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Evaluation of styrene in air by thermal desorption–gas chromatography

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Abstract

A method to quantify the environmental styrene of occupationally exposed workers has been established. A diffusive sampler, that can be analysed by using thermal desorption–gas chromatography, was used to adsorb styrene from the ambient environment. A laboratory study was carried out to evaluate the performance of the sampler and to determine the styrene uptake rate, following the criteria adopted in European Standard 848. Finally, the proposed method has been checked under real conditions by evaluating styrene levels from an exposed population. There were no significant differences with the results obtained by other sampling methods. © 1997 Elsevier Science B.V.

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1. Introduction

Styrene is a widely used compound in several industrial activities. The most extensive exposures to styrene occur in plants manufacturing glass-reinforced polyester products. Commercial unsaturated polyester resins are composed of 40% styrene monomer. As much as 10% of the styrene evaporates into the workplace air during manual laminating or spraying [1,2] and enters the body mainly through the lungs [3].

Exposure to styrene has been associated with effects on the nervous system, irritation of mucous membranes and various other health problems, but more worrying is its potential carcinogenicity [4–6]. Epidemiological studies do not provide firm evidence concerning the carcinogenicity of styrene [7]. However, a potential risk is suggested from recent studies

on the association between occupational exposure to styrene and cytogenetic chromosome damage [8,9].

The International Agency for Research on Cancer, that classifies styrene as a possible carcinogen [7], has been carrying out extensive environmental and biological monitoring. The American Conference of Governmental Industrial Hygienist (ACGIH) proposed an environmental limit value for styrene of 213 mg/m³ for 1995–1996 and a modification of this value to 85 mg/m³ has been proposed [10], based on the hypothesis that the current limit is not protective enough. Styrene is also an ubiquitous air pollutant present both in indoor and outdoor air [11]. It is therefore very important to be able to survey an exposed population, either by air monitoring or biological monitoring.

Use of activated charcoal tube is the traditional way of evaluating the exposure to volatile organic compounds. This method of sampling, called active or dynamic, is based on drawing air by means a portable pump through a tube containing activated

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charcoal, which retains the pollutant. Diffusive monitoring is becoming one of the most important sampling techniques to measure volatile organic compounds in industrial workplaces and indoor air atmospheres. It is based on the diffusion of the pollutant across a convection-free air zone within the sampler to an adequate sorbent.

In most diffusive samplers, the adsorbed vapour is desorbed with a solvent and quantitatively measured by gas chromatography (GC). Another possibility is the use of thermal desorption connected to the gas chromatograph, that offers the advantage of higher sensitivity since the whole sample is available for analysis.

Due to its advantages, there has been great interest in the use of tube-type samplers for thermal desorption (ATD50 diffusive sampler) for the evaluation of workplace environments. The environmental concentration of a contaminant can be calculated from the sampler collection time and the recovered mass on the sampler, if its diffusive uptake rate is known. Since their appearance, lists of diffusive uptake rate values have been available for many contaminants, using mainly Tenax as adsorbent. In many cases uptake rates have been obtained using empirical relationships. However for the same adsorbent–contaminant system there is a great variability of uptake rate values. For example, for Tenax and styrene, values ranged from 2.0 to 2.95 ng/ppm min have been reported [12–15].

The objectives of this work were, first, to establish a method using thermal desorption–gas chromatography in order to quantify the concentration of styrene in ambient air, and to assess the sampler performance against criteria specified in European Standard 838 [16]. And secondly to evaluate the environmental levels of styrene by means of personal sampling from subjects occupationally exposed. Finally, to compare the styrene levels obtained with the proposed method in this paper with those obtained both by an active sampling system and an another diffusive sampler.

2. Experimental

2.1. Thermal diffusive samplers

The thermal diffusive samplers used were the

standard stainless-steel tubes for an ATD50 thermal desorption system (Perkin-Elmer, Beaconsfield, UK) (89 mm×6.4 mm O.D.). The tubes were packed with 150 mg of Tenax TA (SKC, Valley View, PA, USA), selected following the procedure previously described [17]. Prior to use, and during storage, the tubes were protected with Swagelok storage caps; when used, a diffusion cap was fitted to allow controlled exposure to the environment.

