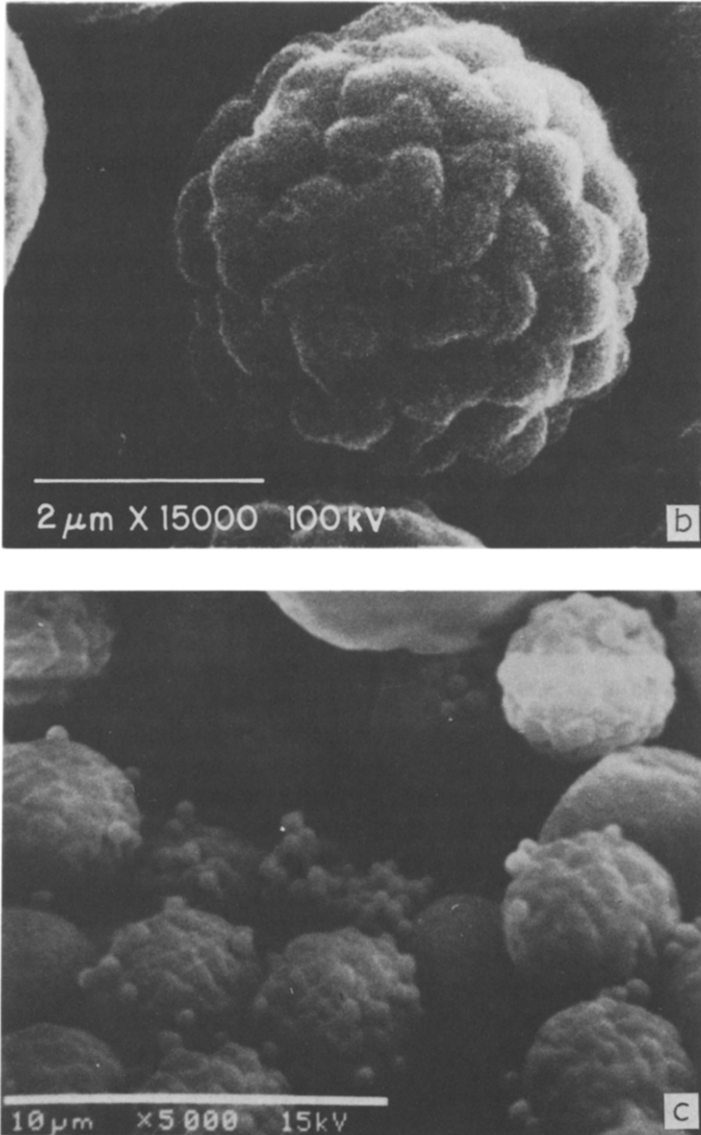


Fig. 2. Electron micrographs of (a) 4.2- μm polystyrene resin particles, (b) a higher magnification showing one polystyrene resin particle and (c) PL-76-PS (strong-base anion-exchanging latex on polystyrene).

Mechanism of latex adsorption

Cantwell and co-workers¹⁴⁻¹⁶ studied the mechanism of organic ion adsorption on a reversed-phase resin, unfunctionalized XAD-2 and sulfonated XAD-2. Using adsorption isotherms, the mechanism was explained by the Stern-Guoy-Chapman (SGC) model of the electrical double layer. According to Cantwell, adsorption of an organic ion onto styrene-divinylbenzene copolymers is due to dispersion forces. As these ions are adsorbed, a resin surface charge is acquired due to the charged

TABLE II
CHARACTERISTICS AND DESIGNATIONS OF COATED RESINS

<i>Designation</i>	<i>Latex*</i>	<i>Resin**</i>	<i>Capacity</i> ($\mu\text{equiv./g}$)	<i>Column size</i>
AL-XAD-1	AL	XAD-1	Variable	—
AL-WB-XAD-1	AL-WB	XAD-1	18	250 mm \times 2.0 mm I.D.
PL-76-PS	PL-76	PS	457	250 mm \times 4.0 mm I.D.
AL-PS	AL	PS	27	250 mm \times 4.0 mm I.D.
AL-PS	AL	PS	48***	250 mm \times 4.0 mm I.D.

* See text for latex descriptions.

** XAD-1 resin is irregularly-shaped and 20 to 26 μm in size. The polystyrene resin (PS) is spherical, non-porous and 4.2 μm in size.

