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Analysis of volatile organic compounds in the ambient air of Algiers by gas chromatography with a β -cyclodextrin capillary column

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Abstract

The concentrations of *para*- and *meta*-xylenes were given together in the majority of measurements of volatile organic compounds (VOCs) because of nonseparation of these two compounds by gas chromatography in usual capillary columns. In order to improve the separation of VOCs in ambient air, a β -cyclodextrin capillary column was used. The pollutants were sampled by two methods, i.e., adsorption on a charcoal cartridge followed by liquid extraction and solid-phase microextraction. About 26 VOCs, mainly aromatics, were identified in urban air of Algiers. The use of a β -cyclodextrin column allowed good separation of aromatic hydrocarbons, as well as of *para*- and *meta*-xylenes. Inversion of elution order was also observed regarding the other aromatics, in particular ethylbenzene and *meta*- and *para*-xylenes. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile organic compounds (VOCs), specifically aromatic ones, play a fundamental role in the pollution of environmental air. Significant levels of these compounds are often emitted into the atmosphere by a partial combustion of fuel petrol in an internal combustion [1–5]. Some of them act as precursors of photochemical oxidants (ozone and peroxyacetyl-nitrates) in the presence of nitrogen oxides and sunlight [5]. The rate of formation of these oxidants

is closely related to the rate at which hydrocarbons are scavenged by hydroxyl radicals, since it is this scavenging that produces organic peroxyradicals which subsequently produce ozone and other oxidants through the oxidation of NO and NO₂ [5].

Three concentration techniques are commonly used: absorption in suitable solution, cold trapping and adsorption in solids at ambient temperature, the latter being the most widely used method [1–4,6–14]. The regeneration of compounds can be done by thermal desorption or solvent extraction.

Solid-phase microextraction (SPME) is recently used as rapid alternative of extraction of organic pollutants in air [15–20]: analytes are adsorbed

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directly from the sample onto a fused-silica fiber that is coated with an appropriate stationary phase.

In usual capillary columns, several studies have reported monitoring of VOCs in ambient air, they show that the concentration of *para*- and *meta*-xylenes were given together in the majority of measurements because of the nonseparation of these compounds.

Cyclodextrins are cyclic oligosaccharides formed by an α -(1,4) linkage of glucopyranose units. The most commonly used oligosaccharides are α -, β - γ -cyclodextrins with six, seven and eight glucopyranose units, respectively. These compounds possess a hydrophilic exterior, which makes them soluble in water, and an interior cavity, which is less polar than water. The structures of solid cyclodextrin were described as cage or channel-type ones [21–23]. The β -cyclodextrin capillary column is widely used in enantiomeric separation of great variety of chiral compounds (ketones, esters, alkanes, acids, ethers, etc.) [22].

In this work, gas chromatography (GC) and GC–mass spectrometry (MS) analysis of VOCs emitted in the urban atmosphere of Algiers were carried out with a β -cyclodextrin capillary column after the sorption of air on charcoal followed by carbon disulfide extraction, and by SPME.

2. Experimental

VOCs were collected in the urban air of Algiers where the autovehicular exhaust emissions are the main source of air pollution. In this respect, it is worth noting that Algiers counts about 560 000 vehicles where 71% of them are older than ten years. All these vehicles use polluted fuels such as leaded gasoline and gasoil. The samples were collected by means of a charcoal sampling technique at a distance of 200 m from the sea, 5 m from the traffic rushing road and about 2 m from the ground.

Air samples were drawn through 90×6 mm I.D. borosilicate glass tubes, containing 100 and 50 mg of charcoal coconut shells (Supelco) as, respectively, first and second layers using a Buck I.H. pump (Supelco), operating at flow-rate of 200 ml min⁻¹ during 10 h from 8:00 a.m. to 06:00 p.m. (rush hours). The both charcoal layers were extracted

during 30 min with 1 ml of CS₂ under slight shaking, and the solutions subjected to analysis.

