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Novel polymeric resins for anion-exchange chromatography

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Abstract

A novel anion-exchange resin containing three amine groups was prepared by reaction of a chloromethylated polystyrene–divinylbenzene (PS–DVB) resin with diethylenetriamine. After being protonated by contact with an aqueous acid, this resin can be used for ion-chromatographic separation of anions. The charge on the resins can be varied from +1 to +3 by changing the pH at which the ion chromatographic separation was carried out. The selectivity of the new ion exchangers for various inorganic anions was quite different from conventional anion exchangers. The performance of this new anion exchanger was studied by changing the pH and the concentration of the eluent, and several different eluents were used with some common anions as testing analytes. Conductivity detection and UV–Vis detection were applied to detect the anions after separation. The new resin can also be used for HPLC separation of neutral organic compounds. Alkylphenols and alkylbenzenes were separated with this new polymeric resin, and excellent separations were obtained under simple conditions. © 1998 Elsevier Science B.V.

Keywords: Anion exchangers; Stationary phases, LC; Inorganic anions; Alkylphenols; Alkylbenzenes

1. Introduction

Ion chromatography is one of the most common and most widely used techniques for the separation of various ionic compounds. Two types of ion chromatography are in practical use now, the suppressor-based system developed by Small et al. [1], and single-column ion chromatography introduced by Fritz et al. [2]. Since the introduction of ion chromatography, a lot of research has been conducted to understand and vary the ion-exchange selectivity and improve ion chromatographic separation of anions [3–13], especially in the development of stationary phases [8–13]. Several types of stationary phases for the separation of anions have been developed, including silica-based anion ex-

changers [13], poly(styrene–divinylbenzene) (PS–DVB) copolymer anion-exchangers [8–11], and macroporous hydroxyethyl methacrylate-based anion-exchanger [12]. There are also mixed-bed ion-exchange materials developed to resolve anions and cations simultaneously [14–16].

In anion-exchange chromatography it is known that a mobile phase containing a 2-anion is generally a more powerful eluent than a 1-anion at the same concentration. This idea has been carried a step further by using the 3-anion of 1,3,5-benzenetricarboxylic acid or the 4-anion of pyromellitic acid in the mobile phase [17,18]. Since ionization of polycarboxylic acids occurs in a stepwise fashion, the average charge on these compounds can be reduced simply by making the pH more acidic. In this way the eluting power of the mobile phase can be varied by changing pH. Although polymer resins containing

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polyethylenimine have been used to separate proteins by anion-exchange chromatography [19,20], most of the anion-chromatographic separations are performed on columns containing single quaternary amine functional groups. Such groups are ionized completely so that changes in pH have little effect on the resins affinity for sample anions. In this paper a new type of anion exchanger is described for the separation of anions by ion chromatography. The anion exchanger is a PS-DVB copolymer containing diethylenetriamine functional groups. Thus, such a group contains three amino groups in the same molecule. The charge on the triamine groups can be varied by changing the pH so that one, two or all three of the nitrogen atoms in each group are protonated. This constitutes a powerful tool to alter the selectivity of the resin.

2. Experimental

2.1. Chromatographic system

The chromatographic system consisted of several components. A Dionex DXP pump (Dionex, Sunnydale, CA, USA) was used to deliver a flow of 1 ml/min. A 7010 Rheodyne injector (Rheodyne, Berkeley, CA, USA) delivered 10- μ l samples which were detected with either a Kratos Spectroflow 783 UV absorbance detector (Kratos Analytical Instrument, Ramsey, NJ, USA) or an Alltech (Deerfield, IL, USA) 320 conductivity detector. Separations were recorded by a Servogor 120 chart recorder (Abb Goerz Instruments, Vienna, Austria) and a Shimadzu C-R3A Chromatopac integrator (Shimadzu Corporation, Kyoto, Japan). Columns were packed with a Shandon Southern (Sewichley, PA, USA) HPLC packing pump at 3000 p.s.i. (1 p.s.i.=6895 Pa).

