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Gas Chromatographic Determination of Styrene in Ambient Air and Emissions

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The method of styrene determination in ambient air and source emissions is described. Styrene undergoes sorption on activated charcoal. Desorption with carbon disulphide is associated with free radical polymerization of styrene which, at low styrene concentrations, results in decreased recovery burdened with large experimental scatter and excessive variability with the lapse of extraction time. Polymerization of styrene is prevented by fortification of carbon disulphide with diethylhydroxylamine. Quantitative analysis is carried out by gas chromatography. The limit of determination is 0.5 μg m^{-3} and 3 μg m^{-3} for capillary and packed columns, respectively.

Praca zawiera opis metody oznaczania styrenu w powietrzu atmosferycznym i w emisji. Styren jest sorbowany na węglu aktywnym. Podczas desorpcji dwusiarczkiem węgla dochodzi do polimeryzacji wolnorodnikowej styrenu; obniża to współczynnik desorpcji, powoduje zwiększony rozrzut jego wartości i zmienność w czasie, tym uciążliwsze, im mniejsze stężenie styrenu. Polimeryzacji zapobiega dodatek dwuetylohydroksyloaminy. Analiza ilościowa metodą chromatografii gazowej pozwala uzyskać próg oznaczalności 0,5 μg m^{-3}, jeśli użyć kolumn kapilarnych, i 3 mg m^{-3} – jeśli pakowanych.

Styrene, vinyl benzene or phenyl ethylene, finds many uses in chemical industry. It is used in the manufacture of polystyrene plastics, protective coatings, styrenated polyesters, copolymer resins of which the most important is styrene-butadiene rubber, and as a chemical intermediate. Although styrene is very slightly soluble in water and has a low vapour pressure of 6.1 mm Hg at 25°C, it has been detected in both ambient air (0.1–100 μg m^{-3}) and finished tap water in many industrial countries

[1–3]. The concentration of the compound at workplaces may exceed 1000 mg m^{-3}. Styrene contributes about 0.75% to all hydrocarbons present in automobile exhaust gases [4]. Reliable data on the environmental fate and distribution of styrene are not available. However, various media are expected to contribute to human exposure; the contribution from air is estimated to be about 50% [5].

There is some albeit inconclusive evidence for an association between styrene exposure and increased risk of lymphatic tumors. The best-documented form of systemic toxicity involves the central nervous system; other adverse effects attributable to styrene include neuropathy, abnormal pulmonary function, and alterations in liver functions. Upper respiratory tract irritation occurs in humans at exposures as low as 100 ppm, and eye irritation at even lower concentrations of 20-50 ppm. An odour threshold is 0.32 ppm [5]. The permissible level for 30 min exposure in Poland (PL_{30}) is fixed at 20 μg m^{-3} for the general area of the country and at 10 μg m^{-3} for the areas of special protection. The occupational threshold limit value for styrene exposure in the United States is fixed at 50 ppm (215 mg m^{-3}) time-weighted average, while ambient air limit goal is imposed at 6.2 ppb (26.3 μg m^{-3}) based on carcinogenicity.

Different analytical techniques have been used to determine styrene: infrared absorption spectroscopy, polarography and colorimetry. Neither is specific. Gas chromatography seems to offer more advantages. Both styrene and its brominated derivative [1] have been sought. The latter method involves the use of an electron capture detector and is very sensitive. It would be very cumbersome, however, under field conditions.

