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A Simple Method to Determine Azobenzene in the Workplace Air

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Abstract: **Background:** In view of the exposure of workers in Poland to azobenzene, there is a need to develop a sensitive method for the determination of this carcinogen in the air. The determination method proposed in this article is simple, using high-performance liquid chromatography with diode array detection.

Material and methods: The method consists of the adsorption of azobenzene using a cellulose filter and silica gel, followed by its extraction with methanol, and an analysis of the received solutions. The methanol as the mobile phase at a flow rate of 0.6 mL min-1 and an Ultra C18 column of 250 mm length at the temperature of 298 K were used for chromatographic separation.

Results: The use of diode array detector at a wavelength of 316 nm makes it possible to quantitatively determine 2 micrograms of azobenzene in a cubic meter of the workplace air (for 120 L air samples) under the conditions of air sampling and determination described in the procedure. The limit of detection is 3.1 ng mL-1, and the limit of quantification is 9.4 ng mL-1.

Conclusions: The method could be useful for determining concentrations of azobenzene in workplace air to assess occupational exposure to this hazardous substance at the workplace.

Keywords: Analysis of Air, Azo Dyes, Carcinogen, Liquid Chromatography, Workplace.

INTRODUCTION

Azobenzene (AZOB, CAS No 100-33-3) is a crystalline solid, orange to red in colour and is poorly soluble in water. On an industrial scale, azobenzene has been used as an intermediate product in the production of dyes and accelerators in the rubber production process (vulcanization). In the past, azobenzene was used as a fumigant in greenhouses against insects and mites, which resulted in its direct release into the environment [1].

Azobenzene is also an intermediate product in the production of hydrazobenzene, benzidine and aniline [2, 3]. Azobenzene can take the form of two geometric isomers: trans and cis. The holographic properties of azobenzene and its derivatives [4, 5] and the possibility of using these substances in the production of photochromic polymers [6-8] is investigated in various research centres. Ko and Yam [9] proposed using azobenzene to create photochromic complexes with metal cations.

Taking the risks to human health into consideration, azobenzene was classified as a carcinogenic substance of category 1B (Carc. 1B) with the health hazard phrase H350 - "may cause cancer", mutagenic substance of category 2 (Muta. 2) with the phrase H341 - "suspected of causing genetic defects" [10]. The routes of potential human exposure to AZOB are inhalation and ingestion. At present, azobenzene occurs in workplaces as a by-product of the production of benzidine and is used in small quantities as a substance used for research purposes, e.g. photochromic polymers.

The analysis of data obtained from the Central Register of Exposure Data on Substances, Factors and Technological Processes with Carcinogenic or Mutagenic Effects, maintained by the Nofer Institute of Occupational Medicine, situated in Łódź (Poland), shows that the number of people exposed to azobenzene in Poland in the years from 2012 to 2015 varied. The largest number of people exposed to azobenzene,

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reported by analytical laboratories in both 2014 and 2015, was 54. Other notifications concerned employees of higher education institutions and scientific institutes.

The presence of carcinogens in work environments poses a big problem for employers, not to mention the personnel exposed to them. EU legislation [11] requires employers to assess occupational risks, to take action to prevent damage from exposure to harmful substances, as well as provide workers with information on potential exposure and the results of workplace examination. Therefore, according to legal regulations in Poland, employers must take measures to deal with the presence of carcinogens in work environments. Monitoring the amount of carcinogen is useful not only to check that the exposure limit values are not exceeded, but also that the technical measures work well enough. Monitoring results are also needed to assist in selecting the appropriate personal protective equipment and to ensure proper medical surveillance. They should be kept with documentation of occupational activities, as the effects of carcinogens on workers' health are often distant from the initial contact.

No concentration limit values for azobenzene have been established and there are no methods developed for its determination in the air at workplaces, therefore the possibility of assessing and documenting occupational risks is limited. In scientific literature, methods of determination of the content of azobenzene in different environmental samples are available. For Huaihe river's sediments in China, at 6 different sampling sites, the azobenzene content was determined to be in the range of 0.13-0.29 mg kg^{-1} [12]. Soil samples were filtered and analysed using gas chromatography and mass spectrometry.

