Personal Air Sampling for Vapors of Aniline Compounds

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A method has been developed for air sampling and laboratory analysis of vapors of seven aniline compounds: aniline, N,N-dimethylaniline, o-toluidine, 2,4-xylidine, p-anisidine, o-anisidine, and p-nitroaniline. Air is drawn by a personal sampling pump from a worker's breathing zone through a tube containing silica gel to collect any anilines present. In the laboratory each silica gel section is transferred to a glass-stoppered tube and desorbed with ethanol. An aliquot of this is analyzed by gas chromatography to determine the amount of each aniline compound present. The sampling tube can be used for short-term sampling at 1000 cm^3/min or for sampling up to eight hours at 200 cm^3/min. Maximum interference effects of water vapor have been considered. Results of retention, desorption, storage, accuracy, and precision studies are presented.

Introduction

AN IMPORTANT PART OF THE WORK OF AN industrial hygienist is the identification and measurement of chemical vapors to which workers may be exposed in their occupational environments. The tools he needs for this purpose are convenient and reliable sampling methods and associated analytical methods.

Three commonly used methods for sampling and analysis of aniline in air are summarized in an American Industrial Hygiene Association Analytical Abstract.[1] These methods involve sampling by drawing air through bubblers containing ethanol or acid solutions and analyzing by spectrophotometry or fluorimetry.[2-4] A fourth commonly used method of aniline vapor determination is by drawing a small volume of air through a detector tube and measuring the length of stain produced.[5] Another method has been described which uses silica gel columns to collect aniline from air, ethanol to dissolve the aniline, and ultraviolet spectrophotometry for analysis.[6] These five methods lack two often important capabilities: 1) sampling air from the worker's breathing zone for extended periods during normal activities to obtain a time-weighted average estimate of his exposure; and 2) readily identifying the specific compounds present. The latter requirement may be quite important since Threshold Limit Values vary from 0.1 ppm for o- and p-anisidine (methoxyaniline) to 5 ppm for aniline.[7] Also, for some detector tubes, ammonia and possibly also some aliphatic amines give false positive results when testing for anilines.[5]

The objective of the work reported here has been development and evaluation of a method for determining concentrations in air of vapors of aniline and substituted aniline compounds which would also have these two capabilities. The approach has been directed toward a procedure similar to the widely used charcoal tube procedure for organic solvent vapors:[8] (1) Air is drawn from the breathing zone through a tube containing an adsorbent by means of a portable sampling pump, (2) the tube is capped and sent to a central laboratory, (3) the collected sample is eluted from the adsorbent

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by a solvent, and (4) the resulting solution is analyzed by gas chromatography. The proposed method will be described in detail along with discussions of experimental tests of it.

Apparatus and Reagents

Sample Collection

Sampling pumps: (1) Model 1531-V107-288 from Gast Mfg. Corp., a stationary pump used for some of the experiments; (2) Model SP-1 Sipin Personal Sampling Pump (50 to 200 cm^3/min flow rate); and (3) Model G Mine Safety Appliance Co. portable sampling pump (1000 cm^3/min flow rate).

Sampling tubes were constructed from the following parts: (1) Pyrex glass tubing, 8mm I.D. (10mm O.D.) and 5mm I.D. (7mm O.D.); (2) Silica Gel D-08, chromatograph grade; activated and fines free, 45/60 mesh from Applied Science Laboratories, Inc., State College, Penn.; (3) 100 mesh stainless steel screen discs, 7.5mm diameter; (4) cylindrical Teflon supports 8.05 ± 0.03mm O.D., 6mm I.D., 3mm long; and (5) polyethylene caps, 10mm I.D.

Sample Analysis

Perkin-Elmer Model 900 gas chromatograph operated under the following conditions: carrier flow (25 cm^3/min He); injection port (150°C); flame ionization detector (250°C, 50 cm^3/min H_2, 470 cm^3/min air): Oven temperature programming capability is desirable when more than one compound is to be analyzed.

Gas chromatographic column (1.22 m x 3mm O.D.) stainless steel packed with Silicone OV-25 liquid phase, 10% on 80/100 mesh Supelcoport.

Varian Model A-25 recorder.

Autolab System IV electronic digital integrator for gas chromatograph peak integration.

Glass-stoppered tubes or flasks, 1 and 10 cm^3, and other common laboratory glassware.

Hamilton syringes, 10mm^3 (10μl).

Eluting mixture: 95% ethanol with 0.1% (by volume) n-heptanol added, both reagent grade.