Direct sampling of air into gas chromatograph is feasible at styrene concentration lying above the 0.5–5 mg m^{-3} threshold. Ambient air environmental samples involve as a rule much lower concentrations, and one or another enrichment procedure becomes mandatory. Absorption in liquids such as ethanol [6] has in more recent literature been superseded by solid sorbents, mostly activated charcoal [7,8] and porous polymers [9]; both dynamic and passive approaches were reported [10–15]. In some cases, the diffusive passive samplers appeared to perform even better with respect to precision than the charcoal tubes but only at high occupational concentrations [14,15]. Generally diffusive sampling is sensitive to aerosols, suffers from insufficient air movement around samplers (starvation effect), and from loss of material by back diffusion. The U.S. National Institute for Occupational Safety and Health recommends only the active sampling for styrene determination [16]. Desorption from the charcoal tube can be either thermal or involve the use of proper solvents. The former technique is simple and very sensitive. However, costly auxiliary equipment is needed and there is a risk of partial styrene polymerization at elevated temperature [9,17]. Carbon disulphide is very effective as a desorbent from the activated charcoal and does not interfere much with the performance of a flame ionization detector. Desorption coefficient as high as 98% has been reported [12], although 83–85% seems to be more realistic [18]. Simultaneous exposure to acetone and dichloromethane affected neither the desorption efficiency nor the uptake rate of styrene by the charcoal [18]. Unfortunately, desorption coefficient is very sensitive to analytical conditions and exhibits pronounced batch-to-batch variability [7,17].

Other solvents such as dimethylformamide [7] or cyclohexanone [19] are not significant improvement over CS_2.

In this work we have opted for sorption on activated charcoal and desorption with CS_2. The problems to be solved are: 1) how to obtain high and reproducible desorption coefficient, and 2) how to avoid interferences with gas chromatographic analyses without compromising simplicity and low cost of analyses.

EXPERIMENTAL

Chromatography

The HP-5890 (Hewlett-Packard) and the GC-14A (Shimadzu) gas chromatographs, both equipped with flame ionization detectors, computer acquisition and processing systems and split/splitless injection port units were used for capillary columns while the GCHF 18.3 chromatograph, also equipped with computer assisted acquisition of data, was used for packed columns.

Chemicals

Analytical reagent grade carbon disulfide used for extraction was further purified to remove any traces of interfering hydrocarbons.

Activated charcoal, grain size 0.4–0.8 mm, was obtained from ZSDD Hajnówka. Treatment involved heating under vacuum for 8–12 h at a temperature of 250°C.

Diethylhydroxylamine was analytical reagent grade; styrene was stabilized by addition of hydroquinone.

RESULTS AND DISCUSSION

Preliminary experiments

Effectiveness of styrene desorption with carbon disulphide was found to deteriorate with the lapse of extraction time. At low mass of styrene (1 μl of styrene dissolved in CS_2 to a concentration of 1 mg ml^{-1}), recovery amounted to *ca.* 65% after 5–10 min, decreased to 45% after 1 h and to about 40% after 2 h. Precision of these measurements was low. A 10-fold increase in styrene concentrations alleviated the problem; recovery increased up to about 80%. A decrease with increasing extraction time was slight, if any; within the limits of experimental error.

The effects of a number of additives to carbon disulphide were examined. Diethylhydroxylamine, DEHA, which is a well known free radical scavenger, yielded the best results. DEHA introduced at a concentration of 0.05–0.1 mg ml^{-1} in CS_2 increased styrene recovery, eliminated variability with the lapse of time, and decreased scatter in experimental results. DEHA adsorbed on the charcoal surface prior to styrene addition was no less effective. Apparently, radical polymerization of styrene occurs in the absence of DEHA. As the effects are only observed at low concentrations, a small number of active centres and diffusion seem to be a limiting factor.

Sorption properties of activated charcoal

An assembly was designed to sample aliquots of either styrene or its solution into a stream of purified air with a microsyringe [20]. Styrene undergoes evaporation followed by sorption in a tube filled with the activated charcoal. The tubes were 8–10 cm long, 0.4 cm i.d.; 60 mg of charcoal was followed by a backup layer of 30 mg of charcoal. To establish the effect of styrene concentration on the recovery, the amount of styrene was varied over the range from 0.23 μg to 600 μg. About 80–100 l of air was drawn through the tube at a flow rate of 80–100 l h^{-1}. Carbon disulphide containing 0.1 mg ml^{-1} of DEHA was used for desorption. As small amount as possible of carbon disulphide should be used to avoid dilution. We found a volume of 1 ml to be convenient; should the analysed air be very dry, this volume can be diminished to 0.5 ml. In separate experiments the effects of humidity were examined by passing the air through the bubbler filled with water. Also the effects of sunlight exposure and prolonged storage of the styrene samples absorbed on the charcoal were investigated. The most representative results are shown in Table 1.

