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Development of a thermal desorption-gas chromatography-mass spectrometry method for determination of styrene in air. Application to workplace air

V. Fernández-Villarrenaga Martín, P. López Mahía*, S. Muniategui Lorenzo and D. Prada Rodríguez.

Department of Analytical Chemistry. University of A Coruña. Campus da Zapateira s/n, E-15071 A Coruña. Spain

Abstract. Styrene is a compound commonly used in several industries, especially in those that manufacture glass-reinforced products. A thermal desorption-gas chromatography-mass spectrometry method for determination of styrene in industrial indoor and outdoor air is presented. Split valves of the thermal desorption unit were fixed at flows of 150 mL/min for indoor air and 5.3 mL/min for outdoor air, which regarded detection limits of 1.21 and 0.08 ng of adsorbed compound, respectively. The method was checked at a fibreglass boat manufacturing workshop. Samples were taken by diffusive and active sampling. Both methods were applied to outdoor samplings with similar results, while indoor samples were taken by diffusive sampling. Results confirm industrial activity as main styrene source in the workplace studied and its surrounding area.

Keywords. Diffusive sampling – thermal desorption – styrene: Tenax TA – occupational exposure – source emissions.

Introduction

Styrene or vinylbenzene (CAS 100-42-5) is a compound commonly found in the environment. It has mainly an anthropogenic origin but it can also arise from natural sources like the sap of some tree species.

This compound is widely used in several industrial activities, mainly in the production of rubbers and resins and the manufacturing of glass-reinforced polyester products. Commercial unsaturated polyester resins contain 40 % styrene monomer and nearly 10 % of it evaporates during laminating or spraying [1]. Other possible sources are adhesives, paints, varnishes [2], cigarette smoke and uncomplete combustion of gasoline in motor vehicles [3,4].

In the atmosphere hydroxyl radicals and tropospheric ozone are major reactants that rapidly degrade styrene. In the presence of nitrogen oxides and natural sunlight, styrene is oxidised, while nitrogen oxide is converted to nitrogen dioxide. Atmospheric half-life values ranging from 3.5 to 9 hours have been reported.

Exposure to styrene has short-term effects on human health as irritation of mucous membranes, dermatitis, headache, dizziness and fatigue. Some effects become evident at 43 mg/m^3 and all of them are immediate at 430 mg/m^3. At long term it can lead to damage of the nervous system and it is a potential carcinogen.

All these effects have led several organisations to establish environmental limit values for styrene in occupational ambient. Thus, the American Conference of Governmental Industrial Hygienists (ACGIH) [5] proposed a threshold limit value time weighed average (TLV-TWA) of 213 mg/m^3 for 1995-1996 and a reduction to 85 mg/m^3 was adopted in May 1997. In Spain styrene limit value was fixed at 85 mg/m^3 in 1999 [6].

Different ambient and occupational air sampling methods have been proposed. US EPA TO-14 Method for determination of airborne volatile organic compounds, and therefore styrene, is based on the collection of whole air samples in passivated stainless-steel canisters, followed by capillary column gas chromatography coupled to mass spectrometry detection or conventional multidetector techniques [7]. Active and diffusive sampling methods have been proposed for determination of styrene in workplace air. With the NIOSH 1501 Method, samples are collected onto sorbent tubes, packed with coconut shell charcoal, by means of a personal pump. Nowadays, diffusive monitoring has become one of the most important techniques in occupational monitoring since it avoids workers to change their working practices because they have to carry a sampling pump. The INSHT (Spanish National Institute of Work Safety and Hygiene) proposes the sampling of styrene with diffusive bag samplers that contain a wafer of activated charcoal inside [8]. In both methods analytes are desorbed with a

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*Correspondence and reprints.

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solvent, often carbon sulphide, and analysed by gas chromatography. An alternative is the thermal desorption method. This technique, used in the US EPA IP-1B Method [9], presents clear advantages, as the improvement of sensitivity, since the whole sample is available for analysis, and the reduction of sample manipulation, which minimises its contamination.

The objectives of this study are to establish a thermal desorption-gas chromatography-mass spectrometry method to determine styrene in air and evaluate styrene levels in a workplace and its surrounding area.

Experimental

Reagents

Styrene as stock solution (5000 µg/mL in methanol) and Tenax TA (60-80 mesh) were purchased from Supelco (Supelco, Bellefonte, PA, USA). Methanol HPLC grade (Romil, UK) was used to prepare working standards.

