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PROGRESS REPORT

Quarterly Report

Development of Air Sampling Techniques

LASL Project R-059

January 1 through March 31, 1973

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scientific laboratory
of the University of California
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Work performed by

Bio-Analytical & Chemical Section
Industrial Hygiene Group

Evan E. Campbell, Section Leader
Gerry O. Wood and Robert G. Anderson

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DEVELOPMENT OF AIR SAMPLING TECHNIQUES

by

Evan E. Campbell, Section Leader, Gerry O. Wood, and Robert G. Anderson

ABSTRACT

Breakthrough and desorption studies have been done for o-toluidine, N,N-dimethylaniline, o-anisidine, o-chloroaniline, and mixed xylidines to determine whether the proposed sampling and analytical method for aniline is applicable to these substituted aniline compounds as well. Breakthrough results by two methods indicate that these compounds are adequately absorbed and retained on silica gel for an eight hour sampling period.

Desorption efficiencies of essentially 100% were found for these compounds. Some observations on the analyses of charcoal tubes and the usefulness of standard reference charcoal tubes are presented.

I. ANILINE COMPOUNDS

The tentative method for aniline sampling and analysis has been tested for several aniline substituted compounds. The chemicals (TLV): o-toluidine (5 ppm), N,N-dimethylaniline (5 ppm), o-anisidine (0.1 ppm), and mixed xylidines (5 ppm) were chosen for the initial studies because they have established and published threshold limit values. O-chloroaniline has been studied also.

A. Breakthrough

A tube containing two 50 mg sections of 45/60 mesh silica gel has been proposed for air sampling for aniline at 200 ml/min for 8 hours. The effectiveness of the first sorbent section can be described by the quantity of material which it will collect and retain before some of the material passes through to the second section (i.e., breakthrough occurs). If the concentration in air is constant during the sampling period this breakthrough can be expressed as parts per million.

One way in which breakthroughs have been determined may be called the bulk addition method. Microliter quantities of the chemical were added to glass wool in front of the initial sorbent section. After passing air through the tube for 8 hours at 200 ml/min, both silica gel sections of the tube were analyzed. Several such experiments with increasing amounts of liquid added result in a graph of percent retention vs mg from which the breakthrough amount can be determined by extrapolation. Such graphs for the five compounds listed above are shown in Figures 1-5. Each point represents one measurement only. Breakthrough amounts from these graphs are listed in Table I.

The second way in which breakthrough of the first silica gel section was measured was to sample several constant concentrations for 8 hours at 200 ml/min. Both sections of each tube were then analyzed. Preliminary results for o-toluidine and N,N-dimethylaniline are shown in Figures 6 and 7 and Table I.

These breakthrough studies indicate that the silica gel sampling method for aniline can also be used for substituted anilines. In all cases examined so far the minimum breakthrough amount (bulk addition method) for the first 50 mg section exceeds the equivalent of one TLV level. Breakthrough studies have not been made for two 50 mg sections; however, it is expected that even for xylidines many times the TLV level can be sampled for 8 hours at 200 ml/min without complete breakthrough.

B. Desorption

Desorption efficiency measurements have been carried out for ethanol elution from silica gel of six aromatic amines: aniline, o-toluidine, N,N-dimethylaniline, o-anisidine, o-chloroaniline, and xylidines.

Two microliters of each liquid were added to five glass tubes containing 50 mg of 45/60 mesh silica gel. The liquid was injected directly onto the silica gel using an air flush technique with a 10 μ l syringe. The tubes were sealed with Parafilm and allowed to stand for at least one day with occasional shaking to evenly distribute the liquid on the sorbent. Each 50 mg section was then transferred to a glass stoppered test tube, eluted with 1 ml ethanol for at least 30 min with occasional shaking and analyzed by gas chromatography. For each compound and set of five samples five identical standards were prepared immediately before the analyses. The same syringe and technique was used to inject 2 μ l of each liquid into 1 ml of ethanol in a glass stoppered test tube. Each solution was mixed by shaking and analyzed twice, alternating the samples and standards.

Peak height ratios (compound/ethanol) were used for the calculations to compensate for slight variations in amount injected into the gas chromatograph. An average and a standard deviation of peak height ratios were calculated for ten analyses of five standards for each compound. This average corresponds to 2 μ l/ml ethanol or the concentration listed in the second

column of Table II with the corresponding standard deviations. For the ten analyses of five desorption mixtures an average and standard deviation of peak height ratios was calculated for each compound. This is given in the third column of Table II in terms of concentration. An average desorption efficiency and a combined uncertainty determined from each set of averages and standard deviations are listed in the fourth column of Table II.

It is clear from these results that well within the uncertainties of these measurements desorption efficiencies are essentially 100% for these six compounds. Standard deviations for the preparation and analysis of sets of standards vary from $\pm 1.25\%$ to $\pm 2.61\%$ with an average of $\pm 2.00\%$. Standard deviations for the preparation, desorption, and analysis of sets of samples vary from $\pm 1.81\%$ to $\pm 4.47\%$ with an average of $\pm 2.49\%$. This information suggests that the desorption step does not significantly decrease the precision of the analytical procedure.

