# Air Sampling and Liquid Chromatographic Determination of Ethylenimine

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**Sampling and analytical methods are described for the determination of airborne exposures of individuals to ethylenimine—an OSHA designated carcinogen. The personal sampler consists of a midget bubbler containing Folin's reagent capable of quantitatively absorbing ethylenimine vapors. The derivatized imine is extracted with chloroform and determined by high-performance liquid chromatography. The method was evaluated with dynamically generated samples in the range of 1.2–794 μg/sample and yielded an average recovery of 92.1% with a pooled coefficient of variation of 0.042.**

Ethylenimine, also known as aziridine, has a molecular weight of 43.07, a density of 0.835 g/mL at 20 °C, a vapor pressure of 171 mmHg at 21 °C, and a normal boiling point (*1*) of 56.7 °C. It has been a commercially important compound finding use in such diverse industries as the textile, paper, pharmaceutical, rocket, agricultural, etc. Production of ethylenimine in the United States is estimated at several million pounds—primarily for the synthesis of poly(ethylenimine).

The high toxicity (*1–4*) of ethylenimine makes it difficult to handle and the toxic effects are quite often determined after some delay. Because of the high vapor pressure of the compound there is an inhalation hazard; and although its ammonia-like odor has a reported (*1*) threshold of 2 ppm, it cannot be relied upon to prevent overexposure. Carcinogenicity of ethylenimine in man has not been demonstrated, but in 1974 the Occupational Safety and Health Administration (OSHA) listed the imine as a potential carcinogen and promulgated standards (*5*) for its production and use. The inclusion of ethylenimine in the standards was based on the extrapolation of animal studies which had demonstrated the imine to be carcinogenic in mice (*6*) and rats (*7, 8*). The Environmental Protection Agency's list (*9*) of potential human carcinogens includes ethylenimine. The American Conference of Governmental Industrial Hygienists (*10*) has adopted a time-weighted average exposure of 0.5 ppm (v) or 1 mg/m$^3$.

The awareness that exposure to ethylenimine presents a significant health hazard in the occupational environment generated a need for a sensitive procedure for air sampling and analysis. A survey of the literature indicated that although several procedures for the analysis of ethylenimine have been reported, very little work appears to have been conducted in the area of air sampling. The sampling methods that have been reported made use of impingers containing 1,2-naphthoquinone-4-sulfonate (*11*) or 0.01 N hydrochloric acid (*12*). In the latter sampling solution ethylenimine proved unstable, requiring fairly rapid analysis. In such solutions the imine is unstable because of its tendency to hydrolyze or polymerize. On-site sampling (*13*), involving the collection of a 10-cm$^3$ air sample with a syringe or an automatic gas injection valve has been used by Dow Chemical U.S.A.

Procedures for the analysis of ethylenimine or derivatives have included titrimetry (*2, 14*), visible spectrometry (*11, 15–18*), and chromatography (*13, 19–21*). The titrimetric procedures are primarily assay procedures and nonselective. The spectrometric methods are inherently selective because the derivatives formed contain the three-membered ring structure of the imine rather than a decomposition product such as ethanolamine. This inherent selectivity is lost, however, when an extract containing the derivative is measured at a wavelength at which derivatives of primary and secondary amines also absorb. Limits of quantitation for ethylenimine with the spectrometric procedures are ≥1 mg/m$^3$. Published gas chromatographic procedures (*19, 20*), other than Dow's (*13*), do not provide data for the quantitative determination of ethylenimine. The minimum level of quantitation of the Dow procedure is 176 μg/m$^3$ using a flame ionization detector. The high-performance liquid chromatography (HPLC) procedure of Evans et al. (*21*) is quite selective and sensitive with a derived minimum level of quantitation of 10 μg/m$^3$ (50-L sample and 100-μL injection). The procedure makes use of the reaction (*11, 16, 18*) between ethylenimine and 1,2-naphthoquinone-4-sulfonate (Folin's reagent) to produce 4-(1-aziridinyl)-1,2-naphthoquinone. The chromatographic system employs a Micro-PAK Si-10 column, dichloromethane/2-propanol (99/1, v/v) as the mobile phase, and a 254-nm UV detector. Evans' HPLC procedure eliminates interferences from many amines, thus providing greater accuracy, and extends the sensitivity for quantitative analysis down to 0.01 ppm of ethylenimine in solution.

