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Determination of benzene, aniline and nitrobenzene in workplace air: a comparison of active and passive sampling

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Abstract

There have been numerous investigations on methods for assessing the relative performance of pumped and diffusive sampling techniques for the determination of airborne contaminants. Diffusive sampling is a convenient and cost-effective analytical tool for measuring exposure to chemical hazards in air and has been available as a replacement for pumped sampling for around 20 years. In spite of the considerable amount of work put into their evaluation, diffusive samplers have only been partially successful in replacing pumps. Generally, evaluation studies on diffusive samplers have been concentrated primarily on their accuracy at high concentrations, neglecting the vital aspect of their applicability at lower concentrations (below mg/m^3) in the field. The present evaluation demonstrates that a Perkin-Elmer-type sampling tube, filled with Tenax TA and operated diffusively, provides a means of sampling that is sufficiently sensitive to measure benzene, aniline and nitrobenzene at concentrations as low as 0.10 mg/m³. This method gives precise and accurate results that are well within the National Institute for Occupational Safety and Health (NIOSH) acceptability criteria of $\pm 25\%$ accuracy. No correlation is observed between active and diffusive sampling at concentration levels below 0.01 mg/m³. Retention volumes, thermal desorption recoveries, sampling efficiencies, diffusive uptake rates and concentration effect on sampling performance were investigated. There are no previous reports, on determination of aniline and nitrobenzene in air by diffusive sampling and thermal desorption.

1. Introduction

The ability to achieve a safe workplace depends largely upon proper sampling techniques for the representative assessment of workplace exposure. Sampling is an integral and vital element of industrial hygiene in air pollution monitoring. Hence the sampling devices and analytical methods employed must be sufficiently sensitive and accurate to allow reasonable interpretation of the results, which are usually presented as time-weighted average exposure over a given period. The basic sampling techniques for the collection of substances in air using solid sorbents are active and passive sampling. The more popular and traditional active sampling utilizes volumetric pumps to draw a known volume of air through a bed of solid sorbent. The passive sampling techniques utilizes diffusion of compounds into a chamber containing solid sorbent. The diffusion of organic vapours

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from the environment to the sorbent occurs according to Fick's first law of diffusion [1].

The traditional preconcentration of organic vapours used in most National Institute for Occupational Safety and Health (NIOSH) procedures utilizes charcoal or silica gel as the sorbent, followed by solvent extraction and gas chromatographic (GC) analysis [2]. A newer technique uses a porous polymer adsorbent and thermal desorption with cryofocusing into the gas chromatograph [3-8]. This technique offers better limits of detection than solvent extraction because the whole sample is injected into the chromatographic system as a narrow band, and it has become increasingly popular [9-14]. Further, this technique is perfectly amenable to complete automation of the analysis, which may become an important feature when a large number of samples have to be analysed and processed [15].

Some tube-type monitors can be used in the active or in the diffusive (passive) mode [16]. In workplace monitoring, it is highly desirable that each worker is monitored for his or her individual exposure in addition to measuring the general level of toxic vapours in workplace air. The drawback with pumped sampling, however, is the high cost involved in mass personal screening projects. Further, good-quality volumetric pumps are required for each person or for each location involved. It is also necessary to have spare pumps in case of breakdown and the pumps require calibration and servicing at regular intervals. Hence, in recent years, a costeffective and simple sampling system has been developed in the form of "diffusive" (passive) samplers. Diffusive samplers are inexpensive, light, reusable and safe for use in flammable atmospheres.

Methods of comparing the performances of pumped and diffusive sampling have been widely investigated [17–21]. To date, there has been a mixed reception amongst occupational hygienists as to the acceptability and applicability of commercially available diffusive monitors. In order to allow the determination of air composition from the amount of analyte adsorbed, the exposure has to be done in a way that ensures a defined, diffusion-limited step that controls the rate of uptake from the atmosphere. The sampling rate of such diffusive samplers is low, owing to the slow rate-determining diffusion step. Consequently, at low atmospheric concentrations, the amount of sample is too small to analyse. To overcome this limitation, the exposure periods should be extremely long [22]. These problems of diffusive sampling have to be considered before taking into account their advantages such as simplicity of use and low cost.

