# The Validation of Methods for the Analysis of Some Volatile Organic Compounds by GC-MS

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## Abstract

*The validation of GC-MS methods for the analysis of some volatile organic compounds (benzene, toluene, o-xylene, styrene, isoprene) from the air samples are presented. It was carried out by setting sensitiveness, the limits of detection, linearization, precision and selectivity of working procedures. The validation of GC-MS methods for determination of some volatile organic compounds showed that the used methods are sufficiently sensitive and the range of linearity was 4-5 size grades for all analyzed compounds. The studied methods have a good repeatability precision for the volatile organic compounds analyzed.*

**Key words:** *benzene, toluene, styrene, o-xylene, GC-MS*.

## Introduction

VOCs emissions have a negative 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.

For this reason, there is a growing interest in the last time for the determination of volatile organic compounds (VOCs) from the air. Gas chromatography /mass spectrometry (GC/MS) represents one of the most accurate techniques for organic pollutants analysis from the environment. Recent researches [1-4] have followed the elaboration of some rapid analyses methods. By this technique there can be analyzed traces of volatile organic compounds (to $10^{-12}$ g) [5-8].

As a continuation of previous work [9] related to the determination of volatile organic compounds by GC/MS, it was realized the validation of methods for benzene, toluene, *o*-xylene, styrene and isoprene determination.

## Experimental Method

The analyses have been made with high purity chromatographic reagents. The purity of all the chemicals (benzene, toluene, *o*-xylene, styrene and isoprene) was stated to be more than 99.5 %. The apparatus used was Gas Chromatograph with FID detector and mass spectrometer Varian

4000. There was used a Factor-Four type capillary Column VF-5ms (30 m $\times$ 0.25 mm ID, DF=0.25 $\mu$ m), and adsorbent tubes of type AMA CBR 150.1.

Operating conditions for the gas chromatograph: temperature of injector: $200^0$C; pressure - 16 psi; carrier gas - helium; carrier gas flow rate - 1.5ml/min.; air flow rate - 300 ml/min; detector type – FID; detector temperature - 250 $^0$C; oven working regime (see Table 1):

**Table 1.** Oven working regime

| Temperature ($^0$C) | Heating rate ($^0$C/min) | Residence time (min) | Total time (min) |
|---|---|---|---|
| 50 | - | 4 | 4 |
| 90 | 20 | 7 | 13 |
| 140 | 10 | 0 | 18 |

## Results and Discussion

The validation of GC-MS methods for the determination of some volatile organic compounds (benzene, toluene, o-xylene, styrene, isoprene) was realized by setting the following parameters: sensitivity, detection limit, method linearity, linearization, precision, and selectivity.

### Sensitivity of the methods for volatile organic compounds determination

The sensitivity, *S*, of a gas-chromatographic method is defined by the following equation:

$$S = \frac{\Delta R}{\Delta C} \tag{1}$$

where $\Delta$C represents the concentration variation and $\Delta R$ is the variation of detector signal.

The variations of detector signal with the concentration of organic compound analyzed are shown in figs. 1-5 and offer the possibility to calculate the sensitivity S. The values obtained are presented in table 2.

**Table 2.** Detection sensitivity of some organic compounds

| Organic compound | Sensitivity *S*, mV/ppm | Minimum of detection limit $C_m$, ppm |
|---|---|---|
| benzene | 0.1968 | 0.101 |
| toluene | 0.1691 | 0.118 |
| styrene | 0.1133 | 0.176 |
| *o*-xylene | 0.00921 | 2.173 |
| isoprene | 0.1372 | 0.145 |

### Detection limit of the methods

FID minimum detection limit $C_m$ can be calculated with the formula:

$$C_m = \frac{2N}{S} \tag{2}$$

where *N* is the noise level of the chromatogram;

   *S*- the sensitivity.

Considering a noise level $N = \pm 0{,}01$ mV, the values for minimum detection limits of the organic compounds analyzed are also presented in table 2. The values are higher than those reported in similar studies [10].