Standard solutions prepared by adding milligram amounts of one or more aniline compounds to 10 cm^3 of the eluting mixture. Aliquots of these solutions may be further diluted to obtain desired concentrations.

Vapor Generation

Model 309 and 307 Calibration Systems from Analytical Instrument Development, Inc., with 12mm O.D. test tubes containing the liquid or solid aniline compound in the

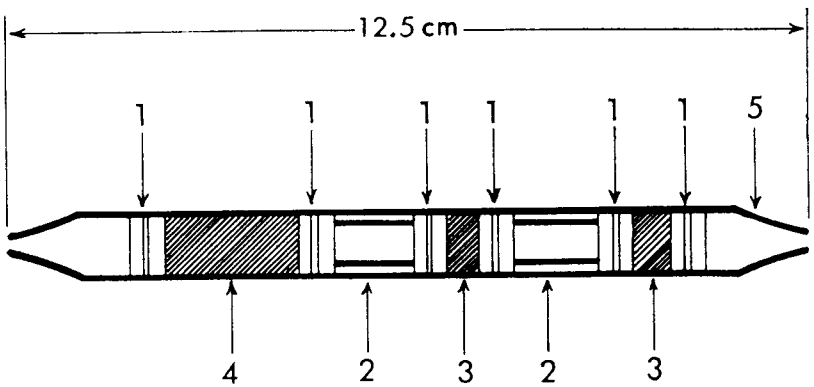

Figure 1. Silica gel sampling tube for aromatic amines. (1) 100 mesh stainless steel screen plugs; (2) 12mm glass tube separator; (3) 150 mg silica gel section, 45/60 mesh; (4) 700 mg silica gel section, 45/60 mesh; (5) 8mm I.D. glass tube.

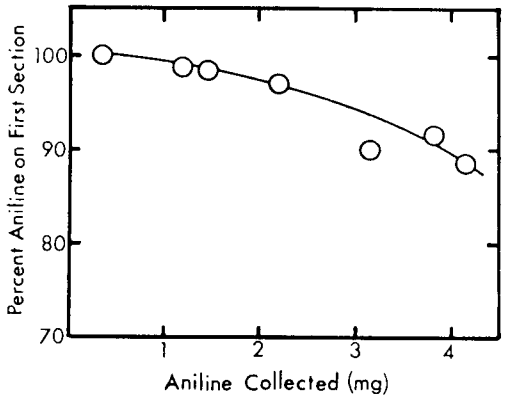

Figure 2. Retention of aniline on 150 mg silica gel after sampling 35 mg/m³ at 1000 cm³/min. High humidity.

heated glass chamber through which heated air flowed. To obtain higher vapor concentrations this glass chamber was attached in a Model LO-200C Grieve Laboratory Oven capable of higher temperatures. The generated contaminated air was cooled to approximately 25°C in a coil of copper tubing prior to sampling.

A 0.03 m³ Pyrex glass chamber containing an electric fan was used for mixing large volumes of contaminated air.

Sampling

Sampling Tube

The 10mm O.D. (8mm I.D.) tube used for sampling aniline compounds in air is about 12.5 cm long including tapered and flame-sealed ends (Figure 1). One 700 mg section and two 150 mg sections of 45/60 mesh silica gel are held in place by stainless steel screen plugs supported with Teflon rings. With these porous plugs the total pressure drop of this tube averages 510 Pa (52mm H_2O) at an air flow rate of 200 cm³/min and 3200 Pa (24mm Hg) at 1000 cm³/min. The sections are separated by 12mm lengths of 7mm O.D. Pyrex tubing to reduce sample migration after sampling (see below).

Silica gel of 45/60 mesh range size was selected on the basis of aniline adsorption capacity, sample desorption efficiency, and pressure drop. More than 50 materials were screened, including gas-liquid and gas-solid chromatography packings and other adsorbents.

Experimental Verification

Dynamic adsorption and retention characteristics of 150 mg and 850 mg sections of this silica gel in 8mm I.D. tubes were determined under simulated sampling conditions. It was found that water vapor in the air significantly reduced retention times of aniline. In order to take into account effects of high humidity, compressed air entering the contaminant vapor generator was first passed through bubblers containing distilled water. The resulting humidity was measured to be essentially 100 at 23°C and 78000 Pa (585mm Hg) which corresponds to 15.5 g/m³ H_2O. Various concentrations of aniline in the effluent from the generator were sampled at 200 or 1000 cm³/min with two-section tubes for varying periods. The initial (test) section (150 or 850 mg) and backup section (150 mg) were later analyzed to determine the fraction of the total sample retained on the test section. Breakthrough was arbitrarily defined as 2% of the total sample on the backup section.

