Short Communication

Thermal desorption–gas chromatography for the determination of benzene, aniline, nitrobenzene and chlorobenzene in workplace air

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ABSTRACT

Sampling on Tenax TA of different mesh sizes followed by thermal desorption and gas chromatography was evaluated as a simple method for the determination of benzene, aniline, nitrobenzene and chlorobenzene in the workplace air. An alternative sampling technique in place of pump sampling was developed. Quantitative recoveries were obtained in the mass range 0.04–10 μg. It was found that air humidity had no effect on recovery. The charged tubes can be stored at room temperature for 5 days with no change in recovery. The particle size of Tenax TA has no significant effect on adsorption and desorption.

INTRODUCTION

The demand for accurate, reliable and sensitive techniques for the monitoring of organic trace pollutants in the workplace atmosphere has increased tremendously. Chromatography is a widely used technique which allows the identification and the determination of organic compounds in sub-nanogram amounts. Because of the relatively low concentrations of organic contaminants in the workplace air, most chromatographic methods for monitoring these contaminants requires a preconcentration step before the actual analysis. Traditional preconcentration of organic vapour used in most NIOSH procedures [1] utilizes charcoal or silica gel as the adsorbent, followed by solvent desorption and chromatographic analysis. A newer alternative technique uses a porous polymer adsorbent and thermal desorption into a gas chromatograph [2–5], which offers the best sensitivity with respect to solvent extraction as the whole sample is injected [6,7]. Hence this technique has gained wide acceptance in a variety of applications, including environmental trace analysis [8–14], industrial hygiene [15], stack sampling [16] and personal monitoring [17].

Among the various organic environmental pollutants, benzene, aniline, nitrobenzene and chlorobenzene are particularly poisonous with acute and chronic effects. The threshold limit values (TLVs) for aniline, nitrobenzene, benzene and chlorobenzene are 10, 5, 30 and 350 mg/m³, respectively, for an

8-h exposure [18]. The inhalation and absorption through the skin of nitrobenzene and aniline lead to cynosis with the formation of methaemoglobin [19]. Benzene is a known carcinogen causing aplastic anaemia, leukaemia and other types of cancer [20].

In a recent report, aniline in air was adsorbed on silica and desorbed with methanol for determination by HPLC with a desorption efficiency of 96% [21]. Nitrobenzene was detected in workplace air by adsorption on charcoal and Tenax GC with desorption efficiencies of 91% with toluene and 100% with diethyl ether [22]. Regarding the determination of benzene in the workplace air using solid sorbent adsorption and thermal desorption, Brown [23] has carried out extensive work and reviewed the subject. However, to our knowledge, no work has been reported so far on the thermal desorption of aniline and nitrobenzene.

The aim of this work was to determine trace levels of benzene, aniline, nitrobenzene and chlorobenzene in the workplace air in plants involving the processes of nitration of benzene to nitrobenzene and the reduction of nitrobenzene to aniline. Chlorobenzene occurs owing to the chlorination of benzene being carried out in an adjacent plant. The development of an alternative sampling technique in place of the conventional pump sampling method is also reported.

EXPERIMENTAL

Benzene, chlorobenzene, aniline, nitrobenzene and methanol were of analytical-reagent grade from Fluka (Buchs, Switzerland). Tenax TA of different mesh sizes (20–35, 35–60 and 60–80) was purchased from Alltech (Deerfield, IL, USA) and from Chrompack (Middelburg, Netherlands).

A Perkin-Elmer gas chromatograph equipped with an automatic thermal desorption system (ATD-50) was used. The ATD-50 was coupled via a heated transfer capillary to the GC column. GC analysis was carried out with flame ionization detection detector using a GP-100 printer–plotter. Stainless-steel sample tubes (Perkin-Elmer) of 89 mm × 5 mm I.D. with stainless-steel wire gauges on both ends to hold the adsorbent and having metal sealing caps on both sides for storage were used.

Solid adsorbent

Commonly used adsorbents are the Chromosorb Century series [13,15], the Porapak series [2,4], Amberlite XE [24] and Tenax GC, the most popular being Tenax GC (a polymer of 2,6-diphenyl-*p*-phenylene oxide), which has excellent properties for trapping the pollutants and of thermal stability [25–27].

Although Tenax GC, after proper pretreatment, has been shown to be useful as a trapping material, some problems still exist. Often significant amounts of aromatic hydrocarbons are observed in blank chromatogram of this material. However, by changing the process conditions during the preparation of Tenax, a new type of material, Tenax TA, was obtained. Tenax TA shows a substantial reduction in the contribution of impurities to the blank values, especially with regard to aromatic hydrocarbons. Hence, the adsorption characteristics of three different particle sizes of Tenax TA were evaluated and its utility in workplace air monitoring of benzene, chlorobenzene, aniline and nitrobenzene was studied.

