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Short communication

Simultaneous determination of ethylbenzene, indan, indene and acenaphthene in air by capillary gas chromatography

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Abstract

An attempt was made to establish a method for the simultaneous determination of ethylbenzene, indan, indene and acenaphthene by capillary gas chromatography with flame ionization detection. The air was sampled on charcoal tubes and extracted with carbon disulfide–methanol (60:1, v/v). The four analytes were separated by gas chromatography using a capillary column of cross-linked 5% phenylmethylsilicone. Under the applied conditions the method showed detection limits of $1.8 \mu\text{g}/\text{m}^3$ for ethylbenzene, $2.1 \mu\text{g}/\text{m}^3$ for indan, $2.8 \mu\text{g}/\text{m}^3$ for indene and $3.4 \mu\text{g}/\text{m}^3$ for acenaphthene. Relative standard deviations were as follows: ethylbenzene, 6.2%; indan, 9.9%; indene, 13.6%; and acenaphthene, 14.4%. The recoveries for these compounds were 98.6, 97.9, 55.7 and 52.1%, and the accuracies were 2.5, 3.0, 44.3 and 47.8%, a working range of 1.5–30 ng/ μl for ethylbenzene and 0.75–15 ng/ μl for indan, indene and acenaphthene. The method was found to be suitable for the determination of environmental and occupational analysed ethylbenzene, indan, indene and acenaphthene exposure. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Air analysis; Environmental analysis; Ethylbenzene; Indan; Indene; Acenaphthene

1. Introduction

Research efforts in the field of occupational exposure to mixtures of toxic volatile organic compounds are steadily increasing.

Occupational exposure to benzene, toluene, naphthalene and xylene in coke plants has been estimated by the determination of benzene homologues and naphthalene in the breathing zone air [1]. The compounds were separated using gas chromatography [2]. Up to now, the simultaneous determination of indan, indene, ethylbenzene and acenaphthene has not been reported.

Analysis of indene, styrene, coumarone, cyclopentadiene and dicyclopentadiene in air by TLC was described by Tsendrovskaya [3]. Bianhi et al. [4]

reported a modified purge-and-trap gas chromatographic method of volatile organic carbon compounds (e.g., ethylbenzene, indene) in water samples. Ethylbenzene is usually determined by the method recommended by NIOSH [5]. Acenaphthene may also be analyzed according to NIOSH by gas chromatography with flame ionization detection [6] or by HPLC with fluorescence detection [7].

Analytical methods for the determination of ethylbenzene together with benzene, toluene and xylenes in air were described by Riedel et al. [8]. The analytes were desorbed thermally by a microwave device coupled to a gas chromatograph interfaced to a mass spectrometer.

According to data presented by Elke et al. [9], the analytes were extracted from a charcoal pad with

carbon disulfide (containing 1% methanol). After removal of carbon disulfide by xanthation reaction, the hydrocarbons (benzene, toluene, ethylbenzene and xylenes) were enriched on a Carboxen–poly(dimethylsiloxane) solid-phase microextraction fiber, thermally desorbed and analyzed by high-resolution gas chromatography–flame ionization detection.

In this work, an attempt to establish a simple method for the simultaneous determination of ethylbenzene, indan, indene and acenaphthene in air is presented.

2. Experimental

2.1. Reagents

All chemicals were of reagent grade quality or better and were used as received without further purification. Acenaphthene 99% (CAS registry No. 83-32-9), indene 99% (95-13-6), indan 97% (496-11-7), ethylbenzene 99% (100-41-4), carbon disulfide 99.9% (75-15-0) were obtained from Aldrich (Milwaukee, WI, USA). Methanol of gradient grade obtained from Riedel-de Haën (Seelze, Germany). Charcoal tubes (catalog No. 226-01) were purchased from SKC (Eighty Four, PA, USA). Distilled water was used in all analyses.

2.2. Standard solutions

In order to prepare a stock solution, ethylbenzene, indan, indene and acenaphthene were dissolved in carbon disulfide–methanol (60:1, v/v) at a concentration of 30 ng/ μ l. This solution was further diluted to yield appropriate working concentrations for the preparation of the calibration standards. The final concentrations were as follows: 1.5, 3, 6, 12 and 30 ng/ μ l for ethylbenzene and 0.75, 1.5, 3, 6, 15 ng/ μ l for indan, indene and acenaphthene. The solutions were kept at 4°C until use.

2.3. Air sampling and sample preparation

Air was pumped through the charcoal tubes with the flow-rate of 0.5 l/min for 6 h (180 l). The analytes were released from the charcoal by treatment with 1 ml of carbon disulfide–methanol (60:1,

v/v) in an ultrasonic bath for 15 min. The amount of the compounds in the back-up layer showed not more than 10% of the compound in the sampling section. Otherwise the measurement was repeated.

