Separation chemistry and analysis of toxic substances International conference – Papers selection

ESTIMATING SUBSTANCE CONCENTRATIONS IN THE AIR SAMPLED BY TENAX SORBENT TUBES

Tomáš ČAPOUN*, Jana KRYKORKOVÁ*

*Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, Na Lužci 204, 533 41 Lázně Bohdaneč, Czech Republic, jana.krykorkova@ioolb.izscr.cz ; tomas.capoun@ioolb.izscr.cz

ABSTRACT:

The article describes a semi quantitative determination of volatile organic compounds in the air by the gas chromatography with mass detection (GC/MS) method. In particular, we studied a procedure for air sampling using the Tenax sorbent tube followed by GC/MS analysis of the sample. Concentration of the given substance can be estimated based on its chromatographic peak area, sampled air volume, and the boiling point of the substance.

KEYWORDS:

gas chromatograph with mass detector, volatile organic substances, sorbent tube, thermal desorption unit

1. Introduction

Chemical reconnaissance and subsequent laboratory investigation are the first measures taken by the Fire Rescue System (FRS) regional units when facing incidents associated with the spills of dangerous substances or chemical warfare agents, in order to protect the population, integrated rescue systems personnel, and material and cultural assets.

The dangerous chemical substances potentially contaminating the environment encountered during such incidents may exhibit varying properties and require appropriate approach for the sample preparation and analytical handling. Inhalation poisoning poses the greatest risk both for the population as well as for the rescue personnel, and the dangerous substance may be encountered in the form of gas, aerosol and dust. Air analysis therefore represents an important chemical countermeasure, including detection of dangerous substances in the air, air sampling and eventual analysis of the samples in a stationary laboratory.

2. Use of Tenax sorbent tubes for the analysis of air contaminants

All regional FRS units associated with dangerous substance incidents are equipped with Tenax sorbent tubes. Tenax is a synthetic, widely used sorbent used to trap substances from the air. The trapped substances are then thermally desorbed in a thermal desorption unit and analysed. Using the GC/MS method, the tubes are used both for the analysis of external air [1–15], internal air including workplace environment [2,6,16–20], and owing to their high sensitivity, they are also applied for the analysis of

dangerous substances emitted from various products and materials [21–25], food and beverage [26,27] or air exhaled by people [28,29]. However, the GC/MS is not the only analytical coupling, and alternatives include the analysis of desorbed substances by the ICP/MS method [30].

Active sampling usually traps Analytes from the air, i.e., by passing a flow of air through the sorbent tube. A sampling pump or a suction cup can achieve this. However, passive (diffusion) sampling based spontaneous diffusion of the substances into the sorbent without using air flow through the tube may also be used [6,10,14,16,18].

Analysis of various substances may require optimisation to achieve high overall adsorption and desorption yield and hence best sensitivity for various analytes. Many pieces of work have been dedicated to the optimisation of sorption and desorption parameters including flow time and rate, air humidity, and GC/MS measurement conditions [6,23,29,31,32]. Attention was also given to the comparison of Tenax to other sorbents. These conclusion are always specific for the analysed substances in question, though: While some describe the best yield with Tenax [7,15,26,33], other describe better results with Carbopack or molecular sieve-based sorbent [11,34], and some authors conclude the yields are comparable with the sorbents studied [14]. Yet, these studies show that Tenax is a very suitable sorbent for the most important volatile organic substances including alkanes, aromatic hydrocarbons, and chlorinated hydrocarbons, both in terms of sorption from the air as well as subsequent thermal desorption.

The Tenax sorbent tubes are primarily intended for the identification of substances present in the air. For substance monitoring in the air, the procedure can be also quantitatively, assuming calibration of the tubes. Absolute calibration based on dosing (spiking) a known amount of the analyte directly into the tube is usually used for such analytes [7,9,10,14,17–20,29,33,35]. In some cases, mixtures of the substances with clean air or nitrogen are prepared in special gas generators [11,14,29,32,35] or gas sampling vessels by dilution with air [4,7,12].

The internal standard method is also applied for the determination of substances in the air. For the determination of benzene, toluene, xylene and ethylbenzene, deuterated toluene-d_8 [3,16] or ethylbenzene-d_{10} [10] could be used. Similarly, DDT in the air could be determined using a ^{13}C-labelled analogue [9]. Even compounds structurally different from the analyte could be used as the internal standard. For example, deuterated trifluarin-d_{13}, trans-permethrin-d_6 and nitrophenol-d_4 could be used for the determination of 28 pesticides [6], tetrabromodiphenyl ether (PDBE-77) for the determination of 18 fire retardants [36], benzyl benzoate for the determination of dialkyl phthalates [25] or anisole for the determination of various volatile substances in the air [35].

As shown by the literature overview, substances monitored in the air or otherwise studied require a calibration of the sorbent tubes. Nevertheless, each FRS incident is unique and may be associated with the spill of a different substance, which the chemical laboratory is not likely to have the calibration data for. This makes the procedure impractical or even unrealistic in real FRS life. Despite that, the field investigators are often requested by the incident commander or other body to make an estimate of the identified substance concentration, and the literature provides no general procedure for the concentration estimate of unknown substances in the air.

3. Air sampling performed by the regional FRS units

Air sampling procedures used by the regional FRS units are defined the Czech FRS Chemical Service Regulation [37]: air is sampled using sampling bags, trapping onto a dust filter, or adsorption on

sorbent tubes. Both passive sampling (based on diffusion of the substance into the Tenax tube) and active sampling (air flow through the tubes using a gas sampling pump) may be used [37,38].

The dependence of adsorbed amounts on air flow rate and time was studied in the past by the Czech FRS for various volatile organic substances with different properties [32]. Flow optimisation [32] yielded a unified procedure for the air sampling by the Tenax tube using a flow rate of 0.5 L/min for 20 min, i.e., with a total air sample volume of 10 L. This procedure was practically implemented by the Czech FRS units [37,38].

4. Experiments performed

Our study included representatives of various organic substances with different properties shown in Table 1.

Table 1

Overview of analysed substances

Substance	*Specification*	*Boiling point, °C*
Dichloromethane	Uvasol, spectroscopy grade, Merck	40.7
Acetone	p.a., Penta	56.2
1,2-Dichloroethylene	pur., Merck	60.0
Chloroform	p.a., Lachema	61.3
Ethyl acetate	p.a., Penta	77.1
Benzene	p.a., Merck	80.5
Trichloroethylene	pur., Lachema	87.0
n-Propyl acetate	pur., Merck	101.6
Toluene	p.a., Merck	110.8
n-Butyl acetate	p.s., Merck	126.5
Ethylbenzene	pur., Merck	135.5
1,2-Dichlorobenzene	p.s., Merck	180.5

Exact concentrations of these substances were prepared by dosing a solution of the compound in methanol (SupraSolve, for GC/MS, Merck) into a flow of filtered air using a dynamic calibration unit SYCOS K-DPG (Ansyco, Germany) with regulated airflow and regulated mixing chamber temperature up to 180°C (Figure 1). The calibration unit was able to prepare aerial mixtures of the substances in the concentration range of *ca.* 0.001–0.050 ppm (1–50 ppb). The desired airflow rate was set. The calibration unit output was passed through the Tenax TA adsorption unit (Markes Inc., USA) for the selected time. Total air volume sample was calculated from the airflow rate and time.

Figure 1. Dynamic calibration unit SYCOS K-DPG

Substances trapped in the adsorption tube were analysed by the GC/MS method on a 7890A gas chromatograph with 5975C mass spectrometer (Agilent) with the HP-5MS column (length 30 m, diameter 250 µm, phase 0.25 µm). Trapped substances were desorbed from the tube using a TD 100 (Markes Inc., USA) thermal desorption unit using following parameters: purification: time 1 min, flow rate 20 mL/min; desorption: time 5 min, temperature 280°C, flow rate 20 mL/min, trap module setting: purification 1 min, temperature –10 to 250°C, flow rate 20 mL/min.

GC/MS analysis was performed using the following chromatographic programme and measurement conditions: carrier gas 5.6 helium 1.0 mL/min, inlet temperature 230°C, GC/MSD interface temperature 230°C, scan range 35–800 amu, splitless, GC programme: 40°C for 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 for 1 min.

Two parallel measurements were performed for each substance and concentration. Area of the individual peaks was then evaluated in the resulting chromatograms which were integrated by the DataAnalysis software.

5. Measurement results

5.1. Sorbent tube calibration

The relationship of peak area as a function of the substance concentration in aerial mixture was constructed and evaluated using the statistical software [39] for the individual substances listed in Table 1. For simplification, the substance chromatographic peak area is given in million abundance units in the following results, equations and tables.

We observed that this relationship is linear within the concentration range described in Table 2 which also summarises parameters of the linear relationship between the substance concentration in the aerial mixture and the corresponding peak area, as described by the equation

A = k × c + q   */1/*

where *A* is the chromatographic peak area in million abundance units, *c* is the substance concentration in the aerial mixture in ppb units, *k* is the gradient and *q* is the intercept on the peak area axis.

The calibration results show that the peak area axis intercept *q* is negligible as compared to real peak areas and hence that the calibration curves approximately pass through the origin.

Table 2

Parameters of the linear relationship between the chromatographic peak area and the substance concentration in the aerial mixture sampled by the Tenax TA sorbent at following conditions: flow rate 0.5 L/min, sampling time 20 min, sampled air volume 10 L

Substance	*Concen-tration range, ppb*	*Gradient k* [TIC × 10^{-6}/ppb]	*Intercept q* [TIC.10^{-6}]	*SD k* [TIC.10^{-6}/ppb]	*SD q* [TIC.10^{-6}]
Dichloromethane	1 – 40	11.2	-0.52	0.090	0.49
Acetone	1 – 40	12.6	-0.37	0.11	0.28
1,2-Dichloroethylene	1 – 40	13.8	0.54	0.14	0.56
Chloroform	1 – 40	14.6	0.70	0.14	0.73
Ethyl acetate	1 – 30	19.1	-0.89	0.093	0.41
Benzene	1 – 30	20.5	1.00	0.10	0.59
Trichloroethylene	1 – 30	22.3	0.96	0.17	1.07
n-Propyl acetate	1 – 20	23.7	1.07	0.19	0.66
Toluene	1 – 20	24.2	1.02	0.087	0.79
n-Butyl acetate	1 – 20	29.0	1.36	0.12	0.94
Ethylbenzene	1 – 15	34.9	1.63	0.21	1.23
1,2-Dichlorobenzene	1 – 10	48.8	2.21	0.43	1.14

These linear relationships were studied in detail using the statistical software [39] based on selected statistical parameters, which allowed for following conclusions [40]:

- Based on the values of the correlation and *QC* coefficients, the hypothesis of linear calibration relationship between the substance chromatographic peak area and its concentration in the air sampled by the Tenax sorbent tube could be confirmed,
- Relative standard deviation (SD) of the determination is in the range 5–15%,
- Limit of detection of the method reaches 0.1–0.3 ppb for the substances, the limit of quantification 0.3–0.5 ppb,
- Determination of the substance concentration using its chromatographic peak area yields statistically accurate results

Based on the measurement results and their statistical evaluation, one can conclude that based on the calibration performed it is possible to estimate the concentration of the given compounds in the air based on the corresponding chromatographic peak area.

5.2. Calculation of the substance concentration in the air

From the linear relationship between the chromatographic peak area and the substance concentration in the air (equation /1/), concentration c can be expressed (in ppb units) as:

$$c = (A - q) / k,\qquad\qquad\qquad /2/$$

where A is the chromatographic peak area in million abundance units, q is the intercept on the peak area axis, and k is the gradient of the relationship.

Taking into account that the intercept q is negligible compared to the real peak areas as concluded in section 5.1, it is possible to accept the hypothesis that the calibration curves pass through the origin. The concentration can be then expressed as a product of the peak area A and concentration factor F_C that is the inverted value of the gradient. In our case, the gradient k was obtained using 10 L air sample volume, and the concentration therefore needs to be corrected to account for this:

$$c = A \times F_C / V\qquad\qquad\qquad /3/$$

where c the substance concentration in the air [ppb], A is the chromatographic peak area [TIC $\times 10^{-6}$], V is the sampled air volume [L], and F_C is the concentration factor [ppb $\times$ L / TIC$\times 10^{-6}$] which is equal to 10 / k. Values of the concentration factor F_C are listed in Table 3 for the studied substances.

In practice, the air is sampled by the Tenax tube at the conditions defined, i.e., at flow rate of 0.5 mL for 20 min to sample 10 L of air. The GC/MS analysis, integration of the peak corresponding to the analysed substance (A), and calculation of its concentration according to equation /3/ ensue.

Although the procedure is very simple, it can be used only for those substances the sorbent tube had been calibrated for. This would practically require calibration for every substance potentially encountered. This is a major limitation for the FRS chemical laboratories, which may face different dangerous substances at each incident, and standard of the substance may not be available.

Table 3

Values of the concentration factor for the determination of substance concentration in the air sampled by the Tenax TA sorbent tube

Substance	Concentration factor F_C [ppb × L / (TIC × 10^{-6})]
Dichloromethane	0.89

Acetone	0.79
1,2-Dichloroethylene	0.72
Chloroform	0.68
Ethyl acetate	0.52
Benzene	0.49
Trichloroethylene	0.45
n-Propyl acetate	0.42
Toluene	0.41
n-Butyl acetate	0.34
Ethylbenzene	0.29
1,2-Dichlorobenzene	0.20

5.3. Effect of substance boiling point on the concentration factor

We have compared the results of measurements which yielded the concentration factors enabling the recalculation of peak area into substance concentration (Table 3) to the boiling points of the substances studied (Table 1). This comparison shows that with increasing boiling point of the substance, the concentration factor decreases, or in other words, gradient of the relationship between chromatographic peak area as function of the substance concentration grows.

Other studies on trapping highly volatile substances reached the same conclusion, and found out that substances with very low boiling point are not trapped on Tenax at all or with very low yield only. This is also a reason why Tenax is combined in the tubes with other sorbents, for example of the Carbopack [41], Carboxen, or Carbograph [42] type.

This conclusion also aligns with facts presented by the HPST company, in particular, that the sorption–desorption process yield increases with decreasing volatility. Corresponding lecture [41] indicates that for 5 L air sample volume the yield reach less than 20% for gaseous and volatile compounds such as butadiene or chloroalkenes, 20 to 80% for medium volatile compounds (benzene, di- and trichloroethane, trichloroethylene etc.), and more than 80% for low volatile aromatic and chlorinated hydrocarbons.

Obtained results were plotted graphically, and the best linear fit of the relationship was achieved when a logarithm of the concentration was plotted against the substance boiling point [40], as shown in Figure 2. Relationship between the concentration factor logarithm and substance boiling point fulfils the linearity requirements if the correlation coefficient reaches 0.9910 (critical value 0.99) and *QC* coefficient 4.68 (critical value 5.00) [39].

Taking into consideration that these linear functions have been constructed for substances of highly varying properties, it may be said concentration factor (or the gradient of chromatographic peak area as function of the substance concentration) is influenced by the boiling point rather than by other properties of the compound, such as structure or polarity.

Relationship shown in Figure 2 can be described by the linear function [39]:

$$\log F_C = -0.0047 \times bp + 0.11 \qquad /4/$$

where F_C is the concentration factor (Table 3) and bp is the substance boiling point in °C.

Logarithm of the concentration factor can also be expressed from equation /3/:
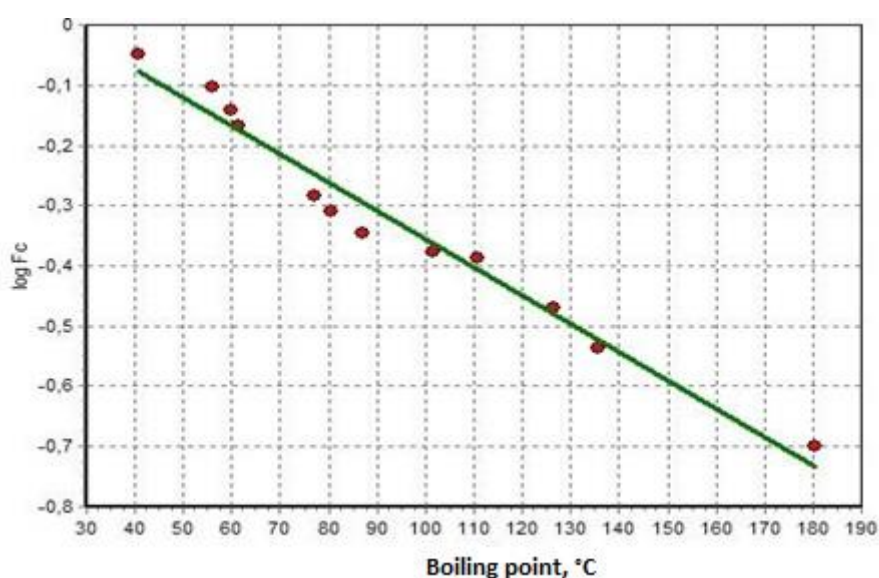
$$\log F_C = \log c + \log V - \log A$$

Figure 2. Logarithm of the concentration factor F$_C$ *as function of the substance boiling point*

Combination of equations /4/ and /5/ allows expression of the logarithm of the determined substance concentration in air and eliminate calculation via the concentration factor:

$$\log c = \log (A/V) - 0.0047 \times bp + 0.11 \qquad /6/$$

where c is the substance concentration in the air in ppb units, A is the chromatographic peak area in million abundance units, V is the air sample volume in litres, and bp is the substance boiling point in °C.

6. Estimating the substance concentration in the air

The equation for the concentration estimate for any compound in the air sampled using the Tenax tube has the general formula:

$$\log c = \log (A/V) + K \times bp + Q \qquad \qquad /7/$$

The aforementioned procedure can be easily applied to other GC/MC systems with a thermal desorption unit and different measurement and thermal desorption parameters, as it circumvents the concentration factor calculation and the construction of a linear relationship between the peak area and concentration. Following procedure is used for the estimate:

- Two substances are selected, one with boiling point around 40°C and the other one around 180°C,
- Aerial mixtures of concentration below 10 ppb are prepared,
- The aerial mixtures are sampled by the Tenax tubes, using a total volume of 10 litres or lower at a flow rate of 0.5 L/min,
- Alternatively, the tube can be spiked with an amount corresponding to the aforementioned concentration in 10 L of air,
- GC/MS analysis using given system with a thermal desorption unit at selected measurement parameters is performed,
- Known concentration of the substance, chromatographic peak area and boiling are plugged into the equation /7/ for each substance
- This results into two equations with the unknown parameters, *K* and *Q*
- Parameters *K* and *Q* are calculated, and plugged into equation /7/ which can then be used for the estimate of concentration of other substances in the air.

An example of such application to estimate the concentration of substances analysed by other GC/MS systems from the chromatographic peak area are the authors' own result from 2008 [32]. Similar to this work, we studied the relationship between the peak area and concentration for nine substances with different properties, sampled from aerial mixtures by flow through the Tenax tubes. However, the air was sampled by flow through Tenax glass adsorption tubes (SKC Inc., USA), and the analysis was performed using a mobile gas chromatograph with mass detector EM 640 (Bruker Daltonik, Bremen, Germany). Desorption was performed using the thermal desorption unit of the EM 640 system for 1.5 minutes at 220°C. Filtered air at a pressure of 300 hPa was used as the carrier gas. The column, measurement parameters, and temperature gradient of the GC analysis were identical to those in this study (see section 4).

Following compounds were studied in [32]: carbon disulfide, hexane, butan-2-one, trichloroethylene, toluene, propan-2-ol, octane, heptan-1-ol, and 1,2-dichlorobenzene. The air sample volume was 10 L in all cases.

Data from publication [32] were assessed as in this work, and the logarithm of concentration factor was plotted against the boiling point (Figure 3).
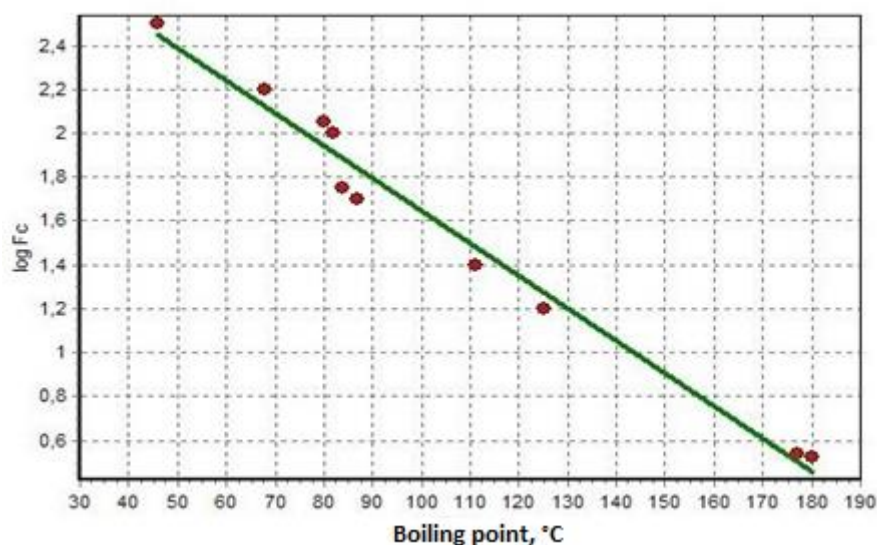
*Figure 3. Logarithm of concentration factor F*C *as function of boiling point for substances studied in 2008 using Tenax glass adsorption tubes (SKC) analysed by mobile GC/MS system EM 640 (Bruker). Data are taken from [32]*

Using statistical software [39], we found out the function shown in Figure 3 can be described by the equation:

$$\log F_C = -0.015 \times bp + 3.2 \qquad\qquad /8/$$

Hence, with the experimental setup described in [32], concentration of the substances in the sampled air could be estimated using the equation:

$$\log c = (\log A/V) - 0.015 \times bp + 3.2 \qquad\qquad /9/$$

7. Verification of the developed procedure

The procedure for the estimation of substance concentration in the air sampled by the Tenax sorbent tube was verified using other organic substances for which the tube calibration had not been performed previously [40]. To verify the estimate, a mixture of the substance and air of exact concentration was prepared using the Dynamic Calibration Unit SYCOS K-DPG (see section 4). Flow rate through the Tenax tube was 0.5 L/min for a certain time shorter than 20 min (i.e., the sampled air volume reached 5 to 10 L). The tube was analysed using a GC/MS system and the area of the peak corresponding to the given substance in the chromatogram was integrated. Two parallel measurements were performed for each substance and concentration. Based on the substance boiling point, mean peak area and sampled air volume, the concentration in the air was estimated using equation /6/. The estimated concentration was then compared to the known concentration, expressing the relative difference of the estimated and known concentration [40].

The substances included, e.g., methyl acetate, cyclohexane, butanal, pentan-3-one, tetrachloroethylene, *n*-octane, *o*-xylene, cumene, sarin, soman, heptan-1-ol, and sulfur mustard.

The results showed that equation /6/ could be successfully applied to estimate the concentration of substances trapped on the Tenax TA sorbent tube. Concentrations of randomly selected organic compounds analysed in the air from the calibration unit were estimated very closely to the real concentration. Maximum relative difference of the estimate and known concentration reached 33% [40]. The only exception from this conclusion was the estimate of sulfur mustard concentration; however, its boiling point lies outside of the range till 180°C. Also, it needs to be noted that study [7] state abnormal behaviour of sulfur mustard on Tenax.

8. Conclusion

The relationship between the substance concentration in an aerial mixture sampled by the Tenax TA tube and their chromatographics peak area was studied for twelve substances of varying properties. We observed that in a certain concentration range depending on the substance properties, these relationships are linear. Hence, for substances calibrated in this manner, the concentration of the given substance can be determined based on the chromatographic peak area.

The linear relationship between the chromatographic peak area and the substance concentration in an aerial mixture was then correlated with the substance boiling point. We found out that with increasing boiling point, the gradient of chromatographic peak area as a function of the substance concentration also increases. Based on this observation, we have derived an equation expressing the relationship between the logarithm of the substance concentration and the logarithm of its chromatographic peak area and the substance boiling point. Use of the equation for the estimate of substance concentration in air sampled by the Tenax sorbent tube was successfully verified for various organic substances. Concentration of randomly selected organic compounds in the air was estimated very closely to real values.

These results were achieved using analysis by the gas chromatography system with mass detector Agilent 7890A/5975C using a thermal desorption unit TD-100. However, we have shown that the procedure is generally applicable for other GC/MS systems with a thermal desorption unit, and for substances for which the relationship between the peak area and concentration is unknown.

LITERATURE

[1] HANG HO, S.S., ZHEN YU, J., Feasibility of Collection and Analysis of Airborne Carbonyls by On-Sorbent Derivatization and Thermal Desorption. *Anal. Chem.,* 2002, Vol. 74, issue 6, pp. 1232–1240.
[2] HANG HO, S.S., ZHEN YU, J., Determination of Airborne Carbonyls: Comparison of a Thermal Desorption/GC Method with the Standard DNPH/HPLC Method. *Environ. Sci. Technol.,* 2004, Vol. 38, issue 3, pp. 862–870.
[3] DUC HOAI, D., et al., Exposure to volatile organic compounds: Comparison among different transportation modes. *Atmosph. Environ.,* 2014, Vol. 94, pp. 53–62.
[4] LIU, J., et al., Atmospheric levels of BTEX compounds during the 2008 Olympic Games in the urban area of Beijing. *Sci. Total Environ.,* 2009, Vol. 408, issue 1, pp. 109–116.

