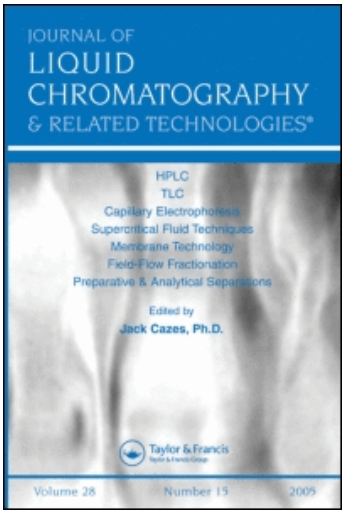

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Preconcentration of Aliphatic Amines from Water Determined by Capillary Electrophoresis with Indirect UV Detection

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PRECONCENTRATION OF ALIPHATIC AMINES FROM WATER DETERMINED BY CAPILLARY ELECTROPHORESIS WITH INDIRECT UV DETECTION

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ABSTRACT

Preconcentration methodology based on adsorption chromatographies for enriching aliphatic amines (C1 to C4 substituted primary, secondary, and tertiary) and alkanolamines in water was studied by free zone capillary electrophoresis (CZE) with indirect UV detection. The solid-phase extraction of amines from water (pH 5) as a preconcentration step was studied for ion exchange solid-phase extraction (SCX) cartridges, cation ion exchange extraction disks, and ion-pairing with C_{18} extraction disks. In the course of the investigations, the electrophoretic properties of the amines was studied in some detail in order to optimize separations and detection limits. The indirect mode is particularly powerful in being able to detect primary through quarternary amines without derivatization. Mobilities of amines were correlated with their Stokes' radii. Increased selectivity for resolving closely related amines under CZE was explored using nonionic surfactants, pH adjustment, and optimized background

electrolyte. Techniques were developed for obtaining stable baselines in the indirect detection mode. Linearity, sensitivity, and efficiency were explored for this mode of detection for a large set of amines.

INTRODUCTION

Aliphatic amines are toxic substances and irritants to mucous membranes[1] that are among the common chemicals of commerce. They are used as corrosion inhibitors in steam boilers and as starting materials in the manufacture of pharmaceuticals, insecticides, herbicides, fungicides, polymers, surfactants, and rubber accelerators. The related alkanolamines function as solvents and starting materials for surfactants, but they appear to be less toxic than the aliphatic amines.

The many commercial uses and natural occurrences of aliphatic amines (here we refer primarily to C_1 to C_4 alkyl-substituted primary, secondary, and tertiary amines) suggest that ultimately they will appear in the environment as pollutants. Thus, they are target analytes of U.S. EPA Method 8260[2] (also Method 624[3]) where they are classified as volatiles.

The U.S. EPA, EMSL-LV, maintains a continuing interest in analytical methods for amines because of their wide occurrence and toxicity and because there is need for determinative methods for amines as a result of the listing activities for various hazardous wastes under RCRA[4] when amines are suspected to be present.

Aliphatic amines are basic compounds with pK_b values[5] of approximately 5×10^{-4}. The replacement of an aliphatic group, or hydrogen, of an amine with an aromatic ring causes a profound change in the basicity, typically reducing the pK_b by six orders of magnitude. Aliphatic amines and their derivatives are essential to life, functioning as neurotransmitters and hormones[6] and occurring in biological tissues and fluids.[7-10]

Aliphatic amines can present chromatographic problems due to their reactivity and extreme basicity. Derivatization has, therefore, been frequently employed. However, derivatization (e.g., Method 8042)[3] has not achieved as wide adoption in environmental analysis as it has in biological and pharmaceutical analysis. Part of the reason may lie in the large number and complex nature of environmental matrices and the possibility of artifact formation from co-extractives.

