

## ANALYSIS OF SUBSTANCES IN AIR BY USING GC/MS METHOD WITH SORPTION TUBES TENAX

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### Abstract

*For the purposes of identification of hazardous substances in the atmosphere a conventional analytical method consisting in a capture on adsorption tube Tenax and subsequent analysis of thermo desorption device of gas chromatograph with mass detector has been studied. In order to achieve maximum sensitivity, an optimization of the air sampling process with devices has been performed (those devices are available at some units of Fire Rescue Services). A possibility of semi-quantitative determination of identified substances has also been evaluated.*

### Keywords

*Air sampling, gas chromatograph with mass detector, volatile organic compounds, adsorption tube, thermo desorption device, chemical detector CHP – 71.*

## INTRODUCTION

Different properties of organic dangerous substances as potential contaminants of the environment during extraordinary events solved by Fire and Rescue Service units require different approaches to modification of samples and analytical elaboration.

Chemical laboratory at Population Protection Institute has at disposal, for above mentioned purposes, mobile chemical chromatograph with a mass detector EM 640. Commonly the procedures of the analysis through the system GC/MC are familiar but for each device and purpose of use it is necessary to optimize and verify familiar common methods. Its part must also be the evaluation of the possibility of implementation in terrain conditions.

## I. PRINCIPLES AND METHODS DESCRIPTION

Methods of substance analysis in the atmosphere through the method GC/MC with sorption tubes Tenax is designed for identification and determination of volatile organic substances in the air<sup>1</sup>. Substances in the flow of air go through the absorption tubes and absorb themselves on the sorbent Tenax. In the thermo-desorption module of the device it comes to the desorption of analyzed substances and further to their separation on a chromatography colony. The software of a mobile gas chromatograph with a mass detector EM 640 Bruker DataAnalysis compares measured mass spectra of analyzed substances to spectra stored in libraries and will perform identification of unknown organic substances in the sample. The area of a

chromatographic peak of a given substance is to a certain extent of concentration proportional to the concentration of a substance in the atmosphere.

The capture of analyzed substances through adsorption has its advantages among them especially belong:

- simple manipulation and transport,
- possibility to concentrate the analyzed components,
- possibility to obtain analyzed component in an original state, i.e. without a chemical change.

Tenax belongs among synthetic sorbents which are used abundantly at present. Their main priority is the fact that through their targeted preparation it is possible to achieve required properties. Tenax is chemically poly-2,6-difenyl-p-fenyleneoxide<sup>2</sup> with a specific surface 19 to 30 m<sup>2</sup>/g. Studying its properties<sup>3,4</sup> it was found out that it is an extremely suitable sorbent of most significant volatile organic substances type alkanes, aromatic carbohydrates and chlorinated carbohydrates both from the air sorption and the following thermal desorption viewpoint.

The principle of the capture of analyzed substances on the sorbent brings the possibility of the application of two approaches which flow from possible elution of analyzed substances out of the sorbent by the flow of analyzed air<sup>5</sup>:

- only such amount of the air is infiltrated by the tube, so there does not occur the elution of the most volatile component from the sorbent,
- such amount of the air is infiltrated by the tube until not only the penetration of analyzed substances through the tube occurs but also fixation of balance between the concentration of analyzed substances in the air and on the surface of the sorbent.

For the analysis of quite unknown substances it is therefore necessary to make the compromise, in order that the extraction of adsorption was the highest and the method for different analytes was that way the most responsive. This is actual just in case of sorbent Tenax whose specific surface is not e.g. in comparison with active coal too large.

In the experimental phase, especially for air sampling, the dependencies of the amount of adsorbed substances on the time and velocity of infiltration for volatile organic substances of different properties were studied.

## **II. OPTIMIZATION OF THE METHODS FOR AIR SAMPLING WITH SORPTION TUBES TENAX**

### **1. Performance of experiments**

During studies, four substances were analyzed as the representatives of organic substances of various properties:

- n-Heptane – non-polar, a little volatile substance,
- n-Butanol – polar, a little volatile substance,
- Methyl ethyl ketone – polar volatile substance,
- Chlorine-benzene – medium polar and medium volatile substance.

