

DETERMINATION OF BENZENE IN AIR BY MICROCOLUMN ADSORPTION AND THERMAL DESORPTION IN GC INLET

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Abstract

The air sample is passed through the glass microcolumn filled with Tenax, which is then transferred into a modified GC injection port for thermal desorption and without cryofocussation analyzed. A linear working range for benzene, toluene, ethylbenzene and p-xylene at the amounts of 4-20 ng per microcolumn was established with correlation coefficients (r^2) within the range, 0.99896 – 0.99952. Limit of detection for benzene (analyzing 200 ml of air sample) lies under $3\mu\text{g}/\text{m}^3$. The method has been successfully applied for the determination of benzene in crossroad air.

Key words: benzene; headspace; solid phase microcolumn extraction; thermal desorption; air analysis

INTRODUCTION

Benzene has been shown to cause cancer in both animals and humans, and therefore is currently classified by the US Environmental Protection Agency (US EPA), the American Conference of Governmental Industrial Hygienists (ACGIH), and the International Agency for Research on Cancer (IARC) as a human carcinogen.

Motor vehicles are a significant source of air pollution emissions, including benzene. Benzene and other volatile organic compounds are substantial contributors to the formation of ozone and other photochemical oxidants^[1]. There is evidence that humans (specifically children) who live close to streets heavily used by motorists or near highways may be at risk of developing cancer, including leukaemia. It is accepted that benzene is a genotoxic carcinogen and that therefore no absolutely safe exposure level can be defined. Nevertheless, for practical purposes some countries (i. e. United Kingdom and Japan) use recommended air-quality control standard for benzene of 1 ppb annual average^[2, 3].

Numerous methods exist for detecting and measuring benzene in ambient air. Air samples for benzene analysis may be preconcentrated by passing the sample through a trap containing a solid adsorbent. Commonly used adsorbents are Tenax resins, silica gel, activated carbon, and carbonaceous polymeric compounds. Benzene in ambient air can be collected in stainless steels canisters or Tedlar bags and can be analysed with or without preconcentration. Preconcentration of benzene can be accomplished by direct on-column cryogenic trapping, or samples may be analyzed directly without preconcentration^[4, 5].

In this work for the analysis of benzene, toluene, ethylbenzene and p-xylene in air a microcolumn containing Tenax was used. The desorption of the analytes was accomplished directly in a modified GC inlet^[6, 7] instead of utilizing a thermal desorption unit.

EXPERIMENTAL

Reagents

HPLC grade standards of benzene and toluene were obtained from Aldrich (Milwaukee, Wisconsin, USA); analytical-reagent grade ethylbenzene was from Merck (Schuchardt, Germany) and p-xylene in neat form was purchased from Dr. Ehrenstorfer (Augsburg, Germany). From these standard materials was prepared by diluting in n-pentane (Uvasol, Merck, Darmstadt, Germany) a stock solution of a mixture of analytes each in concentration of 0.1 mg/ml. From stock standard solutions calibration solutions in n-pentane were prepared with concentrations of each analyte in the range from 10 to 50 µg/ml.

For the preparation of the gaseous standard mixtures previously a liquid mixture of four neat compounds in the ratio 1 : 1 : 1 : 1 was prepared in a vial. From this liquid mixture, 1 µl aliquot was transferred on the strip of aluminium foil, which was inserted in 1-liter flask with ground-glass stopper. The flask was shaken by hand for 1 minute and allowed to equilibrate for 30 minutes. The concentration of each analyte in this high-level gaseous mixture was at 220 µg/l. The glass stopper was replaced by aluminium foil, which was pierced with a narrow glass tube mounted on the gas-tight syringe (with the aid of a short piece of flexible tubing). A volume of 10 ml of stock gaseous mixture was transferred by means of 20-ml all-glass syringe (Poulten & Graf, Wertheim, Germany) into another empty 1-liter flask. The flask was stoppered, shaken, and allowed to equilibrate in the same way as previous one. In the obtained low-level gaseous standard mixture the concentration of each analyte was at 2.2 µg/l.