An overview of several types of passive samplers and their performance was given by Brown and co-workers [23,24]. The important features of their studies include a diffusive sampler evaluation protocol (HSE protocol), effects of exposure variables on sampler performance and a method for comparison of the diffusive sampler with an independent pumped method. Most of the applications of passive samplers are in the monitoring of indoor pollution at fairly high levels (mg/m³). There have been few measurements of organic pollutants below mg/m³ levels by the diffusive sampling technique.

The organic pollutants benzene, aniline and nitrobenzene are known poisons with acute and chronic effects. The inhalation and absorption through the skin of these chemicals may lead to cyanosis with formation of methaemoglobin [25]. Benzene is also a known carcinogen, causing aplastic anaemia and leukaemia [26].

Nitrobenzene and aniline are the basic raw materials widely used in the polymer, rubber, agricultural and dye industries. It is estimated that nearly $3.5 \cdot 10^9$ lbs. (1 lb. = 0.4536 kg) of aniline and $2.5 \cdot 10^9$ lbs. of nitrobenzene are produced currently worldwide. It is interesting that about 300 chemical products are currently manufactured from aniline alone, involving thousands of workers exposed to these chemicals.

For the determination of aniline and nitrobenzene in air, there are validated methods (NIOSH and OSHA) using adsorption and solvent desorption [27,28]. Recently, we have reported the determination of trace levels (mg/m^3) of these pollutants at fixed locations in the workplace by adsorption and thermal desorption techniques making use of active sampling methods [29]. Many of the published assessments of passive samplers are from laboratory trials making use of exposure chambers. Such trials are a useful preliminary step in the evaluation of a new technique, but can in no way be considered a sufficient validation of a personal monitoring method, because it does not reproduce the conditions and variables that occur in real field use [30]. The aim of this study was to extend this work to personal monitoring by assessing the accuracy of the passive sampling technique in comparison with active sampling.

2. Experimental

2.1. Chemicals

Benzene, aniline and nitrobenzene were of analytical-reagent grade from Fluka (Buchs, Switzerland). Methanol used as a solvent was of analytical-reagent grade from S.D. Fine Chemicals (Bombay, India). Tenax TA of 60–80 mesh (180–250 μ m) was obtained form Ohio Valley Specialty Chemicals (Marietta, OH, USA).

2.2. Apparatus

A Perkin-Elmer gas chromatograph equipped with an automatic thermal desorption system (ATD-50) was used. The ATD-50 was coupled with the heated transfer capillary to the gas chromatograph. GC analysis was carried out with a flame ionization detector and GP-100 printer-plotter. Stainless-steel sample tubes (Perkin-Elmer) 89 mm \times 5 mm I.D. with stainless-steel wire gauges on both ends to hold the adsorbent and having metal sealing caps on both side for storage were used. During the determination of laboratory uptake rates and workplace air sampling, diffusion caps of $50-\mu m$ pore size, 0.2 cm^2 area and 1.5 cm path length were used on one side of tubes. The storage caps were replaced with analytical end-caps during analysis.

2.3. Determination of retention volumes

A glass chromatographic column (1 m \times 2 mm

I.D.) was packed with a known mass of Tenax TA (60-80 mesh). After packing, the column was conditioned at 25°C for 45 min. Thereafter, the temperature was increased at 2°C/min to a final temperature of 300°C, which was maintained for 24 h with a nitrogen flow of 20 cm³/min. After conditioning of the column, a standard solution of benzene, aniline and nitrobenzene were injected separately at different column temperatures with a nitrogen flow-rate of 20 cm³/min. The retention volumes were recorded along with the absolute column temperature.