2.4. Instrumentation

The analysis of the charcoal extracts was performed with a Hewlett-Packard 5890 II gas chromatograph equipped with a flame ionization detector, an autosampler/autoinjector (HP7673) and an integrator (HP3396II). The hydrocarbons were separated chromatographically using a capillary column Ultra 2 (cross-linked 5% phenylmethylsilicone), 25 m \times 0.32 mm I.D., 0.52 μ m film thickness (HP Part No. 19091 B-112) with injector and detector temperatures of 230 and 250°C, respectively. An efficient separation was achieved using the following temperature program: 40°C for 1 min, increase by 8°C/min to 80°C, increase by 12°C/min to 220°C; carrier gas, helium at a flow-rate of 2.5 ml/min; injection volume, 1 μ l; splitless time, 1 min; split ratio, 1:30.

2.5. Determination of the desorption coefficient

Ten μ l of standard solution (concentrations given above) were injected into five charcoal tubes, while the other five charcoal tubes were left untreated and used as a control. All samples were tightly closed and stored overnight at ambient temperature (20°C). Then 1 ml of carbon disulfide–methanol (60:1, v/v) was added to each sample and the same procedure was applied as for air samples. Arithmetic mean value of the desorption coefficient based on five samples was calculated for each compound according to the method of OSHA [10].

2.6. Applications

The described method was applied with air samples collected in a coke plant. Breathing zone air samples were collected by 10 workers during their workshift. Personal sampling was performed using a battery-operated pump (Type AFC 123, Casella, London, UK) connected to a filter holder attached to the shoulder of the subject.

3. Results and discussion

In Fig. 1 typical chromatograms from the analysis of a standard solution and an air sample are shown. Retention times obtained are as follows: 5.1 min for ethylbenzene; 8.5 min for indan; 8.7 min for indene; and 14.8 min for acenaphthene.

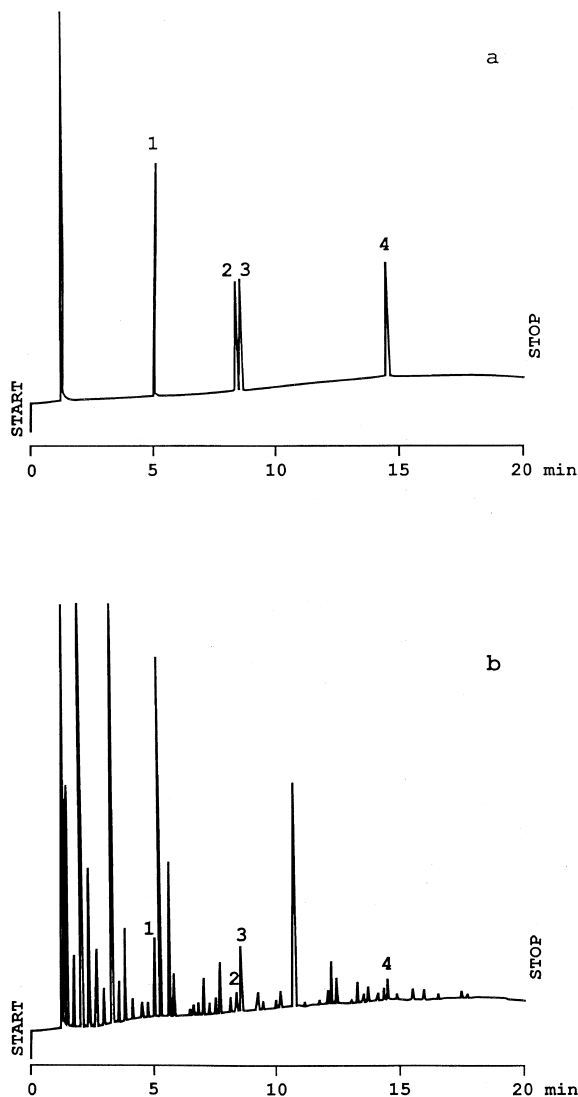


Fig. 1. Gas chromatogram of (a) a standard solution and (b) a breathing zone air sample of a coke plant worker exposed to aromatic hydrocarbons. Peaks: (1) ethylbenzene; (2) indan; (3) indene; (4) acenaphthene.

Samples collected on activated charcoal were extracted with carbon disulfide–methanol (60:1, v/v). The average desorption efficiency for ethylbenzene over a concentration range of 1.5–30 ng/ μ l was 98.6%. The average desorption efficiencies for indan, indene and acenaphthene over a concentration range of 0.75–15 ng/ μ l were 97.9, 55.7 and 52.1%, respectively. The low desorption efficiencies for indene and acenaphthene were taken into consideration in the concentration calculations.

The precision and accuracy were evaluated using samples spiked at concentrations of 1.5, 3, 6, 12 and 30 ng/ μ l for ethylbenzene and 0.75, 1.5, 3, 6 and 15 ng/ μ l for indan, indene and acenaphthene. The accuracy was expressed as the percentage difference between the mean measured concentration of six samples and the theoretical concentration. Each concentration was calculated on the basis of peak area using calibration curves. An integrator program (external standard) was employed. The precision and accuracy of the proposed method are shown in Table 1.

