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Development of Air-Sampling Techniques

LASL Project R-059

October 1, 1973, through March 31, 1974

Work performed by

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DEVELOPMENT OF AIR-SAMPLING TECHNIQUES

October 1, 1973 through March 31, 1974

by

Evan E. Campbell, Project Manager, Gerry O. Wood, and Robert G. Anderson

ABSTRACT

Thermal desorption-gas chromatographic analysis of formaldehyde collected on alumina has been abandoned in favor of a colorimetric method. This modified chromotropic acid method has been found to have much greater sensitivity and specificity and acceptable precision and accuracy. Capacity and breakthrough measurements have been made for a selected alumina sorbent by sampling air containing formaldehyde. As a result, a sampling tube has been designed capable of sampling for up to 1600 s (27 min) under extreme humidity conditions.

Additional breakthrough measurements have been done for aniline, o-toluidine, and xylydine in a high-humidity atmosphere sampled with 45/60-mesh silica gel. From these results a new sampling tube has been designed for sampling aromatic amines. The precision of the total sampling and analysis method has been determined. The accuracy of the method was also confirmed by comparison with an independent sampling and analysis procedure.

Approximately fifty sorbents were screened for methylamine capacity before selecting the same silica gel used for aromatic amines. An efficient desorption procedure was developed for methylamine collected on silica gel. An analytical method of good precision was also developed. Preliminary work has begun with other aliphatic amines.

Six charcoals supplied by NIOSH were tested for benzene and carbon tetrachloride adsorption capacity. Charcoal from an MSA Organic Vapor Respirator Cartridge was tested for benzene capacity at two temperatures and the heat of adsorption was calculated.

A plug has been developed for holding sorbent sections in sampling tubes which has negligible pressure drop.

I. FORMALDEHYDE

The development of thermal desorption, gas chromatographic analysis of formaldehyde on alumina sorbent has been abandoned. Reasons for this decision included the lack of sensitivity necessary for short-term (up to 3600 s) samples and the analytical interferences of substances present on alumina and collected from air. These analytical interferences could be eliminated only

by time-consuming temperature programming of the gas chromatography column.

An alternate colorimetric method involving elution with water and coupling of formaldehyde with chromotropic acid¹ has been explored. This analysis is quite specific for formaldehyde with no common interferences. The sensitivity (0.5 µg) is

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more than required. The analytical precision ($2\sigma = \pm 4.5\%$ at $402 \mu\text{g}$) is quite adequate. Once reagents are mixed only a few steps are required to prepare the sample for absorption measurements. An alumina section is removed from a sampling tube and added to a measured volume of eluent; after thorough shaking an aliquot of the eluent is transferred to a test tube; chromotropic acid solution and concentrated sulfuric acid are added to develop the violet color; upon cooling the absorbance of the solution is measured at 580-nm wavelength. Standards prepared similarly have shown that Beer's Law is obeyed up to an optical density of 1.2 ($\sim 20 \mu\text{g HCHO/aliquot}$).

Desorption of formaldehyde from alumina initially was done with 100 cm^3 of distilled water. The desorption efficiency was measured to be 88% ($2\sigma = \pm 2.4\%$), independent of the amount of formaldehyde over the range of 10 to $400 \mu\text{g}$. The precision of this desorption efficiency includes uncertainties from microliter syringe injections of standards onto alumina sections. To improve this desorption efficiency solutions of 1% chromotropic acid, 1% sodium bisulfite, and distilled water and these eluents heated to 80°C were also tried. None of these attempts resulted in a greater desorption than obtained with distilled water at ordinary room temperature.

As a result of these experiments this colorimetric method is recommended as the method of choice for analyzing formaldehyde collected on alumina. Compensation for incomplete desorption can be made by using standards prepared by injecting solutions of formaldehyde onto alumina sections.