Determination of retention volumes and safe sampling volumes

Glass chromatographic columns (2 m × 2 mm I.D.) were packed with known weights of Tenax TA of 20–35, 35–60 and 60–80 mesh sizes. After packing, each column was conditioned by passing pure nitrogen through for 45 min at room temperature, then heating at a rate of 2°C/min to 300°C and maintaining this temperature for 16 h. Standard solutions of benzene, chlorobenzene, aniline and nitrobenzene were injected at various temperatures (150–275°C) with a nitrogen flow-rate of 25 ml/min.

Standardization of the method by GC

Standard solutions. Stock standard solutions (1%) of benzene, chlorobenzene, aniline and nitrobenzene were prepared in methanol. Working standard solutions to cover the range of interest (0.04–10.0 $\mu g/\mu l$) were prepared by serial dilution of the stock standard solution with methanol.

Calibration. A 1-μl volume of each standard solution was injected on to the GC column under the conditions specified below.

GC conditions. The following conditions were used: column, stainless steel (2.25 m × 2 mm I.D.);

column packing, Tenax TA (60–80 mesh); injection port temperature, 250°C; flame ionization detector temperature, 275°C; oven temperature 185°C for 1 min, increased at 30°C/min to 240°C, held for 6 min; carrier gas (nitrogen) flow-rate, 30 ml/min; and chart speed, 5 mm/min.

The values of area under the curve are the means of five independent observations for each concentration of the standard sample of interest.

Thermal desorption recovery

To determine the thermal desorption efficiency of Tenax TA adsorbent of three different mesh sizes, 0.3 g of material was placed in sample tubes and conditioned under a flow of nitrogen (20 ml/min) at 350°C overnight. The conditioned sample tubes were fitted into GC injection port maintained at 250°C with a nitrogen flow-rate of 15 ml/min. A set of five tubes for each mesh size of Tenax TA were spiked with 1 μl of each standard solution at room temperature. The spiked tubes were disconnected after 2 min and thermally desorbed under the following optimum desorption conditions: desorption temperature, 250°C; desorption time, 10 min;

transfer line temperature, 150°C; cold trap low, −30°C; cold trap high, 300°C; and cold trap adsorbent, Tenax TA (60–80 mesh).

The samples were analysed under GC conditions given above.

Workplace air sample collection

Generally, workplace air sampling on a solid sorbent has been carried out by drawing the air with a constant flow-rate pump. The high capital expenditure for large numbers of such pumps limits the number of sampling locations and the sampling frequency in the workplace. Further, repeated pump failure and maintenance forced us to develop an alternative air sampling technique which is economical and as accurate as pump sampling. In this sampling technique, water is displaced from an air-tight glass bottle (10 l) by siphoning to obtain an accurate and constant flow of air into the bottle through the sample tube. To keep the back-pressure constant to achieve a constant flow, each sample tube was filled with an identical amount (0.3 g) of Tenax TA adsorbent of three mesh sizes. To maintain a constant flow of water withdrawal from the
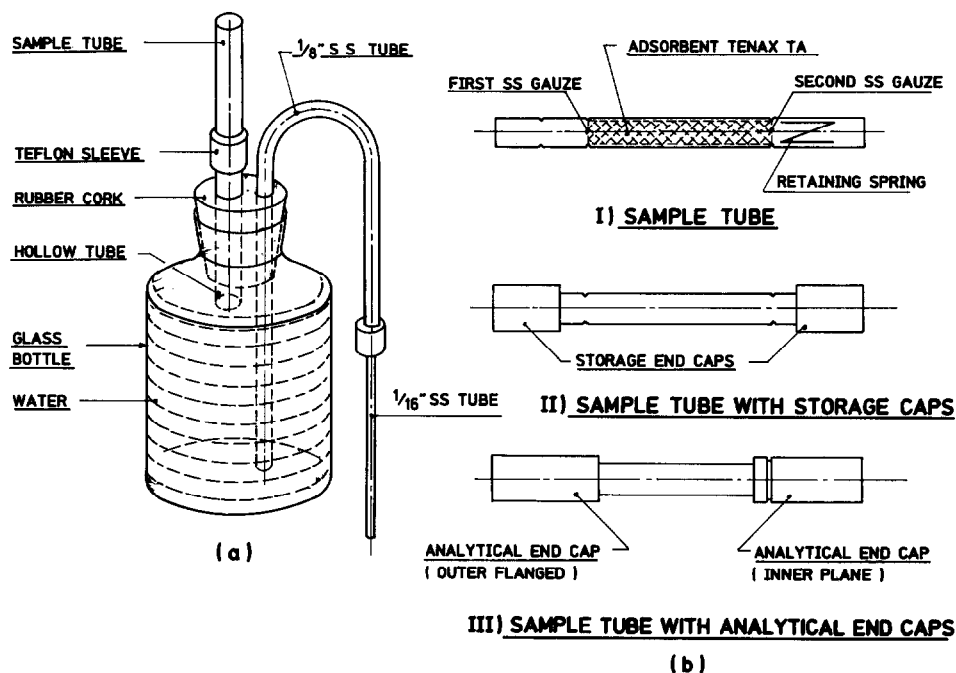

