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Journal of Chromatography A, 778 (1997) 263–268

JOURNAL OF
CHROMATOGRAPHY A

Evaluation of environmental levels of aromatic hydrocarbons in gasoline service stations by gas chromatography

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Abstract

The volume of gasoline sold in refuelling operations and the ambient temperature, can increase significantly the environmental levels of aromatic hydrocarbon vapours and subsequently, the occupational risk of gasoline service station attendants, specially in the case of benzene. We have evaluated the occupational exposure to aromatic hydrocarbons by means of personal-breathing-zone samples of gasoline vapours in a service station attendant population. This evaluation was carried out using diffusive samplers, in two periods at quite different temperatures (March and July). A significant relationship between the volume of gasoline sold during the shift and the ambient concentration of benzene, toluene, and xylenes was found for each worker sampled. Furthermore a significant difference was found between the time-weighted average concentration of aromatic compounds measured in March, with ambient temperatures of 14–15°C and July, with temperatures of 28–30°C. In addition, 20% of the population sampled in the last period were exposed to a time-weighted average concentration of benzene above the proposed Threshold Limit Value of 960 $\mu\text{g}/\text{m}^3$ of the American Conference of Governmental Industrial Hygienists (ACGIH). © 1997 Elsevier Science B.V.

Keywords: Gasoline; Air analysis; Benzene; Toluene; Xylenes; Volatile organic compounds

1. Introduction

Gasoline is a complex mixture of low-molecular-mass compounds, mainly paraffinic, naphthenic, olefinic, and aromatic with carbon numbers typically within the range 3–11. The detailed composition of gasoline varies depending on the type of crude oil from which it originated and the type of processing undergone by the various refinery streams from which it is blended. An important group of aromatic components of gasoline is constituted by benzene, toluene and xylenes.

From a toxicological point of view, benzene is the most hazardous component, because it is considered as a confirmed human carcinogen by several organi-

sations such as the International Agency of Research on Cancer (IARC) [1], the American Conference of Governmental Industrial Hygienists (ACGIH) [2] and the MAK Commission [3].

During refuelling, the subjects can easily be exposed to extremely high levels of gasoline vapours for a short time. However, this fact is particularly relevant in the case of occupational exposure of service station attendants, as it has been recently investigated by several authors [4–8].

Monitoring methods, based in dynamic or diffusive procedures for personal exposures to gasoline vapour, were typically aimed at benzene as the most hazardous component, although they are also capable of measuring toluene and other higher aromatics such xylenes [9,10].

In practice, the composition of the gasoline vapour

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to which exposure occurs in the refuelling areas is very different from that of the liquids from which it evaporates. This is due to fractional distillation effects which occur on evaporation from a bulk liquid. The vapour composition is similar to the liquid only where rapid total evaporation occurs. Other factors, such as the volume of gasoline sold and ambient temperature, can increase significantly the environmental levels of gasoline vapours and subsequently, the risk of the occupationally exposed workers.

The aim of this work is to evaluate the environmental levels of benzene, toluene and xylene in air, by means of personal sampling of subjects occupationally exposed to gasoline vapours as service station attendants. This evaluation was carried out in two different periods of time at quite different ambient temperature. For every sampling time, a variable volume of gasoline was sold. The influence of both temperature and volume sold, on the levels of aromatic hydrocarbons in air, have been analysed.

2. Experimental

2.1. Occupational exposure

The evaluation of occupational exposure to gasoline vapours was carried out in six gasoline service stations located on three roads around a city in southeast Spain. In all station services three different types of gasoline were dispensed: 97 I.O. leaded; 95 I.O. and 98 I.O., both unleaded. Twenty-one subjects occupationally exposed in refuelling operation were sampled using personal diffusive samplers. The samples were collected in March and July, in order to have quite different ambient tem-

peratures. In both periods, the same sampling days, Thursday morning and Friday afternoon, were chosen. During exposure, the concentration of benzene, toluene and xylenes in ambient air were monitored continuously for each worker with 3M-3500 personal diffusive samplers (3M España, Madrid) attached to the clothing within the breathing zone. These samplers are designed to measure average concentrations over a measured time interval. It requires no sampling pump because the contaminants enter to monitor by diffusion and are adsorbed on activated charcoal inside the badge. The amount of contaminant adsorbed is determined by exposure time and contaminant concentration present in the sampled environment. The mass of every organic contaminant, determined by gas chromatographic analysis, is converted to time-weighted average concentration by means of their specific sampling rates [11]. The experimental conditions of sampling are shown in Table 1.

