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# Ion chromatography of alkylamines and alkanolamines using conductivity detection*

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ABSTRACT

A number of separation modes, including ion-exchange and ion interaction chromatography, were investigated for the determination of alkylamines and alkanolamines by ion chromatography with conductivity detection. The use of a poly(butadiene–maleic acid)-coated silica column and a mobile phase of EDTA–nitric acid containing acetonitrile or methanol proved to be the most versatile of the separation methods studied for amine analysis. The use of this highly efficient and flexible separation approach enabled the determination of a wide variety of amines, alkali metals and alkaline earth cations at low μg/l levels when using indirect conductivity detection. The analysis of amines in variety of complex sample matrices is presented.

## INTRODUCTION

The determination of amines is of considerable interest as these compounds are widely used in industrial processes. Ethanolamines are used in the chemical and pharmaceutical industries for the production of emulsifying agents and medicines, for gas purification and as corrosion inhibitors [1]. Amines, such as morpholine and cyclohexylamine, are also used as corrosion inhibitors in the water cycles of power plants [2]. Low-molecular-mass alkylamines are emitted in automobile exhaust fumes, hence the determination of amines is also of significant environmental concern [3]. The ion chromatographic (IC) determination of alkylamines and alkanolamines is complicated by the fact that they are often difficult to resolve from other amines, and the potential alkali metal and alkaline earth cation interferences, using either cation-exchange or reversed-phase ion interaction chromatography [4]. In addition, most amines and the inorganic cations have no UV–Vis absorption characteristics, which limits detection options to either amperometry, conductivity, refractive index or indirect methods. These detection approaches are often difficult to use in conjunction with gradient chromatography, hence separations typically use isocratic elution conditions.

The determination of low-molecular-mass amines by IC is typically achieved using either a silica- or resin-based cation-exchange column with a dilute mineral acid eluent and either direct [5,6] or indirect conductimetric detection [7,8]. As the alkali metals also elute within the same retention time window under these conditions, mobile phases have to be optimized to avoid co-elution between the

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amines and inorganic cations; and generally, the range of amines which can be resolved in one run is limited. Addition of a complexing agent, such as diaminopropionic acid, to the mobile phase has been shown to permit the simultaneous determination of alkali metals, alkaline earth cations and low-molecular-mass amines [2] when using conductivity detection. The use of a UV absorbing eluent, benzyltrimethylammonium chloride, allows the indirect UV detection [9] of ethanolamines and other amines such as piperidine and cyclohexylamine [10]. Indirect UV detection has also been used in conjunction with ion interaction chromatography for the determination of low-molecular-mass amines [11], as has pulsed amperometric detection [1].

It has been demonstrated that a column packed with poly(butadiene–maleic acid)-coated on a 5-$\mu$m silica support offers a unique selectivity for the separation of mono- and divalent cations [12]. The use of this column with an eluent of EDTA–nitric acid and indirect conductivity detection permits the isocratic separation of alkali metal and alkaline earth cations with detection limits at the low $\mu$g/l level [13]. The selectivity characteristics of this column also make it suitable for the analysis of a wide range of amines. This paper compares the use of a poly(butadiene–maleic acid)-coated silica-based column for the analysis of low-molecular-mass alkylamines and alkanolamines to the conventional IC separation approaches of cation-exchange and ion interaction chromatography.

## EXPERIMENTAL

### *Instrumentation*

The liquid chromatograph consisted of a Waters Chromatography Division of Millipore (Milford, MA, USA) Model 600 solvent delivery system, either a U6K injector or a WISP 712 autoinjector, Model 431 conductivity detector and either an 820 Maxima or 860 DEC data station. The following analytical columns were used in this study: a TSK IC Cation SW (50 × 4.6 mm I.D.) silica-based cation exchanger, a Waters IC-Pak Cation (50 × 4.6 mm I.D.) polystyrene-based cation exchanger, a Waters IC-Pak Ethanolamine (50 × 4.6 mm I.D.) polystyrene–divinylbenzene-based cation exchanger, a Waters Nova-Pak $C_{18}$ (300 × 3.9 mm I.D.) functionalized silica-based reversed-phase column and a Waters IC-Pak Cation M/D (150 × 4.6 mm I.D.) butadiene–maleic acid copolymer-coated silica-based cation exchanger. All eluents were prepared daily, filtered and degassed with a Waters solvent clarification kit.