One series of studies was done with 100 mg silica gel sections in 4mm I.D. tubes and

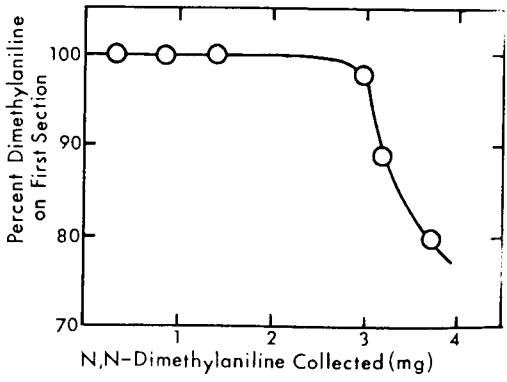

Figure 3. Retention of N,N-dimethylaniline on 150 mg silica gel after sampling 23 mg/m³ at 1000 cm³/min. High humidity.

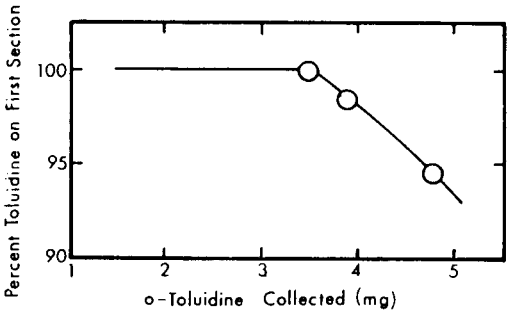

Figure 4. Retention of o-toluidine on 150 mg silica gel after sampling 25 mg/m³ at 1000 cm³/min. High humidity.

aniline vapor. For these 2% breakthrough occurred at approximately 0.9 mg at 90, 60, and 45 mg/m³ for aniline sampled at 1000 cm³/min. This indicates that breakthrough amounts are concentration independent (see later Discussion).

Tubes containing 150 mg silica gel initial sections were used to collect aniline, N,N-dimethylaniline, o-toluidine, and 2,4-xylidine separately from high humidity air at 1000 cm³/min. Breakthrough plots for each compound are shown in Figures 2-5. Table I lists the amounts collected at the 2% breakthrough point as determined from these graphs. A linear correlation between the amounts of these compounds in μmoles retained at 2% breakthrough and the $\log_{10}$ of their corresponding vapor pressures at 25°C[9-12] is shown in Figure 6. The lower

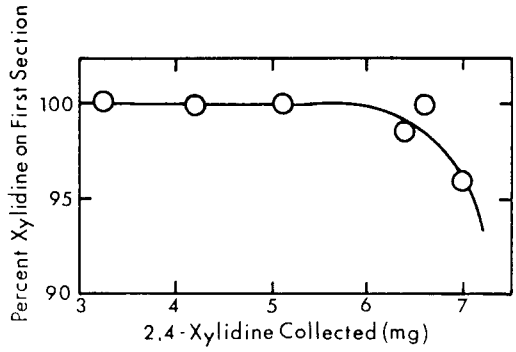

Figure 5. Retention of 2,4-xylidine on 150 mg silica gel after sampling 14 mg/m³ at 1000 cm³/min. High humidity.

the vapor pressure of an aniline compound, the more can be collected on the silica gel sections before breakthrough occurs. Since all substituted aniline compounds have lower vapor pressures than aniline, a sampling tube designed to collect aniline quantitatively would be even more effective for substituted anilines. Predicted 2% breakthrough amounts for p-anisidine, o-anisidine, and p-nitroaniline are also given in Table I from extrapolations of Figure 6.

Figure 7 shows a breakthrough plot for aniline vapor collected on an 850 mg silica gel section in an 8mm I.D. tube from high humidity air. In this case the sampling time

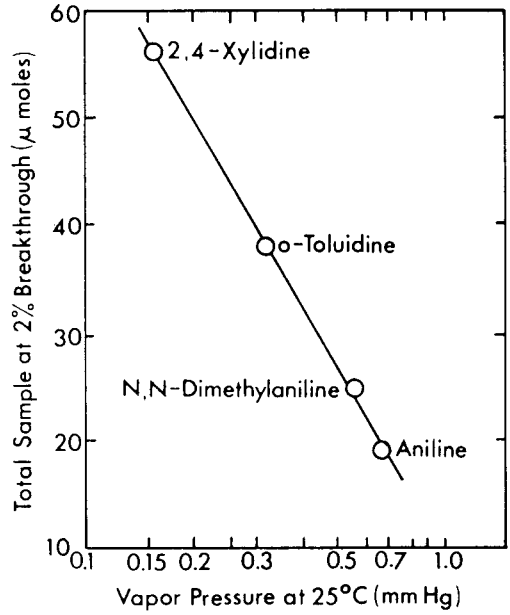

Figure 6. Relationship between amounts collected on 150 mg silica gel at 2% breakthrough and vapor pressure at 25°C.

