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Development of Air-Monitoring Techniques Using Solid Sorbents

LASL Project R-059

NIOSH-IA-77-12

October 1, 1976—December 31, 1977

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ABSTRACT

A project for developing personal sampling and analytical methods for vapors of amine and hydrazine compounds in air is completed with this report. Silica gels and acid-coated silica gels were evaluated for vapor collection, stability, and recovery of amines for analysis. The compounds 2-aminoethanol, ethylenediamine, and diisopropylamine were used for most of these experiments as representatives of aminoalcohols, aliphatic polyamines, and aliphatic amines, respectively. A silica gel tube was designed for sampling and its adsorption capacities were defined for several amines. Stabilization of samples for storage and transportation was accomplished by the addition of concentrated hydrochloric acid. An analytical procedure was developed that involves sample elution with methanol-water solvent, reaction of primary amines with benzaldehyde, and analysis by gas chromatography. Each phase of this procedure was tested to select the optimum conditions and define the limitations. The final sampling and analysis procedure developed for 2-aminoethanol, 2-diethylaminoethanol, and 2-dibutylaminoethanol is summarized and detailed. The procedure for ethylenediamine and diethylenetriamine and an improved method for methylamine is given. Recommendations for improvements in the analysis of methylhydrazine are also given.

I. INTRODUCTION AND SUMMARY

The goals of this program have been to develop methods for monitoring vapors of selected toxic compounds in air representative of that breathed during occupational exposures. A small, wearable sampling system is required to monitor the air in a worker's breathing zone without interfering with normal work activities. Compounds for which sampling and analytical methods have been developed are listed in Table I with their current Threshold Limit Values (TLV).[1] Federal standards[2] for 8-h time-weighted-average concentration exposure limits are currently the same as these values except where otherwise noted. A capability of measuring vapors at concentrations of 0.2-5 times the standards for periods of 0.25-8 h is desirable.

The approach we selected to fulfill these objectives involves collecting vapors on a solid sorbent in a tube through which air is drawn by a personal sampling pump. The tube is transported to a laboratory where it may be stored before the sample is recovered from the sorbent. The compounds in the sample are then analyzed for identification and quantification. Experiments have been performed to select materials and procedures for collection, storage, recovery, and analysis of the compounds of Table I.

TABLE I

EXPERIMENTAL COMPOUNDS AND THEIR TIME-WEIGHTED AVERAGE CONCENTRATION LIMITS

Class	Compound	Standard Limits[a] (ppm)	(mg/m^3)
Anilines	Aniline	5	19
	N,N-Dimethylaniline	5	25
	o-Toluidine	5	22
	2,4-Xylidine	5	25
	p-Anisidine	0.1	0.5
	o-Anisidine	0.1	0.5
	p-Nitroaniline	1	6
Aliphatic Monoamines	Methylamine	10	12
	Ethylamine	10	18
	Isopropylamine	5	12
	Butylamine	5	15
	Cyclohexylamine[b]	10	40
	Dimethylamine	10	18
	Diethylamine	25	75
	Diisopropylamine	5	20
	Triethylamine	25	100
Hydrazines	Hydrazine[c]	0.1	0.1
	Methylhydrazine	0.2	0.35
	1,1-Dimethylhydrazine	0.5	1
	Phenylhydrazine	5	22
Aminoethanols	2-Aminoethanol	3	6
	2-Diethylaminoethanol	10	50
	2-Dibutylaminoethanol[b]	2	14
Aliphatic Polyamines	Ethylenediamine	10	25
	Diethylenetriamine	1	4

[a]Threshold limit values (Ref. 1) given are the same as the Federal standards (Ref. 2) except as noted in b and c.

[b]No Federal standard.

[c]Federal standard is 1 ppm (1.3 mg/m^3).

The first basis for selecting a sorbent is its capacity for collecting and retaining the vapor of interest at anticipated air sampling flow rates and volumes. High capacities make possible the use of smaller amounts of sorbent and, therefore, smaller sampling tubes. The sample is also more concentrated for subsequent analysis. In measurements of such capacities, effects of humidity must be considered. Personal sampling pumps impose limitations on the pressure drops of sampling tubes at selected sampling flow rates. Pressure drops are determined by the particle size range of the sorbent and by the diameter, depth, and packing of the sorbent beds. In designing a sampling tube, the effects of these parameters on both capacity and pressure drop must be measured and considered. A third consideration in the selection of a sorbent is the ease with which the collected sample can be removed for laboratory analysis. Simple procedures that yield high (>80%) and reproducible (≤10% relative standard deviation) sample recoveries without excessive dilution are desirable. The sample must be removed in a form suitable for analysis.

In previous work,[3-12] silica gels and sulfuric acid-coated silica gels in the 42/60-mesh size range have been found to be useful for collection of vapors of amine and hydrazine compounds. These vapors have been shown to be efficiently recovered by solvent elution with dilute acids or distilled water, respectively. Sampling tubes and conditions have been proposed for aniline compounds,[3,4,13] aliphatic amines,[6,10] hydrazines,[9,11,14] and aminoethanols.[12] In the subsequent work we report here, adsorption and desorption properties of silica gels and acid-coated silica gels were studied further, particularly for vapors of 2-aminoethanol and ethylenediamine. Additional sorbent parameters that were varied included source, mesh size, and geometry. Effects of these on retention capacities and pressure drops were determined. A sampling tube was designed and is reported for aminoethanol and polyamine compounds in air.

The method chosen for analysis should be qualitative, quantitative, sensitive, precise, and rapid. Since all these qualities are interrelated, the goal is an optimum and acceptable balance. Gas chromatography with flame ionization detection has been selected as the instrumental method, since it is widely available and provides the desired characteristics for a variety of analyses. The detectability of hydrazine compounds by flame ionization was enhanced in earlier work[9,11] by forming derivatives with 2-furaldehyde. This report describes the development of this approach for other low molecular weight amines, such as 2-aminoethanol, ethylenediamine, and methylamine. Benzaldehyde was preferred to 2-furaldehyde as a derivatizing reagent for primary amines. Gas chromatographic columns and conditions are described for various compounds and derivatives.

The stabilities of amines adsorbed on silica gel have been found to be a problem. Primary amines are particularly susceptible to oxidation when in contact with air. It was because of rapid sample losses that a sulfuric acid-coated silica gel was invented for collecting hydrazine compounds.[6] The acid apparently stabilizes these compounds by formation of salts more resistant to oxidation. This report describes further development of this sample stabilization approach, adding concentrated hydrochloric acid to silica gel beds after sampling is completed.

A photoionization detector was briefly studied as an alternative to the flame ionization detector for the analysis of amines. It produced signals 11-56 times larger than a parallel flame ionization detector for five compounds. However, the derivatization of primary amines and flame ionization detection was selected as a more general and widely available approach to analysis of these compounds.

Experimental work described in this report has resulted in sampling and analytical methods being prepared for three aminoethanol compounds, two polyamine compounds, and methylamine. These methods, written in the format used by the National Institute for Occupational Safety and Health (NIOSH),[13] are included as Appendices A, B, and C. Suggestions are also made for improving the analysis of methylhydrazine.

II. EXPERIMENTAL

A. Reagents

Matheson, Coleman, and Bell was the source of 2-aminoethanol (mp 9-10°C), ethylenediamine (99% minimum), 1,1-dimethylhydrazine (99% minimum), n-butylamine (bp 76-78°C), and 2-furaldehyde (bp 39-40°C at 5 torr). Eastman Kodak Company was the source of 2-dibutylaminoethanol (practical), diethylenetriamine (technical), hydrazine (95% minimum), methylhydrazine (bp 87-88°C), phenylhydrazine (97% minimum), isopropylamine (bp 31-33°C), triethylamine (bp 59-61°C at 15 torr), azobenzene (mp 67-69°C), and benzaldehyde (99% minimum). J. T. Baker Chemical Company was the source of methylamine (40% in H_2O) and diisopropylamine (bp 82-84°C). Ethylamine (99% minimum) was purchased from the Linde Division of Union Carbide Corporation in a cylinder and bubbled through distilled water to make a concentrated aqueous solution. Other chemicals used included 2-diethylaminoethanol (99% minimum) from Aldrich Chemical Company, Inc.; sulfuric acid (95-98%) from Mallinckrodt, Inc.; and methanol (bp 64-65°C) and cyclohexane (bp 81-82°C) from Burdick and Jackson Laboratories, Inc. Aqueous solutions of methylamine, ethylamine, and isopropylamine were standardized acid by titration. It was necessary to redistill the 2-furaldehyde prior to use to remove dark-colored oxidation products.

Three silica gels were used. The first, identified in this report as CEL, was prepared by Coast Engineering Laboratories and sold by Applied Science Laboratories, Inc. of State College, Pennsylvania. It was 42/60-mesh chromatograph grade, D-08, activated and fines free. The second, identified as SKC, was 20/40-mesh silica gel taken from sampling tubes purchased from SKC, Inc., Eighty-Four, Pennsylvania. The third, Davison silica gel, was 6/16-mesh activated desiccant, grade 05, from the Grace Division of Davison Chemical Company, Baltimore, Maryland. This latter silica gel was crushed in a ball mill and separated with US standard sieves into various particle size fractions. The 20/30-mesh silica gel was used in most cases.

Sulfuric acid-coated silica gels were prepared as follows: A selected amount, W, of silica gel was weighed in a glass bottle. Sulfuric acid, concentrated or diluted with water, was added directly and evenly to the silica gel with a glass dropper until the total weight was 1.25 W. The bottle was immediately capped and shaken to uniformly distribute the sulfuric acid on the silica gel. Mixing was repeated intermittently for an hour as the mixture cooled. The resulting material is quite hygroscopic and should not be exposed to humid air any longer than is necessary. Unless otherwise stated, the sulfuric acid-coated silica gel used was 20% by weight concentrated (95-98%) sulfuric acid.

B. Apparatus

Vapor retention on and distribution through sorbent beds in tubes was determined using the system diagrammed in Fig. 1 and pictured in Fig. 2. It was constructed of the following components: Nitrogen flow rate from a cylinder was measured using a Type 1000-500 flow sensor and a Model 800-L linear flowmeter from Datametrics of Wilmington, Maryland. The graduated valve in parallel with this sensor extended the useable flow rate range by acting as a bypass flow controller. A bubble flowmeter was used to calibrate the flowmeter reading for selected valve adjustments. A 1-L/min flow rate through the system was controlled by the pressure regulator and flow controller of a Model 307 calibration system from Analytical Instrument Development, Inc. of Westchester, Pennsylvania. For high humidity experiments, the regulated nitrogen flow passed through two bubblers containing distilled water and through an aerosol respirator filter. For low humidity experiments, a parallel valve was opened, allowing the flow to bypass the bubblers.

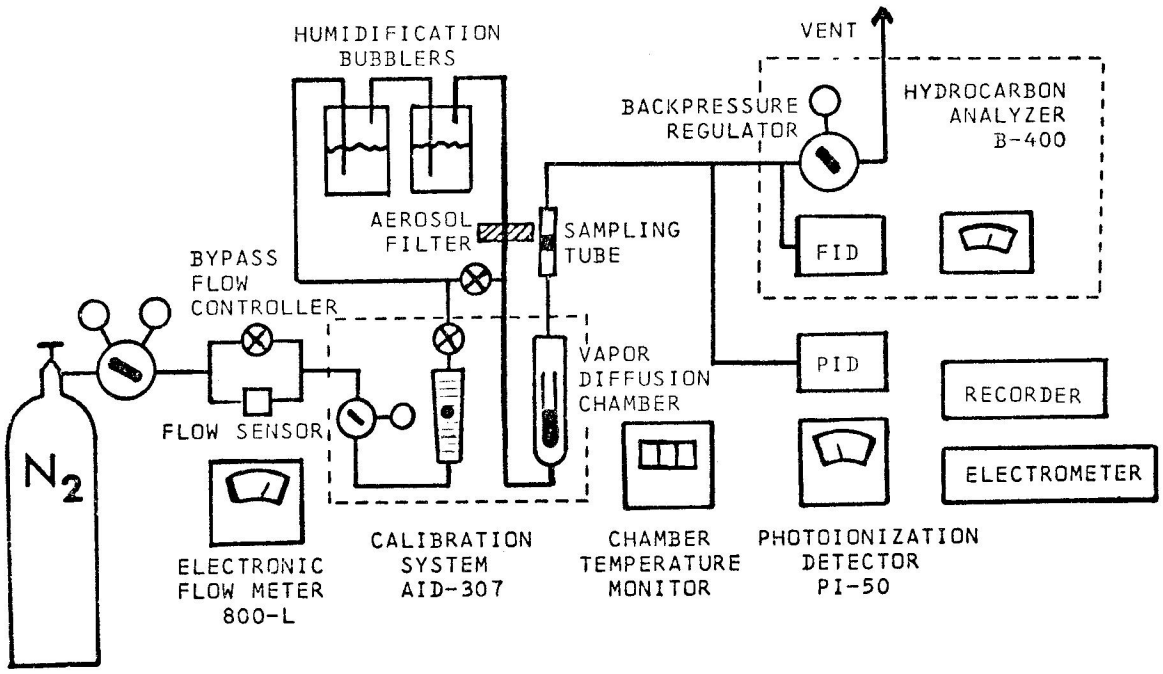

Fig. 1.
Diagram of the apparatus used for testing sorbents for collecting vapors of amines in sampling tubes.

The nitrogen stream then entered a glass chamber in a temperature-regulated zone (30-70°C, ± 0.1°C) of the calibration system and flowed past a test tube (12-mm-diam) containing the compound of interest in liquid form. Vapors evaporating in nitrogen carrier passed through glass wool-packed stainless steel tubing (not shown in Fig. 1) where mixing and cooling to near ambient temperature (22 ± 2°C) took place. At this point in the system a sampling tube or a bubbler was placed for vapor concentration monitoring. Effluent from a sampling tube passed through a back-pressure regulator and was vented to a hood. The back-pressure regulator (Model 12023-5 from Moore Products Company, Spring House, Pennsylvania) was adjusted to maintain a constant pressure of 760 torr at the exit of the sampling tube. This also maintained a constant sample pressure at a capillary leak to the detector used to monitor vapors in the tube effluent. A Model PI-51 gas chromatography photoionization detector (with 10.2-ev lamp) from HNU Systems, Inc., Newton, Massachusetts, was used primarily as the detector. In a few experiments the detector was a Model 400 hydrocarbon analyzer (with flame ionization detector) from Beckman Instruments, Inc., Fullerton, California.

A Perkin-Elmer 900 gas chromatograph and a Hewlett-Packard 7620A gas chromatograph equipped with flame ionization detectors were used for the analyses of organic bases and their derivatives. A PI-51 photoionization detector from HNU Systems, Inc. was also attached to the Hewlett-Packard instrument. Chromatographic columns, packings (Supelco, Inc., Bellefonte, Pennsylvania) and conditions used are described later in this report with the classes of compounds analyzed. An electronic digital integrator (Autolab IV from Spectra-Physics of Mountain View, California) was used to determine areas of gas chromatographic peaks recorded on a strip chart recorder (Model SR-255B from Health Company, Benton Harbor, Michigan).

A Cary 14 spectrophotometer (Applied Physics Corporation, Monrovia, California) was used for colorimetric measurement of azobenzene in cyclohexane. Absorbances were measured at 450 nm in Beckman quartz cells of 10-mm path lengths.

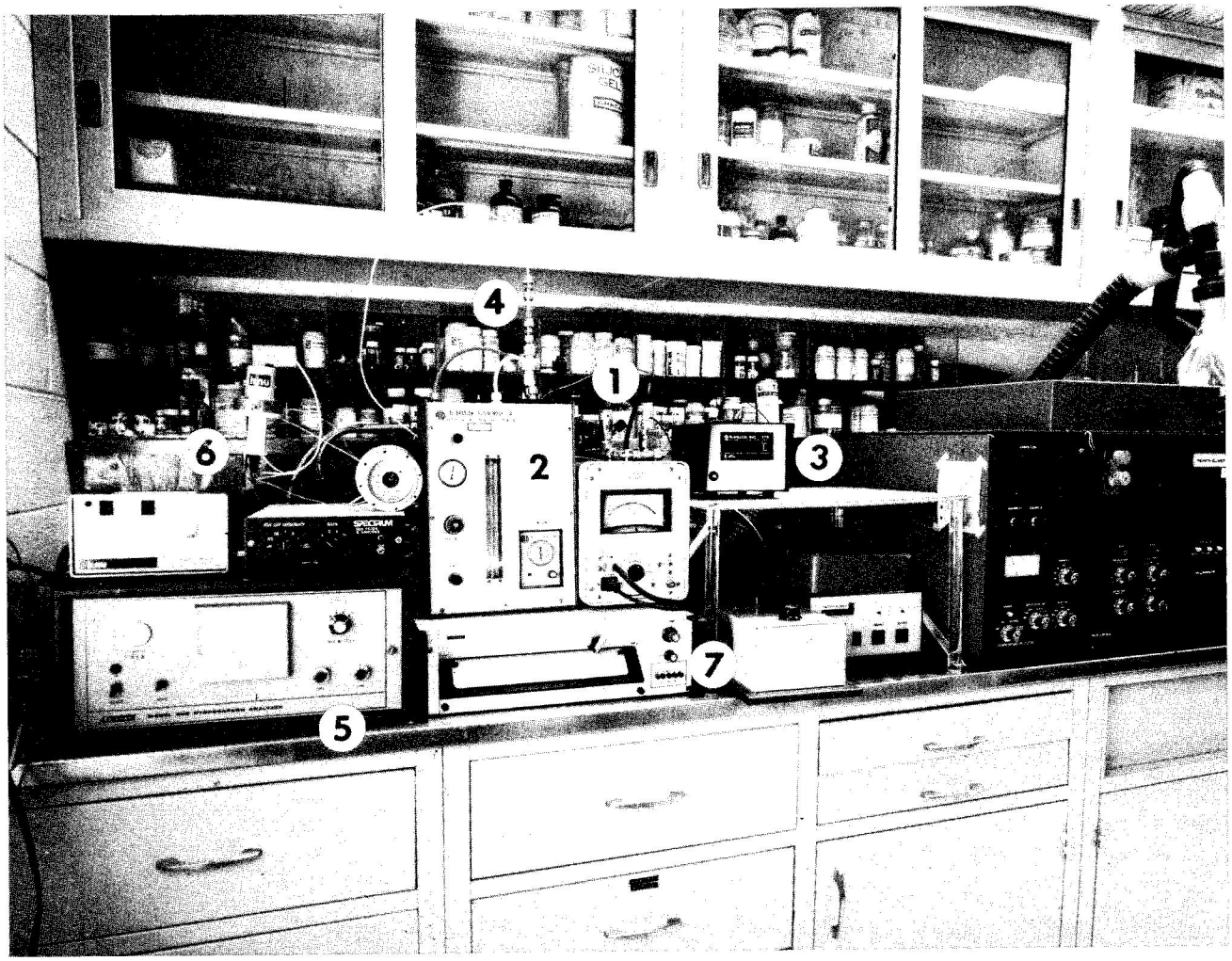

Fig. 2.
Sorbent and sampling tube test system: (1) electronic flowmeter, (2) amine vapor generator, (3) diffusion tube chamber temperature monitor, (4) test sampling tube, (5) hydrocarbon analyzer with flame ionization detector, (6) photoionization detector, and (7) recorder and electrometer.

III. SOLID SORBENT EVALUATIONS

A. Silica Gels

Silica gels have been evaluated in four types of experiments to determine retentions of vapors of amines, distributions of adsorbed amines through beds, adsorption activities, and desorption efficiencies. These silica gels, described in the Reagents section above, varied in source, mesh size range, bed diameter, bed depth, water content, and thermal conditioning.

The first type of experiment, referred to as a retention experiment, involved generating an amine vapor in nitrogen, passing it through a selected silica gel bed at 1-L/min flow rate, and monitoring the effluent of the bed. The system is described in the Apparatus section above and in Fig. 1. Dry nitrogen was used as the carrier gas to eliminate oxidation in the vapor generator, which was heated as high as 74°C in some cases. High vapor concentrations were needed in order to have reasonable experimental times over which the vapor output was consistent. Bed

diameters (tube inner diameters) and depths (weights of silica gel) were varied. The bed effluent was monitored for challenge vapor concentration using a photoionization detector to identify the point of first detectable breakthrough (0.2 to 0.4% of the challenge concentration) and, in some cases, to graph the entire breakthrough curve. Challenge vapor concentrations were determined either by collecting amine vapors in a bubbler containing water and titrating them with standard acid or by collecting vapors on silica gel and measuring them by the analytical methods described in Appendix A.

Retention (capacity at breakthrough) results for 2-aminoethanol are listed in Table II. Two commercially available silica gels of large particle size ranges were used in these experiments. The first conclusion is that the amount of 2-aminoethanol retained on a given amount of silica gel with all other parameters constant is independent of the concentration of the vapor sampled. The second conclusion shown in Fig. 3 is that the amount of 2-aminoethanol retained is a linear function of sorbent amount. In the case of the 42/60-mesh silica gel in a 6-mm-i.d. tube, the amounts are proportional to silica gel amounts with an average of 0.10-mg 2-aminoethanol/mg silica gel (11% relative standard deviation). For the 20/40-mesh silica gel in the 4-mm-i.d. tube, the retention amounts are given approximately by W_R (mg) = 0.25 W_{SG} - 15.7, where W_{SG} is the weight of silica gel in mg. This intercept, corresponding to 62 mg of silica gel, may be due to a zone of turbulence at the front end of the tube, which does not exist for the lower linear velocity in the larger diameter tube.

Retention results for ethylenediamine are listed in Table III. Four silica gels from three sources were studied in these experiments. As in the case of 2-aminoethanol, retention amounts were independent of vapor concentration. However, when retention amounts were plotted vs sorbent amounts for the more extensive sets of experiments (42/60-mesh CEL and 20/30-mesh Davison in 6-mm-i.d. tubes), the curves were nonlinear. Plots of the logarithms of retention amounts vs bed depth (or sorbent amount) were linear as shown in Fig. 4. This indicates that the bed retention increases exponentially, rather than linearly, with sorbent amount. A mathematical model for gas indicator tubes proposed by Saltzman[15] (his Model #3) describes such an exponential distribution. Previous data on the adsorption of aniline[3,5] and methylamine[5] by silica gel fit this model well. Basic assumptions in the derivation of this model are that the sorbed concentration

TABLE II

RETENTION OF VAPORS OF 2-AMINOETHANOL ON SILICA GELS

Silica Gel			Tube	Bed	Vapor	First Detectable Breakthrough	
Source[a]	Mesh Range	Amount (mg)	i.d. (mm)	Depth (mm)	Conc (mg/m^3)	Volume (L)[b]	Amount (mg)
CEL	42/60	40	6	2.0	6.5	570	3.7
		75		3.7	7.7	1000	7.7
		75		3.7	53.2	114	6.1
		75		3.7	53.2	122	6.5
		150		7.5	30.4	507	15.4
		150		7.5	54.1	243	13.1
		150		7.5	58.7	282	16.6
		300		14.9	27.3	1382	32.8
		300		14.9	54.1	572	30.9
		300		14.9	54.1	592	32.0
SKC	20/40	75	4	8.4	61.8	62	3.8
		150		16.8	61.8	336	20.8
		225		25.2	61.8	671	41.5

[a] CEL = Coast Engineering Laboratories; SKC = SKC, Inc.