B. Sampling

A Fisher alumina, 8/14-mesh, has been selected as the most effective sorbent for formaldehyde. One basis for this selection was the water adsorbing capacity. Experiments have shown that water vapor easily displaces adsorbed formaldehyde, probably due to a similarity in molecular structure

and polarity. Therefore, water vapor must be removed as efficiently as possible to prevent formaldehyde displacement from the sorbent section(s). Water capacities at 23°C of 0.25-cm^3 sections of several aluminas, silica gels, and molecular sieves were measured by passing humid air through them until no further weight increase was observed. The 8/14-mesh Fisher alumina had a greater water capacity than even finer mesh aluminas from other sources.

Water vapor breakthrough studies were also done for this Fisher alumina. Helium with 92% relative humidity at 23°C and 7780 Pa (585 mm Hg) was flowed at 1.5 and $3 \text{ cm}^3/\text{s}$ (0.18 l/min) through various volumes of the sorbent. The time of breakthrough was observed by the response of a thermal conductivity detector behind the sorbent tube. The results of these experiments are shown in Fig. 1 as a plot of $\log W_B$ (W_B =weight in mg of water on the section at 1% breakthrough) vs alumina volume. A conservative choice for extrapolation to larger volumes is to say that this plot is linear above 1.0 cm^3 . On the basis of these results and assuming the extreme conditions of 30°C (86°F), 7720-Pa (580-mm) pressure, and 100% relative humidity ($39.74 \text{ g H}_2\text{O/m}^3$), breakthrough of water vapor through a 2-cm^3 section would occur after sampling 5300 cm^3 , or after sampling 1600 s (27 min) at 3.53

Fig. 1. Water collected on Fisher 8/14 alumina at 1% breakthrough. W_B in mg.

cm^3/s ($0.2 \text{ l}/\text{min}$). By extrapolation the breakthrough of a 4-cm^3 section would occur after sampling 0.097 m^3 , or after sampling 29000 s (8 h) at $3.33 \text{ cm}^3/\text{s}$.

Formaldehyde breakthrough studies have also been done for the same alumina. To avoid water vapor displacement air was dried before flowing into the formaldehyde generator. The formaldehyde concentration was varied by changing the temperature of the chamber in which paraformaldehyde was decomposed. At each of three concentrations samples were taken at $3.33 \text{ cm}^3/\text{s}$ for varying periods of time with tubes containing two 1-cm^3 sections of Fisher 8/14-mesh alumina. Figs. 2 and 3 show percent retention of the first section as a function of the total sample collected for formaldehyde air concentrations from 0.46 to $40 \text{ mg}/\text{m}^3$. The amounts of formaldehyde at 1% breakthrough (99% retention) are plotted against formaldehyde concentration in air in Fig. 4. From this graph it is seen that up to 0.08 mg of formaldehyde can be retained on 1 cm^3 of this alumina when sampling a dry air concentration of $15 \text{ mg}/\text{m}^3$ (5 times the Threshold Limit Value²). At a sampling rate of $3.33 \text{ cm}^3/\text{s}$ this corresponds to a maximum sampling time of 1600 s (27 min).

Fig. 2. Formaldehyde retention of a 1-cm^3 section of Fisher 8/14 alumina. $\circ$, $0, 40 \text{ mg}/\text{m}^3$; Δ , $25 \text{ mg}/\text{m}^3$.

Fig. 3. Formaldehyde retention of a 1-cm^3 section of Fisher 8/14 alumina at $0.46 \text{ mg}/\text{m}^3$.

C. Conclusions

With the information above a sampling and analysis method can be written which has the capability of sampling formaldehyde for up to 1600 s (27 min) at $3.33 \text{ cm}^3/\text{s}$ in extreme concentration and humidity conditions. The proposed sampling tube contains three sections of Fisher 8/14-mesh alumina in an 8-mm-I.D. glass tube. The first section has 2 cm^3 of alumina to remove water vapor from up to 5300 cm^3 of sampled air (see above). The second section has 1 cm^3 of

Fig. 4. Formaldehyde collected on a 1-cm^3 section of Fisher 8/14 alumina at 2% breakthrough as a function of concentration in air.

