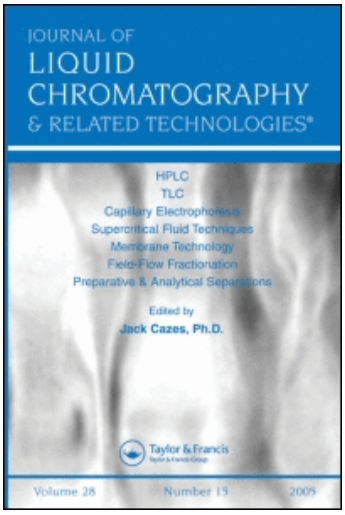

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Race Analysis of Ethanolamine in Water Using Ion Pair Chromatography with On-Line Preconcentration

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TRACE ANALYSIS OF ETHANOLAMINE IN WATER USING ION PAIR CHROMATOGRAPHY WITH ON-LINE PRECONCENTRATION

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ABSTRACT

A simple and rapid method for the determination of ethanolamine in water was developed. The problem of ethanolamine preconcentration was solved by adding octane-1-sulfonic acid (OSA) to the water sample and ion pair was sorbed on the precolumn C18. After flushing ion pair of ethanolamine was desorbed to the analytical column with lower concentration of OSA in mobile phase. Electrochemical detection was used. The limit of the detection at 0.88 V and signal/noise ratio of 5 was about 2 ppb. The mean relative standard deviation was 10% at 10 ppb level.

INTRODUCTION

The sources which discharge ethanolamine into the waste water are varied a numerous. These sources include industrial processes of manufacture of dyes, drugs, plastics and detergents. Ethanolamine has been found to be toxic to most organisms, therefore, legal requirements of many countries are increasing, making it necessary to determine etanolamine at very low level (0.5 mg/litre) [1]. Environmental samples can

have very complex matrices, therefore detection and separation methods are preferred for the determination of ethanolamine.

The widely used method is gas-liquid chromatography of derivate of ethanolamine with flame ionization detection [1,2]. Ion exchange liquid chromatography with photometric or fluorometric detection after derivatization provides an alternative which avoids the necessity for producing a volatile derivate [3-5]. However, the reaction of derivatization and work-up required are time-consuming, and the formation of derivates can be complicated, giving rise to erratic results.

For this reason, we have investigated the development of a sensitive method for the determination of ethanolamine. The method takes advantage of the well-known reaction with octane-1-sulfonic acid (OSA) in mobile phase which proceeds ion pair. The goal of this study is to optimise of composition of mobile phase as well as to introduce a selective enrichment step for ethanolamine from water. The use of solid-phase extraction for this purpose is growing rapidly in popularity in comparison to liquid/liquid extraction or other concentration techniques. The advantage include the speed and selectivity of the solid-phase extraction.

EXPERIMENTAL

The chromatographic system with on-line preconcentration consisted of two pumps (Waters Model 501), a chromatographic column (0.32 x 15 cm) packed with 5 μm particles Separon SGX C18 (Tessek, Prague, Czech republic), an electrochemical detector (Waters Model 460) and a preconcentration column (0.32 x 3 cm) packed with 5 μm particles Separon C18 (Tessek, Prague, Czech republic). The scheme of the LC system is shown in Figure 1. All solvents and the modifiers should be as clear as possible. The flow rate was only 0.5 ml/min because the lower flow rate has the lower noise level at the electrochemical detection.

Before introduction of the sample the preconcentration column was washed with 0.01 M OSA solution. The concentration of OSA in the water sample was adjusted to 0.01 M by addition of solid OSA. The sample is then injected via a loop (0.5 ml) and pumped through the preconcentration column. After flushing ion pair of ethanolamine is desorbed to the analytical column with 0.00076 M OSA in 34% methanol - water. Electrochemical detection was performed with ampermetric detector using carbon electrode. The applied potential with respect to argento-chloride electrode (as reference) was +0.88V.

River water was filtered over a 0.5 μm membrane filter (Millipore type AA). For the recovery experiment the river water was spiked with ethanolamine up to

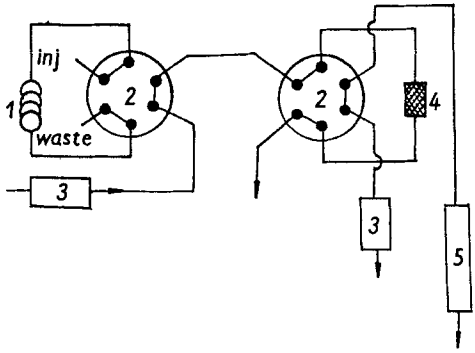

Fig.1. Schematic diagram of the LC apparatus. 1-injection loop (0.5 ml); 2-valve; 3-pump; 4-preconcetration precolumn; 5-analytical column.

concentration 10 ppb. Water solutions for calibration experiments were made starting from 2 ppb to 200 ppb. Preconcentration of 0.5 ml was found possible on 3 x 0.32 cm I.D. preconcentration precolumn without breakthrough.