In the first step, a few microliters of solution were analyzed with a Hewlett-Packard (HP) 5708 A gas chromatograph equipped with a flame ionization detector, and a CP Sil 8 CB fused-silica capillary column (25 m×0.2 mm, 0.25 μ m film, Chrompack). The stationary phase is poly(dimethylphenylsiloxane). The programmed temperature used was 8 min at 40°C, then 2°C min⁻¹ to 200°C (Table 1). Injector and detector temperatures were 250°C.

In the second step, the extract was analyzed by a gas chromatograph (HP 5890 Serie II) combined with a HP 5971 mass spectrometer (mass-selective detector) under the following conditions: potential ionization 70 eV, source temperature 280°C and scan number (40–550 u) with the same column and the same temperature program described above (Fig. 1, Table 2).

In order to improve the separation of VOCs, the analysis was carried out under the same chromatographic conditions with a β -DEX 120 fused-silica capillary column (30 m×0.25 mm, 0.25 μ m film, Supelco). The stationary phase is 10% β -cyclodextrin in SPB-35 poly(35% diphenyl/35% dimethylsiloxane) with the same programmed temperature described above (Fig. 2). Before the sample analysis, a standard solution of *n*-heptane, benzene, toluene, ethylbenzene, *meta*-xylene, *para*-xylene,

Table 1
VOC identification by GC–FID in Algiers atmosphere

| Compound | Retention index | % ^a |
|-------------------------------------|-----------------|----------------|
| <i>n</i> -Hexane | 600 | 3.8 |
| Benzene | 658 | 15.4 |
| <i>n</i> -Heptane | 700 | 5.9 |
| Toluene | 757 | 21.0 |
| <i>n</i> -Octane | 800 | 3.7 |
| Ethylbenzene | 849 | 5.4 |
| <i>para</i> -/ <i>meta</i> -Xylenes | 859 | 14.1 |
| <i>ortho</i> -Xylene | 886 | 6.0 |
| <i>n</i> -Nonane | 900 | 2.1 |
| 1-Ethyl-3-/4-methylbenzenes | 949 | 2.3 |
| 1,3,5-Trimethylbenzene | 958 | 6.4 |
| 1-Ethyl-2-methylbenzene | 964 | 3.2 |
| 1,2,4-Trimethylbenzene | 976 | 2.1 |
| Isobutylbenzene | 998 | 6.5 |
| 1,2,3-Trimethylbenzene | 1007 | 2.1 |

^a Figures are the percent of the sum of components identified.