The purpose of this work was to develop and evaluate a method for the determination of ethylenimine in air so that exposures of individuals working with this compound could be monitored. Attempts were made to adopt the HPLC procedure of Evans et al. for the analysis of ethylenimine in environmental air, but the silica columns in our laboratory yielded irreproducible results after 2 weeks. A Lichrosorb Diol column was evaluated with various compositions of several mobile phases and an analytical procedure was developed by using the diol column and a hexane/chloroform/2-propanol mobile phase. It was found necessary, however, to protect the 4-(1-aziridinyl)-1,2-naphthoquinone chloroform solutions from light. Evan's paper made no mention of the photoinstability of this compound, but other authors have reported on it as well as that of other similar derivatives (*11, 16, 17, 22*).

## EXPERIMENTAL SECTION

The protocol outlining the facilities and health practices used for working with potential carcinogens has been reported elsewhere (*23*).

**Generation of Test Atmospheres.** Ethylenimine test atmospheres were generated with a syringe and syringe pump—a common procedure for generating test atmospheres (*24*) of volatile liquids. In this work, two different air-flow systems were used to generate the ethylenimine challenge atmospheres. In both cases, a syringe pump (Model 355, Sage Instruments) was used to inject neat ethylenimine into a flowing airstream. Concentrations from 0.16 to 204 μg/L were generated by selecting the appropriate syringe and pump carriage speed.

The first system (system A, Figure 1) was used to carry out preliminary experiments and breakthrough studies and consisted of a $^1/_4$ in. o.d. stainless steel manifold with six outlets. Manual valves controlled the flow of compressed air at approximately 3.5

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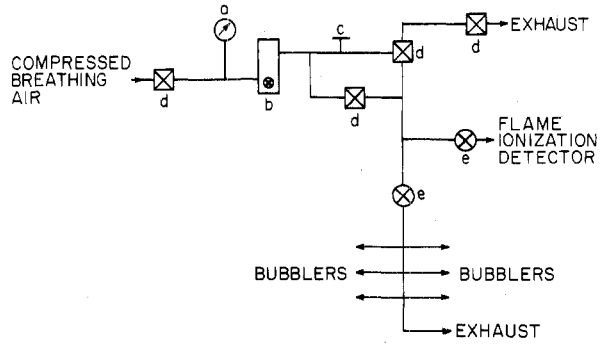


**Figure 1.** System A. Test atmosphere generation and air-sampling system for preliminary experiments: (a) pressure gauge, (b) rotameter with metering valve, (c) septum for insertion of syringe needle, (d) on–off valves, and (e) metering valves.

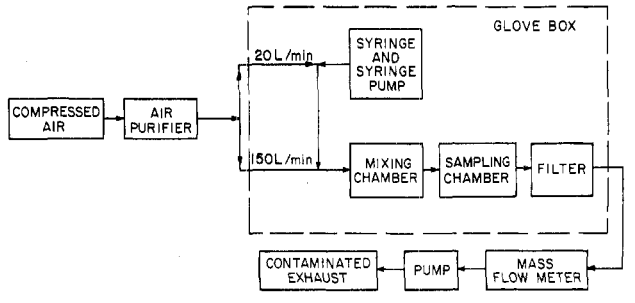


**Figure 2.** System B. Test atmosphere generation and air-sampling system for final experiments.

L/min. A calibrated rotameter measured the total airflow. Critical orifices controlled the flow through each individual sampling bubbler at approximately 0.2 or 0.8 L/min. In addition, bubble flowmeters were used to measure the total flow through the manifold and through each individual sampler at the beginning of each sampling run. To ascertain that the ethylenimine concentration in the test atmosphere had reached a constant level, a flame ionization detector monitored the concentration before the start of each run. This system was installed in a hood with a face velocity greater than 150 ft/min.

Most of the samples used in the evaluation of the method were collected with system B (Figure 2) contained within a ventilated glovebox. All components were made of stainless steel, glass, or Teflon except where stated otherwise. The imine atmosphere, produced at a volumetric flow of 20 L/min, was diluted with an additional 150 L/min of air and then mixed prior to entering the sampling chamber (Figure 3). Up to 10 simultaneous samples could be withdrawn from the chamber. A mass flowmeter (Model AHL-10, Hastings Raydist) measured the total airflow (~170 L/min) which passed through the chamber. Individual critical orifices controlled the flow through the samplers to approximately 0.2 L/min.