[5] ALONSO, L., et al., Determination of Volatile Organic Compounds in the Atmosphere Using Two Complementary Analysis Techniques. *J. Air Waste Manag. Assoc.*, 1999, Vol. 49, issue 8, pp. 916–924.

[6] RAEPEL, C., et al., Analysis of airborne pesticides from different chemical classes adsorbed on Radiello® Tenax® passive tubes by thermal-desorption-GC/MS. *Environ. Sci. Pollution Res.,* 2015, Vol. 22, issue 4, pp. 2726–2734.

[7] KANAMORI-KATAOKA, M., SETO, Y., Measurement of breakthrough volumes of volatile chemical warfare agents on a poly(2,6-diphenylphenylene oxide)-based adsorbent and application to thermal desorption–gas chromatography/mass spectrometric analysis. *J. Chrom. A*, 2015, Vol. 1410, pp. 19–27.

[8] GALLEGO, E., et al., Characterization and determination of the odorous charge in the indoor air of a waste treatment facility through the evaluation of volatile organic compounds (VOCs) using TD–GC/MS. *Waste Manag.*, 2012, Vol. 32, issue 12, pp. 2469–2481.

[9] MARTIN, N., et al., Dichlorodiphenyltrichloroethane determination in air by thermal desorption gas chromatography-mass spectrometry. *Pest Manag. Sci.* 2012, Vol. 68, issue 10, pp. 1360–1367.

[10] WALGRAEVE, C., et al., Uptake rate behavior of tube-type passive samplers for volatile organic compounds under controlled atmospheric conditions. *Atmosph. Environ.*, 2011, Vol. 45, issue 32, pp. 5872–5879.

[11] TRABUE, S.L., et al., Field Sampling Method for Quantifying Odorants in Humid Environments. *Environ. Sci. Technol.,* 2008, Vol. 42, issue 10, pp. 3745–3750.

[12] KANG, Y., et al., Direct quantitative analysis of phthalate esters as micro-contaminants in cleanroom air and wafer surfaces by auto-thermal desorption–gas chromatography–mass spectrometry. *J. Chrom. A*, 2005, Vol. 1070, issue 1/2, pp. 137–145.

[13] BAROJA, O., et al., Optimization and validation of a method of analysis for fenitrothion and its main metabolites in forestry air samples using sorbent tubes with thermal desorption cold trap injection and gas chromatography–mass spectrometry. *J. Chrom. A*, 2004, Vol. 1059, issue 1/2, pp. 165–170.

[14] WIDEQVIST, U., et al., Comparison of measurement methods for benzene and toluene. *Atmosph. Environ.*, 2003, Vol. 37, issue 14, pp. 1963–1973.

[15] HOLLENDER, J., et al., Sensitive indoor air monitoring of monoterpenes using different adsorbents and thermal desorption gas chromatography with mass-selective detection. *J. Chrom. A*, 2002, Vol. 962, issue 1/2, pp. 175–181.

[16] WALGRAEVE, C., et al., Diffusive sampling of 25 volatile organic compounds in indoor air: Uptake rate determination and application in Flemish homes for the elderly. *Atmosph. Environ.*, 2011, Vol. 45, issue 32, pp. 5828–5836.

[17] UNWIN, J., GROVES, J.A., Measurement of Bis(chloromethyl) Ether at the Parts per Billion Level in Air. *Anal. Chem.*, 1996, Vol. 68, issue 24, pp. 4489–4493.

[18] CHIEN, Y.C., WU, L.J., LWO, J.H., The Application of Diffusive Sampling Combined with Thermal Desorption in Occupational Exposure Monitoring — Field Evaluation. *Appl. Occup. Environ. Hyg.*, 2003, Vol. 18, issue 5, pp. 368–373.

[19] CHEN, X., et al., Analyses on influencing factors of airborne VOCS pollution in taxi cabins. *Environ. Sci. Pollution Res.,* 2014, Vol. 21, issue 22, pp. 12868–12882.

[20] CLAUSEN, P.A., WOLKOFF, P., Evaluation of automatic thermal desorption–capillary GC for determination of semivolatile organic compounds (SVOCS) in indoor air. *J. High Res. Chrom.*, 1997, Vol. 20, issue 2, pp. 99–108.

[21] VILLBERG, K., VEIJANEN, A., Analysis of a GC/MS Thermal Desorption System with Simultaneous Sniffing for Determination of Off-Odor Compounds and VOCs in Fumes Formed during Extrusion Coating of Low-Density Polyethylene. *Anal. Chem.*, 2001, Vol. 73, issue 5, pp. 971–977.

[22] HUANG, W., et al., Influence of Thermal Treatment Conditions on the Release of Volatile Organic Compounds from Bamboo. *BioResources.* 2016, Vol. 11, issue 3, pp. 7296–7304.

[23]YAMASHITA, K., et al., Compositions of Volatile Organic Compounds Emitted from Melted Virgin and Waste Plastic Pellets. *J. Air Waste Manag. Assoc.*, 2009, Vol. 59, issue 3, pp. 273-278.

[24]TIRENDI, S., et al., Chemical emissions from toys - the case of stink blasters. *Int. J. Environ. Anal. Chem.*, 2009, Vol. 89, issue 8–12, pp. 929–938.

[25]LIU, H.C., et al., Analysis of trace contamination of phthalate esters in ultrapure water using a modified solid-phase extraction procedure and automated thermal desorption–gas chromatography/mass spectrometry. *J. Chrom. A*, 2008, Vol. 1188, issue 2, pp. 286–294.

[26]LAAKS, J., et al., In-Tube Extraction-GC-MS as a High-Capacity Enrichment Technique for the Analysis of Alcoholic Beverages. *J. Agric. Food Chem.*, 2014, Vol. 62, issue 14, pp. 3081–3091.

[27]KU, K.L., CHEN, T.P., CHIOU, Y.Y., Apparatus Used for Small-Scale Volatile Extraction from Ethanol-Supplemented Low-Salt Miso and GC–MS Characterization of the Extracted Flavors. *J. Agric. Food Chem.*, 2000, Vol. 48, issue 8, pp. 3507–3511.

[28]REYNOLDS, J.C., et al., Detection of Volatile Organic Compounds in Breath Using Thermal Desorption Electrospray Ionization-Ion Mobility-Mass Spectrometry. *Anal. Chem.*, 2010, Vol. 82, issue 5, pp. 2139–2144.

[29]MAURER, F., et al., Validation of liquid and gaseous calibration techniques for quantification of propofol in breath with sorbent tube Thermal Desorption System GC–MS. *J. Pharm. Biomed. Anal.*, 2017, Vol. 143, pp. 116–122.

[30]LARSSON, T., FRECH, W., Species-Specific Isotope Dilution with Permeation Tubes for Determination of Gaseous Mercury Species. *Anal. Chem.*, 2003, Vol. 75, issue 20, pp. 5584–5591.

[31]AMES, J.M., GUY, R.C.E., KIPPING, G.J., Effect of pH, Temperature, and Moisture on the Formation of Volatile Compounds in Glycine/Glucose Model Systems. *J. Agric. Food Chem.*, 2001, Vol. 49, issue 9, pp. 4315–4323.

[32]ČAPOUN, T., KRYKORKOVÁ, J., Analýza látek v ovzduší metodou GC/MS se sorpčními trubičkami Tenax. *The Science for Population Protection*, roč. 0, L. Bohdaneč: Ministry of Interior – Directorate General of the Fire REscue Service of the Czech Republic, Population Protection Institute, 2008, s. 17–30.

[33]KIM, Y.H., KIM, K.H., Novel Approach to Test the Relative Recovery of Liquid-Phase Standard in Sorbent-Tube Analysis of Gaseous Volatile Organic Compounds. *Anal. Chem.*, 2012, Vol. 84, issue 9, pp. 4126–4139.

[34]JUILLET, Y., et al., Optimisation of sorbent trapping and thermal desorption–gas chromatography–mass spectrometric conditions for sampling and analysis of hydrogen cyanide in air. *Analyst*, 2005, Vol. 130, pp. 977–982.

[35]BROOKES, B.I., Gas analysis using an internal standard in adsorption tubes. *Analyst*, 1979, Vol. 104, pp. 698–699.

[36]LAZAROV, B., et al., Air sampling of flame retardants based on the use of mixed-bed sorption tubes - a validation study. *Environ. Sci. Pollution Res.,* 2015, Vol. 22, issue 22, pp. 18221–18229.

[37]*Pokyn generálního ředitele Hasičského záchranného sboru ČR č. 6/2017, kterým se vydává Řád chemické služby Hasičského záchranného sboru České republiky*. [Order of the Czech Fire Rescue Service General Director no. 6/2017, by which the FRS Chemical Service Regulations are issued.] Praha: Ministry of Interior – Directorate General of the Fire REscue Service of the Czech Republic, 2017.

[38]ČAPOUN, T., ULBRICH, J. *Metodika vzorkování pro účely chemické analýzy v laboratořích HZS ČR. (Metodika certifikovaná komisí MV – GŘ HZS ČR, osvědčení č. CERO 9/2015 ze dne 13. 10. 2015)*. [Sampling methodology for the purposes of chemical analysis in Czech FRS laboratories. (Methodology certified by the Ministry of Interior – Directorate General of the Czech Fire Rescue Service, certificate no. CERO 9/2015 from October 13, 2015.] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire REscue Service of the Czech Republic, Population Protection Institute, 2015. 36 pp.

[39]EffiValidation 3.0. EffiChem, Oulehla, 2002.

[40]ČAPOUN, T., KRYKORKOVÁ, J. *Odhad koncentrace organických látek ve vzduchu odebraném na sorpční trubičku Tenax. (Výzkumná zpráva)* [Estimate of organic substance contretation in the air

sampled the Tenax sorbent tube. (Research Report)] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire REscue Service of the Czech Republic, Population Protection Institute, 2017. 43 pp.

[41]KIM, Y.H., KIM, K.H., Extent of Sample Loss on the Sampling Device and the Resulting Experimental Biases When Collecting Volatile Fatty Acids (VFAs) in Air Using Sorbent Tubes. *Anal. Chem.*, 2013, Vol. 85, issue 16, pp. 7818–7825.

[42]ČAPLYGIN, M. *Základy termální desorpce. Sborník XXII. Mezinárodní konference o separační chemii a analýze toxických látek*. (Basics of thermal desorption. Proceedings of the XXII. International Conference on Separation Chemistry and Toxic Substance Analysis.) Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire REscue Service of the Czech Republic, Population Protection Institute, 2017.

DEVELOPMENT AND PROPERTIES OF A SPECIALIZED FILTER FOR THE USE IN A FIRE-FIGHTING EMERGENCY TRUCK

Vlastimil SÝKORA*, Čestmír HYLÁK*

* Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, Na Lužci 204, 533 41 Lázně Bohdaneč, Czech Republic; email: vlastimil.sykora@ioolb.izscr.cz ; cestmir.hylak@ioolb.izscr.cz

ABSTRACT:

Emergency vehicles, whether fire-fighting or military ones, require installed filters to protect the personnel during their operations in contaminated areas. Those filters, in contrast to the conventional filters for the protection of individuals, differ not only in construction, but also in their higher sorbent content and sorption at higher airflow rates. The aim of this work was to test a novel filter on selected hazardous substances, which include cyclohexane, ammonia, sulfur dioxide and hydrogen sulfide. Measurements were performed at a test substance concentration of 500 ppm and at an airflow rate of 200 m^3 h^{-1}. Results obtained clearly demonstrate that such filters are able to absorb the given substances for times complying with the ČSN EN 12941 norm requirements.

KEYWORDS:

specialized filter, measurement method, sorption, properties, cyclohexane

1. Introduction

Dust or chemical filters or combinations thereof are used for the protection against hazardous substances. Those filters vary in shape (cylindric, beveled drop), size (from small ones used for personal protection to large ones intended for collective protection in shelters), intended use (industrial, NBC), amount of sorbent used (from tens of grams up to kilograms) and its composition (determining the use of the filter), and they can exhibit other features based on the requirements (filter housing materials, screw and its location, possibility to connect in series, etc.).

Protective equipment may be combined with a single filter. For example in combination with protective masks or hoods [1, 2, 3], or with multiple filters, such as in protection bags, filtration–ventilation units (typically 2–3 filters or up to 5–7 in special applications) [4], or in air mixing devices [5] (intended for use in improvised collective protection, with up to 8 filters).

The filters are typically used for individual or collective protection in a stationary installation. Special filters containing greater amounts of the sorbent, allowing higher flow rates and requiring a special connection and location in the vehicle are used for mobile equipment such as armoured fighting vehicles and special rescue and fire-fighting vehicles. Development, testing, and production of such filters is not straightforward, and it requires more complex equipment and considerable financial investment.

We have tested ABEK filters, developed in co-operation with the MOLPIR GROUP CZ Company, based in Olomouc, Czech Republic, and produced by the DELBAG company, based in Liberec, Czech Republic, for such use. Sorption capacity of the filters was tested according to the ČSN EN 12941 norm requirements [6] for use with cyclohexane, ammonia, sulfur dioxide, and hydrogen sulfide.

2. Experimental tests

a) Apparatus, equipment and auxiliary materials used

Following apparatus, equipment and auxiliary materials were used:

- Special chamber constructed for the testing on non-standard filters,
- SYCOS K-DPG mixing chamber,
- MFLEX peristaltic pump,
- AZURA P2 high pressure pump,
- Gasmet FTIR DDX-4000 IR spectrometer,
- MultiRAE detector,
- SKF-240 ventilator,
- TESTO 435-2 flowmeter,
- Hanhart laboratory stopclock,
- TESTO 0609 thermometer,
- 25 L sampling bags.

b) Filters tested

Combined filter KFM 200 (Figure 1) was used for the measurement. The filter consisted of a steel housing equipped with steel lids removed before the measurements. Filtration cartridge was prepared from Lydall AX 6650 paper, the ABEK type sorbent (8 kg) came from the Pleisch Company. Overall weight of the filters reached ca. 18 kg.

Figure 1. KFM 200 filter

c) Chemicals used

Following chemicals were used for the testing of the newly developed ABEK-type filter:

- Cyclohexane, C_6H_{12} (colourless, highly flammable liquid, harmful, toxic in the environment, MW 84.16 g mol^{-1}, bp 80.75°C, ρ 778.5 kg m^{-3}),
- Ammonia, NH_3 (colourless, pungent gas lighter than air, very well soluble in water, dangerous for the environment, MW 17.03 g mol^{-1}, bp –33.34°C),
- Sulfur dioxide, SO_2 (colourless, pungent gas, well soluble in water, 2.26× higher density than air, toxic, MW 64.07 g mol^{-1}, bp –10.02°C)
- Hydrogen sulfide, H_2S (colourless gas heavier than air, very well soluble in water, extremely flammable, highly toxic, dangerous for the environment, MW 34.08 g mol^{-1}, bp –60.28°C)

d) Measurement method and conditions

As indicated above, four test substances were used, one of them in the liquid and three in the gaseous state. The measurement setup had to account for these differences to comply with the required conditions.

Cyclohexane measurements

The measuring installation for the cyclohexane sorption testing consisted of a SYCOS K-DPG mixing chamber (including a heated block), AZURA P2 high pressure pump to deliver the required amounts of the substance tested (Figure 2), moisturising equipment to adjust the temperature and humidity of the gas–air mixtures, special chamber for the filter testing, the SKF-240 ventilator fitted with the TESTO

435-2 flowmeter and TESTO 0609 thermometer to regulate the desired air flow (Figure 3) and two Gasmet FTIR DX-4000 IR spectrometers to test the input and output concentration.

The measurement was performed at the gas–air flow of 200 m^3 h^{-1} (3,330 L min^{-1}), analyte concentration of 500 ppm, temperature 24 ± 2°C, relative humidity 50 ± 10% and pressure 985 ± 10 hPa.

For cyclohexane, the ČSN EN 12941 norm requires the minimum penetration time of 70 minutes.

Figure 2. Left view of the measurement setup Figure 3. Right view of the measurement setup

The measurements involved preparation of the gas–air mixture at the given flow rate, concentration, temperature and humidity, and its retention at the filter tested. Flowmeter and then ventilator were connected through the filter side opening. The penetration concentration (10 ppm) was measured on the entry to the ventilator. The input concentration was measured before entry to the filter using silicone tubing. Gasmet FTIR DX-4000 were used in both cases (Figure 4).

Figure 4. IR spectrometer setup

3. Gaseous substances measurement

The gaseous substance measuring installation (ammonia, sulfur dioxide, hydrogen sulfide) consisted of a sampling bag (containing the corresponding gaseous substance), MFLEX peristaltic pump to displace the gas from the bag and to prepare the gas–air mixture of desired concentration, moisturising equipment to adjust the temperature and humidity of the gas–air mixture, special chamber for the filter testing (Figure 1), SKF-240 fitted with the TESTO 435-2 flowmeter and TESTO 0609 thermometer to regulate the desired air flow, and either two Gasmet FTIR DX-4000 IR spectrometers to measure the input and output concentration of ammonia and sulfur dioxide, or the MultiRAE detector to measure the penetration concentration of hydrogen sulfide.

Measurement of the gaseous substances was performed at conditions identical to the cyclohexane measurement. The ČSN EN 12941 norm requires minimum penetration of 50 minutes for ammonia, 20 minutes for sulfur dioxide, and 40 minutes for hydrogen sulfide. However, unlike the cyclohexane measurement, the gas–air mixture was prepared by removal of the gas from the sampling bag using a peristaltic pump to yield the gas–air mixture of desired flow rate, concentration, temperature and humidity. The gas-air mixture was then introduced to the filter tested by means of the ventilator.

Again, the penetration concentration was measured at the entry to the ventilator. For ammonia (25 ppm) and sulfur dioxide (5 ppm) the Gasmet FTIR DX-4000 IR spectrometer was used, while the MultiRAE detector was used for hydrogen sulfide (10 ppm). The input concentration was measured as for cyclohexane.

e) Calculation of dynamic sorption capacity

Dynamic sorption capacity (DSC) was calculated according to the following equation:

$$DSC\ (g)\ = \frac{MW \times c \times Q \times RT}{2447000} \qquad (1)$$

MW   molecular weight [g mol^{-1}]

c   concentration [ppm]

Q   flow rate [l min^{-1}]

RT   residence time [min]

f) Results

Table 1 shows the sorption values for small protective filters for each substance tested at the required flow rate of 3,330 L min^{-1} (200 m^3 h^{-1}). Taking into account that no national norm exists for the filters we have studied, the sorption requirements are taken as per the ČSN EN 12941 [6] norm for class 1 small protective filters, i.e., for concentration of 500 ppm and required minimum retention period (so-called residence time, *RT*). The *DSC* values corresponding to these requirements are also listed.

Table 1. Filter sorption according to ČSN EN 12941 for class 1 small protective filters (SPF)

Filter	Substance tested	*c* [ppm]	*Q* [l min^{-1}]	*RT* [min]	*DSC* [g]
SPF	cyclohexane	500	3,330	70	401.3
SPF	ammonia			50	58.0
SPF	sulfur dioxide			20	87.3
SPF	hydrogen sulfide			20	46.4

Table 2 then shows the resulting *RT* values tested and *DSC* values calculated for each measurement condition and substance tested, including mean values ($DSC_\emptyset$), standard deviations (DSC_s) and variation coefficients (DSC_v).

Table 2. Special TITAN filter sorption

Filter	Manufacturing number	Substance tested	c [ppm]	Q [L min^{-1}]	RT [min:sec]	DSC [g]	$DSC_{\emptyset}$ [g]	DSC_s [g]	DSC_v [g]
TITAN 1	0010819	Cyclohexane	500	3,330	92:45	531.7	512.8	26.8	5.2
TITAN 2	0030819				86:15	493.8			
TITAN 3	0050819	Ammonia			66:15	76.8	99.3	31.8	32.0
TITAN 4	0010720				105:00	121.8			
TITAN 5	0040819	Sulfur dioxide			51:40	225.4	200.0	35.9	18.0
TITAN 6	0020720				40:00	174.6			
TITAN 7	0020819	Hydrogen sulfide			103:35	240.4	242.1	2.3	1.0
TITAN 8	0030720				105:00	243.7			

The results shown in Table 2 clearly indicated that the required RT (or DSC) values could not only be complied with but even highly exceeded. When comparing the average values to the theoretical ones (Table 1), the requirements have been exceeded by 27.8% for cyclohexane, by 71.2% for ammonia, by 129.1% for sulfur dioxide, and by 421.8% for hydrogen sulfide. Moreover, both measurements have reached very similar results for hydrogen sulfide, and the standard deviation DSC_s (2.3 g) and variation coefficient DSC_v (1.0%) were very low. There was a very good match of both measurements for cyclohexane, too (DSC_s 26.8 g and DSC_v 5.2%). The other gases exhibited greater differences – DSC_s reached 31.8 g and DSC_v 18.0% for sulfur dioxide, and 31.8 g and 32.0% for ammonia. However, even the lower values obtained still significantly exceeded the requirements listed in Table 1. For sulfur dioxide, the theoretical values have been exceeded by 100.0% for the DSC of 174.6 g, and for ammonia, by 32.4% for the DSC of 76.8 g.

4. Conclusion

The results obtained have clearly shown that the filters tested are able to protect the rescue truck occupants from the tested hazardous substances for the times required by the ČSN EN 12941 norm. The hazardous substances include cyclohexane (representing organic compounds, especially organophosphates), ammonia (representing also other amines), sulfur dioxide (representing acidic gases) and hydrogen sulfide (representing inorganic compounds).

Sorption capacity of the filter produced (containing ca. 8 kg of the sorbent) not only fulfils the minimum required penetration times or dynamic sorption capacity, but significantly exceeds them.

It can be concluded that these filters are useful both in military as well as fire-fighting emergency trucks.

LITERATURE

[1] Sýkora, V.: *Prostředky pro ochranu dýchacích cest. 1. vyd.* [Respiratory Tract Protective Devices, 1st Edition.] Ministry of Interior, Directorate General of the Fire Rescue Service of the Czech Republic, 2008, 71 pp. ISBN 978-80-86640-95-2.
[2] Sýkora, V.; Hylák, Č.: *Ochranné masky – chrání nebo nechrání, popř. proč?* [Protective masks – do they protect or not, any why?] Proceedings from the international conference DEKONTAM 2013, Fire and Safety Engineering Association, Faculty of Safety Engineering, VSB – Technical University Ostrava, 2013, 161–166, ISBN 978-80-7385-122-4.
[3] Hylák, Č.; Sýkora, V.; Urbanová, D.; Kovaličová, H.: *Testování ochranných masek nabízených na tuzemském trhu na těsnost.* [Testing the tightness of protective masks on the Czech market.] Proceedings from the 1st HAZMAT PROTECT 2014 conference, Kamenná–Milín 2014, section "*Testování ochranných prostředků* [Protective devices testing]", 12–22.
[4] Sýkora, V.: *Filtroventilační jednotky jako moderní nástroj v ochraně dýchacích cest.* [Filtration–ventilation units as a modern tool in respiratory tract protection.] *112* **2018**, *16*, 26–27.
[5] Pivovarník, J.; Hylák, Č.; Sýkora, V.: *Technické řešení možného využití domácích spotřebičů ke konstrukci filtroventilačního zařízení improvizovaného úkrytu, etapa E-6* [Technical solution to possible use of home appliances for the filtration–ventilation unit of an improvised shelter, Phase E-6] and *Posouzení využitelnosti filtroventilačního jednotek určených k individuální ochraně pro improvizované úkryty, etapa E-7* [Utility assessment of filtration-ventilation units intended for individual protection for improvised shelters, Phase E-7]. Interim report to *DÚ 2* [Partial Assignment 2], Lázně Bohdaneč 2014, 44 pp.
[6] ČSN EN 12941:1999 *Ochranné prostředky dýchacích orgánů – Filtrační prostředky s pomocnou ventilací připojené k přilbě nebo ke kukle – Požadavky, zkoušení a značení"* [Respiratory protective devices – Powered filtering devices incorporating a helmet or a hood – Requirements, testing, marking]. Issued October 1, 1999, 52 pp.

IDENTIFICATION OF CANNABIS GENUS TERPENES IN THE AIR

Henryk SIKORA*, Daniel LEPIČ*

*Třemošná Training Centre and Laboratory, Fire Rescue System of the Plzeň Region, Ku staré cihelně 1111, 330 11 Třemošná, Czech Republic e-mail: henryk.sikora@hzspk.cz ; daniel.lepic@hzspk.cz

ABSTRACT:

Cannabis farms are difficult to detect and their number has been steadily growing. Yet, cannabis growing is associated with the release of terpenes into the air, giving rise to the plant's characteristic odour. Sampling the air at an adequate distance is one of the possibilities to identify the farm. The thermal desorption technique is a useful method for such work, passing the air sample through a sorption tube, and then subsequently analysing the sample in the laboratory using gas chromatography with mass detection. This method allowed the identification of characteristic monoterpenes proving *Cannabis* farming on the premises.

KEYWORDS:

Thermal desorption, terpenes, *Cannabis*.