Azobenzene was also determined in water by spectrophotometric method (at 320 nm wavelength) while searching for an effective method of water purification with kaolinite [13]. Fujita et al. [14] examined the possibility of using high-performance liquid chromatography and spectrophotometric detection to determine the components of the mixture of azobenzene, hydrazobenzene and azoxybenzene and their chlorinated derivatives. The use of 500 mm long Permaphase ODS column with an internal diameter of 2.1 mm and methanol (50%) aqueous solution as a mobile phase methanol/water with a flow rate of 0.36 mL min^{-1} allowed the determination of azobenzene, hydrazobenzene and azoxybenzene at 240 nm wavelength.

However, there is currently no method for the determination of azobenzene in the occupational environment air.

The article falls within the area of current topics related to air quality; methods for sampling, analyzing and detecting air toxics in the air [15-21], as well as the collection of airborne substance in environmental samples and methods for controlling exposure to chemicals in the air [22-26].

An important aim of this study was to determine how air samples should be sampled and processed in order to obtain a reliable result. The method of personal sampling was chosen, where a sampler is placed in the worker's breathing zone. The sampler was connected to a pump (battery-powered) for active air sampling.

Various sorption materials were tested; the conditions for active sampling and the shelf life of the samples were checked. The conditions for the chromatographic determination of azobenzene in samples were optimized to quantify the exposure of a worker. Validation parameters were determined according to EN 482 [27] to confirm the suitability of the method for the determination of exposure indicators and occupational risk assessment for workers.

EXPERRIMENTAL

Materials and Reagents

The following chemicals were used in the experiment: azobenzene (Sigma-Aldrich, USA), hydrazobenzene (Aldrich, Lithuania), 4-aminoazobenzene (Fluka, Germany), benzidine (Fluka, South Korea), 3,3'-dimethylbenzidine (Fluka, Germany), 3,3'-dimethoxybenzidine (Sigma, USA), 3,3'-dichlorobenzidine (Supelco, USA) and methanol (MeOH) (Merck, Germany). Pure gradient grade reagents for liquid chromatography were used.

Whatman GF/A fibreglass filters of 25 mm diameter (Whatman, England), cellulose filters of 25 mm diameter (POCh, Poland), polypropylene filters of 25 mm diameter (IW Textile Research Institute, Poland), sorbent tubes with silica gel (100/50 mg) (ZUP Analityk, Poland); sorbent tubes with XAD-7 (ORBO-43) (100/50 mg) (Supelco, USA) and sorbent tubes with XAD-2 (ORBO-605) (100/50 mg) (Supelco, USA), were used for air sampling.

Apparatus

In the experiments, the liquid chromatograph Agilent Technologies (Germany), 1200 series equipped with: G1310A iso pump, ALS G1329A autosampler, G1316A thermos tatted column compartment, G1315D diode array detector (DAD) and G1321A fluorescence detector (FLD), was used.

Gilair 5 aspirator (Sensidyne, USA) was used for active sampling. The WL-2000 mechanical shaker (JWElectronic, Poland) was used in recovery studies and the Sartorius TE214S analytical balance (Sartorius Corporation, USA) for weighing. The samples and standard solutions were stored in a refrigerator at a temperature of 278 K.

Chromatographic Conditions

Determination of AZOB was conducted with an Ultra C HPLC column (250 mm × 4.6 mm, 5 μm) with a precolumn of dimensions: 10 mm × 4.0 mm (Restek, USA) at column temperature of 298 K using the mobile phase of methanol at a flow rate of 0.6 mL min^{-1}. The volume of the sample injected onto the column was 20 μL. Diode array detector (DAD) was used at the wavelength of λ = 316 nm.