[b] Flow rate = 1 L/min in dry nitrogen carrier.

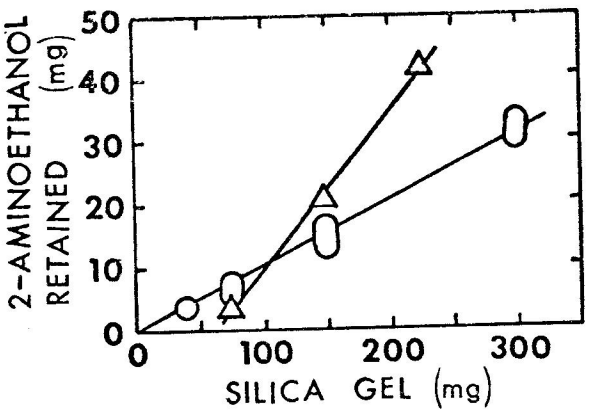

Fig. 3.

Retention amounts of 2-aminoethanol at the first detectable breakthrough points of silica gel beds. O, 42/60-mesh silica gel from Coast Engineering Laboratories, Inc., in 6-mm-i.d. tubes. △, *20/40-mesh silica gel from SKC, Inc., in 4-mm-i.d. tubes.*

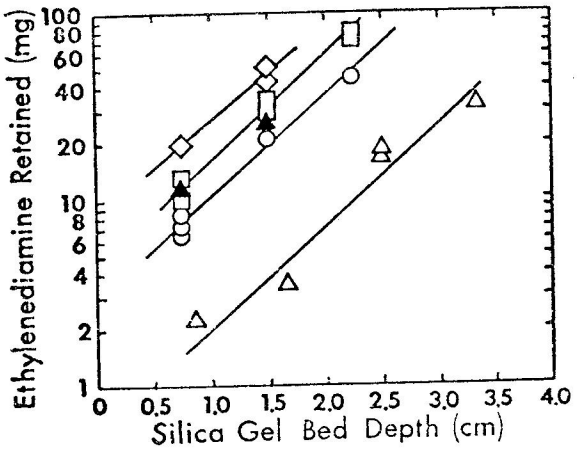

Fig. 4.

Retention amounts of ethylenediamine at the first detectable breakthrough points of silica gel beds. O, 42/60-mesh silica gel from Coast Engineering Laboratories, Inc., in 6-mm-i.d. tubes. □, *20/30-mesh and* ◇, *45/60-mesh silica gels from Davison Chemical desiccant in 6-mm-i.d. tubes.* △, *20/40-mesh silica gel from SKC, Inc., in 4-mm-i.d. tubes, and* ▲, *in 6-mm-i.d. tubes.*

is much less than the saturated value, that the adsorption is essentially irreversible, and that the controlling factor in vapor adsorption is the mass transfer rate. When this model is applied to adsorption tubes,[15]

$$\ln W = L/H + \ln (10^3 b X_L HA) ,$$

where

L = bed depth (cm),
H = height of a mass transfer unit (cm),
W = weight of vapor adsorbed at the first detectable breakthrough of the bed (mg),
A = internal cross section of the tube (cm^2),
b = weight of 1 cm^3 of adsorbent (0.710 g/cm^3),
X_L = concentration of sorbed gas at the bed exit when breakthrough is first detected (g test vapor/g adsorbent).

According to this equation, the slopes of the plots in Fig. 4 are 1/H, the reciprocals of the height of mass transfer units. These slopes are all quite similar (0.9 ± 0.1). This equation is also supposed to take into account differences in bed diameters. However, the points (triangles in Fig. 4) for SKC silica gel in 4-mm-i.d. and 6-mm-i.d. tubes do not fall on the same line. Turbulent flow in the smaller tube may explain this difference. Effects of several other parameters are revealed in these results. Comparing silica gels, retention amounts decreased in the order

TABLE III

RETENTION OF VAPORS OF ETHYLENEDIAMINE ON SILICA GELS

Silica Gel			Tube	Bed	Vapor	First Detectable Breakthrough	
Source[a]	Mesh Range	Amount (mg)	i.d. (mm)	Depth (cm)	Conc (mg/m^3)	Volume (L)[b]	Amount (mg)
CEL	42/60	150	6	0.75	160	46	7.4
		150[c]		0.75	167	50	8.4
		150[c]		0.75	187	38	7.2
		150		0.75	234	28	6.6
		300		1.49	173	125	21.6
		300		1.49	207	102	21.1
		450		2.24	269	165	44.4
SKC	20/40	75	4	0.84	117	20	2.3
		150		1.68	193	18	3.5
		225		2.52	129	140	18.1
		225		2.52	135	125	16.9
		300		3.36	170	190	32.2
		150	6	0.75	282	40	11.3
		300		1.49	324	75	24.3
Davison	45/60	150	6	0.75	158	125	19.8
		300		1.49	165	315	52.0
		300		1.49	177	245	43.4
	20/30	75	4	0.84	116	25	2.9
		225		2.52	116	290	33.6
		150	6	0.75	870	15	10
		150		0.75	890	12	13
		300		1.49	410	80	33
		300[d]		1.49	410	85	35
		300[e]		1.49	410	112	46
		300		1.49	670	51	34
		300		1.49	750	40	30
		450		2.24	460	163	75
		450		2.24	580	135	78

[a] CEL = Coast Engineering Laboratories; SKC = SKC, Inc.; Davison = Davison Chemical (Grace).

[b] Flow rate = 1 L/min.

[c] 30 mg water added to sorbent before sampling.

[d] Thermally conditioned at 160°C in helium flow.

[e] Thermally conditioned at 225°C in helium flow.

Davison>SKC>CEL. The smaller particle 45/60-mesh range Davison silica gel retained more ethylenediamine in 6-mm-diam beds than did the 20/30-mesh silica gel from the same original material. In two experiments (footnote C of Table III) 30 mg of water was added to 150 mg of silica gel and distributed by mixing until the sorbent was again free flowing. Retention of ethylenediamine was essentially the same with the wet as with the dry silica gel within observed experimental variations. Effects of thermal conditioning on the retention were also examined. Portions of the 20/30 Davison silica gel were purged with helium while being heated to 160°C or 225°C for at least 4 h. The results (footnotes d and e of Table III), though limited, suggest that 160°C conditioning has no effect, but that 225°C conditioning significantly improves retention.

Diethylenetriamine retention was measured for the 20/30-mesh silica gel prepared from Davison desiccant. The object of these more limited experiments was to determine retention for the selection of sorbent beds. The results obtained are given in Table IV. For 300 mg of silica gel the molar retention of diethylenetriamine is about half that of ethylenediamine. This is

reasonable since diethylenetriamine is about twice as large a molecule and should occupy twice the surface area as ethylenediamine.

Methylamine retention on three silica gels was also measured in a similar experiment. In this case, both methylamine vapor (400 ± 10 mg/m^3) and water vapor (16.2 g/m^3 or 94% relative humidity at 20°C) were generated by syringe pump injection (16.7 μL/min) of an aqueous methylamine solution (24.0 g/L) into a heated block through which air flowed (1000 cm^3/min). A photoionization detector was used to measure breakthrough vapor concentration. Beds tested for methylamine retention under these conditions contained 600 mg of silica gel in 8-mm-i.d. tubes. The lowest detectable breakthrough concentration was about 0.1 mg/m^3. Volumes of air passed and total methylamine adsorbed at the measured breakthrough times are listed in Table V. These results indicate that the 20/30-mesh Davison silica gel and the 20/40-mesh SKC silica gel were equivalent with an average capacity of 23 ± 2 mg methylamine. The capacity of the 42/60-mesh Coast Engineering Laboratories silica gel was lower at 16 ± 0.4 mg. This latter value is plotted in Fig. 5 vs bed depth along with results reported previously for this same silica gel.[5] In the earlier experiments the relative humidity was 92% at 24°C and the sample flow rate was 200 cm^3/min, rather than 1000 cm^3/min. The new data point is consistent with the earlier three points in spite of the difference in sampling flow rate. Such a flow rate independence was also observed for aniline vapor.[5] The linearity of the semilogarithmic plot of Fig. 5 is also consistent with Saltzman's Model #3 for adsorption indicator tubes discussed earlier in this section. A mass transfer unit height of 0.44 cm is obtained.

The second type of experiment, referred to as a distribution experiment, involved the same apparatus as the retention experiments; however, the silica gel was packed into the tubes as multiple 150-mg sections and each section was analyzed separately for adsorbed vapor. Objectives of these measurements were to determine the distribution of adsorbed vapor through beds and to determine the effects of humidity in sampled vapor on these distributions. Analyses of adsorbed vapors were performed by elution, reaction, and gas chromatography (Appendices A and B). The silica gel used in these experiments was 20/30 mesh prepared from Davison desiccant and conditioned at 225°C. Bed diameters were 6 mm. Average vapor concentrations were calculated from measured sampling volumes and measured total adsorbate. The extreme sampling condition of 100% relative humidity was obtained by bubbling the nitrogen stream through water before it entered the generator. The 50% relative humidity stream was obtained by diluting the water saturated nitrogen with an equal flow of dry nitrogen before it entered the amine vapor generator. Filters and traps were used to guarantee removal of any aerosols formed in the humidity generation or by condensation.

TABLE IV

RETENTION OF VAPORS OF DIETHYLENETRIAMINE ON SILICA GEL

Silica Gel[a] Amount (mg)	Bed Depth[b] (cm)	Vapor Conc (mg/m^3)	First Detectable Breakthrough[c] Volume (L)	First Detectable Breakthrough[c] Amount (mg)
150	0.75	40.5	358	14.5
150	0.75	44.0	309	13.6
150	0.75	109	139	15.2
300	1.49	57	460	26.3
300	1.49	190	136	25.8
300	1.49	213	10.3	22.2
450	2.29	98	1090	107

[a] 20/30 mesh from Davison Chemical desiccant.

[b] 6-mm-i.d. tubes.

[c] Flow rate = 1 L/min.

TABLE V

RETENTION OF VAPORS OF METHYLAMINE ON SILICA GELS

Silica Gel Source[a]	Mesh Range	First Detectable Breakthrough[b] Volume (L)	First Detectable Breakthrough[b] Amount (mg)
CEL	42/60	40.8	16.3
		39.0	15.6
SKC	20/40	58.8	23.5
		61.8	24.7
Davison	20/30	51.6	20.6
		62.2	24.9

[a] CEL = Coast Engineering Laboratories; SKC = SKC, Inc.; Davision = Davision Chemical (Grace).

[b] Flow rate = 1 L/min; humidity = 94% at 20°C; bed = 600 mg silica gel in an 8-mm-i.d. tube; challenge concentration = 400 mg/m^3 methylamine.

Distribution data for 2-aminoethanol and 2-diethylaminoethanol vapors adsorbed on 20/30-mesh silica gel in 6-mm-diam beds are given in Table VI. Per cent of total sample collected on the first 150 mg vs total sample measured is plotted in Fig. 6 for 2-aminoethanol at the relative humidity extremes of 0 and 100%. It appears that there is no large effect, if any, on collection efficiency by water vapor in the sample. Retention amounts of 2-aminoethanol are greater than 23 mg and 62 mg for 150- and 300-mg silica gel, respectively, at the 100% relative humidity extreme. Similar curves are shown in Fig. 7 for 2-diethylaminoethanol at 100% relative humidity measured on 150 mg, 300 mg, and 450 mg of this silica gel. In retention experiments discussed above for 2-aminoethanol, it was found that the quantity adsorbed at the first detectable breakthrough point was proportional to the amount of sorbent tested. Assuming this also holds for 2-diethylaminoethanol, the distribution data in Table VI and Fig. 7 have been "normalized" to 300 mg with the result shown in Fig. 8. Only one point does not fall on a common curve, which confirms the assumption of a linear relationship between quantity adsorbed and quantity of adsorbent. Retention amounts are estimated to be greater than 0.08-mg 2-diethylaminoethanol/mg silica gel.

Distribution results for ethylenediamine and diethylenetriamine similarly adsorbed and measured are listed in Table VII. Per cents of the total sample collected on the first 150 mg and 300 mg of silica gel are plotted vs total sample in Fig. 9 for ethylenediamine. Vapors were sampled at three relative humidities, 0, 50, and 100%. As with 2-aminoethanol,no large humidity effect was seen. This is also in agreement with ethylenediamine retention studies (Table III), in which adding water to silica gel did not significantly affect quantities retained. The retention data indicated an exponential decrease of ethylenediamine through the silica gel beds, so that at a given bed depth the fraction of total sample retained should be constant. The distribution data of Table VII does not agree with this conclusion, particularly for the largest two samples collected. The first two 150-mg sections contained 41.8 mg and 42.1 mg of 111 mg collected on one sampling tube. This suggests that these sections have become saturated with vapor, reducing the effective bed depth. In such cases a much more complicated mathematical model (Saltzman's Model #4) is required to describe the bed distributions and retentions.[15] The data of Table VII shows that ethylenediamine vapor retention on 150- and 300-mg silica gel beds was greater than 9 mg and 42 mg, respectively. Retention of diethylenetriamine on 150- and 300-mg beds was at least 14 mg and 39 mg, respectively. These lower limits for 150-mg beds are in agreement with the results from retention experiments (Tables III and IV), but the lower limits for two 150-mg beds are higher than for one 300-mg bed.

Another type of experiment in which silica gels were compared was gel activity measurement by the method of Jones, Reilich, and O'Neill.[16] Azobenzene dye in cyclohexane (5.0 mL of 0.550 g/L) was equilibrated with each silica gel (500 mg). The absorbances (A) of azobenzene in the original and equilibrated solutions were measured colorimetrically at 450 nm in a 10-mm path cell using a Cary 14 spectrophotometer. Relative gel activity (RGA) is listed in Table VIII for 10 silica gels calculated by $RGA = (A_{STD} - A_{SAM})\ (100)/A_{STD}$. Molar adsorptions in moles azobenzene/g silica gel are also given. Measurements from duplicate samples were averaged (estimated standard deviation = 0.4 μmoles/g). In a second set of these experiments, effects of water on gel activity was determined by adding 100 mg of water to five 500-mg silica gel samples and distributing it by gentle mixing. These samples were then equilibrated with a water-saturated cyclohexane solution of azobenzene. Results for these "wet" measurements are also listed in Table VIII.

Relative gel activities allow some interesting comparisons. The three original untreated silica gels decrease in azobenzene activity in the order Davison>CEL>SKC. The order of the latter two is reversed from the order of ethylenediamine retention found above. As expected, relative gel activity decreases as particle sizes increase and, therefore, as surface areas decrease. This is

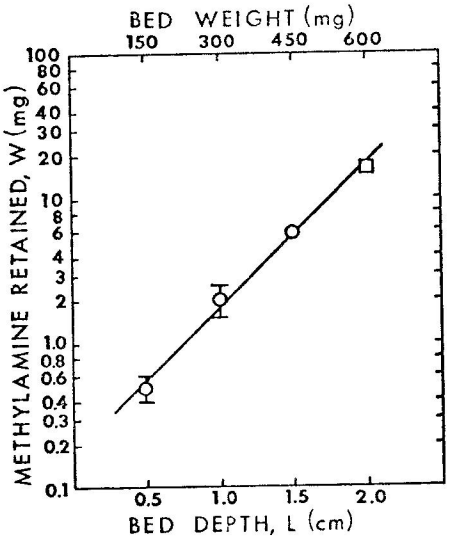

Fig. 5.
Methylamine retention on beds of 42/60-mesh silica gel from Coast Engineering Laboratories. 8-mm-diam beds, 94% RH, 20°C: ○, 200 cm³/min and □, 1000 cm³/min airflow rates.

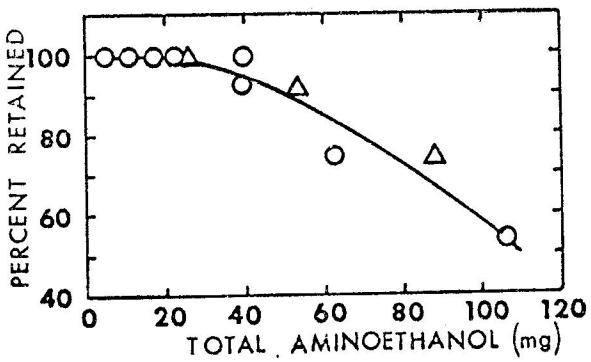

Fig. 6.
Retention of 2-aminoethanol vapors on 150-mg sections of 20/30-mesh silica gel from Davison Chemical desiccant, O, at 100% and, △, at 0% RH.

TABLE VI

DISTRIBUTION OF 2-AMINOETHANOL AND 2-DIETHYLAMINOETHANOL THROUGH SILICA GEL BEDS[a]

Sample Volume[b] (L)	RH (%)	Adsorbed Vapor on Each 150-mg Section (%) #1	#2	#3	#4	Total Amount (mg)	Vapor Conc (mg/m³)[c]
2-Aminoethanol							
240	0	100.0	0	0	0	25.4	106
480	0	91.4	8.6	0	0	53.8	112
725	0	73.2	26.8	0	0	87.8	121
120	100	100.0	0	0	0	4.8	40
260	100	100.0	0	0	0	10.8	42
480	100	100.0	0	0	0	17.0	35
480	100	100.0	0	0	0	23.3	48
960	100	100.0	0	0	0	39.7	41
960	100	92.1	7.9	0	0	39.3	41
960	100	74.2	25.8	0	0	62.3	65
1710	100	53.8	37.7	8.5	0	106.5	62
2-Diethylaminoethanol							
60	100	93.4	6.6	0	0	15.1	250
120	100	73.0	26.3	0.6	0	31.5	260
240	100	47.0	36.8	13.8	2.4	57.4	240
300	100	40.5	34.8	20.0	4.5	64.0	210

[a] 20/30-mesh silica gel (Davison) in 6-mm-diam beds.

[b] Flow rate = 1 L/min.

[c] Calculated from sample volume and total amine measured.

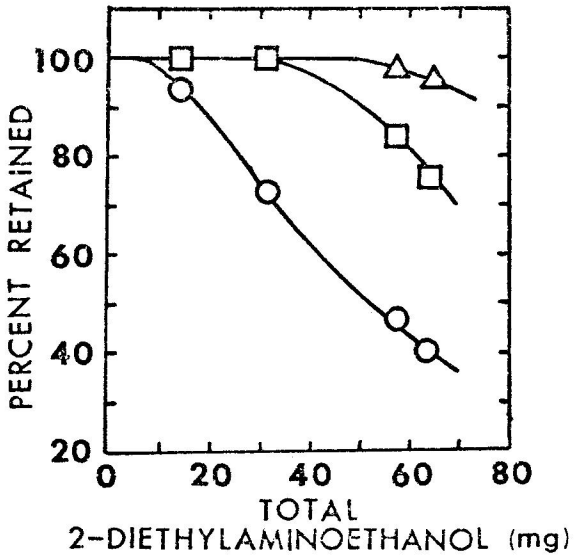

Fig. 7.
Retention of 2-diethylaminoethanol vapors on, ○, 150-mg and □, 300-mg and △, 450-mg of 20/30-mesh silica gel from Davision Chemical desiccant at 100% RH.

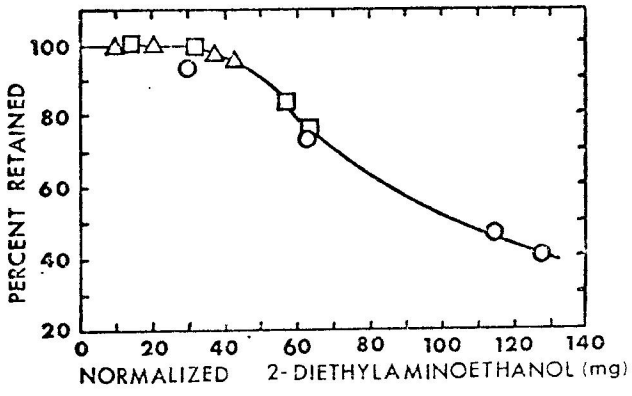

Fig. 8.
Retention data of Fig. 7 normalized to 300 mg by multiplying the total 2-diethylaminoethanol in each sample by the amount of silica gel and dividing by 300 mg. ○, 150-mg, □, 300-mg, and △, 450-mg total silica gel.

TABLE VII

DISTRIBUTION OF ETHYLENEDIAMINE AND DIETHYLENETRIAMINE THROUGH SILICA GEL BEDS[a]

Sample Volume[b] (L)	RH (%)	Adsorbed Vapor on Each 150-mg Section (%) #1	#2	#3	#4	Total Amount (mg)	Vapor Conc (mg/m^3)[c]
Ethylenediamine							
480	0	82.1	17.9	0	0	35.1	73
480	0	44.4	41.2	13.7	0.7	91.7	191
1000	0	37.6	37.8	21.0	3.6	111.3	111
480	50	70.7	29.3	0	0	23.9	50
480	50	66.3	33.2	0.5	0	57.0	119
420	100	100.0	0	0	0	4.0	10
480	100	100.0	0	0	0	8.7	18
480	100	67.1	32.9	0	0	42.5	89
Diethylenetriamine							
90	100	100.0	0	0	0	13.9	150
180	100	80.6	19.4	0	0	38.2	210
300	100	75.1	24.9	0	0	38.6	130

[a] 20/30-mesh from Davison in 6-mm-diam beds.

[b] Flow rate = 1 L/min.

[c] Calculated from total measured sample amount and volume.

in agreement with the ethylenediamine retention trend observed. Thermal conditioning improved the relative gel activities of the 20/30 Davison and the 42/60 CEL silica gels. Thermal conditioning at 225°C improved ethylenediamine retention significantly. The effect of adding water to the silica gels was to reduce gel activities and molar adsorptions in all cases. However, the silica gels with lowest molar adsorptions of azobenzene in the original condition were most affected by water.