1. Introduction

The number of in- and outdoor *Cannabis* farms has been steadily growing according to the Czech National Drug Headquarters 2019 annual report. The overall number of grow houses secured has remained almost constant in the past seven years [1]. Most grow houses are detected due to illicit electricity consumption [2]. However, such proof is insufficient for small-scale farms. Confirmation of the cannabinoid presence by obtaining chemical samples, usually swabs, is most useful. However, this practically means entering a private property or its imminent vicinity, which leads to a number of complications. This article describes a method for the collection of air samples from the surrounding, and subsequent identification of characteristic terpenes, which allows for a reliable confirmation of *Cannabis* farming.

Table 1. Development of the seized amounts between 2010 and 2020 [1]

	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Cannabis [kg]	278	441	563	735	570	655	722	1,094	948	546	655
Cannabis plants [ths]	64.9	62.7	90.1	73.6	77.7	30.8	57.7	54.4	28.3	26.9	16.0

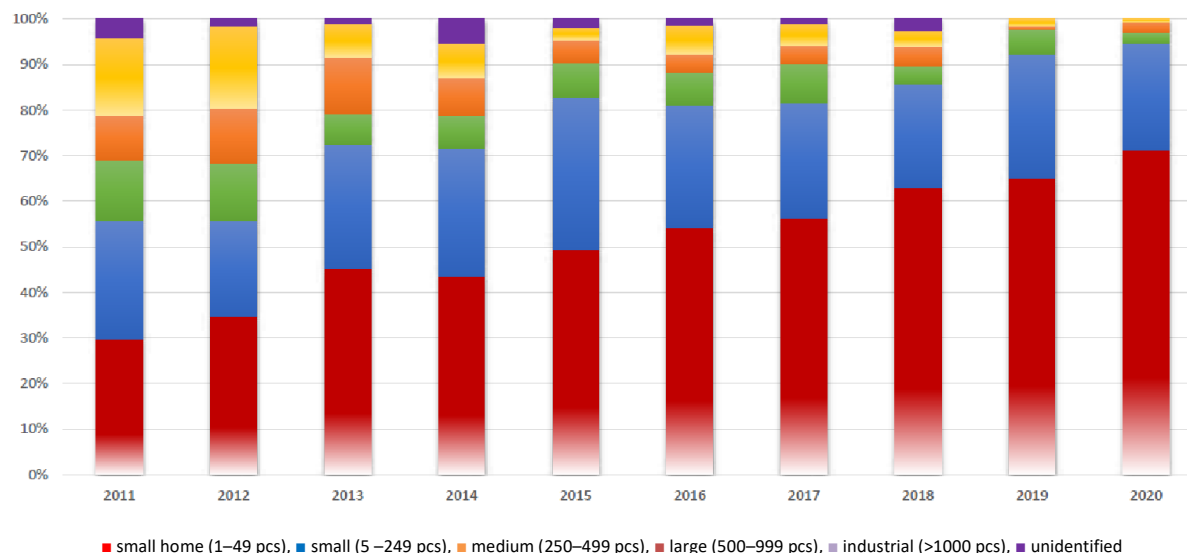| Farms	145	165	199	276	301	220	299	305	202	258	167
Hashish [kg]	9.4	2.4	20.5	1.3	14.9	7.6	6.6	9.1	2.9	1.7	1.2

Figure 1. Number of *Cannabis* farms seized between 2011 and 2020 by size (in %) [1]
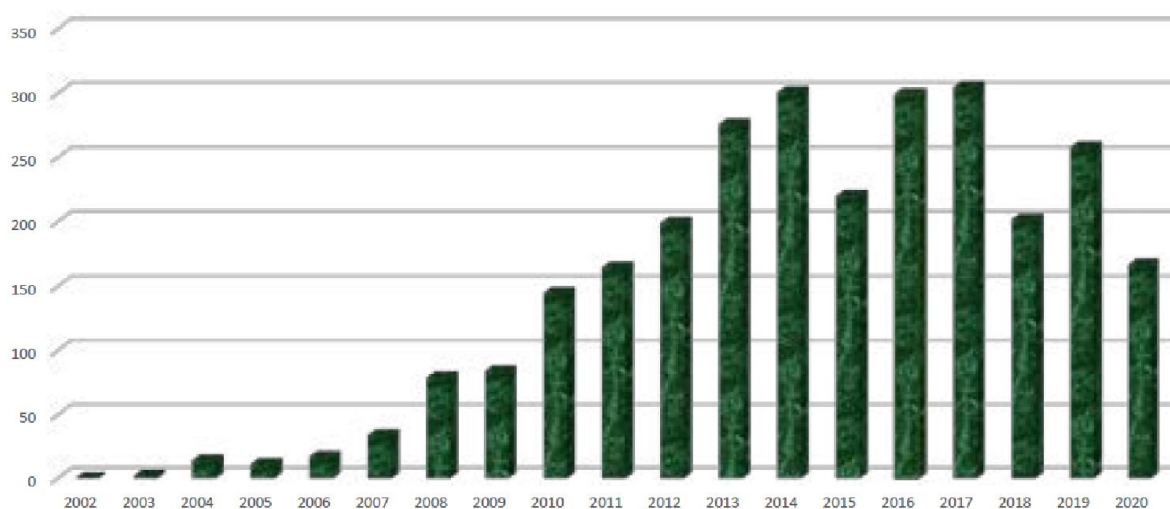

Figure 2: Overall number of *Cannabis* farms seized in the Czech Republic in 2002–2020 [1]

2. Terpenes

Cannabis farming is associated with the release of volatiles into the air. The volatile compounds are terpenes, giving rise to the intensive and characteristic odour of these plants. Some authors describe up to 200 compounds are released into the air, most including monoterpenes or sesquiterpenes [4, 5, 6]. Together, these compounds create a fingerprint proving the presence of *Cannabis* plants at the given location. However, more sophisticated object security measures and dwelling inviolability make

it impossible to collect samples from the interior or immediate vicinity of the farms. Collection of air samples at an adequate distance (meters to tens of meters) may be the only option. Terpenes released into the air may be detected sensorically in very low concentrations around 0.1 ppm [7, 8].

Five-carbon isoprenoid building blocks isopentenyl diphosphate (IPP) and dimethyl allyl diphosphate (DMAPP) represent the basic building blocks for the biosynthesis of terpenes and cannabinoids in *Cannabis.* The building blocks condense to yield geranyl diphosphate (GPP) (C_{10}) or farnesyl diphosphate (C_{15}). Terpene synthases (TPS) convert GPP or FPP to terpenes. Aromatic prenyl transferases (aPT) condense GPP with olivetolic acid to produce cannabigerolic acid (CBGA) which is cyclised by cannabinoid synthases to give cannabinoids [5].

Terpene composition depends on the phenotype, and there are certain differences between the *Cannabis* subtypes. Most terpenes found in *Cannabis* are hydrocarbons directly produced by the terpene synthases (TPS) unlike more complex terpenes, which require modification by other enzymes such as cytochrome P450. The chemical diversity of *Cannabis* terpenes reflects the diversity of the TPS enzymes coded in the *Cannabis* TPS family [5]. Composition of terpenes in the *Cannabis* resin can significantly vary depending on the genetic, environmental and development factors [4, 9].

In our case, we were interested in monoterpenes. Booth and Bohlmann list twelve basic monoterpenes [5], including: β-pinene, α-pinene, β-thujone, 3-carene, terpinolene, D-limonene, terpineol, 1,8-cineol, α-terpinene, linalool, myrcene and (*Z*)-β-ocimene. When extracting the terpenes, Booth, Page, and Bohlmann found that regardless of the inflorescence state, the most abundant monoterpenes include α-pinene, D-limonene, β-pinene, terpinolene and (*E*)-β-ocimene [6]. Other source lists five prominent terpenes from a group of thirteen monoterpenes and fourteen sesquiterpenes, including myrcene, terpinolene, α-pinene, β-pinene, and limonene as monoterpenes, and caryophyllene as a sesquiterpene. The concentration of monoterpenes drops in dried plants [9]. It was shown that hashish from fresh and dried plants can be distinguished through the presence of 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane. This compound is formed from β-myrcene by UV irradiation [4].

Recent studies show that *C. indica* contains 60–80% more myrcene than *C. sativa.* This makes myrcene the dominant terpene present in the *Cannabis* genus plants [10].

α-Pinene and β-pinene are important for identification as they represent 10–20% of the overall amount of terpenes in Cannabis, and moreover, their high volatility contributes to their dominant peaks in the chromatograms. However, pinenes are a predominant constituent in coniferous trees, and sufficient distance from such trees must be maintained when sampling, or additional samples needed to be included into the analysis for comparison purposes [10]. D-Limonene is the second most abundant terpene in *Cannabis*. However, it is also frequently used as an aromatic principle in various cosmetic and cleaning products. It occurs naturally in citrus fruits. This needs to be taken into account when sampling [10, 11].

Linalool is a terpene, which contributes the most to the characteristic odour of *Cannabis* [11]. Eucalyptol (1,8-cineol), carene, phellandrene and terpinolene are important terpenes shown by scientific studies to occur only in the *C. sativa* species [10].

Caryophyllene belongs to the sesquiterpenes; however, it can be detected under suitable conditions in the air due to its highest volatility within the group. Its advantage is lack of decarboxylation, making it the easiest component to detect in *Cannabis* extracts [10].
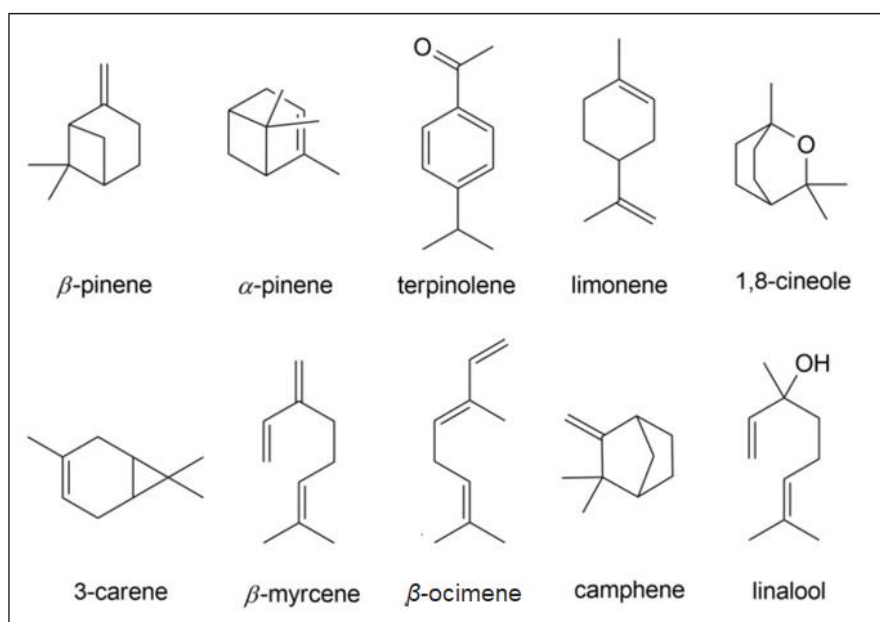
Figure 3: Chemical structure of selected monoterpenes

3. Methodology for the analysis of terpenes in the air

Current analyses show that amounts detectable sensorically represent a borderline concentration for air sampling and subsequent analysis. Yet, the odour is so characteristic the sensoric identification is an important trigger for more sophisticated analysis. Analysis of such low concentration by PID detectors is impractical due to interferences from other volatile compounds in the environment. Using the canine sense of smell can be problematic as the dogs are trained for dried plant material or hashish which contain lower monoterpene concentrations. Moreover, the dogs are trained to locate the particular location of the given substance (explosives, drugs, accelerants, etc.). Persistent odour in the air disorients the dogs and makes the source location more difficult.

The thermal desorption method has been the most convenient for the air analysis. Air is sampled using a sorption tube, which is subsequently analysed, in a laboratory equipped with a gas chromatograph unit with mass detection. Both passive and active sampling can be used; however, passive sampling has been impractical in the field, and active sampling (using a flow of 500 mL/min and 30–60 min sampling time) has been preferred. Short sampling times could be insufficient for the identification of the analysed terpenes; longer sampling times may decrease efficiency due to sorption of other volatile compounds from the environment. Sorption tubes with combined sorbents (strong and weak) have proven most convenient; we have used the combination of Tenax TA 35/60 (100 mg) and Carbograph 5TD 40/60 (100 mg). Solid particles (pollen, dust) adsorbed on the sorption tube may significantly interfere with the analysis due to thermodegradation during the thermal desorption in the absence of oxygen, and make identification of the analysed terpenes difficult. Suitable prefilters are therefore recommended for the sampling.

3.1. Sample collection

Sampling low concentrations in the exterior requires thorough and precise work to avoid the risk of sorption tube (and resulting sample) contamination. Sample collection by the professional who

eventually performs the analysis worked best. The sorption tubes should be prepared and conditioned just shortly before the analyses, and they should be tightly wrapped in the protective tube double cover. They must be sufficiently protected from contact with other volatile compounds during the transport to and from the site of interest, especially from the fuel in vehicles. They should only be manipulated in gloves.

The meteorological situation has to be known before the sampling. It is advantageous to collect the sample at high ambient temperature when the terpenes evaporate more easily. An important contributing factor is the wind direction. The samples should be collected at the downwind side, often in the narrow band of spread. Locations with possible presence of naturally occurring terpenes should be avoided (flowers, shrubs and trees in flower, coniferous trees, etc.). The sorption should be performed neither at elevated location nor on the ground due to higher exposure to pollen, dust, etc.

A control sample may be collected in a similar manner on the upwind side or where appropriate while ensuring sufficient distance from other terpene sources.

It may be necessary to dampen the air pump noise and cover light sources to minimise the risk of discovery. It is recommended to collect at minimum two samples. Both may be collected at the same time to minimise the on-site presence.

After the sampling, it is necessary to tightly enclose the sorption tubes in a clean protective tube double cover, and rapidly transport them to the laboratory for subsequent analysis.

3.2. Sample analysis

The terpenes were analysed using the contributions of other authors dealing with similar topics [12, 13, 14, 15, 16, 17].

Own chromatograms of the terpene standard should be available before the analysis. In our case, we used RESTEK standards [18]. We do not recommend testing the standard immediately before the analysis itself to avoid false positives from the terpene residues. The thermal desorption unit should be ready before the air sample collection, i.e., before conditioning the sorption tubes. All elements including the Cold Trap should be preheated to remove potential impurities. Equipment sensitivity may be verified using a standard before the analysis; however, the standard should differ from the terpenes analysed. Subsequently, the system purity check may be performed.

Table 2

Cannabis terpene standard #1 & #2, Rxi-624Sil MS column [18]

	Name	*RT* (min)	Group
1	α-Pinene	5.399	monoterpene
2	Camphene	5.768	monoterpene
3	β-Myrcene	6.203	monoterpene
4	(−)-β-Pinene	6.290	monoterpene
5	δ-3-Carene	6.816	monoterpene

6	α-Terpinene	7.026	monoterpene
7	Ocimene 1	7.158	monoterpene
8	ᴅ-Limonene	7.281	monoterpene
9	*p*-Cymene	7.362	aromate
10	Ocimene 2	7.539	monoterpene
11	Eucalyptol	7.629	monoterpenoid (ether)
12	Gamma terpinene	7.990	monoterpene
13	Terpinolene	8.887	monoterpene
14	Linalool	9.845	monoterpenoid (alcohol)
15	(−)-Isopulegol	10.874	monoterpenoid (alcohol)
16	Geraniol	11.991	monoterpenoid (alcohol)
17	β-Caryophyllene	13.303	sesquiterpene
18	α-Humulene	13.531	sesquiterpene
19	Nerolidol 1	13.855	sesquiterpenoid (alcohol)
20	Nerolidol 2	14.012	sesquiterpenoid (alcohol)
21	(−)-Guaiol	14.393	sesquiterpenoid (alcohol)
22	Caryophyllene oxide	14.483	sesquiterpenoid (epoxide)
23	(−)-α-Bisabolol	14.747	sesquiterpenoid (alcohol)
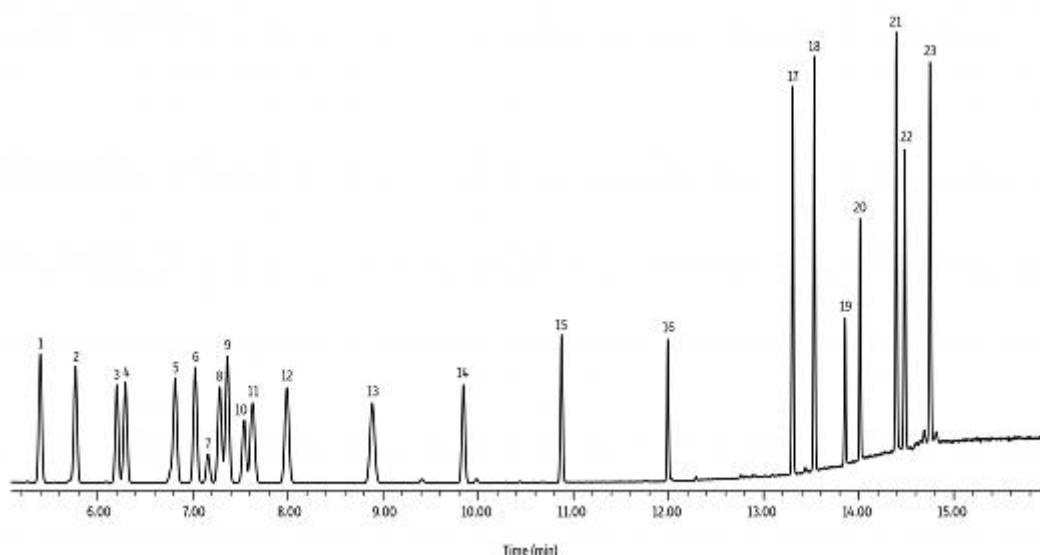
Column	Rxi-624Sil MS, 30 m, 0.25 mm ID, 1.40 μm (cat.# 13868)
Standard/Sample	Cannabis terpenes standard #1 (cat.# 34095)
	Cannabis terpenes standard #2 (cat.# 34096)
Diluent:	Isopropanol
Conc.:	25 μg/mL (5 μg/mL on-column after 5:1 split)
Injection	
Inj. Vol.:	1 μL split (split ratio 5:1)
Liner:	Topaz 4.0 mm ID Precision inlet liner w/wool (cat.# 23305)
Inj. Temp.:	250 °C
Split Vent Flow Rate:	6 mL/min
Oven	
Oven Temp.:	55 °C to 130 °C at 25 °C/min (hold 6 min) to 280 °C at 30 °C/min (hold 2 min)
Carrier Gas	He, constant flow
Flow Rate:	1.2 mL/min

Figure 4. *Cannabis* Terpenes Standard #1 & #2, Rxi-624Sil MS column, injection, FID [18]

Sample analysis should be performed as soon as possible to avoid contamination. The split ratio for primary and secondary desorption and in the injection module should be set to lower values. In our case, the overall split was 1:50.

The control samples should be analysed first to disprove any contamination during sampling, transport or analysis.

Clean split tube should be prepared before the analysis in case the analysis fails and needs to be repeated.

3.3. Interpretation

The sample may exhibit high background despite the most thorough analysis due to the contents of other volatile compounds at the sampling site, thermal degradation of adsorbed solid particles, or sorption tube contamination. Therefore, the chromatograms should be extracted using the characteristic *m/z* 93 typical for these terpenes while fine-tuning the processing parameters. Use of deconvolution is important. In our experience, mass spectrometers with Time of Flight analysers have been convenient for this. Examples of chromatograms extracted at *m/z* 93 are shown in Figures 5 and 6.

Terpenes found are identified using their mass spectrum and compared to the NIST library, and comparison of the retention times to the standard. Smaller peaks corresponding to less volatile terpenes may prove difficult to evaluate. Presence of the *m/z* 93 peak and matching retention times may indicate possible presence of other terpenes.

Reliability of the proof that *Cannabis* plants are present grows with the number of terpenes identified in the air sample. We have established that confirmation of at least five main terpenes – which is straightforward – confirms the presence of *Cannabis* plants with very high probability. The presence of specific terpenes (eucalyptol, carene, phellandrene, terpinolene) highly increases the confidence of the result.

Following chromatogram (Figure 5) illustrates main volatile terpenes α-pinene, camphene, β-pinene, β-myrcene, 3-carene, ᴅ-limonene, eucalyptol, β-ocimene, γ-terpinene, terpinolene, linalool, isopulegol, and two sesquiterpenes β-caryophyllene, and α-humulene.
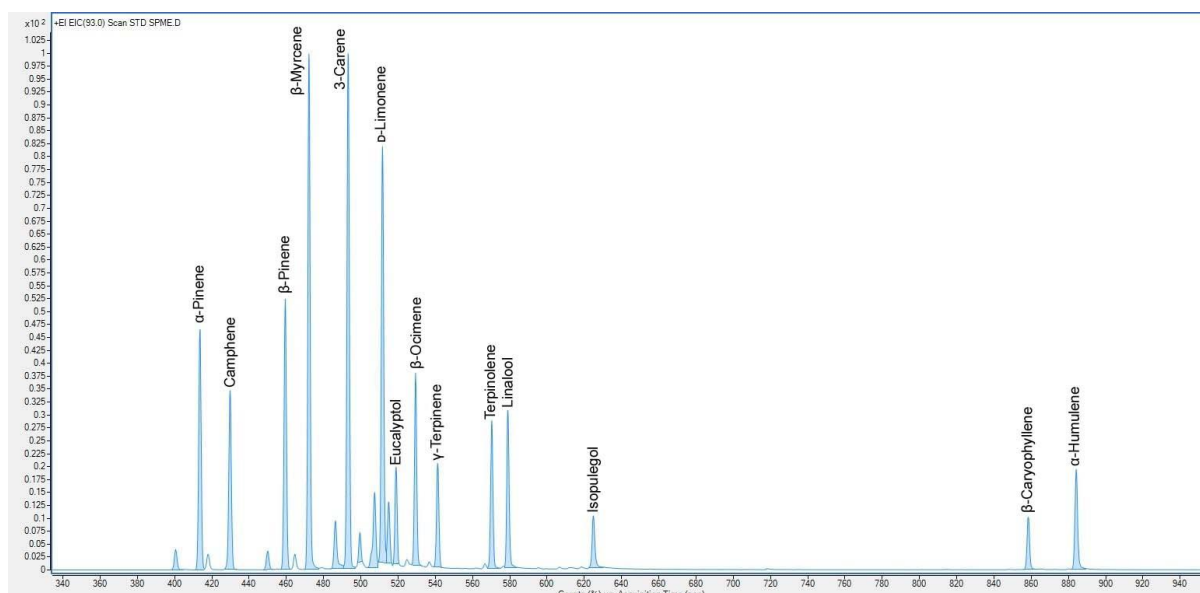

Figure 5. Chromatogram of the RESTEK standard, SPME

The next chromatogram (Figure 6) shows a real sample taken 20 m from the premises. The sorption time reached 60 minutes. Monoterpenes α-pinene, camphene, β-pinene, 3-carene, ᴅ-limonene, and

eucalyptol could be identified by their mass spectra. Monotorpenes ocimene, terpinene, terpinolene, linalool, and isopulegol could be identified by the retention times.
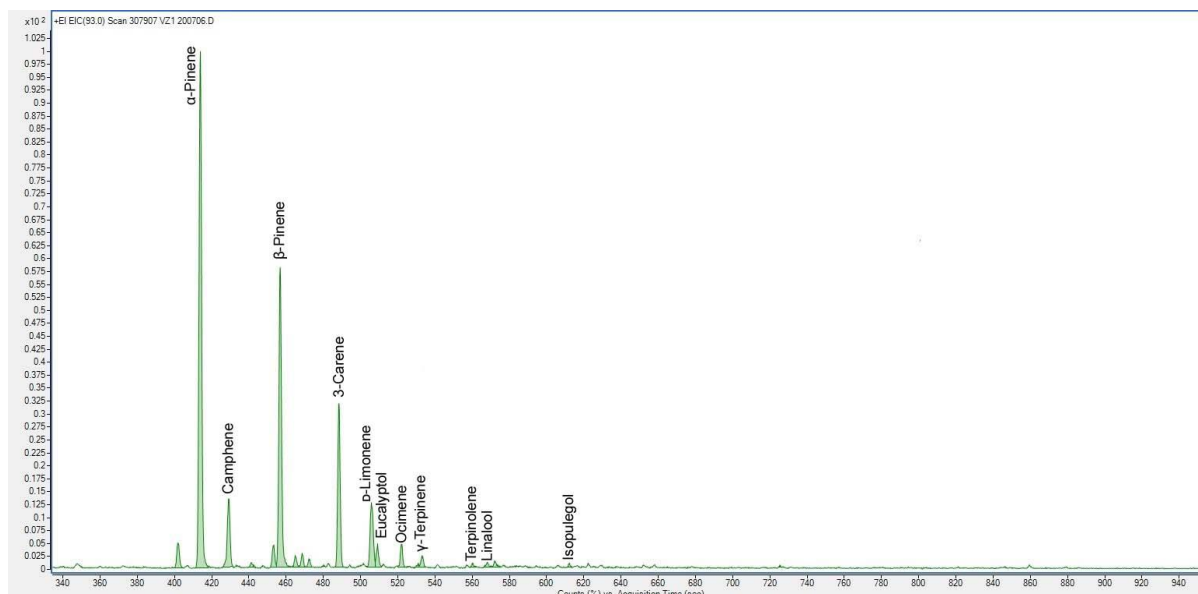

Figure 6. Real sample chromatogram

4. Conclusion

The presence of *Cannabis* plants can be identified by the analysis of air samples taken in the surroundings by the thermal desorption and gas chromatography with mass detection method. The precise methodology for the sampling and analysis has been developed. Main terpenes selected for the identification are α-pinene, camphene, β-pinene, β-myrcene, 3-carene, ᴅ-limonene, ocimene, terpinolene, linalool, eucalyptol, and the sesquiterpene β-caryophyllene. Successful identification of these terpenes in the air proves the presence of *Cannabis* plants or products thereof at the given location with high probability without the need to enter the plots and objects and ingress private property.