alumina to collect and retain formaldehyde from the dried air. The third section has 0.5 cm^3 of alumina to test for breakthrough of the first two sections and to provide an estimate of air concentration if breakthrough does occur. The pressure drop of such a tube is 49 Pa (5 mm H_2O) at $3.33 \text{ cm}^3/\text{s}$, well within the capability of most commercially available personal sampling pumps. The three sections are analyzed separately by the chromotropic acid method after elution with 100 ml distilled water. The desorption efficiency can be determined experimentally or it may be compensated by using as standards alumina sections onto which known amounts of formaldehyde have been added. Extension of the sampling period to at least 14400 s (4 h) will require additional formaldehyde breakthrough studies.

II. AROMATIC AMINES

A. Sampling

Additional breakthrough measurements have been done for aniline, o-toluidine, and 2,4-xylydine in high-humidity air sampled with 45/60-mesh silica gel. The air was saturated with water vapor before passing into the aromatic amine generator (100% R.H. at 23°C and 7780 Pa corresponds to $15.5 \text{ g}/\text{m}^3 \text{H}_2\text{O}$). For each series of experiments the aromatic amine concentration was kept constant as the sampling time was varied. The average concentration was calculated by comparing the analytical results with the volumes of air sampled.

Fig. 5 shows a breakthrough graph for aniline sampled at $3.33 \text{ cm}^3/\text{s}$ with an 850-mg silica gel section. The 2% breakthrough occurred at 14.4 mg total sample. With a 100 mg silica gel section breakthrough occurred at 0.9 mg at 90, 60, and 45 mg/m^3 for aniline sampled at $16.67 \text{ cm}^3/\text{s}$ (1 l/m). This lack of concentration dependence is in contrast with the formaldehyde results of Fig. 4. Different adsorption mechanisms must be occurring.

Fig. 5. Retention of aniline on 850 mg silica gel after sampling 28800 s (8 h) at $3.33 \text{ cm}^3/\text{s}$ (0.096 m^3).

Tubes containing 150-mg silica gel initial sections have been used to sample aniline, o-toluidine, and 2,4-xylydine in high-humidity air at $16.67 \text{ cm}^3/\text{s}$. Breakthrough graphs are shown in Figs. 6-8. A correlation between the measured 2% breakthrough amounts (in μmoles) of these compounds and the logarithms of their vapor pressures at 25°C is shown in Fig. 9. This graph allows the prediction of breakthrough amounts for substituted anilines (and perhaps other aromatic amines) if their vapor pressures at 25°C are known.

Fig. 6. Retention of aniline on 150 mg silica gel after sampling $35 \text{ mg}/\text{m}^3$ at $16.67 \text{ cm}^3/\text{s}$. High humidity.

Fig. 7. Retention of o-toluidine on 150 mg silica gel after sampling 25 mg/m^3 at $16.67 \text{ cm}^3/\text{s}$. High humidity.

It also indicates that a sampling tube developed for aniline would be good for sampling substituted anilines since the latter have equal or lower vapor pressures.

A new sampling tube (Fig. 10) has been designed for aromatic amines based on these results. This three-section tube replaces the two tubes proposed previously. For low concentrations, low humidity, and low volume samples the air is drawn first through the 150-mg short sections which may be eluted with only 1 cm^3 of ethanol. For high concentrations, high humidity, or high volume samples the 700-mg larger section is used as the initial section. It is eluted with 5 cm^3 ethanol. In Table I recommended ranges of sampling volumes are given for

Fig. 8. Retention of 2,4-xylydine on 150 mg silica gel after sampling 14 mg/m^3 at $16.67 \text{ cm}^3/\text{s}$. High humidity.