A fourth test of silica gels examined the effects of source particle size and thermal conditioning on the recovery by solvent desorption of 2-dibutylaminoethanol. Triplicate samples of 150-mg sorbent were spiked with 1 μL of amine, eluted with 1 mL of 0.4 N HCl 4:1 methanol-water solution, and analyzed by gas chromatography. The average relative standard deviation for triplicate samples of 2.7 % included variations in spiking the samples with a microliter syringe. Recoveries measured for eight silica gels are given in Table IX. When these recoveries are compared with relative gel activities of Table VIII, no correlations are apparent. Thermal conditioning had no significant effect on the recoveries obtained from two of the silica gels. Likewise, within experimental precision, particle size did not significantly affect recoveries.

B. Acid-Coated Silica Gels

In the development of a sampling and analytical method for hydrazine compounds, it was necessary to coat silica gel with concentrated sulfuric acid to prevent losses of sample by oxidation during sampling.[6] This acid-coated silica gel was also found to have a higher capacity for amines than uncoated silica gel, especially at high humidities.[7] During this reporting period, additional experiments have been done to determine the usefulness of acid coating of silica gel for sampling and stabilizing amine compounds.

Procedures described in Sec. III.A were used to measure retentions of diisopropylamine and ethylenediamine vapors on silica gel and sulfuric acid-coated silica gels. Diisopropylamine results at the relative humidity extremes of 0 and 100% are listed in Table X and plotted in Fig. 10. Retention amounts at 100% relative humidity increase with sorbent amounts. Retention amounts measured for 300 mg of silica gel indicate that within experimental uncertainty there are no significant effects on sorbent retention capacity by either acid or humidity alone. However, when the acid-coated silica gel was used to sample high humidity air, the retention capacity was increased by more than four times. Apparently, water collected from the air diluted and activated the coating of concentrated sulfuric acid for reaction with this amine. The effects of water and sulfuric acid were studied further in retention experiments for ethylenediamine listed in Table XI. Coatings of 20% by weight on 42/60-mesh silica gel of solutions ranging from pure water to concentrated sulfuric acid were prepared and tested at 0% relative humidity. Added water alone had no effect on retention capacity. All of the acid coatings reduced the retention capacity for ethylenediamine. The optimum acid-coated sorbent was 16% sulfuric acid, 4% water, and 80% silica gel by weight. These results again show activation of the acid coating by water.

Acid coating of silica gel has also been studied as a means of reducing losses of amines during shipment of a sample to a laboratory and storage awaiting analysis. Concentrated sulfuric acid, which has been found to be effective for this purpose for hydrazine compounds, reacts with aminoalcohols to form sulfate esters that are difficult to analyze. Sorbent precoating with concentrated hydrochloric acid, which does not form such esters, was found to be ineffective since this acid was too volatile to remain on the sorbent during sampling. Concentrated sulfuric acid was completely retained under the same conditions. An alternate procedure of adding concentrated hydrochloric acid after adsorbing 2-aminoethanol or ethylenediamine on silica gel was

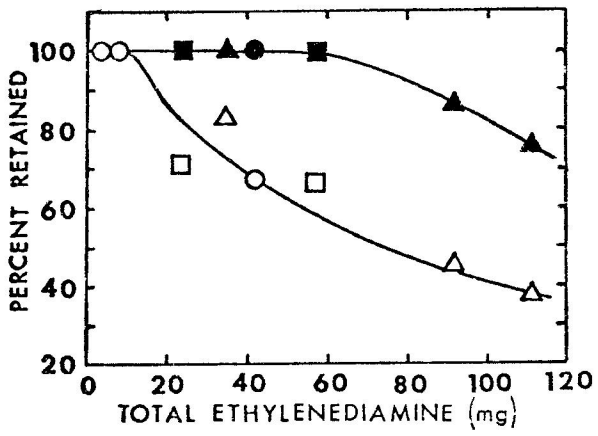

Fig. 9.
Retention of ethylenediamine vapors on 150 mg (open symbols) and 300 mg (solid symbols) of 20/30-mesh silica gel from Davision Chemical desiccant at △, 0% and □, 50% and ○, 100% RH.

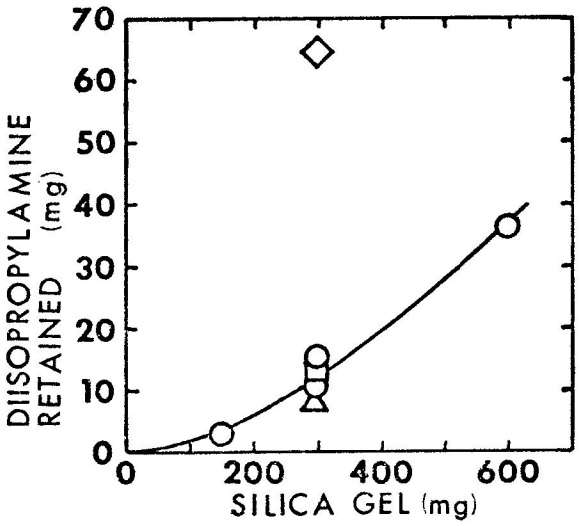

Fig. 10.
Retention of diisopropylamine vapors on 20/30-mesh silica gel from Davision Chemical desiccant in 6-mm-i.d. tubes: △, 0%, and ○, 100% RH with no acid coating; □, 0%, and ◇, 100% RH with sulfuric acid coatings on the silica gel.

TABLE VIII

RELATIVE GEL ACTIVITIES AND MOLAR ADSORPTIONS OF AZOBENZENE

Silica Gel			Relative Gel Activities		Adsorption (μmoles/g)	
Type[a]	Mesh	Size (μ)[b]	Original	Wet[c]	Original	Wet[c]
Davison	80/100	165	87.8		26.4	
	60/80	215	87.5		26.4	
	45/60	285	85.7		25.8	
	30/45	410	80.1		24.2	
	20/30	610	78.9	39.9	23.8	12.1
	20/30[d]	610	85.4	47.5	25.7	14.4
	20/30[e]	610	84.1	49.9	25.4	15.1
CEL	42/60	300	66.8	22.3	20.1	6.8
	42/60[d]	300	87.1		26.2	
SKC	20/40	610	46.1	9.6[f]	13.9	2.9[f]

[a] Davison = Davison Chemical (Grace); CEL = Coast Engineering Laboratories; SKC = SKC, Inc.

[b] Average particle size in the mesh range.

[c] 100 mg water/500 mg silica gel.

[d] Conditioned at 160°C in helium flow.

[e] Conditioned at 225°C in helium flow.

[f] 50 mg water/500 mg silica gel.

TABLE IX

SOLVENT DESORPTION OF 2-DIBUTYLAMINOETHANOL FROM SILICA GELS

Silica Gel Type[a]	Mesh	Relative Gel Activity	Conditioning Temp (°C)	Recovery[b] (%)
Davison	45/60	85.7		89
	30/45	83.1		89
	20/30	73.9		86
	20/30	85.4	160	84
	20/30	84.1	225	85
CEL	42/60	65.8		94
	42/60	87.1	160	94
SKC	20/40	46.1		94

[a]Davison = Davison Chemical (Grace); CEL = Coast Engineering Laboratories; SKC = SKC, Inc.

[b]1 µL of amine eluted from 150 mg silica gel with 1 mL of 0.4 N HCl in 4:1 methanol in water.

TABLE X

RETENTION OF DIISOPROPYLAMINE ON SILICA GEL AND ACID-COATED SILICA GEL

Silica Gel[a] (mg)	Conc Sulfuric Acid Added (mg)	RH (%)	Vapor Conc (mg/m^3)	First Detectable Breakthrough Volume[b] (L)	First Detectable Breakthrough Amount (mg)
150		100	340	10	3.4
300		100	120	89	10.7
300		100	330	47	15.6
600		100	120	304	36.5
300		0	120	70	8.4
300		0	308	30	9.2
300	75	100	280	230	65.1
300	75	0	280	53	15.0

[a]20/30-mesh from Davison, conditioned at 225°C.

[b]Flow rate = 1 L/min.

TABLE XI

RETENTION OF ETHYLENEDIAMINE ON SULFURIC ACID-COATED SILICA GELS AT LOW HUMIDITY

Silica Gel[a] (mg)	Conc Sulfuric Acid Added (mg)	Water Added (mg)	Vapor Conc (mg/m^3)	First Detectable Breakthrough Volume[b] (L)	First Detectable Breakthrough Amount (mg)
150	0.0	0.0	160	46	7.4
	0.0	37.5	160	46	7.4
	7.5	30.0	160	16	2.6
	15.0	22.5	160	16	2.6
	22.5	15.0	160	22	3.5
	30.0	7.5	160	24	3.8
	37.5	0.0	160	16	2.6
300	0.0	0.0	170	125	21.3
	37.5	0.0	190	55	10.5

[a]42/60 mesh from Coast Engineering Laboratories in a 6-mm-i.d. tube.

[b]Flow rate = 1 L/min.

tested. In one set of experiments duplicate samples of 1-mg 2-aminoethanol were added to 150-mg sections of 42/60-mesh silica gel stabilized with 40 μL of concentrated hydrochloric acid, eluted with 2 mL of 4:1 methanol-water and analyzed. Recoveries measured for samples eluted after 1 h and after three days of storage at 20°C were the same, 94%. For uncoated silica gel sections, recoveries of 85% were measured after three days under the same conditions. In similar preliminary experiments with ethylenediamine recoveries of 98% were obtained after seven days when acid was present compared with 80% on the uncoated silica gel. More extended storage stability studies will be discussed later in this report. However, these preliminary experiments demonstrated the usefulness of post-sampling addition of hydrochloric acid for stabilizing collected amine samples. A 50-μL glass syringe with nonferrous parts (platinum needle and Teflon-tipped plunger) was found to be most useful for adding the concentrated hydrochloric acid to silica gel sections.

C. Pressure Drop Measurements

An important feature of a sorbent bed used to remove vapors from air is its resistance to flow usually expressed as pressure drop at a selected flow rate. Parameters that affect flow resistance include bed cross section, bed depth, particle size, and linear flow velocity. Components of a sampling tube other than the sorbent bed, such as the plugs that hold the beds in place or separate, may contribute significantly to flow resistance. The upper limits for acceptable flow resistance of a sampling tube are determined by the capabilities of sampling pumps used with the tube. Many battery-operated personal sampling pumps are now commercially available with differing flow rate and flow resistance capabilities. A general rule of thumb used in this work is that the pressure drops should not exceed 24 torr (13 in. of water) at 1000 cm^3/min volumetric flow rate or 4.7 torr (2.5 in. of water) at 200 cm^3/min. Effects of bed diameter (sampling tube inner diameter) and volumetric flow rate on pressure drops for 200 mg of 42/60-mesh sulfuric acid-coated silica gel (160-mg silica gel base) have been reported in an earlier progress report.[8] Pressure drop was proportional to flow rate and increased in the ratios of 1:3:18 for beds of 8-mm-, 6-mm-, and 4-mm-diam, respectively. The measured pressure drop for 200 mg of this sorbent was 17 torr at 1000 cm^3/min. Some additional pressure drop measurements, which have been made to demonstrate effects of silica gel particle size, sorbent amount (bed depth), and glass wool plugs, are shown in Table XII and Fig. 11. Urethane foam, a very porous material of negligible pressure drop, was used to hold silica gel beds in place in the first set of experiments. The plots of pressure drop vs silica gel amount in Fig. 11 show a proportional relationship with a 4:1 pressure drop ratio for 42/60- and 20/30-mesh sorbents, respectively. Glass wool, on the other hand, introduces significant pressure drop to a tube when it is used as a bed retainer. Furthermore, the contribution to flow resistance depends on how much glass wool is used and how firmly it is packed, two variables that are difficult to control. Two curves in Fig. 11 (solid symbols) show the tube pressure drops when two plugs of a minimum amount of glass wool were used to hold the silica gel beds in place. The pressure drop increases, due to the glass wool, are significant for smaller beds, but become less significant for larger amounts of silica gel. Pressure drops of the glass wool and the silica gel are not additive.

Two commerical silica gel tubes from SKC, Inc. were also tested for pressure drop. The smaller tube of 4-mm-i.d. (6-mm-o.d.) contained 20/40-mesh silica gel in two beds measured to be 147 mg and 75 mg. Polyurethane plugs were behind the two sections and a small amount of glass wool supported by a wire was in front of the larger first section. The second tube measured, also from SKC, Inc., was of similar construction, but contained beds of 737 mg and 389 mg of 20/40-mesh silica gel in a 6-mm-i.d. (8-mm-o.d.) glass tube. Pressure drops for these two tubes, also listed in Table XII, are within the pump capabilities assumed above.

IV. SAMPLING AND ANALYSIS FOR AMINOETHANOLS

A. Summary of the Method

A method for sampling and analyzing vapors in air of three aminoalcohol compounds of recognized toxicity has been developed. The three compounds are 2-aminoethanol (ethanolamine), 2-diethylaminoethanol, and 2-dibutylaminoethanol, which have the TLVs[1] listed in Table I. These bifunctional compounds act as both amines and alcohols with boiling points much higher than the corresponding monofunctional amines or alcohols. The method is summarized in the text below and is detailed in Appendix A in the format of the **NIOSH Manual of Analytical Methods.**[13] Discussion of the experimental basis of the method will also follow.

The sampling tube that was designed for collecting these compounds from air is shown in Fig. 12. It contains two 150-mg sections of 20/30-mesh activated silica gel in a glass tube of 8-mm-i.d., held in place by Teflon screens supported by fluorocarbon rings of 1-mm thickness. Glass wool may be used instead to enclose and separate the sections in 6-mm-i.d. tubes, but is less desirable. Urethane foam will dissolve in concentrated HCl added for sample stabilization. Using a calibrated personal sampling pump, air is drawn from the worker's breathing zone through the tube at a flow rate of 200 to 1000 cm^3/min. The flow rate to be used depends upon the duration of the sampling period, the pump capability, and the concentration in air expected. After sampling for a measured time or volume, silica gel sections are transferred to test tubes and eluted with 2 mL of 4:1 methanol-water with 20 μL of concentrated hydrochloric acid added. If this cannot be done immediately because of the necessity of shipping and/or storing samples, 20 μL of concentrated hydrochloric acid is added to each section in the tube and in the laboratory the transferred sections are eluted with 2 mL of 4:1 methanol water only. One hour of elution with occasional shaking of the samples is sufficient. Standards are also prepared in the acidic eluent mixture. Then 0.5 mL of eluted sample or standard is transferred to a septum sealed bottle or tube and 0.5 mL of 0.2 N sodium hydroxide in 4:1 methanol-water is added. This step regenerates the amine for analysis. If 2-aminoethanol is expected in the sample, 10 μL of benzaldehyde is also added to a second such mixture and allowed to react for at least 10 min to form a derivative. For analysis, 3-μL aliquots of the final solutions are injected into a gas chromatograph with 1 μL of methanol solvent flush. A 1.8 (6-ft) by 2-mm-i.d. glass column packed with 10% Carbowax 20 M and 2% KOH phase on 80/100-mesh Chromosorb W AW is used. The carrier flow is 50-cm^3/min helium, and column temperatures range from 90°C to 225°C depending on the amine being analyzed. A flame ionization detector is used.

B. Sampling Tube Selection

The design of the sampling tube in Fig. 12 was based on considerations of target concentrations, data from retention experiments, and data from distribution experiments. It is desirable to be able to quantitatively collect all the sample vapor at concentrations up to five times the TLV for periods up to 8 h. At a sampling flow rate of 200 cm^3/min, this maximum sample is calculated by 5 x TLV (mg/m^3) x 0.096 m^3, i.e., 2.9 mg for 2-aminoethanol, 24 mg for 2-diethylaminoethanol, and 6.7 mg for 2-dibutylaminoethanol. For short sampling periods, the maximum amount of sample on a minimum amount of sorbent is desirable for best sensitivity of the method; therefore, a higher sampling flow rate of 1000 cm^3/min is recommended. Minimizing the sorbent amount also minimizes the resistance of the tube to flow and minimizes requirements on the pump selected.

TABLE XII

PRESSURE DROP MEASUREMENTS FOR SILICA GEL BEDS IN SAMPLING TUBES

Type of Plug	Silica Gel Mesh Range	Silica Gel Amount (mg)	Bed Depth[b] (mm)	Flow Rate (cm^3/min)	Pressure Drop (torr)
Urethane foam	20/30	150	7.5	1000	2.1
		300	14.9	1000	4.1
	42/60	150	7.5	1000	7.9
		300	14.9	1000	18.1
		150	7.5	200	1.5
		300	14.9	200	3.3
Glass wool	20/30	150	7.5	1000	6.0
		300	14.9	1000	6.9
	42/60	75	3.7	1000	8.0
		150	7.5	1000	11.6
		300	14.7	1000	17.3
		75	3.7	200	1.5
		150	7.5	200	2.2
		300	14.7	200	3.1
Combination[a]	20/40	1128	56.0	1000	12.8
		1128	56.0	200	2.4
		222	24.9[c]	1000	18.6
		222	24.9[c]	200	2.7

[a]Commercial silica gel tubes from SKC, Inc., that have one glass wool plug and two urethane foam plugs. Weights of silica gel are those actually measured in both sections of one sample tube.

[b]6-mm-i.d. tubes unless otherwise indicated.

[c]4-mm-i.d. tube.

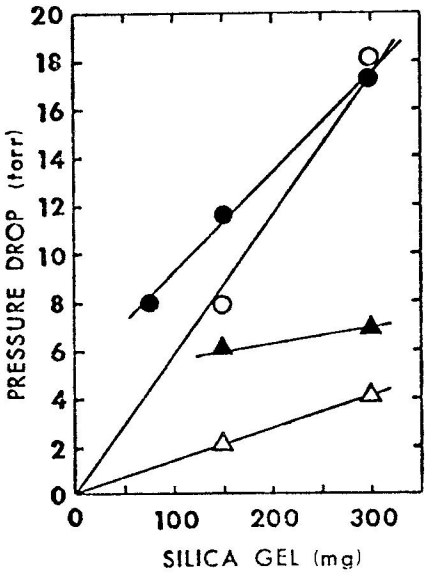

Fig. 11.
Pressure drops of silica gel beds in 6-mm-i.d. sampling tubes at 1000 cm^3/min airflow rate. Open symbols indicate urethane plugs and solid symbols indicate glass wool plugs: △, 20/30-mesh and ○, 42/60-mesh silica gel.

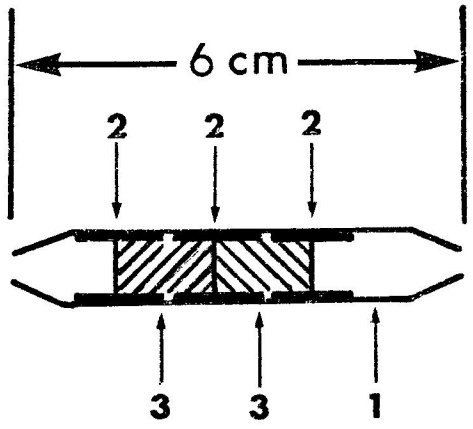

Fig. 12.
Sampling tube for aminoethanols, ethylenediamine, and diethylenetriamine: (1) 8-mm-i.d. glass tube tapered and flame sealed after packing, (2) 100-mesh fluorocarbon screens sandwiched between two fluorocarbon rings, each 3.5-mm wide and 1-mm thick, and (3) 150-mg sections of 20/30-mesh activated silica gel. Alternately, the tube may be 6-mm i.d. if glass wool plugs are used.

Retention experiments (Sec. III.A) for 2-aminoethanol on 42/60-mesh silica gel from Coast Engineering Laboratories in a 6-mm-i.d. tube yielded an average of 0.10-mg 2-aminoethanol/mg silica gel, so that 29 mg of this silica gel should be sufficient. If they could be packed and held in a 6-mm-i.d. tube without channeling, even less of the higher capacity SKC and Davison gels would be sufficient. Distribution results for 2-diethylaminoethanol on 20/30-mesh conditioned Davison silica gel led to the conclusion that retention was at least 0.08-mg/mg silica gel in a 6-mm-i.d. tube. Therefore, 300 mg of this adsorbent is sufficient to meet the maximum sample capability of 24 mg. No data was taken for 2-dibutylaminoethanol; however, previous experience[4-6] has shown that silica gel has higher molar adsorption capacities for higher boiling amines within a homologous series. Even if molar retention capacities were the same, 300 mg would retain 35 mg of 2-dibutylaminoethanol. Also, the retention capability desired for 2-dibutylaminoethanol is much lower than for 2-diethylaminoethanol due to its lower TLV. Therefore, 300 mg of silica gel in a 6-mm-i.d. tube should be more than sufficient for 6.7-mg 2-dibutylaminoethanol.

These data and calculations led to the design of the tube shown in Fig. 12. The silica gel should be equivalent to the 20/30-mesh material prepared from Davison activated desiccant and conditioned at 225°C. It has a relative gel activity for azobenzene of 0.84. The 300 mg of silica gel required is separated into two 150-mg beds to allow more sensitive analysis for small samples, which are completely retained on the first bed. The upper limits of the method have been defined in Appendix A as the capacities of only the first 150-mg bed. This assumes that the second bed is used only to determine any penetration of the first bed. The 6-mm-diam beds have been shown to be more effective than 4-mm-diam beds and to have lower flow resistance. Pressure drops of the described tube are 0.8 torr (0.4 in. water) at 200 cm^3/min and 4.1 torr (2.2 in. water) at 1000 cm^3/min, not including contributions from three plugs when glass wool is used (~5 torr at 1000 cm^3/min).

C. Sample Stabilization

Losses of samples of aminoethanols adsorbed on silica gel may be significant when there is a delay between sample collection and sample elution. Organic bases, particularly primary amines, oxidize when exposed to air. In addition, 2-aminoethanol reacts with carbon dioxide. When the sample is eluted with an aqueous acidic solvent the amines form salts, which are much less reactive to oxygen and carbon dioxide.

