

## PROTECTION OF ADSORPTION TUBES AGAINST CONTAMINATION

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Delivered 10. 3. 2011, revised 15. 4. 2011, accepted 21. 4. 2011.  
Available at [http://www.population-protection.eu/attachments/038\\_vol3n1\\_capoun\\_krykorkova\\_urbanova\\_eng.pdf](http://www.population-protection.eu/attachments/038_vol3n1_capoun_krykorkova_urbanova_eng.pdf).

### Abstract

*For the analysis of dangerous substances of unknown compounds in the air is in the Fire and Rescue Service established a procedure, based on sampling of air samples by means of sucking through Tenax adsorption tube, the release of the captured substances in thermodesorption equipment, and their subsequent analysis in a gas chromatograph with mass spectrometer. The procedure is simple, effective and highly sensitive. High sensitivity nevertheless brings significant interference caused by contamination of tubes stored in the reconnaissance vehicles and transported to the incident-site. The result of this study of tube contamination is the method of optimal protection of the Tenax tubes. This method ensures the reduction of Tenax tubes contamination by volatile substances during the storage, transport and handling to an acceptable minimum.*

### Keywords

*Air sampling, gas chromatograph with mass detector, volatile organic compounds, adsorption tube, thermo desorption device, contamination.*

### INTRODUCTION

To response to the events with dangerous chemicals leakage, their discoveries or terrorist misuse, the chemical laboratories and selected units of the Czech Fire-Brigade (FRS CR) are equipped with mobile chemical laboratories or special emergency vehicles. These means enable to detect, identify and determine dangerous chemicals directly on-site. If there is a need to verify the results of the field analysis in the stationary laboratory, or when the field equipment is not sufficient to accomplish the task on-site, the mobile means enable also sampling and storing of different environmental samples, and their transport to the laboratory.

Sampling is a significant chemical measure. Its aim is to collect sample as fast and accurate as possible, according the methodology, perform on-site analysis and rough analysis in the stationary laboratory. The selection of the sampling procedure is based on the type of sample, purpose and method of the analysis,

which determines specific requirements for sample treatment according to the instrumentation, and a way of storing and transporting of the sample. "Sample" is a specific object or a piece of a material, which is collected in accordance with a prescribed or agreed technique. In the above mentioned examples, the sample is collected to identify a dangerous chemical and its concentration in the original matrix. Mobile units of the FRS CR carry out sample collection - based on the dispatch by the Operation and Information Center of the respective FRS Regional Directorate - according to the orders of the operation commander.

Air sampling represents a special procedure between the individual sampling procedures. It is because the dangerous chemicals in the form of gases, vapours, aerosols and dusts represents a significant risk of inhalation intoxication to the population and mobile unit members.

## AIR SAMPLING PROCEDURES

The key as well as the most significant physical procedure of air sampling is the air-suction. Individual procedures are divided into:

- procedures based on sampling including the matrix (i.e. the air)
- procedures combining sampling and isolation of dangerous substances in the air.

Following techniques belong to the procedures based on sampling including the air: sampling using the sampling bags, different vacuum bottles, special vessels etc. On the other hand, dangerous substances isolation from the air needs to suck air through appropriate solvents, sorbents, dust filters<sup>1,2</sup>, etc.

Sample with the highest concentration of the dangerous substance is collected as close as possible to the leakage source, coloured gas cloud, dust or aerosol in the air. In the events, when it is not possible to detect the place with the highest concentration of the contaminant, the air sample is collected in a height of 20 - 30 cm above the ground<sup>1,2</sup>.

One of the sampling procedures, which is an official standard at the Czech Fire-brigade<sup>1</sup>, is taking the air through the Tenax tube<sup>3,4</sup>. The tube serves to collect samples of gases and vapours based on the adsorption. Air intake through the tubes is provided by a sampling gas pump with adjustable air-flow 0 - 5 l/min, equipped with an air-flow meter. Mobile chemical laboratories of FRS CR or special emergency response vehicles are equipped with a sampling pump PCXR4 or chemical detector CHP - 71.

When sampling with adsorption tubes, both ends must be broken or released. After that the tube is connected by a hose to the inlet and the pump is switched on. The air-flow rate and air intake time should follow the instructions of the manufacturer.