Detection limit for MS: according to selected method, molar masses of organic compound studied are situated in range 50-106 m/z.
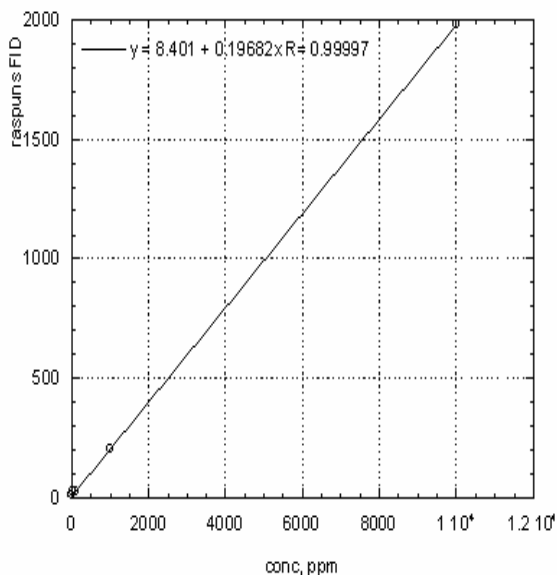


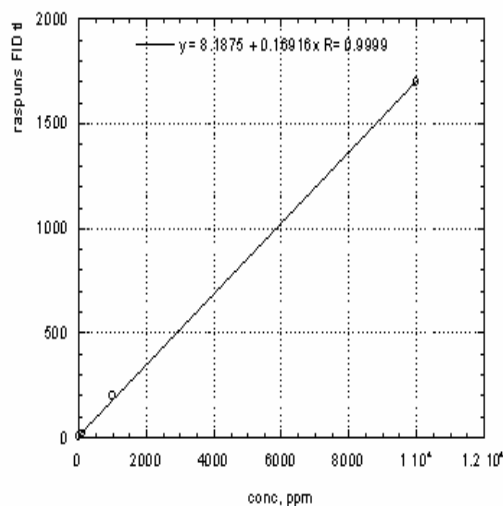**Fig.1**. FID detector response for different benzene concentrations



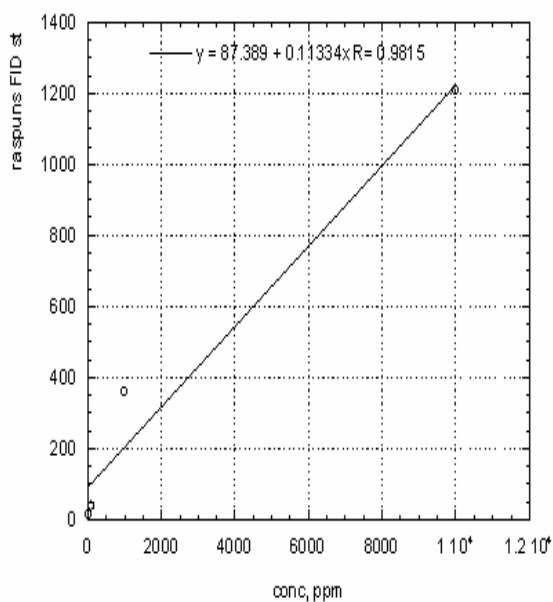**Fig.2.** FID detector response for different toluene concentrations



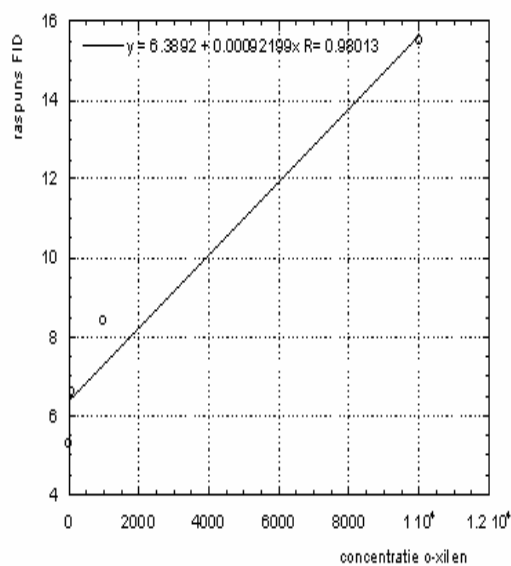**Fig.3.** FID detector response for different styrene concentrations



