

## Analysis of some Volatile Organic Compounds by GC-MS

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### Abstract

*There have been settled the experimental conditions for the separation of some aromatic hydrocarbons from samples introduced in the chromatograph by injection and by thermal desorption. The identification of components has been achieved by means of retention times and also, by means of NIST spectra library. There have been collected air samples by adsorption on adsorbent tubes and there have been identified the separated components.*

**Keywords:** thermal desorption, GC-MS, Tenax, VOCs.

### Introduction

Volatile organic compounds (VOC) are organic substances with a pollutant effect upon the environmental – directly, by their toxicity and indirectly, by their contribution at the greenhouse effect and as precursors of photochemical smog. They present high vapor pressures and in normal conditions, they vaporize significantly and reach the atmosphere. These compounds are represented by any organic substance with an initially boiling point less or equal to 250<sup>0</sup>C, measured at a standard pressure of 101.3 kPa. There are about 150 compounds having this property, predominating hydrocarbons with 4-12 carbon atoms (paraffines, olefines, aromatics). In the presence of light, VOCs react to another pollutant, being in this way, the primary precursors of troposphere ozone formation and of suspension particles, which are the main components of smog. Stratospheric smog is good, because it adsorbs ultraviolet rays and protects people, plants and animals to dangerous radiations exposure. But ozone becomes harmful when it accumulates in the atmosphere, causing respiratory problems and, also, it can have an impact upon cultures and buildings [1].

Internationally organizations of environmental protection classify VOCs sources as following:

- Stationary sources: solvents, oil industry, chemical industry, burning sources, food industry, metallurgical industry, pharmaceutical industry, deposits treating, agriculture;
- Mobile sources: road traffic;
- Natural sources: vegetation (trees are important biological sources of isoprene and terpene) and agriculture crops [2].

VOCs emissions have a negatively impact upon air, soil and groundwater. VOCs affect also human health – they have irritant effects for eyes, nose and throat, leading to headaches, loosing of moving coordination, problems of central nervous system some VOCs cause cancer [3].

Gas chromatography /mass spectrometry (GC/MS) represents one of the most accurately techniques for organic pollutants analysis from the environmental. Recently researches [1,3,4] have followed elaboration of some rapidly analyses methods. By this technique there can be analyzed traces of volatile organic compounds (to  $10^{-12}$  g) [5-8]. The present paper forms a part of our ongoing program of research for the determination of volatile organic compounds according to the environmental legislation.

## Experiments and Results

The analyses have been carried out with high purity chromatographic reagents. The purity of all the chemicals (benzene, toluene, *o*-xylene, styrene and methanol) was stated to be more than 99.5 % mol. The apparatus used was Gas Chromatograph 3800 with FID detector and mass spectrometer Varian 4000. We used a Factor-Four type capillary Column VF-5ms (30 m  $\times$  0.25 mm ID, DF=0.25  $\mu$ m).

### The Experiment 1

The first experiment has aimed the determination of operation parameters, to separate the mixture containing benzene, toluene, *o*-xylene and styrene dissolved in methanol, the sample being introduced by injection in the chromatograph column.

Working procedure was the following: in a round bottom flask of 100 ml which contains about 75 ml methanols, there have been weighted portions of 100 mg from benzene, toluene, *o*-xylene and styrene. This flask has been brought to sign of 100 ml with the solvent methanol. The solution containing these four components has been kept on ice bath. From this solution, there has been extracted with a syringe 1  $\mu$ l and it has been injected in the chromatograph injector and the components detection has been achieved by means of FID detector. The identification of components has been made based on the retention times and by using NIST mass spectra library.

In fig. 1, there are presented the chromatogram and the retention times of the separated components, and in fig. 2-5 there are presented mass spectra of the organic substances separated from the analyzed sample.