When sampling with Tenax tubes No. 226-35-03 of the length 10 cm and diameter 8 mm (polymer sorbent), an optimal air-flow is 0.5 l/min, and air intake time 20 minutes<sup>1,3</sup>. If chemical detector CHP-71 or CHP-5 are used as a pump, the

air-flow of 0.5 l/min is adjusted in the following way: 2 opened and 2 closed mustard detection tubes (with a yellow stripe) are put into the tube chamber - this detection tubes positioning ensures the required air-flow. The air-flow rate regulator is adjusted in a final (zero) position. The adsorption tube is connected to the inlet valve of the detector by a hose. The air-flow regulator is slowly turned until the noise of pump can be heard.

Another option to intake the air through the tubes is utilization of a suction device U66 or other type. In this situation, there must be performed 100 strokes.

The tube has to be closed after finishing of air intake. The special literature<sup>1</sup> states, that it is necessary to prevent the tubes from contamination during manipulation. It means not only to touch them with clean, preferably, cotton gloves, but also to cover them properly. Especially the type of cover is a matter.

After collecting the sample and its transport to the stationary laboratory, the GC/MS analysis follows. In the thermo-desorption module, the substances stuck on the Tenax polymer are firstly desorbed and then they are separated at the chromatographic column. The GC/MS software compares the measured mass spectra of analyzed samples with spectra saved in libraries, and performs identification of unknown organic compounds in the sample. The peak area is, in a specific concentration range, directly proportional to the concentration of a substance in the air. Advantages of this procedure are simple manipulation with detection tubes and their transport, which can be realized even by mail, then also a possibility of increasing the concentration of the analyzed substance, and a possibility of getting the analyzed component in the original form, i.e. without the chemical transformation<sup>4</sup>.

The extreme sensitivity of the whole procedure requires to pay attention to the protection of the Tenax tube against contamination. Respecting the above described sampling directions, the detailed analyses<sup>3-8</sup> performed on GC/MS EM 640 showed, that the detection limit of the whole procedure ranges from 0.01 ppm (for highly volatile substances) to 0.0002 (for low volatile substances). It is obvious, that such a high sensitivity means, in the same time, a very high risk of possible contamination of the tube sorbent by volatile organic substances present in the atmosphere during the storage, transport, and manipulation, when collecting the sample. Even very small concentrations, present in the real environment, can cause contamination of the sorbent. In the conditions of emergency response units, the risk of contamination is particularly represented by fuel, dissolvents, exhaust gases, and any other substance present in the vehicle, garage or incident site. Presence of contaminant on the sorbent layer during the GC analysis can lead to an incorrect interpretation of the analysis results.

Therefore, it was necessary to identify such a cover of the Tenax sorption tube, that would ensure enough protection<sup>9</sup> against the contamination of volatile substances during the storage, transport, and manipulation.

## **ANALYSIS OF PROTECTION POSSIBILITIES OF THE TENAX TUBES AGAINST THE CONTAMINATION**

Generally, it is possible to note, that each user of the Tenax tubes already faced with their tendency to be easily contaminated by substances present in the atmosphere. The contamination can occur not only because of accidental sorption, but also on the surface of the tube. In the laboratory, this issue is simply solved by a so-called blank analysis (background sample), which means testing the tube, that was not applied to the air intake. When processing a background sample, the sorbent is activated in the same time, because of increased temperature (220° C) in the thermodesorption module. This detection tube, used as a background sample, can be consequently used for adsorption. The procedure can not be applied to detection tubes used in the incident site, where they were transported in the response vehicle. It has to be noted, that there is not enough professional literature related to the issue of contamination elimination of detection tubes used for the field air-sampling.

Some possibilities of the protection of detection tubes against contamination were verified in the chemical laboratory of the Pilsen Regional Fire-Brigade<sup>10</sup>. Detection tubes covered and secured in different ways were exposed to the 130 ppm mixture of acetone, hexane, limonene and pentylacetate for 5 days. As a result, all tubes were contaminated. This test however did not follow the real conditions of storing the tubes in the common mobile chemical laboratory, where the potential concentration of organic compounds is usually not so high. That is the reason, why our research was focused particularly on the real conditions.

The first basic protection of Tenax glass tubes represent plastic caps, which are supplied together with the tubes. We can assume, that the covers protect the sorbent against contamination, but surely do not protect the surface of the tube.

The methodology of collecting air samples<sup>1</sup> followed in FRS CR, recommends, after finishing with air-intake, to close the tube with the plastic caps a put it in a glass bottle having a ground cover. During the manipulation with detection tubes, the attention must be paid to the maximal protection of the tube surface against contamination. The tube protection is similarly solved in the standard operational procedure of the Population Protection Institute<sup>11</sup>, where it is stated, that it is necessary, after air intake, to close the tube with plastic caps, put it in a special cover, e.g. ground covered test tube NZ 14, not to touch the tube with bare hands, and to use clean textile gloves.