*** The AL-PS column of a higher capacity was prepared by increasing the latex and sodium chloride concentration in the coating solution.

surface groupings on the adsorbed particle. Following the SGC electrical double layer model, addition of an electrolyte to the coating solution increases the number of counterions in the bulk solution. The surface potential remains constant, so more organic ions must adsorb onto the resin surface in order to maintain this potential, thus creating a heavier organic ion coating.

The adsorption isotherms shown in Fig. 1 for latex-coated XAD seem to follow the trends shown in Cantwell's work. Addition of an electrolyte (sodium chloride) to the coating solution causes more latex particles to adsorb onto the support, giving a higher exchange capacity. This leads to the conclusion that a hydrophobic interaction is responsible for the coating of latex particles onto these resin matrices.

Table I also shows the capacities obtained by coating two latexes which differ in their degree of functionalization onto XAD-1. The latexes are 76% and 100% functionalized strong-base exchanger polystyrene (PL-76 and PL-100). The 76% functionalized latex coated 13 times heavier than the 100% functionalized latex (457 and 36 $\mu\text{equiv./g}$, respectively). With a lower degree of ionic character in the 75.6% functionalized latex, the dispersive forces allow a larger amount of latex to be coated onto the support. This phenomenon also supports the mechanism of hydrophobic interaction between the latexes and the resin supports.

Latex particles held onto the resin surface by a hydrophobic attraction can be washed off by organic solvents. Passing acetonitrile or 2-propanol through a latex-coated column removed part of the latex coating and lowered the column capacity. This observation is similar to results by Iskandarani and Pietrzyk¹⁷ with alkylammonium-coated columns where larger amounts of organic modifiers in the coating solution resulted in a lower degree of resin coating. The latex-coated resins, however, could tolerate low amounts of methanol without significantly affecting the exchange capacity.

The fact that organic solvents alter the column exchange capacity is not a great concern in SCIC. In most cases, aqueous eluents are used and aqueous samples are analyzed. In addition, our work has not found significant advantages from using organic modifiers in the eluents. However, organic solvents can be used to strip the latex off of a fouled or ruined latex-coated column so that the resin can be recoated and used again.

Chromatographic efficiency and selectivity

The best column efficiencies were obtained with the AL-PS (latex-coated 4.2- μm polystyrene) columns. Fig. 3 shows the relationship between the eluent linear velocity (or flow-rate) and the height equivalent to a theoretical plate (HETP) for this column using a 4 mM molybdate eluent. The column efficiencies observed during the course of this work varied with different columns, eluents and test analytes. A typical 250 mm \times 4.0 mm I.D. column produced plate numbers (N) between 12 000 and 72 000 plates/m between flow rates of 0.23 and 1.05 ml/min. The maximum plate number of 72 000 plates/m for sulfate was obtained at a flow-rate of 0.23 ml/min.

The selectivity of the AL-PS (48 $\mu\text{equiv./g}$) column for a series of anions using three different eluents is shown in Table III. The selectivity of this column for these anions is very similar to that obtained previously with coated or chemically functionalized resins^{7,18}, although a few differences were noted. For example, ethyl- and propylsulfonate eluted much earlier than chloride from the AL-PS column. This is unusual because all XAD-based and commercial columns used in our laboratories elute the sulfonates either simultaneously with or later than chloride.

Chromatographic separations

Figs. 4-7 show typical examples of separations that can be achieved with the AL-PS and AL-WB-XAD-1 columns. Fig. 4 shows a good separation of several normally late-eluting anions on a coated XAD column of very low capacity (AL-WB-XAD-1). These latex-coated columns can be prepared very easily with capacities low enough that low eluent concentrations can be used to obtain very sensitive anion determinations. For example, using a AL-XAD-1 column with a capacity of 5 $\mu\text{equiv./g}$ and an eluent concentration of $3.7 \cdot 10^{-5}$ M sodium phthalate (pH 6.0), a 0.4-ng detection limit for sulfate was obtained using indirect spectrophotometric detection.