Validation

The developed determination method was tested in terms of linearity, sensitivity, selectivity, precision and accuracy [27]. The limit of detection (LOD) and the limit of quantitation (LOQ) were determined from the blank sample results which were obtained by extraction of a cellulose filter together with silica gel with 2 milliliters of methanol. To determine the LOD and LOQ, the calculated standard deviation of the blank samples and the slope of the calibration curve were used.

The calculated expanded uncertainty takes account of analytical recovery, analytical precision, as well as the calibration and uncertainty also associated with sampling process.

RESULTS AND DISCUSSION

Determination of Chromatographic Conditions

The possibility of separation of azobenzene in methanol by liquid chromatography using a 25 cm long Ultra C18 column, methanol as a mobile phase and detectors: diode array (DAD) and fluorescence (FLD), was checked (Fig. 1).

Applied chromatographic conditions allow the determination of azobenzene in the presence of benzidine, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, 3,3'-dichlobenzidine, hydrazobenzene and 4-aminoazobenzene with UV/Vis spectrophotometry (wavelengths 240 and 316 nm) (Fig 1A and Fig 1B). As azobenzene exhibits maximum absorbance at 316 nm, the areas of the obtained peaks on the chromatograms are larger than at 240 nm. Hence, for quantitative determination of azobenzene, a diode array detector at a wavelength of 316 nm was used.

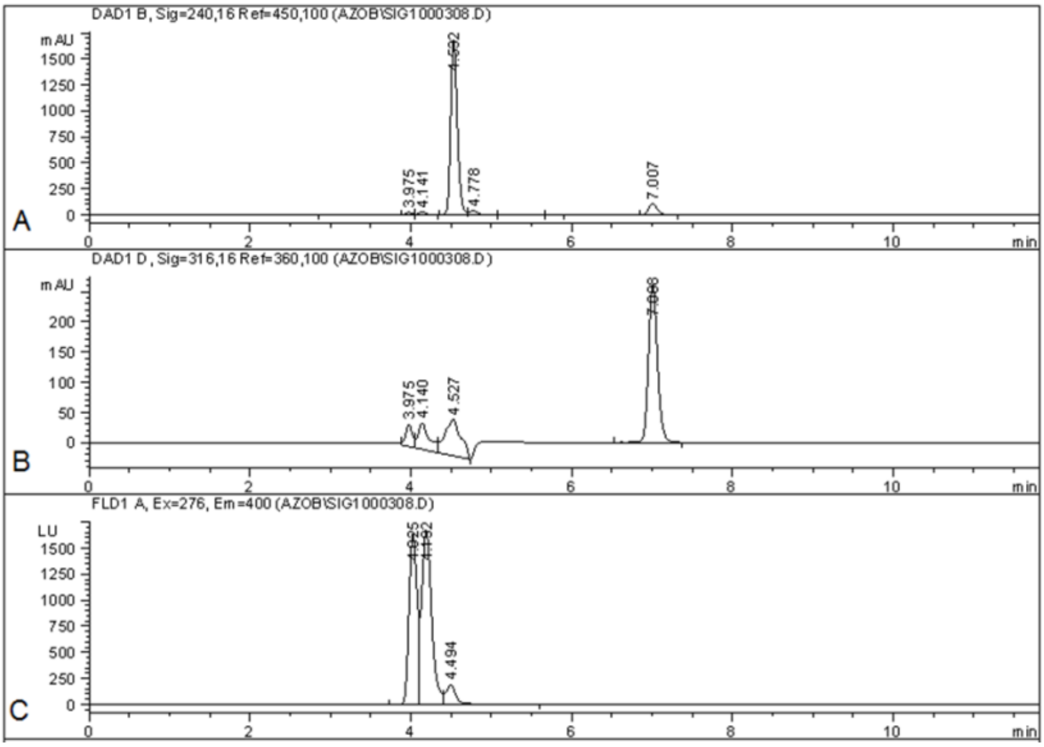

Figure 1: Chromatogram of azobenzene (7.0 min) in the presence of coexisting substances: benzidine (3.98 min), 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine (4.1 min); 3,3'-dichlorobenzidine, hydrazobenzene (4.5 min) and 4-aminoazobenzene (4.78 min)

Determination conditions: Ultra C18 column (250 mm × 4.6 mm, 5 μm), column temp. 298 K; mobile phase methanol; flow 0.6 mL min^{-1}. A: HPLC-DAD: wavelength 240 nm B; HPLC-DAD, wavelength 316 nm; C: HPLC-FLD, excitation wavelength 276 nm, emission wavelength 400 nm.