Gas chromatography (GC) is frequently used to separate amines using a variety of GC detectors. Amines can be chromatographed underivatized on porous polymers such as HayeSep B, even in the presence of water.[11] Chromosorb 102 treated with KOH[12] and liquid-coated supports using ammonia as carrier gas[13] have been reported. Alternatively, a variety of derivatizing agents have been used for the GC of amines.[14-18]

Liquid chromatography has often been the separation technique of choice for amines due to the variety of derivatizing agents available to introduce chromophores for UV detection or fluorophores for fluorescence detection.[14,19-35] Other techniques used to separate amines include supercritical fluid chromatography,[36] thermospray LC/MS,[37] and ion chromatography.[38]

Applications of capillary electrophoresis to environmental analysis have increased dramatically.[39-46] Usually, these applications have depended on UV detection with separations using free zone electrophoresis or micellar electrokinetic chromatography (MEKC). Applications of CE to inorganic cations and anions have been based on indirect UV detection.[47] Beck and Englehardt developed applications of imidazole and other chromophoric amines as background ions for indirect detection of aliphatic amines and alkali ions in water samples.[48] As pointed out by Kuhr and Yeung,[49] indirect detection methods in CE have their origin in ion chromatography applications.[50] Kuhr and Yeung have discussed the conditions for optimization of indirect UV and fluorescence detection.[51] Kuhr has introduced indirect fluorescence detection under MEKC conditions[52] and further discussed indirect fluorescence detection.[53]

In this work, we evaluate various solid-phase extraction (SPE) adsorbents and systems for the preconcentration of aliphatic amines and some alkanolamines in water. The recoveries from these adsorbent systems are determined using capillary zone electrophoresis (CZE) with indirect UV detection. Three adsorbent systems were examined for the concentration of amines from water: (1) cation exchange[54] solid-phase extraction cartridges, (2) ion-pairing with extraction disks, and (3) cation exchange extraction disks. In the course of the recovery studies, procedures were developed to optimize separations and characterize the electrophoretic properties of amines. Correlations of electrophoretic mobilities with structure were made,[55-56] and practical techniques were developed for minimizing baseline fluctuations. Resolution of amines with similar mobilities was effected by adding nonionic surfactants[57] or through pH selection and optimized matching of mobility of amines with that of the background electrolyte.[47]

EXPERIMENTAL

Chemicals

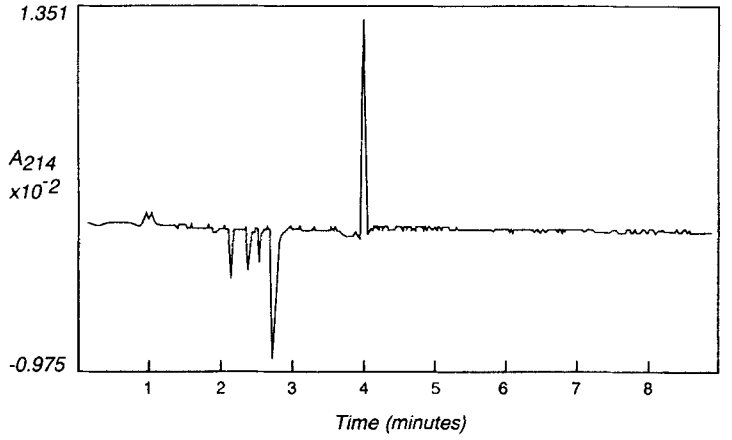
All organic compounds were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA) unless otherwise specified. Other chemicals were from standard sources of supply, and all were used as received. Deionized water (ASTM Type II) was used for all aqueous solutions. Solutions were freshly prepared for each experiment. Liquid amines were measured gravimetrically for preparation of standard solutions.

Capillary Electrophoresis

A P/ACE Model 2050 Capillary Electrophoresis System (Beckman Instruments, Fullerton, CA, USA) was used for all capillary electrophoretic experiments. The instrument was fitted with a capillary 57 cm X 75-μm I.D., 50 cm to the detector, with UV detection at 214 nm. The temperature of the capillary was 25°C, and electrophoretic runs were 10 minutes at 30 kV. The capillary was equilibrated with running buffer at the start of each experiment, and washed extensively with acid, alkali, water, and running buffer between runs. Migration times, peak widths, and dynamic reserves were estimated directly from the monitor of the data system (software System Gold, Ver. 6.1). Corrected peak areas, as computed by the data system (peak area multiplied by the velocity of the ion [length to the detector divided by time]), were normalized to the corrected peak area of the internal standard (tetrabutylammonium ion) as a control for the small variations in the nominal volumes of the pressure injections (ca. 5 nL from 1-s injections).