Sampling methods

Standard PE stainless-steel tubes (Perkin-Elmer, Norwalk, CT, USA) (88 mm × 6.5 mm O.D.) filled with 200 mg Tenax TA were used for both diffusive and active sampling techniques. This sorbent has a breakthrough volume of 1639 L/g for styrene. This volume was determined by means of the gas chromatographic method [10]. Aliquots of 5 µL of the vaporised compound were injected, at different temperatures (60-200 ºC), in a hand-made stainless steel-packed column (40 cm × 2 mm i.d.) filled with 200 mg Tenax TA. Carrier gas was nitrogen at a flow-rate of 20 mL/min. Breakthrough volume at 20 ºC was determined by extrapolation from the plot of logVg *vs.* 1/T, Vg being the specific retention volume, which is calculated by applying the following formula:

$$V_g = 273.15\ (t_R - t_0)\ F_c\ /\ T\ w \qquad (1)$$

where t_R is the retention time of the solute (min), t_0 is the gas hold up time (min), F_c is the volumetric gas flow-rate (mL/min), T is the absolute temperature (K) and w is the weight of the sorbent bed (*g*).

Tubes were conditioned by applying a helium flow (100 mL/min) at 300 ºC for 2 hours and then checked for suitable chromatographic blanks. Once conditioned and prior to use, tubes were stored into glass tubes with Teflon-lined caps to protect them from contamination.

Outdoor samples were collected, by active and diffusive sampling, at several distances from the workshop. Active sampling was performed with a BUCK IH manual pump (AP BUCK, Orlando, Florida, USA). Air was pumped for 20 min at a flow rate of 50 mL/min through two sampling tubes joined by a Swagelok union. For diffusive monitoring, PE stainless-steel tubes were adapted by replacing one of the PTFE storage caps with a diffusion cap to allow a controlled exposure to the environment.

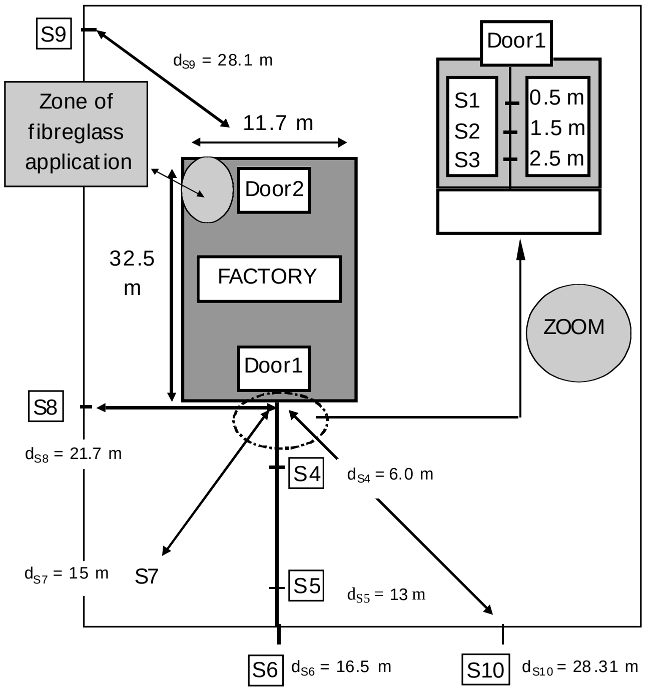

Figure 1. Scheme of the sampling area.

Indoor samples were taken by diffusive monitoring. The samplers were attached to the breast pocket of the workers clothes for 4 hours.

Area of study

The study was performed in a fibreglass boat manufacturing industry. The workshop (Fig. 1) is located in an industrial area with a relatively high traffic density, in the province of A Coruña (NW Spain). It has a surface area of about 380 m^2 and contains two doors, one at the front, which is closed, and the other, at the backside and next to the laminating zone, which is usually open. In addition, the workshop has an air extraction system in this zone.

Samples were taken from the factory and neighbouring area. Each of the five workers, performing different activities in the workplace, represented one sample. Fibreglass laminating is the activity that releases more styrene to environment, so while workers applied fibreglass they wore a protective mask. Outdoor sampling points were placed at 0.5 (S1), 1.5 (S2), 2.5 (S3), 6.0 (S4), 13 (S5), 15 (S7), 16.5 (S6), 21.7 (S8), 28.1 (S9) and 28.3 m (S10) from the workshop.