Table 1. Effects of styrene concentration, air humidity, sunlight exposure and time of prolonged storage on the extraction recovery of styrene from 60 mg of activated charcoal. The uncertainties are 1 σ

Conditions	Number of measurements	Desorption coefficient %
1 μg styrene; 20% humidity	6	83.6±5.7
10 μg styrene; 100% humidity	3	83.0±3.7
1 μg styrene; 100% humidity	8	80.3±3.3
0.23 μg styrene; 100% humidity	8	68.8±6.1
1 μg styrene; 60% humidity; sunlight exposure	6	74.1±4.1
1 μg styrene; 100% humidity; 1-day storage	5	65.0±6.6
1 μg styrene; 100% humidity; 5-days storage	5	68.9±4.3

Inspection of Table 1 reveals that while increase in air humidity is not harmful, the prolonged storage and decrease in styrene concentration are. The 1 μg styrene sample corresponds to PL_{30} for the general area of Poland at 50 l of air, and to PL_{30} for the areas of special protection at 100 l of air. Assuming that storage of the sample up to a few days is unavoidable, conservative estimate gives 67±7% for the value of desorption coefficient. Higher values, up to 98% can be found in literature, but for workplace air analysis at concentrations larger by 1 to 3 orders of magnitude [12,18].

Gas chromatographic analysis

Since a great variety of aromatic and aliphatic hydrocarbons is present in urban areas, the column to be used for styrene analysis should not suffer from interferences. Especially good resolution of styrene from hydrocarbons present in gasoline and Diesel fuel is required, since these hydrocarbons are the most common pollutants. We have examined quite a number of both capillary and packed columns. A Supelcowax-10 capillary column, 60 m×0.32 mm ID, film thickness 0.5 µm, seems to be the best choice; no other compound appears at the location of styrene as can be seen in Figs.1 and 2. Also a weakly polar SPB-5 capillary column, 25 m×0.32 mm ID, 1.5 µm film thickness, is not much inferior. Both the columns offer very good resolution of styrene from gasoline hydrocarbons and sufficient resolution from *o*-xylene. From among the packed columns, a strongly polar 7.5% OV-275 on Chromosorb W-HP, 80/100 mesh, 2.7 m×4 mm ID, releases styrene long after C_{12} paraffins; resolution

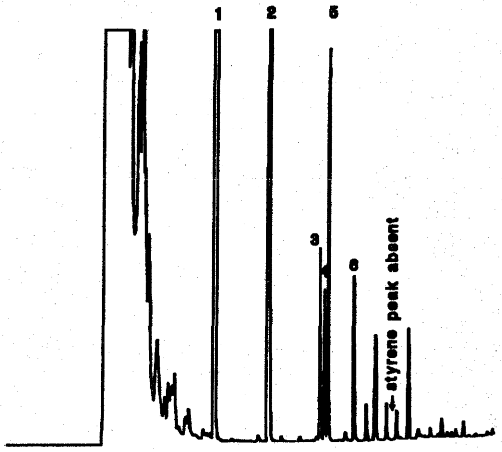

Figure 1. Chromatogram showing relative position of styrene and hydrocarbons from Gasoline-94 elution peaks on a 60 m Supelcowax-10 column: 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – *p*-xylene; 5 – *m*-xylene; 6 – *o*-xylene; styrene is absent but interference would not impede its determination

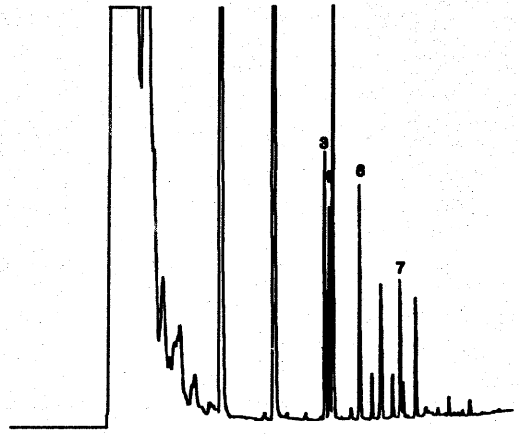

Figure 2. Chromatogram of Gasoline-94 with admixture of styrene on a 60 m Supelcowax-10 column: 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – *p*-xylene; 5 – *m*-xylene; 6 – *o*-xylene; 7 – styrene