A photoionization detector (Model PI 201, H-NU Systems, Inc.) monitored the constancy of the chamber concentration. The detector provided a linear response at relative humidities of 15% or less. The actual generation concentrations of ethylenimine were calculated from the injection rate and total airflow. The method was evaluated for challenge concentrations of 0.16 to 204 μg/L and sampling times of 15–270 min.

**Air Sampling.** The samplers used were 30-mL midget gas bubblers (Model 9110, Misco) containing 15 mL of buffered (pH 7.7) Folin's reagent. In the case of system A installed in the hood, the bubblers were attached to the manifold with $^1/_4$ in. i.d. Teflon-lined, neoprene tubing. For ease of handling, the tubing was attached to the bubbler inlet with $^1/_4$ in. stainless steel compression fittings. Compression fittings were also used in system B to connect the bubbler inlets to the $^1/_8$ in. sampling lines of the sampling chamber.

The downstream sides of the bubblers were connected to critical orifices through 25 mm diameter glass fiber filters and plastic tubing. Without the filters, the orifices tended to become restricted during sampling. In system A the critical orifices were

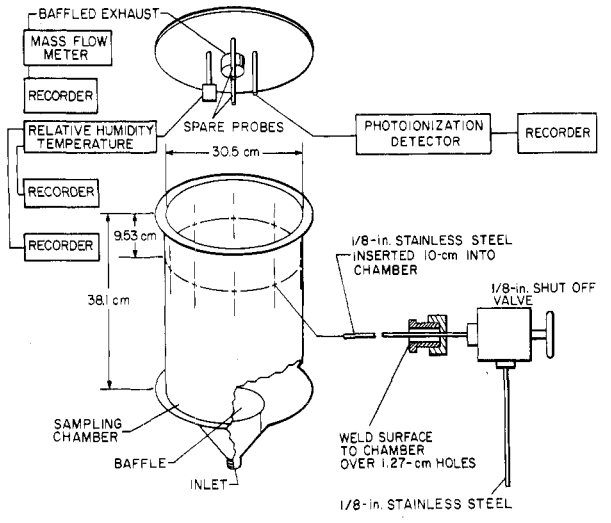


**Figure 3.** Sampling chamber.

connected directly to the sampling pump. With system B the orifices were installed in the common sides of three-way valves located upstream of a mass flow transducer (Model ALL-500/H-500M, Hastings Raydist). This allowed connection of the bubblers either directly to the sampling pump or first through the transducer and then to the sampling pump. By switching through the transducer, we could measure the actual flow through any individual bubbler during a run. These measured flows were used in calculations using system B. With system A, calculations were based on the flows measured with a bubble flowmeter before the run began.

All flow measurements were made with either a bubble flowmeter or with a mass flow transducer, which had been calibrated previously against either a bubble flowmeter or dry test meter. Flow measurements were accurate to ±3%. The syringe pump was calibrated by measuring the speed of the carriage to ±2%.

In general, six or more replicate samples were taken during each run. The challenge atmosphere was close to ambient temperature (25 °C) and usually dry (<15% RH).