and rate were held constant at 8 h and 200 cm³/min and the aniline vapor concentration was varied from 54 to 151 mg/m³. Breakthrough of 2% of the sample occurred at 14.4 ± 0.3 mg total sample. From this it is calculated that the large 700 mg and the center 150 mg sections of the sampling tube described above are more than adequate to retain all the aniline collected in 8 h of sam-

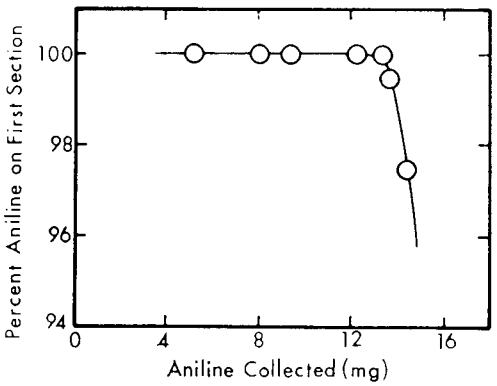

Figure 7. Retention of aniline on 850 mg silica gel after sampling 8h at 200 cm^3/min (0.096 m^3).

pling high humidity air at 200 cm^3/min, even at seven times the Threshold Limit Value.[7] Combining this breakthrough limit for aniline with the data and relationships in Table I and Figure 6, maximum sampling volumes for seven aniline compounds have been calculated and listed in Table II. These maximum volumes assume a concentration of five times the Threshold Limit Value[7] sampled through the large and center sections with less than 2% sample on the third section. For example, the calculation for o-anisidine is $V_{max} = (0.150 m^3)$ (5 ppm/0.1 ppm) (84 μmoles/19 μmoles) = $33.2 m^3$.

Application

The silica gel tube has three adsorbent sections rather than the usual two to allow greater flexibility in its use. For high concentration, high humidity, or high volume samples the 700 mg section is used as the initial section. It is then eluted with 5 cm^3 of ethanol for analysis. Minimum sampling volumes based on analytical sensitivities (discussed below) are given in Table II. However, for low concentrations, low humidity, and low volume samples, the air may be drawn through the tube in the opposite direction, retaining most of the aniline compounds on the 150 mg sections. These then may be eluted with only 1 cm^3 of ethanol, thus increasing analytical sensitivity and reducing the minimum sampling volumes (Table II) by factors of five. The large section still gives the tube its full capacity in case the two smaller sections are overloaded. All sections should be analyzed.

Analysis

Elution

Aniline compounds collected on silica gel were removed for analysis by elution with 95% ethanol containing 0.1% n-heptanol internal standard. One and 5 cm^3 of eluent was used for the 150 mg and 700 mg sections, respectively.

The time necessary for complete elution by ethanol at normal ambient temperatures (~23°C) has been investigated. A sample containing 1.82 mg aniline on 100 mg silica

TABLE I

Amounts at Breakthrough of 150 mg Silica Gel

Compound	Total Sample at 2% Breakthrough: Weight (mg)	Total Sample at 2% Breakthrough: (μmoles)	Vapor Pressure[a] at 25°C [Pa (mm Hg)]	Average Conc. (mg/m^3)
Aniline	1.8±0.2	19±2	89.5 (0.671)	35
N,N-Dimethyl-aniline	3.0±0.1	25±1	74.3 (0.557)	23
o-Toluidine	4.1±0.1	38±1	42.3 (0.317)	25
2,4-Xylidine	6.8±0.1	56±1	20.5 (0.154)	14
p-Anisidine	10.3	84[b]	6.7 (0.050)	—
o-Anisidine	11.2	91[b]	4.9 (0.037)	—
p-Nitroaniline	42.3	306[b]	8.5×10^{-4} (6.4×10^{-6})	—

[a]Reference 9 and extrapolations for other compounds by the method of Reference 9 and data of References 10-12.
[b]From extrapolations of Figure 6.

