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Determination of Ethanolamines in Industrial Waters by Cation-Exchange Chromatography

INTRODUCTION

Ion chromatography has been successfully used to determine amines in a variety of chemical, petrochemical, and environmental applications.^{1,2} However, analysis of some samples can be hampered by large concentrations of one or more amines, which makes the determination of trace concentrations of other amines and cations difficult. The unique selectivity of the IonPac[®] CS11 column with an isocratic methanesulfonic acid (MSA) eluent addresses many of these challenging analyses. This Application Update describes the setup and performance of this method.

EQUIPMENT

Dionex DX-500 Ion Chromatography system consisting of:

- GP40 Gradient Pump, microbore configuration
- CD20 Conductivity Detector with a temperature-controlled conductivity cell (DS3)
- LC20 Chromatography Enclosure, PEEK, with one Rheodyne valve

4-L Plastic bottle assemblies (two for external water mode)

PeakNet Chromatography Workstation

Ion Chromatography Acrodisc[®] filters, 13 mm, 0.2- μ m pore size (Gelman Sciences, P/N 4483) (optional)

CONDITIONS

Column: IonPac CS11 Analytical,
2 x 250 mm (P/N 43127)
IonPac CG11 Guard,
2 x 50 mm (P/N 43128)

Eluent: 35 mM Methanesulfonic acid (MSA)

Flow Rate: 0.25 mL/min

Temp: Ambient

Inj. Volume: 2.5 μ L

Detection: Suppressed conductivity

Suppression: CSRS[®]-II, external water mode, 100 mA

PREPARATION OF SOLUTIONS AND REAGENTS

Standard Solutions

Dissolve the corresponding mass of the compound for each of the cations of interest (see Table 1) in 1000 mL of deionized water. Standards are stable for at least one month when stored at 4 °C.

Table 1 Masses of compounds used to prepare 1 L of 1000 mg/L cation standards

Cation	Compound	Weight (g)
Li ⁺	Lithium chloride (LiCl)	6.109
Na ⁺	Sodium chloride (NaCl)	2.542
K ⁺	Potassium chloride (KCl)	1.907
NH ₄ ⁺	Ammonium chloride (NH ₄ Cl)	2.964
HOCH ₂ CH ₂ NH ₃ ⁺	Ethanolamine (HOCH ₂ CH ₂ NH ₂), 99%	1.010
(HOCH ₂ CH ₂) ₂ NH ₂ ⁺	Diethanolamine [(HOCH ₂ CH ₂) ₂ NH], 99%	1.010
(HOCH ₂ CH ₂) ₃ NH ⁺	Triethanolamine [(HOCH ₂ CH ₂) ₃ N], 99%	1.010
(HOCH ₂ CH ₂) ₂ NH ⁺ CH ₃	N-Methyldiethanolamine [(HOCH ₂ CH ₂) ₂ NCH ₃], 99%	1.010

Working Standard Solutions

Dilute each analyte to the required concentration with deionized water using the 1000 mg/L standards prepared above. Working standards containing less than 100 mg/L cations should be prepared daily.

1 M Methanesulfonic Acid (MSA)

Carefully add 96.10 g of methanesulfonic acid (MSA), 99%, to a 1-L volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly. Fluka or Aldrich brand MSA (> 99% pure) is recommended.

35 mM Methanesulfonic Acid (MSA)

Pipette 35.0 mL of the 1.0 M MSA eluent concentrate into a 1-L volumetric flask containing approximately 500 mL of deionized water. Dilute to 1 L using deionized water. Transfer to an eluent reservoir. Vacuum degas the eluent by placing the filled reservoir in a sonicator and drawing a vacuum for 5–10 minutes.

SAMPLE PREPARATION

For matrices with high concentrations of amines, samples should be diluted to a range where the column capacity will not be exceeded. (For procedures to determine column capacity, see Dionex Technical Note 8 “The Use of Concentrator Columns in IC”.) Samples that contain high amounts of particulate matter should be filtered with filters that will not contribute significant amounts of the analytes of interest. For this work, Gelman Ion Chromatography Acrodisc filters were found to be suitable.

SYSTEM PREPARATION AND SETUP

Connect the columns and suppressor in the IC system by using 0.005-in. (0.125-mm) i.d. tubing. Keep the lengths as short as possible to minimize system void volume and to ensure efficient 2-mm operation. Carefully use a razor blade or plastic tubing cutter so that surfaces of the tubing cuts have straight and smooth edges. Irregularity on the surface of a tubing end can result in unwanted dead volume. Construct a 2.5- μ L sample loop with 7.74 in.

(19.7 cm) of 0.005-in. (0.125-mm) internal i.d. PEEK tubing (1 cm = 0.127 μ L). Establish a blank by loading deionized water as a sample to verify that there is no significant amine or cationic contamination.

RESULTS AND DISCUSSION

A representative separation of monovalent cations and four amines of interest is shown in Figure 1. The eluent is 35 mM methanesulfonic acid at a flow rate of 0.25 mL/min. Under these conditions, there is good separation between diethanolamine (DEA), triethanolamine (TEA), and *N*-methyldiethanolamine (MDEA), facilitating the analysis of matrices with excess concentrations of these amines. This is illustrated in the analysis of a diluted refinery waste water sample, as shown in Figure 2.

