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Note

Chromatography of aliphatic amines on an anion-exchange resin

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The liquid chromatographic determination of aliphatic amines has mainly been performed by ion-exchange chromatography[1–3] and ion chromatography[4,5]. The amines have been separated exclusively on cation-exchange resin columns. In ion-exchange chromatography, the amines eluting from a separating column have been monitored by a spectrophotometric detector based on the reaction of ninhydrin with amines. In ion chromatography, the amines eluting from a separating column, followed by a stripper column, have been monitored by a conductimetric detector. However, no reports have considered the chromatography of aliphatic amines using a system other than the separating column–detector systems mentioned above.

In this work, the chromatography of aliphatic amines was studied with a system consisting of a hydroxide-form anion-exchange resin column and a flow coulometric detector. We have previously used a hydrogen-form cation-exchange resin column and a flow coulometric detector for the analysis of acids[6–9]. The detector was based on the electrochemical reaction of *p*-benzoquinone and hydrogen ion formed by the dissociation of acid as follows: *p*-benzoquinone + $2H^+$ + $2e^-$ → hydroquinone[10,11]. The detector used in this work is based on the electrochemical reaction of hydroquinone and hydroxide ion formed by the hydrolysis of amine as follows: hydroquinone + $2OH^-$ → *p*-benzoquinone + $2H_2O$ + $2e^-$. This paper discusses the chromatographic results with methyl- to octylamine obtained on an anion-exchange resin column with the coulometric detector system.

EXPERIMENTAL

A Hitachi 034 liquid chromatograph was used for isocratic elution and a Spectra-Physics 3500B liquid chromatograph for gradient elution. Each chromatograph was equipped with a Hitachi 030 flow coulometric detector. Details of the detector have been described by Takata and co-workers[10,11]. The electrolytes for flow coulometric detection were as follows: 0.01 *M* hydroquinone–0.001 *M* *p*-benzoquinone–0.1 *M* potassium chloride for the working electrode reaction and 0.5 *M*

potassium iodide for the reference electrode reaction. A glass-jacketted column (550 × 9 mm I.D.) packed with a Hitachi 2632 hydroxide-form anion-exchange resin (particle size 18 ± 2 μm and degree of cross-linking 8%) was used. The column was thermostated at 50° except for experiments on the effect of column temperature. In general, a hydroxide-form anion-exchange resin is unstable at elevated temperature. However, of column temperatures up to 60°, reproducible chromatograms could be obtained in repeated chromatographic runs without re-packing the column. Deionized water or deionized water–acetone was used as the eluent at a flow-rate of 1 ml/min.

The aliphatic amines studied were methyl- to octylamine of reagent grade. All stock solutions of these amines were prepared by dissolving the amine in deionized water or 50% ethanol. The sample solution (0.5 ml) was injected into the column with a loop injector. A chromatogram was recorded with a National VP-651A strip-chart recorder. The peak areas and retention times of the amines were recorded by an Auto Lab System I computing integrator.

RESULTS AND DISCUSSION

Flow coulometric detection of amines

An aliphatic amine eluting from a separating column is in equilibrium with protonated amine and hydroxide ion:

$$RNH_2 + H_2O \rightleftarrows RNH_3^+ + OH^- \quad (1)$$

where R represents an alkyl group. The electrochemical reaction of hydroquinone and the hydroxide ion takes place at the working electrode of the flow coulometric detector:

$$H_2Q + 2OH^- \rightarrow Q + 2H_2O + 2e^- \quad (2)$$

where H_2O and Q represent hydroquinone and *p*-benzoquinone, respectively. The amine is determined by measuring the current resulting from the electrolytic oxidation of hydroquinone according to eqn. 2.

For the electrochemical reaction represented by eqn. 2, a potential applied between the working and reference electrodes is an important factor. Potentials were applied to the working electrode in the range 0.2–0.7 V *versus* the reference electrode, and the optimal potential was determined by measuring the peak area of sodium hydroxide liberated by anion exchange of sodium chloride.

Fig. 1 shows the relationship between the applied potential and the detector response (peak area). As shown, the optimal potential was 0.45 V. Subsequent experiments were carried out at 0.45 V.

Retention volumes

Table I shows the retention volumes of aliphatic amines tested with water as the eluent. The retention volumes of *n*-alkyl amines increased with increase in carbon number or boiling point. The detector responses obtained decreased with increase in carbon number. The peak of octylamine was not detected because of the adsorption effect on the resin bed. The retention volume of isopropylamine was lower than that