A linear relationship was found between the peak area and the mass of compound for each measurement consisting of six samples spiked at the levels given in Section 2. The parameters of the calibration lines (peak area versus ng of each compound per 1 μ l of the injected sample) are shown in Table 2. Concentrations of the analysed compounds in air were calculated according to the relation:

$$C = \frac{MV_s}{V_a R} \quad (\text{ng/m}^3)$$

where M is the mass (ng) of the compound contained in the 1 μ l injected sample, V_s is the volume of the carbon disulfide–methanol solution (1000 μ l) used for the extraction, V_a is the actual air volume sampled (m^3) and R is the recovery coefficient.

The detection limit was determined at a signal-to-noise ratio of 3. The detection limits for ethylbenzene, indan, indene and acenaphthene were found to vary from 1.8 to 3.4 $\mu\text{g/m}^3$.

To demonstrate the suitability of our method, we monitored the air quality in a coke plant. The air concentrations of ethylbenzene, indan, indene and acenaphthene at breathing zone levels are summarized in Table 3. It was found that operators working in the tar distillation process are exposed to relatively

Table 1
Precision and accuracy^a

Compound	Concentration added (ng/ μ l)	Concentration measured mean \pm SD (ng/ μ l)	RSD ^b (%)	Accuracy ^c (%)	Recovery (%)
Ethylbenzene	1.5	1.46 \pm 0.16	10.9	-2.7	97.3
	3	3.07 \pm 0.26	8.5	2.3	102.3
	6	5.75 \pm 0.24	4.2	-4.1	95.8
	12	12.06 \pm 0.40	3.3	0.5	100.5
	30	29.17 \pm 1.23	4.2	-2.8	97.2
Indan	0.75	0.71 \pm 0.10	14.1	-5.3	94.7
	1.5	1.46 \pm 0.16	10.9	-2.7	97.3
	3	3.04 \pm 0.28	9.2	1.3	101.3
	6	6.05 \pm 0.44	7.3	0.8	100.8
	15	14.30 \pm 1.12	7.8	-4.7	95.3
Indene	0.75	0.42 \pm 0.08	19.0	-44.0	56.0
	1.5	1.88 \pm 0.13	14.8	-41.3	58.6
	3	1.57 \pm 0.23	14.6	-47.6	52.3
	6	3.62 \pm 0.38	10.5	-39.7	60.3
	15	7.68 \pm 0.69	8.9	-48.8	51.2
Acenaphthene	0.75	0.40 \pm 0.09	22.5	-46.7	53.3
	1.5	1.76 \pm 0.17	22.3	-49.3	50.6
	3	1.61 \pm 0.20	12.4	-46.3	53.6
	6	3.29 \pm 0.27	8.2	-45.2	54.8
	15	7.25 \pm 0.47	6.5	-51.7	48.3

^a Analyses were carried out under the experimental conditions described in the Experimental section.

^b Relative standard deviation.

^c Defined as the percentage deviation between the average concentration obtained from the experiment and the theoretical concentration.

Table 2
Linear regression of the calibration lines

Compound	Relation ^a	r^2
Ethylbenzene	$M = -1.68 \times 10^{-1} + 3.81 \times 10^{-3}y$	0.9999
Indan	$M = -3.11 \times 10^{-1} + 4.08 \times 10^{-3}y$	0.9997
Indene	$M = -2.06 \times 10^{-1} + 4.11 \times 10^{-3}y$	0.9998
Acenaphthene	$M = -2.18 \times 10^{-1} + 3.80 \times 10^{-3}y$	0.9997

^a Peak area (y) versus mass M (ng) of each compound per 1 μ l of the injected sample.

Table 3
Time-integrated exposure to hydrocarbons of 10 coke plant workers

Exposure	Concentration in breathing zone air (μ g/ m^3)	Range (μ g/ m^3)
Ethylbenzene	47.2 \pm 96.9	2.1–303.0
Indan	31.8 \pm 26.2	2.0–83.1
Indene	21.9 \pm 17.3	5.0–27.5
Acenaphthene	10.8 \pm 13.6	0.3–13.2

low concentrations of the investigated hydrocarbons. In the breathing zone air, the concentrations of ethylbenzene, indan, indene and acenaphthene are relatively low in comparison to the permissible exposure levels. The threshold limit values for the time-weighted average concentrations for ethylbenzene and indene proposed by the Chemical Substances TLV Committee [11] in the year 1997 are equal to 434 and 48 mg/ m^3 , respectively.

4. Conclusions

The described method presents, for the first time, a quick and efficient analytical procedure for the simultaneous quantitative determination of ethylbenzene, indan, indene and acenaphthene in air for applications in occupational and environmental studies.

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