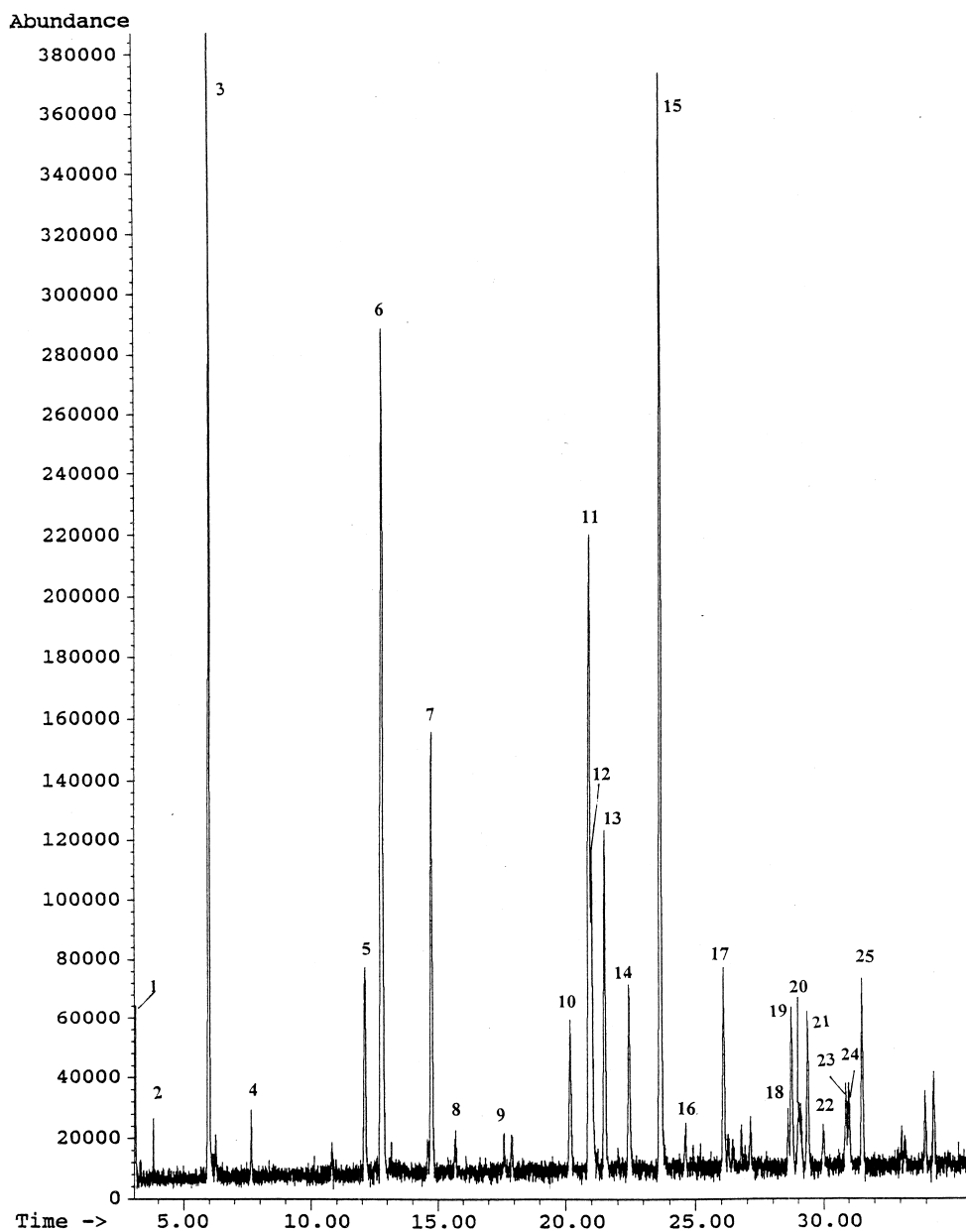


Fig. 1. GC-MS profile of the air sample collected in the urban area of Algiers: numbering as in Table 2. Time scale in min.

ortho-xylene, propylbenzene, 1-ethyl-3-methylbenzene, 1,3,5-trimethylbenzene, *n*-octane, *n*-nonane and 1,2,3-trimethylbenzene (Fluka, GC grade) was analyzed under the same conditions.

The sampling of VOCs by SPME was carried out after that the 100 μm film thickness poly(di-

methylsiloxane) coated fiber (Supelco) was conditioned at 200°C under a helium stream for 2 h. For the first fiber blanks test, some extraneous peaks primarily from the glue used to attach the fibers were observed. The monomers in the glue were released from the fiber after a second desorption lasted for 5

Table 2
 m/z ion current traces used for identification and qualitative evaluation of VOCs by GC–MS in Algiers atmosphere