Another option is storage in a special gas tight box designed for sorption tubes (Fig. 1). The tube is put into a metal box and tighten with a teflon seal from both sides. The box is then screwed up by a double cover, whereas the outer one is unscrewed during the air intake (Fig. 2), and the inner one, when the tube is taken out from the box just before the analysis (Fig. 3). The great advantage is the fact, that it is not possible for the operator to touch the tube, so the surface contamination can be excluded. Relatively high price of this procedure is one of the disadvantages. The boxes mentioned above are used by special chemical fire-

brigade units in Germany. In some situations, it is recommended to pack the box into a tinfoil, and to put it into a hermetically sealed container<sup>10</sup>.

The ideal protection represents such cover, which excludes any potential interference between the tube and the air. This can be done for example by flame sealing of the test tube into a glass tube.



*Fig. 1.*

*Gas tight box made for storage and transport of sorption tubes*



*Fig. 2.*

*Gas tight box made for air intake by sorption tubes*



*Fig. 3.*  
*Taking the sorption tube out of the gas tight box*

## **PERFORMING OF EXPERIMENTS**

All experiments were carried out with new Tenax adsorption tubes (charge No. 4681, expiration VIII/2012, SKC Inc., USA). Tubes were first opened and activated in a drier at the temperature of 200 °C for 2 hours. After cooling, they were immediately provided with a cover. The following options were tested:

1. tubes closed only by plastic caps (Fig 4);
2. tubes closed by plastic caps and stored in a ground-glass test tube NZ 14; the stopper was secured by a Parafilm (Fig. 5);
3. tubes stored in a gas tight box designed for sorption tubes (Fig. 1-3); the boxes used for the testing were from Frybert company, Pribram;
4. tubes closed by plastic caps and flame-sealed in a glass tube realized either by a glass tube with inner diameter of 9 mm, or by a flame sealed test tube (Fig. 6).

The tubes together with covers were put in a paper box, which was put and stored in a mobile chemical laboratory. Every time regularly the tube was taken out from the box, and the analysis of potential contaminants was carried out by the GC/MS method.

Mobile chemical laboratory runs on diesel oil. All the time during the test, the vehicle was parked in a garage together with another box vehicle filled with diesel oil, and a passenger car running on petrol. Any other chemicals were not

present in a garage. The mobile chemical laboratory set out from the garage only once in 14 days - the same as the other two vehicles.



*Fig. 4.  
Tube closed by plastic caps.*



*Fig. 5.  
Tube closed by plastic caps and stored in a ground-glass tube*



*Fig. 6.  
Tube closed by plastic caps and flame-sealed in a glass tube (test tube).*

Chromatographic analysis of substances stuck on the tube sorbent, i.e. contaminants of the sorbent, was carried out by the mobile gas chromatograph with mass detector EM 640 (Bruker Daltonic GmbH, Bremen, Germany).

The Tenax tube was put in a desorption unit of the device after some time of the storage in a vehicle. The desorption ran under the following conditions: T Inlet 230 °C, T Injection 220 °C, desorption time 1.5 min at 220 °C, injection time 20 s.

Separation and analysis of the substances were carried out in all tests under the following conditions:

- Colony: Rxi-5ms, length 30 m, Ø 0.32 mm, phase 1 µm.
- Carrier gas: nitrogen without CO (Linde Technoplyn).
- Scan range: 30-400 amu.
- GC program:
  - 40 °C – 2 min,
  - from 40 °C to 280 °C - dT/dt 10 °C/min,
  - 280 °C – 10 min,

Identification of separated substances was carried out in accordance with the respective standard operational procedure<sup>11</sup>. Except the type of a substance, the peak areas, which are directly proportional to the amount of sorbed substances, were also evaluated.