Precise concentrations of above mentioned substances were prepared in the flow of filtrated air with the aid of Dynamic calibration unit SYCOS K\_DPG (Ansyco, SRN) with adjustable air discharge. This way the aerial mixture of substances with concentration of 2 – 4 ppm and then the mixture with concentration say about 2,5 times higher were prepared. The output of calibration unit was conducted through the adsorption tube Tenax (SKC Inc., USA charge n. 3106) for definite time and at definite air flow.

The analysis of substances was performed with the thermo-desorption equipment of a gas chromatograph with a mass detector EM 640. GC/MS analysis was performed during the following chromatograph program and parameters of measurement:

- Column: HP-5 MS, length 25 m, Ø 0,32 mm, phase 1 µm.
- Carrier gas: filtrated air 300 hPa.
- Temperature: T Inlet 180 °C, T Injection 200 °C.
- Scan range : 30-400 amu.
- Desorption : 1,5 minuts at 220°C.
- Spray: 20 s.
- GC program : 40 °C – 2 min, from 40°C to 130°C dT/dt 5 °C/min, from 130 °C to 220°C dT/dt 20°C/min. 220°C – 1 min.

## 2. Dependence of the extraction of adsorption on the time of air infiltration

Time dependence of the amount of substances which entrap on the tube adsorbent are stated in picture 1 and 2. For illustration of the effect of the infiltration time, various concentrations of substances were chosen, respectively 2 till 4 ppm (pict. 1) and further concentration say about 2, 5 times higher (pict. 2).

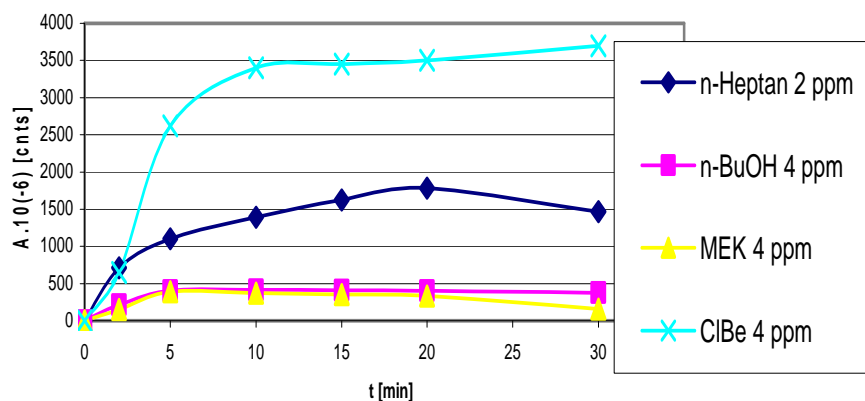
Dependencies in the pictures prove that for both chosen spheres of concentration the dependence of the amount of entrapped substance on adsorbent, expressed by the area of a chromatographic peak after GC/MS analysis is similar to the time of infiltration.

The amount of entrapped **n-Heptane**, as a non-polar, little volatile substance grows with the time of infiltration but with relatively low steepness up to 15 – 20 minutes. During longer times of infiltration the amount moderately drops as a consequence of the elution of non-volatile substance from the tube by flowing air.