2.2. Preparation of anion-exchange resins

Fig. 1 shows the chemical structures of the anion-exchange resin made in our laboratory. This resin was prepared from 5- μ m macroporous polystyrene-divinylbenzene (Sarasep, Santa Clara, CA, USA). A 5-g amount of resin was wetted with glacial acetic acid (ca. 5 ml/g resin) then filtered and rinsed with concentrated hydrochloric acid. A 75-ml vol-

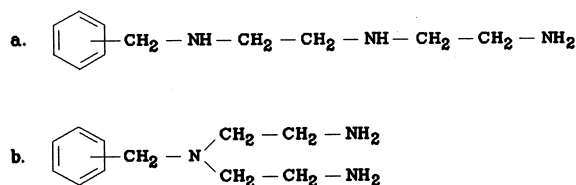


Fig. 1. Structure of the new anion-exchange resins.

ume of concentrated hydrochloric acid with 2.2 M formaldehyde was added to the resin with stirring. The resin mixture was reacted for 2.5 min then poured into ice water to quench the reaction. After filtration and washing with deionized water and methanol, the chloromethylated PS-DVB resin was mixed with 25–40% diethylenetriamine in methanol. This resin mixture was reacted for 24 h at a temperature of 70–80°C, after which the reaction was quenched with ice water. The resultant resin was washed with deionized water, 2-propanol and methanol, and then dried in air for overnight. Four batches of resin were prepared by this procedure. The capacity of the protonated resin, measured by acid-base titration with sodium hydroxide, was 0.175 ± 0.013 meq/g of dry resin. The average nitrogen content by elemental analysis was 0.26 meq/g. The lower exchange capacity could be due to incomplete protonation of the three nitrogens or caused by some nitrogens being located deep within the resin.

2.3. Reagents and chemicals

Methanol, 2-propanol and acetonitrile were of HPLC grade and used as obtained from Fisher Scientific (Pittsburgh, PA, USA). Diethylenetriamine was 99+% and obtained from Aldrich (Milwaukee, WI, USA). All salts and other reagents were of the best grade available and used as obtained from Fisher Scientific, Aldrich, J.&T. Baker (Phillipsburg, NJ, USA) and Lancaster (Windham, NH, USA). All eluents were prepared daily. Stock solutions were used to prepare all sample solutions by diluting to desired concentrations with D.I. water or mobile phase. A Barnstead Nanopure II system (Sybron Barnstead, Boston, MA, USA) was used to further deionize distilled water for all eluents and sample mixtures.

2.4. Chromatographic procedures

A flow of 1 ml/min was selected for all chromatographic separations. The column was protonated with 50 mM hydrochloric acid before the desired eluent was used. Sample injections were made when the baseline was stable. The eluted species were detected by UV–Vis detector at 200 nm or 254 nm with an output range of 0.010 AUFS, or by a conductivity detector with the output range of 0.5 S.

Capacity factors, k' , were calculated according to expression: $k' = (t_r - t_0)/t_0$. The system dead time, t_0 , used to calculate the capacity factor k' , was measured by injecting D.I. water into the system. An average of at least three replicates was used to perform all calculations.

3. Results and discussion

3.1. Conditions for separation

Several anions were separated chromatographically at pH 7.5–7.7 using different salts in the mobile phase with direct UV detection at 200 nm. The results in Table 1 show that perchlorate is a significantly better eluting anion than chloride. However, sulfate and hydrogen phosphate both give even shorter retention times by virtue of their 2[−] charge.

Not all anions absorb sufficiently to use direct UV detection. When conductivity detection was used, potassium hydrogen phthalate (KHP) or sodium benzoate was the preferred material to be used in the mobile phase. The relatively large phthalate or benzoate anions have lower conductivities than the anions to be separated and detected. Chromatograms for separation of inorganic anions are given in Fig.

Table 1
Retention times of several anions with different eluents

Anion	Retention time (min)			
	NaClO ₄ ^a	Na ₂ SO ₄ ^a	NaCl ^a	Na ₂ HPO ₄ ^a
Bromide	3.45	2.15	4.51	1.98
Nitrate	3.98	2.75	5.55	2.54
Iodide	6.25	7.01	12.4	5.95
Thiocyanate	13.7	ND ^b	25.6	17.4

^a Each eluent is 5.0 mM at pH 7.5–7.7.