### *Reagents*

Water (18 M$\Omega$) purified using a Millipore Milli-Q water purification system (Bedford, MA, USA) was used for all solutions. Ultrex nitric acid and EDTA (both free acid and disodium salt) were obtained from J.T. Baker (Gaithersburg, PA, USA). Acetonitrile and methanol (both HPLC grade), Pic-B8 and $C_{18}$ Sep-Pak sample preparation cartridges were obtained from Waters. All amines were obtained as the free base (or hydrochloride salt) from either Sigma (St. Louis, MO, USA) or Aldrich (Milwaukee, WI, USA) in approximately 98% purity.

## RESULTS AND DISCUSSION

### *Cation-exchange separation of ethanolamines*

The primary aim of this investigation was to establish conditions to enable the simultaneous determination of alkali metals and ethanolamines at sub-ppm levels in matrices, such as wastewaters and scrubber solutions, using conductivity detection. Ideally, the method would allow the determination of these solutes in addition to the alkaline earth metals and other alkylamines, which are also likely to be present in such samples. The use of cation exchange appears to be an appropriate starting point for the separation of alkali metals and ethanolamines as low-molecular-mass amines have previously been separated using a variety of cation-exchange columns [5–8]. Initially, a relatively high capacity (450 $\mu$equiv./g) TSK IC Cation SW silica-based cation-exchange column and an eluent of 10 m*M* nitric acid–0.05 m*M* disodium EDTA was used to attempt the separation of a standard solution containing sodium, ammonium, mono-, di- and triethanolamine. All the alkali metals and ammonium were fully resolved under these conditions, however the ethanolamines and sodium eluted unresolved as a group with this column and eluent combination. Weakening the mobile phase did not significantly improve the ethanolamine separation, suggesting that a strictly cation-exchange mechanism was of limited utility for the analysis of these

solutes. As expected, the alkaline earths did not elute under these conditions as the disparate ion-exchange affinities of the alkali metal and alkaline earth cations typically requires that the monovalent and divalent cations be determined using different eluents with conventional cation-exchange columns [13].

A Waters IC-Pak Cation low-capacity (12 μequiv./g) polystyrene-based cation-exchange column was then investigated for the separation of sodium, ammonium, mono-, di- and triethanolamine using an eluent of 2 m*M* nitric acid–0.05 m*M* disodium EDTA. All the alkali metals and ammonium were fully resolved using these conditions and the ethanolamines again eluted unresolved as a group. However, the selectivity of this column was different to the silica-based cation exchanger discussed above, as the ethanolamines now co-eluted with ammonium rather that sodium. This result suggested that perhaps the amines were exhibiting some degree of reversed-phase retention, based on their hydrophobicity, as polymeric ion exchangers typically show more reversed-phase character than silica-based ion-exchange columns [14]. As was the case with the silica-based column, weakening the mobile phase did not significantly improve the ethanolamine separation. The higher capacity (560 μequiv./g) polystyrene–divinylbenzene-based Waters IC-Pak Ethanolamine column was designed to specifically exploit the dual reversed-phase/cation-exchange retention behaviour of the ethanolamines and permits complete resolution of sodium, ammonium and mono-, di- and triethanolamine using an eluent of 4 m*M* nitric acid–0.05 m*M* disodium EDTA and 5% methanol. The addition of the 5% methanol to the mobile phase reduced the retention and improved the peak shape of the ethanolamines. While the ethanolamines were fully resolved under these conditions, the alkali metal cations and ammonium were not separated; lithium and sodium co-eluted, as did ammonium and potassium. Also, the detection limits obtained for the ethanolamines were only in the order of 1 ppm as a consequence of relatively low efficiency (*ca.* 700 plates) of the IC-Pak Ethanolamine column. Hence, while the ethanolamines could be separated with this column, the relative insensitivity combined with the poor separation efficiency limited the general applicability of this approach.