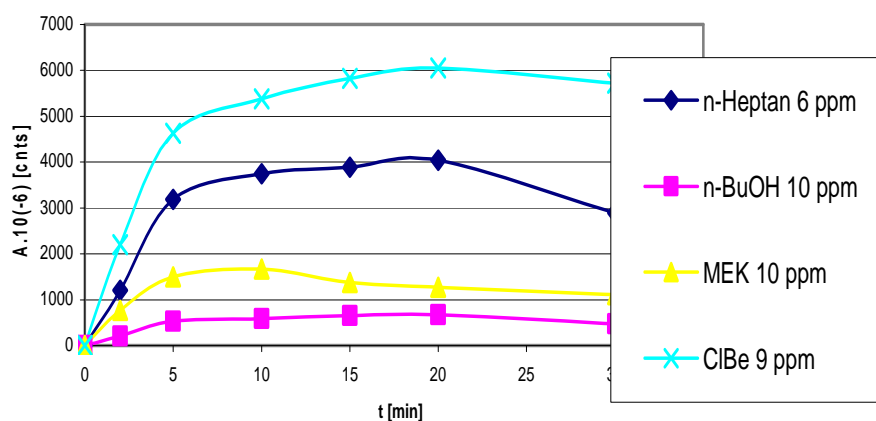
Quite different is the time dependence of the amount of entrapped **1-Butanole**, ie. polar, little volatile substance. Just after 5 minutes the balance between concentration of the substance in the infiltrated air and the concentration on the surface of the adsorbent originates. Therefore with further prolongation of time of infiltration at the air flow of 0,5l/min the adsorbed amount does not almost change.

The most volatile of studied substances – **Methylethylketone** – the amount of entrapped substance grows with the time of infiltration up to 5 – 10 minutes, which is maximal. By further air flow the take down of already adsorbed substance occur and also decrease of the extraction of the adsorption which up to 20 minutes is not substantial; however, distinctly manifests during infiltration of 30 minutes.

*Picture 1*  
Time dependence of the vapour capture on the tube Tenax,  
air flow 0,5 l/min



*Picture 2*  
Time dependence of the vapour capture by sorption tube Tenax,  
air flow 0,5 l/min



The amount of adsorbed **Chlorine Benzene** as the representative of medium polar and medium volatile substances grows with the time steeply up to time of 5-minute infiltration. After the steepness of the grow of the amount of entrapped substance drops and during the time of infiltration of 15 – 20 minutes the balance between concentration of the substance in infiltrated air and the concentration on the

surface of the adsorbent occur and is characterized by minimal changes of the amount of adsorbed substance with the time of infiltration.

Globally it is possible to assess that the optimal time for infiltration during the air flow of 0,5l/min and in a given extent of substance concentration in the air amounts 20 minutes and from the viewpoint of the extraction of adsorption it represents the compromise for substances of various properties.

### 3. The dependence of the extraction of adsorption on the air flow

The influence of the air flow speed ( $Q$ ) on the amount of the substance entrapped on the adsorbent was studied during the time of air infiltration for 20 minutes and concentration of analyzed substances in the air 2 -4 ppm. The air flow was adjusted from 0,1 – 5,0 l/min. Dependencies are graphically expressed in picture 3.

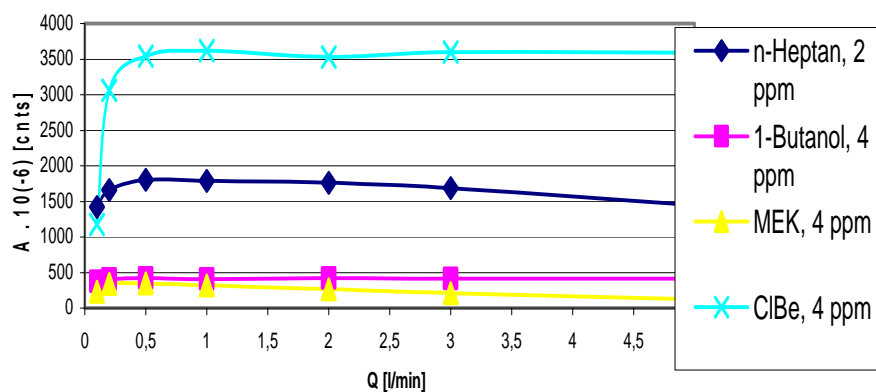
With the growing air flow, **Chlorine Benzene** and **1-Butanol** are reacting in the Tenax tube similarly. The amount of the absorbed substance grows during 20-minute time of infiltration into the air flow of 0,5l/min and further increase of the speed of the flowing air does not influence the extraction of adsorption.