TABLE II

Recommended Ranges of Sampling Volumes

Compound	Threshold Limit Value (ppm)	Threshold Limit Value (mg/m^3)	Volumes of Air (m^3) Minimum	Volumes of Air (m^3) Maximum
Aniline	5	19	0.005	0.150
N,N-Dimethylaniline	5	25	0.005	0.197
o-Toluidine	5	22	0.005	0.300
2,4-Xylidine	5	25	0.005	0.442
p-Anisidine	0.1	0.5	0.250	33.2
o-Anisidine	0.1	0.5	0.250	35.9
p-Nitroaniline	1	6	0.080	12.1

gel was stored for three weeks. It was then eluted with 1.0 cm^3 ethanol, shaken in a glass-stoppered tube, and analyzed at 10-min intervals after reshaking each time. The aniline concentration in the ethanol eluent increased to a maximum at 30 min where it remained at successive intervals up to 50 min. Therefore, a 30-min period with occasional shaking is sufficient for complete elution.

Two studies were made to determine the efficiency of this desorption step. In the first experiments, 2mm^3 of an aniline compound were injected with a syringe onto 50 mg of 45/60 mesh silica gel in a small test tube. Five identical samples were prepared for each of the following compounds: aniline, N,N-dimethylaniline, o-toluidine, 2,4-xylidine, p-anisidine, and o-anisidine. The test tubes were sealed with Parafilm and allowed to stand for at least one day with occasional shaking to evenly distribute the liquid. Each 50 mg section was then transferred to a glass-stoppered test tube, eluted with 1 cm^3 ethanol for at least 30 min with occasional shaking, and analyzed by gas chromatography. For each compound, five identical standards were prepared immediately before the analysis by injecting 2 mm^3 of the liquid into 1 cm^3 of ethanol in a glass-stoppered test tube. Each solution was mixed by shaking and analyzed twice, alternating the samples and standards.

In the second set of experiments, 1, 2, 3, 4, 6, and 8mm^3 of aniline, o-toluidine, and 2,4-xylidine were added to 1.0 g of 45/60 mesh silica gel. After thorough mixing and equilibration overnight, each sample was eluted with 5 cm^3 of ethanol and analyzed by gas chromatography. Standards prepared with the same amounts of compounds added to 5 cm^3 ethanol were analyzed simultaneously.

Results of these desorption efficiency measurements are given in Table III along with uncertainties of two standard deviations calculated from uncertainties in both samples and standards. It is clear that within the precision of these experiments desorption from silica gel by ethanol of aniline compounds can be considered complete and quantitative.

TABLE III

Percent Desorption Efficiencies

Compound	Amount/Weight of Silica Gel: 2mm^3/50 mg	1 to 8mm^3/1.0 g
Aniline	98.4 ± 6.6[a]	97.4 ± 2.8[b]
N,N-Dimethylaniline	99.7 ± 7.8	
o-Toluidine	101.8 ± 7.2	95.6 ± 2.0
2,4-Xylidine	98.6 ± 13.4	99.2 ± 8.4
o-Anisidine	100.5 ± 10.0	
o-Chloroaniline	100.5 ± 9.4	

[a]Uncertainty includes one standard deviation from five duplicate samples and one standard deviation from five duplicate standards, each analyzed twice.
[b]Uncertainty includes two standard deviations from six sets of samples and standards, each analyzed twice.

Gas Chromatography

Ethanol solutions of aniline compounds eluted from silica gel and standard solutions were analyzed by gas chromatography on the