2.2. Determination of diffusive uptake rate and performance of thermal diffusive sampler for styrene

The procedure for the determination of the effect of exposure concentration and time on sampler performance includes the exposure of at least six diffusive samplers in a calibration gas mixture of styrene according to the scheme shown in Table 1. This requires the generation of controlled atmospheres having different concentrations of the pollutant (21 and 364 mg/m³ were used for styrene).

Standard atmospheres of styrene vapour in air were dynamically generated using the syringe injection technique. Styrene 99.5% (Fluka, Buchs, Switzerland) was used. Fig. 1 illustrates the scheme of the system used. The atmospheres were checked by active samplers consisting of activated charcoal tubes connected to the atmosphere by means of a sampling pump. In all cases the concentration measured by the activated charcoal tubes agreed to the theoretical concentration calculated from airflow and syringe speed within 10% [16], so this value of the theoretical concentration can be considered as the true concentration of styrene in the test atmosphere. The coefficient of variation, as determined by on-line chromatography, was 4%.

The humidity of the atmosphere could be adjusted

Table 1
Scheme of the procedure to evaluate the effect of exposure concentration and time on sampler performance

| Concentration (ppm) | Sampling time (h) | | |
|---------------------|-------------------|---|---|
| | 0.5 | 4 | 8 |
| 0.1LV | X | | X |
| LV | | X | |
| 2LV | X | | X |

LV=Limit value, 50 ppm for styrene.

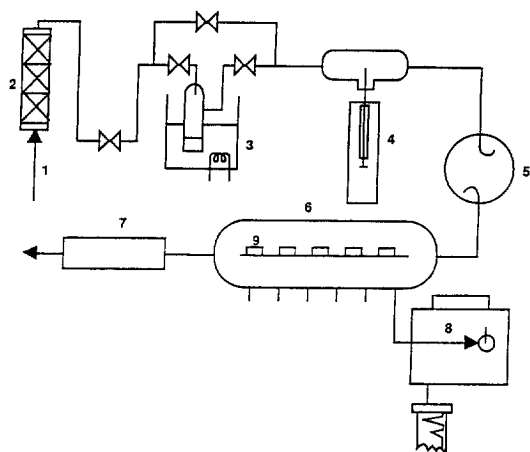


Fig. 1. Scheme of the system used to generate the controlled atmosphere of styrene. (1) Air intake; (2) filter; (3) humidifier; (4) automatic injector; (5) mixing chamber; (6) sampling chamber; (7) humidity sensor; (8) gas chromatograph; (9) diffusive samplers.

by introducing water bubblers into the incoming airflow. A temperature of 20–25°C, a relative humidity (RH) of 40–45% and a relative air speed on the surface of the diffusive monitors of 0.7–1 m/s was used in all these experiments.

Thermal desorption of the styrene collected was carried out in two stages with nitrogen as a carrier

gas (68.95 kPa), an oven temperature of 200°C, 10 min of desorption time, trap lower and upper temperatures of –30 and 300°C, respectively, and a transfer line temperature of 120°C. The GC analyses were performed with a fused-silica capillary column (25 m×0.2 mm I.D., free fatty acid phase 0.3 μm film thickness) (Hewlett-Packard, Palo Alto, CA, USA), using nitrogen at 68.95 kPa as carrier gas. The oven and detector temperatures were 120 and 200°C, respectively (Table 2). A gas chromatogram from a typical sample is shown in Fig. 2.

Diffusive uptake rates (U) were calculated for each one of the samplers, according to the following equation derived from Fick's law

$$U = \frac{m_d - m_b}{d\rho t} \quad (1)$$

where m_d is the mass of the analyte which is desorbed, in nanograms; m_b is the mass of the analyte which is desorbed from the blank sampler, in nanograms; d is the desorption efficiency, the ratio of the mass of analyte desorbed from the sampler to that applied; ρ is the atmosphere concentration, in milligrams per cubic metre and t is the exposure time in minutes.