Similar are also dependencies of the amount of entrapped **n-Heptane**, as non-polar non-volatile substance, and **Methylethylketone**, i.e. volatile substance. With the growing air flow the extraction of adsorption increases up to the velocity of infiltration 0,5 l/min. With further increase of the flow the entrapped amount does not almost change up to the speed of 2 l/min, whilst even higher flows cause elution of substances of the sorbent.

From the dependence flows that during 20 minutes of infiltration the optimal air flow through the tube amounts 0,5 l/min.

Picture 3

*The dependence of the capture of vapourized substances by a sorption tube Tenax on the velocity of the air-flow, time of infiltration 20 minutes*



#### **4. The conclusions of the optimization of the methods of sampling and their implementation in the practice of FRS**

Studying the capture of the vapours of substances of various properties (polar, non-polar, volatile and little volatile) by sorption tubes Tenax in order to do consequent analysis by a mobile gas chromatograph with a mass detector EM 640 and by the usage of thermo-desorption device it was found out that from the viewpoint of the achievement of a maximal sensitivity of the analysis, the procedure of the adsorption of air infiltration by the tube for **20 minutes** at the air flow **0,5 l/min.** is optimal. This corresponds to the amount of 10 l of infiltrated air.

The main final goal of the study was determination of optimal methods of air sampling both for Units of Fire Protection and chemical laboratories of regional FRS. Some of the units – not all of them though – are equipped with a gas consumption pump PCXR 4 where the flow 0,5l/min is adjusted. All units dealing with the air sampling are, however, equipped with a chemical probating device CHP-71. Therefore in the frame of the task solution the attention was also given to the possibility of the reach of required flow on this device.

For this purpose various tubes (regarding their different resistance) which are delivered with this device and their number in the chamber of the probator and measurement of the amount of flowing air were tested.

The result of these tests was the discovery that the flow of 0,5l/min is possible to achieve with satisfactory exactness in this way: Into the chamber of probating tubes are placed (from the left side while looking opposite the chamber) 2 open probating tubes for mustard gas (with a yellow stripe) and 2 closed tubes. The regulator of the air flow is adjusted up to the utmost zero position. On the intake of the probator is added by the hose the adsorption tube and the probator is switched on. You slowly turn the regulator of the air flow until you hear the pump work. Consulting the producer we discovered that this method is possible to use also with the innovated probator CHP-5.

This procedure of air sampling was introduced into the practice of chemical laboratories and in some units of FRS by classifying into the Order of chemical service of FRS CR<sup>6</sup>.

In practice of intervening teams of Population protection institute and chemical laboratories of FRS of regions is the optimized procedure currently used for the identification of substances. However, very often the applicants ask the intervening teams to estimate the concentration of identified substances. So far, for this, however, the chemical laboratory has not got needed groundwork. Therefore it was necessary to deal with the dependence of the response of the gas chromatograph on the concentration of substances in the air taken by a sorption tube Tenax<sup>7</sup>.

### **III. SEMIQUANTITATIVE DETERMINATION OF SUBSTANCES IN THE AIR**

#### **1. Performance of experiments**

During the study the substances were analyzed as the representatives of organic substances of various properties as stated in table 1.