To verify proper quantification of analytes in such a matrix, increasing concentrations of three different amines were added into samples of 150 mg/L MDEA and 150 mg/L of DEA. Spikes of 0.1, 0.3, 1.0, 3.0, and 10 mg/L of DEA and MEA and 1.0, 3.0, and 10 mg/L of TEA in 150 mg/L MDEA yielded coefficients of determination (r^2) values greater than 0.998. Spikes at 0.3, 1.0, 3.0, and 10 mg/L of MDEA and TEA and at 1.0, 3.0, 10, and 30 mg/L for MEA in 150 mg/L DEA also yielded r^2 values greater than 0.998.

Detection limits for this method are summarized in Table 2. If sensitivity below these levels is required, the injection loop size can be increased. However, it is important to make sure that the capacity of the column is not exceeded.

PRECAUTIONS

Divalent cations, such as calcium and magnesium, cannot be determined with this method. If these cations are present in samples, they will concentrate on the column and take up cation-exchange sites, thus reducing the capacity. To elute retained divalent cations, it is advisable to always have the system on. In this way, the retained divalents will, with time, be eluted from the column. Another approach would be to periodically run a 100 mM methanesulfonic acid eluent for one hour as a clean up step.

Table 2 Method detection limits for amines

Amine	MDL* [mg/L (ppm)]	Matrix
Ethanolamine	0.055	150 mg/L Methyl-diethanolamine
Diethanolamine	0.15	150 mg/L Methyl-diethanolamine
Triethanolamine	1.1	150 mg/L Diethanolamine
<i>N</i> -Methyl-diethanolamine	0.062	150 mg/L Diethanolamine

* Based on a signal-to-noise ratio of 3 using a 2.5- μ L sample loop.

REFERENCES

- Jensen, D. *LABO Analytica*. **1992**, 92, 64–74.
- Weiss, J. *Ion Chromatography*, 2nd Ed., VCH, Weinheim, Germany, 1995, 182–185.

LIST OF SUPPLIERS

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Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, P.O. Box 355, Milwaukee, Wisconsin, 53233, USA. Tel.: 1-800-558-9160.

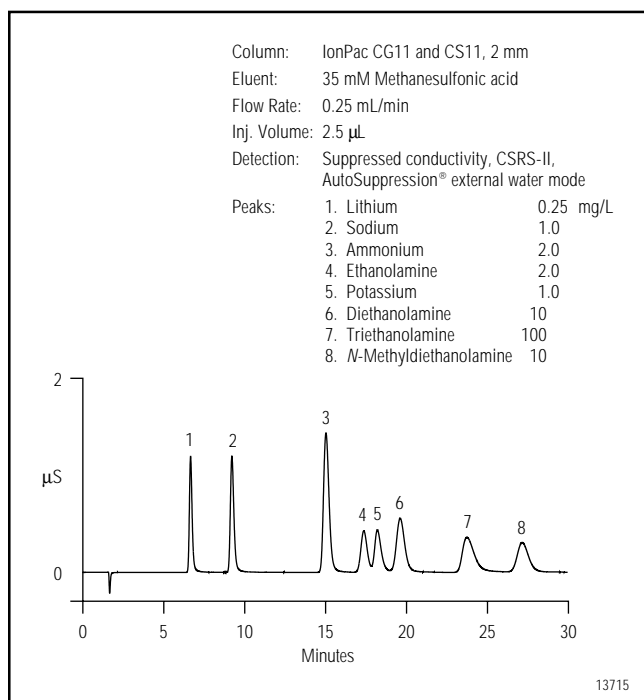


Figure 1 Isocratic separation of ethanolamines and the monovalent cations on the IonPac CS11 column.

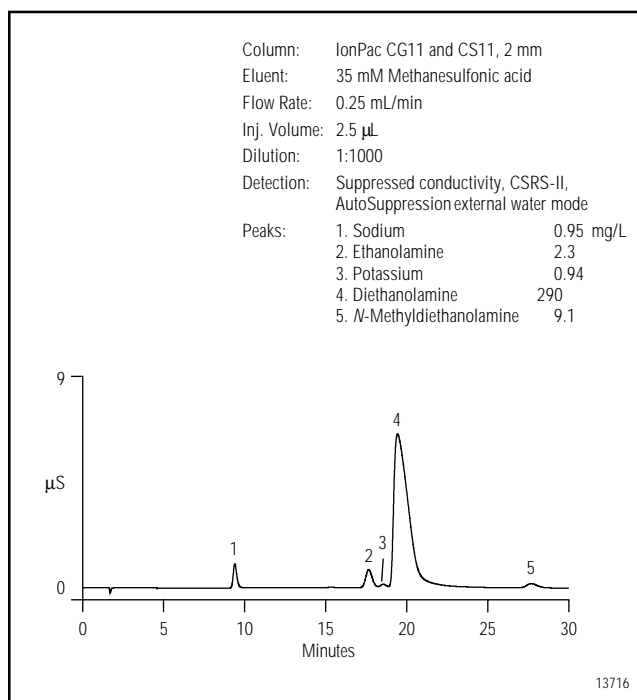


Figure 2 Analysis of refinery waste water using the IonPac CS11 column.

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