2.4. Calibration of method by GC

Stock standard solutions (1%) of benzene, aniline and nitrobenzene were prepared in methanol. Working standard solutions to cover the range of interest $(0.01-10 \text{ mg/cm}^3)$ were prepared by serial dilution of the stock standard solution with the methanol. A 1-mm³ volume of each standard solution was injected on to the GC column under the following optimum conditions: column, stainless steel (2.25 m \times 2 mm I.D.); column packing, Tenax TA (60-80 mesh); injection port temperature, 250°C; flame ionization detector temperature, 290°C; oven temperature, 185°C for 1 min, then increased at 30°C min to 240°C, held for 6 min; carrier gas (nitrogen) flow-rate, 30 cm³/min; and chart speed, 5 mm/ min.

2.5. Thermal desorption recovery

Tenax TA (0.3 g) of 60-80 mesh was used to fill sample tubes, which were then conditioned under a flow of nitrogen ($20 \text{ cm}^3/\text{min}$) at 300°C overnight in a specially made laboratory oven (Skylab, India). The conditioned sample tubes were fitted into the GC injection port maintained at 250°C with a nitrogen flow-rate of 20 cm³/ min. A set of five tubes were spiked with 1 mm³ of each standard solution ($0.01-10 \text{ mg/cm}^3$) 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 analyses were performed using the optimized GC conditions used for calibration of the method.

2.6. Generation of test atmosphere

Test atmospheres for benzene, aniline and nitrobenzene were generated in the concentration range 0.12-8.34 mg/m³ as described [31]. The test substance was fed as a liquid by means of an HPLC pump (880 PU, Jasco, Tokyo, Japan) and diluted with air stream with help of mass flow controllers (Porter Instrument, Hatfield, PA, USA). Provisions were made for water injection into the system to obtain atmospheres of controlled relative humidity. The air stream after appropriate dilution and thorough mixing was fed into the exposure chamber consisting of a 5-dm³ glass vessel with an air-tight lid. The concentration in the exposure chamber was monitored at 30-min intervals using Tenax sampling tubes and were analysed by GC for control purposes.

2.7. Efficiency of active sampling

The efficiency of the active sampler was determined by drawing samples of test atmospheres through three samplers at a flow-rate of 20 cm³/ min for 2–8 h simultaneously, using precalibrated pumps (SKC, USA). During the sampling, the relative humidity was maintained at 50 and 90%, which was achieved by mixing dry air with the air that had been bubbled through deionized water. The exposure chamber was provided with two outlets for sampling and a third outlet was left in water to maintain the atmospheric pressure in the exposure chamber during sampling. Different concentrations were obtained by varing the flow-rate of the dilution air with the help of a mass flow controller.

2.8. Determination of laboratory uptake rate

After independent validation of the active sampling method, a set of three passive samplers

with diffusive caps were exposed to test atmospheres for the determination of passive sampling rates. Samples were collected in the concentration ranges 0.12-8.34, 0.11-7.16 and 0.098-4.56 mg/m³ for benzene, aniline and nitrobenzene, respectively, for 300 min. During the sampling, the relative humidity in the exposure chamber was maintained at 50 and 90%. The concentration in the exposure chamber was directly monitored by GC and was also checked by drawing sample actively over a Tenax TA sampling tube at a rate of 20 cm³ min for 2-8 h for control purposes.

After the exposure, passive sampling tubes were analysed by GC with the thermal desorption system under the conditions specified above. Diffusive uptake rates for each compound were calculated as follows.

uptake rate $(cm^3/min) =$

mass of compound on diffusive tube (ng) concentration in exposure × exposure time (min)

2.9. Workplace air sample analysis

Air samples were collected in chemical plants involving the processes of nitration of benzene to nitrobenzene and the reduction of nitrobenzene to aniline. When selecting the locations, emphasis was placed on the sources of potential exposure, such as manholes, drains, sampling points and the control room where the employee might be exposed to the process chemicals during the duty hours. Sampling tubes containing 0.3 g of Tenax TA of 60-80 mesh, conditioned as mentioned earlier, were used in the passive mode for sampling at each location. Samples were collected for 2-8 h in the passive mode. For the comparison of passive and active sampling results, a few sets of samples were also collected in the active mode at a distance of 10 cm from the passive sampling sets with the help of precalibrated pumps. The humidity and temperature of the workplace air during the period of investigation were found to vary between 50 and 90% and 20 and 40°C, respectively.