2.2. Analysis

Diffusive samplers were desorbed in the same sampler, with carbon disulphide free of benzene (Panreac, Barcelona, Spain), for 30 min. Desorption volume used was 1.5 ml. Volumes of 3–5 μ l were injected into a Hewlett-Packard 5890 gas chromatograph (Palo Alto, CA, USA), equipped with split-splitless injector and flame ionisation detector. The compounds were separated in a crosslinked methyl silicone capillary column measuring 50 m \times 0.2 mm I.D., with phase thickness of 0.5 μ m (Hewlett-Packard, Palo Alto, CA, USA). We used Helium as carrier gas at 180 kPa of pressure with split-ratio 1:20. Injector and detector temperature of 200°C, and

Table 1
Environmental and personal sampling conditions on refuelling stations

Period	Shift	Number of samples	Sampling time (min)	Ambient temperature (°C)	Relative humidity	Gasoline sold (l)
March	Morning	10	375–390	14	50–90%	589–3454
March	Afternoon	11	345–450	15	49–52%	700–2676
July	Morning	11	370–455	28	34–66%	936–3006
July	Afternoon	10	370–450	30	44–49%	1172–3355

oven temperature programmed from 40 to 130°C, a gas chromatogram of a sample is shown in Fig. 1. The mass of every organic contaminant, determined by gas chromatographic analysis, is later converted to time-weighted average concentration in air. The sampled volume was used to calculate the concentration of each one of the contaminants in air, when sorbent tubes were used. For diffusive sam-

plers, the time-weighted average concentration is calculated by means of specific sampling rate [11].

3. Results and discussion

The results found in the evaluation of the occupational exposure of refuelling station workers are