Apparatus

Analyses were performed using a Varian Model 3400 gas chromatograph (Zug, Switzerland) equipped with a modified split-splitless inlet and flame ionization detector. The split-splitless inlet was modified so that it was possible to put a glass microcolumn in and out of the chamber, where a liner was previously placed^[6,7]. The microcolumn was packed with 100 mg of 60-80 mesh Tenax-TA (Alltech, Deerfield, IL, USA) with a length of filling 55 mm. The inside of the exit end of the microcolumn was conically broadened (Just as in glass press-fit connectors) to make a gas-tight connection when it was put on the end of a capillary column inserted into the inlet chamber. A carrier gas line system including gas regulator with pressure gauge was rebuilt so that the carrier gas was passing through the microcolumn connected to the capillary column and it was possible to manually regulate the gas pressure in the inlet. For the separation of analytes a 60 m × 0.53 mm I.D. fused-silica Stabilwax capillary column with a film thickness of 1.0 µm (Restek, Bellefonte, PA, USA) was used. Nitrogen (purity: 5.5, SIAD TP, Braňany u Mostu, Czech Republic) was used as the carrier and make-up gas. The FID and inlet were both held at 250 °C. The GC column was temperature programmed from 35°C (2 min) to 100 °C at 10°C/min and then to 200°C (2 min) at 20°C/min.

Procedure

The calibration lines and other performance characteristics of the developed method for the determination of investigated analytes in air were obtained by direct injection of calibration solutions on the Tenax filling of microcolumn using 1-µl injection syringe (Hamilton, Series 7 000, Reno, NV, USA).

For the study of adsorption and desorption process on the microcolumn a low-level gaseous standard mixture was used. Aliquots of 2 and 4 ml of gaseous mixture were withdrawn by means of 2-ml gas-tight syringe (JENA-THERM, GDR) from the flask capped with aluminium foil and passed through the microcolumn packed with adsorbent.

For the study of breakthrough curve of benzene on the microcolumn and for the sampling of crossroad air an AirChek 2000 sampling pump (SKC Inc., Eighty Four, PA, USA) was utilized. High-level gaseous standard mixture and air samples were passed through the microcolumn at a flow rate of 40 ml/min.

In all cases the loaded microcolumn was transferred into a GC injection port, in which the gas pressure was decreased to 1 psi. The trapped analytes were desorbed by heating of the microcolumn at 250 °C for 2 minutes, then the carrier gas pressure was increased to 10 psi and the temperature programme was started. A computer equipped with Varian GC Star Workstation (Serial Number B 20841035, Varian Associates, 1989-1992) was used for data acquisition.

RESULTS AND DISCUSSION

The optimization of the method for the determination of benzene, toluene, ethylbenzene and p-xylene in air resulted in setting chromatographic conditions and development of procedure described in previous sections. Recovery of the analytes from loaded microcolumn was investigated depending on temperature, time and applied pressure of carrier gas. The best recoveries were achieved at the desorption temperature of 250 °C, which is for Tenax the maximum allowable temperature. The time dependence of the recovery of analytes (expressed as chromatographic peak area) from the microcolumn loaded with 4 ml aliquots of low-level gaseous mixture (with concentration of analytes of 2.2 µg/l) indicates that for all the selected aromatic hydrocarbons the sufficient desorption time is 1-2 minutes (Table I).

Table I Desorption time dependence of chromatographic peak area (counts) of selected aromatic hydrocarbons

Compound	Desorption time			
	1 min	2 min	4 min	7 min
Benzene	7027	7296	6238	6722
Toluene	6415	6617	5730	6127
Ethylbenzene	9509	9793	8828	9164
p-Xylene	8198	8772	7091	7676

During the desorption step, because of obtaining narrow analyte bands introduced into the chromatographic column, the applied pressure of carrier gas passing through the microcolumn was decreased to a minimum value of 1 psi.

When establishing the performance characteristics of the method developed, it was considered a well-known fact that with the decrease of the concentration of analytes in gaseous sample unfavourable side effects of the material of the container wall can occur. For instance in case of a glass container Si-OH groups present on the wall surface can interact with the analytes just like the case with silica gel. At extremely low concentrations of analytes, therefore, the time dependent decrease of analyte concentration in gaseous phase can be observed. This results in non-linear calibration lines and in poor repeatability of analysis of gaseous mixtures at levels of analytes under 1 µg/l. This was the reason for direct dosing of analytes on microcolumn in the form of liquid – as a n-pentane solution.