Analytical methods

Analyses were performed using a PE ATD-400 Automatic Thermal Desorption System coupled to a Q-Mass 910 gas chromatography-mass spectrometry system (Perkin-Elmer, Norwalk, CT, US). A 5 %-diphenylmethylsilicone (Sugelabor, Madrid, Spain) capillary column (50 m × 0.25 mm × 0.25 µm) was used and the temperature program was 40 ºC (5 min), 5 ºC/min to 160 ºC (1 min) and 10 ºC/min to 210 ºC. Carrier gas was helium (purity $\geq$ 99.999 %) at a flow-rate of 0.9 mL/min. This multiramp temperature program allowed the identification of other compounds present in the sample. Mass spectrometer was operated in the ionisation mode (70 eV) and the scan range was from 35 to 200 amu at a scan speed of 125 amu/s. Ion source temperature was 230 ºC and the GC/MS transfer line was kept at 210 ºC.

Thermal desorption conditions adopted for outdoor and indoor air are presented in table I.

Table I. Thermal desorption conditions for indoor and outdoor samples.

		Indoor Samples	**Outdoor Samples**
Flows	Tube Desorption	100 mL/min	
	First Split	-	
	Second Split	150 mL/min	5.3 mL/min
	Cold Trap Desorption	150.9 mL/min	6.2 mL/min
Temperatures	Tube Desorption	300 ºC	
	Cold Trap Low	–30 ºC	
	Cold Trap High	300 ºC	
	Transfer Line	200 ºC	

Compound identification was accomplished by comparing with NIST library spectra. Quantitation was achieved with external standard calibration method. Working standard solutions were prepared by dilution, with an automatic micropipete, of the stock solution with methanol. A multipoint calibration was performed spiking working standards into tubes. Styrene 104 m/z relation was selected for quantitation.

Results and discussion

Study of thermal desorption conditions

The selection of suitable thermal desorption conditions is determinant in achieving good analysis performance. Desorb flows and temperatures of sample tubes were fixed, in basis of previous studies [11], at 100 mL/min and 300 ºC, respectively. The ATD-400 is provided with two split valves before and after the cold-trap. These valves control the amount of analyte that reaches the detector and adapt the cold-trap desorption flow to that required by a capillary column.

High styrene concentrations were expected due to the industrial activity, so several tests were performed with real samples to select split flows. Back valve flow was varied, keeping the front one closed to allow the concentration of the whole sample in the cold trap. 5.3, 14, 40 and 150 mL/min flows were tested with several samples taken inside and outside the workshop. 5.3 and 150 mL/min split: flows, that correspond to 1:6 and 1:167 column:vent ratios, were selected for outdoor and indoor samples, respectively, because they provide a non-saturated detector response and a good peak shape. Recoveries from tubes were quantitative because second desorptions of tubes gave styrene responses below detection limits. Final thermal desorption conditions are summarised in table I.

Figure 2 shows the calibration curve. Area was plotted *versus* nanograms of detected compound, which are directly

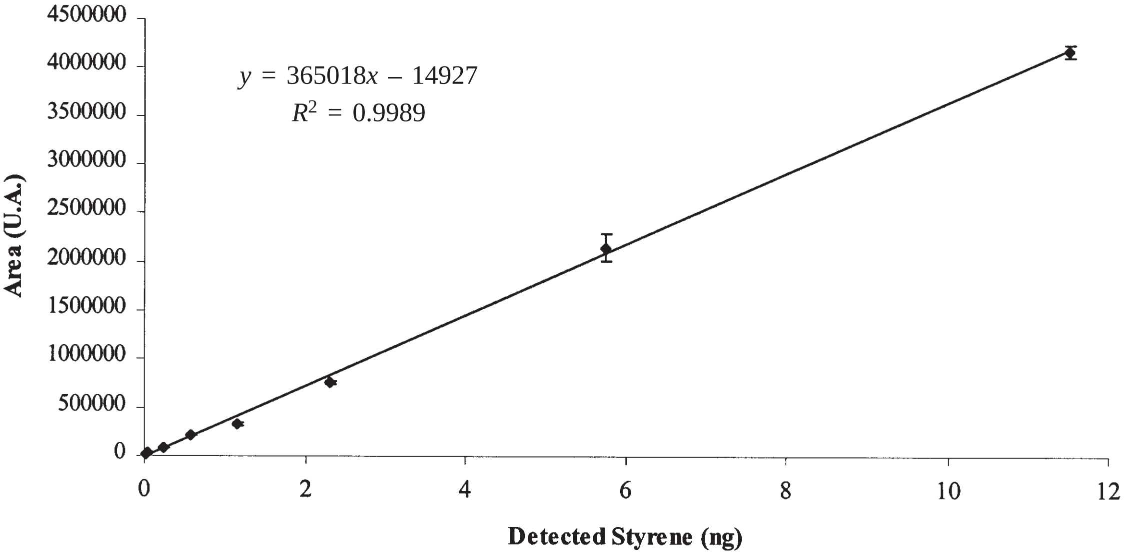

Figure 2. Calibration curve of styrene.