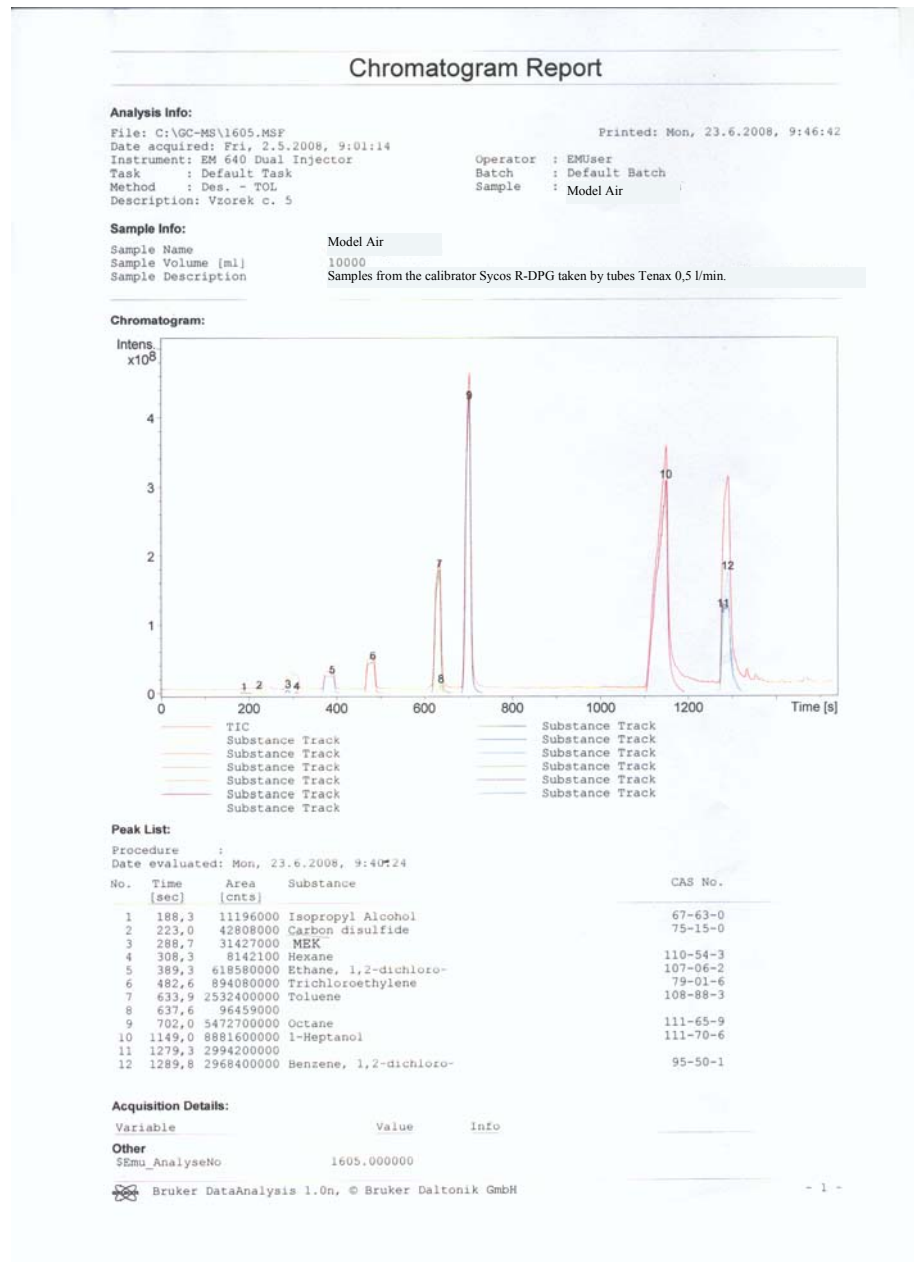
Exact concentration of these substances were prepared in the flow of filtrated air with a Dynamic calibration unit SYCO K-DPG (Ansyco, SRN) described in optimization methodology. The air flow was set up on 0,5l/min. The output of the calibration unit was conducted through the adsorption tube Tenax (SKC Inc., USA, charge n. 3106) for 20 minutes, so the conditions for the air intake was followed according to the Order of chemical service of FRS CR<sup>6</sup>.

*Table 1*  
*List of analyzed substances*

<i>Substance</i>	<i>Specification</i>	<i>Characteristics</i>	<i>Range of measured Concentrations [ppm]</i>
Carbon disulphide	p.a., Merck, charge n. EB 125 514	non-polar, highly volatile	0,063 – 5,0
n-Hexane	pa, 96%, Anasolv-V, Analytics Prague	non-polar, volatile	0,029 – 2,3
2-Butanone	p.a., Riedel-de Haën	medium polar, volatile	0,042 – 3,3
Ethane, 1,2-dichloro	Lachema	non-polar, medium volatile	0,048 – 3,8
Trichlorethylene	pur., Merck, charge n. K 31883158	medium polar, medium volatile	0,042 – 3,3
Toluene	p.a., Merck, charge n. K 20567325	non-polar, medium volatile	0,035 – 2,8
Isopropyl Alcohol	p.a., Lachema	highly polar, medium volatile	0,049 – 3,9
n- Octane	Lachema	non-polar, non-volatile	0,023 – 1,8
n-Heptanole	pur., Fluka, charge n. 2630391087	polar, non-volatile	0,027 – 2,1
Benzene, 1,2-dichloro	pro synt., Merck, S 3891938	medium polar, non-volatile	0,033 – 2,6