*Ion interaction separation of ethanolamines*

Ion interaction chromatography is often used as an alternative to cation exchange for the separation of amines [1,11]. The main advantage of this approach is that both reversed-phase and ion-exchange retention parameters can be used to manipulate the retention of solutes [4]. The other advantage is that the separations are carried out on reversed-phase columns, which typically have much greater efficiencies than polymeric ion-exchange columns. A Waters Nova-Pak 4-μm silica-based $C_{18}$ reversed-phase column and an eluent of 5 m*M* Pic-B8–5% acetonitrile was used for the separation of sodium, ammonium, mono-, di- and triethanolamine. The ethanolamines were well resolved and also separated from sodium and ammonium, although the detection limits were very similar to those obtained using the Ethanolamine column. The major drawback of this approach, however, was the presence of system peaks [14,15]. The magnitude of these peaks was dependent upon the ionic strength of the injected sample and real sample injections resulted in large, interfering system peaks, making the use of this separation approach impractical when using conductivity detection.

*Separation of amines on a butadiene–maleic acid copolymer-coated silica-based column*

A poly(butadiene–malic acid)-coated silica-based column has previously been used with a nitric acid–EDTA eluent and conductivity detection for the simultaneous, isocratic determination of both alkali metal and alkaline earth cations at the low μg/l level [13]. This column has weak acid cation-exchange functional groups and also considerable reversed-phase character as a result of the polymeric coating. These characteristics make it not only suitable for the isocratic separation of mono- and divalent cations, but also the separation a wide range of amines. Fig. 1 shows a chromatogram of a standard solution containing sodium, ammonium, monoethanolamine, diethanolamine, triethanolamine, and also methyldiethanolamine obtained using the Waters IC-Pak Cation M/D column and an eluent of 2 m*M* nitric acid– 0.1 m*M* EDTA with conductivity detection. This column completely resolved sodium, ammonium and the four ethanolamines, in addition to magnesium and calcium, in a single isocratic run. The separation selectivity can be altered by varying

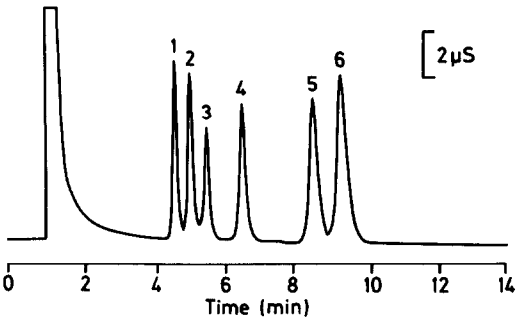


Fig. 1. Separation of sodium, ammonium and four ethanolamines using the IC-Pak Cation M/D column. Conditions: column, Waters IC-Pak Cation M/D; eluent, 2 m*M* nitric acid–0.1 m*M* EDTA; flow-rate, 1.0 ml/min; injection volume, 100 μl; detection, conductivity. Solutes: 1 = sodium (1.0 ppm); 2 = ammonium (1.0 ppm); 3 = monoethanolamine (2.0 ppm); 4 = diethanolamine (4.0 ppm); 5 = triethanolamine (10 ppm); 6 = methyldiethylethanolamine (10 ppm).

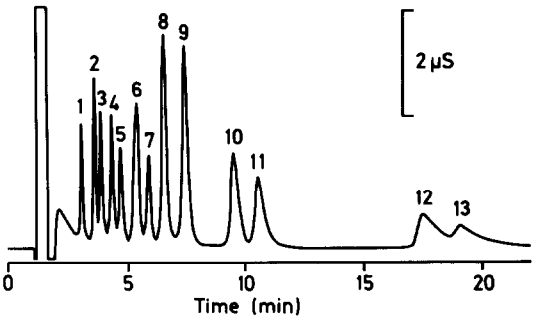


Fig. 2. Separation of lithium, sodium, ammonium and ten low-molecular-mass amines using the IC-Pak Cation M/D column. Conditions as for Fig. 1 except: eluent, 3 m*M* nitric acid–0.1 m*M* EDTA–5% methanol. Solutes: 1 = lithium (0.1 ppm); 2 = sodium (0.5 ppm); 3 = ammonium (0.5 ppm); 4 = monomethylamine (1.0 ppm); 5 = monoethylamine (1.0 ppm); 6 = *n*-propylamine (3.0 ppm); 7 = morpholine (2.0 ppm); 8 = diethylamine (5.0 ppm); 9 = trimethylamine (5.0 ppm); 10 = cyclohexylamine (5.0 ppm); 11 = dipropylamine (5.0 ppm); 12 = triethylamine (5.0 ppm); 13 = dibutylamine (5.0 ppm).