Fig. 1. (a) Diagram of sampler; (b) diagrams of sample tube. I = Sample tube; II = sample tube with storage caps; III = sample tube with analytical end-caps. SS = Stainless steel.

bottle siphoning, the water was siphoned through 1/8- and 1/16-in. stainless-steel tubing connected to each other. The variation in the length of each piece of tubing gave different constant flow-rates over a period of time with an accuracy of $\pm 2\%$, which is comparable to that with pump sampling. It was ensured that the water taken in the bottle was free from particles. The sampling system and sample tube with different end-caps are shown in Fig. 1.

The sample tubes containing 0.3 g of Tenax TA of three mesh sizes, conditioned as mentioned earlier, were used for sampling at each location. When selecting the four locations, emphasis was placed on the sources of potential exposure, such as sample taps, vents, manholes and drains, where the operator may be exposed to the process chemicals. During sampling, care was taken to keep each sampling set as close as possible to each other at every location so as to have the same concentration over three sampling tubes. The amounts of sample collected ranged from 4 to 8 l at rates of 25–30 ml/min. Tubes were sealed immediately for analysis.

RESULTS AND DISCUSSION

In order to establish the retention volume and safe sampling volume, standard solutions of benzene, chlorobenzene, aniline and nitrobenzene were injected at various temperatures (150–275°C) with a nitrogen flow-rate of 25 ml/min. The retention volumes of each analyte at different temperatures were recorded. The logarithm of specific retention volume was plotted against the reciprocal of the absolute column temperature, which gave a linear

relationship. The retention volumes at 20 and 25°C were obtained by extrapolation [24] (Table I). Half of the retention volume was taken as the safe sampling volume, which is defined as the volume of air containing a particular vapour contaminant that may be sampled under a variety of circumstances without significant breakthrough [28].

The calibration graph for each analyte was obtained by plotting average peak area against known concentrations of the compounds in the range 0.04–10.00 $\mu g/\mu l$. A typical chromatogram of a mixture is shown in Fig. 2. The results for the concentration of each compound injected and measured are presented in Table II, together with standard deviation for each measurement. The calibration graphs were linear; the equations of the regression lines and regression coefficients for benzene, chlorobenzene, aniline and nitrobenzene are presented in Table III.

Recovery studies on the thermal desorption were carried out using different mesh sizes of Tenax TA for various concentrations of organic compounds. In general, no differences in recoveries were found on the different mesh sizes of Tenax TA, except for the recoveries of aniline, which were marginally better on Tenax TA (20–35 mesh). The results given in the Table IV indicate nearly quantitative recoveries of all the analytes at all levels of spiking in sample tubes. As the recoveries of the analytes were found to be independent of the mesh size of Tenax TA, only the data for 60–80-mesh Tenax TA are presented in Table IV. A typical chromatogram of thermal desorption is shown in Fig. 3. It was consistently observed that the blank values in ther-

TABLE I

ADSORPTIVE PROPERTIES OF TENAX TA

Compound	Retention volume (l/g)[a]			
	Tenax TA (60–80 mesh)	Tenax TA (35–60 mesh)	Tenax TA (20–35 mesh)	Tenax GC (60–80 mesh)
Benzene	38 (57)	22 (31)	13 (19)	36 (54)
Chlorobenzene	270 (400)	200 (314)	160 (221)	181 (284)
Aniline	1408 (2208)	1635 (2697)	943 (1480)	1212 (1900)
Nitrobenzene	1270 (7331)	6002 (9897)	2565 (4230)	3463 (5710)

[a] Values at 25°C; values in parentheses are retention volumes at 20°C.

TABLE II

STANDARDIZATION OF GC METHOD

Each value is average of five independent measurements.