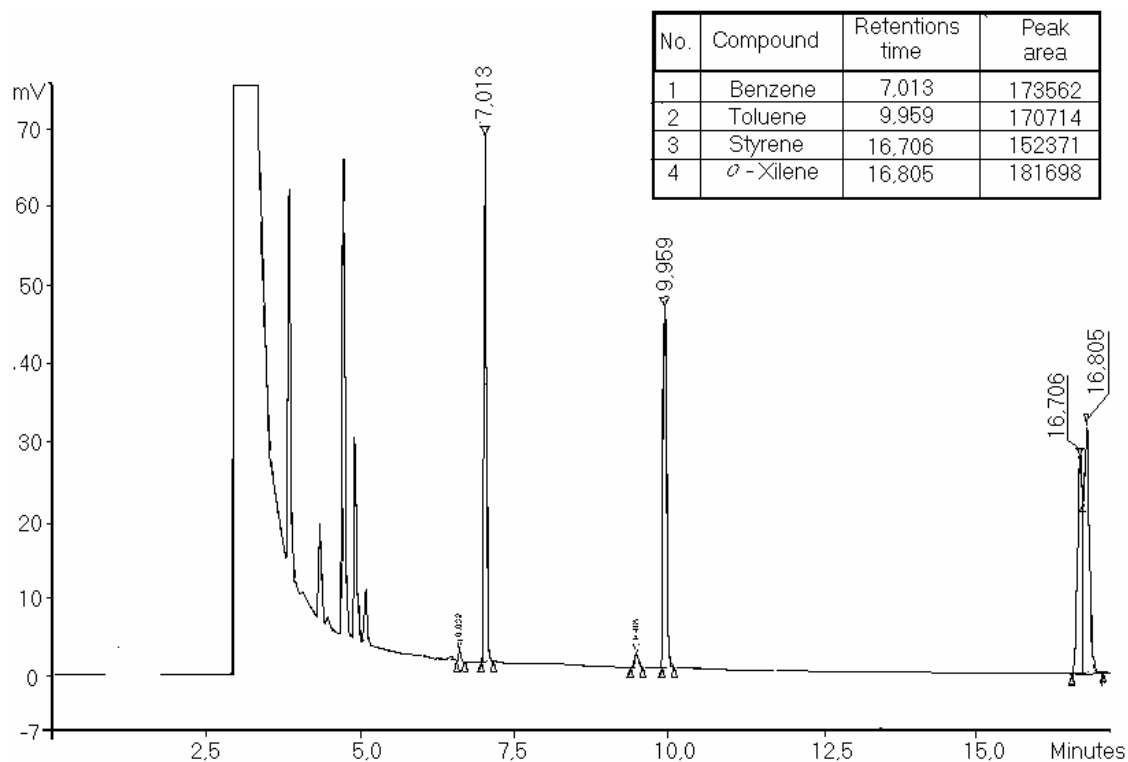
### The Experiment 2

This experiment has aimed the determination of operation parameters, to separate the mixture containing benzene, toluene, *o*-xylene dissolved in methanol, the sample being introduced by thermal desorption from adsorption tube in the chromatograph column.

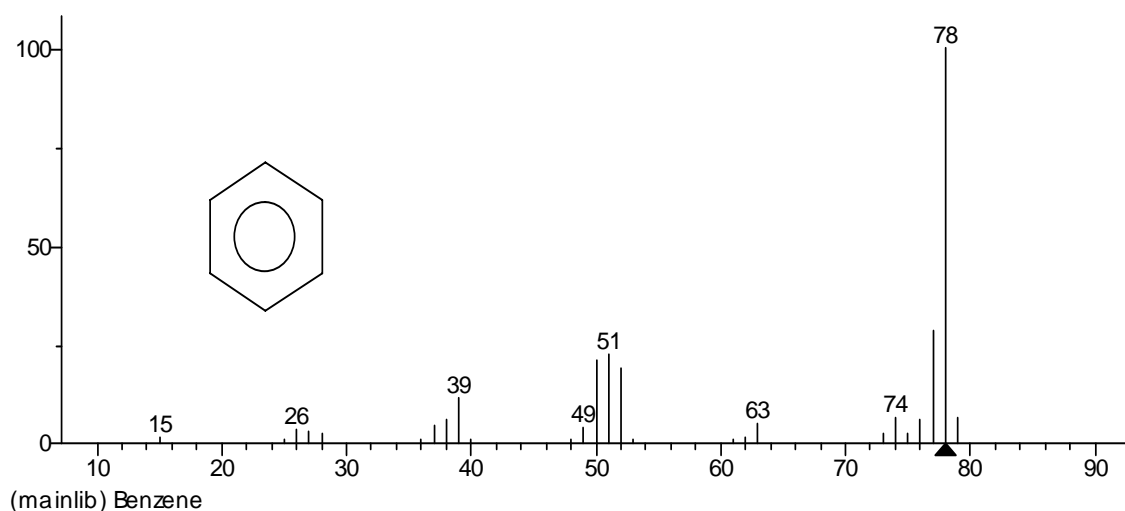
Working procedure was the following: in a flask of 100 ml which contains 75 ml methanol, there have been weighted portions of 10 mg benzene, toluene and *o*-xylene. This flask has been brought to sign of 100 ml with the solvent methanol. The solution containing these three components has been kept on ice bath. From this solution, there has been extracted with a syringe 1  $\mu$ l and it has been injected in the adsorbent tube. The adsorbent tube has been introduced in the desorption device of the chromatograph and the components detection has been achieved by means of FID detector.