the concentration of either nitric acid or organic modifier in the mobile phase. Plots of log capacity factor *versus* log nitric acid concentration were linear for sodium, ammonium and the ethanolamines with slopes of approximately −1, as would be expected for the cation-exchange separation of monovalent cations obtained using a univalent eluent [16]. A plot of log capacity factor *versus* the % organic modifier in the eluent for the ethanolamines was not linear, indicating that a strictly reversed-phase retention mechanism was not operating [17]. The fact that retention can be manipulated by adjusting either the ion-exchange or reversed-phase nature of the mobile phase, combined with the high efficiency of the butadiene–maleic acid copolymer column, enables a large number of amines to be separated in a single chromatographic run. Fig. 2 shows a chromatogram of a standard solution containing lithium, sodium, ammonium and ten low-molecular-mass amines obtained using an eluent of 3 m*M* nitric acid–0.1 m*M* EDTA and 5% methanol. Quaternary amines can also be separated with this column by using increased concentrations of organic modifier in the mobile phase. Fig. 3 shows a chromatogram of a standard solution of tetramethyl, tetraethyl, tetrapropyl and tetrabutylamine obtained using an eluent of 4 m*M* nitric acid–0.1 m*M* EDTA and 30% acetonitrile. As opposed to the case for the ethanolamines, plots of log capacity factor *versus* the % organic modifier in the eluent were linear for the quaternary amines. This result was not entirely surprising, as the more bulky quaternary amines would be expected to exhibit considerably more reversed-phase character than the ethanolamines.

*Applications of amine analysis*

Calibration plots obtained using the IC-Pak Cation M/D column were linear for the ethanolamines from the detection limit (of approximately 0.025

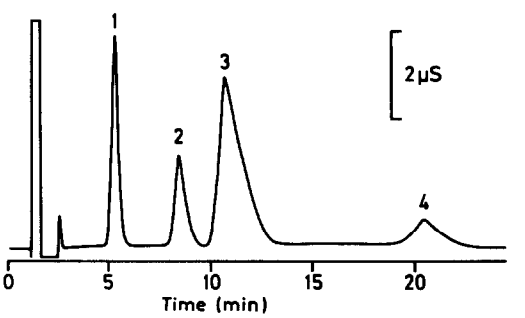


Fig. 3. Separation of quaternary amines using the IC-Pak Cation M/D column. Conditions as for Fig. 1 except: eluent, 4 m*M* nitric acid–0.1 m*M* EDTA–30% acetonitrile. Solutes: 1 = tetramethylamine (25 ppm); 2 = tetraethylamine (25 ppm); 3 = tetrapropylamine (25 ppm); 4 = tetrabutylamine (25 ppm).

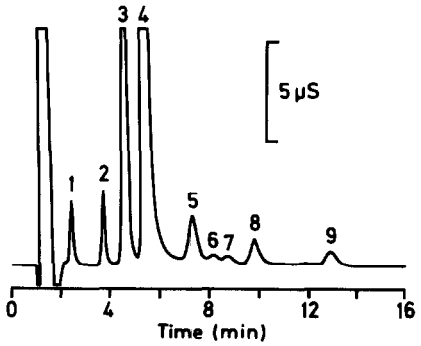


Fig. 4. Analysis of an ethanolamine-based scrubber using the IC-Pak Cation M/D column. Conditions as for Fig. 1 except: sample preparation, 5000× dilution in water. Solutes: 1 = unknown; 2 = sodium; 3 = monoethanolamine; 4 = diethanolamine; 5 = triethanolamine; 6 = unknown; 7 = unknown; 8 = magnesium; 9 = calcium.