A set of four experiments was carried out at two different styrene concentrations (21 and 365 mg/m³)

Table 2
Experimental conditions for desorption and gas chromatography

| Sampler | ATD 50 | 3M-3500 | SKC tube |
|---------------------------------|--|---|---|
| Adsorbent | Tenax TA | Activated carbon wafer | Coconut charcoal |
| Amount | 150 mg | Standard | 200/400 mg |
| U | 0.53 ml/min | 28.12 ml/min | 200 ml/min (flow-rate) |
| <i>Desorption conditions</i> | | | |
| Desorption | Thermal, two steps | Solvent | Solvent |
| Desorption coefficient | >0.95 | 0.90 | 0.87 |
| Desorption volume | – | 1.5 ml, S ₂ C | 3 ml, S ₂ C |
| Oven temperature | 200°C | – | – |
| Trap temperature | –30–300°C | – | – |
| <i>Chromatographic analysis</i> | | | |
| Apparatus | PE 8700 | HP 5890 | HP 5890 |
| Calibration | standard tubes spiked with solution of styrene in methanol | standard solutions of styrene in S ₂ C | standard solutions of styrene in S ₂ C |
| Carrier Gas | N ₂ | N ₂ | N ₂ |
| Column | Capillary, FFAP | Apiezon L | Apiezon L |
| Temperature | Isotherm, 120°C | 75–150°C, at 15°C/min | 75–150°C, at 15°C/min |
| Detector | FID | FID | FID |

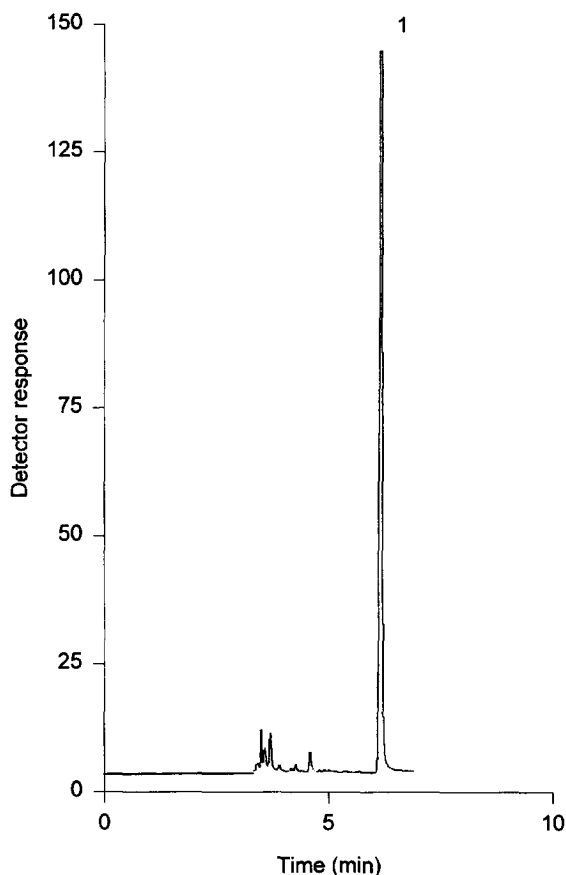


Fig. 2. Gas chromatogram obtained from the thermal desorption of a ATD50 diffusive sampler. (1) styrene.

and two exposure times (30 and 480 min), to determine the effect of humidity on the uptake rate.

2.3. Experimental studies in occupational exposures

The method was checked in subjects habitually exposed to styrene in the workplace. The environmental concentration of styrene in breathing zone air was measured using three different sampling devices: two diffusive samplers and an active one.

The diffusive samplers were: the ATD50 sampler, that has been already described (Section 2.1), and the 3M-3500 badges (3M, Madrid, Spain).