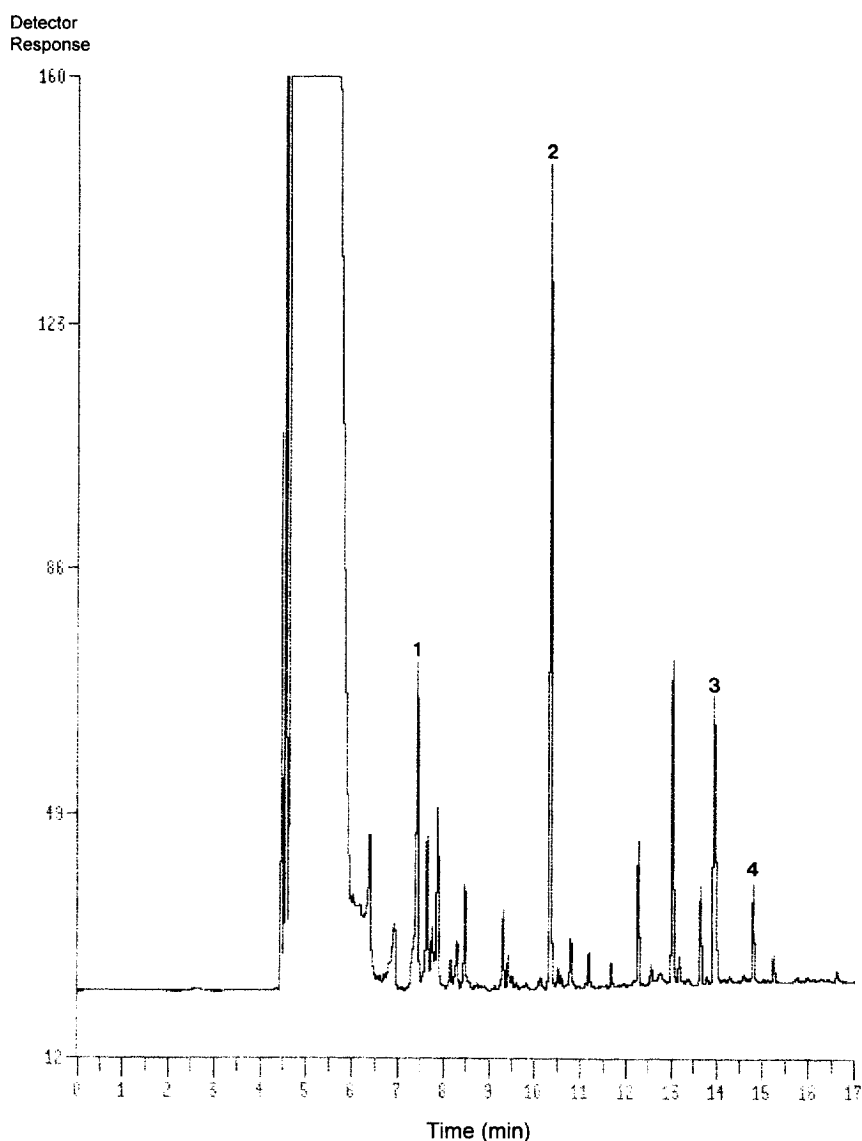


Fig. 1. Gas chromatogram of a personal sample. Initial temperature 80°C, maintained for 8 min, then programmed to 135°C at 8°C/min. Benzene (1); toluene (2); *m,p*-xylenes (3); *o*-xylene (4).

Table 2

Time-weighted average concentrations of aromatic compounds in occupationally exposed workers of refuelling stations

Period	Shift	No. of samples	Compound	Mean	Range
March	Morning	10	Benzene	551	104–897
			Toluene	656	167–1000
			Xylenes	191	95–335
March	Afternoon	11	Benzene	472	164–774
			Toluene	621	222–838
			Xylenes	184	94–370
July	Morning	11	Benzene	726	281–1515
			Toluene	1145	773–2258
			Xylenes	463	265–788
July	Afternoon	10	Benzene	746	272–1603
			Toluene	1192	597–2324
			Xylenes	604	377–1119

Results are expressed in $\mu\text{g}/\text{m}^3$.

shown in Table 2, where the mean values and the concentration ranges are expressed for each compound. The mean value of benzene in all the periods evaluated are lower than those obtained by Lagorio et al. [12] and higher than those obtained in field experiences by Purdhan et al. [9] with a mean concentration of $250 \mu\text{g}/\text{m}^3$ (230–510). This later study was carried out in March and April.

The levels of aromatic compounds in air were higher in July than in March. Two variables, temperature and volume of gasoline sold, could affect the ambient concentration of aromatic compounds. During the refuelling operation, an air stream saturated with gasoline vapour is evacuated from the fuel-tank of the car. The volume of air is exactly equal to the volume of gasoline pumped. For this reason, the volume of gasoline sold during the shift could have a decisive influence in the contamination of the air near to the respiratory zone of each exposed subject.

We analysed the relationship between the volume of gasoline sold during the shift and the ambient concentration of benzene, toluene, and xylenes for each worker sampled. The plot of this relationship for benzene is shown in Fig. 2. Moreover, Table 3 summarises the parameters of the regression lines for each compound. A significant relationship between the levels of aromatic compounds in air and the volume of gasoline dispensed was found, both in March and in July periods. A similar statistical association was obtained for Lagorio et al. between

the levels of benzene in air and the volume of gasoline sold [12].

As the relationship between levels of aromatic compounds in air and the volume of gasoline sold has been confirmed, a normalisation of aromatic hydrocarbon concentrations on air (dividing the time weighted average concentration of each compound by the volume of gasoline sold during the shift) must be carried out before applying statistical tests. Using these normalised values, the net influence of temperature in the time-weighted concentration of aromatic compounds in air, between the two periods studied, can be seen in Fig. 3. The results of the

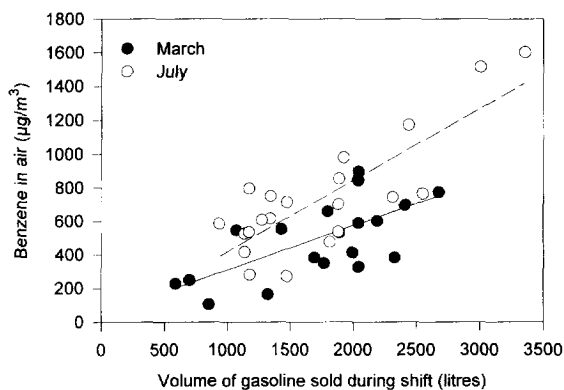


Fig. 2. Relationship between time-weighted average concentration of benzene in air and daily volume of gasoline sold for each occupational exposed worker. Both, March and July sampling periods, are shown separately.