The standard calibration lines of the area versus the concentration of each analyte in adsorbent packing of microcolumn were plotted for the amounts of analytes ranging from 4 to 20 ng per microcolumn. In Fig. 1 an example of calibration line for benzene is illustrated.

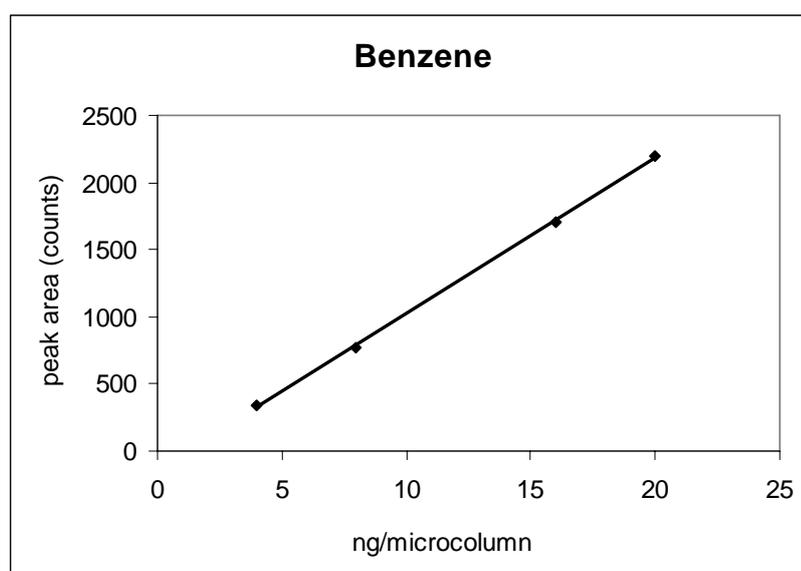


Figure 1. Calibration line for benzene.

For the selected concentration range good linearity was achieved for all the investigated analytes and the obtained correlation coefficients (r^2) were 0.99896-0.99952 (Table II).

In Table II are also listed other performance characteristics of the developed method. Limits of detection (LOD) and quantification (LOQ) were calculated from reliability bands using Adstat Calibration Program, version 1.20 (TriloByte, Czech Republic, 1989-1991) and show good sensitivity.

Table II Linearity, limits of detection, limits of quantification and repeatability for selected aromatic hydrocarbons from direct dosing of n-pentane solution of analytes on microcolumn

Compound	r^2	LOD [ng]	LOQ [ng]	s_r % (n=6)	
				4 ng	8 ng
Benzene	0.99952	0.6	3.8	1.35	1.56
Toluene	0.99896	0.8	4.8	1.06	1.51
Ethylbenzene	0.99921	0.7	4.2	0.77	2.24
p-Xylene	0.99910	0.8	4.6	1.61	2.32

The repeatability of the method was investigated by direct injection of n-pentane solution of analytes on adsorbent (at 4 and 8 ng of analytes per microcolumn) and also by passing 2 ml aliquots of low-level gaseous mixture through the adsorbent packing of microcolumn (Table III).

Table III Statistical evaluation of the following 4 analyses of low-level gaseous standard mixture

Compound	Chromatographic peak area				Average	s	s_r %
Benzene	3998	4020	4165	4062	4061	74.1	1.82
Toluene	4350	4338	4505	4479	4418	86.2	1.95
Ethylbenzene	4361	4325	4496	4515	4424	95.3	2.15
p-Xylene	3970	3944	4106	4125	4036	92.5	2.29
Sum	16679	16627	17272	17181	16939	348.1	2.06

s – standard deviation, s_r – relative standard deviation

The results obtained in Table II and III show very good repeatability of desorption of analytes applied on the microcolumn in the form of liquid as good as repeatability of sorption and desorption in case of application of gaseous mixture. In both cases the relative standard deviations (s_r) were about 2 %.

The limit of detection of the method for the analysis of gaseous samples is also given by the breakthrough volume of the analyte for the microcolumn packed with certain amount of adsorbent. Analysing the model gaseous samples, volume dependence (passed through the microcolumn) of the chromatographic peak area was studied for benzene. In Fig. 2 the plot from measured values that also represents the breakthrough curve is shown. From this curve it is evident that breakthrough volume of benzene is about 200 ml, which corresponds with the value of limit of detection of $3 \mu\text{g}/\text{m}^3$ for the gaseous samples analysis.