This methodology has been developed for the Police of the Czech Republic to make the collection of operative information related to the illicit production and handling of narcotics and psychotropic compounds faster, easier and more reliable.

LITERATURE

[1] B. KUDLÁČKOVÁ, 2020. *Výroční zpráva NPC za rok 2020.* [National Drug Headquarters 2020 Annual Report.] National Drug Headquarters of the Criminal Police and Investigation Service, Police of the Czech Republic.

[2] D. HRAZDÍRA, *Konopný ráj to na pohled…?* [Cannabis Eden All Around…?] Electronic magazine KRIMI-info, Criminalistic Institute Prague, Police of the Czech Republic.

[3] M. ROMAN, L. KOMOROUSOVÁ, *Profil kanabionoidů ve vzorcích konopí (*Cannabis sp. L., Cannabaceæ*).* [Cannabinoid profiles in *Cannabis* samples (*Cannabis sp. L., Cannabaceæ*).] Electronic magazine KRIMI-info, Criminalistic Institute Prague, Police of the Czech Republic.

[4] M. MARCHINI, C. CHARVOZ, L. DUJOURDY, N. BALDOVINI, J.J. FILIPPI, 2014. *Multidimensional analysis of cannabis volatile constituents: Identification of 5,5-dimethyl-1-*

vinylbicyclo[2.1.1]hexane as avolatile marker of hashish, the resin of Cannabis sativa L. Journal of Chromatography A, 1370. 200–215.

[5]   J.K. BOOTH, J. BOHLMANN, 2019. *Terpenes in Cannabis sativa – From plant genome to humans*. DataPlant Science. 284, 67–72. ISSN: 0168-9452, DOI: 10.1016/j.plantsci.2019.03.022.

[6]   J.K. BOOTH, J.E. PAGE, J. BOHLMANN, 2017. *Terpene synthases from Cannabis sativa*. PLOS ONE 12(3): e0173911. DOI: 10.1371/journal.pone.0173911.

[7]   J.E. COMETTO-MUÑIZ, W.S. CAIN, H.A. ABRAHAM, R. KUMARSINGH, 1998. *Sensory Properties of Selected Terpenes: Thresholds for Odor, Nasal Pungency, Nasal Localization, and Eye Irritation*. Annals of the New York Academy of Sciences. 855. 648–51. DOI: 10.1111/j.1749-6632.1998.tb10640.x.

[8]   R. GMINSKI, R. MARUTZKY, S. KEVEKORDES, F. FUHRMANN, W. BÜRGER, D. HAUSCHKE, W. EBNER, V. MERSCH-SUNDERMANN, 2011. *Sensory irritations and pulmonary effects in human volunteers following short-term exposure to pinewood emissions*. Journal of Wood Science - J WOOD SCI. 57. DOI: 10.1007/s10086-011-1182-1.

[9]   P. GOMÉZ, 2017. *Terpene Content in Cannabis – The Variability Problem*, Prof of Pot. Avaiable from: https://profofpot.com/terpene-content-cannabis/ (Accessed August 31, 2022).

[10]FUNDACIÓN CANNÁ. *Terpenes*, Available from: https://www.fundacion-canna.es /en/terpenes (Accessed August 31, 2022).

[11]GREEN CULTURED. *15 Cannabis Terpenes Explained (Complete Visual Guide)*, Available from: https://www.greencultured.co/15-cannabis-terpenes-explained-complete-visual-guide/ (Accessed August 31, 2022).

[12]S.J.B DUNHAM, V.L. NOAD, B.S. ARAKELIAN, D.B. CARDIN, 2019. *Cannabinoid & Terpene Profiling of Cannabis by Solvent-Free Headspace Extraction and Thermal Desorption–GC-MS*, Entech Instruments.

[13]R. HONNOLD, R. KUBAS, A. MACHERONE, 2017. *Analysis of Terpenes in Cannabis Using the Agilent 7697A/7890B/5977B Headspace GC-MSD System*, Application Note, Agilent Technologies, Inc.

[14]M. HALPENNY, K.K. STENERSON, 2017. *Quantitative Determination of Terpenes in Cannabis Using Headspace Solid Phase Microextraction and GC/MS*, GERSTEL Application Note No. 189.

[15]K.K. STENERSON, *Headspace SPME-GC/MS Analysis of Terpenes in Hops and Cannabis*, FOOD & BEVERAGE. Available from: https://www.sigmaaldrich.com/tech nical-documents/articles/analytix-reporter/analysis-terpenes-hops-cannabis.html (Accessed August 31, 2022).

[16]J. WESTLAN, 2019. SPME *Arrow Sampling of Terpenes in Cannabis Plant Material*, Application Note, Sample Preparation, Agilent Technologies Inc.

[17]MARKES INTERNATIONAL. *Thermal Desorption: A Practical Applications Guide*, III. Defence and Forensic. Available from: https://www.restek.com/pdfs/ CFTG1036.pdf (Accessed August 31, 2022).

[18]RESTEK, Pure Chromatography. *Analytical standard, Cannabis Terpenes Standard #1, Cannabis Terpenes Standard #2*. Available from: https://www.restek.com/catalog/vie w/45361, https://www.restek.com/catalog/view/45362 (Accessed August 31, 2022).

PROTECTIVE PROPERTIES OF HOODS AVAILABLE ON THE CZECH MARKET

Čestmír HYLÁK*, Vlastimil SÝKORA*, Dagmar URBANOVÁ*

*Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, Na Lužci 204, 533 41 Lázně Bohdaneč, Czech Republic; cestmir.hylak@ioolb.izscr.cz ; vlastimil.sykora@ioolb.izscr.cz ; dagmar.urbanova@ioolb.izscr.cz

ABSTRACT:

Protective helmets, which are substantially more comfortable than protective masks are often preferred by users of respiratory protective equipment.

Higher comfort of those protective devices, in addition to their design, is also attained by an integrated filtration–ventilation unit. The question is: What are the protective parameters of the currently offered protective hoods? According to the measured penetration values with 25 test users and 9 protective hoods selected on the Czech market, the hoods not only meet the requirements of the current standard ČSN EN 12 941, but in many cases reach the values required according to ČSN EN 136 for protective masks.

KEYWORDS:

Impenetrability, protective hood, filtration–ventilation unit, overpressure, test user, European norm

1. Introduction

The combination of a protective mask (PM) and a protective filter represents the basic method of respiratory system protection from dangerous chemicals in the form of gases, vapours and aerosols. Current trend is to increase the comfort for the personal protective equipment (PPE) users. In the area of respiratory system protection, this endeavour translates into the possibility of using protective helmets (PHs) with powered ventilation in situations where PMs have once been required. Protective properties of the PMs need to fulfil significantly higher normative requirements than PHs. However, PHs whose protective properties are comparable to PMs yet are much more comfortable for their wearers have become available on the market.

Similar to the investigation performed several years ago at the Population Protection Institute (PPI), in which eighteen types of protective masks were assessed in terms of penetration tightness,[1] we have performed the assessment of nine types of PHs in this work.[2]

The results obtained are useful in connection to the current covid-19 pandemics and may assist the selection of appropriate PPEs for the Integrated Rescue System (IRS) personnel in the first line of the pandemic battle.

2. Objective evaluation of penetration into PHs available on the Czech market

From the wide range of PHs available on Czech market, we have selected nine helmets from five suppliers. All of those are offered as professional protective equipment.

Most helmets (five) were selected from a Czech PPE manufacturer, the CLEAN-AIR S.R.O. Company based in Jablonec nad Nisou. Three are offered commercially both in the Czech Republic and abroad (PHs CA – 1, CA – 2, and CA – 10), two had been developed for the protection of the Czech integrated rescue system personnel (PH DOCTOR) and Czech population (PH SENIOR). Four PHs were manufactured abroad – by German companies DRÄGER and MSA AUER, US company SCOTT, and Swedish company SUNDSTRÖM. All these companies have a high reputation in the PPE field, and are involved in the long-term research and development of such devices, and their products fulfil the most stringent requirements. Our reason for choosing CLEAN-AIR S.R.O. was the fact they are the Czech leader in the field of powered filtration–ventilation units, competing with the abovementioned leading manufacturers from abroad.

Figure 1: Protective helmet CA-1 Figure 2: Protective helmet CA-2 Figure 3: Protective helmet CA-10

Figure 4: Protective helmet DOCTOR   Figure 5: Protective helmet SENIOR

Figure 6: Protective helmet 8 000 Hoods

Figure 7: Protective helmet 3000 Hoods

Figure 8: Protective helmet FH-51

Figure 9: Protective helmet SR 562

3. Proband selection

First, we had to select a suitable group of probands, which would undergo the measurement of SF_6 penetration into the PHs. Two criteria were decisive for the selection: First, to select a balanced co-educated group of people with previous experience in protective mask testing. At the same time, the group should exhibit a wider range of facial parameters to challenge the PH tightness. The facial parameters are not as important for the PHs as for the PMs, but they may contribute to their correct function. Second, a more subjective one was linked to the willingness of the given individual to undergo the physically and psychologically demanding measurements of the PH tightness.

Eventually, we have been able to select 25 probands (13 males and 12 females) during 2018 and 2019. These were employees of the PPI from Lázně Bohdaneč and of the Malina Safety Company, based in Jablonec nad Nisou, which co-operates with the PPI in PPE research in the long term.

4. Measurement of SF_6 penetration into PHs

Measurement of SF_6 penetration into the cheek side of the PHs were performed in a KOMPIO testing chamber belonging to our Institute. This is a mobile chamber based on a modification of the Biobox

EBXT 06 manufactured by the EGO Company from Zlín. This chamber may be set up both in the building interior as well as in the exterior.

Measurement of SF_6 penetration into the PHs was performed according to the methodology elaborated by our Institute "Method for the tightness measurement of PHs". The results were evaluated according to two norms. The penetration into the PHs was performed according to ČSN EN 12 941 "Respiratory protective devices – Powered filtering devices incorporating a helmet or a hood – Requirements, testing, marking"[3], which divides the PHs into three classes based on their properties:

- TH 1: penetration of the testing substance into the PH may not exceed mean value of 10% during inhalation
- TH 2: penetration of the testing substance into the PH may not exceed mean value of 2% during inhalation
- TH 3: penetration of the testing substance into the PH may not exceed mean value of 2×10^{-1} % during inhalation

Comparison of protective properties of the PHs with PMs was also performed according to ČSN EN 136 "Respiratory protective devices – Full face masks – Requirements, testing, marking",[4] according to which penetration of the testing substances into the protective masks may not exceed mean value of 5×10^{-2} % during inhalation in ten probands. Based on these criteria, the PMs (or PHs in our case) are evaluated as "Compliant" or "Noncompliant".

Each proband put the PH on and entered the testing chamber containing the testing atmosphere of 1000 ppm of SF_6. The proband then underwent a series of exercises listed by the ČSN EN 136 and ČSN EN 12 941 on a treadmill:

- Walking for 2 min without head movement or speech;
- Turning the head from side to side (15×) for 2 min as if checking the tunnel walls;
- Raising and lowering the head (15×) for 2 min as if checking the tunnel ceiling and floor;
- Loud alphabet spelling or speech to a colleague for 2 min,
- Walking for 2 min without head movement or speech.

The series of exercises was performed twice for each proband and PH at two different air supply rates (140 L×min⁻¹ and 180 L×min⁻¹) with the second series immediately following after the first one.

Penetration of SF_6 into the protective hood (P) was calculated from the measurements performed during the last 100 seconds of each exercise to avoid overlapping results from each exercise. The Innova 1412 Photoacoustic Field Gas-Monitor used usually records three values. Their mean was used for each partial calculation.

Penetration P can then be calculated according to the formula

$$P\ (\%) = C_2/C_1 \times 100$$

where C_1 is the testing concentration and C_2 the mean concentration measured in the PH corrected for background.

5. Evaluation of the penetration into PHs according to ČSN EN 136

Results obtained from the measurement of penetration into the PHs for 25 probands are quite extensive, and are therefore presented as quantitative evaluation of each helmet's success rate in Tables 1–3 and Figure 10. Table 1 summarises the results across both genders, Tables 2 and 3 summarise each gender.

The results of penetration for each exercise and PH (Table 1) show that seven out of nine PHs evaluated fulfil the requirements of ČSN EN 136 for penetration, i.e., observed penetration is below 5×10^{-2} %. Penetration exceeding the allowed limit was mostly observed during the speaking test.

The best results were observed for the DOCTOR PH, which failed in only one proband for both air supply rates tested. For other probands, this helmet was compliant with ČSN EN 136 for both air supply rates. Immediately following were two PHs: FH 51 from SCOTT (now 3M) and CA-10 from CLEAN-AIR. The FH 51 helmet failed in one proband at both air supply rates, and in another proband at 140 L×min^{-1}. The CA-10 failed in one proband at both air supply rates, and in additional three probands at one air supply rate. The X-PLORE 8000 Hoods (DRÄGER, Germany) ranked fourth. It failed in two probands at both air supply rates, and in additional two probands at 140 L×min^{-1}. The PHs CA-1 and SENIOR from the CLEAN-AIR company both failed in two probands for both air supply rates, and in additional three probands at one air supply rate. Least protective were the SR 562 (SUNDSTRÖM, Sweden) and OPTIMAIR 3000 Hoods (MSA, Germany) helmet. They could not comply with ČSN EN 136 in any proband, not even at an air supply rate of 200 L×min^{-1}.

Table 1: Overall quantitative evaluation of PH impenetrability according to ČSN EN 136 – [males (♂) + females (♀)]

Protective helmet type	Complying probands [1]	Complying probands [%]	Rank for individual air supply rate	Overall rank (sum at both air supply rates)
CA – 1 (140 L×min^{-1})	21	84	5–6	5–6
CA – 1 (180 L×min^{-1})	22	88	4– 5	
CA – 2 (140 L×min^{-1})	16	64	7	7
CA – 2 (180 L×min^{-1})	18	72	7	
CA – 10 (140 L×min^{-1})	23	92	2–4	3
CA – 10	22	88	4–5	

(180 L×min⁻¹)				
PH – 2015 (SENIOR) (140 L×min⁻¹)	23	92	2–4	**5–6**
PH – 2015 (SENIOR) (180 L×min⁻¹)	20	80	6	
CLEAN-AIR DOCTOR (140 L×min⁻¹)	24	96	1	**1**
CLEAN-AIR DOCTOR (180 L×min⁻¹)	24	96	1	
SCOTT FH 51 (140 L×min⁻¹)	23	92	2–4	**2**
SCOTT FH 51 (180 L×min⁻¹)	23	92	2–3	
DRÄGER X-PLORE 8000 Hoods (140 L×min⁻¹)	21	84	5–6	**4**
DRÄGER X-PLORE 8000 Hoods (180 L×min⁻¹)	23	92	2–3	
MSA OPTIMAIR 3000 Hoods (140 L×min⁻¹)	0	0	8–9	**8–9**
MSA OPTIMAIR 3000 Hoods (180 L×min⁻¹)	0	0	8–9	
SUNDSTRÖM SR 562 (140 L×min⁻¹)	0	0	8–9	**8–9**
SUNDSTRÖM SR 562 (180 L×min⁻¹)	0	0	8–9	

Table 2 (males only) shows that the best ranking PHs according to ČSN EN 136 are again the DOCTOR and FH 51, as in the overall comparison across both genders. The DOCTOR PH complied in 100% male probands, the FH 51 in 92% cases, i.e., it failed in one proband for both air supply rates. Protective hoods CA-1 and X-PLORE 8000 Hoods ranked third to fourth place. The remaining helmets ranked identical as in Figure 1, i.e., across both genders.

Table 2: Overall quantitative evaluation of PH impenetrability according to ČSN EN 136 – [males (♂)]

Protective helmet type	Complying probands [1]	Complying probands [%]	Rank for individual air supply rate	Overall rank (sum at both air supply rates)
CA – 1 (140 L×min^{-1})	10	80	5–6	6
CA – 1 (180 L×min^{-1})	10	80	5–6	
CA – 2 (140 L×min^{-1})	6	46	7	7
CA – 2 (180 L×min^{-1})	9	69	7	
CA – 10 (140 L×min^{-1})	11	85	3–4	3–4
CA – 10 (180 L×min^{-1})	11	85	4	
PH – 2015 (SENIOR) (140 L×min^{-1})	11	85	3–4	5
PH – 2015 (SENIOR) (180 L×min^{-1})	10	80	5– 6	
CLEAN-AIR DOCTOR (140 L×min^{-1})	13	100	1	1
CLEAN-AIR DOCTOR (180 L×min^{-1})	13	100	1	
SCOTT FH 51 (140 L×min^{-1})	12	92	2	2
SCOTT FH 51 (180 L×min^{-1})	12	92	2–3	
DRÄGER X-PLORE 8000 Hoods (140 L×min^{-1})	10	80	5–6	3–4

Protective helmet type	Complying probands [1]	Complying probands [%]	Rank for individual air supply rate	Overall rank
DRÄGER X-PLORE 8000 Hoods (180 L×min^{-1})	12	92	**2–3**	
MSA OPTIMAIR 3000 Hoods (140 L×min^{-1})	0	0	**7–8**	**7–8**
MSA OPTIMAIR 3000 Hoods (180 L×min^{-1})	0	0	**7– 8**	
SUNDSTRÖM SR 562 (140 L×min^{-1})	0	0	**7– 8**	**7–8**
SUNDSTRÖM SR 562 (180 L×min^{-1})	0	0	**7–8**	

Table 3 (females only) shows that the best ranking PHs according to ČSN EN 136 are the CA – 10 and CA – 1 from the CLEAN-AIR company. These failed in one and two probands, respectively. Results obtained for the DOCTOR (CLEAN-AIR), FH 51, X-PLORE 8000 Hoods (DRÄGER) and PH-2015 (SENIOR – CLEAN-AIR) were comparable. Remaining helmets ranked similar to the previous tables, i.e., OK CA – 2 ranked seventh, and OPTIMAIR 3000 Hoods (MSA) and SR 562 (SUNDSTRÖM) ranked eighth to ninth.

Table 3: Overall quantitative evaluation of PH impenetrability according to ČSN EN 136 – [females (♀)]

Protective helmet type	Complying probands [1]	Complying probands [%]	Rank for individual air supply rate	Overall rank (sum at both air supply rates)
CA – 1 (140 L×min^{-1})	11	92	**3–6**	**1–2**
CA – 1 (180 L×min^{-1})	12	100	**1**	
CA – 2 (140 L×min^{-1})	10	83	**7**	**7**
CA – 2 (180 L×min^{-1})	9	75	**7**	
CA – 10	12	100	**1–2**	

(140 L×min⁻¹)				**1– 2**
CA – 10 (180 L×min⁻¹)	11	92	**2– 5**	
PH – 2015 (SENIOR) (140 L×min⁻¹)	12	100	**1–2**	**3–6**
PH – 2015 (SENIOR) (180 L×min⁻¹)	10	83	**6**	
CLEAN-AIR DOCTOR (140 L×min⁻¹)	11	92	**3–6**	**3–6**
CLEAN-AIR DOCTOR (180 L×min⁻¹)	11	92	**2–5**	
SCOTT FH 51 (140 L×min⁻¹)	11	92	**3–6**	**3–6**
SCOTT FH 51 (180 L×min⁻¹)	11	92	**2–5**	
DRÄGER X-PLORE 8000 Hoods (140 L×min⁻¹)	11	92	**3–6**	**3–6**
DRÄGER X-PLORE 8000 Hoods (180 L×min⁻¹)	11	92	**2–5**	
MSA OPTIMAIR 3000 Hoods (140 L×min⁻¹)	0	0	**8–9**	**8–9**
MSA OPTIMAIR 3000 Hoods (180 L×min⁻¹)	0	0	**8–9**	
SUNDSTRÖM SR 562 (140 L×min⁻¹)	0	0	**8–9**	**8–9**
SUNDSTRÖM SR 562 (180 L×min⁻¹)	0	0	**8–9**	

When considering the ČSN EN 12 941 norm for the evaluation of penetration into the PHs, i.e., maximal penetration 10% for TH 1, 2% for TH 2, and 2×10^{-1} % for TH 3, it is clear that all PHs except MSA OPTIMAIR 3000 Hoods and SUNDSTRÖM SR 562 fulfil the TH 3 requirements. The latter two did not fulfil the ČSN EN 12 941 requirements in any proband, neither at air supply rate of 140 L × min⁻¹ nor at 180 L × min⁻¹. This may be attributed to the fact the air supply must exceed 200 L × min⁻¹ for the

SUNDSTRÖM SR 562 PH. The Swedish manufacturer declares a requirement of 175–225 and 240 L × min^{-1}, respectively. For the SR 562 PH, the TH 2 class requirements were met in 15 probands, only TH 1 (< 10% penetration) in the remaining 10 probands. For the German PH MSA OPTIMAIR 3000 Hoods, the TH 2 protection class is declared for air supply rates of 130–160 L × min^{-1}. This requirement was met in 24 probands (the requirements of TH 1 class were met in the last proband).

There was no significant difference in terms of (non-)compliance with the TH 3 class requirements between the two rates of air supply into the PH tested (140 and 180 L × min^{-1}).

The TH 2 class requirements were not met in any proband and measurement at 140 L × min^{-1} by the SR 562 helmet. For the OPTIMAIR 3000 Hoods, this requirement was not met in one proband. At 180 L × min^{-1}, the TH 2 class requirements were not met in 5 probands with the SR 562 helmet, and in 1 proband with the PH 2015 (SENIOR) and OPTIMAIR 3000 Hoods PHs.

Figure 10: Overall quantitative evaluation of PH impenetrability according to ČSN EN 136
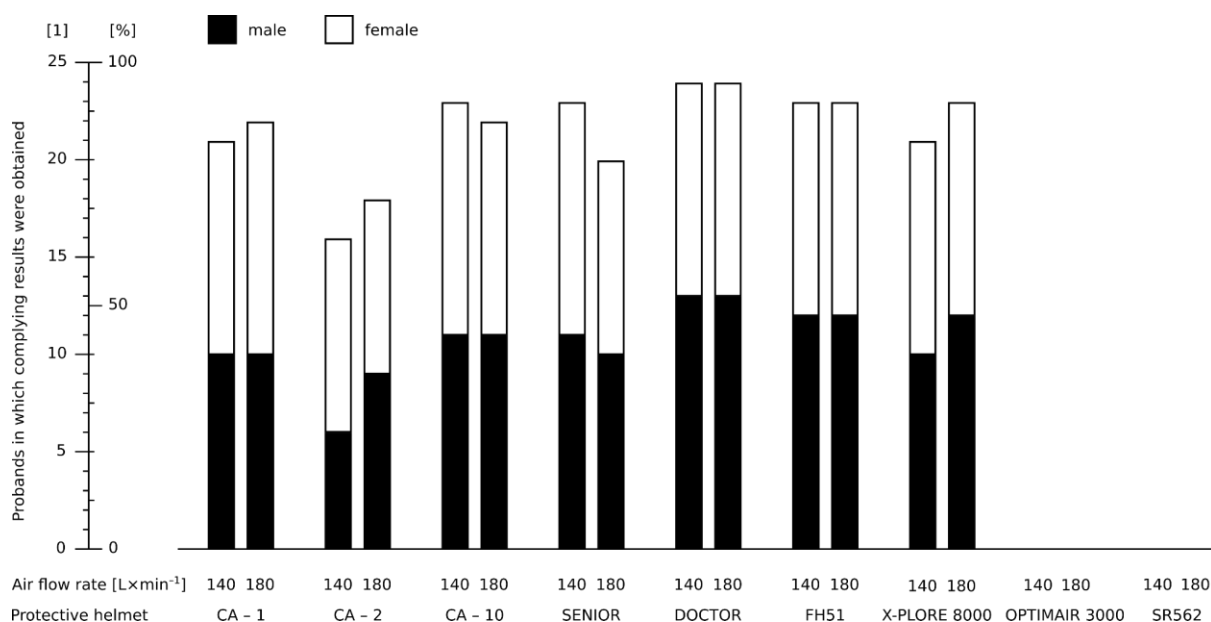
Table 4: Overall quantitative evaluation of PH impenetrability according to ČSN EN 12 941 (TH 3) – [male (♂) + female (♀)]

Protective helmet type	Probands complying with TH 3	Probands complying with TH 2	Probands complying with TH 1	% complying the TH class
CA – 1 (140 L×min^{-1})	25	25	25	**100 % TH 3**
CA – 1 (180 L×min^{-1})	25	25	25	
CA – 2 (140 L×min^{-1})	24	25	25	96 % TH 3

CA – 2 (180 L×min^{-1})	24	25	25	100 % TH 2
CA – 10 (140 L×min^{-1})	25	25	25	100 % TH 3
CA – 10 (180 L×min^{-1})	25	25	25	
PH – 2015 (SENIOR) (140 L×min^{-1})	24	25	25	96 % TH 3 98 % TH 2
PH – 2015 (SENIOR) (180 L×min^{-1})	24	24	25	100 % TH 1
CLEAN-AIR DOCTOR (140 L×min^{-1})	25	25	25	100 % TH 3
CLEAN-AIR DOCTOR (180 L×min^{-1})	25	25	25	
SCOTT FH 51 (140 L×min^{-1})	25	25	25	100 % TH 3
SCOTT FH 51 (180 L×min^{-1})	25	25	25	
DRÄGER X-PLORE 8000 Hoods (140 L×min^{-1})	25	25	25	100 % TH 3
DRÄGER X-PLORE 8000 Hoods (180 L×min^{-1})	25	25	25	
MSA OPTIMAIR 3000 Hoods (140 L×min^{-1})	0	24	25	0 % TH 3 96 % TH 2
MSA OPTIMAIR 3000 Hoods (180 L×min^{-1})	0	24	25	100 % TH 1
SUNDSTRÖM SR 562 (140 L×min^{-1})	0	0	25	0 % TH 3 30 % TH 2
SUNDSTRÖM SR 562 (180 L×min^{-1})	0	15	25	100 % TH 1

6. Overpressure impact on tightness

For each air supply rate, the resulting overpressure under each proband's PH was measured during the SF_6 penetration into the helmet. The overpressure values are listed in Tables 5a and 5b. Overpressures at which the helmet did not comply with the 5×10^{-2} % penetration requirement are highlighted. Logically speaking, the higher the overpressure, the lower the penetration should be and the PH should be tighter. However, the results obtained do not really prove this relationship, except the OPTIMAIR 3000 Hoods (MSA) and SR 562 (SUNDSTRÖM). It is clear that greater air supply air rate and hence greater overpressure under the PH do not positively influence the penetration (and tightness). Better results in terms of tightness were obtained at the higher air supply rate (i.e., 180 L × min^{-1}) for three types of PHs. For two helmets, better results were obtained at the lower air supply rate (i.e., 140 L × min^{-1}) , and for two helmets, there was no significant difference in tightness between the air supply rates. Worse results in case of higher air supply rates can be explained by turbulence in the air flow forced into the helmet. The turbulence is influenced by the air supply rate and obstructions the flow encounters. This turbulence may cause ingress of outside air into the helmet, which explains the individual differences observed in the 25 probands – each having a differently sized face, and also differently sized skull, its protrusions, such as supraorbital ridge, nose, cheekbones, chin, and depressions, such as fossa temporalis and infratemporalis.