The quantitative evaluation was based on the regression analysis where the dependence between the area of peak of ethanolamine and the quantity was determined. The linearity range was between 2 and 200 ppb of ethanolamine.

RESULTS AND DISCUSSION

Reversed ion-pair liquid chromatography has become a well established method for the separation of ionic compounds, in which the retention can be regulated by the nature and concentration of organic modifier and ion pair reagent as well as by a competing ion with the same charge as that of the analyte.

To find the optimal composition of mobile phase (contents of methanol and OSA) with the minimal number of measurements, Doehlert matrix design [6] was used. The retention of ethanolamine in ion-pairing reversed phase chromatography was modelled via changing the volume percentage of methanol and concentration of ion-pairing agent octylsulfonic acid in the mobile phase. To fit the second-order polynomial of eq. 1, Doehlert matrix design was employed.

$$\ln(k) = a_0 + a_1 \cdot X_1 + a_2 \cdot X_2 + a_{11} \cdot X_1^2 + a_{22} \cdot X_2^2 + a_{12} \cdot X_1 \cdot X_2 \qquad (1)$$

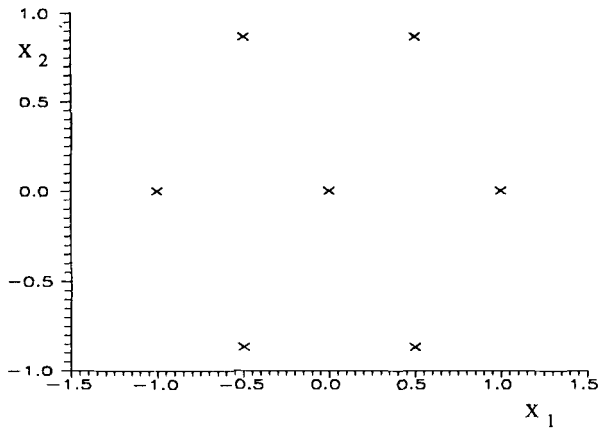

Fig. 2. Doehlert matrix design for two factors X_1, X_2. The experimental points in our procedure are listed in Tab.1.

Tab. 1. Doehlert matrix design for modelling of ethanolamine retention.

Point	Variables in coded units		Variables in original scale	
	X_1	X_2	φ(MeOH) volume fraction	c(OSA) [mol\L]
1	1	0	0.30	0.0010
2	-1	0	0.30	0.0002
3	0.5	0.866	0.45	0.0008
4	-0.5	0.866	0.45	0.0004
5	0.5	-0.866	0.15	0.0008
6	-0.5	-0.866	0.15	0.0004
7	0	0	0.30	0.0006

Tab.2. Analysis of classical residuals.

Point	Response measured $y_{exp[i]}$ {ln(k)	Prediction calculated $y_{calc[i]}$ {ln(k)}	Standard deviation $\sigma(y_{calc[i]})$ [x10^{-8}]	Classical residual [x10^{-8}]
1	1.4400	1.4400	3.9151	2.1653
2	1.3600	1.3600	4.2887	2.0238
3	0.9900	0.9900	3.9151	0.4506
4	2.2700	2.2700	3.8254	2.1535
5	2.4300	2.4300	3.6325	0.4495
6	0.6800	0.6800	2.8954	2.1367
7	0.0700	0.0700	2.5588	0.9876

Residual sum of squares = $1.8393.10^{-15}$

where k is the capacity factor, X_1 is the volume fraction of methanol in the mobile phase, X_2 is the concentration of ion-pairing agent in the mobile phase and a_0, a_1, a_2, a_{11}, a_{22} are parameters of regression function.

Doehlert described how to generate the designs up to at least ten factors [7]. An experiment in two factors (X_1, X_2) may be thought as a point in two-dimensional space. The two factors Doehlert design requires seven experiments (Fig.2).

The results of regression using model in eq.1. are shown in Tab.2. The analysis of residuals shows a very good fit of experimental data. According to eq. 1. the contour plot (Fig. 2) can be constructed.

The contour plot of dependence ln (k) = f {φ(MeOH); c (OSA) } according to eq. 1 is shown in Fig.3. The contour of 1.3 (capacity ratio 3.7) was most available because the symmetrical shape of ethanolamine peak was achieved. From this point of view the concentration of OSA was 0.00076 M in 34% methanol - water. As it can be seen from Fig.3 the value of capacity ratio of ethanolamine is very high at low concentration of methanol and higher concentration of OSA in mobile phase using C18 column. This phenomena was applied to preconcentration of ethanolamine in the precolumn and from this reason OSA must be added to the water sample before injection.