| Peak No. | Basic peak | Molecular ion | Compound |
|----------|------------|---------------|-----------------------------|
| 1 | 78 | 78 | Benzene |
| 2 | 43 | 100 | <i>n</i> -Heptane |
| 3 | 91 | 92 | Toluene |
| 4 | 43 | 114 | <i>n</i> -Octane |
| 5 | 91 | 106 | Ethylbenzene |
| 6 | 91 | 106 | <i>p/m</i> -Xylenes |
| 7 | 91 | 106 | <i>o</i> -Xylene |
| 8 | 43 | 128 | <i>n</i> -Nonane |
| 9 | 105 | 120 | Isopropylbenzene |
| 10 | 91 | 120 | Propylbenzene |
| 11 | 105 | 120 | 1-Ethyl-3-methylbenzene |
| 12 | 105 | 120 | 1-Ethyl-4-methylbenzene |
| 13 | 105 | 120 | 1,3,5-Trimethylbenzene |
| 14 | 105 | 120 | 1-Ethyl-2-methylbenzene |
| 15 | 105 | 120 | 1,2,4-Trimethylbenzene |
| 16 | 105 | 120 | 1,2,3-Trimethylbenzene |
| 17 | 68 | 136 | Limonene |
| 18 | 105 | 134 | 1-Methyl-3-propylbenzene |
| 19 | 105 | 134 | 1-Methyl-4-propylbenzene |
| 20 | 105 | 134 | Butylbenzene |
| 21 | 119 | 134 | 1-Ethyl-3,5-dimethylbenzene |
| 22 | 105 | 134 | 1,2-Diethylbenzene |
| 23 | 119 | 134 | 2-Ethyl-1,4-dimethylbenzene |
| 24 | 119 | 134 | 4-Ethyl-1,2-dimethylbenzene |
| 25 | 119 | 134 | 1,2,4,5-Tetramethylbenzene |

min at 200°C, which prevented that no contaminants were in the fiber coating prior to exposure to a given air sample. The technique was used for the extraction of VOCs by direct exposure of the SPME fiber to the exhaust gas of petrol vehicles during 20 min (Fig. 3).

3. Results and discussion

The use of charcoal tubes with two beds (100 and 50 mg as, respectively, first and second layers) under the sampling conditions provided a good information about the breakthrough volumes since the absence of the compounds in the second layer confirm the fact that the sampling was done without breakthrough and hence the compounds were mostly adsorbed in the first layer.

Some important observations can be drawn through the analysis of VOCs emitted in the urban atmosphere of Algiers by GC–flame ionization detection (FID) (Table 1) and GC–MS (Fig. 1, Table 2) with a CP Sil 8 CB capillary column. The number

of peaks obtained by GC–MS (total ion current mode, see Fig. 1) and by GC–FID analysis were 40 and 30, respectively. Many of the compounds were identified by direct interpretation of the mass spectra obtained by GC–MS analysis; others were identified by combining MS data with retention index information calculated with Van Den Dool and Kratz equation [24] and with those reported in literature [25]; this last approach was requisite for many isomeric arenes owing to the similarity of their mass spectral fragmentation patterns.

The alkylbenzenes have a molecular ion at m/z 92, 106, 120, 134. Their ion fragments are at m/z 50, 51, 52, 63, 65, 76, 77, 91, 105 and 119. Certain isomers present similar spectra with a basic peak at: (1) m/z 91 (i.e., toluene, ethylbenzene, *ortho*-, *para*- and *meta*-xylenes); (2) m/z 105 (i.e., isopropylbenzene, 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, 1,3,5-trimethylbenzene, 1-ethyl-2-methylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1-methyl-3-propylbenzene, 1-ethyl-4-propylbenzene, butylbenzene and 1,2-diethylben-