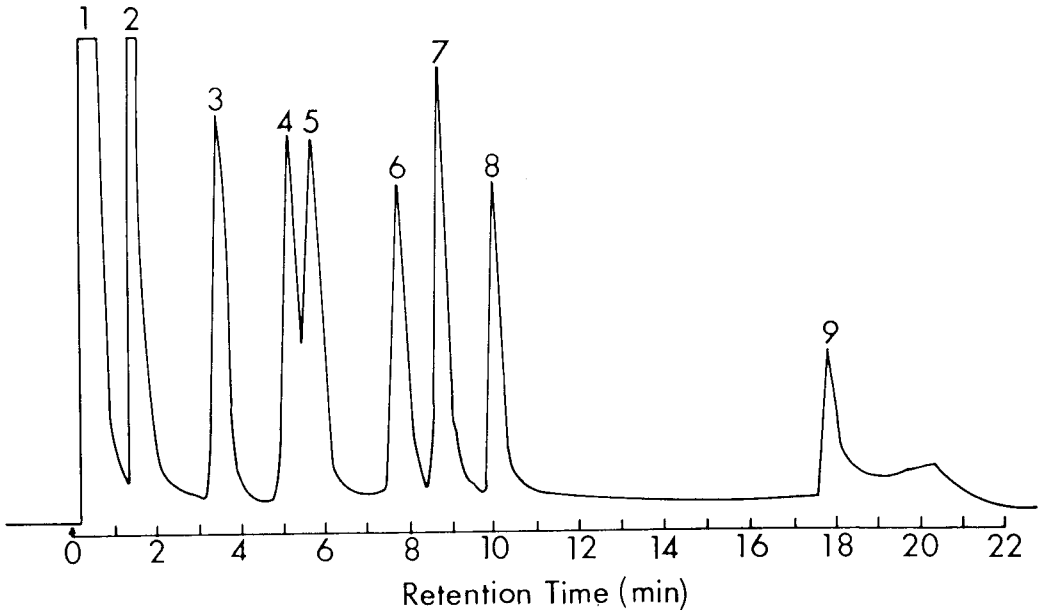

Figure 8. Gas chromatogram: (1) ethanol solvent, (2) 0.1% n-heptanol internal standard, and 0.4 mg/cm³ of (3) aniline, (4) N,N-dimethylaniline, (5) o-toluidine, (6) 2,4-xylidine, (7) o-anisidine, (8) p-anisidine, and (9) p-nitroaniline. Conditions described in text.

Silicone OV-25 column described previously. As an internal standard 0.1% by volume n-heptanol was added to the ethanol used for both elution and standards. Figure 8 is a chromatogram that was obtained when a mixture containing approximately 0.4 mg/cm³ of each of seven aromatic amines in ethanol/ heptanol was analyzed with temperature programming (100°C for four min, then increased at 8 C°/min to 230°C). The simultaneous analysis of all eight required 20 min plus cool-down time per injection. However, if only one compound was expected, a much more rapid analysis was obtained under appropriate isothermal conditions. For example, aniline in ethanol containing n-heptanol was conveniently analyzed at 110°C on this column in only four min.

When interferences are suspected from other compounds an alternate analysis on another column may be useful. On Chromosorb 103 (6.1m x 6mm O.D. 80/100 mesh at 250°C, 50 cm³/min He) elution times relative to ethanol are: aniline, 73 sec; N,N-dimethylaniline, 103 sec; o-toluidine, 105 sec; o-chloroaniline, 143 sec; o-anisidine, 164 sec; and xylidine, 153 sec. Decomposition of p-nitroaniline occurs under these conditions.

The sensitivity of this analysis has also been investigated. Injections of 1 mm³ of ethanol solutions containing seven aniline compounds gave reliable peaks for concentrations as low as 0.02 mg/cm³ for all but p-nitroaniline (0.1 mg/cm³). Assuming that 0.096m³ of air (200 cm³/min for eight h) is sampled on 700 mg of silica gel which is then eluted with 5 ml of ethanol, the sensitivities given above correspond to 0.055 TLV aniline, 0.042 TLV N,N-dimethylaniline, 0.047 TLV o-toluidine, 0.042 TLV xylidine, 0.87 TLV p-nitroaniline, and 2.1 TLV of o- and p-anisidine. For the latter three compounds it is necessary to extend the sensitivity of the method to below the TLV level. This can be done by injecting larger volumes of ethanol solution. For 10mm³ injections the sensitivity is extended

to 0.002 mg/cm^3 (0.01 mg/cm^3 for p-nitroaniline) or 0.21 TLV for o- and p- anisidine and 0.087 TLV for p-nitroaniline.

Precision of the gas chromatographic analysis was measured by multiple injections of ethanol solutions of seven aniline compounds also containing n-heptanol internal standard. Peak areas and ratios were calculated with the Autolab IV electronic integrator with calculation module. For the solution containing approximately 0.4 mg/cm^3 of each aniline compound (Figure 8) the analytical precision (relative standard deviation) ranged from 2% for o-ansidine to 14% for p-nitroaniline with an average of 6%. At approximately 0.12 mg/cm^3 the average analytical precision was also 6% relative standard deviation. Analytical precision was usually improved when only one compound was present and chromatographic conditions and integrator parameters were optimized for it.

Storage

The effects of several factors on the short-term and long-term storage of sampling tubes have been examined. To avoid contamination of the silica gel between tube preparation and air sampling, the ends of each tube should be tapered and flame sealed.

The short-term (up to 8 h) effects examined were low pressures or high temperatures to which a used sampling tube might be subjected during transportation to a laboratory. A batch of aniline evenly distributed on silica gel (18.25 mg/g) was prepared. This was used to prepare six identical tubes containing 100 mg of this mixture each. Without sealing, these tubes were subjected to the following conditions for 8h: two at 50°C, 78000 Pa (585mm Hg); two at 25°C, 66700 Pa (500mm Hg); two at 25°C, 78000 Pa (585mm Hg). An atmospheric pressure of 78000 Pa is normal for Los Alamos. Subsequent analysis showed the aniline on the three sets of tubes to be the same. Therefore, brief periods of elevated temperatures (50°C) or reduced pressures (to 500mm Hg) do not affect the retention or recovery of an aromatic amine sample collected on silica gel.