^b ND=not detected.

2A and Fig. 2B using KHP at pH 3.8 and in Fig. 2C using sodium benzoate at pH 6.4. At pH 3.8, the triamine resin is more fully protonated than it is at pH 6.4. This pH effect is demonstrated particularly well for the divalent sulfate anion. The retention time for sulfate is ca. 21 min at pH 3.8, but is only ca. 15 min at pH 6.4 despite the fact that benzoate is generally considered to be a weaker eluent than phthalate.

In Fig. 2C it will be noted that a good separation was obtained for eight anions with the divalent anions sulfate, molybdate and chromate eluting much later than the monovalent anions. This unique selectivity with the new resin is quite different from that on the conventional anion exchangers, such as trimethylamine modified PS–DVB resin where sulfate and chromate ions were eluted earlier than iodide [21]. The classical plate numbers were calculated for the first six peaks (Table 2). The average plate number ($N=2900$ for a 10-cm column) compares well with ordinary commercial columns.

3.2. Effect of pH

Perhaps the most interesting aspect of the triamine resin is its ability to assume a 3+, 2+ or 1+ charge with varying degrees of protonation. The higher the charge on the protonated triamino functional groups, the more strongly a sample anion should be retained. The effect of pH was studied by using a fixed concentration (15 mM) of sodium perchlorate in the mobile phase and carefully equilibrating both the resin and the mobile phase at various pH values. Since perchlorate is the anion of a strong acid, sodium perchlorate should be completely ionized over the entire pH range that was used.

The results of the pH study for six anions are given in Fig. 3. As expected, the capacity factors for bromide, nitrate and iodide decrease steadily as the pH is raised and the resin nitrogens become less fully protonated. Thiocyanate, which is more strongly retained by the resin, shows a larger change in k' with pH. The decrease in k' is particularly great going from approximately pH 2.2 to pH 3.4.

Chromium (VI) shows a more complicated pattern with respect to changing pH. The k' of chromate ion decreases at pH 2 to pH 3.5, then increases at pH of 3.5 to 6, and decreases again as pH increases further.

