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Collection of Ethanolamines in Air and Determination by Mobile Phase Ion Chromatography

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A method is described for the collection and determination of monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) in air. Samples were collected by pulling air through a glass tube containing alumina, cleaned especially to remove interfering inorganic ions. The ethanolamines were desorbed with water and determined by Mobile Phase Ion Chromatography (MPIC). The recovery and total relative precision for MEA, DEA and TEA — all collected from air at a flow rate of 100 mL/min for 7 hr — was 93.1 ± 17%, 92.7 ± 15% and 89.4 ± 21%, respectively (95% confidence level). The method was validated for all three compounds from approximately the limit of detection (3 × noise) to ten times the limit of detection. Based on a sample size of 42 L, MEA was validated over the range from 0.12 to 3.0 ppm v/v (TLV®=3), DEA over the range from 0.25 to 3.3 ppm v/v (TLV=3) and TEA from 0.31 to 3.7 ppm v/v (no TLV assigned). No effect on recovery was observed when sampling at high humidity or on storage of the samples for up to 31 days.

Introduction

Ethanolamines are used widely in the chemical industry in applications such as chemical intermediates, coatings, plasticizers, detergents, cosmetics and pharmaceuticals. The acute industrial hazards associated with the production and handling of ethanolamines are skin and eye irritation.[1] The exposure guideline for both monoethanolamine (MEA) and diethanolamine (DEA) is a TLV of 3 ppm v/v while no TLV has been set for triethanolamine (TEA) at this time.[2] A sensitive and specific method for the determination of ethanolamines and isopropanolamines was published in 1980.[3] In this method, alkanolamines are collected from air on alumina sampling tubes and desorbed with aqueous 1-octanesulfonic acid. The extract is freeze-dried, derivatized and analyzed by gas chromatography. Although this method is sensitive and necessary for complex mixtures, it is time intensive and may not be necessary for many less complex samples. A rapid procedure for the direct analysis of the alumina extract is described here. If further sensitivity or specificity is needed, then the derivative/GC method can be used on the remaining extract.

Experimental

Apparatus

Detector: WESCAN conductivity meter, Model 212, and a Model 219-200 microcell.

Recorder: Sargent-Welch, Model SRG-2.

Separator: Mobile Phase Ion Chromatographic (MPIC) column: (4) MPIC-NSI #35321, available from Dionex Corp., Sunnyvale, CA 94086.

Guard column: MPIC-NG1 #35320, available from Dionex.

Suppressor: 4 × 240 mm AG1-X10, 200-400 mesh in the borate form. The suppressor was prepared from AG1-X10 resin in the chloride form (BIO-RAD Laboratories, Richmond, Calif.). First, it was converted to hydroxide form with 0.8N NaOH at about 1 mL/min for 1 hr. After the column was rinsed with deionized water until the effluent was neutral to pH paper, the column was converted to borate form with 0.5M H_3BO_3 at 1 mL/min for 1 hr. The column was rinsed with deionized water for about 20 min before use.

Mobile Phase: 0.005 M hexane sulfonic acid in water at 1.0 mL/min flow rate.

Injection Valve: Rheodyne, Model 7125, Liquid Chromatographic Injection Valve.

Sample Loop Size: 200 μL.

Temperature: Ambient.

The apparatus was set up in the normal liquid chromatographic configuration: injection valve, guard column, analytical column, suppressor and detector. The detector was connected to a recorder with an adjustable range control.

Reagents

Reagent-grade materials were used to prepare standards and experimental samples. The aqueous solutions of ethanolamines used to prepare the samples were prepared every day from a high concentration mixed standard in deionized water, which contained 9000 ppm MEA, 36 000 ppm DEA and 71 000 ppm TEA. This mixed standard was stored in a refrigerator and was used for up to two weeks. Microliter aliquots (10-15 μL) were injected into alumina tubes to prepare experimental samples with the desired amounts of ethanolamines. Standards, which were prepared by diluting the original mixed standard with deionized water, were used to prepare experimental samples containing low amounts of ethanolamines. The concentrations of the diluted standards were such that the aliquots added into the alumina tubes were not more than 20 μL in any of the prepared samples. The standards used for the analysis of amines were