Solid Phase Extraction Studies

Solid phase extraction disks (Bakerbond Octadecyl C18; J.T. Baker, Inc., Phillipsburg, NJ, USA) and SCX cartridges containing 500 mg benzenesulfonic acid and used for cation exchange (Varian Associates Inc., Sunnyvale, CA, USA) were prepared according to the manufacturers' instructions. An experimental product cation exchange disk was a gift of 3M Industrial and Consumer Sector, New Products Department, St. Paul, MN, USA. Aqueous solutions of analytes were applied at flow rates of about 1 L/h. Increasing flow rates to 1 l/15 min for disk extractions did not adversely affect recovery.



Compound	Migration Time Seconds	Mobility μ_e $10^{-4}Cm^2V^{-1}S^{-1}$	Response Factor Per mM	10^4 Theoretical Plates
propylamine	119	3.76	0.385	5.48
dipropylamine	135	2.83	0.421	3.13
tripropylamine	144	2.39	0.395	5.55
tetrabutylammonium bromide	155	1.81		0.75

Figure 1. Electropherogram demonstrating the separation of propylamine, dipropylamine, and tripropylamine. The background ion was imidazole (5.0 mM, pH 5.0). The internal standard was tetrabutylammonium ion (1.0 mM). Analytes were detected as decrements in absorbance at 214 nm caused by the displacement of the background ion. For other conditions and calculations see text.

RESULTS AND DISCUSSION

Capillary Electrophoresis: Indirect Detection of Organic Amines

Figure 1 shows an electropherogram of propylamine, dipropylamine, and tripropylamine by CZE. A solution containing propylamine (6.0 mM), dipropylamine (3.7 mM), tripropylamine (2.6 mM), tetrabutylammonium bromide (1.0 mM), and imidazole (5.0 mM, pH 5.0) was injected (5.0 nl) into the capillary; thus, the analytes were dissolved in the running buffer. The system peak (displaced imidazole) reached the detector window at 240 seconds. From these times (column 2 of the inset), the apparent mobilities (μ_a) may be

Table 1

Relative Response and Effective Mobility (μ_c) of Selected Organic Compounds

Compound	Slope[1] (response/mM)	Mobility[2] (10^{-4} cm^2 V^{-1}s^{-1})
Morpholine	0.318	3.46
Pyrrolidine	0.305	3.65
Diaminobutane	0.656	4.72
Diamiopropane	0.491	4.81
Diaminopentane	0.555	4.28
Ethanolamine	0.450	3.83
Diethanolamine	1.28	3.10
Triethanolamine	0.991	2.83
Diethylamine	0.306	3.37
Triethylamine	0.342	3.02
Butylamine	0.311	3.33
Dibutylamine	0.363	2.42
Tributylamine	0.385	2.01
Propylamine	0.311	3.64
Dipropylamine	0.380	2.76
Tripropylamine	0.379	2.35
Dimethylamine	0.258	4.33
Triethylamine	0.188	4.17

[1] Slopes (relative response per mM) are based on 5-10 determinations for each compound and were taken from plots like those presented in Figure 2. Linear regression analyses were performed on each data set. Values for R^2 exceeded 0.99 in each case. For other methods, see Figure 1 and text.

[2] Effective mobilities ($^{10-4}$ cm^2 V^{-1} s-1) were calculated from measured migration times by the following equation: μ_a = apparent mobility; μ_c = effective mobility; μ_{EOF} = mobility provided by electroosmotic flow.

$$\mu_a = /L/tV$$

where $\mu_a = \mu_c + \mu_{EOF}$

V = applied voltage

/ = effective capillary length (to detector)

t = migration time

L = total capillary length

calculated. The effective mobilities (μ_e; column 3 of inset) are then obtained from familiar equations of CE (see also Table 1).[58] The relationship between the mobility of the amines and the background electrolyte is of interest, and we shall correlate the mobility with an empirical relationship for a large class of amines. The relationship between the response factor (corrected area of analyte ion/corrected area of internal standard ion) of each peak and the concentration of that particular analyte in the test solution injected into the capillary is shown in column 4 (inset). The proportionality between concentration of analyte and the response factor of its peak was constant over a 150-fold concentration range.

Theoretical plate number, or the height equivalent to a theoretical plate (HETP) is a measure of zone broadening and of efficiency of separation and will be discussed in a later section of this paper (cf. Figure 4). The analyte peaks shown in Figure 1 exhibited plate numbers (column 5) from about 10,000 to more than 50,000.