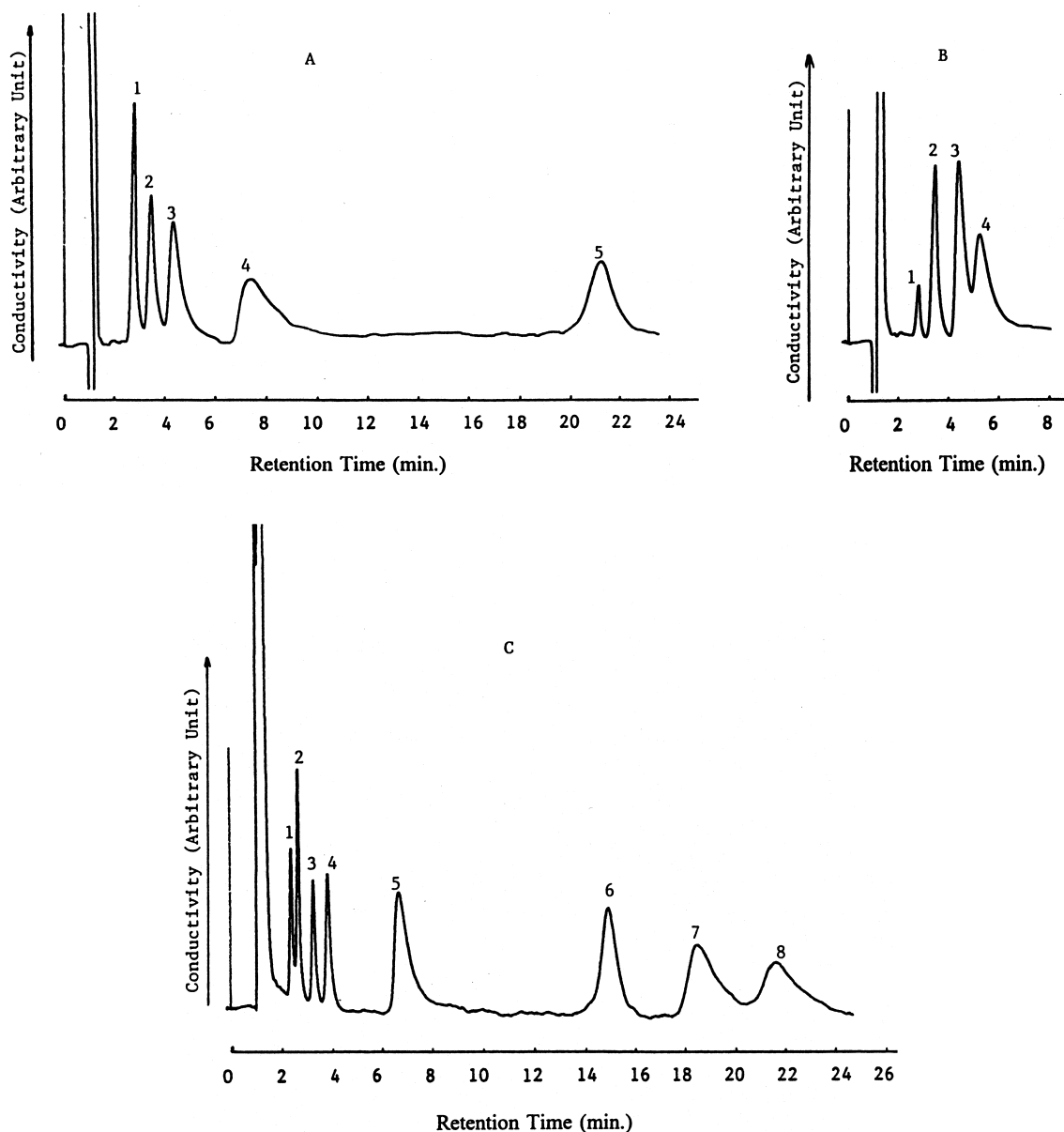


Fig. 2. Separations of inorganic anions on PS–DVB triamine resin. Column: 100×4.6 mm; detection: conductivity. (A) Eluent: 2.5 mM potassium hydrogen phthalate, pH: 3.77. Peaks: 1=chloride (30 ppm); 2=bromide (118 ppm); 3=nitrate (85 ppm); 4=iodide (300 ppm); 5=sulfate (100 ppm). (B) Eluent: same as (A) Peaks: 1=iodate (200 ppm); 2=bromate (200 ppm); 3=nitrite (80 ppm); 4=chlorate (150 ppm). (C) Eluent: 5.0 mM sodium benzoate, pH: 6.40. Peaks: 1=fluoride (22 ppm); 2=chloride (20 ppm); 3=bromide (63 ppm); 4=nitrate (45 ppm); 5=iodide (200 ppm); 6=sulfate (100 ppm); 7=molybdate (200 ppm); 8=chromate (200 ppm).

The possible reason is that chromate ion undergoes some chemical reactions at acidic conditions, e.g.: $\text{CrO}_4^{2-} + \text{H}^+ = \text{HCrO}_4^-$ (for chromic acid, H_2CrO_4 ; $\text{p}K_{a1}=0.74$, $\text{p}K_{a2}=6.49$), and the resultant mono-

valent anions are retained more weakly than chromate ions due to the charge difference. Another possible reaction is the conversion of chromate ions to dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$), which can be proton-

Table 2

Theoretical plate numbers (N) for anions separated on a triamine resin column

Peak no.	Anion	N
1	Fluoride	4900
2	Chloride	3800
3	Bromide	2100
4	Nitrate	2100
5	Iodide	2000
6	Sulfate	2500

Conditions: 100×4.6 mm column, 5.0 mM sodium benzoate at pH 6.4, conductivity detection.

ated in acidic solution to produce the monovalent ions, such as HCr_2O_7^- . That would also give a decreased retention time. A spectral shift, presumably from dichromate to chromate or hydrogen chromate, occurs with rising pH and particularly between about pH 5–6 (Fig. 4).