These samplers are designed to measure average concentrations over a measured time interval. It

requires no sampling pump because the contaminants enter into the monitor by diffusion, and are adsorbed on a wafer of activated charcoal inside the badge. The amount of contaminant adsorbed is dependent both on the exposure time and on the contaminant concentration present in the sampled environment. The mass of styrene, determined by GC analysis, is converted to environmental concentration by means of its specific sampling rate [18].

The active sampler consists of activated charcoal tubes connected to a sampling pump giving a 0.2 l/min flow-rate. The charcoal tubes used consist of a glass tube (110 mm long by 8 mm in diameter), packed with 20–40 mesh activated coconut charcoal, divided into two sections of 400 and 200 mg each (SKC, Valley View, PA, USA). The second section was used only as a check for possible saturation of the first one. The fused ends of the sorbent cartridge are broken before sampling and sealed at the end for transport and storage. In this case, ambient concentration is determined as a function of the mass of the styrene analysed and the volume of air passed through the tube.

The three samplers were attached all together to the clothes of the workers near to the breathing zone. During an approximately 4 h exposure period, the concentration of styrene was monitored continuously for each worker.

2.4. Instrumental analysis

ATD samplers were thermally desorbed and analysed as described in Section 2.2. The charcoal from the other samplers (either as wafer from the 3M-3500 sampler or as granular form from the tubes) were desorbed with carbon sulphide (Panreac, Barcelona, Spain) using *n*-propyl benzene as internal standard, and the resulting sample was injected in a gas chromatograph (Hewlett-Packard 5890, Palo Alto, CA, USA) with a flame ionisation detector. The operating conditions are summarised in Table 2.

3. Results and discussion

The concentration of the contaminant in the workplace ambient can be calculated from the sampler collecting time and the recovered mass on the

sampler, if the diffusive uptake rate (U) of the sampler is known. For a diffusive sampler to be appropriate, U must be constant for any combination of concentration and exposure time, since it is this parameter that allows the amount of contaminant collected by the sampler to be correlated with its ambient concentration. Therefore, it is necessary to determine U under controlled laboratory conditions, and the effect of changes in variables such as concentration of styrene in air, sampling time and moisture content of air have to be established.

The European Standard EN 838 [16] has been used to evaluate the performance of the sampler for styrene. Following this standard, the first stage was the determination of nominal diffusive rate. The exposure of six samplers in a 40.58 ppm atmosphere of styrene during an 8 h period has been used to determine this nominal uptake rate according to Eq. (1), resulting in a mean value of 2.29 ng/ppm min (Table 3).

The second stage was the determination of the effect of exposure concentration and time, consisting in the exposure of six diffusive samplers under the exposure combinations that can be seen in Table 1. The recommended procedure is to start with the four

Table 4
Analysis of experimental data

| Concentration (ppm) | Measured concentration/true value | | | |
|---------------------|-----------------------------------|------|---------|------|
| | 30 min | | 480 min | |
| 4.98 | 1.00 | 1.04 | 0.98 | 0.98 |
| | 0.99 | 0.96 | 0.96 | 1.01 |
| | 1.01 | 1.00 | 1.06 | 1.09 |
| 85.41 | 1.01 | 1.04 | 1.00 | 1.04 |
| | 1.01 | 0.99 | 0.97 | 1.00 |
| | 1.02 | 0.98 | 0.97 | 1.00 |

combination 0.1 limit value (LV), 2LV, 30 min and 8 h. And if the statistical analysis shows no significant effects the other combination may be omitted. For each exposure combination the measured concentration has to be calculated for each one of the six replicate samplers using the previously calculated U value of 2.29 ng/ppm min, in Eq. (1). The measured concentration obtained are summarised in Table 3. Each one of these values have been divided by the true value of the concentration (Table 4). On these results an analysis of variance has been carried out in order to determine whether there are any significant