Recoveries of aminoethanol compounds adsorbed on silica gel in sealed tubes have been measured for up to 28 days and are listed in Table XIII and plotted in Fig. 13. Samples of 1 μL of an amine were injected into 150 mg of 42/60-mesh silica gel in a tube and sealed with Parafilm. Some samples were kept at room temperature (20 ± 2°C). For one set of 20 samples, 40 μL of concentrated hydrochloric acid (37%) was injected into each section and the tubes were resealed. They were stored at ambient conditions until eluted and analyzed at intervals of seven days. Recovery of 2-aminoethanol (Fig. 13) from samples in sealed tubes at 20°C decreased rapidly by 15% in the first three days, followed by a slower decrease over succeeding weeks. Recoveries remained above 80% for two weeks of storage. When samples on silica gel were stored in a freezer at -17°C, only the slower decrease occurred. For the samples to which the acid was added, no significant decrease in recovery was observed for at least four weeks. Sample losses for the other two compounds, which are tertiary amines, were less significant than with 2-aminoethanol. On the basis of these experiments, it is recommended that samples be eluted immediately after sampling or that samples be stored for short periods only in a freezer, or that samples be stabilized with concentrated hydrochloric acid for shipping and awaiting analysis. Formation of salts by

TABLE XIII

STORAGE STABILITIES OF AMINOETHANOLS ADSORBED ON SILICA GEL[a]

Compound	Storage Period (days)	Recoveries (%) Ambient[b] (20°C)	Freezer[b] (-17°C)	Hydrochloric Acid Coated[c]
2-Aminoethanol	0	100		
	3	85	94	
	7	87	99	96
	10	87	94	
	14	80	96	100
	21	68	73	98
	28	62	82	96
2-Diethylaminoethanol	14	92	100	
	28	82	88	
2-Dibutylaminoethanol	14	89	100	
	28	70	78	

[a] 1 µL injected onto 150 mg of 42/60-mesh silica gel and mixed.

[b] Averages of duplicate samples and standards, ±3%.

[c] 40 µL of concentrated HCl (37%) injected after the sample. Averages of five samples and standards, 3% RSD.

acid addition to amines greatly reduces sample volatility, virtually eliminating sample migration between sorbent sections and sample loss due to accidental heating or atmospheric pressure reduction.

D. Sample Desorption

It has been found that a strong acid and a high ethanol concentration in an aqueous solution is required to efficiently recover 2-diethylaminoethanol adsorbed on silica gel.[9] Further studies were done with 1 mg of 2-aminoethanol eluted from 150-mg of 42/60-mesh silica gel by 1 mL of 0.4 N HCl in 80% alcohol. There were no significant differences in recoveries measured between experiments using 80% ethanolic eluent and 80% methanolic eluent. A cleaner chromatogram with a smaller solvent peak was obtained in the gas chromatographic analysis when methanolic eluent was used. Therefore, for subsequent method development an eluent of 0.4 N HCl in 4:1 methanol-water (by volume) was used. The acid strength is not important in determining desorption efficiency as long as it is present in excess over the amount of amine.[9] In the final method, 0.2 N HCl is recommended.

Desorption efficiencies were studied to select an eluent/sorbent ratio and to determine effects of sample size. In one experiment, 1-µL (1.02 mg) of 2-aminoethanol was added to six sections of 150 mg of 42/60-mesh silica gel and also to duplicate aliquots of 1, 2, or 3 mL of methanolic acid solution, which served as standards. After shaking the silica gel samples to distribute the amine, duplicates of these were immediately mixed with 1, 2, or 3 mL of the eluent solution. The next day all samples and standards were analyzed by duplicate injections into the gas chromatograph. Average analytical precision was 4% relative standard deviation. Averages of the duplicate eluted samples and prepared standards were compared to obtain the desorption efficiencies of Table XIV. Differences of the duplicates were used to estimate the relative standard deviations of the calculated desorption efficiencies. The second set of three experiments with

results shown in Table XIV were similarly performed, except that the amount of 2-aminoethanol was varied from 0.2 to 1.0 mg. Only one sample and one standard were prepared and analyzed at each concentration. The relative standard deviations given were calculated from differences in peak areas from duplicate gas chromatographic analyses. The third set of experiments approached the desorbed sample equilibrium from another direction. A solution of 1.02-mg/mL 2-aminoethanol in eluent was mixed in the ratios of 0.5-4 mL per 150 mg of 42/60-mesh Davison silica gel conditioned at 160°C. After equilibrating overnight, the original solution and each equilibrated solution were analyzed. This procedure has been reported to give results equivalent to desorption.[17] Average analytical precision was 2.4% relative standard deviation, or 3.5% for the calculated desorption efficiencies. The desorption efficiencies of Table XIV are all greater than 90%. Within experimental uncertainties there are no significant differences due to variations in either sample size or eluent volume. Sensitivity of the method decreases with increases in eluent volume, so that the minimum volume that gives acceptable desorption efficiency should be used. A ratio of 2 mL of eluent per 150 mg of silica gel was selected for most experimental work. Experience has shown that when samples with eluent in a sealed tube are shaken occasionally, 2 h are sufficient to maximize desorption. Longer periods of elution may also be used.

Desorption efficiencies of 2-diethylaminoethanol and 2-dibutylaminoethanol were also greater than 90% when 2 mL of methanolic acid eluent was used. In one case of 0.09 mg of 2-diethylaminoethanol eluted from 150 mg of 42/60-mesh silica gel, desorption efficiencies of 89 and 92% were measured for eluent volumes of 1 mL and 2 mL, respectively. Other examples of recoveries are the data in Table XIII.

E. Derivatization of 2-Aminoethanol

Difficulties in analyzing 2-aminoethanol by standard gas chromatography techniques result from sample tailing on the column and low sensitivity to detection by flame ionization. The tailing, common to primary aliphatic amines, can be reduced by using a basic column packing. The low sensitivity of the flame ionization detection is due to the small number of carbon atoms (2) and the presence of nitrogen and oxygen in the molecule, which inhibit the formation of C_n^+

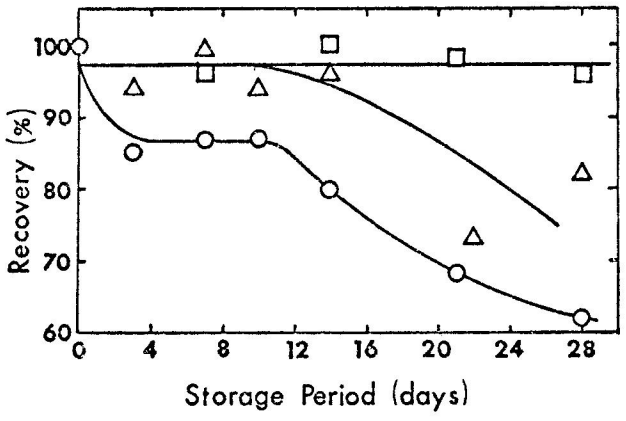

Fig. 13.
Recoveries of 2-aminoethanol from silica gel after storage periods, ○ at 20°C, and △ at -17°C, and □ at 20°C with concentrated acid added for stabilization.

TABLE XIV

EFFECTS OF ELUENT VOLUME AND SAMPLE SIZE ON DESORPTION EFFICIENCY OF 2-AMINOETHANOL

Sample Size[a] (mg)	Eluent Volume[b] (mL)	Desorption Efficiency	RSD[c] (%)
1.02	1	0.93	2.5
1.02	2	1.02	4.0
1.02	3	0.96	3.6
1.02	2	0.94	2.0
0.51	2	0.93	3.1
0.20	2	1.05	12.3
0.51	0.5	0.93	3.5
1.02	1	0.92	3.5
2.04	2	0.93	3.5
4.08	4	0.96	3.5
0.10[c]	2	0.97	6.8

[a]For 150-mg of 42/60-mesh silica gel from Coast Engineering Laboratories.

[b]Acidic methanol, 0.4 N HCl, 80% methanol.

[c]RSD = relative standard deviation.

[d]For 150 mg of 20/30-mesh silica gel from Davision.

detectable ions. One way to overcome these analytical difficulties is to form organic derivatives with more carbon content. Requirements for a derivative are that it be formed rapidly and completely, that it be soluble in the medium to be analyzed, and that it be volatile and stable enough for gas chromatography.

Reaction of 2-aminoethanol with benzaldehyde has been selected to form a derivative with these desired characteristics. The formation of benzylidenes from primary amines for gas chromatographic analysis has been reported.[18-20] However, it was necessary to demonstrate that this reaction would also proceed at low concentrations in the aqueous alcoholic solution used for sample desorption from silica gel. Experiments showed that this derivative did not form sufficiently in acidic eluent or in sodium acetate buffered eluent (pH = 4). However, in basic solution the reaction of 2-aminoethanol and benzaldehyde did go to completion within an hour. The dehydration step of the condensation is catalyzed in basic solution.[21] 2-Benzylideneaminoethanol was readily analyzed on a Carbowax 20/KOH column selected for unreacted 2-aminoethanol, 2-diethylaminoethanol, and 2-dibutylaminoethanol. Linear calibration curves (over two orders of magnitude in concentration) and enhanced sensitivities (by a factor by 12.5) were obtained by analyzing the derivative of 2-aminoethanol. The other two aminoethanols, because they are tertiary amines, do not react with benzaldehyde. The procedure for derivatization is detailed in Appendix A.

Kinetics of product formation were also studied to determine reagent concentrations and reaction times required. Standards of 2-aminoethanol in methanolic acid eluent were alkalinized with an equal volume of base and mixed with benzaldehyde. At selected reaction times, samples were injected into a gas chromatograph for analysis. Figure 14 shows two product formation curves of product peak area vs reaction time. The benzaldehyde concentration was 10 μL/mL in alkalinized mixture or 0.10 moles/L. Concentrations of 2-aminoethanol were 8.3×10^{-2} moles/L or 8.3×10^{-4} moles/L in the alkalinized solution. The similar shape of the product formation curves for these two reactant concentrations differing by a factor of 100 indicates that the reaction is first order in 2-aminoethanol. Therefore, the extent of reaction for a fixed concentration of benzaldehyde is a function of time only, and not a function of 2-aminoethanol concentration. This is a convenient situation since sample sizes are usually unknown. At a benzaldehyde concentration of 0.10 moles/L the reaction is essentially complete by 20 min. Figure 15 shows other product formation curves for 4.2×10^{-4} moles/L 2-aminoethanol and three concentrations of benzaldehyde 0.05, 0.01, and 0.20 moles/L. For a reaction rate first order in a large excess of benzaldehyde, the extent of derivative formation should be a function only of the product of benzaldehyde concentration and reaction time. The results shown in Fig. 15 indicate that this is indeed the case. Again we conclude that the reaction in essentially complete by 2-min moles/L, or 20 min for 0.10 moles/L benzaldehyde. Reaction time required varies inversely with benzaldehyde concentration. In a number of other cases such reactions have been reported to be first order in carbonyl compound and first order in amine compound.[22]

F. Gas Chromatographic Analysis

Several gas chromatograph columns and conditions were used and tested. One column was selected for analyzing 2-diethylaminoethanol, 2-dibutylaminoethanol, and the derivative of 2-aminoethanol with benzaldehyde. It is capillary glass 1.8-m (6-ft) long and 2-mm i.d. (0.25-in. o.d.) filled with a column packing of 10% Carbowax 20M and 2% KOH by weight on 80/100-mesh Chromosorb W/AW support. Carbowax is a good liquid phase for alcohols, and potassium hydroxide reduces tailing by amines.[23] This column can also be used for underivatized 2-aminoethanol if the sample size is large.

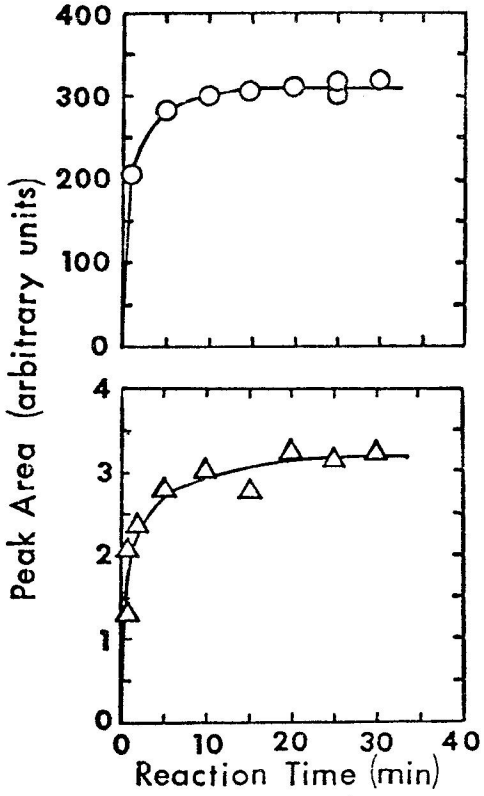

Fig. 14.
2-Benzylideneaminoethanol formation curves from the reaction of benzaldehyde (0.1 moles/L) and 2-aminoethanol, O at 8.3 x 10^{-2} moles/L, and Δ at 8.3 x 10^{-4} moles/L.

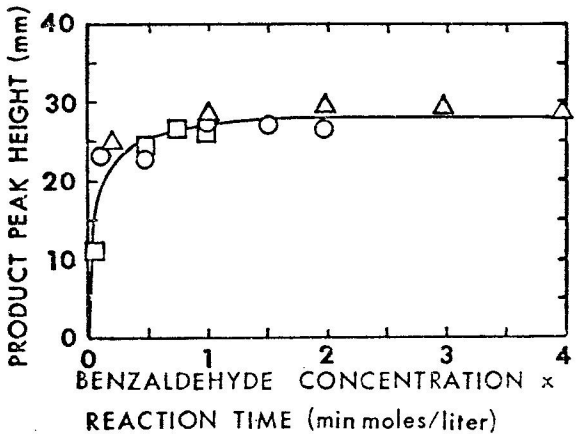

Fig. 15.
2-Benzylideneaminoethanol formation curves from the reaction of 2-aminoethanol (4.2 x 10^{-4} moles/L) and benzaldehyde, □ at 0.05 moles/L, and O at 0.10 moles/L, and Δ at 0.20 moles/L.

Chromatographic conditions selected were: a helium carrier gas flow rate of 50 cm^3/min, an injection port temperature of 150°C, a detector temperature of 250°C, and column temperatures of 90-225°C. Hydrogen and airflows to the flame ionization detector were adjusted to optimize the response for the instrument used (Perkin-Elmer 900 or Hewlett Packard 7620A). When only one compound was present, isothermal analysis gave the best analytical precision. At 90°C for 2-diethylaminoethanol, 150°C for 2-dibutylaminoethanol, and 225°C for the derivative of 2-aminoethanol, retention times of 280, 180, and 195 s, respectively, were obtained. All three compounds were measured in the same injection in some cases by temperature programming of the column, holding at 90°C for 3 min, heating to 225°C at 16°C/min, and holding at 225°C for 6 min. A chromatogram for this program is shown in Fig. 16. Sample sizes of 2.8 μL were injected using a methanol flush technique.

Precision of the gas chromatographic analysis has been determined experimentally for the three aminoethanols at several concentration levels for the conditions given above. Table XV lists estimates of relative standard deviations calculated[24] from the ranges of peak areas obtained from replicate (usually five) injections. These results represent the precision of a standard curve, which would be used for calibration.

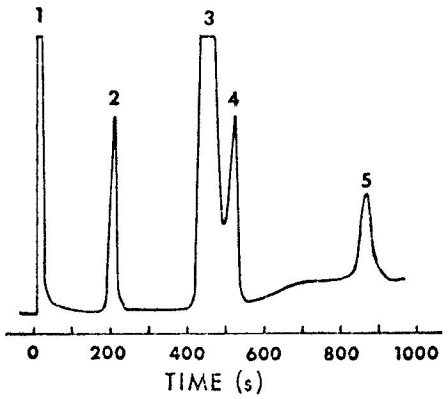

Fig. 16.
Gas chromatogram obtained by temperature programming of the 10% Carbowax 20M, 2% KOH column. Conditions are given in the text. (1) Methanol solvent, (2) 2-diethylaminoethanol, (3) excess benzaldehyde, (4) 2-dibutylaminoethanol, and (5) 2-benzylideneaminoethanol.

TABLE XV

PRECISIONS OF THE GAS CHROMATOGRAPHIC ANALYSIS OF AMINOETHANOL COMPOUNDS

Compound	Conc of Original Std (μg/mL)	Amount of Amine Injected[a] (ng)	RSD (%)
2-Aminoethanol	10 200	14 100	3
	1 020	1 410	2
	102	141	8
	51	70	13
	20	28	10
	10	14	40
2-Diethylaminoethanol	8 900	12 300	2
	890	1 230	2
	89	123	6
	45	62	60
2-Dibutylaminoethanol	860	1 190	1
	86	119	8
	17	24	9
	9	12	31

[a] In a volume of 2.8 μL reacted solution.

G. Precision and Accuracy

In addition to random errors from the gas chromatographic analysis, precision of the total method is affected by random errors from the volume of air pumped, the desorption process, and sample preparation. The contribution of the sampling pump to the precision of the method is difficult to estimate since factors such as pump type and condition and battery charge must be considered. The best that can be expected is a volume reliability of ±2%. Pump errors are often systematic (due to incorrect calibration or weak battery), as well as random, and affect the accuracy, rather than the precision of a method.

Desorption of an amine from silica gel is an equilibration process between the eluent and the silica gel. The variation of this equilibrium contributes to the precision of the total method by affecting the desorption efficiency. What are the effects of volumetric errors on the desorption efficiency? Consider a ±5% variation in the amount of silica gel packed into a bed and a ±2% pipetting error in adding eluent to this section. The desorption efficiency (or recovery) is given by $R = y/(y + xK_D)$, where x is the weight of sorbent in mg (S_x = 5%) and y is the volume of eluent in mL (S_y = 2%) and K_D is the equilibrium constant (mL/mg). By a propagation of errors calculation[25] the relative standard deviation of the recovery is $S_R = (1\text{-}R)(S_x^2 + S_y^2)^{1/2}$. At a recovery of 0.90, S_R = 0.5%. Therefore, relatively large errors in this step contribute only small errors to desorption efficiency as long as the recovery is high.

Precision of sample preparation has been determined experimentally. A solution containing 0.86 mg/mL of 2-dibutylaminoethanol in eluent was aliquoted five times and each sample was prepared and analyzed separately. The variation in the analytical results was 3.3% relative standard deviation, while the variation of the GC analysis determined by five injections of a single sample was 1.2%. The precision of the sample preparation was, therefore $[(3.3\%)^2 - (1.2\%)^2]^{1/2}$ = 3.1% relative standard deviation. This value implies a pipetting precision of 500 μL ± 16 μL, which is rather large and certainly could be improved.[26]

The concentration of amine in air sampled using this method is calculated by $W_T = (W \times F_D)/(R \times V)$, where W_T is the amount of amine obtained from a standard curve, F_D is the volumetric dilution factor in sample preparation (±3%), R is the recovery in the desorption step (±0.5%), and V is volume of air drawn by the pump (±2%). If the minimum level of measurement is defined as the sample level at which the total precision is 10% relative standard deviation, the gas chromatographic precision must be less than $[(10\%)^2 - (3\%)^2 - (0.5\%)^2 - (2\%)^2]^{1/2} = 9.3\%$. Using precision data of Table XIV, the minimum levels of measurement defined in this way are approximately 100 μg/mL (200 μg/sample) of 2-aminoethanol, 80 μg/mL 2-diethylaminoethanol, and 20 μg/mL 2-dibutylaminoethanol.

The accuracy of the total sampling and analysis procedure is determined principally by the accuracy of air sample volume measurement and by the recovery of sample from the silica gel adsorbent. Collection efficiency is 100% until breakthrough of the sorbent beds occurs. Adsorbed samples can be stabilized by acid to prevent losses during shipping and storage. In the analytical procedure, eluted samples are treated in the same way as the standards prepared in eluent to which they are compared. As has been shown, desorption efficiencies of aminoethanols are usually greater than 90%. If greater accuracy is desired, the desorption efficiency must be measured or taken into account.

A procedure for determining desorption efficiencies is detailed in Appendix A. It involves adding a known amount of an amine of interest to 150 mg of silica gel and to 2 mL of eluent solution. The silica gel is then eluted with 2 mL of the same solution. Eluted sample and standard solutions are analyzed together. It must be noted, however, what precision can be expected for such a desorption efficiency determination. One contribution to the precision of determining desorption efficiency is from the addition of a known amount of amine or solution of an amine to a sorbent section. This random error is estimated to be ±2% at best, since volumes less than about 50 μL would be involved. A second source of error is the determination of the amount of sample recovered by desorption (recovery ± 0.5%), sample preparation (volume ±3%), and analysis (±2% minimum) for a minimum estimated precision of ±3.6%. Since desorption efficiency is the amount measured/amount added, total precision of desorption efficiency measurement is ±4.2%, at best. This might be reduced slightly by extra careful attention to volumetric transfers. However, the estimated error significantly increases as the analytical uncertainty increases for smaller sample sizes (Table XV). Therefore, it is probably not helpful to measure desorption efficiencies unless values significantly less than 90% are expected from previous experience with a given silica gel adsorbent.

An alternate procedure, which compensates for desorption efficiencies less than 100%, may be preferred. It involves the preparation of calibration standards on, and subsequent elution from, the same silica gel used for sample collection. A solution of amine in water or methanol (≤40 μL) is added by syringe to a 150-mg section of silica gel in a septum sealed tube. The silica gel is shaken and allowed to equilibrate for an hour to distribute the amine. Then these standards are eluted and analyzed in the same way and at the same time as the unknown samples collected from air. This procedure involves no more effort or sources of error than preparing standards in solution. And it does not introduce added uncertainty from a separate determination of desorption efficiency.

Precision and accuracy of the desorption, preparation, and analysis procedure have been determined at 102-μg/sample 2-aminoethanol, 89-μg/sample 2-diethylaminoethanol, and 86-μg/sample 2-dibutylaminoethanol. Four samples and standards were prepared for each compound by injecting with a syringe 10 μL of 1% by volume solution (in 4:1 methanol water) onto 150 mg of 20/30-mesh Davison silica gel or into 2 mL of eluent. Concentrated hydrochloric acid (40 μL) was added to each silica gel section and standard solution. After 1-2 h, samples were desorbed with 2 mL of eluent for 2-3 h. Standards and desorbed samples were analyzed as described previously. Precisions of the amounts determined in four samples are given in Table XVI as relative standard deviation estimates from ranges of results. All sample precisions were

TABLE XVI

DESORPTION EFFICIENCIES AND PRECISIONS OF THE ANALYSIS OF AMINOETHANOLS AT THE LOWER LIMIT OF THE METHOD

Compound	Sample Amount (mg)	Average Desorption Efficiency	Analytical Precision (RSD, %)[a]		
			Samples	Standards	Desorption Efficiency[b]
2-Aminoethanol	0.10	0.97	3	6	7
2-Diethylaminoethanol	0.09	0.85	7	22	23
2-Dibutylaminoethanol	0.09	0.93	2	2	3

[a]Four samples and four standards in 2-mL eluent.