## DISCUSSION OF RESULTS

The chromatographic analysis showed, that if any contamination of the detection tubes stored in the vehicle appears, the most frequent contaminants are aromatic hydrocarbons as toluene, xylene, ethylbenzene, propylbenzene, isopropylbenzene, ethylmethylbenzene, trimethylbenzene, naphthalene, and n-alkanes as tridecane, tetradecane and pentadecane. Besides, other substances also appeared (e.g. alkylbenzenes C4 and C5, methyl naphthalenes, alkanes from octane to hexadecane). Generally, they are components of the fuel. The contamination was however evaluated just according the presence of the substances, which were found in the contaminated tubes in each measuring, and they are displayed in the following graphs:

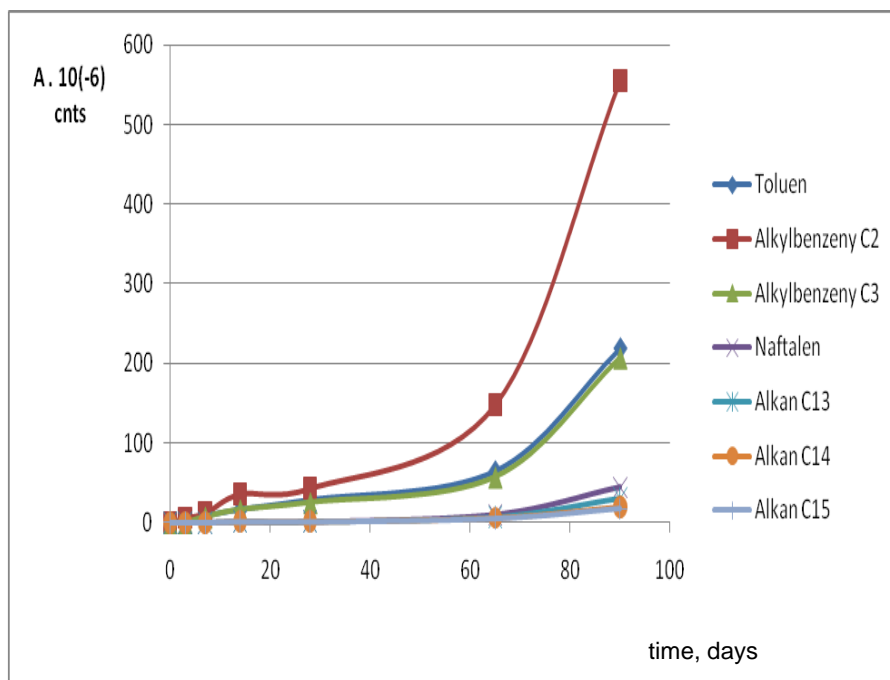
- toluene,
- alkybenzenes C2 (sum of xylenes and ethylbenzenes)
- alkylbenzenes C3 (sum of propylbenzenes, isopropylbenzenes, ethylmethylbenzenes, and trimethylbenzenes),
- naphthalene,
- alkane C13 (tridecane),
- alkane C14 (tetradecane),
- alkane C15 (pentadecane).

The results of the analysis of the Tenax tube **closed only by plastic covers** (according the Fig. 4) without any other covering are shown in the Fig. 7,



which displays the relation between the amount of sorbed substances in the tube (expressed by the chromatographic peak area) and the storage time of the tube in the mobile chemical laboratory. Just after 3 days of the storage, the tube was contaminated by a small amount of the toluene, xylene and ethylbenzene. After one week, all above mentioned substances were present in the tube. The amount of the sorbed substances increases with a time, and after 2 months of the storage starts to increase very steeply.

Finally, we can say, that it is not possible to store the Tenax tubes, intended to collect the air samples, covered only with the plastic caps, because they are getting contaminated by hydrocarbons immediately after few days.



*Fig. 7.*

*Relation between the amount of sorbed substances in the Tenax tube closed by the plastic caps, expressed by the chromatographic peak area, and the storage time of the tube in the mobile chemical laboratory.*

The results of the analysis of the Tenax tube **closed by the plastic caps and stored in the ground-glass tube** (according the Fig. 5) are shown in the Fig. 8. It is obvious, from the Fig. 8, that the ground-glass tube improves the Tenax tube protection against the contamination in comparison with the case, that only plastic caps were used. The tube was fully protected, without any contaminant

present, for a 1 week period. But after 2 weeks of the storage, the analysis started to show the presence of the most above mentioned hydrocarbons, and their amount started to increase significantly with the time.

It is obvious, from the results, that even this way of the storage of Tenax adsorption tubes in the mobile chemical laboratory is not suitable, because it provides protection only for a 1 week period.