**Analytical Procedure.** Fifteen milliliters of Folin's reagent was added to midget bubblers with fritted glass stems. (Folin's reagent and the aziridinylnaphthoquinone solutions must be contained in either low-actinic or aluminum-wrapped glassware to minimize their photodecomposition.) After being sampled, the collection solution was extracted with two 4-mL portions of pure, UV grade, distilled in glass, chloroform (Burdick and Jackson Laboratories, Inc.). The extract was placed in a 10-mL low-actinic glass volumetric flask. The flask's volume was brought to 10 mL with chloroform, and a 10-μL aliquot was injected into an HPLC (Model ALC 202/401; Waters Associates) which was factory equipped with a U6K injector and a UV detector (254 nm). 4-(1-Aziridinyl)-1,2-naphthoquinone eluted from the 4.6 mm by 25 cm Lichrosorb Diol column (Rheodine, Inc.) in 5 min at a mobile phase flow rate of 1.3 mL/min (300 psi). The mobile phase consisted of 59.5/40/0.5 (v/v) *n*-hexane/chloroform (1% ethanol)/2-propanol, all UV grade and distilled in glass (Burdick and Jackson Laboratories). The efficiency and capacity factor for the chromatographic system were 1936 theoretical plates and 0.9, respectively. Peak areas were determined electronically with an Autolab System IV-B integrator (Spectra-Physics). At 0.04 AUFS, 3.3 ng of 4-(1-aziridinyl)-1,2-naphthoquinone per 10-μL injection could be quantitated as shown in Figure 4. Corresponding ethylenimine weight equivalents, in nanograms, are shown in parentheses. The detection limit for the naphthoquinone derivative was 1.6 ng/injection (0.3 ng of ethylenimine) at a signal-to-noise ratio of ~2 to 1.

**Synthesis of 4-(1-Aziridinyl)-1,2-naphthoquinone.** Samples were analyzed by calibrating with standard solutions of 4-(1-aziridinyl)-1,2-naphthoquinone, which was synthesized as follows. Two grams of the sodium salt of 1,2-naphthoquinone-4-sulfonic acid (Pfalz and Bauer) was dissolved in 250 mL of distilled water and the solution transferred to a 1-L separatory funnel wrapped

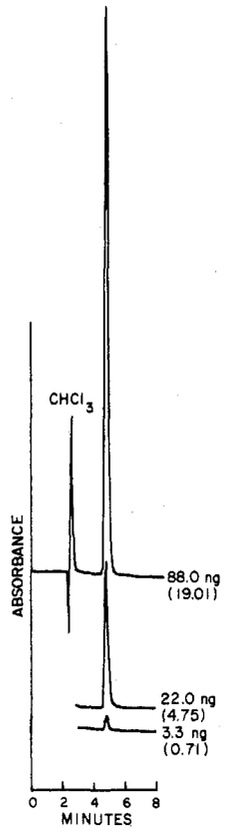


**Figure 4.** Representative chromatograms of 4-(1-aziridinyl)-1,2-naphthoquinone calibration solutions. Ethylenimine weight equivalents are shown in parentheses [column, 25 mm × 4.6 mm Lichrosorb Diol; mobile phase, hexane/chloroform (1% ethanol)/2-propanol, 59.5/40/0.5 (v/v) at 1.3 mL/min; detector, UV at 254 nm and 0.04 AUFS].

in aluminum foil. Thirty-five milliliters of 0.5 M trisodium phosphate was added and the solution shaken. The pH was determined to be between 10.5 and 11.5. After 0.3 mL of ethylenimine (Pierce Chemical Co.) was added and the funnel was shaken intermittently for 10 min, the precipitated 4-(1-aziridinyl)-1,2-naphthoquinone was extracted with six 200-mL portions of pure chloroform. The extracts were collected in a 2-L beaker. An aluminum foil cover, through which three holes were made, was placed on top of the beaker and the chloroform evaporated with a nitrogen purge. The orange residue was transferred to a 50-mL beaker, 35 mL of methyl alcohol and 1 mL of chloroform were added to it, and the mixture was stirred. The beaker was placed in an ice water bath for 10 min and the solution filtered through Whatman No. 42 paper. The residue in the filter paper was rinsed with 4 mL of chilled methyl alcohol, dried with nitrogen, transferred to a brown-glass bottle, and dried overnight in a desiccator. The melting point of the dry compound was found to be 173–175 °C. The sample was introduced into a double sector mass spectrometer (DuPont 21–492, E. I. du Pont) by programmed heating of the solid. The measured molecular mass was found to be 199.06328 which compared well with the calculated mass of 199.06337 for 4-(1-aziridinyl)-1,2-naphthoquinone. The 4-(1-aziridinyl)-1,2-naphthoquinone (51% yield) was stored in a freezer and used for the preparation of standard solutions. A linear calibration curve was obtained with solution concentrations in the range of 1–38 μg per 10 mL.