[b]Combined contributions of samples and standards.

less than 7% relative standard deviation at these levels. Sample recoveries were calculated by comparing average amounts measured in samples and standards. These values are also given in Table XVI.

Precision and accuracy of the total sampling and analysis procedure has been measured for vapors of 2-aminoethanol and 2-diethylaminoethanol. Vapors generated in a diffusion tube system were passed at 1 L/min through sampling tubes. No sampling pumps were used. Sampling tubes of 6-mm i.d. contained two 150-mg sections of silica gel 45/60 mesh for 2-aminoethanol and 20/30 mesh for 2-diethylaminoethanol. In experiments to measure total precision, tube samples were taken consecutively. In experiments to determine accuracy also, tube samples were alternated with samples collected under the same conditions in a fritted glass bubbler containing 10 mL of distilled water. Tube samples were analyzed by the procedure developed. Bubbler samples were analyzed to determine total amine collected by titration with standard acid using methyl red indicator. Results of these experiments are given in Table XVII. Accuracy of the method is confirmed by the agreement between amounts measured by both independent procedures. The bubbler procedure is more precise, but has the disadvantages of no specificity for amines, much less sensitivity, and difficulty of sample collection, storage, and shipping.

V. SAMPLING AND ANALYSIS OF ALIPHATIC POLYAMINES

A. Summary of the Method

A method has also been developed for sampling and analyzing vapors in air of ethylenediamine (1,2-diaminoethane) and diethylenetriamine (2,2'diamino-diethylamine). A detailed description of the procedure selected is given in Appendix B in the format of methods published in the **NIOSH Manual of Analytical Methods.**[13] A summary of the method and discussion of the experimental basis of it are given below.

The sampling tube described in Sec. IV.B and Fig. 12 is also used for polyamine compounds. Sample collection on silica gel, stabilization with acid, elution with 80% methanol, and derivatization with benzaldehyde are done in the same ways described for 2-aminoethanol. After 30 min of reaction, 3-μL aliquots of sample or standard solutions are injected into a gas chromatograph with 1 μL of methanol solvent flush. A 60-cm (2-ft.) long by 4-mm-i.d. glass column packed with 10% SE-30 silicone phase on 80/100-mesh Supelcoport is used. The carrier flow is 30-cm^3/min helium at column temperatures of 200°C for ethylenediamine and 235°C for diethylenetriamine. A flame ionization detector is used.

B. Sampling Tube Selection

Desirable sampling tube capacities for the two polyamines are calculated by 5 x TLV (mg/m^3) x 0.096 m^3 for sampling at concentrations up to five times the permissible levels (Table I) for 8 h at 200 cm^3/min flow rate. These values are 12 mg for ethylenediamine and 2 mg for diethylenetriamine. Retention experiments for ethylenediamine and diethylenetriamine were discussed in Sec. III.A of this report. Results of ethylenediamine vapor retention (Table III) showed that 150 mg of all silica gels tested in 6-mm-diam beds at 1000 cm^3/min flow rate had capacities ranging from 7 mg for the 42/60-mesh silica gel from Coast Engineering Laboratory to 20 mg for the 45/60-mesh silica gel from Davison desiccant. At a lower flow rate of 200 cm^3/min, capacities would be the same or greater. Two 150-mg silica gel beds have more than twice the capacity of one such bed. Distribution data revealed little, if any, effect of humidity on these capacities. Similar retention data in Table IV showed that 14 ± 1 mg of diethylenetriamine was retained on 150-mg silica gel at 1000-cm^3/min sampling rate. Combining this value with the relative amounts of ethylenediamine retained (Table III) on the 42/60-mesh Coast Engineering Laboratory silica gel (7 mg) and the 20/30-mesh Davison silica gel (11 mg) gives 9 ± 2 mg as an estimate for the retention of diethylenetriamine on 150 mg of the Coast Engineering Laboratory silica gel. More sample of diethylenetriamine collected at the higher flow rate would result in better sensitivity and precision. The conclusion is that the sampling tube shown in Fig. 12, having two 150-mg 6-mm-diam silica gel beds, is more than adequate for ethylenediamine and diethylenetriamine adsorption requirements. If all the sample is to be retained on the first bed with the second used to determine breakthrough, the sample limits are defined by the capacity of the first bed only (Appendix B).

C. Sample Stabilization

Recoveries of ethylenediamine and diethylenetriamine adsorbed on silica gel have been measured for periods up to 28 days to determine sample stabilities. Results are shown in Table XVIII for storage in sealed tubes at room temperature (20°C), at freezer temperature (-17°C), and ambient temperature with concentrated hydrochloric acid added (40-μL/150 mg silica gel). There was a rapid intial loss of 15% of the ethylenediamine during the first three days of storage at room temperature just like that observed for 2-aminoethanol, another primary amine (Table XIII). Storing samples in the freezer reduced the loss rate by a factor of about 7, so that after 14 days, recovery was still 86%. However, adding hydrochloric acid stabilized ethylenediamine to the extent that no significant loss was measured up to 28 days. Storage losses of diethylenetriamine at room and freezer temperature were much less than those of ethylenediamine for two weeks of storage. Therefore, if samples cannot be eluted immediately after sampling, they should be stored in a freezer for short periods or stabilized with acid for shipping and extended storage periods.

D. Sample Desorption

Desorption efficiencies measured for ethylenediamine and diethylenetriamine are listed in Table XIX. Relative standard deviations given were estimated from the ranges of analytical results. For each compound the first set of data was obtained by injecting 1 μL of liquid onto 150 mg of 42/60 Davison silica gel, mixing the sample, and eluting it with acidic methanol solution. The second sets of data were obtained by equilibrating 0.5-2 mL volumes of prepared solutions with 150 mg of silica gel. Except for the equilibrated solutions of ethylenediamine, which

TABLE XVIII

STORAGE STABILITIES OF POLYAMINES ADSORBED ON SILICA GEL

Compound[a]	Storage Period (days)	Recovery (%) Ambient[b] (20°C)	Freezer[b] (-17°C)	Hydrochloric Acid Coated[c]
Ethylenediamine	0	101		
	1	95		
	2	93		
	3	85	98	
	7	82	91	99
	10	81	92	
	14	68	86	101
	21			99
	28			95
Diethylenetriamine	14	96	106	
	28	75	84	

[a] 1-μL injected onto 150 mg of 42/60-mesh silica gel and mixed.

[b] Averages of duplicate samples and standards, 3% range.

[c] 40 μL of concentrated HCl (37%) injected after the sample. Averages of five samples and standards with a combined RSD average of 3%.

TABLE XVII

ACCURACY AND PRECISION DETERMINATIONS FOR VAPORS OF 2-AMINOETHANOL AND 2-DIETHYLAMINOETHANOL

Number of Samples	Volume of Samples[a] (m^3)	Amounts Determined by Analysis: Solid Sorbent Tube (mg)	Solid Sorbent Tube RSD[b] (%)	Bubbler[c] (mg)	Bubbler RSD[b] (%)
2-Aminoethanol					
2	0.02[d]	0.59	1.8		
2	0.08[d]	2.48	4.5		
4	0.03	0.31	7.3	0.35	3.4
5	0.03	1.91	5.0	1.74	1.5
5	0.03	1.79	6.2		
2-Diethylaminoethanol					
6	0.03	3.69	3.7		

[a] 1 L/min flow rate.

[b] RSD estimated from ranges of results.

[c] 10 mL of water absorbent titrated with acid.

[d] 20-L and 80-L samples were taken alternately at the average concentration of 30.3 mg/m^3.

TABLE XIX

DESORPTION EFFICIENCIES OF ETHYLENEDIAMINE AND DIETHYLENETRIAMINE

Compound	Sample Size[a] (mg)	Eluent Volume[b] (mL)	Desorption Efficiency	RSD (%)
Ethylenediamine	0.90	1[c]	0.98	2.0
	0.90	2[c]	0.99	1.6
	0.45	0.5	0.91	2.6
	0.90	1.0	0.96	2.6
	1.80	2.0	0.89	2.6
Diethylenetriamine	0.96	1.0	1.06	11.8
	0.48	0.5	0.99	1.7
	0.96	1.0	0.96	1.7
	1.92	2.0	0.97	1.7

[a] For 150 mg of 42/60-mesh silica gel from Davison.

[b] Acidic methanol, 0.4 N HCl, 80% methanol, except where otherwise specified.

[c] 0.24 N HCl, 80% methanol.

averaged 92% in solution, the desorption efficiencies were all essentially 100%. For 1 mL of eluent per 150-mg section, recoveries were consistently greater than 96%. This is the ratio used for most subsequent experiments. One hour of elution with occasional agitation of the mixtures of silica gel in eluent is sufficient for maximum desorption. In another experiment, there was no difference in recoveries of ethylenediamine measured after 1 h and after 24 h of elution.

E. Derivatization

Ethylenediamine and diethylenetriamine both have two primary amino groups that contribute to tailing on gas chromatographic columns. Such tailing has been eliminated by reacting these compounds with benzaldehyde to form the dibenzylidene derivatives. This reaction also forms larger organic molecules for more sensitive detection by flame ionization.

Rates of formation of the dibenzylidene derivatives were studied. Prepared solutions of ethylenediamine and diethylenetriamine in alcoholic acid eluent were alkalinized and mixed with benzaldehyde. Subsequent periodic analyses of the reaction mixture were done by gas chromatography. Figure 17 shows product peak heights vs reaction time for a solution 7.5×10^{-4} moles/L in ethylenediamine, 4.6×10^{-4} moles/L in diethylenetriamine, and 0.25 moles/L in benzaldehyde. These reactions were complete within 10 min. Two other product formation curves are shown in Fig. 18 for 9.3×10^{-3} and 9.3×10^{-4} moles/L diethylenetriamine reacting with 0.10 moles/L benzaldehyde. At the higher concentration, the reaction was complete in about 30 min. At the 10 times lower concentration data scatter was greater, but the reaction certainly did not take 10 times longer. Therefore, this reaction is apparently first order in both reagents like the reaction of benzaldehyde with 2-aminoethanol and similar condensation reactions.[21-22] The conclusion from these experiments and other experience with this method is that 30 min of reaction is sufficient at 0.10 moles/L benzaldehyde.

F. Gas Chromatographic Analysis

A column was selected for analysis of 1,2-(dibenzylideneamino)ethane from ethylenediamine and 2,2'-(dibenzylideneamino)diethylamine from diethylenetriamine. It is made of glass tubing 60-cm (2-ft.) long and 4-mm i.d. (0.25-in. o.d.) packed with 10% silicone SE-30 by weight on 80/100-mesh Supelcoport. Chromatographic conditions selected were: a helium carrier gas flow rate of 30 mL/min, an injection port temperature of 200°C, a detector temperature of 250°C, and column temperatures of 200-235°C. At 200°C, 1,2-(dibenzylideneamino)ethane eluted at 300 s, and at 235°C 2,2'-(dibenzylideneamino)diethylamine eluted at 345 s. Samples of 2.8-μL solutions were injected using a methanol flush technique with a 10-μL syringe.

Precision of the gas chromatographic analysis has been determined experimentally for standards of the two polyamines at the conditions described above. Table XX lists estimates of relative standard deviations calculated from the ranges of peak areas[24] obtained from 3-14 replicate injections for each standard. The precision of the analysis is greater than 9% relative standard deviation for concentrations in the original eluent solution less than about 90 μg/mL for ethylenediamine or diethylenetriamine. A previous discussion in this report (Sec. IV.G) showed that this precision corresponds to a 10% relative standard deviation for the total method.

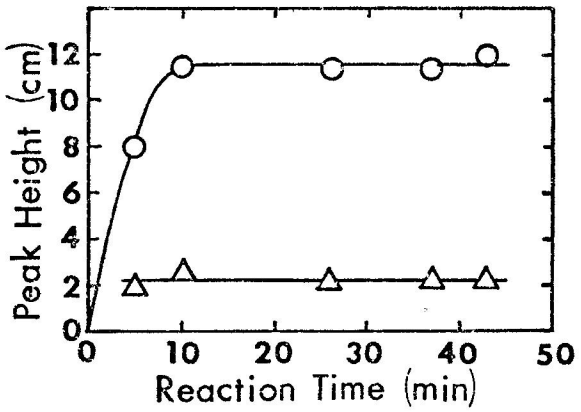

Fig. 17.
Product formation curves for the reactions of benzaldehyde (0.25 moles/L), O with ethylenediamine (7.5 x 10^{-4} moles/L), and Δ with diethylenetriamine (4.6 x 10^{-4} moles/L).

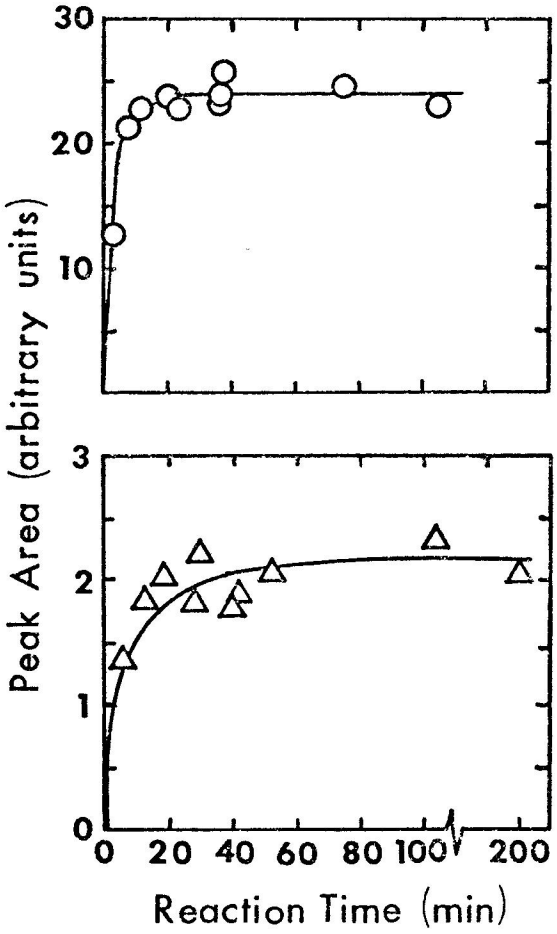

Fig. 18.
Product formation curves for the reaction of benzaldehyde (0.10 moles/L) with diethylenetriamine, O at 9.3 x 10^{-3} moles/L, and Δ at 9.3 x 10^{-4} moles/L.

TABLE XX

PRECISIONS OF GAS CHROMATOGRAPHIC ANALYSIS OF ALIPHATIC POLYAMINES

Compound	Conc of Original Std (μg/mL)	Amount of Amine Injected[a] (ng)	RSD (%)
Ethylenediamine	9 000	12 500	1
	900	1 250	4
	90	125	12
	45	62	5
	18	25	20
	9	12	20
Diethylenetriamine	91	126	8
	45	63	22

[a]In a volume of 2.8-μL reacted solution.

G. Precision and Accuracy

Precision and accuracy of the desorption, preparation, and analysis procedure have been determined at 45 μg/mL ethylenediamine and 48 μg/mL diethylenetriamine. Four samples and standards were prepared for each compound by using a syringe to inject 10 μL of 1% by volume solution in 4:1 methanol-water (about 0.1 mg) onto 150 mg of 20/30-mesh Davison silica gel or into 2 mL of eluent. Concentrated hydrochloric acid (40 μL) was added to each silica gel section and eluent standard. After 1-2 h, samples were desorbed with 2 mL of eluent for 2-3 h. Standards and desorbed samples were analyzed as described previously. Precisions of the amounts determined in four samples are given in Table XXI as relative standard deviation estimates from ranges. These precisions include unknown variations in preparing samples. Precision of ethylenediamine measurement at 45 μg/mL is acceptable, but for diethylenetriamine acceptable precision would probably be obtained only at twice the level of these experiments, or 96 μg/mL. Desorption efficiencies calculated by comparing average amounts measured in samples and standards are also given in Table XXI. These values indicate that essentially complete recovery was obtained. No decrease in recovery is expected at higher sample levels.

Precision and accuracy of the sampling and analysis method has been measured for ethylenediamine. Vapors were sampled at 1 L/min flow rate from the diffusion tube generation system (Fig. 1). Sampling tubes of 6-mm-i.d. contained 150 mg of 45/60-mesh silica gel. Air samples were collected for 30 min (0.03 m^3) on six tubes or in six bubblers containing 10 mL of water. Tube samples were analyzed by the procedures described in Appendix B and bubbler samples were titrated with standard acid. The average results (and relative standard deviations) were 3.30 mg (4%) for the tube samples and 3.42 mg (2%) for the bubbler samples. This agreement was satisfactory.

VI. SAMPLING AND ANALYSIS OF ALIPHATIC AMINES

A. Introduction

In earlier work on this project, we developed and reported a sampling and analysis method for vapors of eight aliphatic amines in air.[10,27] This method was subsequently proven for cyclohexylamine as well.[7] A known amount of vapor is drawn by a pump through a tube containing silica gel to trap the vapors. The silica gel is transferred to glass-stoppered tubes and treated with 1.0 N sulfuric acid for sample desorption. A portion of this solution is made alkaline with an equal

TABLE XXI

DESORPTION EFFICIENCIES AND PRECISIONS OF ANALYSIS OF POLYAMINES NEAR LOWER LIMIT OF METHOD

Compound	Sample Amount (mg)	Average Desorption Efficiency	(RSD, %) Samples and Standards[a]	(RSD, %) Desorption Efficiency[b]
Ethylenediamine	0.09	1.02	14	20
Diethylenetriamine	0.10	1.02	14	20

[a] Four samples and four standards in 2-mL eluent.

[b] Combined contributions of samples and standards.

volume of 1.1 N sodium hydroxide. Then an aliquot of this alkaline solution is analyzed by gas chromatography using an Ascarite precolumn, a Chromosorb 103 column, and a flame ionization detector.

Although the method reported was useful, there were some limitations in it that needed to be removed. One difficulty was insufficient sensitivity for methylamine. Several factors explain this problem. Methylamine is an organic compound with only one carbon atom per molecule and is, therefore, not as readily detected by flame ionization as larger organic compounds. As a primary amine, it tends to tail and produce unsymmetrical and difficult to measure peaks when chromatographed. In addition, it elutes from the chromatographic column simultaneously with water in the sample. In recent work, we have observed that water vapor quenches the ionization and detection of amines in flame ionization and photoionization detectors (Sec. VIII). A second difficulty with the method was the chromatographic separation of methylamine, dimethylamine, and ethylamine. A third problem was less than quantitative recovery of higher boiling aliphatic amines, such as butylamine, diisopropylamine, and triethylamine. After further experience with methods development for other organic bases, we have found solutions for these difficulties in the analysis of aliphatic amines.

B. Derivatization

The insufficient detectability of low molecular weight hydrazines, 2-aminoethanol, and ethylenediamine by flame ionization was solved by allowing these primary amines to react with aldehydes to form compounds of higher carbon content. Such derivatives also tail less on chromatographic columns than the primary amines from which they are formed. The need for the often troublesome Ascarite precolumn is eliminated. This approach was successfully applied to the analysis of primary aliphatic amines. Standards of methylamine (0.078 moles/L), ethylamine (0.030 moles/L), isopropylamine (0.056 moles/L), and butylamine (0.101 moles/L) were prepared in 4:1 methanol-water acidified to 0.4 N with hydrochloric acid. Aliquots of 0.5 mL of these standards were alkalinized with an equal volume of 0.5 N sodium hydroxide in 4:1 methanol-water, mixed with 10-25 μL of benzaldehyde or 2-furaldehyde, and reacted for 1 h. The derivatives formed were analyzed on a 1.8-m long 4-mm-i.d. glass column packed with 10% silicone SE-30 on 80/100-mesh Supelcon AW DMCS. Helium carrier flow rate was 50 cm^3/min. Column temperatures ranged 100-150°C for individual compounds. Figure 19 shows a chromatogram obtained for the benzylidene derivatives when the column temperature was programmed 100°C for 6 min before heating to 150°C at 8°C/min rate. Figure 20 shows a chromatogram for the 2-furylidene derivatives under the same conditions. These derivatives elute from the column faster than the benzylidenes. With both aldehydes, derivatives were easily formed and analyzed. Derivative peaks were well separated from solvent and reagent peaks and from each other. Peak tailing was not excessive.

Further studies were done forming and analyzing the benzylideneaminomethane derivative of methylamine. The reaction of 0.043 moles/L methylamine and 0.10 moles/L benzaldehyde was observed to be complete within 2.5 min at 22°C. Table XXII lists relative peak areas and analytical precisions obtained from the analyses of standards varying in methylamine concentrations over more than two orders of magnitude. The practical lower limit of this analytical method appears to be about 8.6×10^{-4} moles/L (0.027 mg/mL) methylamine in the original eluent or standard. Below this concentration analytical precision exceeds 9% relative standard deviation. For 2 mL of eluent per sample, this limit corresponds to 54 μg/sample or 4500 cm^3 of air sampled at the TLV concentration of 12 mg/m^3. A 25-min sampling period and a 1000 cm^3/min sampling flow rate would be sufficient to precisely determine a concentration of 0.2 times the TLV or more. This is adequate analytical sensitivity.

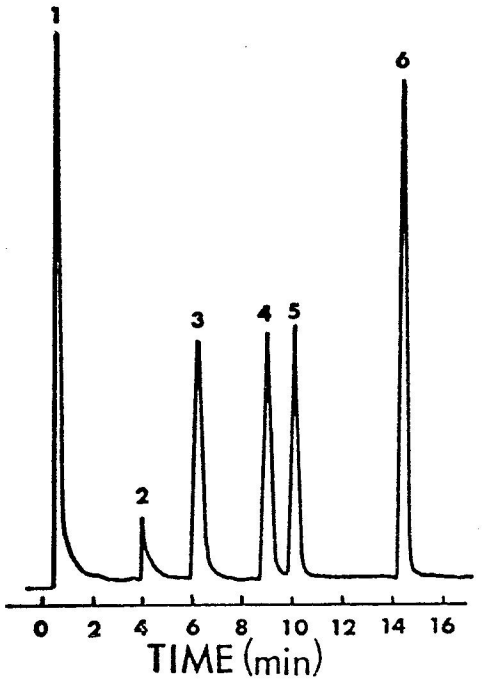

Fig. 19.
Gas chromatogram of benzaldehyde derivatized primary aliphatic amines obtained by temperature programming of a silicone SE-30 column. Conditions are given in the text. (1) Methanol solvent, (2) excess benzaldehyde, (3) benzylideneaminomethane, (4) benzylideneaminoethane, (5) 2-benzylideneaminopropane, and (6) 1-benzylideneaminobutane.