Table 3
Experimental data for different combinations of exposure time and styrene concentration

| True concentration (ppm) | Time (min) | U (ng/ppm min) | | Measured concentration (ppm) | |
|--------------------------|------------------|------------------|------|------------------------------|-------|
| 40.58 ^a | 480 ^a | 2.30 | 2.28 | | |
| | | 2.29 | 2.29 | | |
| | | 2.28 | 2.28 | | |
| 4.98 | 30 | 2.29 | 2.39 | 4.98 | 5.20 |
| | | 2.27 | 2.20 | 4.94 | 4.78 |
| | | 2.30 | 2.29 | 5.01 | 4.98 |
| 4.96 | 480 | 2.25 | 2.25 | 4.87 | 4.87 |
| | | 2.21 | 2.31 | 4.79 | 5.02 |
| | | 2.43 | 2.50 | 5.28 | 5.42 |
| 85.41 | 30 | 2.32 | 2.37 | 86.48 | 88.64 |
| | | 2.31 | 2.27 | 86.39 | 84.78 |
| | | 2.34 | 2.24 | 87.50 | 83.74 |
| 83.21 | 480 | 2.29 | 2.37 | 88.39 | 86.20 |
| | | 2.23 | 2.30 | 80.93 | 83.49 |
| | | 2.21 | 2.29 | 80.42 | 83.09 |

^a Experimental conditions used to calculate nominal diffusive uptake rates.

Table 5
Analysis of experimental data

| Source of variation | Sum of squares | Degrees of freedom | Mean square | F-ratio | Sig. level |
|---|----------------------|--------------------|----------------------|---------|------------|
| Between concentrations | $1.04 \cdot 10^{-4}$ | 1 | $1.04 \cdot 10^{-4}$ | 0.094 | 0.766 NS |
| Between sampling times | $4.16 \cdot 10^{-6}$ | 1 | $4.16 \cdot 10^{-6}$ | 0.004 | 0.952 NS |
| Concentration \times time interaction | $9.38 \cdot 10^{-4}$ | 1 | $9.38 \cdot 10^{-4}$ | 0.847 | 0.378 NS |
| Errors | 0.0222 | 20 | 0.0011 | | |
| Total | 0.0232 | 23 | | | |

Analysis of variance.

NS=not significant at 5% level.

main effects or interactions with respect to the two factors, concentration and time. Table 5 shows that no factors are found to be significant at 5% level.

The relative overall uncertainty of the method, as calculated from the absolute bias plus two times the standard deviation [19], was 6.6%.

The influence of the humidity was analysed at two different concentrations and exposure times as can be seen in Table 6, that shows the values obtained by dividing the measured concentration in each one of the six samplers exposed by the true concentration. The analysis of variance (Table 7) show no signifi-

Table 6
Analysis of the effect of humidity

| Concentration/time (ppm)/min | Measured concentration/true value | | | |
|---------------------------------|-----------------------------------|------|----------|------|
| | HR = 40% | | HR = 92% | |
| 4.97/30 | 1.00 | 1.04 | 0.91 | 1.02 |
| | 0.99 | 0.96 | 1.01 | 0.99 |
| | 1.01 | 1.00 | 1.01 | 0.97 |
| 82.70/480 | 1.00 | 1.04 | 1.01 | 0.98 |
| | 0.97 | 1.00 | 1.03 | 1.01 |
| | 0.97 | 1.00 | 0.99 | 0.95 |

Table 7
Analysis of the effect of humidity

| Source of variation | Sum of squares | Degrees of freedom | Mean square | F-ratio | Sig. level |
|---|----------------------|--------------------|----------------------|---------|------------|
| Between concentrations | $6.67 \cdot 10^{-5}$ | 1 | $6.67 \cdot 10^{-5}$ | 0.070 | 0.797 NS |
| Between humidity | $4.16 \cdot 10^{-4}$ | 1 | $4.16 \cdot 10^{-4}$ | 0.438 | 0.523 NS |
| Concentration \times humidity interaction | $2.67 \cdot 10^{-4}$ | 1 | $2.67 \cdot 10^{-4}$ | 0.280 | 0.608 NS |
| Errors | 0.0190 | 20 | $9.52 \cdot 10^{-4}$ | | |
| Total | 0.0198 | 23 | | | |

Analysis of variance.