**Buffered Folin's Reagent.** An alkaline buffer solution was prepared by mixing 100 mL of 0.1 M $KH_2PO_4$ with 93.4 mL of 0.1 N NaOH. One-hundred milliliters of the buffer was placed in a 500-mL volumetric flask, 0.40 g of 1,2-naphthoquinone-4-sulfonic acid (sodium salt) was added, and the contents were shaken and diluted to 500 mL with distilled water. The flask was wrapped with aluminum foil and stored in a refrigerator. Folin's reagent provided a pH 7.7 buffered solution. The reagent was discarded after 5 days.

**Effect of pH.** Solutions were prepared in low actinic glass volumetric flasks which contained 15 mL of 0.1% 1,2-naphthoquinone-4-sulfonate, 1 μL (835 μg) of ethylenimine, and 3 mL of one of the following buffers: pH 7.7, 8.9 ($KH_2PO_4$ + NaOH) and pH 10.0, 10.7 (Borax + NaOH). One-milliliter aliquots were extracted with 10 mL of chloroform at various time intervals and the extracts chromatographed using the HPLC procedure. (All solutions were maintained at ~22 °C for the duration of the experiment.) Blanks were run for compensation purposes. The effect of pH on the recovery of ethylenimine is shown in Figure 5.

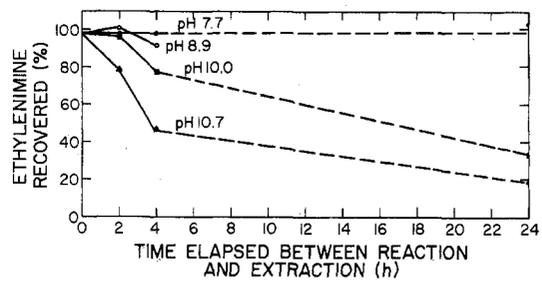


**Figure 5.** Effect of pH on the recovery of 4-(1-aziridinyl)-1,2-naphthoquinone.

**Table I. Recovery of 4-(1-Aziridinyl)-1,2-naphthoquinone from Bubblers Challenged with Air and $N_2$ (835 μg of Ethylenimine Added)**

| time, h | recovered[a] air | recovered[a] $N_2$ |
|---|---|---|
| 0 | 96, 105 | 99, 91 |
| 2.5 | 101, 96 | 99, 98 |
| 5 | 99, 98 | 103, 97 |
| 24 | 98, 90[b] | 96, 95[b] |

[a] Values given are for primary bubblers. [b] Only in these two cases was any of the added ethylenimine (less than 2%) found in any backup bubbler.

**Effect of Air.** Fifteen milliliters of pH 7.7 buffered Folin's reagent was added to midget bubblers wrapped with aluminum foil. Four bubblers were assembled in pairs. The first bubbler in each pair contained 835 μg of the imine and the second bubbler served as a backup. Blanks were run for compensation purposes. House air was passed through each pair of bubblers at the rate of 0.2 L/min. A parallel experiment using a purified nitrogen challenge atmosphere was run simultaneously to serve as reference. One-milliliter aliquots from each of the eight bubblers were taken at various time intervals and treated as already described. The effect of air on the recovery of the imine is presented in Table I.

**Effect of Storage Temperature.** Eight and ten microliters of ethylenimine in chloroform solutions (2.088 and 0.167 μg/μL, respectively) were added to 15 mL of buffered, pH 7.7, Folin's reagent contained in low-actinic glass volumetric flasks. Blanks and six samples each of the spiked solutions stored under ambient (~22 °C) and refrigerated (5 °C) conditions were analyzed as already described. Time intervals and the results of the experiment are shown in Table II.

## RESULTS AND DISCUSSION

To determine the dynamic collection efficiency of the bubblers, two runs were made in which two bubblers in series were used to collect the samples. In both cases, ~800 μg ($1.9 \times 10^{-5}$ mol) of ethylenimine was collected. This amount corresponded to ~40% of the total derivatizing agent in each bubbler. The concentrations in the test atmospheres and sampling times were 20.6 μg/L for 270 min and 204 μg/L for 26 min. Analyses of the solutions in the bubblers (Table III) show 95% recovery in the first bubblers and negligible amounts in any of the backup units. These data also show that at least 800 μg of ethylenimine can be collected by a single bubbler before any appreciable amount is found downstream.