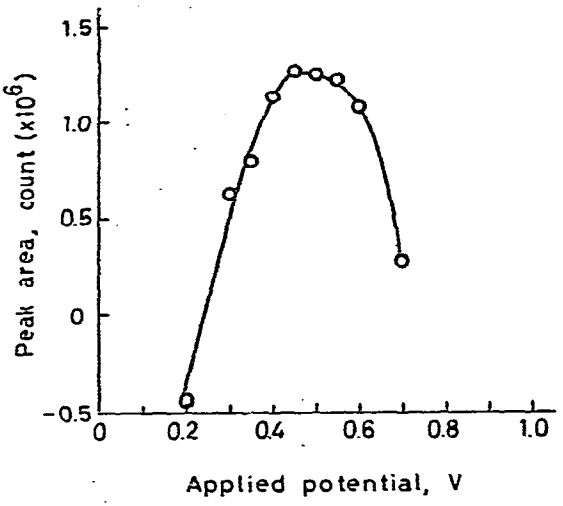

Fig. 1. Relationship between peak area and applied potential. Sample concentration: 100 mg/l of sodium chloride; 0.5-ml injection.

TABLE I

RETENTION VOLUMES AND DETECTION LIMITS OF AMINES

Amine	*Retention volume (ml)* *	*Boiling point (°C)*	*Detection limit (mg/l)* **
Methylamine (MeA)	17.3	−6.6	0.06
Ethylamine (EtA)	17.4	16.6	0.11
Diethylamine (Et_2A)	18.0	56	0.23
Triethylamine (Et_3A)	21.5	89.5	0.30
n-Propylamine (PrA)	19.3	48.7	0.16
Isopropylamine (i-PrA)	18.3	33	0.16
n-Burylamine (BuA)	23.6	76	0.19
n-Amylamine (AmA)	30.0	104	0.24
n-Hexylamine (HxA)	49.5	129	0.26
n-Heptylamine (HpA)	76.0	153.5	0.29
n-Octylamine (OcA)	—	180	0.32

* Eluent: water.

** Eluent: water–40% acetone.

of *n*-propylamine; those of di- and triethylamine were higher than that of ethylamine. These results suggest that the separation of the amines on the hydroxide-form anion-exchange resin column is based on the adsorption effect on the resin matrix.

Effect of column temperature

The effect of column temperature on the retention volumes of *n*-alkylamines was investigated in the temperature range 30–60° (Fig. 2). The retention volumes of methyl and ethylamine were hardly affected by the column temperature, whereas those of propyl- to heptylamine slightly decreased with increase in column temperature. It is considered that the increase in the solubilities of the amines in water at elevated temperature decreased the retention volumes.

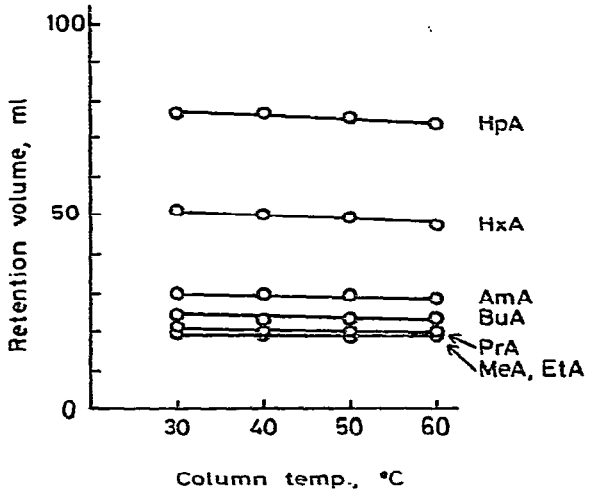

Fig. 2. Effect of column temperature on retention volumes of amines.

Effect of acetone concentration in water–acetone eluent

The solubilities of aliphatic amines are higher in water–acetone than in water as the eluent. Mixtures containing water and up to 40% (v/v) of acetone were used as eluent. The peak heights and areas of methyl- and ethylamine did not vary with an increase of acetone concentration in the eluent, whereas those of propyl- to octylamine increased with an increase in acetone concentration in the eluent. In particular, the peak of octylamine, which was not detected with water as the eluent, could be observed in an eluent containing 10% of acetone.

Fig. 3 shows the effect of acetone concentration on the retention volumes of *n*-alkylamines. The retention volumes of methyl- to propylamine were not affected

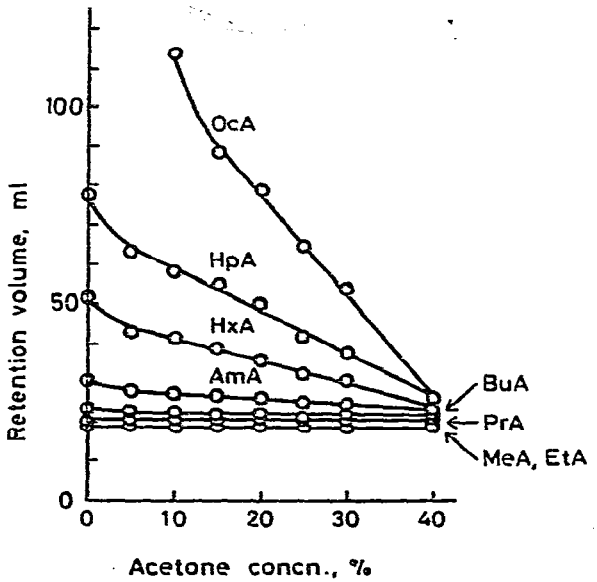

Fig. 3. Effect of acetone concentration on retention volumes of amines.

by the acetone concentration, whereas those of butyl- to octylamine decreased with increase in acetone concentration in the eluent. This behaviour shows that the solubilities of amines increased with increase in acetone concentration.

