Gas-chromatographic determination of airborne monoethanolamine using reagent-coated adsorbent tubes*

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Summary. A sampling and analytical procedure was developed for the monitoring of airborne monoethanolamine (MEA). The analyte is collected by drawing air through the adsorbent tubes containing XAD-4 resin coated with cyclohexanone as a derivatising reagent. Derivatisation takes place during sampling. After desorption with methanol, the MEA derivative was quantified by gas chromatography using a thermionic specific detector (TSD) in the nitrogen mode. Application of cyclohexanone as a derivatising reagent gives a more stable product and TSD allows subsequent GC analysis in the presence of excess reagent. The structure of the MEA derivative was confirmed by mass spectrometry. The lower limit of detection for MEA was 1 μg and the detector response was linear between 5 and 200 μg. The working range of the method is 0.5 to 20 mg/m³ in a 10 l air sample. Collected samples were stable for at least 2 weeks at 4 °C and room temperature. The efficiency of sampling was evaluated using a Test Atmosphere Generation System.

Introduction

Monoethanolamine (MEA), also known as 2-aminoethanol, is a reactive, bifunctional compound, combining the properties of an alcohol and an amine. MEA is widely used in the chemical industry in applications such as chemical intermediates, coatings, plasticizers, detergents, emulsifier in cosmetic formulations, thickener, wetting agent, and alkalisising agent.

The acute industrial hazards associated with the production and handling of MEA are skin and eye irritation [1, 2]. The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a threshold limit value for an 8-h time-weighted average (TLV-TWA) of 7.5 mg/m³ (3 ppm) for MEA [3].

Several non-selective methods are available for the determination of MEA in air [4, 5], but a chromatographic procedure provides the best selectivity and sensitivity. Since direct chromatographic determination of the free monoethanolamine is difficult, most methods employ derivatisation.

MEA in air has been collected on alumina sampling tubes, derivatised with 1-(heptafluorobutyryl)-imidazole and separated by a gas-chromatographic technique using a flame-ionisation detector (FID) [6]. A simplified version, using ion chromatography (IC) without derivatisation, has also been developed [7]. The National Institute of Occupational Safety and Health (NIOSH) recommends silica gel for the collection of MEA in the workplace, desorption with methanol, followed by reaction of MEA with benzaldehyde forming N-benzylidene-2-aminoethanol, and then quantification employing GC-FID [8]. This sampling and analytical method is cumbersome and requires the addition of concentrated hydrochloric acid to the tubes immediately after sampling to stabilise the analyte and alkalisisation of the sample before derivatisation reaction.

None of the above sampling methods utilised in situ derivatisation to stabilise the analyte. Attempts have been made to use the 1-naphthylisothiocyanate-coated sorbent for the collection and derivatisation of monoethanolamine and diethanolamine in air, followed by high-performance liquid chromatography analysis [9].

But the present authors found this sorbent to be impractical because of the problems encountered in the separation of the excess reagent and the instability of the coating materials towards the passage of air through the tubes.

This paper describes a highly sensitive and specific sampling and analytical procedure for the determination of airborne MEA. It is based on the derivatisation and stabilisation of MEA by its reaction with cyclohexanone in situ during sample collection, which results in the formation of the stable and non-volatile Schiff's base (Fig. 1). The analyte is collected by drawing air through the solid sorbent sampler containing XAD-4 resin coated with cyclohexanone. After desorption with methanol, the MEA derivative is quantified by gas chromatography using a thermionic specific detector (TSD), which is not sensitive to the excess of the derivatising reagent.

The efficacy of the cyclohexanone-coated XAD-4 sorbent as a collecting medium and a derivatising agent was established by conducting tests on a Test Atmosphere
H₂N-CH₂-CH₂-OH + \( \xrightarrow{60^\circ C} \) \( \xrightarrow{60^\circ C} \) \( \xrightarrow{60^\circ C} \) H₂N-CH₂-CH₂-OH + H₂O

Fig. 1. Derivatisation reaction of MEA with cyclohexanone

Generation System (TAGS), which simulates real-life sampling conditions.

Application of reagent-coated sorbents provided the stabilisation of the reactive analyte, increased the yield of the derivatisation reaction through the use of excess of the coating material and enhanced the sensitivity of the analysis by employing nitrogen specific detection.

Experimental

Reagents

Monoethanolamine, cyclohexanone and Amberlite XAD-2 and XAD-4 resins were supplied by Aldrich (Milwaukee, WI, USA).

All solvents were of glass-distilled quality and purchased from Caledon Laboratory (Georgetown, Ontario, Canada).

Apparatus

A Hewlett-Packard (HP) Model 5890A gas chromatograph, equipped with a thermionic (nitrogen-phosphorus) specific detector (TSD), a Model 3396A integrator, and a Model 7672A autosampler were used for GC. Mass spectra were obtained on an HP Model 5985 gas chromatograph—mass spectrometer, equipped with an HP 7920 data system. The sampling tubes and the portable air-sampling pump Aircheck Sampler Model 224-PCXR3 were from SKC (Eighty Four, USA).

The Test Atmosphere Generation System (TAGS) was from SRI (Menlo Park, CA, USA). It could generate multiple (up to 12) uniformly loaded samples from a dynamically generated test atmosphere.

Standards preparation and sampling procedure

The reference standards were prepared by adding microliter aliquots of the MEA stock solution to 1 ml of methanol containing 10 µl of cyclohexanone. The vials were capped and allowed to stand for 1 h at room temperature.

The authentic N-cyclohexylidene-2-aminoethanol (CHAQ) standard was prepared by the condensation reaction of 1.6 g of cyclohexanone with 1.0 g of monoethanolamine in 30 ml of benzene [10]. The mixture was allowed to reflux under a Dean & Stark continuous water separator for 4 h; then the solvent was evaporated under vacuum. This crude product was purified by vacuum distillation (88—90°C, 16 mm) and was used only to optimise the derivatisation reaction condition and select the suitable sorbent.

Samples collected on the cyclohexanone-coated XAD-4 sorbent were prepared for analysis by transferring front and back sections to separate vials. After adding 1 ml methanol, the vials were crimp-sealed with PTFE-lined caps and shaken at room temperature for 1 h.

Gas chromatography

An aliquot (2 µl) of methanol solution was withdrawn and injected into the gas chromatograph operating under the following conditions:

Column: a DB-Wax megabore silica fused column (J&W Scientific, Folsom, CA, USA), 15 m × 0.53 mm i.d., 1.0 µm film thickness.

Oven: 120°C.

Detector: thermionic specific at 240°C.

Injector: 220°C (splitless injection).

Carrier gas: helium at a flow-rate 1.2 ml/min.

A typical chromatogram obtained under the above conditions is shown in Fig. 2 and represents 10 µg of MEA [retention time (RT) = 2.9].

Preparation of reagent-coated sorbent tubes

Prior to coating, commercially obtained XAD-2 and XAD-4 resins were treated as follows: the resin beads were added to water, the mixture stirred and the particles were allowed to settle. The supernatant was removed by aspiration and this procedure was repeated until the water layer was clear. The resin was then rinsed several times in methanol, extracted in a Soxhlet extractor for 24 h and dried under vacuum.

The reagent-coated sorbent was prepared by dissolving 0.1 g of cyclohexanone in 10 ml of methylene chloride, then stirring with 1.0 g of XAD-4 resin. This slurry was allowed...