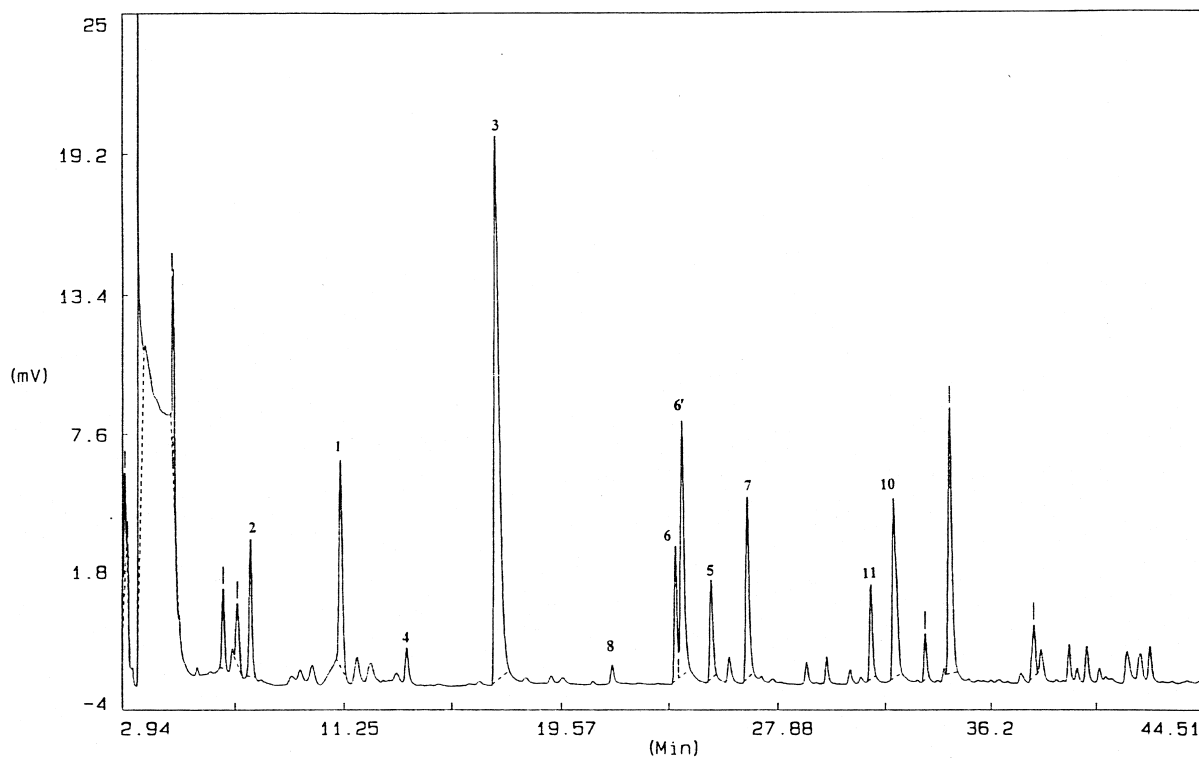


Fig. 2. GC-FID profile of the air sample collected in the urban area of Algiers separated into β -DEX 120: numbering as in Table 2 (6: *para*-xylene; 6': *meta*-xylene).

zene); (3) m/z 119 (i.e., 1-ethyl-3,5-dimethylbenzene, 2-ethyl-1,4-dimethylbenzene, 4-ethyl-1,2-dimethylbenzene and 1,2,4,5-tetramethylbenzene).

The alkanes *n*-heptane, *n*-octane and *n*-nonane

have been identified using their characteristic ion fragments, combined with retention times.

From about 40 compounds detected in the air samples, 26 (mainly aromatics ones) were identified.