Preliminary Investigations of AZOB Recovery Efficiency

Azobenzene is solid under normal conditions. When released into air, it occurs primarily in the form of an aerosol, although the vapour pressure of 0.48 Pa at 298 K indicates that it will also occur in the air in the form of vapours [1]. To ensure the quantitative separation of this compound from the air, sampling conditions were adjusted. Polypropylene, cellulose and fiberglass filters, as well as absorption tubes containing silica gel and polymeric sorbents XAD-7 and XAD-2, were used for the study. Methanol (in which AZOB dissolves very well) was used to recover azobenzene from the filter and sorption materials.

25 μL of azobenzene solution (approx. 2.08 mg mL^{-1}) was applied to the selected filters and sorbents. After drying (about 1 hour at room temperature), 2 mL of methanol was added. After 30 minutes of shaking the prepared samples, the determination of AZOB was performed in the obtained solutions under the determined chromatographic conditions. Azobenzene was also determined in reference solutions. The recovery and desorption coefficients were calculated on the basis of the AZOB peaks areas on the chromatograms of the tested solutions (Table 1). Among the sorbents, satisfactory recovery was obtained for silica gel.

Table 1: Results of determination of AZOB recovery and desorption coefficients from selected filters and sorbents (approx. 52 μg AZOB)

Material		Peak area of azobenzene in the reference solution	Peak area of azobenzene in solution after recovery/desorption	Average recovery/ desorption coefficient
Filter	fibreglass	2994.7	2916.6	0.99
		2991.9	2909.8	
		2932.7	2971.6	
		2929.9	2977.4	
		2994.0	2951.6	
		2964.0	2949.1	
	polypropylene	2984.1	2411.3	0.80
		2993.2	2388.5	
		3003.0	2386.3	
		2997.9	2398.4	
		2934.0	2350.6	
		2991.0	2349.5	
	cellulose	30670.0	31315.0	0.99
		30615.0	31250.0	
		31654.0	30795.0	
		31625.0	30730.0	
		31570.0	30960.0	
		31535.0	30940.0	
Sorbent	silica gel	2974.1	2373.6	0.85
		2973.2	2357.8	
		2695.3	2421.1	
		2694.8	2420.1	
		2834.0	2431.6	
		2864.0	2499.1	
	XAD-7	2974.1	801.2	0.28
		2973.2	799.2	
		2695.3	847.3	
		2694.8	847.3	
		2834.0	750.6	
		2864.0	749.5	
	XAD-2	2974.1	792.1	0.28
		2973.2	791.7	
		2695.3	825.3	
		2694.8	826.1	
		2834.0	789.2	
		2864.0	788.8	

Satisfactory results were obtained for the same tests carried out with the cellulose filter and fibreglass filter. Due to the lower price of cellulose filter, this type of filter was chosen for further experiments.

Air Sampling Optimization

During the optimization of the air sampling stage, the ability of cellulose filter and silica gel to retain azobenzene during air permeation and the durability of air samples was checked.

In the study, air from above the azobenzene (the standard in the form of a fine powder - about 3 mg) scattered on the Petri dish was absorbed. A cellulose filter was used for the study (placed in the collection head of the inhalable fraction of aerosol), which was connected in series with an sorbent tube containing one layer of 100 mg of silica gel (two layers of gel gave too much resistance at airflow of 2 L min^{-1} and throttled the sampling pump). Ten liters of air (2 L min^{-1}) were drawn through for 5 minutes. The test was repeated twice. In solutions after recovery from cellulose filter 87.3 % of azobenzene and in solutions after recovery from silica gel 12.6% was determined. The results show that the cellulose filter retains azobenzene in the form of an aerosol, the silica gel - vapour of azobenzene.