To check the accuracy of the combined sampling and analytical method, we conducted eight runs in which at least

Table II. Storage Stability of 4-(1-Aziridinyl)-1,2-naphthoquinone

| storage time, days | ethylenimine level, μg | % found ± std dev[a] at 5 °C | at 23 °C |
|---|---|---|---|
| 0 | 16.7 | 96.5 ± 5.2[b] | 96.5 ± 5.2[b] |
| 3 | 16.7 | 99.8 ± 2.9* | 95.5 ± 1.3* |
| 7 | 16,7 | 94.5 ± 2.5* | 86.3 ± 3.5* |
| 14 | 16.7 | 92.2 ± 3.8 | 72.5 ± 1.8 |
| 28 | 16.7 | 86.2 ± 4.4 | 60.2 ± 1.7 |
| 0 | 1.67 | 104.2 ± 4.0[b] | 104.2 ± 4.0[b] |
| 3 | 1.67 | 92.8 ± 2.8 | 100.3 ± 5.7 |
| 7 | 1.67 | 93.8 ± 9.7 | 98.8 ± 13.1 |
| 14 | 1.67 | 94.2 ± 8.9 | 81.2 ± 4.4 |
| 28 | 1.67 | 94.2 ± 8.5 | 56.2 ± 5.5 |

[a] All standard deviations are based on six samples except for those marked with an asterisk, which are based on four samples. [b] Results of samples analyzed 1 h after spiking.

six simultaneous samples were taken. These data are shown in Table IV. Challenge concentrations in these experiments ranged between 0.16 and 206 μg/L and sampling times ranged from 15 to 270 min. The average recovery from these eight runs, Table IV, was 92.1% with a pooled coefficient of variation of 0.042 (25).

The experimental data indicate that pH and storage conditions have a significant effect on the recovery of ethylenimine reacted with Folin's reagent. Folin's reagent buffered at pH 7.7 produced the best recoveries (>86%), even when the reacted ethylenimine samples had been allowed to stand at ambient temperature for up to 7 days (Figure 5 and Table II). Refrigeration of the samples allowed for recoveries >86% even after 28 days (Table II). Possible degradation (for example, oxidation) of the derivatized imine during or after sampling, as a result of an air atmosphere is not a critical factor as indicated in Table I where the results for both air and nitrogen atmospheres are comparable.

Two dynamic runs were conducted with solutions of possible contaminants in ethylenimine. The results from these experiments are shown in Table V. Calculation of the amount of ethylenimine to be expected in these samples was based upon the volumes of the components that were used in making up the solutions and no corrections were made for possible volume changes on mixing. The ethylenimine recoveries from these samples compare favorably with those from the other dynamic runs in which these other compounds were not present. Chromatograms of these dynamically generated samples exhibited no extraneous peaks to suggest possible decomposition products of the analyte.

Static (that is, addition of the contaminant to a solution containing the analyte, derivatization, extraction, and subsequent chromatography) interference studies were also conducted with various amines. For solutions containing ethylenimine at 17 ng/μL, the following amines were found not to interfere (because of different retention times or low extinction coefficients of the derivatized analyte) when their concentrations were 2 ng/μL: methylamine, diethylamine, ethanolamine, butylamine, dihexylamine, dicyclohexylamine, benzylamine, dibenzylamine, and aniline. The propylenimine and ethylenimine derivatives have the same retention time.

Table III. Collection Efficiency (Dry Test Atmosphere)

| no. of samples | av sampling rate, L/min | sampling time, min | av vol sampled, L | challenge concn, μg/L | av amt expected, μg | % recovered ± std dev first bubbler | second bubbler | total |
|---|---|---|---|---|---|---|---|---|
| 4 | 0.158 | 26 | 4.11 | 204.2 | 840 | 95.3 ± 10.4 | 0 | 95.3 ± 10.4 |
| 6 | 0.143 | 270 | 38.5 | 20.6 | 794 | 95.2 ± 6.3 | 0.01 ± 0.02[a] | 95.3 ± 6.3 |

[a] Ethylenimine, 0.4 and 0.2 μg, respectively, was found in two of the backup bubblers. No measurable amount was found in any of the others.