related with the mass sorbed onto tubes. Reproducibility was calculated as the relative standard deviation of six sequential injections of a standard of 50 ng/µL for the split-flow of 5.3 mL/min and 200 ng µl when the split-flow was 150 mL/min. In both cases RSD was between 4.3 and 5.4 %. The detection limit expressed in area was calculated by means of the expression:

$$LOD_{area} = x + 3\sigma \tag{2}$$

where LOD_{area} is the detection limit in area units, x is the average value of six blank tubes desorbed under the same conditions as those of a sample tube and σ is the standard deviation of those blanks. The detection limit in mass units was obtained by introducing the LOD_{area} value in the calibration plot. The detection limits obtained were 0.08 and 1.21 ng of adsorbed styrene on the tube for the split-flows of 5.3 and 150 mL/min, respectively.

Application

Occupational air samples were collected on diffusion tubes attached to the clothes of the workers for middle working day. Average values were under the limit value (85 mg/m^3) and ranged from 14.2 to 69.9 mg/m^3. Daily average concentrations showed appreciable differences, 23.5 and 55.7 mg/m^3 for instance, possibly as a result of the discontinuous activity of the factory. Differences were also observed in concentrations obtained from each personal sampler within the same sampling day (Fig. 3), these being due to the different activities undertaken by each worker at the workplace: fibreglass laminating, carpentry, painting, etc. Since occupational concentrations of a chemical substance depend directly on the materials and working practices, no similar situations were found in the literature.

However, styrene is also a pollutant present in other industrial activities, for example, in the varnish sections of furniture industries. Studies carry out by this laboratory determined an average concentration of 144 mg/m^3 at the varnish section of a door manufacture industry, while Mangani *et al.* [12] found 307 mg/m^3 for a similar situation.

Outdoor samples were taken at several distances from the workshop to study the possible influence of the factory on its surrounding area. Samples were collected on working and non-working days. The temperature was between 15 and 19 ºC during sampling period.

Figure 4 presents the variation of styrene concentration with distance over a perpendicular line to the workshop that contains S1 to S6 sampling points, taking as reference mean indoor concentration. Styrene concentrations decrease as the distance from the workshop increases, ranging from the 7.5 mg/m^3 at 0.5 m (S1) to 0.02 mg/m^3 at 16.5 m (S6). This tendency is specially marked between S1 and the other sampling sites because this point is close to the workshop front door. But it is broken at sampling point S5 (13 m), presenting a slightly greater concentration (0.4 mg/m^3) than that at the previous point (S4: 6 m and 0.2 mg/m^3). This can be due because the door was opened while the sample was taken. This fact shows the clear influence of indoor concentrations on ambient values.

Samples were also taken round the perimeter (sampling points S6, S8, S9 and S10) on working and non-working days (Fig. 5). In general, styrene concentrations (1.1-23.5 µg/m^3) on working days were twice those (1.4-10.7 µg/m^3) on non-working days, in agreement with the 9-hour styrene lifetime in the atmosphere. This relationship does not apply at S9 (1.1 and 1.4 µg/m^3) since this point is not directly influenced by indoor air and is exposed to wind. The highest concentration values were found at the point near the back door (S9) (23.5-10.7 µg/m^3). It appears that closeness of the sampling point to this door seems to be determinant in the concentrations found, because it is next to the laminating zone and stays open during the entire day.

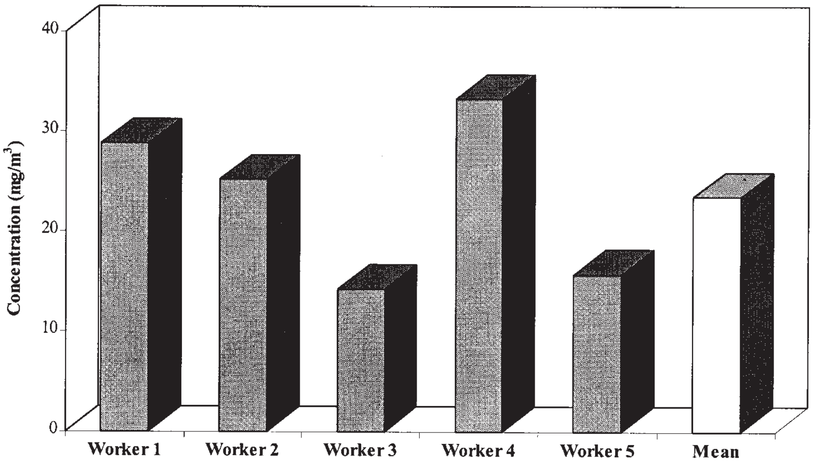

Figure 3. Occupational concentrations of styrene in a working day.