There have been tested two types of adsorbent materials (Carbotrap-C/Carbotrap/Carbosieve – SIII and Tenax), but only Tenax has adsorbed all the analyzed compounds. Tenax is recommended for adsorption of aromatics, non-polar compounds with a boiling point higher than  $>100\text{ }^{\circ}\text{C}$  and polar components with a boiling point higher than  $150^{\circ}\text{C}$ . For thermal desorption of the analyzed hydrocarbons, there have been used adsorbent tubes of type AMA CBR 150.1 (Tenax).

In fig. 6, there are presented the chromatogram and the retention times of the separated components.



**Fig. 1** Chromatogram of volatile organic compounds separated from the sample introduced by injection



**Fig. 2** Mass spectrum of benzene

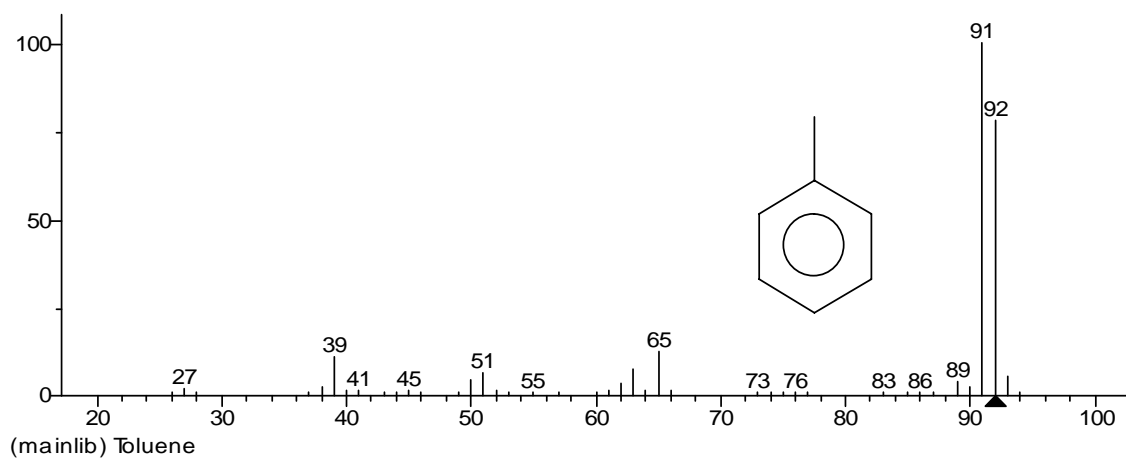


Fig. 3 Mass spectrum of toluene

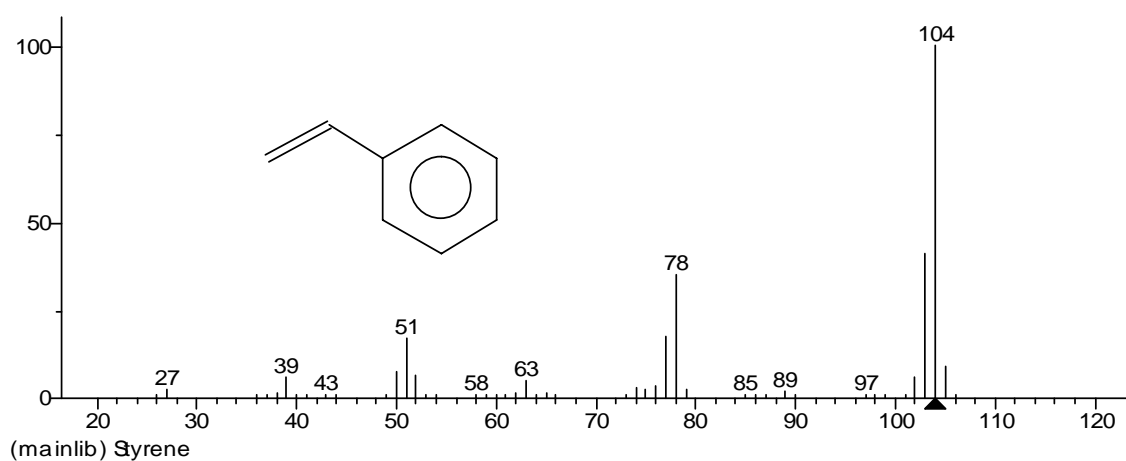


Fig. 4 Mass spectrum of styrene

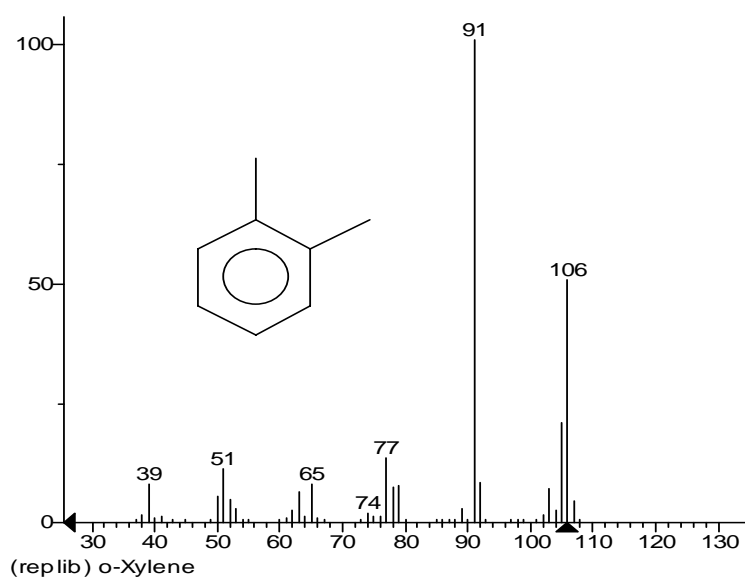
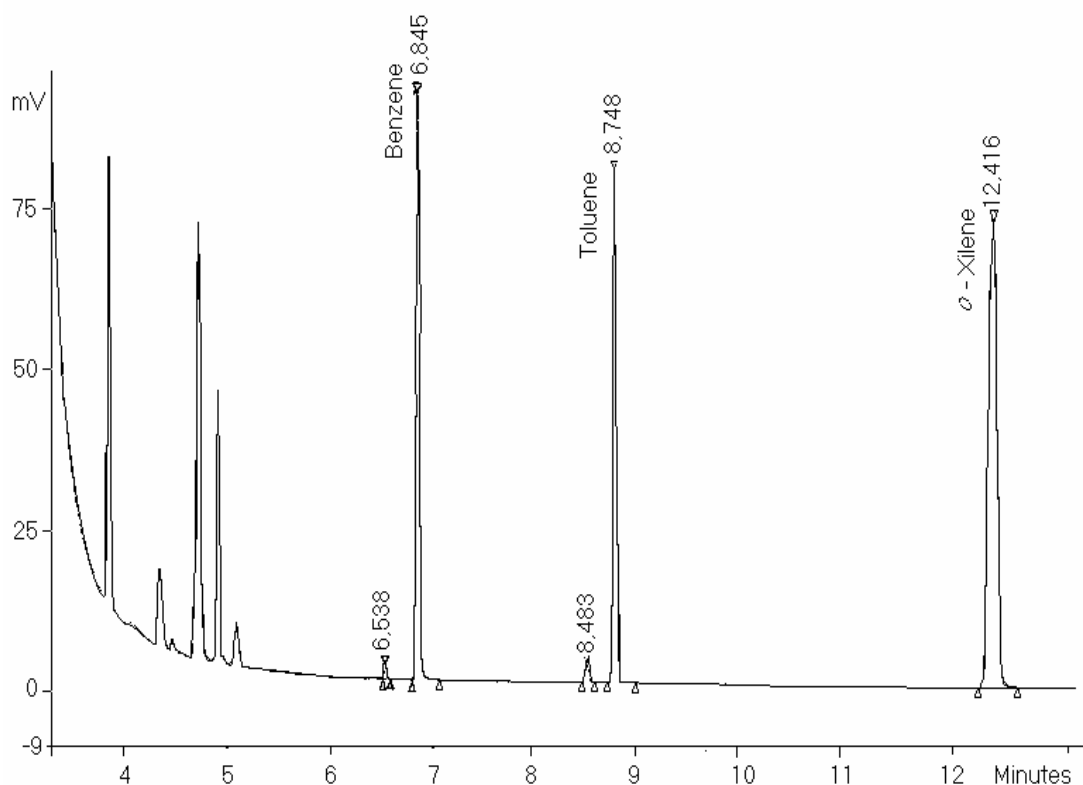