Surprisingly, we observed lower overpressure at the high air supply than at the low supply air rate in 16 cases. This anomaly may be explained by the PH changing position on the proband's head during the exercise prescribed by the ČSN EN 12 941 norm and by loosening of the head straps.

Table 5a: Overpressure in the PH at the air supply rate listed

Protective helmet / Air supply rate (L × min^{-1})	Proband ID – Protective helmet overperssure (Pa)													Average overpressure (1–25)
	1 ♂	2 ♂	3 ♀	4 ♀	5 ♀	6 ♀	7 ♂	8 ♀	9 ♂	10 ♀	11 ♀	12 ♀	13 ♀	
CA – 1 140	6	64	63	43	46	70	63	63	58	41	48	51		59
CA – 1 180	70	74	70	59	51	75	72	76	68	53	61	61		66
CA – 2 140	50	41	49	39	42	48	50	43	51	39	31	42	62	47
CA – 2 180	53	45	60	47	52	50	55	52	61	45	38	46		53
CA – 10 140	78	69	71	70	50	64	83	77	72	74	63	49	66	73

CA – 10 180	86	76	70	77	62	72	96	89	93	84	65	55	78	81
OK – 2015 140	59	72	41	72	56	44	78	72	83	42	32	81	100	71
OK – 2015 180	84	82	82	75	58	58	96	82	–	71	–	86	–	83
DOCTOR 140	82	–	75	84		79	75	85	82	58	38	47	62	76
DOCTOR 180	87	–	93	86		78	77	103	101	74	77	73	57	85
SCOTT FH 51 140	62	54	30	45	29	23	48	33	53	28	35	30	14	42
SCOTT FH 51 180	69	62	39	72	58	90	61	36	72	41	15	43	48	60
X-PLORE 8000 Hoods 140	58	57	54	59	55	45	60	62	56	48	57	46	58	54
X-PLORE 8000 Hoods 180	63	63	59	62	60	50	66	57	66	49	62	48	67	59
OPTIMAIR 3000 Hoods 140	27	22	31	40	48	29	50	32	23	15	26	26	21	29
OPTIMAIR 3000 Hoods 180	35	28	38	52	39	31	62	42	30	18	36	30	25	34
SR 562 140	71	–	45	54	64	52	63	58	56	37	49	53	64	59
SR 562 180	77	–	60	59	81	58	72	64	66	47	59	58	74	67

Note: Fields highlighted in red – PHs not complying with ČSN EN 136

Fields with "–" – overpressure not measured

Table 5b: Overpressure in the PH at the air supply rate listed

Protective helmet Air supply rate (L × min⁻¹)	Proband ID – Protective helmet overperssure (Pa)												Averagee overpressure (1–25)
	14 ♀	15 ♀	16 ♂	17 ♂	18 ♂	19 ♂	20 ♂	21 ♀	22 ♂	23 ♂	24 ♂	25 ♂	
CA – 1 140	60	62	57	70	53	62	66	67	60	49	60	67	59
CA – 1 180	65	72	56	77	56	65	75	72	64	54	63	74	66
CA – 2 140	46	54	33	55	48	39	57	51	56	50	45	50	47
CA – 2 180	50	57	28	64	49	47	65	65	62	59	54	57	53
CA – 10 140	78	72	63	87	56	88	86	102	80	67	81	74	73
CA – 10 180	84	92	66	96	81	89	99	85	82	68	87	88	81
OK – 2015 140	72	70	95	95	47	84	91	91	62	67	72	93	71
OK – 2015 180	98	99	112	112	87	63	–	–	86	56	81	93	83
DOCTOR 140	68	87	87	94	72	87	85	84	63	87	77	87	76
DOCTOR 180	85	100	110	106	47	83	106	95	60	87	82	94	85
SCOTT FH 51 140	34	52	33	67	47	29	40	59	58	40	43	67	42
SCOTT FH 51 180	31	62	53	128	31	46	85	68	78	66	70	83	60

X-PLORE 8000 Hoods 140	26	43	55	61	52	56	54	63	61	48	59	58	54
X-PLORE 8000 Hoods 180	33	46	59	68	62	58	62	69	66	55	62	58	59
OPTIMAIR 3000 Hoods 140	13	27	21	41	25	26	35	36	29	24	32	22	29
OPTIMAIR 3000 Hoods 180	15	31	28	45	27	32	42	37	31	32	32	21	34
SR 562 140	78	57	65	61	54	52	73	66	71	60	62	61	59
SR 562 180	55	66	77	73	63	55	76	76	79	70	75	71	67

7. Subjective evaluation of the PHs by the probands

Once the penetration measurements were finished, 24 probands (all except proband #1) performed a subjective evaluation of the given PH. The evaluation was performed according to ČSN EN 13 274 (Respiratory protective devices – Methods of test – Part 2: Practical performance tests).[5] In compliance with the norm, we elaborated a questionnaire listing twelve parameters, which the probands evaluated (1 as best result, 5 was worst results).

Following parameters as per the norm were evaluated:

- Ease of application and removal of the PH
- Harness (application, removal, adjustability, safety, and comfort)
- Comfort of the chek part
- Skin tolerance
- Ease of wear and mass balance of the equipment
- Clear vision through the visor
- Field of vision
- Communication by speech, noise of the filtration-ventilation unit
- Safety of the attachment and connections
- Ease of breathing (e.g., temperature, pressure, quantity)
- Any stress or discomfort experienced due to air flow or turbulence

A total was calculated to rank the PHs (lowest number being the best ranking PH, the highest number being the worst ranking PH).

Table 6a: Subjective evaluation of PHs

Overall rank of protective helemts	Proband										Evaluation total
	2	3	4	5	6	7	8	9	10	11	
CA −1	3	1	8	4	1	1	7	1	1	1	28
CA − 2	2	2	7	5	9	1	1	5	4	5	41
CA − 10	1	6	2	1	4	1	1	8	3	2	29
SENIOR	5	2	3	8	3	7	4	1	4	4	41
DOCTOR	5	2	4	1	8	1	1	5	1	2	30
FH-51	4	8	5	3	4	8	6	7	8	8	61
X-PLORE	7	7	1	5	2	1	7	1	7	7	47
OPTIMAIR	9	9	9	9	4	9	9	9	9	9	85
SR-562	8	5	6	5	4	1	4	1	4	5	43

Table 6b: Subjective evaluation of PHs

Overall rank of PHs	Proband										Evaluation total
	12	13	14	15	16	17	18	19	20	21	
CA −1	2	1	1	2	1	1	4	1	4	2	19
CA − 2	1	−	3	2	5	1	8	3	2	2	27
CA − 10	6	2	2	4	2	1	6	3	1	1	28
SENIOR	8	5	4	6	4	1	4	5	5	5	47
DOCTOR	3	4	6	1	2	6	1	2	2	6	33
FH-51	5	8	9	8	6	6	8	7	8	8	73
X-PLORE	7	6	6	4	7	1	2	6	6	7	52
OPTIMAIR	8	7	8	9	9	9	2	8	8	9	77
SR-562	3	2	4	7	8	6	6	9	7	2	54

Table 6c: Subjective evaluation of PHs

Overall rank of PHs	Proband				Evaluation total	Rank
	22	23	24	25		
CA −1	1	1	2	1	28 + 19 + 5 = 52	**1.**
CA − 2	5	2	3	4	41 + 27 + 14 = 82	**3.**
CA − 10	7	2	5	3	29 + 28 + 17 = 74	**2.**
SENIOR	9	7	8	8	41 + 47 + 32 = 120	7.
DOCTOR	3	4	8	6	30 + 33 + 21 = 84	4.
FH-51	5	6	3	7	61 + 73 + 21 = 155	8.
X-PLORE	3	9	5	1	47 + 52 + 18 = 117	6.
OPTIMAIR	7	7	5	9	85 + 77 + 28 = 190	9.
SR-562	1	5	1	4	43 + 54 + 11 = 108	5.

The Tables 6a–6c show that the probands ranked the CA – 1 helmet as the best one in the subjective evaluation (smallest score). On the contrary, the OPTIMAIR PH ranked worst in the evaluation (highest score). In general, we can conclude the subjective evaluation of the PHs corresponds to the penetration measurements. The FH 51 helmet (SCOTT, USA) is an exception: although it ranked 8th in the subjective evaluation, it ranked 3rd in the penetration measurements. This may be due to its construction as it protects not only the head, face and respiratory system, but also the shoulders and part of the torso. This makes it less convenient and its setup is a bit more complicated.

8. Conclusion

The Czech market offers a wide selection of PHs, which compare well to the protective masks as shown for nine representatives by penetration measurements and subjective evaluation by probands. This was confirmed by the penetration measurement which showed that 5 out of 9 PHs complied both with the ČSN EN 12 941 requirement of the TH 3 class (2×10^{-1}%) and the ČSN EN 136 requirement for protective masks (5×10^{-2}%).

The best PH as evaluated by the penetration measurements was the DOCTOR PH (CLEAN-AIR). This helmet was non-compliant in only one proband (at both air supply rates tested.). It ranked 4th in the subjective evaluation, which is a very good result considering it is of the oldest design (2008). Under the covid pandemic conditions, it would represent a very good protective device for the first line healthcare professionals, offering the best possible protection of the respiratory system and eyes.

Protective helmets CA-10 (CLEAN-AIR) and FH 51 (SCOTT, now 3M) would represent no worse PPEs for the first-line healthcare professionals.

Additional four PHs, CA-1, CA-2 and PH-2015 SENIOR (CLEAN-AIR) and X-PLORE 800 Hoods (DRÄGER, Germany) were evaluated above the standard, and would in many cases comply with the penetration requirements of the ČSN EN 136 norm.

The measurement results show that the relationship between the penetration and rate of air supplied by the filtration–ventilation unit is somewhat illogical: The penetration may be higher at the higher air supply rate than at the lower. Based on two years' experience and findings from the measurements, we can conclude that this is due to subjective differences between the probands influencing the results. These include the placing the helmet on the proband's head, adjustment of the straps, and physiological parameters of the proband due to the age, gender, height, physical conditions etc.

Overall, we can say the construction of current PHs is very good. In terms of penetration into the helmet as the most important parameter for respiratory system protection, the helmets surpass the requirements of the ČSN EN 12941 and ČSN EN 12942 norms, and are at the level of the ČSN EN 136 norm for protective masks, which is 5×10^{-2}%.

LITERATURE

[1] HYLÁK, Č. – SÝKORA, V. – URBANOVÁ, D. – KOVALIČOVÁ, H.: *Měření průniku do lícnic ochranných masek v roce 2014 (Průběžná zpráva k DÚ 3 „BOKR")* [Measurement of penetration into cheek parts of protective masks in 2014 (Interim report to DÚ 3 "Public Safety – Crisis Management")]. Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, Lázně Bohdaneč 2014.

[2] HYLÁK, Č. – SÝKORA, V. – URBANOVÁ, D.: *Měření průniku SF$_6$ do ochranných kukel dostupných na tuzemském trhu (2018–2019). (Průběžná zpráva k DÚ 3 projektu „CAVHZS ")* [Measurement of SF6 penetration into protective helmets available on the Czech market (2018–2019). (Interim report to DÚ 3 of the Targeted Applied Research project of the Fire Rescue Service] Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, Lázně Bohdaneč 2019.

[3] ČSN EN 12 941 *„Ochranné prostředky dýchacích orgánů - Filtrační prostředky s pomocnou ventilací připojené k přilbě nebo ke kukle - Požadavky, zkoušení a značení"* [Respiratory protective devices – Powered filtering devices incorporating a helmet or a hood – Requirements, testing, marking].

[4] ČSN EN 136 *„Ochranné prostředky dýchacích orgánů – Obličejové masky – Požadavky, zkoušení a značení"* [Respiratory protective devices – Full face masks – Requirements, testing, marking].

[5] ČSN EN 13 274 – 2 *„Ochranné prostředky dýchacích orgánů – Metody zkoušení – Část 2: Praktické zkoušky"* [Respiratory protective devices – Methods of test – Part 2: Practical performance tests].

New trends in HazMat analysis via Infrared and Raman spectroscopy

František KESNER**, Karel ŠEC*

*Nicolet CZ s.r.o., Křelovická 970/6, 10400 Prague 10, Czech Republic, email: nicoletcz@nicoletcz.cz

***Corresponding author e-mail:* kesner@nicoletcz.cz *, tel.:* +420 603 554 788

ABSTRACT:

Article presents some possibilities of analysis of unknown samples directly on crime scene using sophisticated mobile spectrometers with a focus on operators who do not have chemical education. There are a large number of such devices on the market and they are based on many different principles, in this article we focused on only two of them: Infrared and Raman spectroscopy.

KEYWORDS:

infrared spectroscopy, FTIR, Raman spectroscopy, fluorescence spectroscopy.

1. Introduction

There is a growing interest in fast, simple and cost-effective analysis of hazardous substances nowadays. The ideal solution is that analysis takes place in the field, for example at accident site, with staff who may not always have any chemical education. These requirements therefore place high demands on the simple control of these analytical systems, as well as on the accuracy and repeatability of the analysis of often very complicated unknown samples. These analytical methods are usually molecular spectroscopy techniques like visible, ultraviolet and infrared spectroscopy, as well as Raman spectroscopy. Each of the above methods has its advantages, but also limitations. It is ideal to combine these analytical techniques.

2. Raman radiation versus fluorescence

Fluorescence is an important phenomenon that often interferes with the measurement of the Raman spectrum. In most cases, this interference is critical factor in the success of our field analysis. Fluorescence arises in a very similar way to Raman scattering, but is based on a photoluminescent mechanism. Fluorescence is also several orders of magnitude stronger than Raman radiation, which means that the fluorescence spectrum can in many cases completely overlap the Raman spectrum and thus destroy the analysis of the investigated material. Strong fluorescence can be seen, for example, when measuring darker and colored samples or organic substances with a chemical bond containing elemental nitrogen. In order to minimize the effect of fluorescence on Raman spectra, laser excitation with a longer wavelength (1064 nm) or, conversely, with a shorter - so-called deep "UV excitation (248

nm) - outside the so-called fluorescence excitation range (approx. 275 – 950 nm) is preferred, see figure 1.

However, each of these solutions has its advantages and disadvantages. In the case of using an excitation laser with a wavelength of 1064 nm, it is necessary to significantly extend the measurement time or increase the excitation laser power (at least a few hundred to thousands of mW), because the Raman spectrum is much weaker than when using an excitation laser with a wavelength in the visible range. When using deep UV excitation, the main problems are higher acquisition cost (special UV optics and monochrome UV radiation source) and worse spectral resolution.
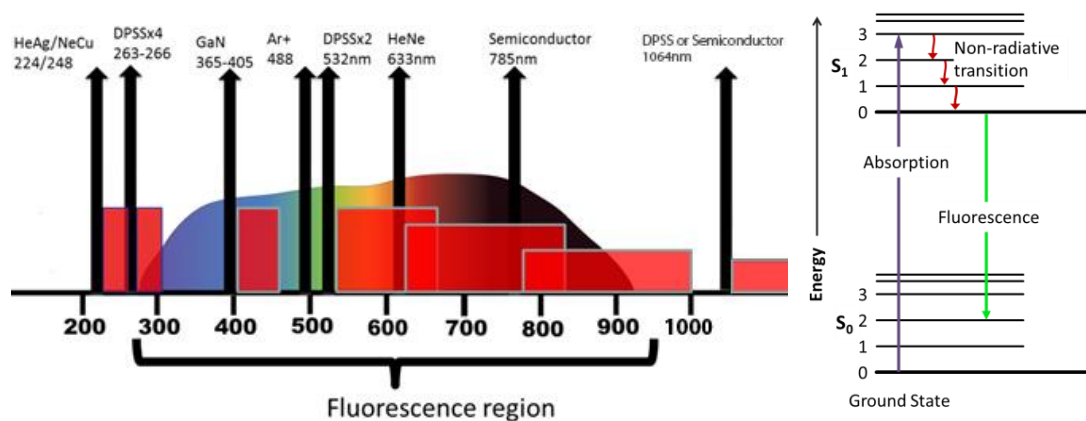
Figure 1 – Fluorescence area versus excitation wavelengths of lasers common for Raman spectroscopy + energetic diagram of fluorescence [1]

3. Raman spectroscopy with excitation 1064 nm

American company BWTek offers in its portfolio (among other things), mobile Raman spectrometers TacticID1064[2], TacticID Mobile[3] and TacticID1064 ST[4] with a robust construction, which use an excitation laser with a wavelength 1064 nm. Their advantage is the possibility of direct measurement of darker and colored samples such as cannabinoids, cathinones or psychoactive substances. Comparison of the MDMA Raman spectra using an excitation laser with a wavelength of 785 nm and 1064 nm: Figure 2
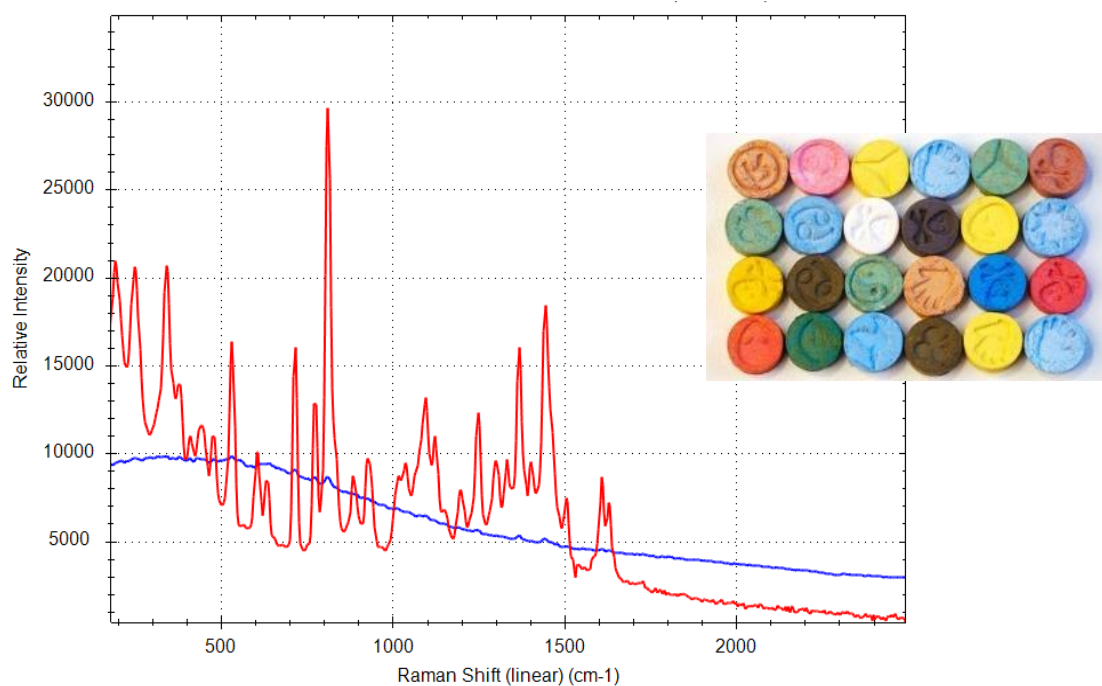
Figure 2 – Comparison of Raman spectra of MDME measured with different excitation lasers: 785 nm (blue) and 1064 nm (red)

Specialty of the TacticID1064 ST4 spectrometer is the possibility of measuring samples through non-transparent packaging, e.g. plastic containers, paper envelopes, etc. For this purpose a patented attachment connected with a special mathematical algorithm is used, see Figure 3.

Figure 3 – Raman spectrometer TacticID1064 ST with the accessory for measurements through non transparent packaging

4. Raman spectroscopy with deep UV excitation (lower than 250 nm)

American company Photon Systems offers, for example, the combined spectrometer Standoff 200[5], which even allows simultaneous measurement of Raman and fluorescence spectra. This combined device allows the identification of a wide range of unknown chemical as well as biological samples, where Raman spectroscopy is used for chemical identification and fluorescence spectrum is

used for biological identification (e.g. biomaterials, proteins, pollens, microbiological materials,…), see Figure 4.
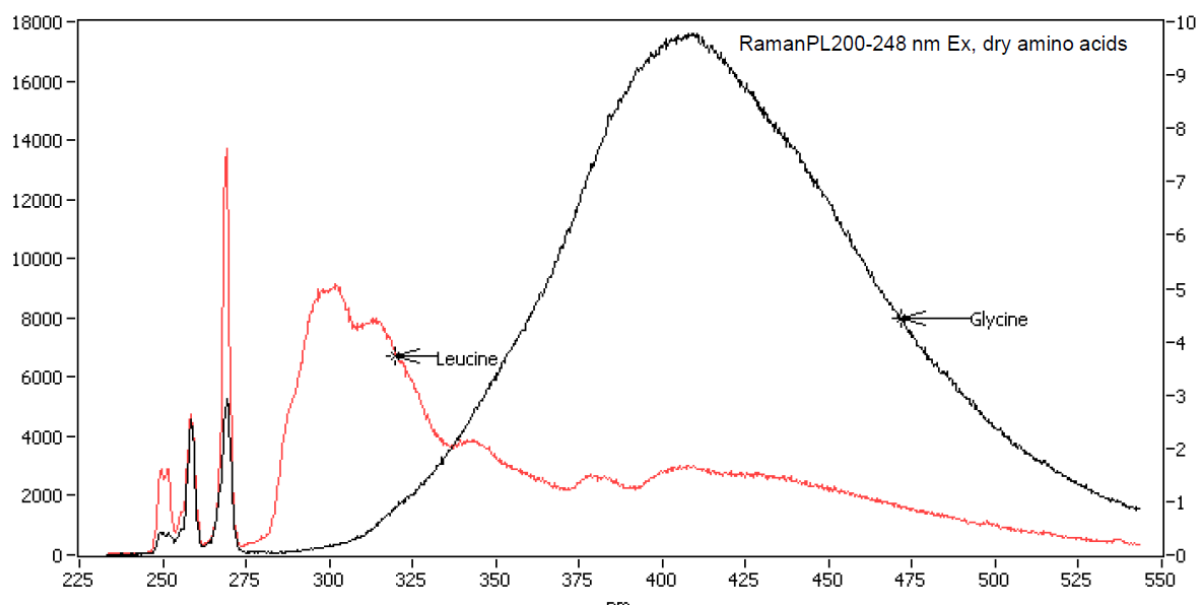
Figure 4 – Raman and fluorescence spectra of glycine and leucine measured with excitation wavelength 248 nm

5. Infrared spectroscopy (FTIR) – analysis of solids, liquids and gaseous substances

The use of mobile infrared spectrometers for the identification of solid and liquid samples is nowadays almost common for many groups of the integrated rescue systems or police. However, this is not so common to combine with the identification of gases and vapors. The new ThreatID-GLS[6,7] case FTIR spectrometer (see Figure 5) from Red Wave Technology solves this problem by identifying samples in different states, via possibility of replacing measurement accessories in the field within minutes.