Table 3

Parameters of linear regression line $y=a+bx$, where y =time weighted average concentration in air of each aromatic compound ($\mu\text{g}/\text{m}^3$) and x =volume of gasoline dispensed by the worker (l)

Compound	Number of samples	<i>a</i>	<i>b</i>	<i>r</i>	<i>P</i>
Benzene (March)	21	45.33	0.264	0.66	<0.001
Benzene (July)	21	-6.502	0.424	0.81	<0.001
Toluene (March)	21	122.8	0.291	0.68	<0.001
Toluene (July)	21	167.9	0.572	0.80	<0.001
Xylenes (March)	21	101.5	0.049	0.45	<0.05
Xylenes (July)	21	126.5	0.231	0.73	<0.001

ANOVA test show a significant difference, for each one of the three compounds, between March, with ambient temperatures of 14–15°C and July, with ambient temperatures of 28–30°C. Both temperature levels are very common in our country.

The current environmental threshold limit values (TLV) and the time weighted average (TWA) adopted by ACGIH for toluene and xylene, are 180 mg/m^3 and 375 mg/m^3 respectively [2]. The TWA concentrations evaluated in the population exposed was always much lower than TLVs cited above.

For benzene, a drastic reduction of TLV–TWA from 32 mg/m^3 to 300 $\mu\text{g}/\text{m}^3$ was proposed as intended change for the ACGIH in 1993–1994. However this proposed value was modified to 960 $\mu\text{g}/\text{m}^3$ before being accepted. In the last edition of

TLVs for 1995–96, this limit value even appears as proposed. If we compare our results with the proposed limit, the mean values of timed weighted average concentration of benzene in air, obtained in the two periods studied, were very close to the proposed TLV, specially in the July period. In fact, 20% of the population sampled in this period was exposed to time weighted average concentrations of benzene up to 960 $\mu\text{g}/\text{m}^3$. This fact could have a great relevance if the proposed limit is accepted.

4. Conclusions

The climatic conditions of countries with high temperatures in summertime, as our country, can increase the risk of exposure during the shift on service stations. Therefore, technical solutions should be designed to reduce the occupational risk to benzene vapour exposure in refuelling operation of service station attendants. In this way, vapour recovery systems has been developed to avoid volatile organic compounds emissions in refuelling station services according to legal regulations, as Council Directive 94/63/EEC [13]. Nevertheless the efficiency of these recovery systems should be verified periodically to reduce the occupational exposure to gasoline vapours, specially benzene because it is a confirmed human carcinogen.

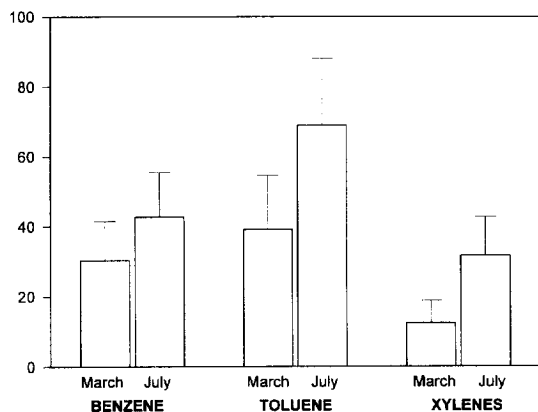


Fig. 3. Plot of mean values and standard deviations of aromatic hydrocarbon concentrations in air obtained from personal-breathing-zone samples of gasoline service station attendants in the two periods studied. The values were normalised by dividing the environmental concentration in air by the volume of gasoline sold during the shift.

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