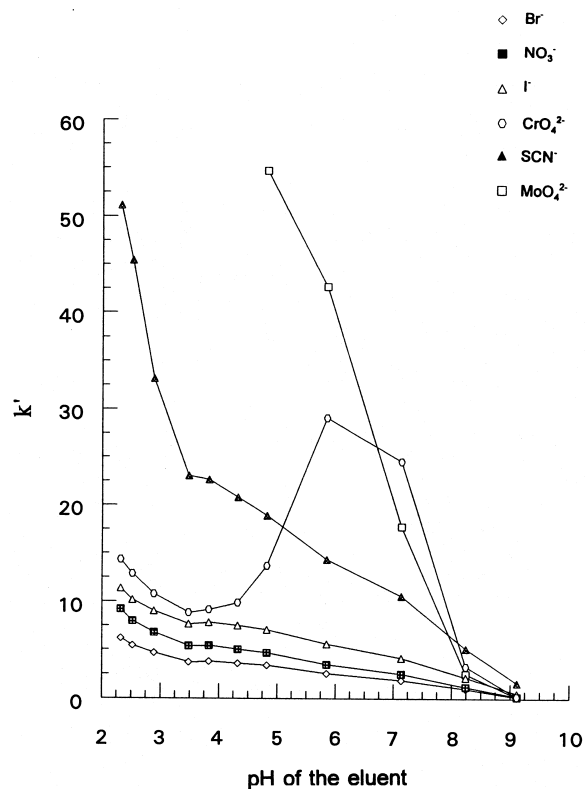


Fig. 3. Eluent pH vs. anion capacity factor, k' . Conditions: 100×4.6 mm column, 15 mM sodium perchlorate, UV detection at 200 nm.

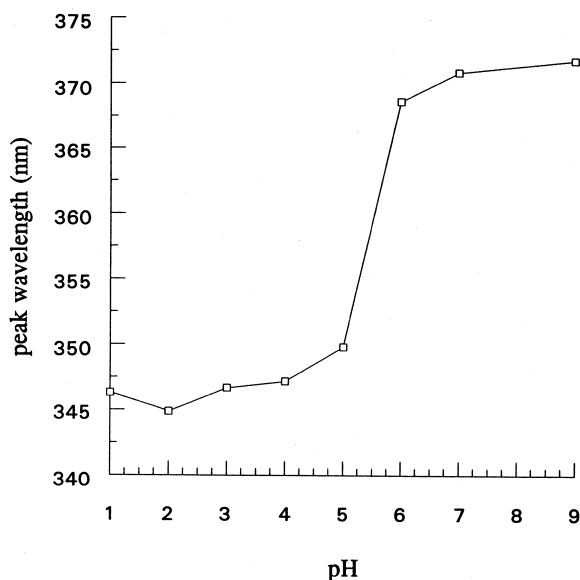


Fig. 4. Effect of solution pH on the wavelength at peak absorbance for chromium (VI).

Molybdate ions were not detected at pH below 4.5. The most likely explanation for this is that molybdenum (VI) is retained too strongly on the stationary phase to be eluted in a reasonable time.

3.3. Other anion separations

Gold (III) and the platinum group elements form stable chloro anions in acidic solutions containing chloride. With conventional anion exchangers, these complex anions are retained so strongly that chromatographic separation is difficult. But with the new triamine resin, a good separation of AuCl_4^- , RhCl_6^{3-} and PtCl_6^{2-} was obtained at pH 2.6 (Fig. 5). At a higher pH, the baseline became more noisy.

The separation of major anions in a tap water sample is shown in Fig. 6. The bicarbonate in the water was undoubtedly converted to carbonic acid by the acidic eluent (pH 3.8) or by the acidic protonated resin. The interesting feature of this separation is the very large difference in retention times between the chloride and sulfate peaks.