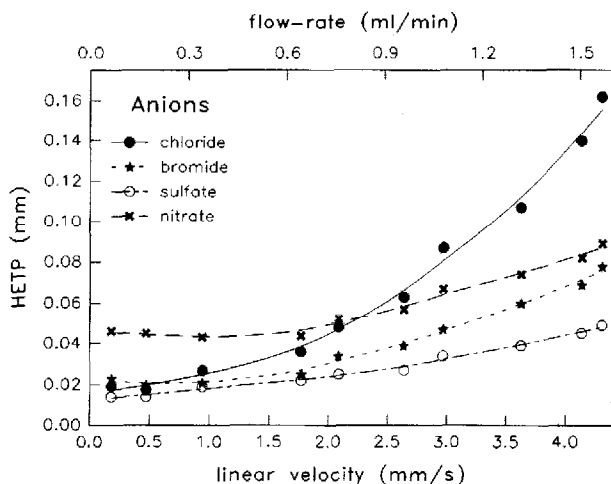


Fig. 3. Plot of HETP versus linear velocity (or flow-rate) using the 250 mm \times 4.0 mm I.D. AL/PS (48 $\mu\text{equiv./g}$) column. The eluent was 4 mM sodium molybdate.

TABLE III
SELECTIVITY DATA FOR AL-PS COLUMN

Conditions: AL-PS column is 4.2- μ m spherical, non-porous polystyrene coated with a strong-base anion-exchanging acrylic latex (48 μ equiv./g capacity); 250 mm \times 4.0 mm I.D. column; 1.0 ml/min flow-rate; conductivity detection.

Anion	Capacity factor		
	90 mM nicotinic acid	2.4 mM sodium phthalate, pH 6.0	4.0 mM sodium molybdate
Methyl acrylate	1.30	—	—
Lactate	1.85	—	—
Formate	3.45	—	—
Fluoride	3.70	0.36	0.21
Acetate	—	—	0.25
Iodate	6.40	0.36	0.21
Dihydrogen phosphate	8.25	—	—
Monochloroacetate	12.25	—	—
Methylsulfonate	13.50	0.73	0.54
Ethylsulfonate	13.60	0.73	0.54
Sulfamate	15.40	—	—
Propylsulfonate	16.95	0.91	0.75
Bromate	27.20	1.27	0.92
Chloride	28.90	1.45	0.96
Nitrite	31.65	2.04	1.42
Malonate	—	4.27	2.21
Bromide	48.90	5.00	3.13
Nitrate	—	6.73	4.17
Chlorate	—	6.91	4.71
Sulfate	—	7.45	3.17
Thiosulfate	—	32.27	13.58
Retention time for Cl ⁻ (min)	55.00	3.00	2.19

Fig. 5 shows an excellent separation of seven common anions using the AL/PS (27 μ equiv./g) column. Baseline resolution was achieved between every peak and the total analysis time was *ca.* 7 min. The molybdate eluent used here serves to elute sulfate immediately after nitrate, and proved to be an excellent eluent for the separation of these anions with these latex-coated columns. Since conductivity detection is not suitable with this eluent, indirect spectrophotometric detection at 250 nm was used.

Fig. 6 shows an excellent separation of 12 anions using the AL-PS (27 μ equiv./g) column and a nicotinic acid eluent. Again, baseline resolution was achieved with every peak. The organic acid eluents such as nicotinic acid are very useful for separating large series of weakly-retained monovalent anions with these latex-coated columns.

Fig. 7 shows a separation using a AL-PS resin of a slightly higher capacity than the column used in Figs. 5 and 6 (48 compared to 27 μ equiv./g). In this separation, sulfate was eluted before nitrate, an inversion which is rarely seen. Dionex has marketed a proprietary column, HPIC-AS2, which also shows this inversion. This column is useful for determining early-eluting anions in nitric acid digests. Supposedly,

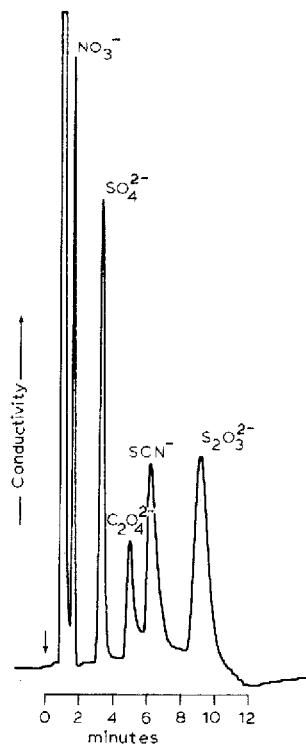


Fig. 4. Separation of late-eluting anions on AL-WB-XAD-1 column using $9 \cdot 10^{-4} M$ sodium phthalate at pH 5.10 as the eluent. The flow-rate was 1.3 ml/min and 13 to 17 ppm of each anion was injected.