During thermal desorption and GC analysis of samples, the diffusion caps were replaced with

an analytical end-caps and the sampling tubes were placed on the turntable of the thermal desorption system for analysis. The tubes were thermally desorbed and analysed using the optimized conditions of thermal desorption and GC. The concentrations for the compounds of interest were determined as follows:

C (passive) (mg/m³) =

mass of compound found on tube (ng) uptake rate $(cm^3/min) \times sampling time (min)$

3. Results and discussion

3.1. Retention volumes

The retention volumes of each compound were recorded at different temperatures. The logarithm of the specific retention volume was plotted against the reciprocal of the absolute column temperature, which gave a linear relationship. The retention volumes of benzene, aniline and nitrobenzene were determined at 20°C and found to be 57, 2208 and 7331 dm³/g, respectively.

3.2. Calibration of method by GC

The calibration graph for each analyte was obtained by plotting average peak area against known concentrations of the compounds injected. A linear graph passing through the origin was obtained for the investigated concentration range of $0.01-10.00 \text{ mg/cm}^3$ for each analyte. The pooled accuracy of the method was found to be better than 100% with relative standard deviations of 0.72-4.21, 0.95-7.14 and 0.94-7.5% for benzene, aniline and nitrobenzene, respectively. A regression coefficient of 0.999 was found for all the chemicals.

3.3. Thermal desorption recovery

The thermal desorption recovery of benzene, aniline and nitrobenzene on solid sorbent tubes packed with Tenax TA (60–80 mesh) was investigated at various concentrations. The tubes were spiked with different concentrations of standard solutions. After the spiking, each tube was connected to the pump and exposed to different relative humidities for 2-6 h in order to check for potential losses during field sampling. The thermal desorption recovery results are given in Table 1. The results indicate nearly quantitative recoveries of all the analytes at all levels of spiking in sample tubes. However, only at lower concentrations of spiking was a positive bias of up to 15% observed. This indicates that the adsorption of substances from the calibration mixture and subsequent thermal desorption were complete under the conditions used. The charged tubes can be stored at room temperature for 5 days with no significant change in recovery. The recoveries were almost complete within the relative standard deviation of the whole method (0.80-12%). This indicates that relative humidity has no effect on sampling over Tenax TA under the specified experimental conditions. Similar observations have been reported previously [3,32].

3.4. Sampling efficiency

The sampling efficiency for different concentrations of benzene, aniline and nitrobenzene was determined by analysing the sampling tubes exposed to known concentrations of test atmosphere. The results for the sampling efficiency with relative standard deviations are given in Table 2. Neither the concentration nor the relative humidity seems to affect seriously the sampling efficiency at a sampling rate of $20 \text{ cm}^3/$ min. Three parallel samplings at a flow-rate of 20 cm³/min were performed at 50 and 90% relative humidity. The overall sampling efficiency at the two relative humidities was found to be more than 98%, showing complete adsorption and thermal desorption of benzene, aniline and nitrobenzene from Tenax TA sampling tubes.

3.5. Laboratory uptake rate

The uptake rates for different concentrations of benzene, aniline and nitrobenzene were de-

Table 1							
Thermal	desorption	recovery	on	Tenax	ΤA	(60 - 80)	mesh)

Benzene		Aniline		Nitrobenzene	
Spiked	Recovery	Spiked	Recovery	Spiked	Recovery
0.010	0.011(110) {0.001]	0.010	0.011(114) [0.001]	0.011	0.012(114) [0.001]
0.040	0.041(103) [0.003]	0.040	0.048(115) [0.004]	0.040	0.041(102) [0.005]
0.400	0.411(103) [0.009]	0.404	0.382(95) [0.015]	0.403	0.401(100) [0.015]
2.000	2.033(102) [0.041]	2.020	1.849(92) [0.046]	2.013	1.936(96) [0.048]
3.600	3.644(101) [0.03]	3.636	3.646(100) [0.045]	3.623	3.698(102) [0.035]
5.200	5.237(101) [0.028]	5.252	5.237(100) [0.105]	5.239	5.248(100) [0.117]
8.000	7.907(99) [0.063]	8.080	8.012(99) [0.083]	8.052	8.060(100) [0.099]
10.000	9.867(99) [0.091]	10.100	10.243(101) [0.109]	10.065	10.064(100) [0.129]