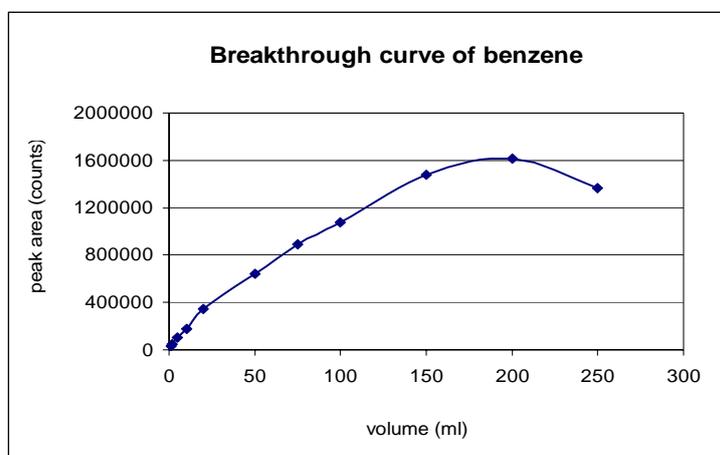


Figure 2. Model gaseous sample volume dependence of chromatographic peak area of benzene at level of $220 \mu\text{g}/\text{l}$.

In Fig. 3 an example of a chromatogram from the analysis of a real air sample is shown. The sample of 200 ml of air from crossroad in Bratislava was preconcentrated on the microcolumn connected to Air Check 2000 sampling pump and analysed by the developed method. The results gave $4.5 \mu\text{g}/\text{m}^3$ of benzene, $9.8 \mu\text{g}/\text{m}^3$ of toluene, $2.4 \mu\text{g}/\text{m}^3$ of ethylbenzene and $1.7 \mu\text{g}/\text{m}^3$ of p-xylene, respectively. For quantification, the calibration lines method with direct dosing of analytes on microcolumn was chosen.

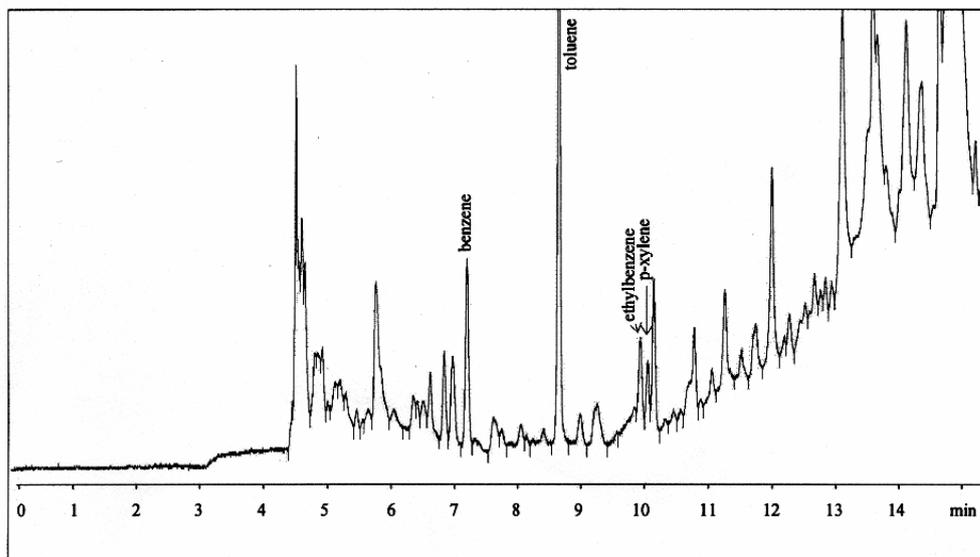


Figure 3. Chromatogram from the analysis of 200 ml air sample from town crossroad.

CONCLUSION

The method developed combines solid phase microcolumn concentration of organic compounds from gaseous samples with the following thermal desorption and analysis in gas chromatograph facilitates relatively simple and inexpensive determination of benzene and other aromatic hydrocarbons in the air. The obtained sensitivity, linearity and repeatability indicate that the method is reliable and enables determination of benzene in air under the regulatory limit of Slovak Republic^[8], which is $5 \mu\text{g}/\text{m}^3$.

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