Subsequently the value of air flow through a sampler with cellulose filter connected to a sorbent tube with silica gel (100/50 mg) was verified in order to determine the total content of azobenzene in the examined air (Table 2). For this purpose: 5 µL of AZOB solution in methanol (2 mg mL^{-1}) was applied to the cellulose filters. Then (after drying) the air (120 L) was passed through the filter placed in sampler and the silica gel in the sorption tube. The tests were carried out for different air flow values (from 0.333 to 2 L min^{-1}). For a pump flow of 2 L min^{-1}, a tube with one layer of silica gel (100 mg) was placed behind the filter. The solutions obtained after elution with methanol from filters and sorbents were determined by chromatography. The results shown in Table 2 show that at an air flow of 2 L min^{-1}, more than 10% of azobenzene is not retained on the filter nor on the 1st layer of sorbent.

Table 2: Results of verification of the value of air flow through a sampler with cellulose filter connected to a sorbent tube with silica gel

Air flow (L min^{-1})	Sampling time (min)	Air volume (L)	Peak area of AZOB in solutions after recovery		
			cellulose filter	silica gel (first layer, 100 mg)	silica gel (second layer, 50 mg)
0 (air was not allowed to pass through)	0	0	629.8	not tested	not tested
0.333	360	120	591.0	28.8	not detected
0.333	360	120	588.5	25.9	not detected
1	120	120	546.7	45.3	not detected
1	120	120	541.2	51.1	not detected
2	60	120	356.0	126.3	not tested
2	60	120	353.4	130.1	not tested

On the basis of the results, the following air sampling method was determined: at the sampling point, through a 25 mm diameter cellulose filter placed in a sampler combined with a sorbent tube containing two layers of silica gel (100/50 mg), pass up to 120 L of tested air with a constant airflow up to 1 L min^{-1}.

Air Sample Storage Test

The durability of air samples, depending on their storage time, was tested as follows: 5 µL of 0.25 mg mL^{-1}AZOB solution in methanol was applied to cellulose filters and silica gel in sorbent tubes. The samples were stored under refrigeration at a temperature of 278 K and analyzed (2 samples each) on subsequent days.

Table 3: Stability of air samples, each containing 1.25 µg of azobenzene stored under refrigeration

Sample	Storage time (days)	Peak area	Average peak area	Variation of average peak areas after air samples storage (%)
cellulose filter	0	62.75 61.55	62.15	--
silica gel	0	60.10 58.85	59.48	--
cellulose filter	1	62.95 65.10	64.02	3.0
silica gel	1	62.80 61.00	61.90	4.1
cellulose filter	3	59.25 59.70	59.48	-4.3
silica gel	3	57.10 56.30	56.70	-4.7
cellulose filter	6	59.05 56.15	57.60	-7.3
silica gel	6	54.15 52.31	53.23	-10.5

On the basis of the obtained results (Table 3), it was found that the samples stored in the refrigerator are stable for at least 3 days. Because the variation in results during the first 3 days of sample storage was less than 5%.

Validation Parameters

During validation, the procedure for the measurement of azobenzene has been tested in terms of linearity, sensitivity, selectivity, precision and accuracy.

The calibration was carried out in the concentration range of 0.125–2.5 μg mL^{-1} (measurement range: 0.002–0.042 mg m^{-3} for 120 L of air sample). Three series of calibration solutions were prepared with increasing concentrations of AZOB in MeOH. Two chromatographic determinations were carried out for each concentration. Then the peak areas were read and the concentration dependence of the AZOB peak area was determined. Table 4 presents the parameters which characterize the calibration curves described by the y = bx + a equation, where y = detector response and x = target analyte concentration.