Each value is average of five independent measurements (μg) with the recovery (%) in parentheses and the standard deviation (μg) in square brackets.

termined by analysing the passive sampling tubes exposed to known concentrations of test atmosphere. The results for passive sampling uptake rates for benzene, aniline and nitrobenzene are presented in Table 3 with standard deviations. The accuracy and precision of the uptake rate determinations were found to be excellent. In laboratory trials, the accuracy and precision of passive sampler were found to be better than those of the pumped sampler. A similar observation has been reported previously [33]. The overall precision of the uptake rate determi-

Table 2

Sampl	ing efficiency of	Tenax	TA	sorbent	tube	in	active	mode	for	different	concentrations	and	relative	humidi	ity
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Analyte	Test atmosphere concentration (mg/m ³)	Concentration found (mg/m ³)	Sampling volume (dm ³)	Sampling efficiency (%)	Precision (R.S.D.) (%)	Standard deviation (mg/m ³)
Benzene	0.120	0.126	5	105	2.38	0.003
	1.363	1.409	7.5	103	3.69	0.052
	8.347	8.221	8	99	2.74	0.226
Aniline	0.110	0.119	10	105	5.04	0.006
	1.481	1.444	9	98	3.04	0.044
	7.167	7.079	8	99	2.51	0.178
Nitrobenzene	0.098	0.103	8	105	7.77	0.008
	2.324	2.398	9	103	4.50	0.108
	4.563	4.489	10	98	3.54	0.159

Average of 4~6 determinations at 50 and 90% relative humidity.

Analyte	Test atmosphere concentration (mg/m ³)	Mass of analyte on diffusion tube (ng)	Uptake rate (cm ³ /min)	Standard deviation (cm ³ /min)	Effective uptake rate (cm ³ /min)
Benzene	0.120	34	0.94	0.03	0.909
	1.363	373	0.911	0.018	
	8.347	2201	0.878	0.018	
Aniline	0.110	28	0.858	0.046	0.852
	1.481	379	0.853	0.020	
	7.167	1820	0.846	0.014	
Nitrobenzene	0.098	27	0.918	0.034	0.881
	2.324	601	0.862	0.010	
	4.563	1183	0.864	0.015	

Table 3		
Laboratory determination of uptake rate in cm/min for di	lifferent concentrations and re	lative humidity

Average of five independent measurements.

Table 4

Results of workplace air sample analyses for 5-8 h

Sample No.	Concentration	n (mg/m ³)									
	Passive sampl	ing		Active sampling							
	Benzene	Aniline	Nitro- benzene	Benzene	Aniline	Nitro- benzene					
1	0.100	0.384	0.311	0.040	0.157	0.124					
	(0.133)	(0.043)	(0.146)	(0.001)	(0.110)	(0.005)					
2	0.030	0.046	0.154	0.028	0.074	0.102					
	(0.005)	(0.011)	(0.034)	(0.008)	(0.003)	(0.017)					
3	0.026	0.245	0.041	0.043	0.265	0.021					
	(0.002)	(0.010)	(0.007)	(0.004)	(0.007)	(0.003)					
4	0.027	0.669	0.045	0.012	0.738	0.031					
	(0.001)	(0.076)	(0.001)	(0.001)	(0.064)	(0.003)					
5	0.066	0.229	0.122	0.018	0.270	0.071					
	(0.053)	(0.173)	(0.102)	(0.0004)	(0.013)	(0.004)					
6	0.065	0.367	0.164	0.077	0.379	0.087					
	(0.005)	(0.033)	(0.131)	(0.003)	(0.048)	(0.008)					
7	0.033	0.164	0. 166	0.026	0.097	0.154					
	(0.055)	(0.041)	(0.011)	(0.005)	(0.019)	(0.007)					
8	0.139	0.561	0.136	0.129	0.529	0.126					
	(0.066)	(0.023)	(0.007)	(0.004)	(0.029)	(0.005)					
9	0.166	0.912	0.055	0.158	0.920	0.042					
	(0.003)	(0.035)	(0.008)	(0.006)	(0.018)	(0.004)					
10	0.071	0.129	0.272	0.071	0.111	0.273					
	(0.009)	(0.003)	(0.017)	(0.004)	(0.011)	(0.008)					

Each value is average of three independent measurements. Values in parentheses are standard deviations.