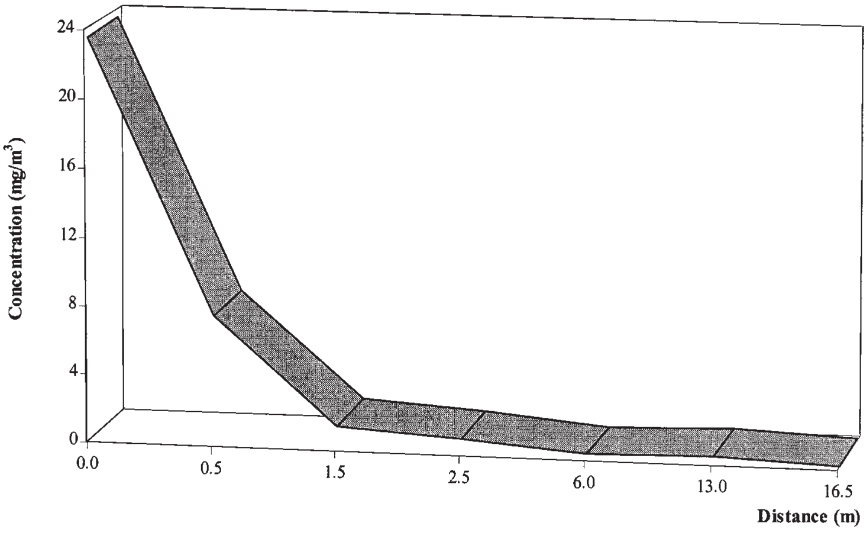

Figure 4. Variation of styrene over a perpendicular line from the factory (S1 to S6 sampling points).

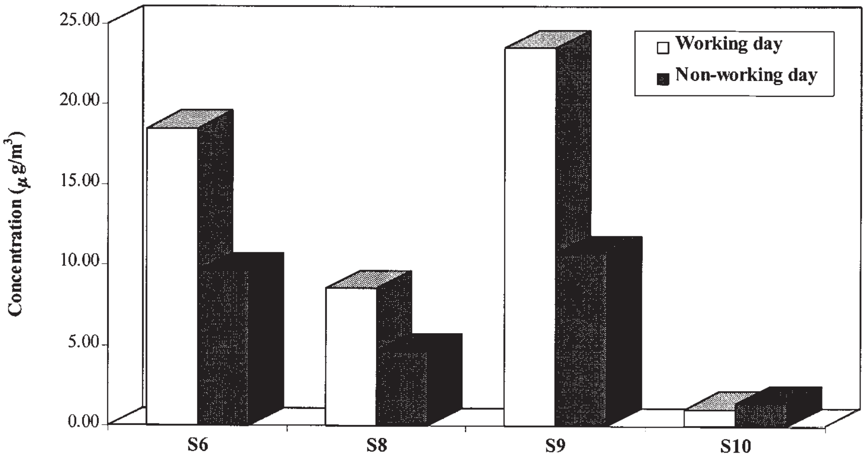

Figure 5. Working *vs* non-working day measurements on the surrounding area of the factory.

Several samples were taken at sampling point S7 by diffusive and active sampling. Average concentrations (113 and 100 µg/m^3, respectively) show that there are no significant differences between both sampling methods.

In general, outdoor concentrations were higher than those for urban air reported by other authors 0.6-1.1 µg/m^3 [13] and 2.9-3.3 µg/m^3 [14], although these two studies were developed in areas with higher traffic densities. This seems to confirm the industrial activity as the main source of styrene at the studied area.

Conclusions

A suitable thermal desorption-gas chromatography-mass spectrometry method for determination of styrene in industrial indoor and outdoor air is developed. Indoor samples were taken by diffusive sampling and ranged from 14 to 70 mg/m^3, levels that never exceed the limit value. Outdoor concentrations varied with distance and with the kind of work performed; active and diffusive sampling methods were used and gave the same results. They confirm the industrial activity undertaken in the workshop as the main styrene source at the studied area.

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