NS=not significant at 5% level.

cant variations between the different conditions of humidity and concentration assayed.

These findings show that the sampler—stainless-steel tube filled with 150 mg of Tenax for the ATD50—comply with the requirements specified by

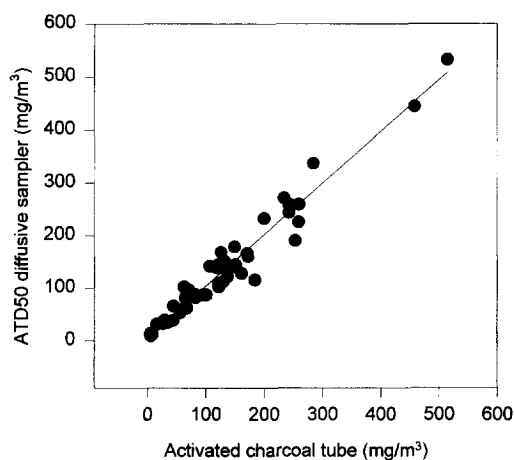


Fig. 3. Correlation between ambient styrene, expressed in mg/m^3 , determined by activated charcoal tubes and by ATD50 diffusive samplers. The samples were taken simultaneously on the same subject.

Table 8
Parameters and confidence limits of the regression analysis

| ATD50 vs. activated carbon | | | | | ATD50 vs. 3M-3500 | | | | |
|------------------------------|----------|----------------|----------------|--------|------------------------------|----------|----------------|----------------|--------|
| Parameter | Estimate | Standard error | 95% confidence | | Parameter | Estimate | Standard error | 95% confidence | |
| | | | Lower | Upper | | | | Lower | Upper |
| Intercept | 6.071 | 5.574 | -5.146 | 17.287 | Intercept | 7.884 | 4.080 | -0.282 | 16.050 |
| Slope | 0.975 | 0.033 | 0.909 | 1.042 | Slope | 0.946 | 0.028 | 0.889 | 1.003 |
| Standard error of estimation | 24.049 | | | | Standard error of estimation | 20.425 | | | |
| Correlation coefficient | 0.974 | | | | Correlation coefficient | 0.975 | | | |

Linear model: $y = a + bx$.

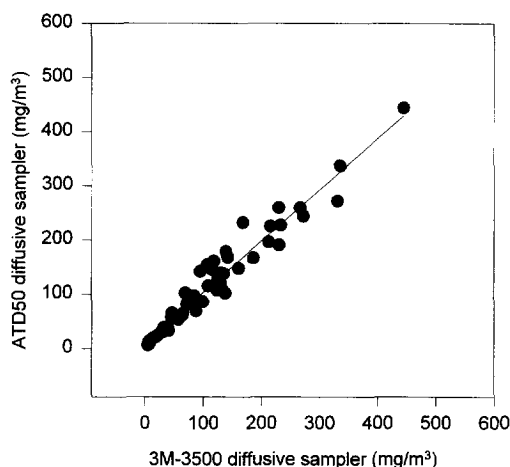


Fig. 4. Correlation between ambient styrene, expressed in mg/m^3 , determined by 3M-3500 and by ATD50 diffusive samplers. The samples were taken simultaneously on the same subject.

the EN838. In addition, the sampler was evaluated in field tests, as the ranges of environmental influences may exceed those in the laboratory tests. For personal sampling trials, seventy comparisons were made between the diffusive ATD50 sampler and the reference sampling system, which has been in one case a pump sorbent system and in another a 3M-3500 diffusive sampler. The three samplers were worn simultaneously, and as close together as possible, on one lapel of an occupationally exposed worker. Figs. 3 and 4 show the results between the methods compared by a linear regression analysis considering the reference method as independent variable. The estimated value of each coefficient in

the regression analysis, the correlation coefficient, the standard error of the estimations as well as the 95% confidence limits, are reported in Table 8. From these results it can be seen that both the slope and intercept for the two regression lines does not show significant differences from ideal values of 1 and 0, respectively, and therefore, there were no systematic differences between both series of results.

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