Figs. 4 and 5 show the chromatograms after preconcentration of 0.5 ml spiked and unspiked river sample. It was not observed the river water contained a trace amount of ethanolamine. From this reason, the river water was spiked with ethanolamine such

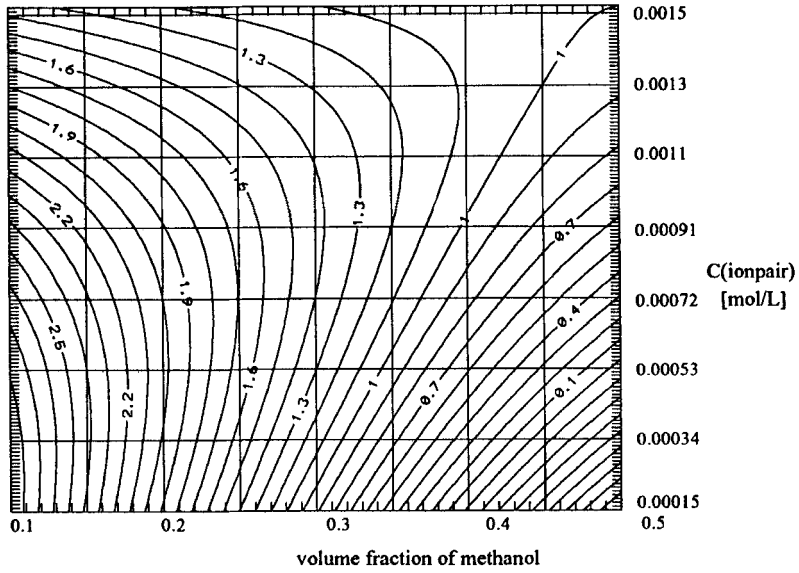

Fig.3. The contour plot of dependence ln(k) = f {φ(MeOH); c (OSA)} according to eq.1.

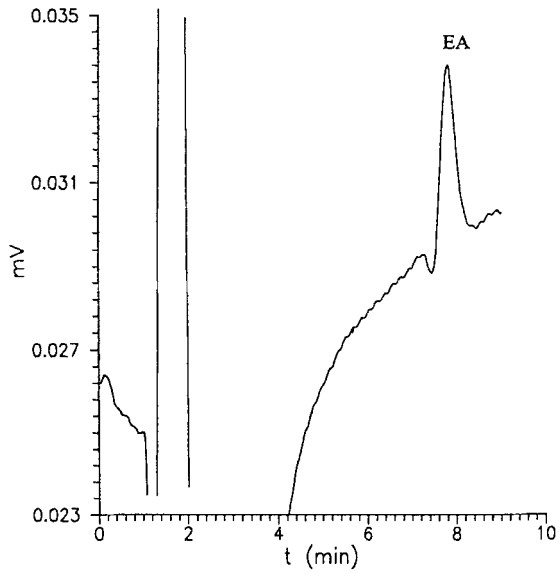

Fig.4. Chromatogram of the spiked river water (10 ppb) after on-line preconcentration (sampling volume 0.5 ml). Chromatographic column Separon SGX C18. Flow rate was 0.5 ml/min., mobile phase - see experimental part, ampermetric detection at +0.88V. EA - ethanolamine

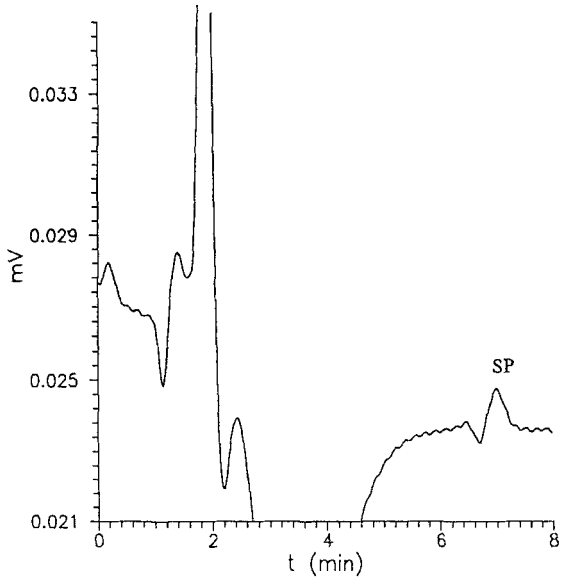

Fig.5. Chromatogram of the unspiked river water after on-line preconcentration (sampling volume 0.5 ml). For the chromatographic conditions see Fig 4.
SP - solvent peak

that the concentration became 5 ppb to demonstrate the possibility of the method. After the experiments the difference between the peak areas of the unspiked and spiked chromatograms was used to calculate the concentration of ethanolamine. The recovery of solid phase extraction was about 75%.

The selectivity of the preconcentration system allows the LC analysis to be performed within about 15 minutes with a detection limit of 5 ppb. Lowest limit has been determined using a peak area integrator signal-to-noise ratio of five. Triplicate injection of ethanolamine (10 ppb) yielded the relative standard deviation of about 10 %.

The results of this study clearly indicate that OSA is a useful ion pairing agent for chromatographic separation of ethanolamine. The work also demonstrates the effectivity of Doehlert matrix design for the optimization of mobile phase composition in ion pair chromatography.

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