Table 4: Calibration parameters for three series of AZOB measurement

Parameter	Measurement series		
	I serie	II serie	III serie
Mean peak area for AZOB solution of 0.125 μg mL^{-1}	14.7	14.7	14.6
Mean peak area for AZOB solution of 0.250 μg mL^{-1}	29.3	29.8	29.6
Mean peak area for AZOB solution of 0.625 μg mL^{-1}	73.9	73.9	73.6
Mean peak area for AZOB solution of 1.25 μg mL^{-1}	147.6	148.9	149.3
Mean peak area for AZOB solution of 2.00 μg mL^{-1}	241.2	238.4	240.0
Mean peak area for AZOB solution of 2.50 μg mL^{-1}	297.3	296.6	296.8
Calibration curve y=bx+a	y = 119.68 x – 0.64	y = 118.89 x – 0.04	y = 119.35 x – 0.29
Correlation coefficient, r	0.9999	1	1
The average value of the calibration factor	118.6		
Standard deviation of the calibration factor	0.87		
Coefficient of variation of the calibration factor (%)	0.73		

A correlation coefficient (r) greater than 0.999 confirms linearity: the response of the DAD detector (at 316 nm) was linear at the selected concentration range.

Also, the test of significance, which compares the significance coefficient with the critical value ($t_{critical}$) of the Student's distribution (for a 95% confidence level), showed that the correlation of these variables is significant (the correlation coefficient differs significantly from zero).

Since the coefficients b and a are subject to uncertainty, their significance has been tested. The mean test score for slope (t_{score} = 136.4) was determined on the basis of the mean value of slope (b) and standard deviation (S_b) and compared with the critical values for the Student's t-distribution on n-2 degrees of freedom (f = 4) at a common level of significance α = 0.05 ($t_{critical}$ = 2.776). t_{score} being greater than $t_{critical}$ indicates that the slope factor was significant

It was found that the method had an acceptable sensitivity. Analogically, the significance of the y-intercept of the regression line (a) was determined. The t_{score} value of 0.695 was calculated on the basis of a and S_a values. Since $t_{score} < t_{critical}$ (2.776) the displacement coefficient was not significant.

The linear calibration curve for azobenzene is therefore presented as a formula y = (118.6 ± 2.4) x.

The slope of the calibration curve was used to estimate the detection limit of the method.

In order to assess the precision of calibration, working standards were prepared in three series of eight working solutions in the following concentrations: 0.125, 0.625 and 1.25 μg mL^{-1} of AZOB in methanol.

The standard deviation and coefficient of variation were calculated from the peak areas obtained on the chromatograms. The values characterizing the precision of calibration determinations, i.e. the coefficients of variation for subsequent concentration levels, were at a low level: 1.0%; 0.98%; 0.58%, respectively.

The minimum concentration of azobenzene that may be determined under the conditions of air sampling and determination described in the procedure is 0.002 mg m^{-3} (for 120 L of air sample). The limit of detection is 3.1 ng mL^{-1}, and the limit of quantification is 9.4 ng mL^{-1}. The expanded uncertainty of the method is 22% and is lower than the value of 30% (required by EN482 [27]).

CONCLUSIONS

As a result of the conducted research, a measurement method for the long-term personal monitoring of the concentration of azobenzene present in the workplace air was developed. Studies have confirmed that azobenzene in the air may occur in the form of aerosol and vapours. A cellulose filter and silica gel were selected for adsorption of azobenzene from the air. Specified chromatographic separation conditions allow the quantitative determination of azobenzene in the presence of other substances. Within the studied range (0.125–2.5 µg mL^{-1}), linear calibration curves were obtained. The determined validation parameters confirm that the application of the developed method will provide reliable results of the concentrations of carcinogenic azobenzene in air. The developed quantitative method for the determination of azobenzene concentrations in the air may be used in the workplace for periodic measurements in order to estimate occupational exposure and to control the effectiveness of actions aimed at risk reduction.

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