Figure 5 – case spectrometer ThreatID-GLS from RedWave Technology[6,7]

First responder teams often already have a number of tools at their disposal to detect and quantify gases. E.g., Photoionization detectors (PIDs) that can quickly detect a wide range of gases and, when properly calibrated, accurately quantify them, but these do not actually identify gas. If identifiable gas is also present in the mixed sample, you still do not know which specific gas mixture it is, and what concentration of this mixture is dangerous. However, the addition of the classic PID technology with the ThreatID-GLS infrared spectrometer provides the ability to quickly detect and locate the monitored gas (using PID) but also to accurately identify it using the long-path gas cell of the infrared spectrometer[8].

Ion Mobile Spectroscopy (IMS) and High Pressure Mass Spectrometry (HPMS) provide sensitive detection of specific targeted threats. Both of these techniques are important tools for the detection and identification of chemical warfare agents (CWA). However, it is not always suitable for general use because the number of materials identifiable by these systems is relatively low. IMS is a very sensitive technique, also focused on chemical warfare agents (CWA) and several selected toxic industrial chemicals (TIC). Currently, this technique provides the identification or classification of approximately 50 compounds. HPMS is more versatile and includes not only chemical warfare agents (CWAs), toxic industrial chemicals (TICs) but also a number of narcotics. Each of the substances can be detected with great sensitivity, but the number of identified compounds is currently in the order of only a few hundred. By comparison, ThreatID-GLS currently has more than 5,500 compounds in the library covering a wide range of toxic industrial substances (TICs) and volatile organic compounds (VOCs). This allows easy and quick identification of many substances found in typical "HazMat" accident sites.

High-sensitivity devices, such as IMS or HPMS, can accurately identify even small amounts of material. This fact is a very desirable parameter in the case of chemical accident analysis. However, it can also be a disadvantage because the measuring system is more easily contaminated via samples with higher concentrations. The ThreatID-GLS infrared spectrometer can identify most compounds at concentrations in the order of ppm. In addition, with a partial filling of the gas cell, it can identify compounds even in much higher concentrations. An example is ammonia, which can be accurately identified/quantified in a concentration range from 25 ppm to more than 0.5 %[8].

6. Conclusion

In the previous text, we wanted to present the current trends in instrumentation for the analysis of hazardous substances in the field. We focused on the advantages of Raman spectroscopy, which use excitation lasers with wavelengths outside the fluorescence region (1064 nm or 248 nm). The second part of the text concerns a mobile infrared spectrometer (FTIR) for the analysis of samples in all states. Special emphasis was placed on the analysis of gases and vapors in concentrations from ppm to several percent.

LITERATURE

BWTEK, Choosing the Most Suitable Laser Wavelength For Your Raman Application (2018/06/05)

[1] BWTEK, Products, https://bwtek.com/products/tacticid-1064/ downloaded 15. 10. 2021
[2] BWTEK, Products, https://bwtek.com/products/tacticid-mobile/ downloaded 15. 10. 2021

[3]   BWTEK, Products https://bwtek.com/products/tacticid-1064-st/   downladed 15. 10. 2021

[4]   PHOTONSYSTEMS,   Products,   https://photonsystems.com/products-hand-held-standoff-200/
      [online15. 10. 2021]

[5]   REDWAVE TECHNOLOGY, Gases, https://redwavetech.com/gases/

[6]   REDWAVE TECHNOLOGY, Powders liquids, https://redwavetech.com/powdersliquids/

[7]   REDWAVE TECHNOLOGY, The Gas Identification Gap https://redwavetech.com/

EXPOSURE AND PHYSIOLOGICAL LOAD OF A FIREFIGHTER'S ORGANISM IN FIREFIGHTING

Petr KOŽENÝ**, Zdeněk HON*

*Czech Technical University in Prague, Faculty of Biomedical Engineering, Department of   Health and Population Protection, Sportovců 2311, 272 01 Kladno, Czech Republic, email: zdenek.hon@fbmi.cvut.cz

 **Corresponding author: e-mail: petr.kozeny@pak.izscr.cz

ABSTRACT:

In recent years, a number of epidemiological studies have been published indicating that firefighters as an occupational group have an increased risk of certain diseases compared to the general population. An important etiologic factor that distinguishes firefighters from other occupational groups and the general population is fire suppression. A number of stress factors are associated with this activity, including exposure to combustion products. Therefore, the efforts of research institutions are currently focused on biomonitoring the working environment of firefighters and the associated characterisation and assessment of health risks in this occupational group. The aim of this paper is to present basic information on the potential health risks of the firefighting profession, including the evaluation of some biomarkers. The paper also presents a project aimed at evaluating the body burden of firefighters in simulated firefighting conditions.

KEYWORDS:

exposure, biomarkers, combustion products, firefighters, firefighting, hazardous chemicals

1. Introduction

It is widely acknowledged that the 'firefighting' profession is one of high-risk activities and this can put a lot of pressure on individuals. Exposure of firefighters to high temperatures, combustion products or intervention in a complicated and stressful environment can cause trauma, death or pathological changes in the body. In recent years, a number of research institutions, in collaboration with fire departments around the world, have attempted to quantify the potential health risks in the firefighter work environment. What distinguishes firefighters from other occupational groups and the general population is exposure to hazardous chemicals (HCH) during firefighting. Firefighters from around the world tackle fires in a variety of environments, i.e. from outdoor and natural fires, confined space fires to process plant fires. Firefighting involves a range of high-risk activities combined with exposure to high temperatures and the complex mixture of HCHs released during a fire. The burning of modern polymeric materials, textiles, furniture, electrical or electronic equipment releases a range of compounds that are classified as known, probable or possible carcinogens, as well as mutagens or endocrine disruptors [1].

Firefighters are exposed to many stressors during their working lives including exposure to HCH, extreme physical, mental, or cardiovascular stress (responding to external stimuli), disruption of circadian rhythms (shift work), increased heat stress associated with exposure to heat while fighting fires, or use of emergency personal protective equipment (PPE) [2-6]. Persistent exposure to occupational stressors can contribute to the development of short – and long-term health consequences. In general, firefighters are expected to have lower mortality (morbidity) and morbidity (mortality) than the general population. This is referred to in occupational risk epidemiology as the healthy worker effect. Given the nature of the 'firefighting' profession, the physical and mental demands of the work and the associated need to undergo regular physical fitness checks, including regular medical examinations, must be taken into account. Nevertheless, a number of foreign studies have been published in recent years which indicate that firefighters, as an occupational group, have a higher incidence of certain diseases compared to the general population. The etiology of some diseases and health problems may therefore be related to the firefighting profession and firefighting.

2. Exposure and potential health risks

To date, a large number of epidemiological studies have been published examining fire departments in different countries. The first major epidemiological studies looking at the health effects of the firefighting profession were published in 1959, by Ernest Mastromatteo, in Toronto. However, the history of health research concerning firefighters is much older. Today, firefighters are one of the most thoroughly studied occupations in terms of epidemiology or occupational medicine, along with asbestos workers. Despite extensive research, epidemiological or toxicological data are not complete [7]. Perhaps the most important source of data on the long-term health effects of the firefighting profession are epidemiological studies covering long time periods (several decades) and examining risk in a large group of tens of thousands of firefighters. These are mainly referred to as cohort studies. The largest epidemiological studies examining morbidity or mortality of various diseases have evaluated groups of up to 30 000 firefighters over a period of more than 40 years. A large proportion of epidemiological studies have come from North America, but research has also been conducted in Australia, New Zealand, South Korea, Germany, France, the UK, Northern European countries, etc.

In 2010, the International Agency for Research on Cancer (IARC) classified firefighter "occupational exposure" as potentially (possibly) carcinogenic to humans (Group 2 B), based on limited evidence in humans and insufficient evidence in experimental animals. According to the IARC, the main etiological factor for cancer among firefighters is repeated exposure to combustion products [8]. All types of fires release some highly hazardous substances in terms of chronic effects on the organism, such as polycyclic aromatic hydrocarbons, (PAHs), benzene, 1,3-butadiene, trichloroethylene, dioxins, furans, vinyl chloride or formaldehyde. The IARC published monograph lists at least 13 substances identified in combustion products with proven carcinogenic effects on humans. Many of the identified carcinogens are volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). These compounds are common in the combustion of most materials. Complex VOC/SVOC mixtures are formed in fires as products of incomplete combustion and many are known to cause significant harm to human health and the environment. Some compounds such as benzene, styrene and phenol are formed in most fires. They occur in combustion products of synthetic (polymer) materials, but also in traditional building materials or wood products [9]. The increased incidence of certain cancers usually associated with exposures leads to the conclusion that a causal link between cancer and firefighting activities cannot be excluded. It can be said that for cancers, according to the result of research over the last 50 years or so, firefighters show lower or comparable overall incidence and mortality rates

compared to controls (non-exposed group), although there is a statistically significant finding of some specific types of cancers.

Heat stress, heat exhaustion, and heat stroke due to prolonged and frequent exposure to high temperatures, especially in response personal protective clothing (response PPE), can lead not only to hyperthermia, but also to dehydration, which can damage the heart, kidneys, liver, or gastrointestinal tract [10]. The physical demands associated with firefighting and the high temperatures in which firefighters operate lead to heavy sweating. Emergency PPE reduces cooling, makes sweating less effective, and disrupts the body's thermoregulatory processes and water balance. Recent research examining U.S. firefighters in training showed that more than half of the probands included in the study were dehydrated prior to training [11]. During training, most probands lost more than 1% of their body weight due to fluid loss, which can affect mental function, strength, and coordination. In addition, increased blood flow, sweating, and body temperature along with decreased body water content may also increase the risk of dermal absorption of some burn products [11-12].

The kidneys are known to be particularly susceptible to damage from some toxic substances, so the combination of dehydration associated with repeated exposure to toxic substances over a number of years may go part of the way in explaining the increased risk of kidney disease [13-14]. There are a number of factors that can affect the gastrointestinal system of firefighters. Long-term exposure to some specific components of combustion products (e.g., acrolein) is known to cause irritation of epithelial cells in the gastrointestinal tract, whereas other components of combustion products (e.g., polychlorinated biphenyls) are associated with histological changes in the liver [15-16].

In the USA, 45% of in-service deaths among US firefighters were found to be due to ischemic heart disease (IHD) [17]. Studies have shown that exposure to certain HCHs such as hydrogen cyanide, carbon monoxide or particulate matter can accelerate cardiovascular disease. Increased risk of myocardial infarction leading to death may also be due to heat stress, extreme physical exertion associated with firefighting, dehydration, shift work, or stress related to fire alarm response [7].

Reduced reproductive health in firefighters is evident in both men and women according to some studies [18,19]. In a 2019 Danish study, it was found that there is an increased likelihood that couples in which the male is in the firefighting profession will seek in vitro fertilization (IVF) treatment [18]. The likely mechanism behind the decline in male fertility is genital heat stress caused by occupational stress [20]. Heat stress can occur, for example, with regular use of intervention PPE. These garments are composed of several layers of functional materials and are primarily designed to protect the firefighter during firefighting operations. However, they are widely used for all types of intervention, including training as part of their regular use. Firefighters are also exposed to a range of HCHs that can adversely affect their reproductive health, whether they are endocrine disruptors or substances with teratogenic effects [18].

A large number of studies show that frequent, prolonged and direct exposure to smoke increases respiratory rate and frequency, resulting in deposition of smoke particles in the respiratory tract. Studies suggest that exposure of lung epithelial cells to particulate matter promotes inflammation due to alveolar macrophage responses [20]. This may contribute to an increased incidence of chronic respiratory disease in firefighters. Exposure of firefighters to combustion products during wildland firefighting has been found to have a significant effect on respiratory immunity and at high doses can cause long-term or permanent lesions in lung tissues. This is mainly the case when firefighters do not consistently use an isolation breathing apparatus during firefighting. Thus, activities during 'firefighting' or immediately after a fire intervention appear to be problematic. The effects on the respiratory system appear to be most strongly associated with the size and composition of the inhaled

particulate matter, which is thought to be extremely harmful to human health [21]. The lungs have an extensive contact surface for gas exchange. Lung injury occurs when an external noxa causes a hypersensitivity reaction or damage to the respiratory system. Chemicals associated with lung cancer according to the IARC include arsenic and inorganic arsenic compounds, beryllium and beryllium compounds, cadmium and cadmium compounds, chromium compounds, nickel compounds, particulate matter, benzo(a)pyrene, phthalates, etc. [23-25]. Several studies have demonstrated the exposure of firefighters to these HCHs during firefighting. [26-28]. After inhalation, NCHLs can enter the respiratory tract leading to local or systemic inflammation [29]. Disorders of lipid metabolism, oxidative stress, DNA damage, epigenetic modifications, and inflammation can develop into respiratory disease or cancer under certain circumstances. Pathophysiological changes due to exposure of firefighters to stress factors such as extreme physical exertion or exposure to HCH all likely contribute to the development of respiratory disease in firefighters.

The profession of firefighting and fire suppression has also been associated with oxidative stress, protein and DNA damage, early inflammation, and the development/worsening of cardiorespiratory, metabolic disorders and cancer [30-32]. The concentration of HCH released during fires is often extreme, but alone cannot explain the overall health burden found in this occupational group. Prolonged exposure to HCH released from fires promotes the continuous production of reactive oxygen species, disrupts the oxidation/antioxidation balance, and may subsequently cause protein and DNA damage [33-35]. Epidemiological studies have also found that heat exposure and physically demanding activities performed by firefighters in response PPE disrupt homeostasis in firefighters [36-39]. Oxidative stress occurs when oxidative activity is not adequately suppressed by intracellular antioxidant systems. Biomarkers of oxidative stress are molecules that participate in biological processes or are its end products (e.g., antioxidant enzymes, lipid radicals, malondialdehyde, and isoprostanes). An imbalance between oxidative and antioxidant activity causes oxidative stress and can lead to severe damage to proteins and DNA. Protein damage has a response within the cell by disrupting enzymatic regulation and related biological functions [40-41].

3. Research project "threat assessment of firefighter exposure to combustion products"

The potential health risks associated with fire suppression are largely determined by the duration and frequency of exposure, the overall toxicity of the HCH (depending on the combustible assemblage and combustion products produced), the route of entry of the HCH into the body, health and physical condition, or genetic predispositions. Exposure to combustion products is probably not the only etiological factor explaining the overall health burden. Rather, it is a complex set of factors that contribute to some health problems of firefighters. In order to understand the results of epidemiological studies and the etiological factors associated with the development of certain diseases, various measurable indicators of biological or pathological processes in the body (biomarkers) are used to assess the burden of disease in firefighters. Biomarkers are valuable tools to elucidate the mechanism of action of certain stressor factors that may lead to the occurrence of disease. Biomarkers of effect (also known as biomarkers of biological response) are observable and quantifiable physiological/biochemical changes that are directly associated with biological responses to pathological processes in the body [42]. These changes may be specific clinical symptoms or markers of clinical disease. Their quantification is of utmost importance for early intervention in disease development. Research on biomonitoring of firefighters has increased significantly in recent years. There is now evidence suggesting a link between firefighting, exposure to combustion products and adverse health effects in firefighters.

Despite the efforts of a number of research organizations and fire departments, there is currently insufficient information on how firefighters' bodies respond to stressors that affect them during real fires. At the same time, the results of biomonitoring are crucial for optimizing the physical load, minimizing firefighter exposure and contamination, or developing PPE.

This issue led to the development of the research project "Assessment of the threat of firefighter exposure to combustion products" at the Czech Technical University in Prague, Faculty of Biomedical Engineering. The project also involves the National Institute of Public Health, Population Protection Institute of the Fire Rescue Service of the Czech Republic, the Technical Institute of Fire Protection of the Fire Rescue Service of the Czech Republic, Department of Occupational Medicine, 1st Faculty of Medicine, Charles University in Prague and Institute of Forensic Medicine and Toxicology of the 1st Faculty of Medicine and General University Hospital in Prague, the Institute of Experimental Medicine, CAS, CASRI - Scientific and Service Institute of Physical Education and Sport and some other institutions. The aim of the project is to evaluate the behavior of the firefighters' organism in conditions of combustion products, extreme heat and intense physical exertion. Special attention was paid to the exposure of the organism to some of the HCHs commonly found in combustion products such as benzene or PAHs. Two field experiments simulating real fire conditions in confined spaces were carried out within the project. The research in both cases took place in Vysoké Mýto, in a facility simulating real fire phenomena (the so-called flashover container), operated by the Fire Rescue Service of the Pardubice Region. The first - pilot experiment took place in 2019 and was attended by 10 probands from the ranks of members of the Fire Rescue Service of the Czech Republic. The aim of the experiment was to verify some methods such as sampling from the inner part of the "flashover" container to determine the concentration of benzene, hydrogen cyanide or carbon monoxide. In addition, probands were subjected to biological material sampling to assess benzene exposure or exhaled air sampling. Based on the experience of the pilot experiment, some methods were modified and supplemented. The methodology was significantly modified to not only assess the effects of exposure of the organism to some of the HCHs, but also to assess the response and adaptation of the probands to the extreme load.

The second field experiment took place in 2021 and involved 24 probands, again from the ranks of members of the Fire Rescue Service of the Czech Republic. They performed a simulation of a firefighting operation in confined spaces associated with the search and rescue of a person. During the experiment, extreme conditions associated with the development of large amounts of combustion products, zero visibility and high temperatures were simulated inside the training facility. The aim of the simulation was to create in probands an intense load and stress response corresponding to the realistic load in a fire response in confined spaces. Thus, conditions inside the facility were simulated similar to those of a fire inside a residential room. That is, the materials used in the combustion ensemble and placed in the incinerator were equivalent to the equipment in the living room. By simulating the fire intervention, the probands were evaluated:

- internal body exposure to some highly toxic substances commonly found in combustion products,

- damage to the genetic material of the cell,

- exposure and extent of damage to the organism from particulate matter,

- physical and stress loads on the body under extreme conditions,

- acute and chronic changes in the respiratory tract,

As part of the field experiment, a number of the following examinations and biological material collections were performed:

- Biological Exposure Tests (BET) - performed when assessing exposure to chemicals in the work environment (occupational exposure) and allows quantification of the total amount of a selected harmful substance absorbed into the body. Benzene metabolites and PAHs were evaluated in the experiment.

- Cytogenetic analysis of peripheral lymphocytes (CAPL), micronucleus examination and the so-called comet assay - this is a very accurate test used to monitor the population exposed to carcinogens and mutagens (genotoxic substances). These NCHL are commonly found in combustion products.

- Nuclear DNA methylation carries the genetic information that encodes in its structure and gives cells their program, thus predetermining the development and characteristics of the whole organism. Simply put, DNA methylation indirectly predetermines the resistance of this nuclear acid to damage. The methylation settings of individual genes can change gradually over the course of a lifetime, depending on living conditions, including exposure to genotoxic substances. It is these changes that will be analyzed in blood DNA samples.

- Determination of carbonylhemoglobin levels in blood was determined both invasively, i.e. by blood sampling, and by CO oximetry, i.e. non-invasively.

- The evaluation of some physiological parameters was performed by a personal biotelemetry system FlexiGuard developed by the Czech Technical University in Prague, Faculty of Biomedical Engineering. Heart rate, temperature under clothing, skin temperature and humidity under clothing were evaluated.

- Examination of biomarkers of oxidative stress - Oxidative stress is a process in which free radicals are formed that can cause acute and chronic diseases. The examination included both blood and urine sampling and exhaled air condensate.

- Determination of the levels of selected hormones (cortisol, testosterone) provide information on the level of load and stress during extreme physical exertion.

- Determination of lactate and glucose indicate the degree of load and the involvement of aerobic/anaerobic metabolism during exercise.

- The acid-base balance test (ASTRUP) provides information on the current state of the internal environment. It determines blood pH, O_2 and CO_2 partial pressures and the status of the blood buffering systems.

- The body composition analysis was performed by the bioimpedance method, where the body composition was determined, especially the proportion of fat and muscle, bone weight, amount of water in the body or body mass index (BMI).

- Exhaled NO to detect possible allergic inflammation in the airways (asthma, etc.) was assessed using a specialized device.

- Spirometry - non-invasive examination of lung volumes and resistance to breathing.

During the experiment, a number of air samples were taken from inside the flashover container. In the samples taken, the concentration of benzene, some polycyclic aromatic hydrocarbons and hydrogen cyanide were quantitatively evaluated. At the same time, a continuous measurement of carbon monoxide concentration was performed during the fire simulation. Along with the HCH sampling,

temperature measurements were made at the reference site inside the container using thermocouples.

The results of the exposed group will be compared with the results of the control so-called occupationally unexposed group. The intent of the investigation is to compare the body response of the exposed group (firefighters) and the body response of the non-exposed group (control group). The control group will perform the same activity and undergo approximately the same workload as the exposed group with the exception of exposure to combustion products and extreme heat. The control group will be examined at the end of this year.

The findings will be used primarily to optimize the physical and stress loads of firefighters during firefighting operations. Furthermore, they will be used for the development of preventive, regimen measures in the field of firefighters' working environment. These measures will provide practical recommendations for reducing firefighters' exposure to HCH and optimizing the physical load during fire intervention.

4. Conclusion

Firefighters may be exposed to a range of carcinogens and mutagens, including those with acute effects on the body, when conducting fire response. In recent years, the results of a number of studies evaluating the working environment of firefighters, including the level of exposure to toxic combustion products, have been published. The concentration of combustion products emitted during fires is extreme, but this alone cannot explain the overall health burdens found in this occupational group. The exposure of firefighters to a range of stress factors of a physical, biological, chemical or psychological nature significantly complicates the assessment of the health impacts of the firefighting profession in the long term. Along with occupational stresses, firefighters are subject to other environmental or social factors to which the general population is exposed. Studies published in recent years assessing the body burden of firefighters, including biomonitoring, provide valuable preliminary information. Most studies assessing the workload of firefighters during firefighting are case-control or cross-sectional studies, but cannot be used to draw conclusions about the causes and consequences of exposure. Thus, there are still significant gaps regarding the underlying biological mechanisms that lead to some pathologies. In addition, evaluated firefighters may have different genetic predispositions and different susceptibilities to the development of certain diseases that may manifest themselves as a result of the often extreme conditions of response activities. These factors can further complicate the quantification of health risks. When evaluating and comparing the results of some studies, we must take into account the different working, environmental and social conditions in which firefighters from various countries of the world live and work. Differences in working conditions, equipment, response activities, professional culture, work organization or different requirements for health and physical fitness may be significant. Psychosocial risks and stress in the workplace may also be related to working conditions. Therefore, for further research it is necessary to find methods and procedures to comprehensively assess stress factors not only in firefighting conditions, but also in other activities related to the firefighters' workload. As a result, well-designed large-scale longitudinal studies (using different types of biomarkers and biological material sampling) are urgently needed to further characterize and understand the effects of the profession on firefighters' health.

LITERATURE

[1] FABIAN, Thomas Z., Jacob L. BORGERSON, Pravinray D. GANDHI, C. Stuart BAXTER, Clara Sue ROSS, James E. LOCKEY, and James M. DALTON. Characteristics of firefighter exposure to smoke. Fire Technology [online]. 2014, 50(4), 993-1019 [cited 2021-11-11]. ISSN 0015-2684. Available from: doi:10.1007/s10694-011-0212-2

[2] ÂNGELO, R. P. and M. J. CHAMBEL. The relationship between job characteristics and burnout and employee engagement: a longitudinal study of firefighters. Stress and health [online]. 2015, 31(2), 106-114 [cited 2021-11-11]. ISSN 15323005. Available from: doi:10.1002/smi.2532

[3] DOBSON, Marnie, BongKyoo CHOI, Peter L. SCHNALL, Erin WIGGER, Javier GARCIA-RIVAS, Leslie ISRAEL, and Dean B. BAKER. Exploring occupational and health behavioral causes of obesity in firefighters: A Qualitative Study. American Journal of Industrial Medicine [online]. 2013, 56(7), 776-790 [cited 2021-11-11]. ISSN 02713586. Available from: doi:10.1002/ajim.22151

[4] KIM, Yun Tae, Woo Jin KIM, Jee Eun CHOI, et al. Cohort Profile: Firefighter Research on the Enhancement of Safety and Health (FRESH), a Prospective Cohort Study on Korean Firefighters. Yonsei Medical Journal [online]. 2020, 61(1) [cited 2021-11-11]. ISSN 0513-5796. Available from: doi:10.3349/ymj.2020.61.1.103

[5] PILLUTLA, Priya, Dong LI, Naser AHMADI, and Matthew J. BUDOFF. Comparison of coronary calcium in firefighters with abnormal stress test findings and asymptomatic non-firefighters with abnormal stress test findings. The American Journal of Cardiology [online]. 2012, 109(4), 511-514 [cited 2021-11-11]. ISSN 00029149. Available from: doi:10.1016/j.amjcard.2011.09.044

[6] SCHNELL, Thomas, Frederike SUHR, and Roland WEIERSTALL-PUST. Posttraumatic stress disorder in volunteer firefighters: the influence of specific risk and protective factors. European Journal of Psychotraumatology [online]. 2020, 11(1) [cited 2021-11-11]. ISSN 2000-8198. Available from: doi:10.1080/20008198.2020.1764722

[7] GUIDOTTI, Tee L., ed. Health risks and fair compensation in the fire service [online]. Cham: Springer International Publishing, 2016 [cited 2021-11-11]. ISBN 978-3-319-23068-9. Available from: doi:10.1007/978-3-319-23069-6

[8] WORLD HEALTH ORGANIZATION (WHO), 2010. IARC monograph on human carcinogenic risk assessment. Volume 98: Painting, firefighting and shift work. Geneva: WHO Press. ISBN 978-92-832-1298-0.