Determination of substances was carried out with the aid of thermo-desorption device of a gas chromatograph with a mass detector EM 640. BC/MS analysis was carried out at the same chromatographic program and parameters of measurements as the optimization of air sampling.

For each substance and concentration 2 parallel measurements were carried out. The result of measurements was a chromatogram of the mixture of substances, example in picture 4. On chromatograms the area of individual peaks was evaluated.



Picture 4  
 Chromatogram of the mixture of analyzed substances



## 2. Calibration

For individual substances the dependence of the peak area in units cnts on the concentration of the substance in the air mixture was made and elaborated with the aid of a statistic software<sup>8</sup>. It was discovered that in the range of concentrations according to the table 1 these dependencies are linear. The example of a calibration straight line is in picture 5.

Parameters of these straight lines described by the formula:

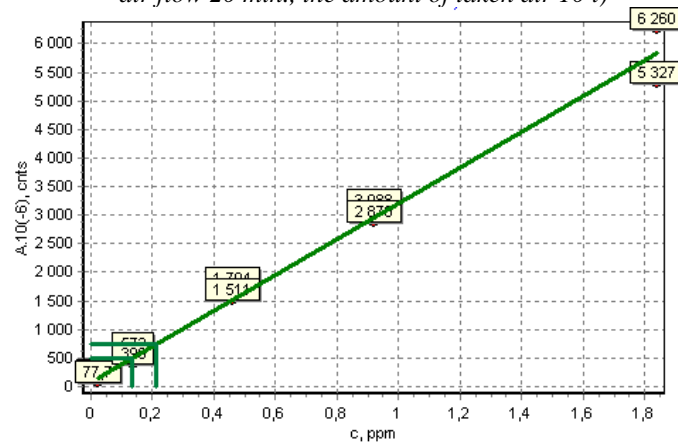
$$A [\text{cnts}] = k \cdot c [\text{ppm}] + q$$

Where **A** is the area of a chromatograph pike and **c** is concentration of a substance in the air, see table 2.

Table 2  
Parameters of linear dependence of the area of a chromatographic peak on the concentration of the substance in the air taken by the sorption tube Tenax

Substance	Direction $k$ [cnts. $10^6$ /ppm]	Sector $q$ [cnts. $10^6$ ]
Carbon disulphide	23,5	-4,30
n-Hexane	42,8	0,80
2-Butanone	16,4	2,15
Ethane, 1,2-dichlor	177	0,91
Trichlorethylene	273	21,4
Toluene	931	20,9
Isopropyl Alcohol	51,7	-0,34
n- Octane	3130	77,2
n-Heptanole	3900	38,5
Benzene, 1,2-dichlor	1840	-169

Picture 5  
The dependence of the area of a chromatographic peak on the concentration of n-Octane in the air taken by the sorption tube Tenax (air flow 0,5l/min, time of air flow 20 min., the amount of taken air 10 l)



### 3. Semi-quantitative determination of the substance in the air

Discovered calibration dependencies described in table 2 enable to estimate concentrations of the substances in the air. The possibility to use estimates for the calculation of concentrations has the following limiting presumptions:

- The air sample was taken by unified prescribed procedure<sup>6</sup>, i.e. the air flow by the sorption tube Tenax 0,5 l/min during 20 minutes.
- For the desorption and analysis of the air mixture the system EM 640 is used and conditions of separation and analysis according to the chapter II.1. of this publication.
- Constant concentration of the substances in the air during the taking-in is at least approximately assured.