from aromatics is satisfactory. A 3% OV-17 on Chromosorb W-HP, 80/100 mesh, 2.7 m×4 mm ID, is not as reliable as the previous column but can be accepted at higher styrene concentrations or at lower concentrations of interfering pollutants. The analytical conditions considered to be the best are listed below:

	Capillary columns	
Flame ionization detector		
Stationary phase	Supelcowax-10	SPB-5
Carrier gas helium	3 ml min^{-1}	3 ml min^{-1}
Split ratio	1/10	1/10
Column temperature		
initial	50°C for 2 min	30°C for 8 min
increase rate	10°C min^{-1}	10°C min^{-1}
final	250°C for 10 min	200°C for 10 min
Injector temperature	200°C	200°C
Detector temperature	280°C	280°C
Sample volume 1 μl		

	Packed columns	
Flame ionization detector		
Stationary phase	OV-275	OV-17
Carrier gas nitrogen	30 ml min^{-1}	30 ml min^{-1}
Column temperature	90°C	60°C
Injector temperature	200°C	200°C
Detector temperature	280°C	280°C
Sample volume 5 μl		

The limits of detection and determination can be established following accepted practice of using twice and 5 times the peak-to-peak noise level, respectively. The values listed in Table 2 refer to 100 l of air passed through the charcoal and to 1 ml of CS_2 used for desorption on the assumption of 70% recovery.

Table 2. The limits of detection and determination for styrene in air and in solution

Column	Solution μg ml^{-1}	Air μg m^{-3}
Capillary columns		
Limit of detection	0.014	0.2
Limit of determination	0.035	0.5
Packed columns		
Limit of detection	0.08	1.1
Limit of determination	0.20	3.0

Estimation of errors

Systematic and random errors contribute to the total error of quantitative analysis. The former ones can be assessed on the basis of known capacity tolerances of microsyringes, volumetric bulbs and pipets taking into account parallax effects. The latter ones refer to the determination of desorption coefficient and chromatographic analysis and were estimated on the basis of standard deviation at the 95% confidence interval. The overall error of styrene determination is evaluated as not exceeding 15%.

Field experiments

To test the influence of the field conditions a sampling stand was located in downtown Warsaw near a busy highway and in the vicinity of the rubber Stomil factory which manufactures foamed styrene-butadiene copolymers. The results shown in Table 3 and Figs. 3 and 4 indicate that determination of styrene at concentration levels below PL_{30} is feasible provided that capillary columns are used.

Table 3. Field experiments on styrene determination. Results are averages from three parallel measurements

Sampling location	Styrene concentration, $\mu g\ m^{-3}$	
	Supelcowax-10 Capillary column	OV-275 Packed column
Downtown Warsaw	0.3	below detection limit
Downtown Warsaw	0.4	below detection limit
Outside Stomil factory 100 m from the stack	0.6	below detection limit

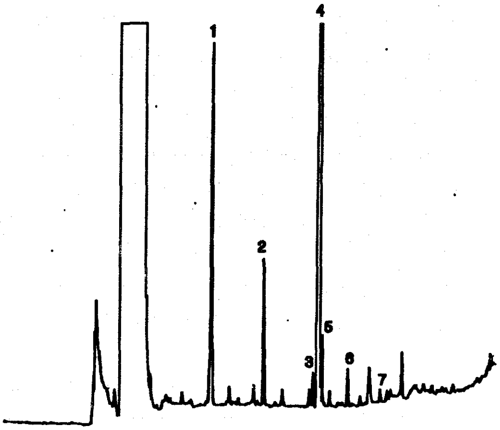

Figure 3. Chromatogram of downtown Warsaw air on a 60 m Supelcowax-10 column: 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – *p*-xylene (overestimated as a result of an artefact in analyses); 5 – *m*-xylene; 6 – *o*-xylene; 7 – styrene. Styrene comes from automobile exhaust gases; its identity was confirmed by mass spectrometry