Table IV. Precision and Accuracy of Sampling/Analytical Method (Dry Test Atmospheres)

| no. of samples | av sampling rate, L/min | sampling time, min | av vol sampled, L | challenge concn, μg/L | av amt found, μg | recovery % ± std dev |
|---|---|---|---|---|---|---|
| 6 | 0.143 | 270 | 38.6 | 20.6 | 757 | 95.3 ± 6.3 |
| 6 | 0.170 | 56 | 9.44 | 19.9 | 178 | 94.9 ± 5.9 |
| 7 | 0.180 | 102 | 18.2 | 8.22 | 137 | 91.7 ± 3.7 |
| 6 | 0.173 | 60 | 10.4 | 8.07 | 73 | 87.4 ± 1.5 |
| 6 | 0.170 | 15 | 2.56 | 19.9 | 49 | 96.1 ± 2.1 |
| 6 | 0.174 | 15 | 2.61 | 6.56 | 15 | 87.0 ± 3.6 |
| 6 | 0.172 | 15 | 2.58 | 6.32 | 14 | 85.6 ± 1.7 |
| 9 | 0.176 | 43 | 7.55 | 0.16 | 1.2 | 98.5 ± 5.3 |

Table V. Effect of Dynamically Generated Interference on the Recovery of Ethylenimine

| challenge atmosphere | no. of samples | av sampling rate, L/min | sampling time, min | av vol sampled, L | ethylenimine challenge concn, μg/L | av amt of ethylenimine found, μg | recovery % ± std dev |
|---|---|---|---|---|---|---|---|
| 50% ethylenimine 50% ethanolamine | 8 | 0.175 | 40 | 7.00 | 1.37 | 9.6 | 91.1 ± 2.2 |
| 50% ethylenimine 25% aniline 25% diethylamine | 6 | 0.178 | 40 | 7.10 | 1.39 | 9.8 | 99.7 ± 1.3[a] |

[a] One sample with 77.4% recovery was discarded.

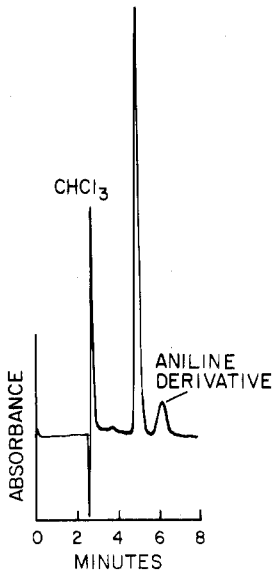


**Figure 6.** Chromatographic separation of ethylenimine, aniline, and diethylamine derivatives (diethylamine derivative produces no response at 254 nm).

2-Bromoethylamine also interferes. The latter compound and its chloro analogue can be expected to interfere positively since they are probably converted to ethylenimine in the alkaline reagent solution. Ammonia, and amines in general, can be considered interferences if their concentrations are so high that they consume Folin's reagent to the extent that a quantitative reaction is not obtained with the analyte. (The ammonia derivative is not extracted into chloroform.) Figure 6 depicts a chromatogram in which 15 mL of buffered Folin's solution was spiked with a chloroform solution containing 5.0, 5.1, and 5.3 μg of ethylenimine, aniline, and diethylamine, respectively, and analyzed according to the ethylenimine procedure. Even at these levels, no bias was detected in the imine recovery when compared to control samples. Although the dynamic interference study (Table V) with ethanolamine produced lower imine recoveries when compared to the static study, the recoveries were within the range encountered when only ethylenimine was generated (Table IV).

## CONCLUSIONS

The personal sampler and analytical procedures described here provide a means for monitoring ethylenimine in air. No data were obtained for imine atmospheres at relative humidities greater than 15% where some degree of hydrolysis could be expected; however, the method is indicative of the concentration of the intact analyte at the time of sampling and thus reflects the potential exposure to workers. In addition, the selective chromatographic procedure provides a sensitivity of 14 $\mu g/m^3$ (50-L air sample, 10-μL injection), which is greater than that cited in the published literature. All materials and instrumentation required to implement the methodology described are commercially available.

Although both the sampling and analytical procedures developed were designed to be applied in the occupational environment, no field samples were obtained to determine the reliability of the methods under various field conditions. The method may have to be modified in certain situations, for example, in the case of a contaminant (not evaluated in this study) that interferes with the analysis.

## ACKNOWLEDGMENT

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