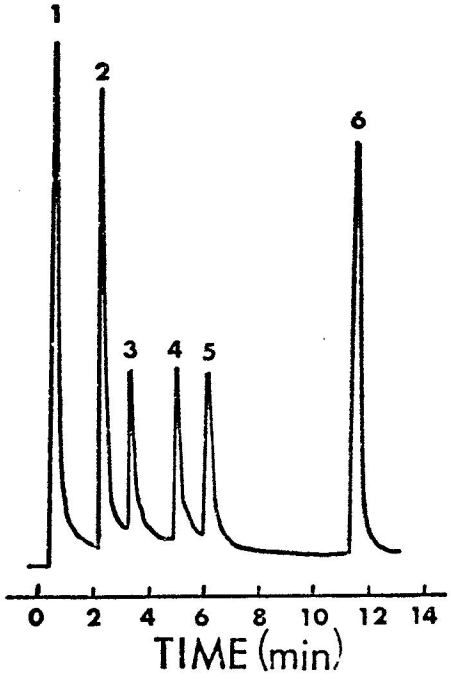

Fig. 20.
Gas chromatogram of 2-furaldehyde derivatized primary aliphatic amines obtained by temperature programming of a silicone SE-30 column. Conditions are given in the text. (1) Methanol solvent, (2) excess 2-furaldehyde, (3) 2-furylideneaminomethane, (4) 2-furylideneaminoethane, (5) 2-(2-furylidene)aminopropane, and (6) 1-(2-furylideneamino)butane.

C. Desorption

Methanol and ethanol were found in earlier work to enhance the desorption by dilute acid of aminoethanol and polyamine compounds from silica gel. Therefore, acidic methanol appeared to be a promising eluent for high boiling aliphatic amines, which are not efficiently desorbed in dilute acid alone. First, the individual effects of dilute acid and aqueous methanol solutions on the desorption equilibrium of butylamine were examined. Solutions of 0.10 moles/L butylamine were prepared in solvents of varying hydrochloric acid, methanol, and water content. Each solution was equilibrated with 45/60-mesh Davison silica gel in the ratio 2 mL:150 mg in sealed bottles. The equilibrated solutions were analyzed along with the original solutions to determine the fraction of butylamine remaining in the former. Figure 21 shows increasing recovery (equilibrium shift) due to increasing volume fraction of methanol in water. The best recovery was 83% for 100% methanol. Figure 22 shows the further enhancement of recovery due to added hydrochloric acid. Acid concentrations of 0.1 N, 0.4 N, and 1.0 N in 1:1 methanol:water gave complete recovery (vs 62% for nc acid present). A solvent of 0.4 N HCl in 4:1 methanol:water was selected for further studies.

TABLE XXII

RESULTS OF REPLICATE GAS CHROMATOGRAPHIC ANALYSES OF BENZYLIDENEAMINOMETHANE OBTAINED FROM DERIVATIZATION OF METHYLAMINE

Conc of Std (moles/L)	Average of Peak Areas (Relative)	Analytical Precision (RSD, %)
0.086	1000	1.2
0.0086	92	1.2
0.00086	17	9.0
0.00043	9	9.9

Equilibrium recoveries were determined in the same way for varying concentrations of butylamine, triethylamine, and diisopropylamine. The results are shown in Table XXIII. Essentially complete recovery (99% average with 3.3% relative standard deviation) was obtained for all butylamine samples. Recoveries of 95% or greater were also obtained for all samples of diisopropylamine and triethylamine measured. At the triethylamine sample of 0.15 mg/2 mL, an unknown interferent in the gas chromatographic analysis prevented precise triethylamine peak measurement. However, with further effort, this problem could have been removed and triethylamine could have been determined at this level or lower.

A diisopropylamine solution 0.007 moles/L in 0.4 N HCl in 4:1 methanol-water was likewise equilibrated with 150 mg of silica gel, but using volumes of 0.5 mL, 1.0 mL, and 2.0 mL. Recoveries measured were 97%, 98%, and 99%, respectively, or essentially the same within analytical error (±3%). This is in contrast to a large variation of desorption efficiency with eluent/sorbent ratios observed in earlier work using dilute aqueous acid to elute butylamine and triethylamine from silica gel.[6,10]

The usefulness of the methanolic hydrochloric acid for eluting methylamine from two different silica gels was also studied. Twenty microliters of five aqueous methylamine solutions (0.078-7.8 moles/L) were added to 150-mg samples of silica gels and to 2 mL of 0.4 N HCl in 4:1 methanol:water eluent. The 42/60-mesh Coast Engineering Laboratory and 20/30-mesh Davison

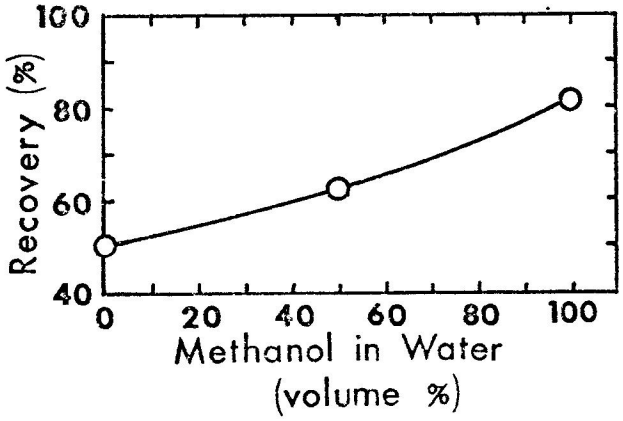

Fig. 21.
Recovery of n-butylamine from silica gel as a function of methanol content of the eluent solution.

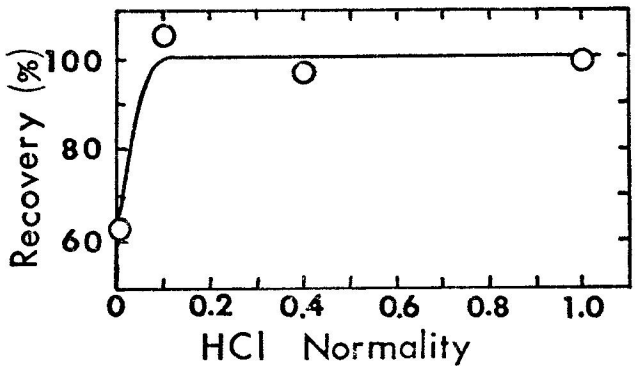

Fig. 22.
Recovery of n-butylamine from silica gel as a function of hydrochloric acid concentration in a 1:1 by volume methanol-water eluent.

silica gels were used. Duplicate samples and standards were prepared. One day later each sample was desorbed with 2 mL of eluent. Samples and standards were analyzed by alkalinization with methanolic sodium hydroxide, reaction with benzaldehyde, and separation by gas chromatography, as described in Appendix C. Chromatographic peak areas for samples and standards were compared to calculate the recoveries listed in Table XXIV. Measured recoveries were apparently higher for the 20/30-mesh silica gel. Desorption efficiencies measured for both silica gels were ≥85%.

D. Recommendations

Based on the more recent experimental results described above, we have some suggestions for improving the sampling and analysis method originally proposed for aliphatic amines (P & CAM 221).[27] First, a methanolic dilute acid, such as 0.4 N HCl in 4:1 methanol-water, should replace the aqueous acid as the eluent for desorption. This results in higher sample desorption efficiencies, especially for higher molecular weight aliphatic amines. Second, primary aliphatic amines, particularly methylamine and ethylamine, should be analyzed as their benzylidene derivatives. This results in enhanced analytical sensitivity and in better chromatographic separation from secondary and tertiary amines and from solvent peaks. Third, samples collected by adsorption on silica gel should be stabilized against oxidation by adding concentrated hydrochloric acid to the silica gel if they cannot be eluted and analyzed with a few days. If this is done, no acid is needed in the methanol-water eluent. These recommendations have been incorporated in a revised sampling and analytical procedure for methylamine in Appendix C.

VII. SAMPLING AND ANALYSIS OF HYDRAZINE COMPOUNDS

A sampling and analysis method was developed and reported in earlier work for vapors in air of methylhydrazine, 1,1-dimethylhydrazine, hydrazine, and phenylhydrazine.[11,14] It involves collection of vapors on sulfuric acid-coated silica gel in sampling tubes, elution with distilled water, reaction with 2-furaldehyde in sodium acetate buffer, extraction of the derivatives with ethyl acetate, and analysis of them by gas chromatography on a silicone OV-7 column. There was one major difficulty in using this procedure for methylhydrazine. The 2-furaldehyde

TABLE XXIII

EQUILIBRIUM RECOVERIES MEASURED FOR THREE ALIPHATIC AMINES

Compound	Sample Amount[a] (mg)	Recoveries (%)
n-Butylamine	14.8	0.98
	7.4	1.01
	3.0	1.00
	1.5	1.01
	0.74	1.01
	0.15	0.98
	0.07	0.92
Diisopropylamine	14.3	0.96
	1.4	0.98
	0.14	1.02
Triethylamine	14.6	0.97
	1.5	0.95

[a]In 2 mL of acidified methanol-water eluent equilibrated with 150 mg of 42/60-mesh Davison silica gel.

TABLE XXIV

RECOVERY OF METHYLAMINE BY DESORPTION WITH ACIDIC METHANOL ELUENT

Amount (mg)	Average Recoveries 42/60 Mesh[a]	Average Recoveries 20/30 Mesh[b]	Analytical Precision[c] (RSD, %)
0.048	0.85	0.93	10
0.240	0.87	0.95	2
0.480	0.99	0.95	8
2.40	0.91	0.97	1
4.80	0.91	0.98	3

[a]Coast Engineering Laboratory.

[b]Davison activated desiccant.

[c]From ranges of peak areas obtained for three pairs of duplicate samples and standards prepared, desorbed, reacted, and analyzed by gas chromatography.

methylhydrazone derivative formed for analysis slowly reacts further with 2-furaldehyde to form a secondary product. Therefore, the reaction time before extraction and chromatographic analysis must be carefully controlled for both samples and standards.

We considered the possibility that using benzaldehyde in place of 2-furaldehyde might reduce or eliminate the secondary product formation. The larger aromatic ring of benzaldehyde should result in greater steric hindrance of the reactive hydrogen on the benzaldehyde methylhydrazone. This, indeed, turned out to be the case. Figure 23 shows the formation of this derivative in three standards for reaction times up to 2 h. No significant change in the amount of derivative formed at 0.019 mole/L was observed between 1- and 7-h reaction time. For all three concentrations, the reaction in 0.1 mole/L benzaldehyde was complete within 2 h. The highest concentration standard may have been completely reacted within 1 h, as were the other two, if the benzaldehyde reagent excess had been greater. Similar kinetic studies with the other three compounds gave approximate complete reaction times of 0.5 h for hydrazine, 12 h for 1,1-dimethylhydrazine, and 2 h for phenylhydrazine in 0.1 mole/L benzaldehyde. At 0.2 mole/L benzaldehyde reaction times were halved.

In these experiments, reaction and analytical conditions were changed from those in the original method. In order to dissolve the benzaldehyde reagent, 4:1 methanol-water was used instead of distilled water as the solvent for standards. Although not proven for these compounds, such an alcoholic solvent should give improved desorption efficiencies when used to elute samples from sulfuric acid-coated silica gel. Another change was to use 0.5 N aqueous sodium hydroxide in place of 0.5 M sodium acetate to prepare acidic solutions for reaction. The resulting solutions were more basic, which may explain the longer reaction times than those observed previously. This type of reaction is often very pH dependent.[21,22] Ethyl acetate used for extraction is immiscible in the 40% methanol (by volume) reaction mixture. In the third change, the benzaldehyde (10-20 μL) was added by injection with a syringe into the final alkalinized mixture rather than dissolved in the buffer or alkalinizing solution. Benzaldehyde has the additional advantage of being less easily oxidized by air than 2-furaldehyde; therefore, it does not need to be purified by redistillation before use. The gas chromatographic column used for these experiments was 1.2-m (4-ft.) long by 4-mm-i.d. stainless steel packed with 10% silicone SE-30 on 80/100-mesh Supelcon AW-DMCS support. Carrier flow was helium at 50 cm^3/min flow rate. The hydrazone derivatives of methylhydrazine and 1,1-dimethylhydrazine had column retention times of 200 s and 197 s, respectively, at a column temperature of 160°C. Retention times of the benzaldazine (from hydrazine) and benzaldehyde phenylhydrazone were 197 s at 230°C and 200 s at 235°C, respectively. These pairs of compounds in mixtures could be separated by temperature programming the column from 80°C to 200°C at 16°C/min.

VIII. PHOTOIONIZATION DETECTOR EVALUATION

A gas chromatography photoionization detector was investigated as an alternative to the more common flame ionization detector in order to obtain enhanced detectability of amine and hydrazine compounds. Compounds such as methylamine, methylhydrazine, 2-aminoethanol, and ethylenediamine have two or fewer carbon atoms per molecule and are, therefore, not very responsive to a flame ionization detector, which forms C_n^+ ions. Furthermore, oxygen and nitrogen atoms in these molecules reduce flame ionization response,[28] likely by forming CO, CO_2, and CN instead. The photoionization detector used in these experiments was a model PI-51 gas chromatography detector manufactured by HNU Systems, Inc., of Newton, Massachusetts. It was mounted on the heated detector block of a Hewlett Packard 7620A research

chromatograph and operated at 250°C. Hydrogen and airflow rates to the flame ionization detector of this instrument were optimized for most sensitivity. Signals from both detectors were amplified by the same electrometer in this instrument. The chromatographic column was 1.8-m (6-ft.) long and 2-mm-i.d. glass packed with 10% Carbowax 20 M and 2% KOH on 80/100-mesh Chromosorb W-AW.

Responses of the two detectors to chromatographed solutions of 2-aminoethanol and 2-diethylaminoethanol in absolute ethanol were compared in the first experiment. Peak heights on chart paper were measured with a ruler and multiplied by the attenuation factor used. Duplicate analyses of 4 μL of each standard were made. The column temperature was 125°C, and the helium carrier flow rate was 35 cm^3/min. Figure 24 shows log-log plots of peak heights vs concentrations for these two compounds. Analyses were made to below the lowest measurable concentrations. Table XXV lists the concentrations of solutions of the two aminoethanols analyzed and the ratios of peak heights measured with the two detectors. Over three orders of magnitude in concentration, the photoionization detector was 27-66 and 15-27 times more sensitive than the flame ionization detector for 2-aminoethanol and 2-diethylaminoethanol, respectively. Under the conditions of this experiment, this meant that the photoionization detector gave minimum levels of measurement lower by a factor of about ten. The ratios of responses of the photoionization detector and the flame ionization detector are greater for smaller samples.

In a second experiment, an ethanol solution of 1% by volume each of ethylenediamine, diethylenetriamine, 2-aminoethanol, 2-diethylaminoethanol, and 2-dibutylaminoethanol was chromatographed on this same column. The temperature was programmed from 90°C to 200°C at 6°C/min. Ratios of observed peak heights (photoionization detector/flame ionization detector) were 41, 30, 32, 12, and 11, respectively. This shows that the sensitivity enhancement using the photoionization detector extends to at least an order of magnitude greater concentration than determined in the first experiment.

Although these results were encouraging, the photoionization detector was not used for further analyses of amines. Unsymmetrical and difficult to measure chromatographic peaks were ob-

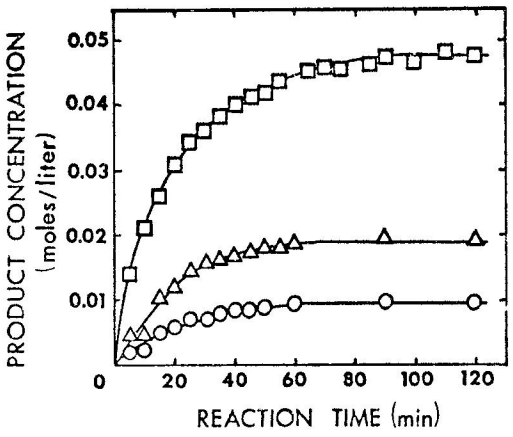

Fig. 23.
Product formation curves for the reactions of benzaldehyde (0.10 moles/L) with methylhydrazine: ○ at 9.49 x 10^{-3} moles/L, and △ at 1.90 x 10^{-2} moles/L, and □ at 4.75 x 10^{-2} moles/L.

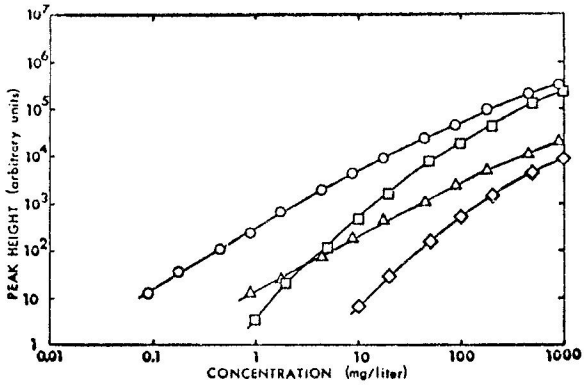

Fig. 24.
Log-log calibration curves obtained with a photoionization detector (○,□) and a flame ionization detector, (△, ◇) for 2-aminoethanol, (□, ◇), and 2-diethylaminoethanol (○, △).

TABLE XXV

RELATIVE RESPONSES OF A PHOTOIONIZATION DETECTOR AND A FLAME IONIZATION DETECTOR TO 2-AMINOETHANOL AND 2-DIETHYLAMINOETHANOL

2-Aminoethanol		2-Diethylaminoethanol	
Conc (mg/L)	Peak Height Ratio[a]	Conc (mg/L)	Peak Height Ratio[a]
1018	27	890	15
509	30	445	19
204	30	178	20
102	36	89	20
51	52	45	23
20	57	18	22
10	66	9	24
		4	28
		2	27
		1	19

[a]Photoionization detector response/flame ionization detector response with the same electrometer.

tained for primary amines in aqueous solution. Therefore, the approach selected was to form benzylidene derivatives of the primary amines, which would not tail excessively and which would be detected with adequate sensitivity using a flame ionization detector.

In another series of experiments the photoionization detector was used as a constant monitor of amines in an airstream. It had good response and stability to vapors such as ethylenediamine, 2-aminoethanol, and diisopropylamine at low humidities. However, at relative humidities approaching 100%, the response to these compounds was greatly decreased and variable. The same effect was observed when the monitor was the flame ionization detector in a Beckman Model 400 hydrocarbon analyzer. An explanation for these observations is that the water vapor mixed with the sample vapor quenches the ions formed from the latter before they can migrate to the ion-collecting electrode. In neither detector is the water vapor itself directly ionized significantly. Therefore, ionization detectors should be used with careful consideration of possible quenching when monitoring high humidity air. In a gas chromatographic application, this is usually not a problem because compounds are separated by the chromatographic process.

REFERENCES

1. Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1977 (American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1977).

2. Federal Register **39**, 23502, June 27, 1974, and redesignated at Federal Register **40**, 27073, May 28, 1975.

3. G. O. Wood and R. G. Anderson, "Personal Air Sampling for Vapors of Aniline Compounds," Am. Ind. Hyg. Assoc. J. **36**, 538 (1975).

4. E. E. Campbell, G. O. Wood, and R. G. Anderson, "Development of Air-Sampling Techniques," Los Alamos Scientific Laboratory report LA-5634-PR (June 1974).

5. E. E. Campbell, G. O. Wood, and R. G. Anderson, "Development of Air-Sampling Techniques," Los Alamos Scientific Laboratory report LA-5973-PR (July 1975).

6. E. E. Campbell, G. O. Wood, and R. G. Anderson, "Development of Air-Sampling Techniques," Los Alamos Scientific Laboratory report LA-6057-PR (September 1975).

7. G. O. Wood and R. G. Anderson, "Development of Air-Monitoring Techniques Using Solid Sorbents," Los Alamos Scientific Laboratory report LA-6216-PR (February 1976).

8. G. O. Wood and R. G. Anderson, "Development of Air-Monitoring Techniques Using Solid Sorbents," Los Alamos Scientific Laboratory report LA-6513-PR (September 1976).

9. G. O. Wood and R. G. Anderson, "Development of Air-Monitoring Techniques Using Solid Sorbents," Los Alamos Scientific Laboratory report LA-6738-PR (March 1977).

10. G. O. Wood and R. G. Anderson, "Sampling and Analysis of Aliphatic Amine Vapors," presented at the 1975 American Industrial Hygiene Conference, Minneapolis, Minnesota, June 6, 1975.

11. G. O. Wood and R. G. Anderson, "Sampling and Analysis of Hydrazine Compounds in Air," presented at the 1976 American Industrial Hygiene Conference, Atlanta, Georgia, May 16-21, 1976.

12. G. O. Wood, R. G. Anderson, and J. W. Nickols, "Sampling and Analysis of Aminoethanols in Air," presented at the 1977 American Industrial Hygiene Conference, New Orleans, Louisiana, May 22-27, 1977.

13. "Aromatic Amines in Air," Method No. P&CAM 168 in the **NIOSH Manual of Analytical Methods**, Vol. 1, Second Edition (US Government Printing Office, Washington, D.C. 1977).

14. "Hydrazine Compounds in Air," Method No. P&CAM 248 in the **NIOSH Manual of Analytical Methods**, Vol. 1, Second Edition (US Government Printing Office, Washington, D.C., 1977).

15. B. E. Saltzman, "Basic Theory of Gas Indicator Tube Calibration," Am. Ind. Hyg. Assoc. J. **23**, 112 (1962).

16. D. R. Jones, H. G. Reilich, H. J. O'Neill, "Subfractionation of Coal For Neutral Fraction," Final Report C6324-5 (Illinois Institute of Technology Research Institute, Chicago, Illinois, 1975).

17. R. A. Dommer and R. G. Melcher, "Phase Equilibrium Method for Determination of Desorption Efficiencies," Am. Ind. Hyg. Assoc. J. **39**, 240 (1978).

18. Y. Hoshika, "Gas Chromatographic Determination of Lower Aliphatic Primary Amines as Their Fluorine-Containing Schiff Bases," Anal. Chem. **49**, 541 (1977).

19. Y. Hoshika, "Gas Chromatographic Separation of Lower Aliphatic Amines," Anal. Chem. **48**, 1716 (1976).

20. Y. Hoshika, "Gas Chromatographic Determination of the Lower Aliphatic Primary Amines as Their Schiff Bases," J. Chromatogr. **115**, 596 (1975).