Standard No.	Concentration (μg/ml)	Benzene	Chlorobenzene	Aniline	Nitrobenzene
1	Taken	0.040	0.040	0.040	0.040
	Found	0.040	0.041	0.042	0.040
	S.D.	0.001	0.003	0.003	0.003
2	Taken	0.200	0.203	0.202	0.201
	Found	0.201	0.206	0.189	0.199
	S.D.	0.007	0.012	0.009	0.007
3	Taken	0.400	0.407	0.404	0.403
	Found	0.403	0.409	0.388	0.405
	S.D.	0.017	0.022	0.018	0.015
4	Taken	1.200	1.220	1.212	1.208
	Found	1.220	1.234	1.223	1.232
	S.D.	0.029	0.034	0.035	0.037
5	Taken	2.000	2.033	2.020	2.013
	Found	1.923	1.950	1.945	1.933
	S.D.	0.046	0.042	0.045	0.041
6	Taken	2.800	2.846	2.828	2.818
	Found	2.957	2.879	2.894	2.855
	S.D.	0.074	0.073	0.073	0.073
7	Taken	3.600	3.659	3.636	3.623
	Found	3.701	3.670	3.788	3.723
	S.D.	0.027	0.029	0.036	0.035
8	Taken	4.400	4.473	4.444	4.429
	Found	4.410	4.475	4.551	4.461
	S.D.	0.073	0.079	0.127	0.118
9	Taken	5.200	5.286	5.252	5.239
	Found	5.202	5.276	5.383	5.258
	S.D.	0.132	0.130	0.085	0.088
10	Taken	6.000	6.099	6.060	6.039
	Found	6.010	6.096	6.205	6.052
	S.D.	0.115	0.125	0.148	0.140
11	Taken	8.000	8.132	8.080	8.052
	Found	7.875	8.031	8.149	7.955
	S.D.	0.312	0.311	0.252	0.252
12	Taken	10.000	10.165	10.100	10.065
	Found	9.763	10.040	10.048	9.899
	S.D.	0.274	0.30	0.252	0.296

TABLE III

LINEARITY OF ANALYTICAL PROCEDURE

Compound	Regression equation[a]
Benzene	$y = 36.739x + 2.049$; $r = 0.999$
Chlorobenzene	$y = 25.142x + 0.936$; $r = 0.999$
Aniline	$y = 28.036x + 0.779$; $r = 0.999$
Nitrobenzene	$y = 22.274x + 1.002$; $r = 0.999$

[a] y = Peak area; x = concentration; r = regression coefficient.

mal desorption on Tenax TA were low (10–20 ng) compared with the values obtained on Tenax GC (40–60 ng).

Comparison of the results in Table II for standardization of the GC method and in Table IV for recovery studies shows good agreement, indicating that the adsorption of substances from the dry nitrogen calibration mixtures and subsequent thermal desorption were complete under the conditions
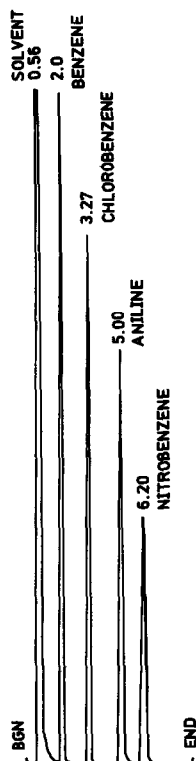
Fig. 2. Typical chromatogram showing the separation of benzene, chlorobenzene, aniline and nitrobenzene. BGN = Start; numbers at peaks indicate retention times in min.
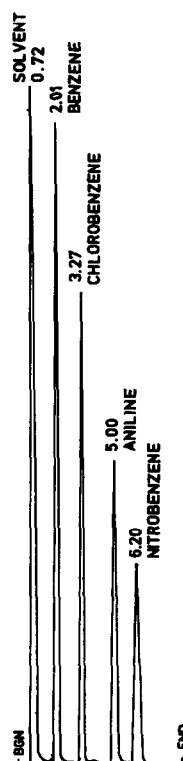

Fig. 3. Typical chromatogram for the thermal desorption recovery of benzene, chlorobenzene, aniline and nitrobenzene.