The volume of the ion-exchange resin bed in the column gradually decreased with increase in acetone concentration in the eluent. When water–40% acetone was used as the eluent, a shrinkage of about 3% was observed. However, the resin bed returned to its original volume after passing water into the column. The column could be used again without re-packing.

Separation of several amines

A mixture of several aliphatic amines was separated by isocratic elution with water as the eluent and by gradient elution with water–acetone. The gradient profile was linear with a continuously increasing acetone concentration from 0 to 20% during the first 30 min. Fig. 4 shows the chromatograms obtained by both methods. Although methyl- to heptylamine were separated by isocratic elution with water, the peak pattern was not clear (Fig. 4A). The chromatogram obtained by gradient elution showed a good separation of methyl- to octylamine (Fig. 4B).

The column used for gradient elution could be used again without re-packing, because the decreased volume of the resin bed was hardly noticeable. Reproducible chromatograms could be obtained on repeated chromatographic runs.

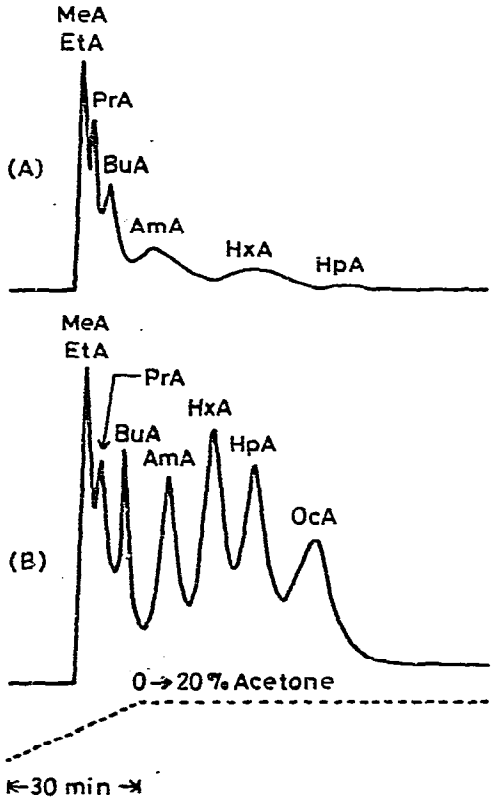

Fig. 4. Chromatograms of a mixture of *n*-alkyl amines. (A) Isocratic elution method; (B) gradient elution method.

Calibration graph and detection limits

A calibration graph was constructed for propylamine in the concentration range 1–200 mg/l (Fig. 5). Bouyoucos[5] has pointed out that the response of a conductimetric detector in ion chromatography is non-linear for amines at concentrations over 100 mg/l. However, as shown in Fig. 5, the present method gave an excellent linear response at concentrations up to 200 mg/l.

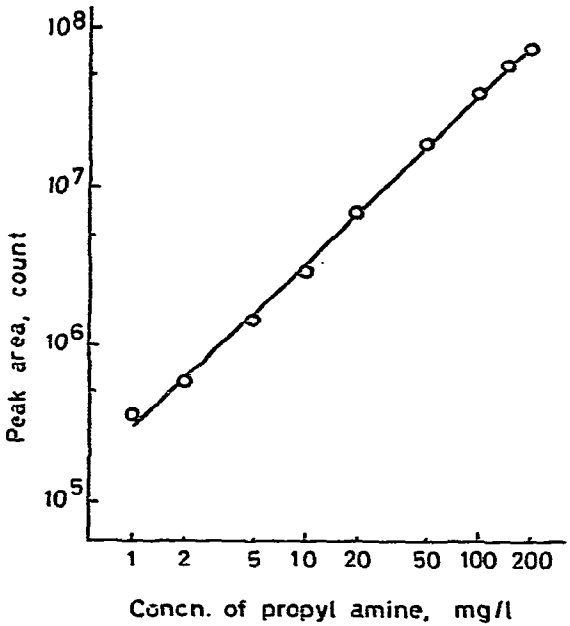

Fig. 5. Relationship between peak area and concentration of *n*-propylamine.

The detection limits of the aliphatic amines were determined with water–40% acetone as the eluent, an injection volume of 0.5 ml and a column temperature of 50°. The detection limit was defined as that concentration which gave a signal twice as strong as that produced by the background noise.

These limits are shown in Table I. The detection limits for the lower amines were lower than those for the higher amines.

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