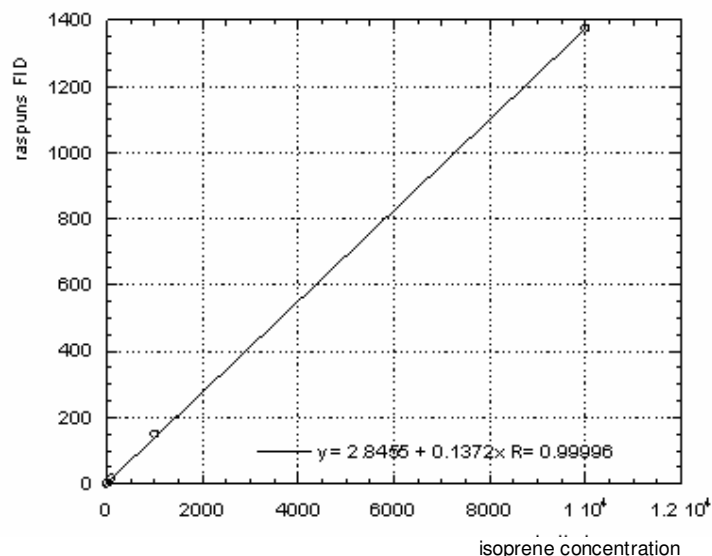**Fig.4**. FID detector response for different *o*-xylene concentrations

**Fig.5**. FID detector response for different isoprene concentrations

## Method linearity

It was traced the calibration plots for different concentrations of benzene, toluene, styrene, isoprene şi *o*-xylene, dissolved in *n*-heptane to settle method linearity. The concentration of standard solutions was 10 mg/ml, 1 mg/ml, 0,1 mg/ml, 10 μg/ml and 1 μg/ml respectively.

The correlation lines for the five studied organic compounds and the values for correlation coefficients are shown in fig. 6-10. The correlation coefficients of the calibrating plots have optimal values, being in the range 0.99-1, which demonstrate a good linearity of the organic compounds method determination for the analyzed compounds.
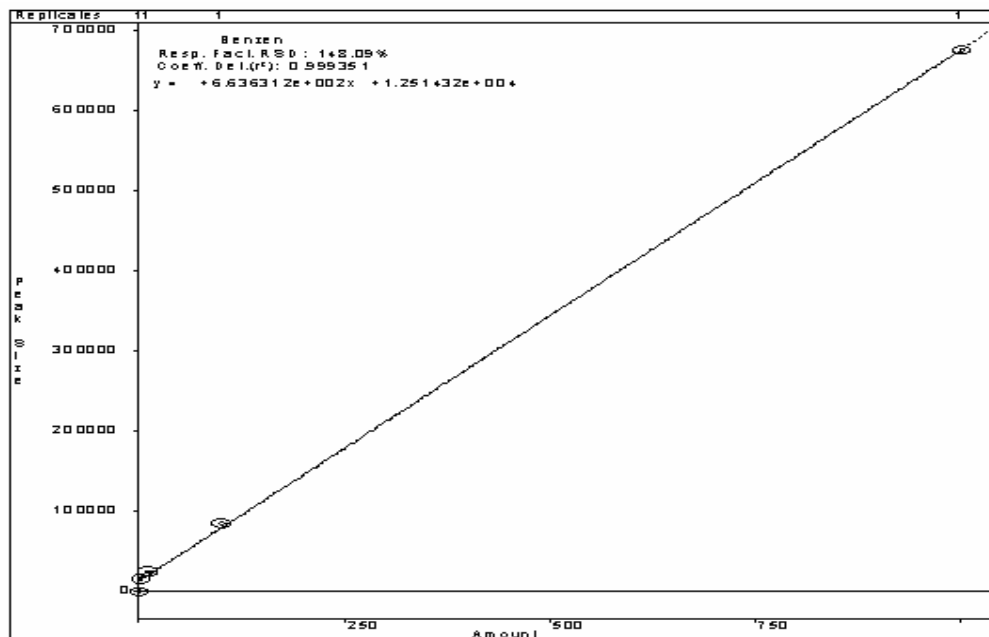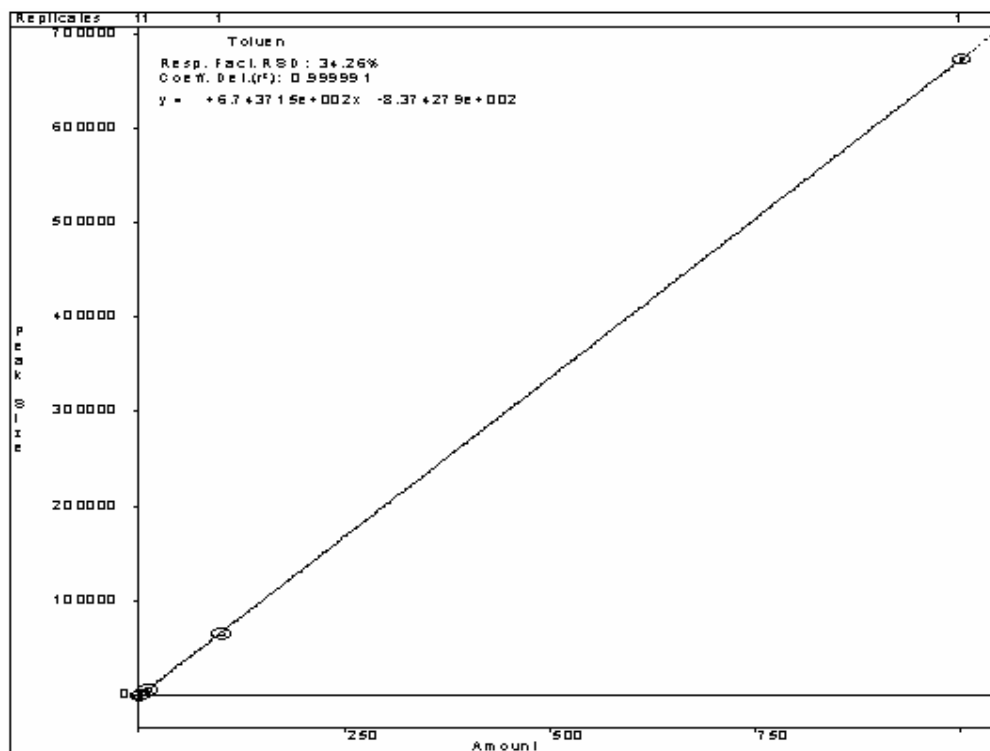