TABLE IV

THERMAL DESORPTION RECOVERY ON TENAX TA (60–80 MESH)

Standard No.	Recovery (μg)[a]			
	Benzene	Chlorobenzene	Aniline	Nitrobenzene
1	0.041 ± 0.006 (102)	0.056 ± 0.010 (121)	0.051 ± 0.006 (122)	0.041 ± 0.01 (93)
2	0.235 ± 0.008 (117)	0.237 ± 0.017 (115)	0.199 ± 0.033 (105)	0.121 ± 0.045 (105)
3	0.411 ± 0.009 (102)	0.414 ± 0.007 (101)	0.354 ± 0.015 (91)	0.394 ± 0.015 (98)
4	1.226 ± 0.018 (100)	1.30 ± 0.013 (105)	1.137 ± 0.039 (93)	1.182 ± 0.039 (96)
5	2.033 ± 0.041 (106)	2.107 ± 0.013 (108)	1.839 ± 0.046 (94)	1.926 ± 0.048 (100)
6	2.853 ± 0.024 (100)	2.953 ± 0.016 (102)	2.695 ± 0.032 (93)	2.746 ± 0.049 (96)
7	3.644 ± 0.030 (98)	3.825 ± 0.028 (104)	3.538 ± 0.045 (93)	3.698 ± 0.035 (99)
8	4.425 ± 0.262 (100)	4.755 ± 0.156 (106)	4.406 ± 0.147 (97)	4.502 ± 0.109 (102)
9	5.237 ± 0.028 (101)	5.545 ± 0.041 (105)	5.227 ± 0.105 (97)	5.248 ± 0.117 (100)
10	6.047 ± 0.052 (101)	6.409 ± 0.033 (105)	6.122 ± 0.052 (99)	6.168 ± 0.072 (102)
11	7.907 ± 0.063 (100)	8.433 ± 0.059 (105)	8.002 ± 0.083 (98)	8.034 ± 0.099 (101)
12	9.867 ± 0.091 (101)	10.640 ± 0.100 (106)	10.243 ± 0.109 (102)	10.054 ± 0.129 (102)

[a] Each value is average of five independent measurements ± standard deviation. The values in parentheses are percentage recoveries.

TABLE V

RESULTS OF ANALYSIS OF WORKPLACE AIR SAMPLES

Sample No.	Mesh size	Concentration (mg/m³)			
		Benzene	Chlorobenzene	Aniline	Nitrobenzene
1	20–35	0.020	0.005	0.401	0.050
	35–60	0.020	0.004	0.417	0.070
	60–80	0.019	0.005	0.394	0.069
2	20–35	0.014	0.006	0.385	0.116
	35–60	0.014	0.006	0.339	0.098
	60–80	0.014	0.007	0.244	0.083
3	20–35	0.012	0.013	0.792	0.098
	35–60	0.013	0.014	0.754	0.092
	60–80	0.011	0.012	0.668	0.085
4	20–35	0.017	0.021	0.259	0.065
	35–60	0.030	0.037	0.280	0.134
	60–80	0.021	0.016	0.174	0.046
5	20–35	0.077	0.074	0.448	0.101
	35–60	0.081	0.067	0.355	0.077
	60–80	0.076	0.073	0.334	0.087
6	20–35	0.018	0.010	0.289	0.072
	35–60	0.019	0.011	0.268	0.074
	60–80	0.019	0.012	0.256	0.069
7	20–35	0.030	0.022	0.557	0.064
	35–60	0.032	0.025	0.546	0.063
	60–80	0.030	0.022	0.575	0.067
8	20–35	0.041	0.021	0.070	0.118
	35–60	0.041	0.020	0.062	0.129
	60–80	0.040	0.022	0.067	0.126
9	20–35	0.027	0.053	0.117	0.099
	35–60	0.025	0.032	0.099	0.086
	60–80	0.024	0.021	0.078	0.078
10	20–35	0.022	0.022	0.072	0.084
	35–60	0.038	0.025	0.078	0.106
	60–80	0.027	0.028	0.083	0.118

specified. In order to check for potential losses during field sampling, charged tubes were exposed to a stream of air with various relative humidities, generated by volumetric mixing of air with water-saturated air. The charged samples tubes were then purged with air at various relative humidities of air over different periods of time. The recoveries were almost complete within the relative standard deviation of the whole method (1–4%), indicating that relative humidity has no effect on sampling over Tenax TA. Similar observations were reported earlier [28,29].

The results of workplace air monitoring of organic pollutants using the proposed sampling technique are shown in Table V. The data obtained at each location on three different mesh sizes of Tenax TA are in reasonable agreement with each other. In conclusion, this work has clearly demonstrated the applicability of Tenax TA for the monitoring of airborne benzene, aniline, nitrobenzene and chlorobenzene in the workplace environment in conjunction with thermal desorption and gas chromatography.

ACKNOWLEDGEMENTS

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