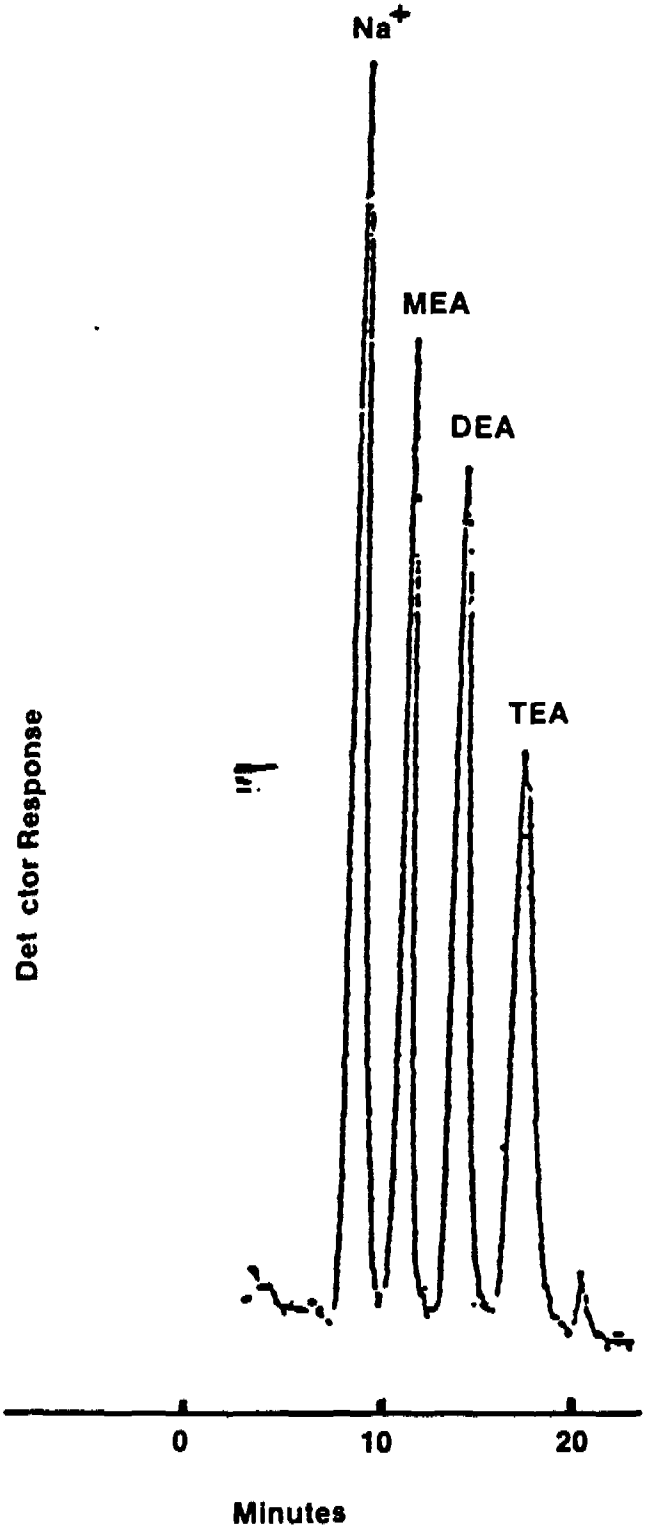

Figure 1 — Typical Chromatogram of an Experimental Sample Containing 75 ppm Monoethanolamine (MEA), 160 ppm Diethanolamine (DEA), and 250 ppm Triethanolamine (TEA). Sensitivity 120 μ Siemens Full Scale.

prepared from the same high concentration standard diluted with aqueous alumina extract (same ratio of alumina to water as used to extract the sample) to simulate the background of the samples. The mobile phase was prepared by the dilution of 50 mL of 0.1 M hexane sulfonic acid (available from Dionex) to 1 L with deionized water.

The 20/40 mesh alumina (obtained in bulk from SKC, Inc., Eighty Four, Pa.) was cleaned to remove interferences prior to its use; the following procedure was used: approximately 100 g of alumina was added to a 1000 mL beaker containing about 800 mL of deionized water. The beaker was placed on a hot plate, and the alumina was extracted with the water boiling for about 15 minutes. The hot water was decanted, and the alumina was washed several times with deionized water. This entire cleaning procedure was repeated for a total of three times, and alumina was filtered and reactivated in an oven at about 150° C for about three hours. Adsorbent was stored in sealed jars.

Disposable glass pipettes (approx. 5 mm × 10.5 cm) with the tips removed were used to prepare the sampling tubes. The cleaned and activated alumina was packed into the glass tube to form a back section (2.7 cm) and a front section (5.3 cm) separated and retained by glass wool. The tubes were approximately equivalent in size to the SKC tubes (Catalog No. 226-18), which had been used in the published gas chromatographic method.[3] In that prior work, no breakthrough is observed for concentrations of MEA, DEA and TEA up to 12 ppm (v/v) in the presence of 100% relative humidity.[3]

An atmosphere generation system to produce a clean stream of humidified air was used to prepare laboratory experimental samples for collection efficiency studies, storage studies, and for a study to investigate the effect of humidity on recovery and breakthrough.[5] Then, known amounts of the aqueous ethanolamine standards were injected directly into the front section of the alumina tube, and the conditioned air (31% and 92% relative humidity at 23 ± 2° C) was pulled through at 100 mL/min for 7 hr. Some of the samples were stored at room temperature and some refrigerated (4° C) for periods up to 31 days.

Analysis

The alumina from the front and back sections of the collection tubes was placed in separate vials. A mechanical shaker was used for about 45 min to extract the front section with 10 mL of deionized water and the back section with 5 mL of water. Approximately 5 mL of the extract was filtered with a 0.45 μm pore size Gelman ACRODISC-CR filter into a vial (precleaned with dilute hydrochloric acid). Ethanolamines were determined in this filtered solution with the instrumental conditions described in the Apparatus Section. Figure 1 shows a chromatogram of an experimental sample. Peak height of each component was used to determine the concentrations in the extract by comparison to a standard with a concentration close to the concentration of the sample or by use of a calibration curve. Calibration curves were linear over the range tested.