[9] AUSTIN, C. C. et al, 2001. Characterization of volatile organic compounds in smoke from experimental fires. Journal of Toxicology and Environmental Health, Part A [online]. 63(3), 191-206 [cited 2021-10-25]. DOI: 10.1080/15287390151101547. ISSN 1528-7394. Dostupné z: http://www.tandfonline.com/doi/abs/10.1080/15287390151101547

[10] CHESHIRE, William P. Thermoregulatory disorders and diseases associated with heat and cold stress. Autonomic neuroscience [online]. 2016, 196, 91-104 [cited 2021-11-11]. ISSN 15660702. Available from: doi:10.1016/j.autneu.2016.01.001

[11] HORN, Gavin P., Jacob DEBLOIS, Inga SHALMYEVA, and Denise L. SMITH. Quantifying dehydration in firefighters using field methods and novel devices. Prehospital Emergency Care [online]. 2012, 16(3), 347-355 [cited 2021-11-11]. ISSN 1090-3127. Available from: doi:10.3109/10903127.2012.664243

[12] WALKER, Adam, Rodney POPE and Robin Marc ORR. The impact of fire suppression tasks on firefighter hydration: a critical review with consideration of the utility of reported hydration measures. Annals of Occupational and Environmental Medicine [online]. 2016, 28(1) [cited 2021-11-11]. ISSN 2052-4374. Available from: doi:10.1186/s40557-016-0152-x

[13] VERVAET, Benjamin A, Patrick C D'HAESE and Anja VERHULST. Acute kidney injury induced by environmental toxins. Clinical Kidney Journal [online]. 2017, 10(6), 747-758 [cited 2021-11-11]. ISSN 2048-8505. Available from: doi:10.1093/ckj/sfx062

[14]RONCAL-JIMENEZ, C., M.A. LANASPA, T. JENSEN, L.G. SANCHEZ-LOZADA, and R.J. JOHNSON. Mechanisms by which dehydration can lead to chronic kidney disease. Annals of Nutrition and Metabolism [online]. 2015, 66(Suppl. 3), 10-13 [cited 2021-11-11]. ISSN 0250-6807. Available from: doi:10.1159/000381239

[15]CRAWFORD, J. O. and R. A. GRAVELING. Non-cancer occupational health hazards in firefighters. Occupational Medicine [online]. 2012, 62(7), 485-495 [cited 2021-11-11]. ISSN 0962-7480. Available from: doi:10.1093/occmed/kqs116

[16]KIM, Hyo-Min, Chang-Ho YOUN, Hae Jin KO, Seon-Hwa LEE, and Yu-Mi LEE. Relationship between blood levels of persistent organic pollutants and common gastrointestinal symptoms. Korean Journal of Family Medicine [online]. 2017, 38(4) [cited 2021-11-11]. ISSN 2092-6715. Available from: doi:10.4082/kjfm.2017.38.4.233

[17]KALES, Stefanos N, Elpidoforos S SOTERIADES, Stavros G CHRISTOUDIAS and David C CHRISTIANI. Firefighters and in-service deaths from coronary artery disease: a case-control study. Environmental Health [online]. 2003, 2(1) [cited 2021-11-11]. ISSN 1476-069X. Available from: doi:10.1186/1476-069X-2-14

[18]JAHNKE, Sara A., Walker S. C. POSTON, Nattinee JITNARIN, and Christopher K. HADDOCK. Maternal and Child Health Among Female Firefighters in the U.S. Maternal and Child Health Journal [online]. 2018, 22(6), 922-931 [cited 2021-10-25]. ISSN 1092-7875. Available from: doi: 10.1007/s10995-018-2468-3

[19]PETERSEN, Kajsa U, Johnni HANSEN, Niels E EBBEHOEJ and Jens P BONDE. Infertility in a cohort of male Danish firefighters: A Register-Based Study. American Journal of Epidemiology [online]. 2019, 188(2), 339-346 [cited 2021-10-25]. ISSN 0002-9262. Available from: doi: 10.1093/aje/kwy235

[20]JUNG, A. and H.-C. SCHUPPE. Effect of genital heat stress on semen quality in humans. Andrologia [online]. 2007, 39(6), 203-215 [cited 2021-10-25]. ISSN 0303-4569. Available from: doi: 10.1111/j.1439-0272.2007.00794.x

[21]HIRAIWA, Kunihiko and Stephan F. VAN EEDEN. Contribution of Lung Macrophages to the Inflammatory Responses Induced by Exposure to Air Pollutants]. Mediators of Inflammation [online]. 2013, 1-10 [cited 2021-11-11]. ISSN 0962-9351. Available from: doi:10.1155/2013/619523

[22]NAEHER, Luke P., Michael BRAUER, Michael LIPSETT, Judith T. ZELIKOFF, Christopher D. SIMPSON, Jane Q. KOENIG, and Kirk R. SMITH. health effects of wood smoke: A Review. Inhalation Toxicology [online]. 2010, 19(1), 67-106 [cited 2021-11-11]. ISSN 0895-8378. Available from: doi:10.1080/08958370600985875

[23]KOLENA, Branislav, Ida PETROVIČOVÁ, Miroslava ŠIDLOVSKÁ, Henrieta HLISNÍKOVÁ, Lenka BYSTRIČANOVÁ, Soňa WIMMEROVÁ and Tomáš TRNOVEC. Occupational risks and hazards associated with phthalates in Slovak firefighters. International Journal of Environmental Research and Public Health [online]. 2020, 17(7) [cited 2021-11-11]. ISSN 1660-4601. Available from: doi:10.3390/ijerph17072483

[24]LOOMIS, Dana, Neela GUHA, Amy L HALL and Kurt STRAIF. identification of occupational carcinogens: an update on IARC monographs. Occupational and Environmental Medicine [online]. 2018, 75(8), 593-603 [cited 2021-11-11]. ISSN 1351-0711. Available from: doi:10.1136/oemed-2017-104944

[25]MOORTHY, Bhagavatula, Chun CHU, and Danielle J. CARLIN. Polycyclic aromatic hydrocarbons: From metabolism to lung cancer. Toxicological Sciences [online]. 2015, 145(1), 5-15 [cited 2021-11-11]. ISSN 1096-6080. Available from: doi:10.1093/toxsci/kfv040

[26]DOBRACA, Dina, Leslie ISRAEL, Sandra MCNEEL, et al. Biomonitoring in California Firefighters. Journal of Occupational & Environmental Medicine [online]. 2015, 57(1), 88-97 [cited 2021-11-11]. ISSN 1076-2752. Available from: doi:10.1097/JOM.0000000000000307

[27]FENT, Kenneth W., Christine TOENNIS, Deborah SAMMONS, et al. Firefighters' and instructors' absorption of PAHs and benzene during training exercises. International Journal of Hygiene

and Environmental Health [online]. 2019, 222(7), 991-1000 [cited 2021-11-11]. ISSN 14384639. Available from: doi:10.1016/j.ijheh.2019.06.006

[28]FENT, Kenneth W., Christine TOENNIS, Deborah SAMMONS, et al. Firefighters' absorption of PAHs and VOCs during controlled residential fires by job assignment and fire attack tactic. Journal of Exposure Science & Environmental Epidemiology [online]. 2020, 30(2), 338-349 [cited 2021-11-11]. ISSN 1559-0631. Available from: doi:10.1038/s41370-019-0145-2

[29]TURNER, Michelle C., Zorana J. ANDERSEN, Andrea BACCARELLI, et al. Outdoor air pollution and cancer: a review of current evidence and public health recommendations. CA: A Cancer Journal for Clinicians [online]. 2020, 70(6), 460-479 [cited 2021-11-11]. ISSN 0007-9235. Available from: doi:10.3322/caac.21632

[30]COKER, Robert H., Carl J. MURPHY, Michelle JOHANNSEN, Grant GALVIN, and Brent C. RUBY. Wildland Firefighting. Journal of Occupational & Environmental Medicine [online]. 2019, 61(3), e91-e94 [cited 2021-11-11]. ISSN 1076-2752. Available from: doi:10.1097/JOM.0000000000001535

[31]REID, Colleen E., Michael BRAUER, Fay H. JOHNSTON, Michael JERRETT, John R. BALMES, and Catherine T. ELLIOTT. Critical Review of Health Impacts of Wildfire Smoke Exposure. Environmental Health Perspectives [online]. 2016, 124(9), 1334-1343 [cited 2021-11-11]. ISSN 0091-6765. Available from: doi:10.1289/ehp.1409277

[32]SOTERIADES, Elpidoforos S, Jaeyoung KIM, Costas A CHRISTOPHI and Stefanos N KALES. Cancer incidence and mortality in firefighters: A State-of-the-Art Review and Meta-Analysis. Asian Pacific Journal of Cancer Prevention [online]. 2019, 20(11), 3221-3231 [cited 2021-11-11]. ISSN 2476-762X. Available from: doi:10.31557/APJCP.2019.20.11.3221

[33]KWON, Jae-Woo, Hee-Won PARK, Woo-Jin KIM, Man-Goo KIM, and Seung-Joon LEE. Exposure to volatile organic compounds and airway inflammation. Environmental Health [online]. 2018, 17(1) [cited 2021-11-11]. ISSN 1476-069X. Available from: doi:10.1186/s12940-018-0410-1

[34]LUO, Kai, Irina STEPANOV, and Stephen S. HECHT. Chemical biomarkers of exposure and early damage to potentially carcinogenic air pollutants. Annals of Cancer Epidemiology [online]. 2019, 3, 5-5 [cited 2021-11-11]. ISSN 26164213. Available from: doi:10.21037/ace.2019.08.01

[35]MOORTHY, Bhagavatula, Chun CHU and Danielle J. CARLIN. Polycyclic aromatic hydrocarbons: From metabolism to lung cancer. Toxicological Sciences [online]. 2015, 145(1), 5-15 [cited 2021-11-11]. ISSN 1096-6080. Available from: doi:10.1093/toxsci/kfv040

[36]GORDON, H. and LARIVIERE, M. Physical and psychological determinants of injury in Ontario forest firefighters. Occupational Medicine [online]. 2014, 64(8), 583-588 [cited 2021-11-11]. ISSN 0962-7480. Available from: doi:10.1093/occmed/kqu133

[37]MONTINE, Kathleen S, Joseph F QUINN, Jing ZHANG, Joshua P FESSEL, L Jackson ROBERTS, Jason D MORROW, and Thomas J MONTINE. Isoprostanes and related lipid peroxidation products in neurodegenerative diseases. Chemistry and Physics of Lipids [online]. 2004, 128(1-2), 117-124 [cited 2021-11-11]. ISSN 00093084. Available from: doi:10.1016/j.chemphyslip.2003.10.010

[38]PARK, Eunju, Yun-Jeong LEE, Sun-Woo LEE, Chang-Hoon BANG, GyuChang LEE, Jun-Kyoung LEE, Jung-Suk KWAN, and Yu-Sub HUH. Changes in oxidative/antioxidative parameters and DNA damage in firefighters wearing personal protective equipment during treadmill walking training. Journal of Physical Therapy Science [online]. 2016, 28(11), 3173-3177 [cited 2021-11-11]. ISSN 0915-5287. Available from: doi:10.1589/jpts.28.3173

[39]SHIA, Regina M., Lindsey K.. MCINTIRE, Josh A. HAGEN, Chuck D. GOODYEAR, Leanne N. DYKSTRA, and Andrea R. MYERS. Biomarkers and biometric indicators of physical exhaustion in firefighters. Production Procedure [online]. 2015, 3, 5081-5087 [cited 2021-11-11]. ISSN 23519789. Available from: doi:10.1016/j.promfg.2015.07.522

[40]BARAIBAR, Martin A., Liang LIU, Emad K. AHMED and Bertrand FRIGUET. Protein Oxidative Damage at the Crossroads of Cellular Senescence, Aging, and Age-Related Diseases. Oxidative Medicine and Cellular Longevity [online]. 2012, 1-8 [cited 2021-11-11]. ISSN 1942-0900. Available from: doi:10.1155/2012/919832

[41] HAWKINS, Clare L. and Michael J. DAVIES. detection, identification and quantification of oxidative modifications of proteins. Journal of Biological Chemistry [online]. 2019, 294(51), 19683-19708 [cited 2021-11-11]. ISSN 00219258. Available from: doi:10.1074/jbc.REV119.006217

[42] NORDBERG, Gunnar F. Biomarkers of exposure, effects and sensitivity in humans and their use in the study of metal-metal interactions in China. Toxicology Letters [online]. 2010, 192(1), 45-49 [cited 2021-11-11]. ISSN 03784274. Available from: doi:10.1016/j.toxlet.2009.06.859

Taxus Poisoning

Ivo BEROUN*

*Police of the Czech Republic, Institute of Criminology, Post Box 62/KÚ, Strojnická 27, 170 89 Prague 7, Czech Republic, ivo.beroun@pcr.cz

ABSTRACT:

3,5-Dimethoxynaphthol is an important market in yew (taxus) poisoning, and its presence is considered to be a proof thereof. This article describes a simple method to increase 3,5-dimethoxynaphthol concentration in native plant material or its extract based on acidic hydrolysis at higher temperature. The GC-MSD method was used for the analysis of samples prepared in this manner. Use of the method was documented on two case studies, both suicide cases of young people. Not only is this suicide method quite rare, but moreover, the first person recorded his self-harming behaviour through video sequences caught on a tablet, and besides, both suicide victims knew each other.

KEYWORDS:

European yew (*Taxus baccata*), 3,5-dimethoxyphenol, hydrolysis, GC-MSD, poisoning, suicide

1. Introduction

Plant species *Taxus baccata* (L.) of the *Taxacea* genus is a coniferous tree, abundant in the Czech Republic in the form of a shrub or short tree, especially in parks. It is generally known this tree is poisonous, with all parts being highly poisonous except the red arils (*epimatium*) formed around the seeds during Autumn. The poisonous substances (pseudoalkaloids of the taxin class, especially dominant taxin B, isotaxin B, and then taxin A, whose concentration can significantly vary throughout the year in an individual plant) are quickly absorbed in the gastrointestinal tract (within 30–60 min) and cause heart failure due to their pronounced effect on the cardiovascular system. The amount of 50–100 g or decoction of this amount is considered to be lethal [1], leading to death usually within 2 hours after consumption. Taxus poisonings exhibit high mortality due to the pronounced cardiotoxic effect of the toxins contained and also due to the fact there are no efficient antidotes which could be administered after the poisoning. The presence of plant residues (needles) in the gastrointestinal tract may point to a poisoning case during an autopsy. However, when the taxus decoction is used for the poisoning, the plant residues may be missing. In such cases, the toxicologist may search for 3,5-dimethylphenol (further as 3,5-DMP), a marker of growing importance in the past years, to confirm his suspicion. [2,3] Why is 3,5-DMP rather than principal toxins (taxin A, B and isotaxin B) analysed? The answer is simple: these toxins are not easily available as standards (none of the established companies offering certified standards of narcotics or psychotropic substances, drugs and toxic substances have these in their product portfolio). Additionally, the analytic procedures for their identification are not straightforward – usually, liquid chromatography coupled with mass detection is used, *e.g.*, as HPLC–ESI–MS–MS system after sample preparation using thin-layer chromatography (TLC) or solid phase extraction (SPE). The 3,5-DMP marker forms in body organs by the cleavage of taxicatin, another taxin typical for taxus, by enzymatic hydrolysis catalysed by β-glucuronidase:
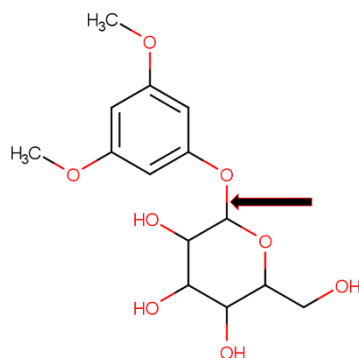
Figure 1: The arrow indicates the cleavage of taxicatin to yield the 3,5-dimethoxyphenol structure (up left)

2. Sample preparation and analysis

As 3,5-DMP is only formed biochemically in the human body, its concentration may be very low both in the native material samples (needles, seeds, decoction etc.) handled by the expert laboratories of the Czech Police (containing high concentration of undecomposed taxicatin) and bodily samples encountered by court toxicologists (as 3,5-DMP may be widely distributed across the body organs and fluids). Hence, it is important to cleave taxicatin present in the evidence before the analysis itself. As the laboratories are not equipped to perform enzymatic decomposition, acidic hydrolysis may be used. Human stomach contains hydrochloric acid produced by the parietal cells at a concentration of 140–160 mmol/L which corresponds to 0.5–0.6%. Hence, the first step was to identify a suitable amount of hydrochloric acid to be added to the analysed material sample. We decided to use a much higher concentration of hydrochloric acid than present in the gastric juice as there are no enzymes to assist the cleavage, namely 7% (ca. 2 N HCl). The sample was then "incubated" at a higher temperature (to 80°C, in a concentrator, drier, or similar) to accelerate the non-enzymatic hydrolysis giving rise to 3,5-DMP. After the incubation period and cooling to ambient temperature, organic solvent immiscible with water (ethyl acetate) is added to extract the marker. After the separation and centrifugation, the sample may be injected without any derivatization directly into a gas chromatograph coupled with a mass detector (GC–MSD). The following analytical conditions were used: Agilent 7890B/Agilent 5977B HESS as the GC–MSD system, column: HP-5MS (30 m × 250 μm × 0.25 μm), inlet: 250°C, Split, flow (He): 1 mL/min, temperature gradient: 60°C (1 min) → 30°C/min → 180°C (0 min) → 10°C/min → 280°C (15 min), i.e., 30 minutes total time per analysis, MS Source: 230°C, MS Quad: 150°C, Acquisition type: Scan.

3. Analytical results

Most commonly, relatively fresh samples of the plant material (up to a few months old) are submitted to the analysis. Incubation of these sample can significantly increase the 3,5-DMP concentration, as shown in Figure 2, comparing samples without incubation (mere extract by ethyl acetate) and with incubation of a taxus sample two days after harvest:
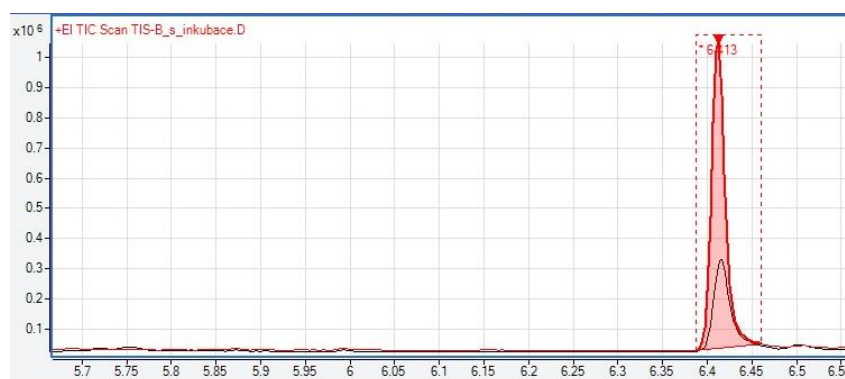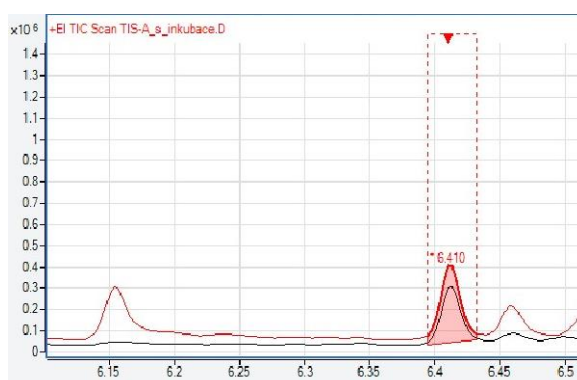
Figure 2: Comparison of identical taxus material (needles) without incubation (black) and with incubation (red), 2 days after harvest (concentration of 3,5-DMP is 2.75× higher based on corresponding peak area)

On the contrary, the difference between incubated and non-incubated taxus samples gets smaller as the sample ages. This is due to fermentation (dry matter "maturing") which leads to the release of 3,5-DMP from taxicatin, as shown in Figure 3 comparing the results of samples from an identical tree (different one than in the previous example) ca. 1 year after harvest without incubation (mere extraction by ethyl acetate) and with incubation. The difference is significantly less pronounced:

Figure 3: Comparison of identical taxus material (needles) without incubation (black) and with incubated (red), 1 year after harvest (concentration of 3,5-DMP is 1.35× higher based on the corresponding peak area)

On long standing of the taxus extracts, the toxicologically active substances may completely decompose. Hence, if a long time passes between the incident and the analysis, the 3,5-DMP marker may not be identified at all. This has been already described in the literature, [4,5] and many researchers notice taxus extracts are unstable in neutral or alkaline environments, leading to a drop in their toxicity. In these, other accompanying substances of simpler structure, *e.g.*, myrtenol or 1-octen-3-ol may be identified. [6]

4. Case study

The aforementioned procedure could be successful used in our laboratory for the elucidation of two recent cases of suicide by lethal intoxication by taxus. These happened shortly after each other in

March and July 2018. Surprisingly, although the two victims were seemingly unrelated, they, in fact, knew about each other.

The first case was a young man (28 years old), and the probable motive of his behaviour was total lack of hope for a better future and disappointment with his previous life. After investigation at the crime scene, an iPod tablet was secured. The tablet was active when discovered, and its investigation yielded 26 video recordings taken during the young man's self-harmful behaviour. The video sequences describing the preparation and ingestion of the toxic taxus material as well as the gradual effect on his organism were very important for the evaluation of the case. The victim started and stopped the recording himself. We found out that the package of video records was shared; however, the physical storage of recordings nor their sharing could be identified, and we were not able to ascertain whether they were shared with more recipients.

The second case was a young woman (24 years old) whose main motive was her serious diagnosis (paranoid schizophrenia). As in the previous case, autopsy followed by a toxicological analysis revealed the the imminent cause of the young woman's death was poisoning by a mixture of taxus toxins. The victim was not under the influence of alcohol or other toxicologically active substances (drugs, narcotics, psychotropic compounds). Investigation at the crime scene revealed the existence of two notebooks apart from the plant material. The victim's mother informed us her daughter used one of the notebooks to write short stories and her book, but that her daughter had deleted the entire hard drive some time ago, and deleted her Facebook account ca. one month before the incident. We were not able to prove direct communication between both victims despite repeated investigation of the electronic devices. However, it was obvious that the young woman knew which toxic plant material was used a family friend for his suicide, and may have been inspired by that. Among others, her mother stated: "She was very struck when my acquaintance's son consumed taxus decoction and died. This happened some time in March this year". Both cases sadly connected when the young man's father, receiving the young man's possessions detained by the police during the course of the investigation, produced the young woman's obituary, stating she died in the same way as his son.

5. Conclusion

The concentration of 3,5-DMP which is an important marker in taxus poisonings could be increased ("multiplication") by acidic hydrolysis of samples containing taxus material, catalysed by hydrochloric acid at a higher temperature of 80°C. This procedure is especially useful for relatively fresh material after harvest. Two case studies, both suicides by consumption of taxus material, confirm high mortality in this type of poisoning.

LITERATURE

[1] DIOCHI.CZ, Tis Cerveny, https://www.diochi.cz/pl/herbar/tis-cerveny , [online, March 5, 2022].
[2] FROLDI R., CROCi P..F, DELL'ACQUA L., FARÈ F., TASSONI G., GAMBARO V.: Preliminary gas chromatography with mass spektrometry determination of 3,5-dimethoxyphenol in biological specimens as evidence of taxus poisoning, J. Anal. Toxicol. 2010 Jan–Feb; 34 (1): 53–56.
[3] STŘÍBRNÝ J., DOGOŠI M., ŠŇUPÁREK Z., TOUPALÍK P., BALÁŽ P., BARTOŠ P: 3,5-Dimethoxyfenol – marker intoxikace tisem červeným [3,5-Dimethoxyphenol – a taxus baccata intoxication marker], Soud Lék. 2010, 55 (3), 36–39.
[4] BRYAN-BROWN T. : The pharmacological actions of taxine. Q. J. Pharm. And Pharmacol. 1932, 5, 205–219.

[5] JENNISKENS L. H. D., van ROZENDAAL E. L. M, van Beek T .A.: Identification of six taxine alkaloids from Taxus baccata needles. J. Nat. Prod. 1996, 59, p.117–123.

[6] VARLET V., AUGSBURGER M.:Monitoring of aglycons of yew glycosides (3,5-dimethoxyphenol, myrtenol and 1-octen-3-ol) as first indicator of yew presence. Drug Test Anal., 2013 Jun; 5 (6); 474–479.

Pre-concentration technique for the determination of hazardous metals in wastewater

Jiří SÝKORA*, Renata KOMENDOVÁ**

*Brno University of Technology, Faculty of Chemistry, Purkyňova 464, Brno, 612 00, Czech Republic
e-mail: xcsykoraj@fch.vutbr.cz

** Brno University of Technology, Faculty of Chemistry, Purkyňova 464, Brno, 612 00, Czech Republic,
email: komendova@fch.vut.cz

ABSTRACT:

We have developed and optimised a pre-concentration technique, using agar as the pre-concentration medium. We have found out that pre-concentration factors of up to 400, depending on the analyte can be achieved using this procedure. Theoretically, this should enable the chemical laboratories of the Fire Rescue System of the Czech Republic to determine the concentration of some hazardous metals at the level of 30 µg/L. We have experimentally confirmed the limit of detection reaches the values of 100 µg/L using the optimised pre-concentration procedure and optimised method for the Olympus Delta Professional device.