 Table 5

 Paired t-test of two independent methods (active and passive)

Analyte	No. of measurements	Paired <i>t</i> -test values				
	incustrements	t (calculated)	t (tabulated)			
Benzene	30	4.930	2.05			
Aniline	30	13.489	2.05			
Nitrobenzene	30	4.712	2.05			

At the 95% confidence level.

nation was found to be in the range 1.00-5.36%. Neither the concentration nor the relative humidity seems to affect seriously the determination of uptake rates in the concentration range studied.

3.6. Workplace sample analysis

A field survey was carried out at nitrobenzene

and aniline manufacturing plants performing nitration of benzene and subsequent reduction of nitrobenzene to aniline. Field measurements were made at four different locations at the workplace air for about 1 year in the passive mode. During the period of investigation, the temperature and relative humidity were found to vary between 20 and 40°C and 50 and 90%, respectively.

In the field evaluation of individual sampling techniques at fixed locations, the results of most of the measurements were within $\pm 6\%$ for active sampling and $\pm 8\%$ for passive sampling. It is generally believed that diffusive samplers are more reliable than pumped samplers because they eliminate pump failure. However, in our field trials with diffusive samplers, we found a variability of the results of 8–10%, wherein the results differed widely. Similar results have been reported previously [34].

The representative field sampling data are summarized in Table 4. The results of paired



Fig. 1. Plot of concentration given by passive sampler versus active sampler for benzene in workplace air: y = 1.009x + 0.002; R = 0.967.

data sets for active and diffusive sampling for benzene, aniline and nitrobenzene were subjected to Students' t-distribution test for comparison. Table 5 gives results of the paired t-test of the two independent methods. According to the paired t-tests, the methods are comparable.

A correlation between the different results obtained from the two methods was also made using linear regression analysis. The data for 30 representative paired samples were evaluated by means of a point correlation diagram, wherein Xand Y correspond to active and diffusive sampling values, respectively. The regression equations and correlation coefficients for benzene, aniline and nitrobenzene are given in Figs. 1, 2 and 3, respectively. The correlation is generally good for benzene, where the regression coefficient is 0.967. For aniline and nitrobenzene. relatively low correlation coefficients were obtained. Careful evaluation of the data indicates that the agreement between pumped and diffusive samplers is concentration dependent. No

correlation was observed at concentration levels below 0.10 mg/m^3 . At concentration levels above 0.10 mg/m^3 , fairly good agreement was observed.

4. Conclusions

The results demonstrate that a Perkin-Elmer tube sampler, operated diffusively, provides a means of sampling that may be sufficiently sensitive for analysis at concentration levels of 0.1 mg/m³ of benzene, aniline and nitrobenzene. Fairly good agreement between the results of pumped and diffusive sampling was observed as the correlation coefficient approached unity at concentration levels above 0.1 mg/m³.

The tube-type diffusive sampler coupled with automatic thermal desorption offers the possibility of fully automated sample recovery. This, in combination with on-line GC chromatographic analysis, is very attractive when one is aiming for



Fig. 2. Plot of concentration given by passive sampler versus active sampler for aniline in workplace air: y = 0.873x + 0.064; R = 0.899.



Fig. 3. Plot of concentration given by passive sampler versus active sampler for nitrobenzene in workplace air: y = 0.947x + 0.029; R = 0.862.

a convenient and cost-effective analytical procedure. Diffusive sampling and automated thermal desorption provide a convenient method for mass screening of workers exposed to organic vapours at a reasonable cost.

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