Fig. 9. Relationship between vapor pressure and amounts collected on 150 mg silica gel at 2% breakthrough.

seven aniline compounds. The minimum volumes are based on detectability of 0.1 times the Threshold Limit Value² when using the large section as the initial section. The maximum volumes are based on breakthrough studies at high humidities and an assumed concentration of five times the Threshold Limit Value when using the large section as the initial section. When the smaller section is used as the initial section these minimum and maximum volumes must be divided by five if the sample is to be retained on the first two sections. The

Fig. 10. Silica gel sampling tube for aromatic amines.
 1) 100-mesh stainless steel screen plugs;
 2) 12-mm glass tube separator;
 3) 150-mg silica gel section, 45/60-mesh;
 4) 700-mg silica gel section, 45/60-mesh;
 5) 8-mm-I.D. glass tube.

TABLE I
Recommended Ranges of Sampling Volumes

	Threshold Limit Value ²		Volumes of Air (m ³)	
	(ppm)	(mg/m ³)	Minimum	Maximum
Aniline	5	19	0.005	0.150
N, N-Dimethylaniline	5	25	0.005	0.150
O-Toluidine	5	22	0.005	0.300
2, 4-Xylidine	5	25	0.005	0.440
O-Anisidine	0.1	0.5	0.250	0.550
p-Anisidine	0.1	0.5	0.250	0.550
p-Nitroaniline	1	6	0.080	2.400

large section still gives the tube its full capacity in case the two smaller sections are overloaded.

The pressure drops of such tubes are kept within the limits of most commercially available personal sampling pumps by using an 8-mm-I.D. tube and wire screen plugs (see below). The pressure drop averages 510 Pa (52 mm H₂O) at 3.33 cm³/s and 3200 Pa (24 mm Hg) at 16.67 cm³/s.

B. Precision and Accuracy

The precision of the overall sampling and analysis method has been determined. A Mine Safety Appliance Company (MSA) Portable Pump was used to take eight consecutive 0.015-m³ samples of aniline in air at 16.67 cm³/s from a 0.030-m³ chamber attached to an aniline generator. Flow through the chamber was approximately twice the sampling rate. The analysis of the silica gel tubes gave an average of 176 µg with 2σ = 8.9%. This uncertainty includes possible fluctuations in the chamber concentration.

The proposed method was also checked against an independent method. Samples of 0.006 m³ aniline in air were taken from the chamber at 3.33 cm³/s with a Sipin Personal Sampler alternately using two bubblers in series containing 10 ml 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.⁴ Absorbances of orange-colored solutions obtained by coupling aniline with 1-naphthol 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/m³ with 2σ = 22%. A different analyst used the proposed method of ethanol elution (with heptanol internal standard) and gas chromatographic analysis for the silica gel tubes. The average result for five tube samples was 46 mg/m³ with 2σ = 12%.

The good agreement of these independent methods, well within experimental uncertainties, confirms the accuracy of the proposed method. Advantages of the proposed sampling method over the use of bubblers include portability and transportability of the tube sampler. Advantages of the gas chromatographic analysis include fewer steps, more specific identification of the aromatic amine collected, and better precision. This specific identification is

quite important since Threshold Limit Values vary greatly for substituted anilines (Table I).

III. ALIPHATIC AMINES

Approximately fifty possible sorbent materials were tested for methylamine adsorption capacity at room temperature. The sorbent with the largest capacity (66 mg/cm³) was found to be the 45/60 mesh silica gel used for aromatic amine sampling. However, unlike the aromatic amines elution of methylamine by ethanol or water was quite inefficient. It was found that 100% (2σ = 4%) recovery of methylamine could be realized by elution with 1 N HCl, separation of half the eluent from the sorbent, and alkalinizing it with an equal amount of 1.2 N NaOH.

Gas chromatographic analysis of the resulting methylamine solution has been done using a 1-m x 5-mm-I.D. Teflon column containing 60/80 mesh Chromosorb 103 at 135° C and 0.42 cm³ He/s (25 cm³/min). With an internal standard of ethanol included in the 1.2 N NaOH, an analytical precision of 2σ = 5.2% has been measured for a 1.8-mg sample.

The acid elutions of ethylamine and butylamine were less efficient, 66% and 55% respectively, which is not satisfactory. As an alternate method some preliminary studies of thermal desorption of these amines have been completed. These results are currently being evaluated.