The area of the positive peak which migrates at the EOF, as verified by measuring the migration time of benzyl alcohol, and represents the displaced chromophoric background ion, imidazole, was very nearly equal to the sum of the areas of the negative peaks representing the positively charged cationic analytes and the internal standard. In a series of 15 electropherograms (not presented here), the ratios of the sums of the negative peaks to the sums of the positive peaks were calculated. The average of these ratios was 1.072, and the standard deviation was 0.031.

These results suggest that the analyte ions effect a nearly 1:1 displacement of background electrolyte ions because the analyte ions are dissolved in the running buffer (background electrolyte).[51]

Detector Response is a Linear Function of Analyte Concentration

The usefulness of any determination depends on its ability to measure a target analyte over a useful range of concentrations with a response that is directly proportional to concentration over the entire range. Several experiments demonstrated that the method permitted detection of the analytes of interest over a 150-fold range of concentrations, from 0.02 mM to 3.0 mM, with as little as 5-nL injections (Fig. 2). The mass limit of detection was about 0.1 pmol of analyte injected on-column.

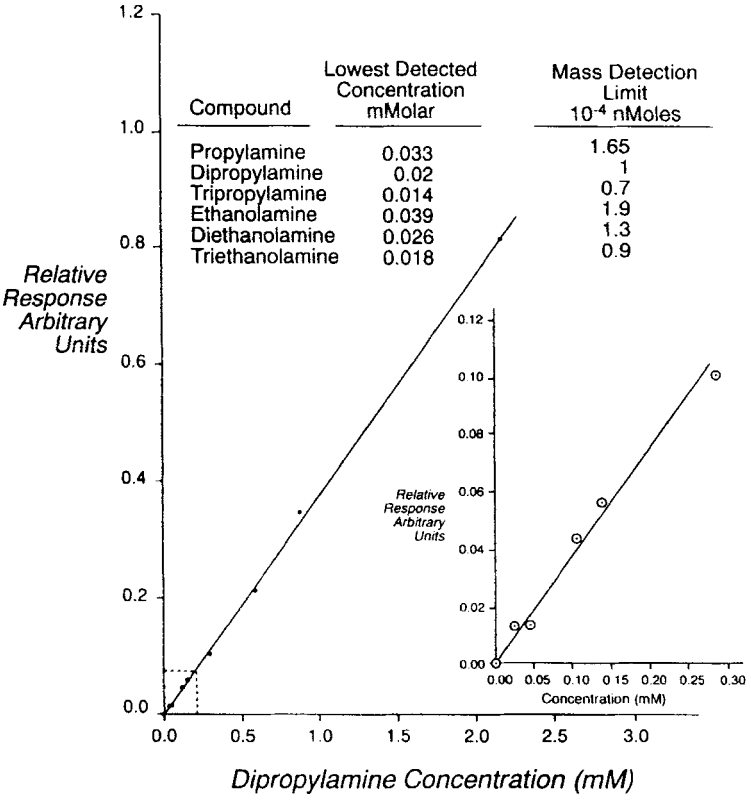


Figure 2. Relative response is a linear function of analyte concentration. Relative responses (corrected area of analyte peak divided by corrected area of internal standard peak) are plotted as a function of the analyte concentrations injected into the capillary. Upper inset gives results for the indicated compounds in similar experiments. Inset at lower right shows enlargement of the plot near the origin surrounded by the dotted line.

The inset in the lower right corner of Figure 2 shows an enlarged plot of that portion of the main figure (dotted outline) representing concentrations of analytes from 0.02 mM to 0.1 mM. Linear regression analyses on data sets like that of Figure 2 gave correlation coefficients (R^2) in excess of 0.99. In the upper inset of the figure are results for six of the organic compounds studied here. Similar analyses were conducted for all of the compounds listed in Table 1, where the slopes of the regressions are given. The detection limit was about 1.5 ppm without preconcentration.

Migration Time and Electrophoretic Mobility Correlations

The electrophoretic mobilities of the organic compounds were calculated from the observed migration times taken directly from data like those presented in Figure 1 and are listed in Table 1. The intrinsic mobility of the internal standard, tetrabutylammonium ion, in these experiments was 1.81×10^{-4} $cm^2V^{-1}s^{-1}$ and varied less than 1% between experiments. In contrast, the value of μ_{eo} in these experiments was quite variable. In a typical experiment, the data permitted 15 determinations of the mobility imparted by the EOF. The average of these was 3.50 with a standard deviation of 0.45.