21. B. M. Anderson and W. P. Jencks, "The Effect of Structure on Reactivity in Semicarbazone Formation," J. Am. Chem. Soc. **83**, 1773 (1960).

22. J. Hine, **Physical Organic Chemistry** (McGraw-Hill Book Company, Inc., 1962) pp. 254-257.

23. E. D. Smith and R. D. Radford, "Modification of Gas Chromatographic Substrates for the Separation of Aliphatic Diamines," Anal. Chem. **33**, 1160 (1961).

24. M. G. Natrella, **Experimental Statistics**, National Bureau of Standards Handbook 91 (U.S. Government Printing Office, Washington, D.C., 1963) p. 2-6.

25. P. R. Bevington, **Data Reduction and Error Analysis for the Physical Sciences** (McGraw-Hill Book Company, Inc., 1968) p. 56.

26. C. F. Emanuel, "Delivery Precision of Micropipettes," Anal. Chem. **45**, 1568 (1973).

27. "Aliphatic Amines in Air," Method No. P&CAM 221 in the **NIOSH Manual of Analytical Methods**, Vol. 1, Second Edition (US Government Printing Office, Washington, D.C., 1977). 1568 (1973).

28. Model 400 Hydrocarbon Analyzer Instruction Manual, 81996-A (Beckman Instruments, Inc., Fullerton, California) p. 21.

APPENDIX A

AMINOETHANOL COMPOUNDS

Analytical Method

Analytes:	2-Aminoethanol (Ethanolamine) 2-Diethylaminoethanol 2-Dibutylaminoethanol	Method No:	P&CAM 270
		Range:	See Paragraph 2
Matrix:	Air		
Procedure:	Adsorption on silica gel, elution with methanolic acid, derivatization of 2-aminoethanol, GC analysis	Precision:	2-9% (Analytical)
		Classification:	E (Proposed)
Date Issued:			
Date Revised:			

1. Synopsis

A known volume of air is drawn through a tube containing silica gel to trap the aminoethanol compounds. Concentrated HCl is added to stabilize amines collected. The sorbent sections are transferred to glass tubes and treated with methanol solution. An aliquot is alkalinized with sodium hydroxide. Benzaldehyde is added to derivatize 2-aminoethanol forming benzylidene-aminoethanol. The solution is analyzed by gas chromatography with flame ionization detection.

2. Working Range, Sensitivity, and Detection Limit

The ranges of the method for the various analytes are at least

2-Aminoethanol	0.1-15 mg/sample
2-Diethylaminoethanol	0.1-12 mg/sample
2-Dibutylaminoethanol	0.1-17 mg/sample

The lower ends of the ranges given are levels where the desorption and analysis procedure was evaluated and found to be acceptably precise (see paragraph 4.3). The upper limits are determined by the capacities of the first section of the sampling tube used to collect the sample. Amounts of individual compounds retained on 150 mg of a 42/60-mesh silica gel in 6-mm-i.d. sampling tubes at 1 L/min sampling flow rate were found to be those given above as the upper limits.

3. Interferences

3.1 Water vapor does not significantly affect collection efficiency.

3.2 Large amounts of ammonia or primary amines will reduce the amount of benzaldehyde available for reaction with 2-aminoethanol. Such interferences should be compensated for by adding additional benzaldehyde.

3.3 Any compound which has nearly the same retention time on the GC column as one of the analytes is an interference. Retention time data on a single GC column cannot be considered as proof of chemical identity. The presence and identity of possible interfering substances may be determined by the analysis of bulk samples from the process or environment.

4. Precision and Accuracy

4.1 The volume of air sampled can be measured to within $\pm$ 2% if a pump with a calibrated volume indicator and an adequate battery is used. Volumes calculated from initially set flow rates may be less accurate ($\pm$ 5-10%) unless changes in flow rate are manually or electronically monitored and compensated.

4.2 Below the following levels precisions of replicate GC analyses of standards were worse than 9% relative standard deviation.

2-Aminoethanol	0.10 mg/sample
2-Diethylaminoethanol	0.08 mg/sample
2-Dibutylaminoethanol	0.02 mg/sample

At the upper limits of the method analytical precision becomes 2% relative standard deviation or better.

4.3 The precision (relative standard deviation) of the method based on analyses of replicate 0.1 mg samples injected by syringe into silica gel sections was

2-Aminoethanol	3%
2-Diethylaminoethanol	7%
2-Dibutylaminoethanol	2%

Replicate samples of vapor at higher sample levels had precisions ranging from 2-7%.

4.4 The precision of the analysis is dependent upon the precision and sensitivity of the technique used to quantitate the GC peaks of samples and standards. An electronic digital integrator with baseline correction capability is best for this purpose.

4.5 Collection efficiency is 100% until breakthrough of the sampling tube beds occurs (see Section 2).

4.6 Desorption efficiencies based on analyses of replicate 0.1 mg samples on silica gel and standards in 2 mL eluent were found to be

2-Aminoethanol	0.97 (7%)
2-Diethylaminoethanol	0.85 (22%)
2-Dibutylaminoethanol	0.93 (3%)

with the relative standard deviations given in parentheses. Measurements at higher sample levels have given desorption efficiencies consistently in the range 90-100%.

4.7 This method has given quantitative results equivalent to an independent method involving adsorption of 2-aminoethanol vapors in water in a bubbler and titration with standard acid. Using each method, four or five 0.030-m^3 vapor in nitrogen samples were taken at 1 L/min. The following sample amounts and relative standard deviations in parenthesis were determined:

Tube and Chromatography	Bubbler and Titration
0.31 mg (7.3%)	0.35 mg (3.4%)
1.91 mg (5.0%)	1.74 mg (1.5%)

5. Advantages and Disadvantages

5.1 The method uses a small, portable sampling device involving no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities. Transportation to the analytical laboratory is simplified with the solid sorbent tube.

5.2 The sorbent tube has a high capacity even at high relative humidities. It can be used for at least eight hours to measure a workday average concentration, or for shorter times to measure excursion concentrations.

5.3 Desorption and preparation of samples for analysis involve simple procedures and equipment.

5.4 Several amines can be collected and determined simultaneously. The GC analysis distinguishes which are present and at what individual concentrations they occur. Interferences by other amines are much less likely than in colorimetric or titrimetric methods.

5.5 A major disadvantage is the tendency of amines to oxidize while adsorbed on surfaces exposed to air. This is overcome by addition of concentrated hydrochloric acid to the sorbent sections soon after sampling.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Sorbent. The silica gel used should be the equivalent of Silica Gel D-08, chromatographic grade, activated and fines

free, 42/60 mesh, as produced by Coast Engineering Laboratories and sold by Applied Science Laboratories, Inc. of State College, Pennsylvania.

6.1.2 Sampling Tubes. Glass tubes 7-cm-long and 6-mm-i.d., tapered and flame sealed at one end, are packed with two 150-mg sections of silica gel. Glass wool plugs are used to separate and enclose the sections. The second end is flame sealed to prevent contamination during storage prior to use.

NOTE: Sampling tubes constructed with metal parts or urethane foam plugs should not be used. Concentrated hydrochloric acid will react with these materials.

6.1.3 Personal Sampling Pump. Battery-operated pumps are required, capable of operation at 0.2 L/min for up to eight hours or at 1.0 L/min for up to two hours with a sampling tube in line. The pump is to be calibrated with a representative sorbent tube in line. A wet or dry test meter or bubble meter capable of measuring a flow rate of 0.2 L/min and/or 1.0 L/min to within $\pm$ 2% may be used in setting the pump flow.

6.2 Gas chromatograph with a flame ionization detector. Temperature programming capability is necessary to determine more than one compound simultaneously.

6.3 GC column, 1.8-m x 2-mm i.d. glass, silanized and packed with 10% (by weight) Carbowax 20M and 2% KOH on 80/100-mesh Chromosorb W AW, or equivalent support.

6.4 Strip chart recorder compatible with the GC. An electronic digital integrator is desirable.

6.5 Test tubes or glass vials, 2-mL, sealed by a septum.

6.6 Syringes, 10-µL.

6.7 Syringe for dispensing concentrated HCl, 50-µL, with glass barrel, fluorocarbon-tipped plunger, and inert (platinum or fluorocarbon) needle.

6.8 Pipettes, 0.5-mL and 2-mL.

6.9 Volumetric flasks, 10-mL.

6.10 File and Forceps.

7. Reagents - All chemicals must be analytical reagent grade.

7.1 2-Aminoethanol (ethanolamine).

7.2 2-Diethylaminoethanol.

7.3 2-Dibutylaminoethanol.

7.4 Water, doubly distilled and aldehyde-free. Deionized water should not be used as it may contain formaldehyde and other impurities leached from the ion-exchange resins.

7.5 Concentrated hydrochloric acid (38%, 12 M).

7.6 Benzaldehyde.

7.7 Eluent solution, 4:1 methanol-water (by volume).

7.8 Alkalinizing solution, 0.20 N NaOH in 4:1 methanol-water (by volume).

7.9 Helium, Bureau of Mines Grade A.

7.10 Hydrogen, prepurified.

7.11 Air, compressed and filtered.

8. Procedure

8.1 Cleaning of Equipment. All glassware is washed with detergent solution, rinsed with tap water and distilled water, and dried in an oven.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before beginning the collection of a sample, break each end of the sorbent tube so as to provide openings at least 2 mm in diameter.

8.2.2 Attach the tubing from the sampling pump to the backup end of the sampling tube. Sampled air must not pass through any hose or tubing before entering the sorbent tube.

8.2.3 With the sorbent tube in a vertical position as much as is practical, sample the air at 1.0 L/min for 15 min-2 hours or at 0.2 L/min for 2-8 hours. Intermediate flow rates and other sampling periods may be used, as appropriate.

8.2.4 Immediately after sampling is completed, add 20 µL of concentrated HCl to each section of silica gel in the tube. Use a 50 µl glass syringe with fluorocarbon-tipped plunger and inert needle, so that the acid does not contact and react with stainless steel. The silica gel will turn yellow upon addition of the acid due to iron impurities in the silica gel.

8.2.5 Seal the sorbent tubes with polyethylene caps.

8.2.6 Obtain a blank sample by handling one tube in the same manner as the sample tubes (break, add acid, seal, and ship) except that no air is pumped through it.

8.2.7 For shipping to the laboratory, pack the tubes tightly to minimize chances of breakage during transit. Tubes should not be subjected to extremes of high temperature or low pressure.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Score each tube with a file 5 mm in front of the glass wool plug that precedes the first sorbent section and break the tube there. Transfer this plug and the initial section to a 2-mL test tube or glass vial that can be septum sealed. Likewise, transfer the second plug and sorbent section to another test tube. Label each appropriately for separate analysis.

8.3.2 Desorption. Add 2 mL of eluent solution to each sorbent section. Seal the samples. Shake the mixtures occasionally over a period of two hours. Tests have shown that complete desorption occurs within two hours and samples are stable for at least a day.

8.3.3 Preparation. Transfer a 0.50-mL aliquot of each eluate to another test tube or vial. Add 0.50 mL of alkalinizing solution and mix thoroughly. Verify the basicity of the solution with litmus paper.

8.3.4 Reaction. If 2-aminoethanol is present in the sample, repeat the preparation step with another 0.50-mL aliquot. Add 10-µL of benzaldehyde to the basic solution, mix thoroughly, and allow at least 20 min for reaction.

8.4.5 Gas Chromatograph Conditions. Typical operation conditions are:

Helium gas flow rate, 50 mL/min.
Injection port temperature, 150 °C.
Detector temperature, 250 °C.
Column temperature, 90 °C for three min, heat to 225 °C at 16 °C/min, and hold for six min.

Under these conditions, retention times are 213 sec for 2-diethylaminoethanol, 365 sec for 2-aminoethanol, 515 sec for 2-dibutylaminoethanol, and 866 sec for 2-benzylidene-aminoethanol. When only one compound is present isothermal analysis is best at 90 °C(retention time, 280 sec) for 2-diethylaminoethanol, 150 °C(retention time, 180 sec) for 2-dibutylaminoethanol, or 225 °C(retention time, 195 sec) for 2-benzylideneaminoethanol.

8.3.6 Injection of Sample. Inject and analyze 3-µL aliquots of each sample and standard. To eliminate difficulties arising from blowback or distillation within the 10-µL syringe, use a solvent flush technique.

8.3.7 GC Peak Measurement. Determine the areas of the peaks of the compounds of interest from analyses of samples and standards.

8.4 Determination of Desorption Efficiency

8.4.1 Importance. Desorption efficiency for a particular compound can vary from one lot of silica gel to another and from one laboratory to another. Also, for a given lot of silica gel the desorption efficiency may vary with the amount of material adsorbed during sampling. Therefore, it is necessary to determine at least once the desorption efficiency for each aminoethanol with each lot of silica gel used for at least two levels within the normal range of samples size. If the desorption efficiencies are significantly different from quantitative recovery, they should be used to correct the measured weight of aminoethanols as described in Section 10.2 below.

8.4.2 Procedure. Place 150 mg of silica gel in a 2-mL glass-stoppered tube. The silica gel must be from the same lot as that used in collecting the sample; it can be obtained from unused sorbent tubes. With a microliter syringe, inject a known amount of the aminoethanol, either pure or in water solution, directly onto the silica gel. Also inject 20 µL of concentrated HCl. Close the tube with the glass stopper and allow it to stand overnight to insure complete adsorption of the amine. Prepare at least three tubes for each at two different levels. These tubes are referred to as samples. Prepare a blank in the same manner, omitting the aminoethanol. Analyze the samples and blank as described in Section 8.3. Also analyze three standards prepared by adding identical amounts of the aminoethanol and 20 µL of concentrated HCl to 2.0 mL of eluent solution. Determine the concentrations of the aminoalcohols in the blank, samples, and standards using calibration curves prepared as described in Section 9. The desorption efficiency is calculated by dividing the concentration of amine found in the sample by the concentration obtained for the corresponding standard.

9. Calibration and Standardization

9.1 Preparation of a Stock Solution. Calculate for each compound i the volume V_i (µL) of pure liquid required for preparation of 10 mL of a stock solution, 10 µL of which contains amounts of aminoethanols equal to those collected from volume of air V_s at concentrations X_i:

$$V_i = \frac{X_i \times V_s}{d_i} \times 1000$$

Where:

X_i - the standard concentration limit, or the anticipated average concentration, (mg/m^3) of compound i in air.

V - volume (m^3) of air sampled.

d_i - density (mg/μL) of a pure compound i.

1000 - aliquot factor.

Add the calculated volumes of each compound to a 10-mL volumetric flask and dilute to the mark with 4:1 methanol-water. Neutral solutions of aminoethanols are subject to oxidation and should be prepared fresh when needed.

9.2 Preparation of Calibration Standards. Add 2.5 μL, 5 μL, 10 μL, 15 μL and 20 μL of the prepared standards to reaction tubes containing 2 mL eluent solutions and 10 μL concentrated hydrochloric acid. Use a 10-μL syringe to inject through septum seals. Shake these tubes. These standards correspond to 0.25, 0.5, 1, 1.5, and 2 times X_i in V_s, respectively. Other standards may be similarly prepared, if desired.

9.3 React and analyze standards with samples according to Section 8.3.

9.4 Prepare a calibration curve for each amine by plotting peak areas obtained from the analyses of standards against nominal amount (mg) in the calibration standards.

10. Calculations

10.1 Read the weights (mg) of each compound corresponding to each peak area from the appropriate calibration curve. Correct each value for the weight found in a blank, if any. Add the weights found in the front and backup sections of the sample tube to obtain the total weight of compound in the air volume sampled.

10.2 Divide the total weight by the desorption efficiency to obtain the corrected sample weight.

10.3 Determine the volumes (m^3) of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min) and $10^{-3} m^3/L$. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$V_s = 10^{-3} \times f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \quad ,$$

where:

f - sample flow rate (L/min)
t - sampling time (min)
P_1 - pressure during calibration of sampling pump (torr)

P_2 - pressure of air samples (torr)

T_1 - temperature during calibration of sampling pump (^oK)

T_2 - temperature of air sampled (^oK)

10.4 Divide the total corrected weight (mg) of each compound by V_s (m^3) to obtain the concentration of the compound in the air sampled (mg/m^3).

APPENDIX B

ETHYLENEDIAMINE AND DIETHYLENETRIAMINE

Analytical Method

Analytes:	Ethylenediamine (1,2-Diaminoethane) Diethylenetriamine (bis(2-aminoethyl)amine)	Method No:	P&CAM 276
Matrix:	Air	Range:	See Paragraph 2
Procedure:	Adsorption on silica gel, elution with methanolic acid, derivatization with benzaldehyde, GC analysis	Precision:	2-8% (Analytical)
Date Issued:			
Date Revised:		Classification:	E (Proposed)

1. Synopsis

A known volume of air is drawn through a tube containing silica gel to trap vapors of the compounds. Concentrated HCl is added to stabilize amines collected. The sorbent sections are transferred to glass vials and treated with methanol solution. An aliquot is alkalinized with sodium hydroxide. Benzaldehyde is added to form dibenzylidene derivatives. The solution is analyzed by gas chromatography with flame ionization detection.

2. Working Range, Sensitivity, and Detection Limit

The ranges of the method for the two analytes are at least

Ethylenediamine	0.2 - 7 mg/sample
Diethylenetriamine	0.2 - 9 mg/sample

Data relating to the lower ends of the range are given in Paragraphs 4.2, 4.3, and 4.6. The upper limits are determined by the capacities of the first section of the sampling tube used to collect the sample. Amounts of individual compounds retained on 150 mg of a 42/60-mesh silica gel in 6-mm-i.d. sampling tubes at 1 L/min sampling flow rate were found to be those given above as the upper limits.

3. Interferences

3.1 Water vapor does not significantly affect collection efficiency.

3.2 Large amounts of ammonia or primary amines will reduce the amount of benzaldehyde available for reaction with the analytes. Such interferences should be compensated for by adding additional benzaldehyde.

3.3 Any compound which has nearly the same retention time on the GC column as one of the analytes is an interference. Retention time data on a single GC column cannot be considered as proof of chemical identity. The presence and identity of possible interfering substances may be determined by the analysis of bulk samples from the process or environment.

4. Precision and Accuracy

4.1 The volume of air sampled can be measured to within $\pm$ 2% if a pump with a calibrated volume indicator and an adequate battery is used. Volumes calculated from initially set flow rates may be less accurate ($\pm$ 5-10%) unless changes in flow rate are manually or electronically monitored and compensated.

4.2 Precision (relative standard deviation) of replicate GC analyses of standards was measured to be:

Ethylenediamine	5% at 0.05 mg/mL eluent
Diethylenetriamine	8% at 0.09 mg/mL eluent

These levels correspond to sample sizes of 0.1 mg and 0.2 mg, respectively. At the upper limits of the method analytical precision becomes 2% relative standard deviation or better.

4.3 The precision (relative standard deviation) of the method based on analyses of replicate 0.1 mg samples injected by syringe into silica gel sections or into 2 mL of eluent was 14% for both compounds.

4.4 The precision of the analysis is dependent upon the precision and sensitivity of the technique used to quantitate the GC peaks of samples and standards. An electronic digital integrator with baseline correction capability is best for this purpose.

4.5 Collection efficiency is 100% until breakthrough of the sampling tube bed occurs (see Section 2).

4.6 Desorption efficiencies for both compounds based on analyses of replicate 0.1 mg samples on silica gel and standards in 2 mL eluent were found to be 102% with a relative standard deviation of 20%. Measurements at higher sample levels have given desorption efficiencies consistently in the range 90-100% with better precision.

4.7 This method has given quantitative results equivalent to an independent method involving adsorption of ethylenediamine vapors in water in a bubbler and titration with standard acid. Using each method six 0.030-m^3 vapor-in-nitrogen samples were taken at 1 L/min. The following sample amounts and relative standard deviations in parentheses were determined:

Tube and chromatography: 3.30mg (4%)

Bubbler and titration: 3.42mg (2%)

5. Advantages and Disadvantages

5.1 The method uses a small, portable sampling device involving no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities. Transportation to the analytical laboratory is simplified with the solid sorbent tube.

5.2 The sorbent tube has a high capacity even at high relative humidities. It can be used for at least eight hours to measure a workday average concentration, or for shorter times to measure excursion concentrations.

5.3 Desorption and preparation of samples for analysis involve simple procedures and equipment.

5.4 Several amines can be collected and determined simultaneously. The GC analysis distinguishes which are present and at what individual concentrations they occur. Interferences by other amines are much less likely than in colorimetric or titrimetric methods.

5.5 A major disadvantage is the tendency of amines to oxidize while adsorbed on surfaces exposed to air. This is overcome by addition of concentrated hydrochloric acid to the sorbent sections soon after sampling.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Sorbent. The silica gel used should be the equivalent of Silica Gel D-08, chromatographic grade, activated and fines free, 42/60 mesh, as produced by Coast Engineering Laboratories and sold by Applied Science Laboratories, Inc. of State College, Pennsylvania.

6.1.2 Sampling Tubes. Glass tubes 7-cm-long and 6-mm-i.d., tapered and flame sealed at one end, are packed with two 150-mg sections of silica gel. Glass wool plugs are used to separate and enclose the sections. The second end is flame sealed to prevent contamination during storage

prior to use. Polyethylene caps are used to seal tubes after sampling is completed.

NOTE: Sampling tubes constructed with metal parts or urethane foam plugs should not be used. Concentrated hydrochloric acid will react with these materials.

6.1.3 Personal Sampling Pump. Battery-operated pumps are required, capable of operation at 0.2 L/min for up to eight hours or at 1.0 L/min for up to two hours with a sampling tube in line. The pump is to be calibrated with a representative sorbent tube in line. A wet or dry test meter or bubble meter capable of measuring a flow rate of 0.2 L/min and/or 1.0 L/min to within $\pm$ 2% may be used in setting the pump flow.

6.2 Gas chromatograph with a flame ionization detector. Temperature programming capability is necessary to determine more than one compound simultaneously.

6.3 GC column, 0.6-m x 4-mm i.d. glass, silanized and packed with 10% (by weight) silicone SE-30 on 80/100-mesh supelcoport or equivalent support.

6.4 Strip chart recorder compatible with the GC. An electronic digital integrator is desirable.

6.5 Test tubes or glass vials, 2-mL, sealed by a septum.

6.6 Syringes, 10-µL.

6.7 Syringe for dispensing concentrated HCl, 50-µL, with glass barrel, fluorocarbon-tipped plunger, and inert (platinum or fluorocarbon) needle.