3.4. Separation of organic compounds

The new resin consists of a hydrophobic resin

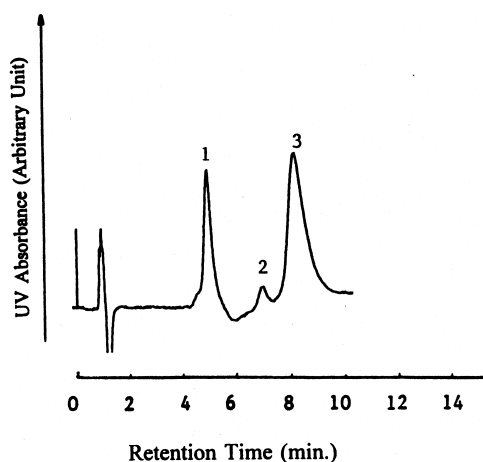


Fig. 5. Separation of anionic chloro-metal complexes. Column: 100×4.6 mm packed with PS–DVB triamine resin; eluent: 15 mM sodium perchlorate at pH 2.58; detection: UV at 200 nm. Peaks: 1= AuCl_4^- (4.0 ppm); 2= RhCl_6^{3-} (3.2 ppm); 3= PtCl_6^{2-} (0.5 ppm).

backbone which is modified by the presence of very polar triamine groups. A 10-cm column packed with the triamine resin was washed with 50 mM aqueous hydrochloric acid to protonate the amine nitrogen. Then the column was washed with water and finally with the aqueous-acetonitrile solution to be used as the mobile phase. Excellent separations of alkyl-

phenols and alkylbenzenes were obtained using 50% and 60% aqueous acetonitrile, respectively (Fig. 7). The average theoretical plate number for the alkylphenols was approximately 2100 for the 10-cm column.

Chromatograms of both sample mixtures were run again after treating the column with dilute sodium hydroxide to eliminate any protonation of the nitrogens. The peaks were significantly broader and retention times were slightly longer. Thus, better results were obtained with the more polar, protonated resin.

4. Conclusions

A polymeric resin with triamine functional groups is an efficient material for ion-chromatographic separation of inorganic anions. A unique feature of this resin is that retention times of sample anions can be varied widely simply by changing the pH of the mobile phase. In acidic solutions 2- anions are much more strongly retained than anions with 1- charge. The new resin is also an effective hydrophilic column packing material for separation of phenols and alkylbenzenes by HPLC with an aqueous-acetonitrile mobile phase.

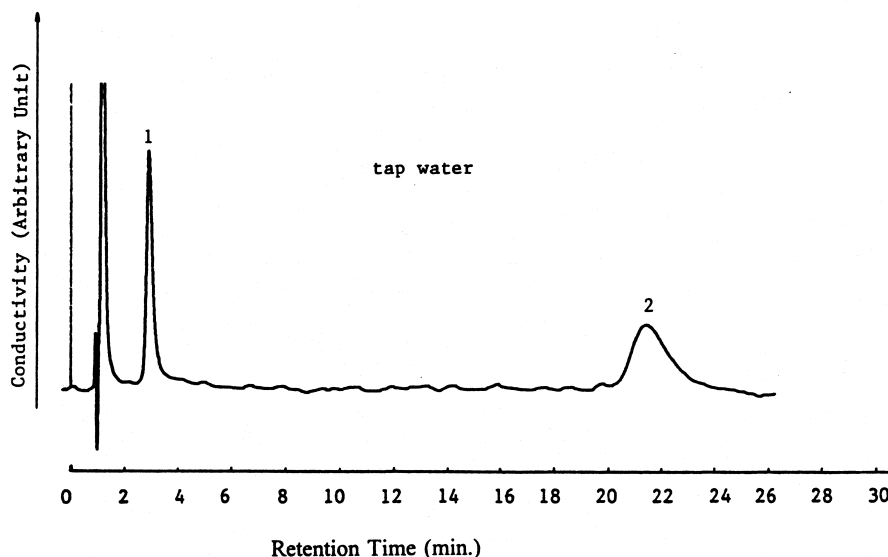


Fig. 6. Application of the new stationary phase for tap water. Column: 100×4.6 mm packed with PS–DVB triamine resin; eluent: 2.5 mM potassium hydrogen phthalate, pH: 3.80; detection: conductivity. Peaks: 1=chloride; 2=sulfate.