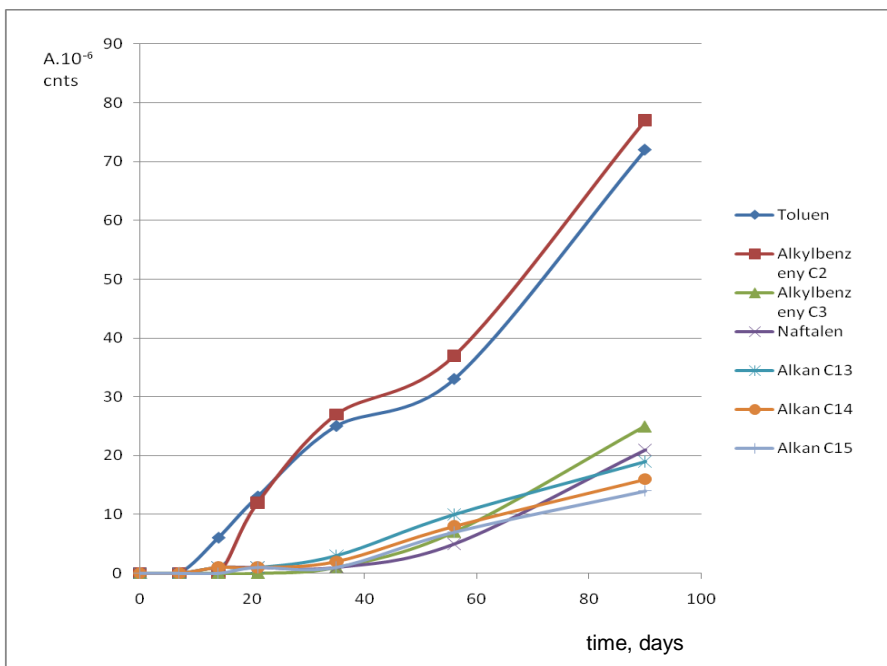


Fig. 8.

*Relation between the amount of sorbed substances in the Tenax tube closed by the plastic caps and stored in the groud-glass tube, expressed by the chromatographic peak area, and the storage time of the tube in the mobile chemical laboratory.*

Contamination of the Tenax tubes protected by other studied ways, i.e gas tight box (Fig 1 - 3), and plastic caps combined with flame-sealing into a special glass tube (Fig. 6), was monitored for a 6 months period. Even **after 6 months** period of the tube storage in the mobile chemical laboratory, **no contamination appeared**.

However, the **flame-sealing of the Tenax tubes into glass tubes**, although it is undoubtedly the most advanced protection against the contamination, is not an ideal solution for several reasons. When opening the glass tube, an increased risk of injury and also damage (e.g. perforation) of the protective suit

becomes an issue, and it might be very serious, if it happens in the contaminated area. Once the glass tube is broken, the Tenax tube has to be transported back to the laboratory without this kind of protection. Flame-sealing of the glass tube inside the mobile chemical laboratory is difficult and does not meet the safety requirements, particularly in the contaminated area. The tube is not protected on the surface during the sample collection as well.

Based on the study of the contamination of Tenax tubes, stored in the mobile chemical laboratory to collect the air samples by a response unit, and based on the experiences from the field work, the most effective way of tubes protection is storage in a gas tight box. It is a very simple way to protect tubes against the contamination during the manipulation, i.e. for a period of transport to the incident site, sampling and transport back to the laboratory.

## CONCLUSION

Tenax adsorption tubes are used by some Fire-brigade units for an air sampling to analyze volatile organic compounds and toxic warfare agents by GC / MS method. The air is sucked through adsorption tubes by sampling gas pump or a chemical detector CHP-71. Due to the extremely high sensitivity of analysis, there is a significant risk of secondary contamination of the tube by volatile organic compounds from the air, and consequently a risk of false results of the analysis.

To ensure the protection of adsorption tubes against contamination, the following options were studied:

- closure only with plastic caps,
- closure with the plastic caps and storage in a ground-glass tube,
- storage in gas-tight boxes for adsorption tubes,
- closure with the plastic caps and storage in a ground-glass tube,

The results show that for practical use the special gas-tight box is the best protection of adsorption tubes. It is a very simple way to protect tubes against the contamination during manipulation, i.e. for a period of transport to the incident site, sampling and transport back to the laboratory. The Tenax tubes in gas-tight boxes placed in mobile chemical laboratory showed no contamination, even after 6 months.

The conclusions of the study are important to ensure the tasks of chemical research and laboratory control in the Fire and Rescue Service. It was proven, that fire-brigade units equipped for sampling with adsorption tubes Tenax, must keep these tubes in special gas-tight boxes. Following this precaution will significantly increase the reliability of the whole expertise from sampling, through analysis to the final interpretation of results.

*This article was created within the project "Security of citizens – Crisis Management" (VF20112015018).*

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