Fig. 5 Mass spectrum of o-xylene



**Fig. 6** The chromatogram of the separated volatile organic compounds from the sample introduced by thermal desorption

After the experimental study, there have been settled the necessary conditions for the separation of volatile organic compounds:

1. Operating conditions for the gas chromatograph 3800:

- temperature of injector 1177 type: 200<sup>0</sup>C;
- pressure: 16 psi;
- carrier gas: helium;
- carrier gas flow rate: 1.5ml/min;
- air flow rate: 300ml/min;
- detector: FID;
- detector temperature: 250<sup>0</sup>C;
- oven column regime (see Table 1):

**Table 1.** Oven column regime

Temperature <sup>0</sup> C	Heating rate <sup>0</sup> C/min	Residence time min	Total time min
50	-	4	4
90	20	7	13
140	10	0	18

2. Adsorbent tubes of type AMA CBR 150.1. Settled parameters for the thermal desorption unit have been the following:

- Desorption temperature: 250 °C;
- Desorption time: 10 min;

- Flowing rate of desorption: 30 ml/min;
- Inferior limit of the secondary trap: +30 °C to -30 °C;
- Carrier gas: helium;
- Carrier gas pressure: 0.90 bar.

3. Operation conditions of the mass spectrometer Varian 4000 are given in table 2.

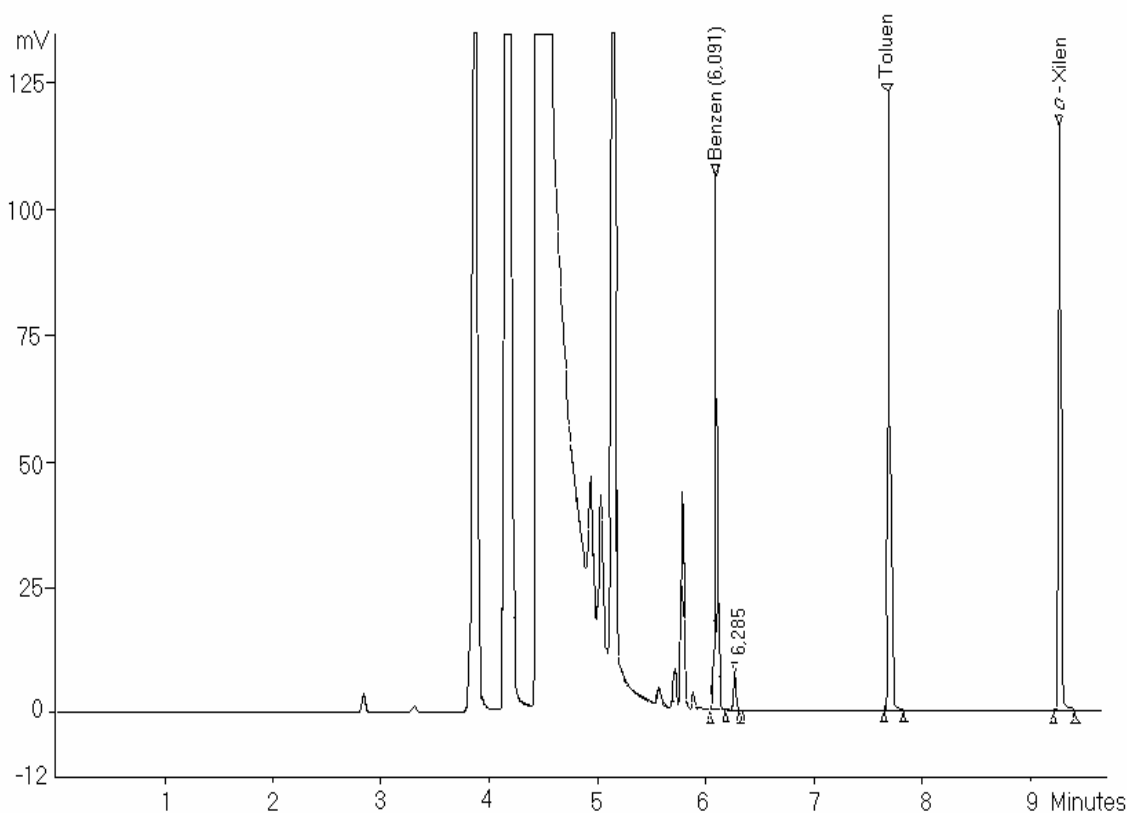
**Table 2.** Operation conditions of the mass spectrometer Varian 4000