From the total amount of each component found, the concentrations in air can be calculated from the following equation:

TABLE I
Summary of Recovery Data

Compound	Range (μg/sample)	(ppm v/v)[A]	% Recovery 92% RH (n=16)	% Recovery 30% RH (n=9)	% Recovery 31 day storage (n=9)	verall Recovery (n=34)	% Total Relative Precision (6) (95% CL)
MEA	13-317	0.12-3.0	92.1 (10)[B]	92.6 (4.6)	96.4 (8.3)	93.1 (8.1)	± 17.2
DEA	45-600	0.25-3.3	90.6 (6.7)	98.6 (3.4)	90.4 (6.3)	92.7 (6.8)	± 15.0
TEA	79-940	0.31-3.7	89.3 (11.3)	92.0 (7.4)	87.9 (11.1)	89.4 (10)	± 21.0

[A]Based on a 42-L sample
[B]Standard deviation in parenthesis

$$\text{ppm (v/v) ethanolamine} = \frac{\mu\text{g found} \times 24.45}{\text{volume of air (L)} \times \text{molecular weight of ethanolamine}}$$

Results and Discussion

It is known from a previous publication that alkanolamines can be collected in alumina sampling tubes.[3] In that previous work, ethanolamines and isopropanolamines are collected on alumina tubes (100 mL/min for 7 hr) and the recovery for MEA, DEA and TEA is shown to be 90% with no breakthrough observed. The samples are desorbed with aqueous 1-octanesulfonic acid, lyophilized and derivatized prior to gas chromatographic analysis.

Advancement of liquid chromatographic technology for these types of compounds led us to believe that a more rapid and less complex procedure could be developed. Mobile Phase Ion Chromatography (MPIC) appeared to have potential for the separation and quantitative determination of ethanolamines.[4] The technique used a hydrophobic column without permanently attached ion exchange sites. The eluent contained an organic anion (hexane sulfonic acid), which adsorbed reversibly to the bed to create ion exchange sites that differentially retarded cations for chromatographic resolution.

The collection properties of alumina are well established in an earlier gas chromatographic publication;[3] however, because water is the most suitable desorbing solvent for ion chromatography, it was necessary to determine if ethanolamines could be desorbed quantitatively from alumina when only water was used. Also, it has not been known if inorganic ions such as Na^+, K^+, Mg^{++}, Ca^{++}, *etc.* (which may be present in the alumina) would interfere with the determination of ethanolamines. Preliminary tests indicated that the extraction efficiency of water was satisfactory; however, it was found that high concentrations of sodium can interfere with the determination of monoethanolamine (MEA), and depending on the amount, with the determination of diethanolamine (DEA). Also, an unknown ion (probably Ca^{++}) eluted after 90-110 min (depending on the flow rate used). Successive peaks of this unknown — the result of several previous sample injections — interfered with the determination of the ethanolamines. Cleaning of the column with extensive elution was needed before any other analyses could be performed. This problem was solved by employing the cleaning procedure described in the Experimental Section in order to remove the interfering water soluble inorganic salts from the alumina collection adsorbent. Recoveries of approximately 90% for the ethanolamines in all samples were obtained.

No bias was observed for any of the compounds with regard to concentration or humidity even for samples stored at room temperature for 29 days or refrigerated (4° C) for up to 31 days. No breakthrough was observed for any of the compounds, and it is probable that larger volumes or higher sampling rates may be used. For example, a 10- to 15-min excursion sample collected at 500 mL/min should be sufficient to determine the ethanolamines at TLV concentrations or greater.

Ammonia elutes at about 9.2 min, just ahead of MEA. Depending on the concentration, separation can be achieved. Monomethylamine (10.2 min) interferes with the determination of MEA. Dimethylamine (12.2 min), if present can interfere with the determination of DEA. Trimethylamine (14.7 min) at high concentration may interfere with the determination of TEA. Ethylamines also may interfere; however, no attempt was made to verify the extent. The overall recovery and total relative precision at 95% confidence level for MEA, DEA and TEA are summarized in Table I. Total relative precision is a term which includes the precision of a single sample analysis, the precision of determining the recovery value and the estimated precision of the sampling pump (±5%).[6]

Conclusions

Ethanolamines can be collected on a collection tube containing precleaned 20/40 mesh alumina at a flow rate of 100 mL/min for 7 hr and analyzed by MPIC. Samples can be stored for 29 days at room temperature or refrigerated (4°C) for up to 31 days. The recovery and total relative precision at the 95% confidence level (assuming ± 5% pump error) for MEA, DEA and TEA are 93.1 ± 17%, 92.7 ± 15%, and 89.4 ± 21% respectively over a range of approximately 1/10 TLV to 1 TLV. Other amines, such as methylamines, may interfere if present. The derivative gas chromatographic procedure can be used to analyze the sample extract if more sensitivity or specificity is needed.[3]

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