C. Interferences

The effects of preabsorbed water, toluene, benzene, or xylene on the retention of o-toluidine on silica gel have been studied. As discussed above, the breakthrough point by the bulk addition method is just above 6 mg o-toluidine for a 50 mg, 45/60 mesh silica gel section; therefore, 6 mg was used for these tests. Tubes were packed with two sections of the equivalent of 50 mg silica gel dry weight. After adding 6 mg o-toluidine to each and drawing air through them for 8 hours at 200 ml/min both sections of each tube were analyzed. For preabsorbed water (24% by weight added) and benzene (26%) there was no breakthrough of the first section. For toluene (24%) and xylene (27%) the breakthroughs were only 0.5% and 0.9%, respectively.

On the Porapak Q gas chromatograph column now being used dimethylaniline and o-anisidine have the same retention time;

therefore, each must be considered as a possible interference in the analysis of the other. Use of another column may remove this difficulty.

II. CHARCOAL TUBE ANALYSES

At the request of NIOSH we have temporarily diverted considerable time and effort to the analysis of two sets of charcoal sampling tubes. One set of approximately 400 tubes is being analyzed as a result of our participation in the collaborative study organized by Scott Research Laboratories, Inc., Plumsteadville, Pennsylvania, and sponsored by NIOSH. The second set of 64 tubes was prepared by the National Bureau of Standards as standard reference charcoal tubes. Both sets contained seven compounds: xylene, benzene, trichloroethylene, chloroform, ethylene dichloride, dioxane, or carbon tetrachloride.

The results of these analyses have been or will be reported to Scott Research Laboratories, Inc., or NIOSH by letter and will not be included in this or future reports. However, some general comments and opinions which seem appropriate follow:

1) As regards the physical characteristics of these charcoal tubes, we suggest the use of glass wool or glass woven cloth instead of the urethane foam sections. The urethane plugs are difficult to remove, increasing the possibility of accidental spillage of charcoal. Also, while struggling to get these plugs out charcoal is easily crushed creating fines which are permanently trapped in the urethane. Even larger charcoal particles are sometimes difficult to release from such plugs. The unknown behavior of the urethane as a sorbent also makes the material undesirable.

2) The charcoal in both sets of tubes contained some chemical which colored the CS₂ eluent, but which did not interfere with the analyses as far as could be determined. Usually the smaller, second section gave more coloration, suggesting that this unknown material is removed from the first

section as air is drawn through the tubes.

3) In the determination of desorption efficiencies several desorption samples and several standards should be prepared and analyzed simultaneously. The procedure described in Section I.B. of this report is time consuming, but reliable. Perhaps it would be even better to determine one desorption efficiency at each of five concentrations rather than to determine five desorption efficiencies at one concentration.

4) In general, we encourage the use of standard charcoal tubes such as those prepared by the National Bureau of Standards for NIOSH. The necessity for determining desorption efficiencies can be avoided and errors such as in pipetting the eluent can cancel.

5) However, due to the variation of desorption efficiencies for different charcoal batches such standards would be useful only when they are part of a set containing blank tubes for sampling packed with the same charcoal.

6) These standard tubes are most useful when all the compound is retained on the first charcoal section. Our results indicate that this is the case for benzene, xylene, and carbon tetrachloride (except for the high excursion standard). It is much easier and faster to confirm a zero on a second section than it is to do multiple analyses to determine the amount present.

7) The published procedure should include a warning to check with the manufacturer to determine if the flame ionization detector used will operate properly with large amounts of carbon disulfide. We discovered after some difficulty that stainless steel flame jets are recommended for CS₂ rather than the nickel ones provided with the Hewlett-Packard 7620 gas chromatograph.

TABLE I

BREAKTHROUGH RESULTS

Compound	Bulk Addition (mg)	Constant Concentration (mg)	TLV Equivalent (mg)
Aniline	5	8.4	1.8
o-Toluidine	6	8.3	2.1
N,N-Dimethylaniline	4	6.0	2.4
o-Anisidine	10		0.5
Xylidines	3		2.4

TABLE II

DESORPTION MEASUREMENT

Compound	Concentrations (mg/ml)		Desorption Efficiency
	5 Standards	5 Samples	
Aniline	2.043±0.029	2.010±0.037	98.4±3.3%
o-Toluidine	1.998±0.025	2.033±0.045	101.8±3.6%
N,N-Dimethylaniline	1.913±0.038	1.906±0.037	99.7±3.9%
o-Anisidine	2.185±0.057	2.196±0.051	100.5±5.0%
o-Chloroaniline	2.425±0.061	2.437±0.053	100.5±4.7%
Xylidines (mixed)	1.929±0.042	1.903±0.085	98.6±6.7%

Fig. 1. o-Anisidine retention. Bulk addition method.

Fig. 2. o-Chloroaniline retention. Bulk addition method.

Fig. 3. o-Toluidine retention. Bulk addition method.

Fig. 5. Xylidines retention. Bulk addition method.

Fig. 4. N,N-Dimethylaniline retention. Bulk addition method.

Fig. 6. o-Toluidine retention. Constant concentration sampling.

Fig. 7. N,N-Dimethylaniline retention.
Constant concentration sampling.