IV. CHARCOAL TESTING

Several air-sampling methods and air-filtration methods using charcoal are in wide-spread use. For reliability of these methods it is essential that the adsorption characteristics of the charcoal be well known and reproducible. One characteristic that should be important is the adsorption capacity at normal temperatures. The adsorption capacities of six charcoals for benzene and carbon tetrachloride have been

measured. Various physical and chemical properties of these six 20/30 mesh charcoals supplied by the National Institute of Occupational Safety and Health have been measured previously.⁵

The isothermal capacity of interest is the amount of compound which a given volume of charcoal will adsorb at a given temperature and which will not desorb unless the temperature is increased or another compound displaces it. This capacity was determined by measuring the amount of compound not retained by a 0.25-cm³ section of charcoal in a 4-mm-I.D. tube when a known amount of the compound was injected into a helium stream flowing through the tube at 3.33 cm³/s.

The results of such measurements at 25° C are given in Table II. For benzene charcoals #3 (an MSA cocoanut shell charcoal) and #5 (a Barnebey Cheney petroleum charcoal) have the highest capacity. For carbon tetrachloride charcoal #2 (a Barnebey Cheney cocoanut shell charcoal) has the highest capacity. For these two compounds charcoal #3 is probably the best compromise. Two other Barnebey Cheney cocoanut shell charcoals (#4 and #6) showed some of the lowest capacities for both benzene and carbon tetrachloride. Charcoal #1 was a cocoanut shell charcoal from SKC, Inc.

These results point out the often mentioned variations in charcoals (factors of nearly two in isothermal adsorption capacities) of the same mesh size, source material, and manufacturer. They also show that the "best" charcoal for adsorbing one compound may be quite poor for another (for example, #5). Therefore, a batch of charcoal should be tested with each of the compounds for which it is to be used for sampling.

Isothermal adsorption capacities were compared with surface area, pore volume, and particle densities of these same charcoal batches.⁵ No correlation was found with any of these three physical properties.

TABLE II
Isothermal Adsorption Capacities at 25°C

Charcoal	Benzene (mg/cm ³)	Carbon Tetrachloride (mg/cm ³)
1	64 ± 2 (2)*	188 ± 40 (3)
2	86 ± 5 (2)	260 ± 30 (3)
3	98 ± 1 (2)	217 ± 17 (3)
4	65 ± 3 (2)	184 ± 11 (3)
5	104 ± 10 (5)	140 ± 29 (4)
6	72 ± 3 (3)	135 ± 34 (5)

*Number of tests given in parentheses.

Another empirical property which may relate to the effectiveness of a charcoal for air sampling or filtering is the heat of adsorption of a compound on it. Isothermal capacities of charcoal from an MSA Organic Vapor respirator cartridge were measured for benzene at 25° C and 100° C yielding 22 mg/cm³ and 4.7 mg/cm³, respectively. From these two points the heat of adsorption of benzene on these most active sites is calculated to be 1.9×10^3 J/mol (4.6 kcal/mol).

The techniques for measuring isothermal capacities and heats of adsorption used in these experiments show promise for the development of standard methods of sorbent screening and quality control and testing.

V. PLUGS FOR SORBENT TUBES

Considerable effort has been made to develop a satisfactory plug for retaining sorbent sections in tubes. Glass wool packing is of questionable usefulness since it introduces considerable and variable pressure drop. Urethane plugs have much lower pressure drop but may react with or absorb the contaminant sought.

Wire screen of 100-mesh copper, brass, or stainless steel has negligible pressure drop and should be unreactive to most organic vapors sampled. When the urethane and glass cloth plugs of a standard organic

vapor charcoal sampling tube (4-mm-I.D.) were replaced with copper screens the total pressure drop of the tube was reduced 20%. However, for much larger tubes the screen alone was found to be incapable of holding sorbent sections firmly in place. This problem was solved by sandwiching a disc of screen between Teflon rings. A materials cost estimate of \$0.02 per plug has been made for such plugs mass produced. They are easily inserted and removed with the appropriate tool. A patent application for this design is being processed.

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