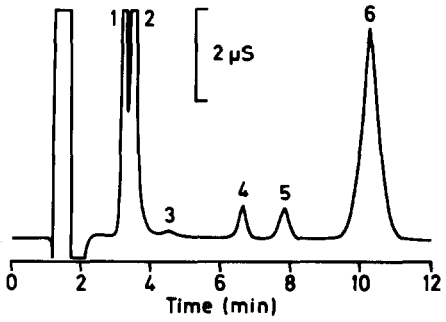


Fig. 6. Analysis of bethanechol in a tablet formulation using the IC-Pak Cation M/D column. Conditions as for Fig. 1 except: eluent, 4 m*M* nitric acid–0.1 m*M* EDTA–5% acetonitrile; sample preparation, one tablet dissolved in 1 l of water followed by $C_{18}$ Sep-Pak clean-up. Solutes: 1 = sodium; 2 = ammonium; 3 = potassium; 4 = magnesium; 5 = calcium, 6 = bethanechol.

ppm at 3× signal-to-noise) up to a concentation of 20 ppm for a 100 μl injection volume, after which the signal generated by the peaks exceeded the computer input of 2.5 V. One of the more common industrial uses of ethanolamines is as scrubber solutions for the removal of $NO_x$ and $SO_x$ from stack gases. Fig. 4 shows a chromatogram of a 5000× dilution of an ethanolamine scrubber solution used for virgin acid gas treatment in a petroleum refinery obtained using the IC-Pak Cation M/D column. Sodium, mono- and diethanolamine, magnesium, calcium and several unidentified peaks, possibly low-molecular-mass amines, were present in the diluted solution. Ethanolamine determination is also of importance in the biotreatment of wastewaters, as elevated levels are detrimental to the biotreater performance. The IC-Pak Ethanolamine column, while of limited utility for trace level amine analysis, proved to be most appropriate for the analysis of low ppm levels of amines in samples containing high levels of sodium and ammonium. Fig. 5 shows a chromatogram a petroleum refinery wastewater containing 12 ppm diethanolamine in the presence of approximately 2000 ppm sodium and 500 ppm ammonium obtained using the IC-Pak Ethanolamine column. As previously mentioned, amines are widely used in pharmaceutical formulations. Fig. 6 shows a chromatogram of bethanechol, a synthetic analogue to choline, in a tablet formulation after dissolution in water and passage through a $C_{18}$ Sep-Pak to remove exipients. The biogenic quaternary amines, choline and acetylcholine, can also be separated from bethanechol using the same conditions with IC-Pak Cation M/D column.

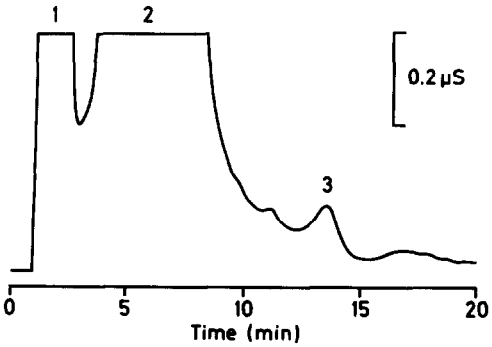


Fig. 5. Analysis of petroleum refinery wastewater using the IC-Pak Ethanolamine column. Conditions as for Fig. 1 except: column, Waters IC-Pak Ethanolamine; eluent, 4 m*M* nitric acid–0.05 m*M* disodium EDTA–5% methanol; flow-rate, 1.2 ml/min; injection volume, 10 μl; sample preparation, $C_{18}$ Sep-Pak clean-up. Solutes: 1 = sodium (*ca.* 2000 ppm); 2 = ammonium (*ca.* 500 ppm); 3 = diethanolamine (12 ppm).

## CONCLUSIONS

A wide variety of amines and inorganic cations, can be separated using a poly(butadiene–maleic acid)-coated silica-based column with a mobile phase of nitric acid–EDTA containing organic

modifier. The amines are retained through a combined ion-exchange/reversed-phase mechanism and the separation selectivity can be altered by varying either the nitric acid or organic modifier concentration in the mobile phase. Cation exchange is the primary retention mechanism, particularly for the ethanolamines and low-molecular-mass alkylamines. The more hydrophobic the R group on the amine, the greater the retention, up to the point where large quaternary amines exhibit "classical" reversed-phase retention behaviour. Calibration plots for low-molecular-mass amines are linear in the range 0.025 to 20 ppm when using conductivity detection and the combination of the highly efficient and flexible separation approach with indirect conductivity detection provides a very versatile method for the determination of amines, mono- and divalent inorganic cations in wide variety of complex sample matrices.

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