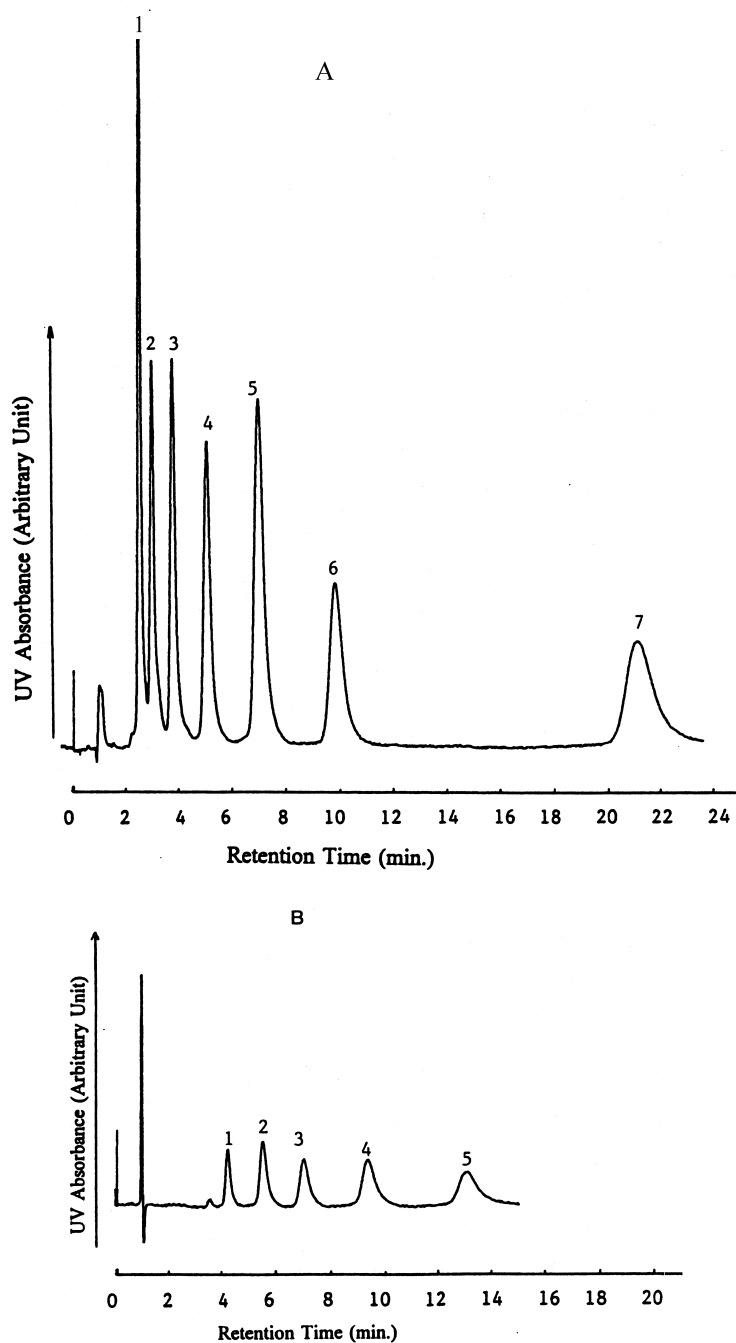


Fig. 7. Separation of alkylphenols and alkylbenzenes. Column: 100×4.6 mm packed with PS–DVB triamine resin; detection: UV at 254 nm. (A) Eluent: 50% acetonitrile–water. Peaks: 1=phenol (7.0 ppm); 2=*p*-cresol (10 ppm); 3=4-ethylphenol (10.0 ppm); 4=4-*n*-propylphenol (8.0 ppm); 5=4-*n*-butylphenol (15 ppm); 6=4-*n*-amylphenol (20 ppm); 7=4-*n*-heptylphenol (25 ppm). (B) Eluent: 60% acetonitrile–water. Peaks: 1=benzene (35 ppm); 2=toluene (35 ppm); 3=ethylbenzene (45 ppm); 4=propylbenzene (60 ppm); 5=butylbenzene (60 ppm).

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