The mobilities calculated for the organic amines were in accord with expectations, which follow from the basic equation describing electrophoretic mobility:

$$\mu_e = q/(6\pi\eta r)$$

where μ_e = electrophoretic mobility
q = ion charge
η = solution viscosity
r = ion radius.

The relationship predicts that small, highly charged species would exhibit high mobilities and that large, minimally charged species would exhibit low mobilities.[59] In some cases, the radius must include the solvation sphere of the ion. Figure 3 presents a plot of the reciprocal of the Stokes' radius, based on the empirical formula $1/(m/z)^{0.7}$,[68] of the organic compounds listed in Table 1 as a function of their calculated electrophoretic mobilities. This plot suggests a qualitative inference may be possible in predicting the m/z value of an unknown amine whose mobility falls on the curve between known compounds. The data point representing the ammonium ion (μ_e = 5.8) fell well off the curve, suggesting that the computation used for the organic amines underestimated the effective radius of this ion. These data represent an extension of previous studies to a larger data set of aliphatic amines of environmental interest.

The ionic radii for several inorganic cations (potential interferences to indirect detection of aliphatic amines) can be plotted as a function of their calculated electrophoretic mobilities (not shown). For these ions, the mobility increased with increasing ionic radius.

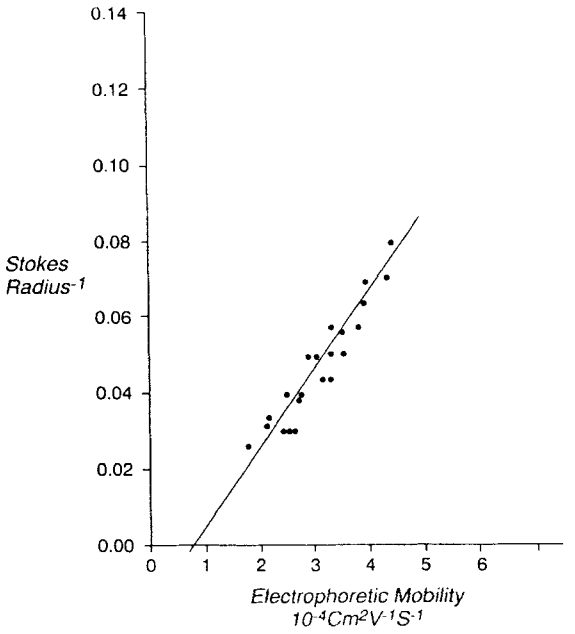


Figure 3. Electrophoretic mobility of several organic amines as a linear function of the reciprocal of their Stokes' radii $[1/(m/z)^{0.7}]$. The mobilities listed in Table 1 are plotted as a function of this parameter for each of the listed compounds. The point lying well off the curve (mobility=5.8) represents the ammonium ion.

One explanation for this, offered by Harned and Owen[60] is that relatively small ions of high charge density would be expected to exhibit relatively large hydration spheres. With increasing radius of given ions, both the hydration number and the radius of the hydration sphere decrease.[61]

Theoretical Plate Number and Efficiency of Separation

The efficiency of separations attainable with electrophoretic methods is determined by a combination of at least two factors. The first is the effective mobility (μ_e), which is determined by charge, size, and resistance to flow of an analyte. The second is dispersion of the analyte ion, which determines the zone length.[59] Dispersion in CE is often dominated by longitudinal diffusion and depends on the molecular diffusion coefficient (D), which can be determined under CZE conditions.[62] Dispersion, or zone length, is also dramatically

influenced by the length of the injection plug and, in the indirect detection method described here, by the difference between the electrophoretic mobility of the analyte and the electrophoretic mobility of the background ion itself, according to the Kohlrausch regulating function.[47,59] Dispersion will be minimal when the mobilities of both the analyte and the background ion are equal or nearly so.[47,63] With indirect detection, peak broadening will increase as the concentration of the analyte approaches that of the background ion.[64] Zone length or broadening of the peak in an electropherogram may be quantified by calculating the plate number according to:

$$N = 5.545\ (t/w_{1/2})^2$$

where t = migration time in seconds

$w_{1/2}$ = peak width, in seconds, at half height

Plate counts of the order of 300,000 are quite satisfactory.[63,65] Zone broadening relative to the concentration of analyte is negligible when the analyte concentration is two orders of magnitude below that of the background ion.