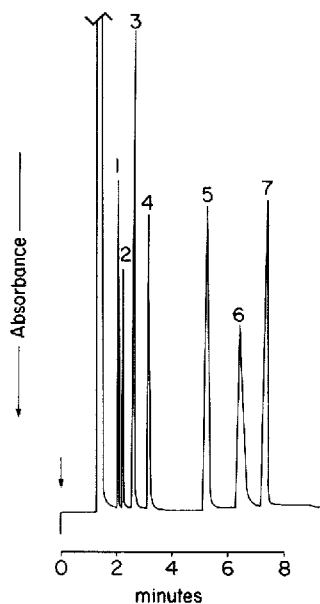


Fig. 5. Separation of 7 common anions on AL-PS (27 μ equiv./g) column using a sodium molybdate eluent run at 0.75 ml/min. Indirect spectrophotometric detection was used at 250 nm with 0.05 a.u.f.s. Peaks: 1 = ethylsulfonate; 2 = propylsulfonate; 3 = chloride; 4 = nitrite; 5 = bromide; 6 = nitrate; 7 = sulfate (10–20 ppm each anion).

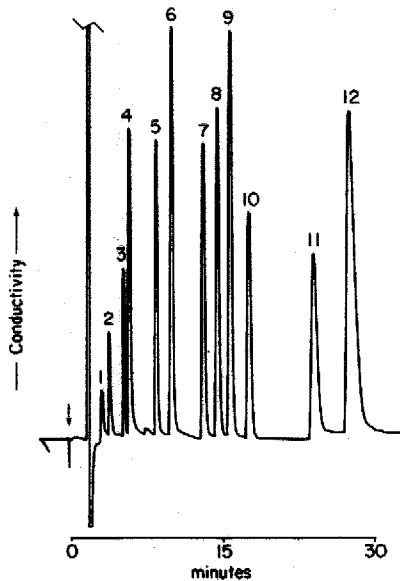


Fig. 6. Separation of 12 monovalent anions on AL-PS (27 $\mu\text{equiv./g}$) using 70 mM nicotinic acid (pH 3.5) as the eluent. The column pressure was 115 bar at a flow-rate of 0.75 ml/min. Conductivity detection was used with 0.1 $\mu\text{S f.s.}$ Peaks: 1 = methyl acrylate; 2 = lactate; 3 = formate; 4 = fluoride; 5 = iodate; 6 = dihydrogen phosphate; 7 = monochloroacetate; 8 = ethylsulfonate; 9 = sulfamate; 10 = *n*-propylsulfonate; 11 = bromate; 12 = chloride (25–100 ppm each).

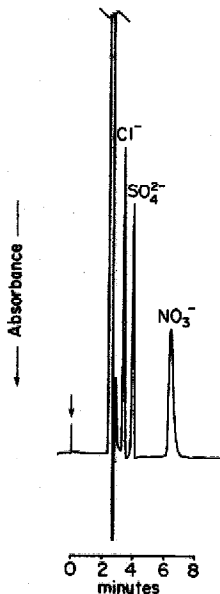


Fig. 7. Separation on AL-PS (48 $\mu\text{equiv./g}$) showing inversion of nitrate and sulfate. The eluent is 16 mM sodium molybdate run at 0.75 ml/min. Indirect spectrophotometric detection is used at 271 nm with 0.01 a.u.f.s.

the nitrate/sulfate inversion on the Dionex resin is brought about because of different resin functional groups. DuVal and Fritz⁷ demonstrated this same inversion using tetraoctylammonium chloride coated on XAD-8 as the anion-exchanging resin.

The "nitrate-selective" column utilized in this work is a strong-base anion-exchanging acrylic latex coated on polystyrene. The exchange site is a typical trimethylammonium functional group. The higher capacity of this resin (as compared to the resin used in Fig. 6) along with the molybdate eluent created the nitrate/sulfate inversion. The retention times of chloride, sulfate and nitrate were 3.3, 3.8 and 6.4 min, with a 2.6-min separation between sulfate and nitrate.

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