**Fig. 6** The calibration plots for benzene

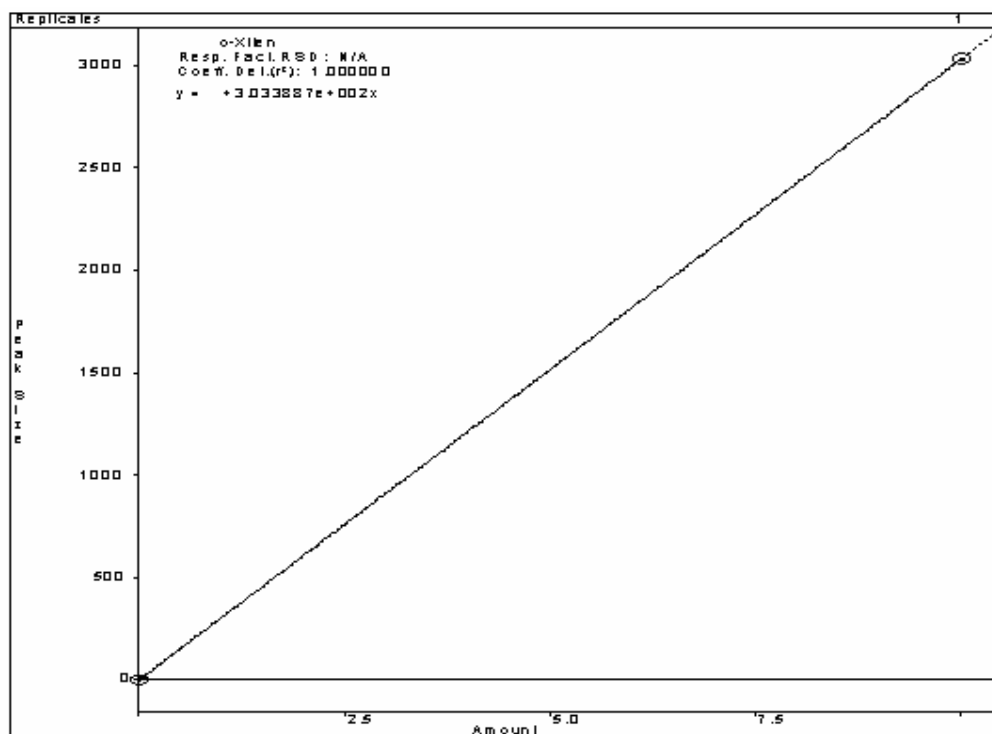**Fig. 7** The calibration plots for toluene