In the work reported here, we have noted the previously observed inverse relationship between theoretical plate number and analyte concentration at constant injection volume. These observations are presented in Figure 4, where the reciprocals of the calculated theoretical plate numbers are plotted as a function of the concentrations of injected tripropylamine solutions. The linear relationship thus obtained permitted extrapolation to infinite dilution of the analyte. From the intercept on the ordinate, we inferred the theoretical plate number at zero analyte concentration. Data for tripropylamine are presented in the figure, and from the ordinal intercept a maximal plate number of 2.22×10^5 was obtained.

Similar plots were prepared for each of the compounds listed in the inset (Fig. 4). As shown, these plate numbers were of the order of 2 to 4 x 10^5, and were comparable to those reported by Gross and Yeung[64] and indicate satisfactory efficiencies.

Maximal theoretical plate numbers were calculated for these compounds based on an assumed value for diffusion coefficients of the order of 1×10^{-5} cm^2s^{-1}. These values were found to vary between 1.8 and 2.9 x 10^6 plates. The plate numbers measured and reported here (1.8 to 3.5 x 10^5) represented 10%

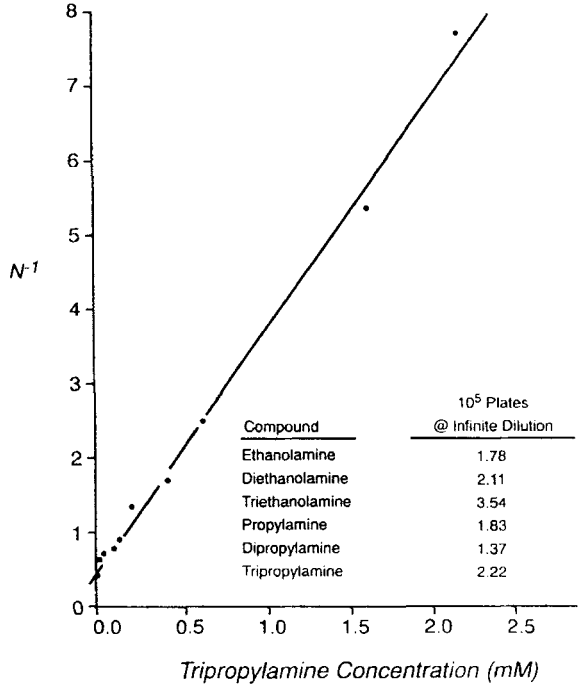


Figure 4. Theoretical plate number at infinite dilution. The concentration of analyte injected into the capillary is plotted as a function of the reciprocal of the theoretical plate number observed at that concentration. Extrapolation to zero concentration permits inference of maximal theoretical plate number at infinite dilution. The inset provides results from similar plots obtained with the indicated compounds.

of the maximally attainable efficiency. It is likely that the size of the injection plug employed in these studies (5 nL, about 10 times the size calculated to give 5% broadening) also accounted for a considerable fraction of the reduction from the maximum attainable efficiency.[59]

Figure 5 shows the importance of migration time and illustrates the difficulty in achieving separation of analytes with similar Stokes' radii (cf Fig. 3) and therefore similar electrophoretic mobilities. Butylamine and diethylamine were not separated when run together in buffer with 5.0 mM imidazole as the background ion since their mobilities differ by only 1.2%. Tripropylamine and dibutylamine, whose mobilities differ by about 3%, were just barely separable in this system. This slight difference may be exploited, and better resolution obtained by electrophoresis, if a background ion is used that