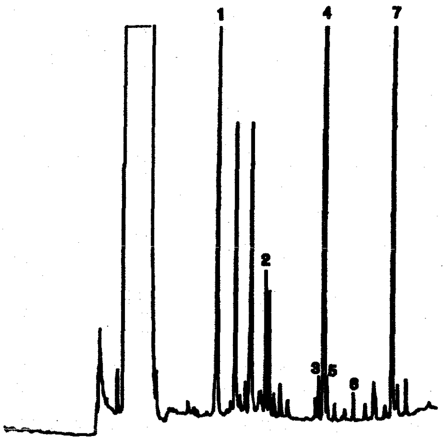

Figure 4. Chromatogram of air sampled 20 m from the ventilation outlet of Stomil factory on a 60 m Supelcowax-10 column: 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – *p*-xylene (overestimated as a result of an artefact in analyses); 5 – *m*-xylene; 6 – *o*-xylene; 7 – styrene

Styrene determination in emissions

Since styrene concentration in source emissions may be very high, losses resulting from polymerization pose not so acute a problem. Temperature of waste gases may surpass ambient temperature considerably, however. Also the saturation effects and concomitant breakthrough may impose limitations on the volume of air to be sampled. To estimate sorption efficiency under such conditions, experiments were performed at elevated temperatures, 50 and 80°C, and 100% humidity. The mass of styrene up to 900 μg per 100 mg of activated charcoal from 20–40 l of air drawn at a flow rate of 40–80 l h^{-1} was found not to exceed the capacity of the first layer of charcoal. Only at much higher styrene concentrations did breakthrough occur. Sampling of 100 l of air from the stack of Stomil factory resulted in absorption of as much as 1–5 mg of styrene in 100 mg of charcoal. The backup layer was found to contain 2-28% of styrene with respect to the first layer under such severe conditions. It can be concluded that the mass of absorbed styrene should not exceed 1% with respect to the mass of charcoal.

To estimate extraction recovery, the series of experiments analogous to those described in Table 1 was performed; only was styrene concentration enhanced considerably. The mass of activated charcoal in a tube was increased to 100 mg in the first layer and to 50 mg in the backup layer. The results are listed in Table 4. It is seen that the desorption coefficient is largely unaffected. The differences are within the limits of experimental error. A mean value of 81.5±5% can be recommended for the determination of emissions.

Table 4. Effects of styrene concentration, air humidity and time of prolonged storage on the extraction recovery of styrene from 100 mg of activated charcoal at ambient and elevated temperatures. The uncertainties are 1 σ

Conditions	Number of measurements	Desorption coefficient %
4 µg styrene	5	80.3±3.4
0.9 mg styrene	5	85.1±3.6
0.9 mg styrene; 100% humidity; 80°C	3	81.4±1.1
0.9 mg styrene; 100% humidity; 50°C	4	83.5±1.0
44 µg styrene; 100% humidity; 4-days storage	4	78.4±1.7

Selection of gas chromatographic conditions that would suit samples of different origin is not possible. Every technological process is unique. Preliminary investigations are necessary to establish the composition of waste gases; also the danger of side reactions should not be overlooked. Gaseous matrices may frequently be so complicated, as to make the use of GC/MS techniques and capillary columns of very high resolution indispensable.

Conclusions

As far as analysis of ambient air is concerned an average value of 67±10% can be recommended for the coefficient of desorption and for routine use. The accuracy of this determination can be improved, were such need to arise, by making more replicate measurements under specific analytical conditions used.

Concentration of styrene in emissions is usually high, and a value for the coefficient of desorption is enhanced to 81.5±5%. The mass of styrene sorbed on 100 mg of charcoal should not exceed 1 mg, *i.e.* 1% with respect to the mass of charcoal. Otherwise breakthrough may occur, especially at large humidity and elevated temperature of waste gases.

The total error of styrene determination falls over the range 10–15%. Control actions can readily be implemented on the basis of such a value.

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