Long-term (up to 1 month) storage effects of interest were migration and sample decomposition. To measure migration of sample from one silica gel section to another, two identical tubes were prepared with a 100 mg section of fresh silica gel and a 100 mg section of contaminated silica gel (18.25 mg aniline/g silica gel) separated by a glass wool plug. After 14 days 3.8 ± 0.4% of the total aniline was found on the originally uncontaminated silica gel sections. This experiment was repeated, but with a 12mm long piece of 5mm O.D. glass tubing and an additional plug between the silica gel sections. After 27 days of storage at 25°C and 78000 Pa (585mm Hg) migration was only 0.7 ± 0.1%. For a set of identical tubes refrigerated for the same 27 days no migration was detectable.

Tubes containing collected aromatic amines on silica gel have been observed to darken in color when stored for long periods. This decomposition of the sample is accompanied by a decrease in sample recovery by ethanol elution. For example, in one case the recovery of aniline from identically prepared tubes (20 mg/g silica gel) dropped from 94% after 14 days to 83% after 33 days. The effects of temperature, light, and air on this decomposition were briefly investigated. Another set of identical tubes was prepared each with a section of silica gel containing aniline. A pair of tubes was stored in a refrigerator (−3°C); a pair was stored in a dark drawer; a pair was stored uncapped in a helium atmosphere; and a pair was left uncapped and exposed to room light and temperatures. These were analyzed after 27 days. A comparison of aniline recoveries showed that the decomposition process was not slowed by storage under refrigeration, was not slowed by storage in the dark, but was significantly decreased by storage in an

inert atmosphere. The decomposition of aniline is apparently an oxidation process due to the presence of air.

The conclusion from these storage studies is that after sampling aromatic amines with silica gel, the tubes should be tightly capped. If the analysis is to be delayed beyond 7 days after sampling, each tube should be filled with an inert gas (helium, nitrogen, etc.) to reduce loss by oxidation and stored under refrigeration to reduce migration.

Testing of the Method

The precision of the overall sampling and analysis method has been determined. An MSA Portable Pump was used to take eight consecutive 0.015 m^3 samples of an unknown concentration of aniline in air at 1000 cm^3/min from a 0.03 m^3 chamber attached to an aniline generator. Flow through the chamber was approximately twice the sampling rate. Analysis of the silica gel tubes gave an average of 176 μg with a relative standard deviation of 4.45%. This uncertainty includes possible fluctuations in the chamber concentration.

The proposed method was also checked for accuracy against an independent method. Samples of 6000 cm^3 aniline in air were collected from the chamber at 200 cm^3/min with a Sipin Personal Sampler, alternately using two bubblers in series containing 10 cm^3 ethanol each and silica gel tubes. No aniline was found in the backup bubblers or on the backup sections of the tubes.

Analysis of aniline in the bubbler samples was done by the colorimetric method of El-Dib.[13] Absorbances of orange-colored solutions obtained by coupling aniline with 1-napthol were measured at 495 nm and compared with those from aniline in ethanol standards. The five bubbler samples gave an average air concentration of 48 mg/m^3 with a relative standard deviation of 11%. A different analyst used the proposed method of ethanol elution and gas chromatographic analysis for the silica gel tubes. The average result for five tube samples was 46 mg/m^3 with a relative standard deviation of 6%.

The good agreement of these independent methods confirms the accuracy of the sampling and analysis methods. Effects of storage losses on the accuracy have not been included in this comparison.

Discussion

All of the breakthrough results for aniline vapor can be described by a model (#3) which has been proposed for gas indicator tubes.[14] This model is derived for a non-equilibrium case where the controlling factor in vapor adsorption is the mass transfer rate. Furthermore, it is assumed that the back pressure due to re-evaporation from the adsorbent is negligible compared with the inlet concentration of test gas. For this situation

$$\frac{L}{H} = \ln\left(\frac{a}{bx_L H}\right) + \ln\left(\frac{CV}{A}\right) \qquad (I)$$

where

L = stain length (cm)
H = height of a mass transfer unit (cm)
C = inlet concentration of test gas (ppm)
V = volume of air sample (cm^3)
A = internal cross section of the tube (cm^2)
a = weight of 10^{-6} cm^3 of pure test gas at STP (g)
b = weight of 1 cm^3 of adsorbent (g)
x_L = concentration of sorbed gas required to produce a detectable stain (g test gas/g adsorbent)