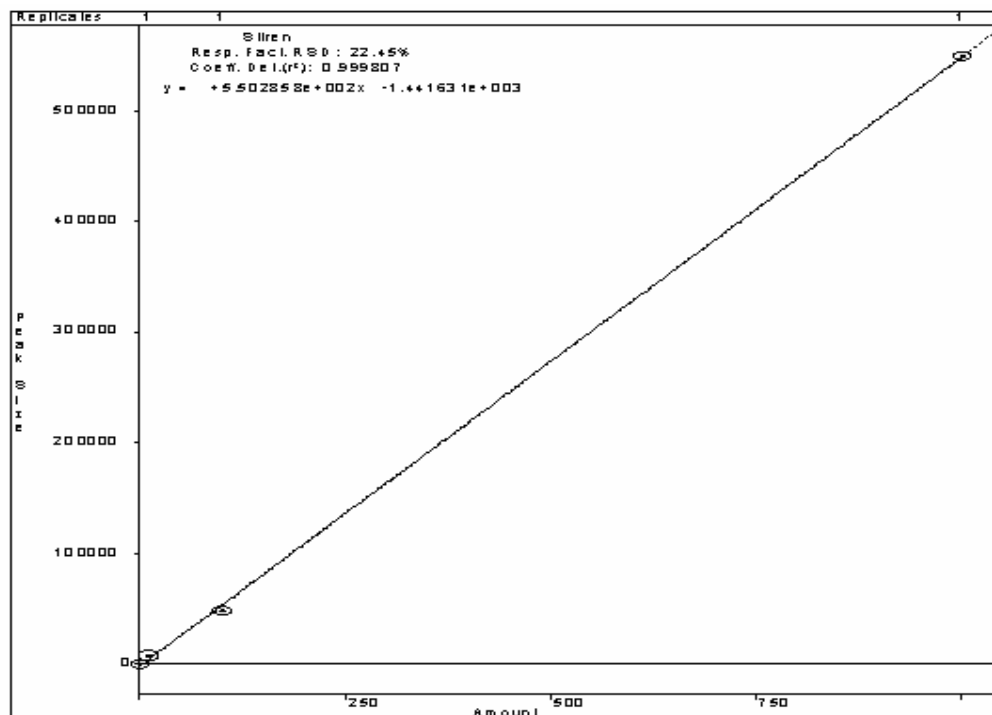**Fig. 8** The calibration plot for *o*-xylene
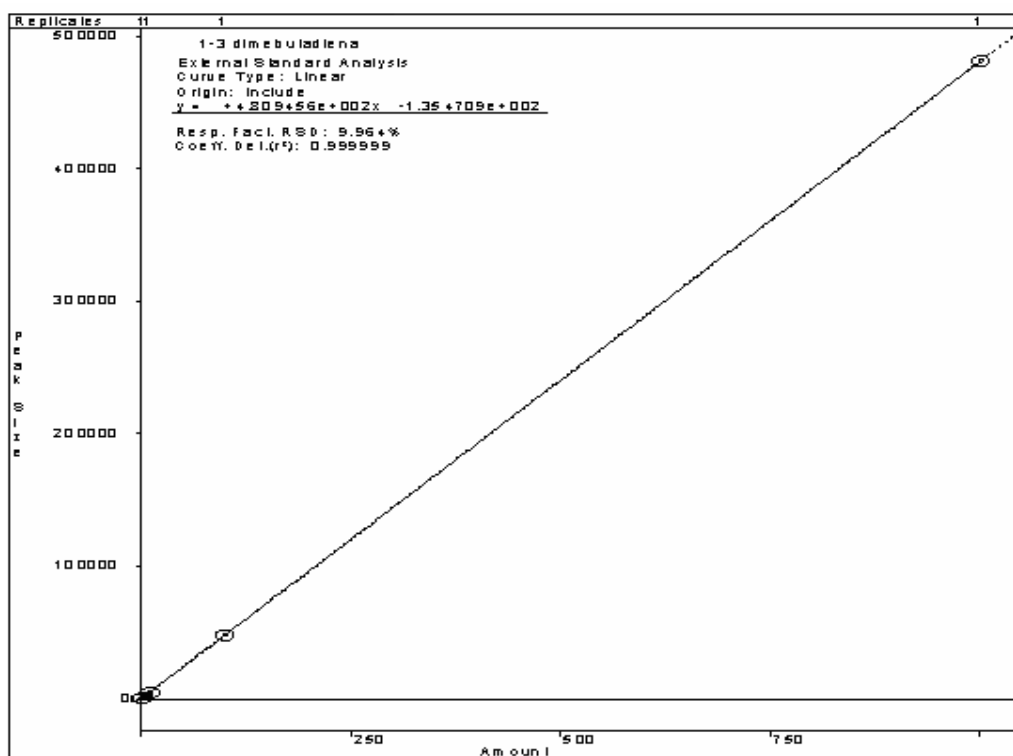
**Fig. 9** The calibration plots for styrene



**Fig. 10** The calibration plots for isoprene

## Method precision

The study of repeatability precision consists in successive analysis of the same sample, in the same day, with the same gear and reagents, realized by the same analyst.