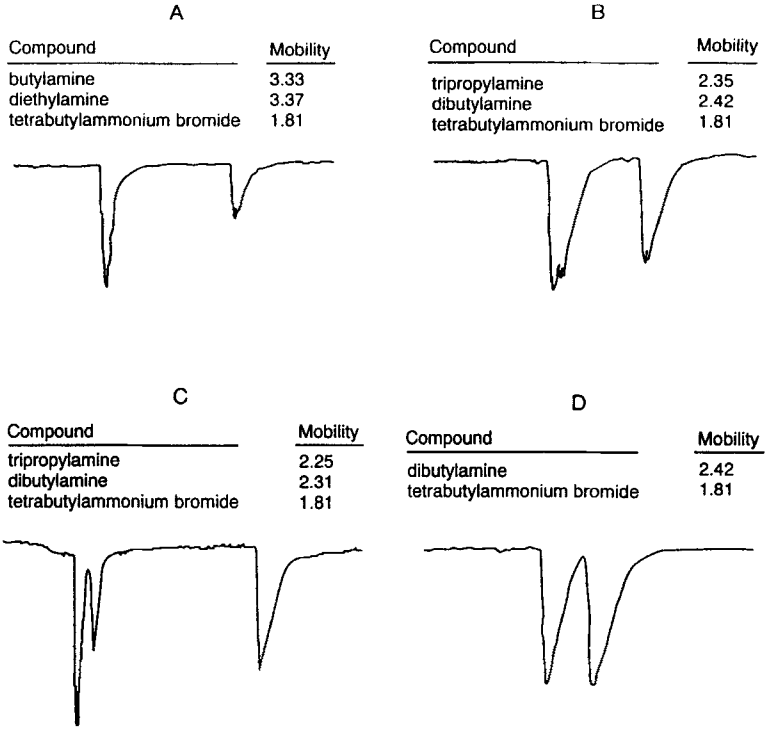


Figure 5. Efficiency of separation depends upon mobility and plate number. Panels A and B show that butylamine and diethylamine are poorly separated and that tripropylamine and dibutylamine are poorly separated in a running buffer consisting of 5.0 mM imidazole at pH 5.0. As shown in panel C, tripropylamine may be separated from dibutylamine by running in buffer consisting of 5.5 mM N-ethylbenzylamine at pH 5.5 and with the detergent POE 20 (2%). Panel D demonstrates that dibutylamine and tetrabutylammonium ion are well separated in either running buffer.

has a mobility more nearly equal to the mobilities of the barely separable pair of analytes. For example, as shown in Figure 5C, when tripropylamine and dibutylamine were run together with N-ethylbenzylamine (pH 5.1, 5.7 mM) as the background ion and in the presence of the nonionic surfactant[57] Tween 20, a considerable improvement in separation was achieved even though no changes in the values of μ_e were observed. The mobilities of dibutylamine and tetrabutylammonium ion differ by 34% and were easily separated in either solvent.

Table 2

Separation of Similarly Migrating Compounds[1]

Compound	Effective Mobility (10^{-4} cm^2 $V^{-1}s^{-1}$)		
	Imidazole (5.0 mM, pH 5.0)	**N-ethylbenzyl amine (5.5mM, pH 5.1)**	**Benzyltriethyl-ammonium chloride (5.0 mM, pH 10.1)**
Tetrabutyl-ammonium ion	1.81	1.81	1.75
Triethanolamine	2.83	N/D	1.75
Dipropylamine	2.76	N/D	2.53
Tipropylamine	2.35	2.35	2.28
Dibutylamine	2.42	2.42	2.29
Butylamine	3.33	N/D	2.23
Diethylamine	3.37	N/D	2.61

[1] See legends of Figure 1 and Table 1.
N/D = not determined.

In Table 2 the results obtained with three buffer systems are compared. Note that triethanolamine and dipropylamine were well separated in benzyltriethylammonium chloride at pH 10.1 but not in imidazole at pH 5.0. Similarly, butylamine and diethylamine were not separated in imidazole but were easily separated in benzyltriethylammonium chloride. These data demonstrate that compounds that are difficult to separate in one electrolyte system may indeed be well separated in another system by taking advantage of slight differences in pK_b values of the target analytes and by optimizing the mobility of the background electrolyte.

This situation is analogous to the recommendation of Terabe et. al. for the separation of weak acids at their respective values of pK_a.[66] To our knowledge, this principle has not been previously applied to the separation of aliphatic amines as shown here.

Addition to the running buffer of nonionic surfactants such as Tween 20 may also enhance resolution of closely migrating analytes. Ionic additives are not recommended in the indirect mode because they may well compete for displacement with the background electrolyte and thereby reduce the response.

Table 3

Recovery of Amines from a More Dilute Aqueous Solution

	------- Percent Recovery[2] -------		
Disk[1]	**Propylamine**	**Dipropylamine**	**Tripropylamine**
1	105	107	108
2	98	112	107
3	96	96	86
4	0	0	0

[1] Empore Bakerbond Octadecyl (C_{18}) extraction disks were prepared following manufacturer's instructions.