To apply this formulation, L is identified with the length of a silica gel test section that retains 98% of the test gas (w mg) which has entered it by time t_L and volume V. The average inlet concentration C' (mg/m^3) = 10^6 w/V = C (MP/RT). Also, a = 4.467 x10^{-11} M. At 25°C and 101325 Pa (760 mm), Equation I becomes

$$\frac{L}{H} = \ln\left(\frac{10^3}{bx_L H}\right) + \ln\left(\frac{W}{A}\right) \qquad (II)$$

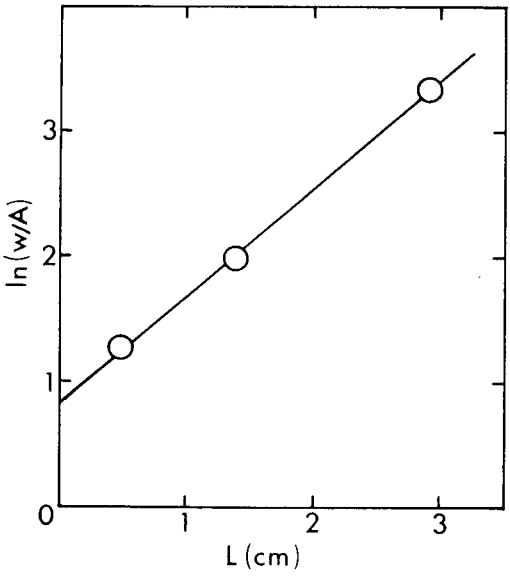

Figure 9. Semilog plot of the ratio of breakthrough amount per cross sectional area vs length of the silica gel section for aniline vapor data.

Equation II predicts that the amount of test vapor w retained by a given adsorbent bed (A,L,b) is independent of the inlet concentration C. This agrees with the experimental results for 100 mg sections (L = 1.4 cm, A = 0.126 cm^2) which retained 0.9 mg of aniline independent of the sampled concentrations in the range 45-90 mg/m^3.

A plot of $\ln \frac{W}{A}$ vs L is predicted to be linear with a slope of 1/H. Such a plot is shown in Figure 9 based on the data in Table IV for aniline vapor in high humidity air. It is indeed linear, yielding a mass transfer unit of H = 1.15 ± 0.05 cm. This unit appears to be independent of flow rate over the range 200-1000 cm^3/min. From the intercept of 0.801 an empirical value of x_L = 3.33×10^{-3} g/g has been calculated for a silica gel density of b = 0.583 g/cm^3. These values of H and x_L can be used to estimate the depth L of a silica gel bed of cross section A necessary to retain 98% of W mg of aniline vapor in high humidity air drawn through it. For example, a 0.096 m^3 air sample (8h at 200 cm^3/min) having 95 mg/m^3 (5TLV) aniline vapor contains 9.12 mg of aniline. If an 8mm I.D. tube (A = 0.503 cm^2) is to be used to collect the vapor, a bed depth of 2.4 cm (705 mg) is calculated to provide 98% collection efficiency at high humidities. At lower humidities the bed depth needed would be less.

It is reasonable to assume that x_L has the same value for all the substituted anilines. From Equation II and breakthrough results for 150 mg sections given in Table I, height of mass transfer units have been calculated to be 0.174, 0.150, and 0.124 for N,N-dimethylaniline, o-toluidine, and 2,4-xylidine, respectively. The information on hand is insufficient to attempt an explanation of the trend of these values or of the related trend shown in Figure 6. However, this again demonstrates that the sampling tube designed to collect and retain aniline vapor under extreme humidity conditions should be even more effective for vapors of substituted aniline compounds.

Conclusions

The sampling and analysis method described can be used for identifying vapors of aniline compounds in the air and for determining personal exposures to them without interference with normal work activities. Capability of sampling for short periods or

TABLE IV

Aniline Vapor Breakthrough Data and Parameters

Silica Gel Test Bed			Total Aniline at Breakthrough		Flow Rate
M (mg)	L (cm)	A (cm^2)	W (mg)	ln (w/A)	cm^3/min
100	1.4	0.126	0.9	1.97	1000
150	0.5	0.503	1.8	1.27	1000
850	2.9	0.503	14.4	3.35	200

for at least 8h, even under high humidity situations, has been demonstrated. The sensitivity, precision, and accuracy of the method have been experimentally determined. Extensive use of the method in actual field sampling situations and routine laboratory analysis situations remains to be done.

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