The repeatability precision was estimated using standard deviation $\sigma$ of 5 independent determinations, using the following formula:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n-1}} \qquad (3)$$

where: $n$ is the number of determinations and $\overline{x}$ - arithmetic average of the $x_i$ values.

The calculated values of the standard deviations are presented in table3.

**Table 3** The method repeatability

| VOC | Retention time, min. | Peak area, V˙s | Arithmetic average of retention time, min. | Standard deviation of retention time, min | Arithmetic average of peak area, V˙s | Standard deviation of peak area, V˙s |
|---|---|---|---|---|---|---|
| Benzene | 7.017 | 84321.36 | 7.012 | 0.008 | 84321.33 | 0.40 |
|  | 6.997 | 84320.63 |  |  |  |  |
|  | 7.014 | 84321.52 |  |  |  |  |
|  | 7.015 | 84321.50 |  |  |  |  |
|  | 7.016 | 84321.64 |  |  |  |  |
| toluene | 9.959 | 65147.00 | 9.958 | 0.002 | 65146.59 | 0.48 |
|  | 9.954 | 65146.25 |  |  |  |  |
|  | 9.958 | 65146.00 |  |  |  |  |
|  | 9.958 | 65146.05 |  |  |  |  |
|  | 9.959 | 65147.64 |  |  |  |  |
| styrene | 14.955 | 48328.67 | 14.955 | 0.002 | 48328.40 | 0.34 |
|  | 14.951 | 48328.89 |  |  |  |  |
|  | 14.956 | 48328.45 |  |  |  |  |
|  | 14.957 | 48328.74 |  |  |  |  |
|  | 14.956 | 48328,24 |  |  |  |  |
| isoprene | 4.011 | 47779.21 | 4.009 | 0.001 | 47779.33 | 0.33 |
|  | 4.008 | 47779.52 |  |  |  |  |
|  | 4.009 | 47779.81 |  |  |  |  |
|  | 4.010 | 47779.01 |  |  |  |  |
|  | 4.009 | 47779.98 |  |  |  |  |
| *o*-xylene | 15.530 | 54557.25 | 15.525 | 0.006 | 54557.45 | 0.36 |
|  | 15.515 | 54557.35 |  |  |  |  |
|  | 15.525 | 54557.85 |  |  |  |  |
|  | 15.528 | 54557.02 |  |  |  |  |
|  | 15.527 | 54557.78 |  |  |  |  |

## Selectivity

GC-MS is a very selective instrumental method of analysis because it allows a good chromatographic separation and VOC identification through their characteristic mass spectra. This technique allows to know the proportion of compound that co-elute at the same retention time thanks to the selection of a VOC characteristic ion that is not present in the mass spectrum

of that VOC which co-elutes with [10]. Chromatographic separation was good for all organic compounds analyzed in this work.

## Conclusions

The validation of GC-MS methods for the determination of some volatile organic compounds showed that the used methods are sufficient sensitive and the range of linearity (ppm) was from 4 to 5 order of magnitude for all analyzed compounds. The studied methods are very selective and have a good repeatability for all the volatile organic compounds analyzed.

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# Validarea metodelor pentru analiza unor compuşi organici volatili prin metoda GC-MS

## Rezumat

*Această lucrare prezintă un studiu asupra validării metodelor GC – MS pentru determinarea unor compuşi organici volatili (benzen, toluen, o-xilen, stiren, izopren) prezenţi în aer, prin stabilirea sensibilităţii, a limitei de detecţie, a liniarităţii, preciziei şi selectiviăţii metodelor de lucru. Validarea metodelor GC – MS pentru determinarea unor compuşi organici volatili a arătat că metodele sunt satisfăcător de sensibile şi că toţi compuşii analizaţi prezintă domenii de liniaritate (ppm) de la 4 la 5 ordine de mărime. Metodele dezvoltate sunt foarte selective şi prezintă o bună repetabilitate pentru toţi compuşii organici volatili investigaţi.*