6.8 Pipettes, 0.5-mL and 2-mL.

6.9 Volumetric flasks, 10-mL.

6.10 File and Forceps.

7. Reagents - All chemicals must be analytical reagent grade.

7.1 Ethylenediamine.

7.2 Diethylenetriamine.

7.3 Water, doubly distilled and aldehyde-free. Deionized water should not be used as it may contain formaldehyde and other impurities leached from the ion-exchange resins.

7.4 Concentrated hydrochloric acid (38%, 12 M).

7.5 Benzaldehyde.

7.6 Eluent solution, 4:1 methanol-water (by volume).

7.7 Alkalinizing solution, 0.20 N NaOH in 4:1 methanol-water (by volume).

7.8 Helium, Bureau of Mines Grade A.

7.9 Hydrogen, prepurified.

7.10 Air, compressed and filtered.

8. Procedure

8.1 Cleaning of Equipment. All glassware is washed with detergent solution, rinsed with tap water and distilled water, and dried in an oven.

8.2 Collection and Shipping of Samples.

8.2.1 Immediately before beginning the collection of a sample, break each end of the sorbent tube so as to provide openings at least 2 mm in diameter.

8.2.2 Attach the tubing from the sampling pump to the backup end of the sampling tube. Sampled air must not pass through any hose or tubing before entering the sorbent tube.

8.2.3 With the sorbent tube in a vertical position as much as is practical, sample the air at 1.0 L/min for 15 min-2 hours or at 0.2 L/min for 2-8 hours. Intermediate flow rates and other sampling periods may be used, as appropriate.

8.2.4 Immediately after sampling is completed, add 20 μL of concentrated HCl to each section of silica gel in the tube. Use a 50-μL glass syringe with fluorocarbon-tipped plunger and inert needle, so that the acid does not contact and react with stainless steel. The silica gel will turn yellow upon addition of the acid due to iron impurities in the silica gel.

8.2.5 Seal the sorbent tubes with polyethylene caps.

8.2.6 Obtain a blank sample by handling one tube in the same manner as the sample tubes (break, add acid, seal, and ship) except that no air is pumped through it.

8.2.7 For shipping to the laboratory, pack the tubes tightly to minimize chances of breakage during transit. Tubes should not be subjected to extremes of high temperature or low pressure.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Score each tube with a file 5 mm in front of the glass wool plug that precedes the first sorbent section and break the tube there. Transfer this plug and the initial section to a 2-mL test tube or glass vial that can be septum sealed. Likewise, transfer the second plug and sorbent section to another test tube. Label each appropriately for separate analysis.

8.3.2 Desorption. Add 2 mL of eluent solution to each sorbent section. Seal the samples. Shake the mixtures occasionally over a period of two hours. Tests have shown that complete desorption occurs within two hours and samples are stable for at least a day.

8.3.3 Preparation and Reaction. Transfer a 0.50-mL aliquot of each eluate to another test tube or vial. Add 0.50 mL of alkalinizing solution and mix thoroughly. Verify the basicity of the solution with litmus paper. Add 10-µL of benzaldehyde to the basic solution, mix thoroughly, and allow at least 20 min for reaction.

8.3.4 Gas Chromatograph Conditions.

Helium gas flow rate, 30 mL/min.
Injection port temperature, 200 °C.
Detector temperature, 250 °C.
Column temperature, 200 °C for
1,2-(dibenzylideneamino)ethane and
235 °C for 2,2'-(dibenzylideneamino)diethylamine.

Under these conditions, retention times are 300 sec for 1,2-(dibenzylideneamino)ethane and 345 sec for 2,2'-(dibenzylideneamino)diethylamine.

8.3.5 Injection of Sample. Inject and analyze 3-µL aliquots of each sample and standard. To eliminate difficulties arising from blowback or distillation within the 10-µL syringe, use a solvent flush technique.

8.3.6 GC Peak Measurement. Determine the areas of the peaks of the compounds of interest from analyses of samples and standards.

8.4 Determination of Desorption Efficiency

8.4.1 Importance. Desorption efficiency for a particular compound can vary from one lot of silica gel to another and from one laboratory to another. Also, for a given lot of silica gel the desorption efficiency may vary with the amount of material adsorbed during sampling. Therefore, it is necessary to determine at least once the desorption

efficiency for each analyte with each lot of silica gel used for at least two levels within the normal range of samples size. If the desorption efficiencies are significantly different from quantitative recovery, they should be used to correct the measured weight of analyte as described in Section 10.2 below.

8.4.2 Procedure. Place 150 mg of silica gel in a 2-mL glass-stoppered tube. The silica gel must be from the same lot as that used in collecting the sample; it can be obtained from unused sorbent tubes. With a microliter syringe, inject a known amount of amine, either pure or in water solution, directly onto the silica gel. Also inject 20 µL of concentrated HCl. Close the tube with the glass stopper and allow it to stand overnight to insure complete adsorption of the amine. Prepare at least three tubes for each at two different levels. These tubes are referred to as samples. Prepare a blank in the same manner, omitting the amine. Analyze the samples and blank as described in Section 8.3. Also analyze three standards prepared by adding identical amounts of the amine and 20 µL of concentrated HCl to 2.0 mL of eluent solution. Determine the concentrations of the analytes in the blank, samples, and standards using calibration curves prepared as described in Section 9. The desorption efficiency is calculated by dividing the concentration of amine found in the sample by the concentration obtained for the corresponding standard.

9. Calibration and Standardization

9.1 Preparation of a Stock Solution. Calculate for each compound i the volume V_i (µL) of pure liquid required for preparation of 10 mL of a stock solution, 10 µL of which contains amounts of analytes equal to those collected from volume of air V_s at concentrations X_i.

$$V_i = \frac{X_i \times V_s}{d_i} = 1000$$

Where:

X_i - the standard concentration limit, or the anticipated average concentration, (mg/m^3) of compound i in air.

V_s - volume (m^3) of air sampled.

d_i - density (mg/µL) of a pure compound i.

1000 - aliquot factor.

Add the calculated volumes of each compound to a 10-mL volumetric flask and dilute to the mark with 4:1 methanol-water. Neutral solutions of amines are subject to oxidation and should be prepared fresh when needed.

9.2 Preparation of Calibration Standards. Add 2.5 µL, 5 µL, 10 µL 15 µL and 20 µL of the prepared standard to reaction tubes containing 2 mL eluent solution and 40 µL concentrated hydrochloric acid. Use a 10-µL syringe to inject through septum seals. Shake these tubes. These standards correspond to 0.25, 0.5, 1, 1.5, and 2 times X_i in V_s, respectively. Other standards may be similarly prepared, if desired.

9.3 React and analyze standards with samples according to Section 8.3.

9.4 Prepare a calibration curve for each amine by plotting peak areas obtained from the analyses of standards against nominal amount (mg) in the calibration standards.

10. Calculations

10.1 Read the weights (mg) of each compound corresponding to each peak area from the appropriate calibration curve. Correct each value for the weight found in a blank, if any. Add the weights found in the front and backup sections of the sample tube to obtain the total weight of compound in the air volume sampled.

10.2 Divide the total weight by the desorption efficiency to obtain the corrected sample weight.

10.3 Determine the volumes (m^3) of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min) and 10^{-3} m^3/L. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$V_s = 10^{-3} \times f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} .$$

where:

f - sample flow rate (L/min)
t - sampling time (min)
P_1 - pressure during calibration of sampling pump (torr)
P_2 - Pressure of air sampled (torr)
T_1 - temperature during calibration of sampling pump (°K)
T_2 - temperature of air sampled (°K)

10.4 Divide the total corrected weight (mg) of each compound by V_s (m^3) to obtain the concentration of the compound in the air sampled (mg/m^3).

APPENDIX C

METHYLAMINE

Analytical Method

Analyte:	Methylamine	Method No:	P&CAM 277
Matrix:	Air	Range:	0.5-120 mg/m^3 in 100-L air sample
Procedure:	Adsorption on silica gel elution with methanolic acid, derivatization with benzaldehyde, GC analysis	Precision:	1-9% (Analytical)
Date Issued:			
Date Revised:		Classification:	E (Proposed)

1. Synopsis

A known volume of air is drawn through a tube containing silica gel to trap methylamine vapors. Concentrated hydrochloric acid is then added to stabilize the sample. Silica gel sections are transferred to glass tubes and treated with a methanol-water solution. An aliquot is alkalinized with sodium hydroxide. Benzaldehyde is added to convert the methylamine to benzylideneaminomethane. The solution is analyzed by gas chromatography with flame ionization detection.

2. Working Range, Sensitivity, and Detection Limit

2.1 The range of the method is at least 0.05-12 mg/sample.

2.2 The lower limit of 0.05 mg/sample is the lowest level at which the desorption and analysis procedure was found to be acceptably precise (see Paragraph 4.2) and quantitative (see Paragraph 4.6). This limit corresponds to 0.5 mg/m^3 monomethylamine in a 0.1-m^3 air sample.

2.3 The upper limit is at least 12 mg of amine per sample. This amount of methylamine was retained by the 600-mg section of silica gel in the sampling tube without breakthrough when 93L of high-humidity air containing 129 mg/m^3 of methylamine was sampled. This limit corresponds to 120 mg/m^3 in a 0.100-m^3 air sample.

3. Interferences

3.1 Large amounts of ammonia or primary amines will reduce the amount of benzaldehyde available for reaction with methylamine. Such interferences should be compensated for by adding additional benzaldehyde.

3.2 Any compound which has nearly the same retention time on the GC column as one of the analytes is an interference. Retention time data on a single GC column cannot be considered as proof of chemical identity. The presence and identity of possible interfering substances may be determined by the analysis of bulk samples from the process or environment.

4. Precision and Accuracy

4.1 The volume of air sampled can be measured to within $\pm$ 2% if a pump with a calibrated volume indicator and an adequate battery is used. Volumes calculated from initially set flow rates may be less accurate ($\pm$ 5-10%) unless changes in flow rate are manually or electronically monitored and compensated.

4.2 Replicate analyses of a standard solution at the level 0.05 mg/sample showed the analytical precision to be 9% relative standard deviation. At the upper limit of the method, analytical precision approached 1% relative standard deviation.

4.3 A sampling and analysis precision of 3% (relative standard deviation) has been measured for 10 samples, each containing 1.2 mg of methylamine collected from 4L of air with a personal sampling pump.

4.4 The precision of the analysis is dependent upon the precision and sensitivity of the technique used to quantitate the GC peaks of samples and standards. An electronic digital integrator with baseline correction capability is best for this purpose.

4.5 Collection efficiency is 100% until breakthrough of the front sampling tube bed occurs (see Paragraph 2.3).

4.6 Desorption efficiencies were measured to be 85% for one 42/60 mesh silica gel at the level 0.05 mg per sample and higher at higher sample levels.

5. Advantages and Disadvantages

5.1 The method uses a small, portable sampling device involving no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities. Transportation to the analytical laboratory is simplified with the solid sorbent tube.

5.2 The sorbent tube has a high capacity. It can be used for at least eight hours to measure a workday average concentration, or for shorter times to measure excursion concentrations.

5.3 Desorption and preparation of samples for analysis involve simple procedures and equipment.

5.4 Several amines can be collected and determined simultaneously. The GC analysis distinguishes which are present and at what individual concentrations they occur. Interferences by other amines are much less likely than in colorimetric or titrimetric methods.

5.5 A major disadvantage is the tendency of amines to oxidize while adsorbed on surfaces exposed to air. This is overcome by addition of concentrated hydrochloric acid to the sorbent sections soon after sampling.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Sorbent. The silica gel used should be the equivalent of Silica Gel D-08, chromatographic grade, activated and fines free, 42/60 mesh, as produced by Coast Engineering Laboratories, and sold by Applied Science Laboratories, Inc. of State College, Pennsylvania.

6.1.2 Sampling Tubes. Glass tubes 12.5-cm long and 8-mm-i.d., packed with three sections of silica gel of weights 600 mg, 150 mg, and 150 mg, in order. These tubes are used for sampling in either direction. Sorbent sections are held in place by 7-mm-diam discs of 100-mesh Teflon screen supported by Teflon rings of 8-mm-o.d., 6-mm-i.d., and 2-mm thick. Pieces of glass tubing 12-mm long and 7-mm o.d. are located between the sorbent sections to inhibit migration of the amines and to facilitate sorbent removal. The ends of the tubes are flame-sealed after packing to prevent contamination prior to sampling. Polyethylene caps should be provided to seal the tubes after sampling has been completed. Pressure drop across such a tube containing 42/60 mesh silica gel is 6-cm of water at 0.2 L/min sampling flow rate.

Note: Sampling tubes constructed with metal parts or urethane foam plugs should not be used, as concentrated hydrochloric acid will react with these materials.

6.1.3 Personal Sampling Pump. A battery-operated pump capable of operation at 0.2 L/min for up to eight hours with a sampling tube in line is required. The pump is to be calibrated with a representative sorbent tube in line. A wet or dry test meter, or bubble meter, capable of measuring a flow rate of 0.2 L/min to within $\pm$ 2% may be used in setting the pump flow.

6.2 Gas Chromatograph with a flame ionization detector.

6.3 GC column, 1.8-m x 4-mm i.d. glass, silanized and packed with 10% (by weight) silicone SE-30 on 80/100-mesh Supelcoport or equivalent support.

6.4 Strip chart recorder compatible with the GC. An electronic digital integrator is desirable.

6.5 Test tubes or glass vials, 2-mL, and 10-mL, sealed by a septum.

6.6 Syringes, 10-µL.

6.7 Syringes for dispensing concentrated HCl, 50-µL and 100-µL, with glass barrel, fluorocarbon-tipped plunger, and inert (platinum or fluorocarbon) needle.

6.8 Pipettes, 0.5-mL and 2-mL.

6.9 Volumetric flasks, 10-mL.

6.10 File and Forceps.

7. Reagents - All chemicals must be analytical reagent grade.

7.1 Methylamine, 40% in H_2O.

7.2 Water, doubly distilled and aldehyde-free. Deionized water should not be used as it may contain formaldehyde and other impurities leached from the ion-exchange resins.

7.3 Concentrated hydrochloric acid (38%, 12 M).

7.4 Benzaldehyde.

7.5 Eluent solution, 4:1 methanol-water (by volume).

7.6 Alkalinizing solution, 0.20 N NaOH in 4:1 methanol-water (by volume).

7.7 Helium, Bureau of Mines Grade A.

7.8 Hydrogen, prepurified.

7.9 Air, compressed and filtered.

8. Procedure

8.1 Cleaning of Equipment. All glassware is washed with detergent solution, rinsed with tap water and distilled water, and dried in an oven.

8.2 Collection and Shipping of Samples.

8.2.1 Immediately before beginning the collection of a sample, break each end of the sorbent tube so as to provide openings at least 2 mm in diameter.

8.2.2 Choose the direction desired for sample air flow, mark the inlet end of the tube with a permanent marker, and attach the other end to tubing from the sampling pump. Sample air must not pass through any hose or tubing before entering the sorbent tube. For low concentrations of methylamine, low humidity conditions, or short sampling periods, pump the sample air through the outer 150-mg sorbent section first; for high concentrations, high humidity, or long sampling periods, pump the sample air through the larger 600-mg sorbent section first.

8.2.3 With the sorbent in a vertical position as much as is practical, sample the air at 200 cm^3/min for the desired period of time. The flow rate and sampling time, or the volume, must be measured as accurately as possible. The temperature and pressure of the air being sampled should be measured and recorded.

8.2.4 Immediately after sampling is completed, add 20 µL of concentrated HCl to each of the smaller sorbent sections and 80 µL to the larger section. The silica gel will turn yellow upon addition of the acid due to iron impurities in the silica gel. If sample desorption and analysis is to be done within one week, and the tube is not subjected to unusually high temperatures or low pressures, this acid stabilization is not necessary. In this case, the 20 µL (or 80 µL) of acid must be added to 2 mL (or 8mL) of methanol-water used for sample recovery (see Paragraph 8.3.2).

8.2.5 Seal the sorbent tubes with polyethylene caps.

8.2.6 Obtain a blank sample by handling one tube in the same manner as the sample tubes (break, add acid, seal, and ship) except that no air is pumped through it.

8.2.7 For shipping to the laboratory, pack the tubes tightly to minimize chances of breakage during transit. Tubes should not be subjected to extremes of high temperature or low pressure.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Score each tube with a file between the sorbent sections and break the tube into three parts. Remove the Teflon screens and transfer the smaller silica gel sections to separate 2-mL glass tubes or vials that can be tightly sealed. Repeat for the larger section and a 10-mL glass container. Label each appropriately.

8.3.2 Desorption. Add 2 mL of methanol-water eluent solution to each of the smaller silica gel sections and 8 mL to the larger one. If no acid was added to the silica gel solutions in the field, add 20 µL of concentrated hydrochloric acid to each 2 mL of eluent and 80 µL to each 8 mL of eluent. Seal the samples. Shake the mixtures occasionally over a period of one hour.

8.3.3 Preparation and Reaction. Transfer a 0.5-mL aliquot of each eluate to another test tube or vial. Add 0.5-mL of alkalinizing solution and mix thoroughly. Verify the basicity of the solution with litmus paper. Add 10 µL of benzaldehyde, mix thoroughly, and allow at least 5 min for reaction.

8.3.4 Gas Chromatographic Conditions. Typical operating conditions are:

Helium gas flow rate, 50 mL/min
Injection port temperature, 150 °C
Detector temperature, 200 °C
Column temperature, 100 °C

Under these conditions, unreacted benzaldehyde elutes at 190 sec and benzylideneaminomethane elutes at 425 sec.

8.3.5 Injection of Sample. Inject and analyze 3-µL aliquots of each sample and standard. To eliminate difficulties arising from blowback or distillation within the 10-µL syringe, use a solvent flush technique.

8.3.6 GC Peak Measurement. Determine the areas of the peaks of the compounds of interest from analyses of samples and standards.

8.4 Determination of Desorption Efficiency

8.4.1 Importance. Desorption efficiency for a particular compound can vary from one lot of silica gel to another and from one laboratory to another. Also, for a given lot of silica gel the desorption efficiency may vary with the amount of material adsorbed during sampling. Therefore, it is necessary to determine at least once the desorption efficiency for methylamine with each lot of silica gel used for at least two levels within the normal range of samples size. If the desorption efficiencies are significantly different from quantitative recovery, they should be used to correct the measured weight of analyte as described in Section 10.2 below.

8.4.2 Procedure. Place 150 mg of silica gel in a 2-mL glass-stoppered tube. The silica gel must be from the same lot

as that used in collecting the sample; it can be obtained from unused sorbent tubes. With a microliter syringe, inject a known amount of standardized 40% methylamine in water solution, directly onto the silica gel. Also inject 40 µL of concentrated HCl. Close the tube with the glass stopper and allow it to stand overnight to insure complete adsorption of the amine. Prepare at least three tubes for each at two different levels. These tubes are referred to as samples. Prepare a blank in the same manner, omitting the amine. Analyze the samples and blank as described in Section 8.3. Also analyze three standards prepared by adding identical amounts of methylamine and 40 µL of concentrated HCl to 2.0 mL of eluent solution. Determine the concentrations of methylamine in the blank, samples, and standards using calibration curves prepared as described in Section 9. The desorption efficiency is calculated by dividing the concentration of amine found in the sample by the concentration obtained for the corresponding standard.

9. Calibration and Standardization

9.1 Standardization of the 40% methylamine solution. Aqueous solutions of methylamine of nominal 40% (0.4 g/mL) concentration can be obtained from commercial sources. Such solution will decrease in methylamine concentration when opened. Therefore, it is necessary to periodically standardize such solutions by titration with standard hydrochloric acid. Add 1 mL of the 40% solution to a 100-mL volumetric flask and add distilled water to the mark. Prepare 0.1 N hydrochloric acid and fill a 10-mL burette with it. Titrate 5 mL of the diluted methylamine solution with the standard HCl, using three drops of methyl red or other suitable acid-base indicator. Calculate the concentration of the nominally 40% methylamine solution (c_i) in g/mL.

9.2 Preparation of a Stock Solution. Calculate the volume V_i (µL) of the 40% solution required for preparation of 10 mL of a stock solution, 10 µL of which contains an amount of methylamine equal to that which would be collected from a volume of air V_s (m^3) sampled at a concentration X_i (mg/m^3):

$$V_i\ (\mu L) = \frac{X_i \times V_s}{C_i} \times 1000$$

where:

X_i - the standard concentration limit, or the anticipated average concentration, (mg/m^3) of compound i in air.

V_s - volume (m^3) of air sampled.

C_i - concentration (mg/µL = g/mL) of the original methylamine solution determined in Paragraph 9.1.

1000 - aliquot factor.

Add the calculated volume of 40% methylamine to a 10-mL volumetric flask and dilute to the mark with 4:1.methanol-water. Neutral solutions of amines are subject to oxidation and should be prepared fresh when needed.

9.3 Preparation of Calibration Standards. Add 2.5 µL, 5 µL, 10 µL, 15 µL, and 20 µL of the prepared standard to test tubes containing 2 mL eluent solution and 40 µL concentrated hydrochloric acid. Use a 10-µL syringe to inject through septum seals. Shake these tubes. These standards correspond to 0.25, 0.5, 1, 1.5, and 2 times X_i in V_s, respectively, for samples collected on the smaller tube sections and eluted with 2 mL of methanol-water. They correspond to 1, 2, 4, 6, and 8 times X_i in V_s, respectively, for the larger section.

9.4 React and analyze standards with samples according to Section 8.3.

9.5 Prepare a calibration curve by plotting peak areas obtained from the analyses of standards against nominal amounts (mg) in the calibration standards.

10. Calculations

10.1 Read the weights (mg) of sample on each tube section corresponding to each measured peak area using the calibration curve. Correct each value for the weight found in a blank, if any. Add the weights found in the front and backup sections of the sample tube to obtain the total weight of compound in the air volume sampled.

10.2 Divide the total weight by the desorption efficiency to obtain the corrected sample weight.

10.3 Determine the volume V_s (m^3) of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min) and 10^{-3} m^3/L. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this corrected volume is:

$$V_s = 10^{-3} \times f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}$$

where:

f - sample flow rate (L/min)
t - sampling time (min)
P_1 - pressure during calibration of sampling pump (torr)
P_2 - pressure of air samples (torr)
T_1 - temperature during calibration of sampling pump (°K)
T_2 - temperature of air sampled (°K)

10.4 Divide the total corrected weight (mg) of methylamine by V_s (m^3) to obtain the concentration of methylamine in the air sampled (mg/m^3).

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