The estimate of the concentration (semi-quantitative determination) is performed on the base of a subtracted area of a chromatographic peak according to the table 3.

*Table 3*  
*Coefficients for the estimate of the concentration of substances in the air taken by the sorption tube Tenax*

<i>Group of substances</i>	<i>Examples</i>	<i>Area of chromatographic pike <math>1 \cdot 10^6</math> cnts = [ppm]</i>
1. Highly volatile and volatile, polar and non-polar	Carbon disulphide, Hexane, Isopropyl Alcohol, 2-Butanone	<b>0,03</b>
2. Medium volatile, medium and little polar (aliphatic chlorine hydrocarbon)	Ethane, 1,2-dichlor, Trichlorethylene	<b>0,005</b>
3. Medium volatile non-polar (aromatic hydrocarbons)	Toluene	<b>0,001</b>
4. Non-volatile polar and non-polar	Octane, Heptanole, Benzene, dichloro	<b>0,0005</b>

For verifying the reliability and reproducibility of stated coefficients for the estimation of concentration of substances in the air may be compared to the results achieved during the optimization of methods for the air sampling extraction by the sorption tube Tenax<sup>1</sup> when the work was performed in May 2006 at identical conditions. As stated above, the optimization was studied on four following testing substances whereas at the final procedure these coefficients were settled: for n-Heptane the peak area  $1 \cdot 10^6$  cnts corresponded to the concentration 0,0007 ppm, for n-Butanole 0,013 ppm, for 2-Butanone 0,02 ppm and for Chlorine Benzene 0,0008 ppm. With regard to the fact that Butanole lies approximately between groups 1 and 2 and Heptane with Chlorine Benzene between groups 3 and 4, it is evident that there is a very satisfactory consistency of results which were achieved in two-year time interval. Here at it is necessary to keep in mind that it is just the estimate of the concentration.

#### IV. CONCLUSION

Studying the capture of the vapours of substances of various properties (polar, non-polar, volatile and little volatile) by sorption tubes Tenax in order to make a consequent analysis by a mobile gas chromatograph with a mass detector EM 640 with the usage of a thermo-desorption device, it was discovered that from the viewpoint of the achievement of a maximal sensitivity of the analysis the optimal procedure of the adsorption of air infiltration by the tube is for twenty minutes during the airflow 0,5 l/min. This corresponds to the amount of infiltrated air 10 l. The methods for air sampling procedure were introduced into practice with Units of Fire Protection and chemical laboratories of regional FRS which for this purpose use a gas consumption pump PCXR 4 or a chemical probator CHP-71.

The research of the dependence of the peak area on the concentration of 10 substances of different properties in the air mixture taken by infiltration through a sorption tube Tenax and their elaboration via statistic software proved that the reproducibility of measured results enables to use these chromatographic data for the estimate of concentration of substances in the air. The condition is that the air sample was taken in a unified and specified manner, for desorption and analysis of the air mixture the system EM EM was used and given conditions of separation and analysis and at least approximately the constant concentration of the substance in the air during the time of the extraction was assured. For the estimate of the concentration under these conditions on the base of the area of a chromatographic peak for individual group of substances the counting coefficients were determined.

#### Résumé

*In order to achieve a maximum sensitivity analysis of volatile organic compounds in the air by using GC/MS method, with adsorption to the sorption tube Tenax, an optimal procedure of sampling the air has been developed and verified. Air is drawn through a tube for 20 minutes at a flow rate of 0.5 l/min - equivalent to 10 l air. The methodology for sampling air using a sampler pump gas or chemical detector CHP-71 has been put into practice for fire protection units and regional chemical laboratories Fire and Rescue Services.*

*A study concerning the dependency of the peak area on the concentration of 10 different substances in the air mixture captured on the sorption tube Tenax showed that the reproducibility of measured results makes the use of chromatography data possible for semi-quantitative determination of substances in the air. To estimate the concentration under prescribed conditions on the basis of the chromatographic peak area, translation rates for each groups of substance were established.*

#### Literature

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