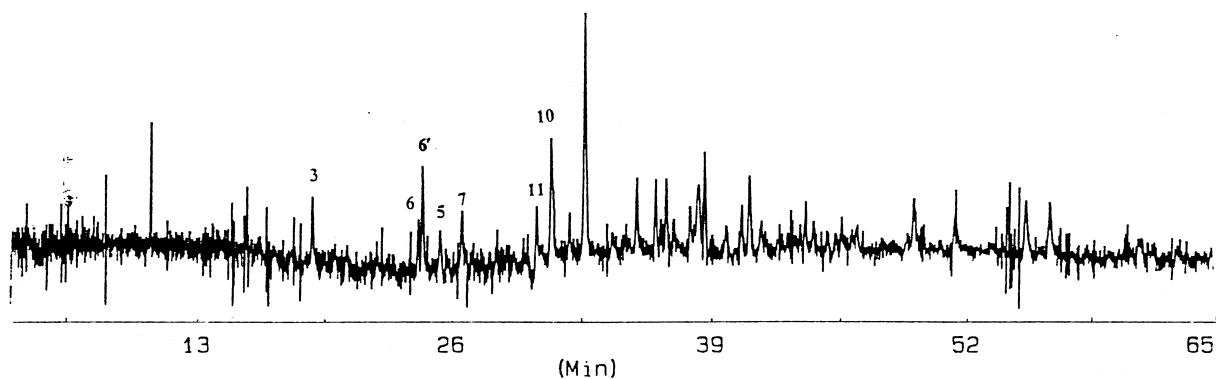


Fig. 3. GC-FID profile of extracts of vapors of petrol vehicles exhaust obtained by SPME separated into β -DEX 120: numbering as in Table 2 (6: *para*-xylene; 6': *meta*-xylene).

Table 3
Elution order of some VOCs separated with CP SIL 8 CB and β -DEX 120 capillary columns

| Elution order in CP Sil 8 CB | Elution order in β -DEX 120 |
|-------------------------------------|-----------------------------------|
| Benzene | <i>n</i> -Heptane |
| <i>n</i> -Heptane | Benzene |
| Toluene | <i>n</i> -Octane |
| <i>n</i> -Octane | Toluene |
| Ethylbenzene | <i>n</i> -Nonane |
| <i>para</i> -/ <i>meta</i> -Xylenes | <i>para</i> -Xylene |
| | <i>meta</i> -Xylene |
| <i>ortho</i> -Xylene | Ethylbenzene |
| <i>n</i> -Nonane | <i>ortho</i> -Xylene |
| Propylbenzene | 1-Ethyl-3-methylbenzene |
| 1-Ethyl-3-methylbenzenes | Propylbenzene |

BTEX compounds (benzene, toluene, ethylbenzene and xylene) were found to be the important pollutants, benzene and toluene were the most predominant compounds, and assess for respectively 15.4 and 21.0% of the total. The aliphatic hydrocarbons were present at lower extent. The presence of limonene may be related to biogenic emission of trees sited near our air sampling equipment.

The most important observation that can be derived by looking at the chromatogram in Fig. 1 and at the data reported in Tables 1 and 2 is that in any cases, the retention indices and the percentage of *para*- and *meta*-xylenes are given together because of their nonseparation in the usual capillary column (like CP Sil 8 CB used in this work). So, the chiral β -cyclodextrin capillary column allows a good improvement of separation of the isomers of alkylbenzene, as well as *para*- and *meta*-xylenes. The inversion of the elution order of some compounds was also observed as shown in Table 3. As these compounds present substituents at isomeric positions, this inversion can be attributed to the conic structure of β -cyclodextrin which leads to the formation of inclusion complexes.

It is worth noting that benzene is more retained in this phase allowing its quantitative analysis with accuracy since it is found to be eluted far from solvent used for extraction (carbon disulfide).

4. Conclusions

The sampling of organic compounds in Algiers

was done in the appropriate conditions; with adsorption through charcoal cartridge followed by solvent extraction with desorption coefficient up to 98%. The analysis of extracts with both GC-FID and GC-MS by combining MS data with retention index information has enabled the identification of 26 compounds, mainly aromatics ones, in the atmosphere of Algiers.

Perfect separation of arene isomers as well as xylene isomers was obtained in the β -cyclodextrin capillary column allowing its utilization in the qualitative and quantitative studies of VOCs in air using different sampling techniques.

The application of SPME in the sampling and extraction of VOCs provided satisfactory results. In particular, this technique was found well effective in adsorption and desorption of analytes, inexpensive, portable, solventless and also gave an interesting gain of time of extraction, desorption and analysis. More than 30 compounds could be detected; among them, the same species identified previously using adsorption-solvent extraction have been found. These studies show also that the road traffic is the dominant source of aromatic VOC emission in the Algiers area.

Finally, these results highlight the need to an intensive control of these VOCs pollutants present in the ambient air of Algiers. Particular concern should be focused onto benzene, due to its toxicity, and toluene owing to its high aerometric levels.

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