Segment	Minimum Ratio, m/z	Maximum ratio, m/z	Storage limit RF m/z	Ionization factor, %	Filament
1	10	99	35	100	Stopped 0-2 min
2	100	249	35	100	Activated 2-15 min
3	250	399	35	100	
4	400	1000	35	100	

### The Experiment 3

This experiment has aimed collecting of some air samples from 4 working points, to identify the presence of some volatile organic compounds by GC-MS method. The samples have been collected conform to standard SR EN ISO 13649-2001 [9].

There has been used a sampling pump AMA type PN 7500. This contains a thermal sensor for an exactly measuring of air volume and Mass Flow Controller for the automatic control of flow rate.



**Fig. 7.** Ion-chromatogram for sample 4

The operating conditions for the sampling pump:

- flow rate 250 ml/min;
- sampled volume 7 l;
- sampling temperature 15 °C;

The sampling pump has been settled in the working point 1. There has been introduced an adsorption tube of type CBR 150.1 in the sampling pump device. There have been settled the working parameters and the pump has been started. At the experiment ending, the tube can be kept for 5-6 hours at ambient temperatures. The adsorbent tube is introduced in the thermo-desorption device. In parallel, it is opened the method for the gas chromatograph. Based on retention times from chromatogram (fig. 7), there have been identified the following components: benzene, toluene, *o*-xylene and styrene in the sample from the working point 1. Similarly chromatograms have been obtained from the working points 2 - 4.

## Conclusions

There have been elaborated two methods of volatile organic compounds analyzes. These methods are different by the samples introducing mode in gas chromatograph – by thermo-desorption and by injection.

Gaseous samples have been adsorbed in adsorbent tubes by means of a special pump. There have been tested two types of adsorbent materials (Carbotrap-C/Carbotrap/Carbosieve – SIII and Tenax), but only Tenax material has adsorbed all the analyzed compounds.

For both methods there have been settled optimal parameters for gas-chromatographic separation of the volatile organic compounds.

For the identification of volatile organic compounds there has been used the spectral library NIST.

In a future paper, there will be presented the calibration of analysis methods for volatile organic compounds, according to the environmental standards.

## References

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## Analiza prin GC-MS a unor compuși organici volatili

### **Rezumat**

*Au fost stabilite condițiile experimentale necesare separării hidrocarburilor aromatice din probele introduse în cromatograf prin injecție și prin desorbție termică. Identificarea componentelor s-a realizat prin indicii de retenție și cu ajutorul bibliotecii de spectre NIST. Au fost colectate probe de aer prin adsorbție pe tuburi adsorbante și au fost identificați componentii separați.*