[2] The test solution contained per L, 45 μmol of total amines; 150 μmol of dodecylbenzene-sulfonate, sodium salt; and 5.0 mL of methanol. The filtrate from disk 3 was passed through disk 4 to check for amines remaining in solution after the first passage.

Solid Phase Extraction Studies

Experiments were conducted for testing solid phase extraction disks in adsorbing an ion-pairing agent (e.g., decanesulfonate) which would in turn sequester ionized organic amines from aqueous solutions at pH 5.0. These experiments revealed that the recovery of each amine tended to decrease as the volume of applied sample increased. Evidently, the retention of decanesulfonate or the ion pair was insufficient and "wash out" resulted.

Table 3 details an experiment that evaluated sodium dodecylbenzenesulfonate as an ion pairing agent. The average recoveries for propylamine, dipropylamine, and tripropylamine were nearly 100%. The improved recoveries suggest that the adsorbent exhibited a higher affinity for the amine/dodecylbenzenesulfonate than for the amine/decanesulfonate ion pair. The concentration of each amine was 15 μM, just at the limit of detection. The concentration was increased by a factor of 100 by use of the solid phase extraction disk (1 L to 10 mL).

In further efforts to recover propylamines from dilute aqueous solutions, we used experimental cation exchange disks in which the sulfonic acid moieties were chemically bonded to a resin, which in turn was embedded in a Teflon

Table 4

Solid Phase Extraction of Organic Amines from Aqueous Solution: Sulfonic Acid Bonded to Poly(styrenedivinylbenzene) as Cationic Exchange Resin[1]

	Percent Recovery			
Compound[2]	**Sample 1**	**Sample 2**	**Sample 3**	**Average**
Butylamine	49	67	60	59
Dibutylamine	50	66	76	64
Tributylamine	42	58	46	49
Dimethylamine	12	15	23	17
Diethylamine	10	14	18	14
Triethylamine	12	16	20	16
Propylamine	79	85	83	82
Dipropylamine	72	84	78	78
Tripropylamine	74	75	68	72

[1] Cation exchange disks (47-mm, sulfonic acid bonded to poly(styrene-divnylbenzene) copolymer, hydrogen form) were a gift of 3M, New Products Department, St. Paul, MN 55144. Disks were prepared by first washing with acetone, methanol, water, then very dilute H_2SO_4 (2 drops/100 mL), and finally with H_2O until the pH reached5.5. Disks were then eluted with four 5.0-mL protions of 4% NH_4OH in methanol (v/v); and following elution, the disks were regenerated as indicated in the washing procedure.

[2] Samples consisting of 1L, were passed through the disk at a flow rate of approximately 200 mL/min.

matrix. Several analytes were examined (Table 4). The recoveries for propyl-, dipropyl-, and tripropylamine compared well with the best ion-pairing results. Recoveries for some analytes, however, were disappointing. In particular, methylamine and ethylamine were not quantitatively recovered from the disks. Butyl-, dibutyl-, and tributylamine approached quantitative recovery levels, and improvements may result from alternative elution conditions. All analytes were quantitatively sequestered. Recoveries were limited by our inability to elute analytes quantitatively from the disks using the 4% ammonium hydroxide in methanol[5,4] (i.e., the system best suited for indirect detection). To our knowledge, these data represent the first report for the application of these disks for recovery of aliphatic amines.[6,7]

CONCLUSIONS

These results have demonstrated the utility of capillary electrophoresis coupled with indirect UV detection to measure the recovery of organic amines in aqueous solutions using various SPE techniques. The limit of detection was in the range of 0.02 mM. The results obtained showed a linear response over a 150-fold range in concentration for the several amines examined, and also that solid phase extraction could routinely achieve concentration factors on the order of 100-fold or more for selected analytes. The indirect detection mode is, however, the least selective and therefore the most subject to interferences. The indirect mode also imposes severe limitations on the choice of electrolytes, their concentrations, additives, and elution systems for solid phase extraction isolation. These restrictions impose practical limitations on the determination of amines in various matrices and to the levels obtainable. The indirect detection mode does offer broad applicability since primary through quarternary amines can be detected under one set of CE conditions. Future work will need to address cleanup techniques for eliminating interferences from inorganic ions such as the alkali metals and alkaline earths using organic solvents and pH. Additional work will examine selective derivatization for laser-induced fluorescence detection.[67]

NOTICE

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, funded and performed the research described here. This work has been subjected to the Agency's peer review and has been approved as an EPA publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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