KEYWORDS:

Hazardous metals, XRF, concentration

1. Introduction

The chemical laboratories of the Fire Rescue Service of the Czech Republic face requests to determine hazardous metals in wastewater or in surface water multiple times per year. Not all the laboratories are equipped with ICP-OES or ICP-MS techniques, which makes the determination of hazardous metals such as arsene, copper, lead, zinc, chromium, nickel, or cadmium difficult. Yet, all these laboratories are equipped with energy dispersive X-ray fluorescence analyser Optimus Delta Professional X (further as ED-XRF) whose limit of detection for these metals reaches the concentration of 10 mg/L. To meet the limits for selected elements present in the surface water and wastewater as defined by the Czech Government Regulation 401/2015, Coll., as amended (tenths mg/L to several mg/L) using the ED-XRF, an efficient pre-concentration technique is therefore required.

### 2. Experimental part

Analyser

The handheld Delta Professional X analyser was equipped with rhodium X-ray anode (power 4 W). Due to optimal geometry, analyser evacuation was not required. The analyser was fitted with a Silicon Drift Detector equipped with an integrated full VGA camera and with the possibility to narrow the X-ray beam from 9 mm to 3 mm [1, 2].

Chemicals

Agar (Dorapis, Prague, Czech Republic), nitric acid (Penta, Chrudim, Czech Republic), distilled water, Multielement standard solution 4 for ICP (Supelco, Darmstadt, Germany), concentration 1,000 mg/mL, Multielement standard solution 8 for ICP (Supelco, Darmstadt, Germany), concentration 100 mg/mL, certified reference material (Astasol®, Prague, Czech Republic), concentration 1,000 mg/mL for these metals: cadmium, arsene, zinc, copper, nickel, chromium, and lead.

Optimised procedure

The development of our procedure was inspired by Kazuki Nakano and his team who used a laboratory-scale wavelength dispersive X-ray fluorescence analyser Rigaku to analyse pre-concentrated heavy metals in agar. Unlike their method, which uses basic pH, our method, provides very good results using acidic pH of the sample analysed. The pH is adjusted before the measurement (Graph 1). The sample is mixed with 70 mg of agar in a both ends open XRF cuvette, prepared upfront. The cuvette is heated to 90°C for 30 min on a hot plate, followed by a free cooling to the ambient temperature, and then by drying at 90°C for ca. 2.5 hours in a drier. The gel was then dispersed to achieve better homogeneity of the sample. The measurement was performed directly in the both ends open XRF cuvette using the Delta X ED-XRF analyser [3].
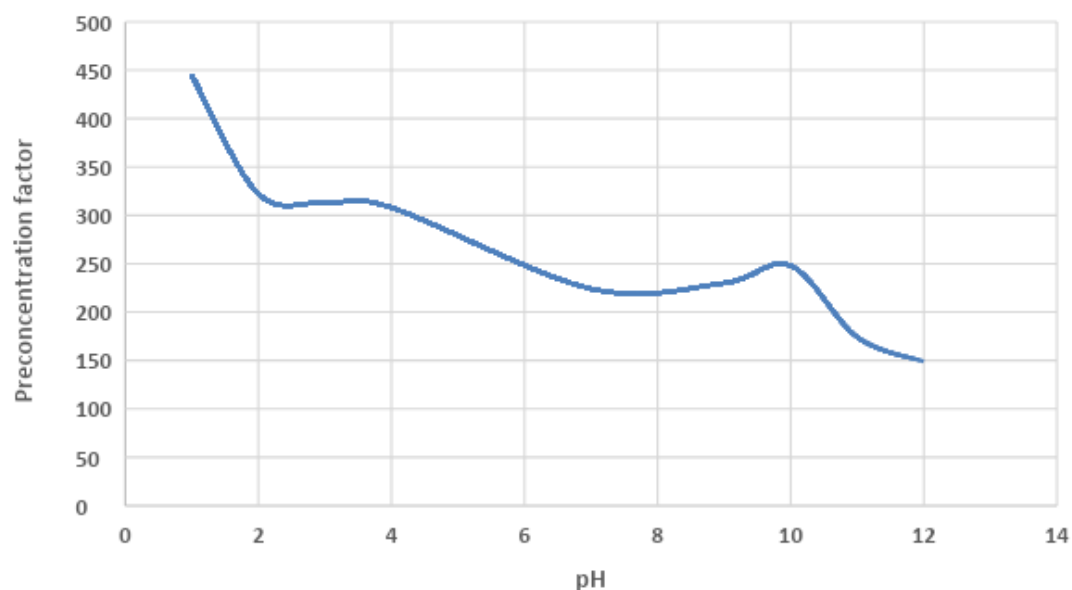
Graph 1. Influence of the pH on the pre-concentration factor for nickel

Analyser setting

The developed method was used for the optimisation of the Delta X ED-XRF setting to allow for the most accurate identification of the analytes possible. The limits of detection and data reproducibility have been improved by the adjustment of the measurement times and by user calibration of the analyser.
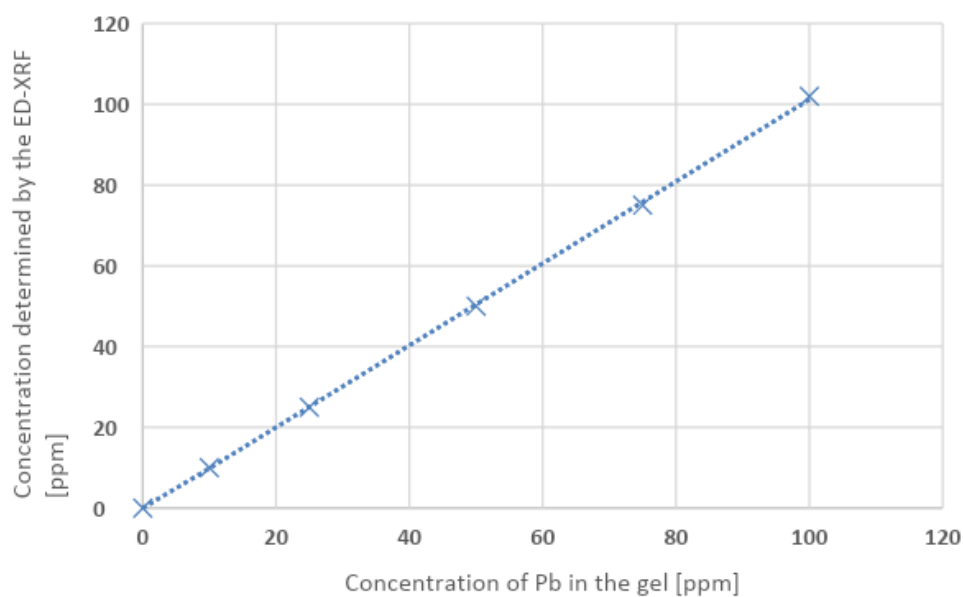
Graph 2. Calibration curve for lead

Determination of pre-concentration factors

Working solutions containing 50 mg/L or 100 mg/L of chromium, nickel,copper, zinc, arsene, cadmium, and lead have been prepared. These solutions have been analysed by the aforementioned optimised procedure using the Delta X analyser. Five samples were prepared for each concentration and each element, and each sample was analysed in triplicate. Pre-concentration factors obtained from these measurements are summarised in Table 1.

Table 1. Pre-concentration factors obtained

	Cr	Ni	Cu	Zn	As	Cd	Pb
50 mg/L	317 ± 5	444 ± 7	397 ± 6	326 ± 7	243 ± 8	110 ± 5	90 ± 5
100 mg/L	315 ± 4	445 ± 6	395 ± 5	330 ± 4	249 ± 7	105 ± 5	94 ± 4

Limits of quantification of the metals

Based on the limit of detection obtained on the Delta X analyser and based on the pre-concentration factors, the limit of quantification can be also calculated. To verify these calculations, we have prepared solutions containing 10 µg/L, 50 µg/L, 100 µg/L, 200 µg/L, 500 µg/L of the metals. Again, these solutions were analysed using the aforementioned procedure. We found that chromium, nickel, copper, zinc and arsene can be reliably determined starting from the concentration of 100 µg/L, while lead and cadmium could be reliably determined from 200 µg/L. The comparison of the theoretical limit of quantification and its experimental verification is summarised in Table 2.

Table 2. The limit of quantification (LoQ) obtained theoretically and confirmed experimentally

	Cr	Ni	Cu	Zn	As	Cd	Pb
Theoretical LoQ [µg/L]	31.6	22.5	25.3	30.5	40.7	93.0	108.7
Confirmed LoQ [µg/L]	100	100	100	100	100	200	200

3. Results and discussion

The pre-concentration results illustrated in Graph 1 indicate that while the method is useful across the wide pH range, the pre-concentration factors differ with pH. Highest pre-concentration factors could be obtained for all metals determined in acidic pH. The pre-concentration factors obtained allowed the calculation of the theoretical limit of quantification. These limits were verified experimentally and the results are summarised in Table 2. The pre-concentration method has two advantages: There is no transfer of liquids from a vessel to a vessel as the pre-concentration is performed in an open two-ended XRF cuvette, and no loss of the analytes therefore occurs. Second, the analysis is very cost-efficient.

4. Conclusion

Our results indicate that the optimised procedure meets the requirement of the chemical laboratories of the Fire Rescue Service of the Czech Republic. Without the pre-concentration technique, the laboratories would not be able to detect the low concentration of metals such as chromium, nickel, copper, zinc, arsene, cadmium, and lead using the Delta X analyser. Employing the pre-concentration procedure using agar, the limits of detection obtained easily meet the requirements of the Czech Government Regulation 401/2015, Coll., as amended, for the acceptable impurity levels in the surface waters and wastewater.

Acknowledgement

LITERATURE

[1] BAS RUDICE, Ruční spektrometr a ruční analyzátor kovů Delta Professional. [Handheld spectrometer and metal analyser Delta Professional.] BAS Rudice [online]. Blansko [cited 2021-10-17]. Available from https://www.bas.cz/rucni-analyzator-kovu-pro-trideni-kovu-pmi/delta-professional-rucni-analyzator-kovu-spektrometr.php.

[2] DELTA PROFESSIONAL Handheld XRF for Positive Material Identification (PMI). Blansko, Czech Republic, 2013.

[3] Kazuhiko NAKANO, Kenta OKUBO, and Kouichi TSUJI. Preconcentration of environmental waters by agar for XRF analysis. Powder Diffraction [online]. 2009, 24 (2), 135–139 [cited 2021-10-17]. ISSN 08857156. Available from: doi:10.1154/1.3132596

CONTRIBUTION TO THE EVALUATION OF RISK OF SECONDARY AIR CONTAMINATION BY THE DESORPTION OF A CHEMICAL WARFARE AGENT FROM CLOTHES

Jana KRYKORKOVÁ*, Tomáš ČAPOUN*

*Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, Na Lužci 204, 533 41 Lázně Bohdaneč, Czech Republic, jana.krykorkova@ioolb.izscr.cz ; tomas.capoun@ioolb.izscr.cz

ABSTRACT:

This article describes the risks of secondary air contamination by sarin desorption from clothing of personnel exposed in a contaminated area. Sorption of amyl acetate as a sarin imitant into various textile materials and its subsequent desorption was tested in laboratory experiments to evaluate this risk. Additionally, we have tested the desorption of amyl acetate from the clothes of a test mannequin to resemble real conditions more closely. This gave us evidence about the rate of sorption of amyl acetate into clothing, the rate of its desorption, and their dependence on ambient concentration and temperature. Tests under real conditions in closed and open space resulted in the evaluation of the risk of secondary air contamination by desorption of sarin from the clothes of contaminated personnel.

KEYWORDS:

chemical warfare agents, sorption, desorption, sarin, amyl acetate, photoionization detector, secondary contamination

1. Introduction

Terrorist and criminal group activities have been increasing in frequency, aggressivity, forms, methods and success rates. Although the ban on development, production, storage and use of chemical warfare agents has entered into force already in 1997, it is obvious that terrorists do not consider themselves bound by any ethical, moral or legal norms. This may lead to the use of chemical warfare agents, or to their abuse to threaten and blackmail. Chemical warfare agents may therefore become a very efficient coercion tool against state officials, institutions, various corporation or civic groups due to their fairly easy methods of production, application if strongly impure, the ability to strike many people, and strong psychological effect not only on the people impacted, but also on the rescue teams.

History has proven multiple times that objects and areas with a high concentration of people are the most efficient for the misuse of chemical warfare agents. Therefore, mass transit connection points, railway stations, airports, subway stations, entertainment facilities (theatres, movies, stadiums,

concert halls, music clubs), public buildings, administrative offices, tourist centres, shopping malls etc. may be considered the most endangered places.

2. Conclusions from previous studies on contaminant distribution in space

Large studies on the distribution of a sarin imitate were conducted in the Prague subway system [1–6], in a shopping mall [7], in an ice stadium [8], and in the lecture hall of the VSB – Technical University in Ostrava, Czech Republic [12]. The most detailed study was performed within the contamination distribution study in the Prague subway [1–6] resulting in the elaboration of a typical activities sheet [9]. Based on these studies, following conclusions regarding secondary contamination were made:

- The rescue system as well law enforcement have to be ready for various scenarios of a chemical terrorist attack while considering the risk of an attack aiming at mass murder must be considered as the worst case scenario,
- Sarin as nerve-paralysing agent is the most dangerous real chemical contaminant in an area with large concentration of people,
- An aerosol represents the most efficient form to use sarin,
- Most probable method of distribution is free evaporation. Explosive distribution is also realistic to be considered.

In the experiments focusing on sarin spread in space, the agent had to be replaced by a suitable imitating compound which would at least partially comply with the following requirements [10]: the imitant should have similar physical-chemical properties, it should be easy to detect, it has acceptable toxicity, it is safe to work with, and it is easily available from the supplier and price point of view. *n*-Amyl acetate (*n*-pentyl acetate) has been selected comparing its basic physical properties with sarin [10,11].

3. Theoretical considerations

The previous study on the spread of amyl acetate in the Prague subway system concluded that any plan to minimise the impact of a chemical terrorist attack needs to consider the contribution of secondary contamination by the chemical warfare agent borne on the passengers' clothes [5,6], i.e., the process of sorption of the chemical warfare agent into the passengers' clothes, their transportation into non-contaminated areas, and subsequent desorption and secondary decontamination.

A test of amyl acetate sorption into a 1 mm thick cotton textile at varying ambient concentration was performed in the laboratories of the Czech National Institute for Nuclear, Chemical and Biological Protection. The results have shown that the amount absorbed into the textile is linearly proportional to the concentration of amyl acetate in the surrounding air.

Additionally, one of the sources [13] describes that each person transports up to 50 L of contaminated air in their clothes, including underwear, outside garments and a coat.

To assess the risk resulting from volume, we have considered the secondary contamination of the subway station entrance lobby whose average volume reaches 4,000 m^3. Assuming complete desorption from passengers' clothes, the contribution of secondary contamination within the entire volume of the lobby corresponds to ca. 0.33 mg/m^3 [6]. This calculation assumes complete evaporation of the contamination without ventilating the station, maximum sorption into the passengers' clothes, complete desorption in the given space, and full rush hour. Hence, it is safe to assume that the real contribution of the secondary contamination would be significantly lower.

Real experiments with the sorption of a chemical warfare agent imitant into textile materials and subsequent desorption should consider rational imitant concentration in the contaminated spaces and sorption times.

We have taken the data measured within previous studies as the basis for our own experiments. The maximum concentration of amyl acetate in the Prague subway system at various setups and arrangements was found to be 35 ppm [5,6], the concentration in a shopping mall reached 22 ppm [7], 18 ppm in an ice stadium [8], and 30 ppm in the lecture hall of the VSB – Technical University Ostrava [12]. Based on these results, we have taken the amyl acetate concentration of 40 ppm as the initial one for our experiments.

The sorption time was set to 10 minutes, considering both the operating times as well as the course of intoxication. The operating times assume that the presence of sarin would be detected within 5 minutes from achieving an efficient concentration, and the evacuation would take 5 additional minutes.

A person present in a space contaminated by sarin at a concentration of 40 ppm for 10 minutes would exhibit the signs of severe toxication, most probably leading to death unless adequate aid is provided. First signs of intoxication would occur within 5 minutes, the person would then leave the contaminated area. The intoxication would fully develop within 15–20 minutes. The characteristic signs of intoxication would include salivation, perspiration, difficult breathing, impaired vision, quickly occurring skeletal muscle cramps, nausea, vomiting, colic-like stomach ache, and possibly diarrhoea and spontaneous urination and defecation. Within 30 minutes, generalised tonic–clonic seizure can be expected, potentially including opisthotonus, unconsciousness and apnea. Untreated intoxication would at these expositions end lethally within 30–60 minutes [14].

4. Experimental setup

4.1. Laboratory experiments with amyl acetate vapour sorption into textile materials

The amount of amyl acetate absorbed into the textile material was obtained gravimetrically. All experiments were performed at 21°C. The following items were placed inside a 100×60×80 cm test chamber made from transparent plastic: analytical balances, weighed sample of the textile (diameter 11.5 cm, area 0.0104 m^2), photoionisation detector AreaRAE Steel Z2 (RAE Systems Inc., San Jose, USA) calibrated to amyl acetate, battery-powered fan, and a Petri disk with a varying amount of amyl acetate (p.a., >98.5%, Fluka, b.n. 1252898 10807295).

The detector and fan were switched on, and once the amyl acetate reached a steady concentration, the textile sample was weighed. The textile weight increments as function of sorption time, textile type and amyl acetate concentration in the chamber were studied.

4.2. Laboratory experiments with amyl acetate desorption from textile materials

The textile sample containing amyl acetate prepared above (at an initial concentration of amyl acetate in the testing chamber of 150 ppm) was placed at the bottom of a gas bubbler. The bubbler was immediately closed, and the inner tube was connected to the inlet of the AreaRAE Steel Z2 photoionisation detector by a silicon tube (Figure 1).

Concentration of desorbing amyl acetate was measured using the photoionisation detector, and its dependence on time and temperature (having placed the gas bubbler in a thermostat) was studied.

Figure 1. Laboratory arrangement for the amyl acetate desorption from textile materials

4.3.   Real-size experiments with amyl acetate desorption from clothes

The experiments were performed using a 170 cm tall test mannequin clad in the following fashion:

- underwear on the torso and legs: polyester–lycra–elastane
- trousers: jeans (cotton)
- jumper: wool–polyester
- scarf: polyester.

Amyl acetate was dispersed in a hermetic testing chamber (5.1 m^3 volume) and its concentration was set to 40 ppm. The AreaRAE Steel Z2 photoionisation detector, calibrated for amyl acetate, was used to measure the concentration. The mannequin was placed into the chamber and exposed to the amyl acetate vapours for 10 minutes.

After the exposure, the mannequin was transported within 1 minute to the testing area. A network of AreaRAE Steel Z2 photoionisation detectors was located around the mannequin. Five detectors were located evenly around the figurine at a constant distance from the figurine (Figure 2). Amyl acetate concentration was measured at the height of 165 cm.

Figure 2. Arrangement of the testing area for the measurements of amyl acetate desorbing from clothes in an open environment

The amyl acetate concentrations were recorded continuously using the ProRAE Guardian software [15] which also evaluates the maximum concentration values in the real time and records the concentration as a function of time. The concentration values recorded by the detectors were downloaded (as numbers or as the graphical representation of concentration as function of time) using the ProRAE Suite software [16].

5. Discussion of results

5.1. Amyl acetate vapour sorption on textile materials

We observed that the sorption of amyl acetate on textile material is a fast process: the textile sample weight increment measurements at given amyl acetate concentration have shown that weight grows within the first 0.5–1 min and then remains constant.

We have also studied the dependence of the amyl acetate amount absorbed on its ambient concentration. Examples for some textile types are shown Figure 3, which depicts the weight increment expressed as the weight ratio, i.e., the ratio of weight increment (Δm) and the sample initial weight (M). As seen in Figure 3, the amount of amyl acetate absorbed by the textile sample grows with increasing amyl acetate ambient concentration. The amount absorbed rapidly grows up to 100 ppm of amyl acetate in the ambient air; however, the increase is not as pronounced at higher concentrations. At the initial concentration of amyl acetate 40 ppm (see section 3.2), the weight increment reached 0.33% m/m for the wool sample, 0.17% m/m for corduroy, 0.13% m/m for cotton (denim), 0.11% m/m for cotton (T-shirt), 0.10% for canvas, 0.08% m/m for a polyester–cotton mixture, and 0.06% m/m for pure polyester.
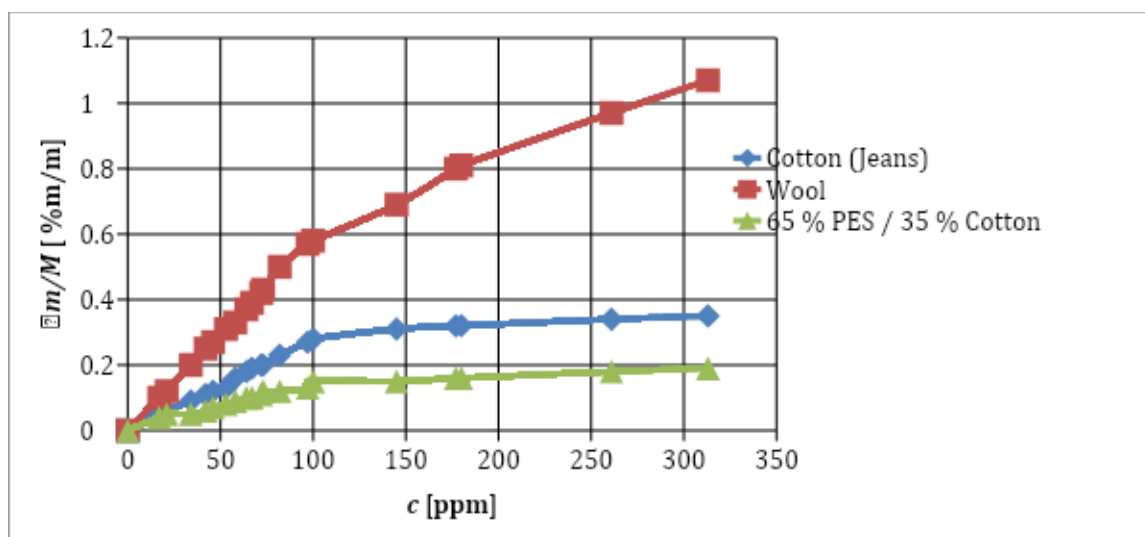

Figure 3. Relationship between the mass increment of textiles samples due to amyl acetate sorption and amyl acetate ambient concentration

The most important conclusions from these measurements are:

- Contaminant sorption from the environment is a fast process in which common textiles reach the equilibrium within one minute;
- The amount absorbed by the textile increases with increasing ambient concentration. It is therefore important to maintain constant concentration during the sorption phase before studying the contaminant desorption from the samples.

5.2. Amyl acetate desorption from textile samples at laboratory scale

The dependence of amyl acetate concentration in immediate proximity to the contaminated textile surface on time at the aforementioned experimental conditions at varying temperatures is shown in Figure 4, using corduroy as an example. This indicates that the desorption rate is significantly smaller than the sorption rate. The concentration above the textile has not dropped zero within 40 minutes at any temperature tested. The experiments also show that the temperature has major impacts on the desorption process as it influences:

- The maximum amyl acetate concentration reached above the textile material
- Time within which the maximum concentration is reached

At these experimental conditions, the desorption curves exhibit similar behaviour beyond 10 minutes regardless of the temperature.

The influence of temperature on the maximum amyl acetate concentration is also illustrated in Figure 5 which only shows the curves in the first 12 minutes.
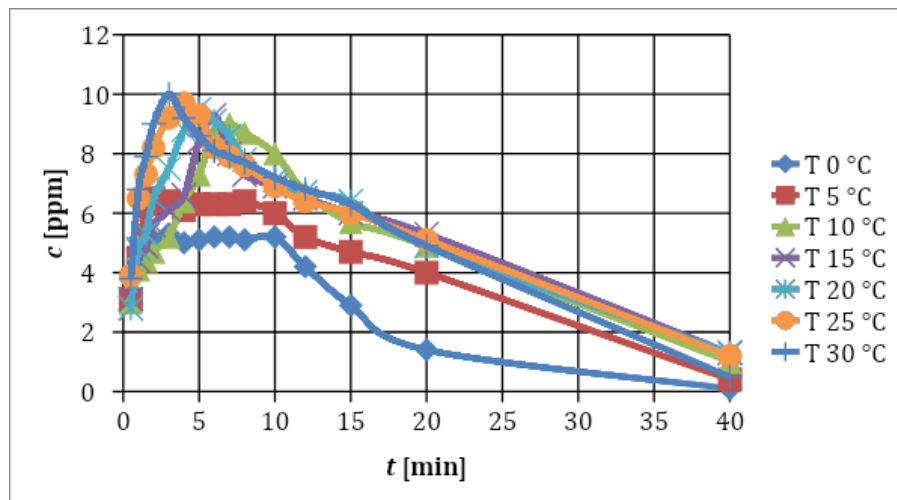

Figure 4. Dependence of amyl acetate concentration above the contaminated corduroy sample on time at varying temperatures
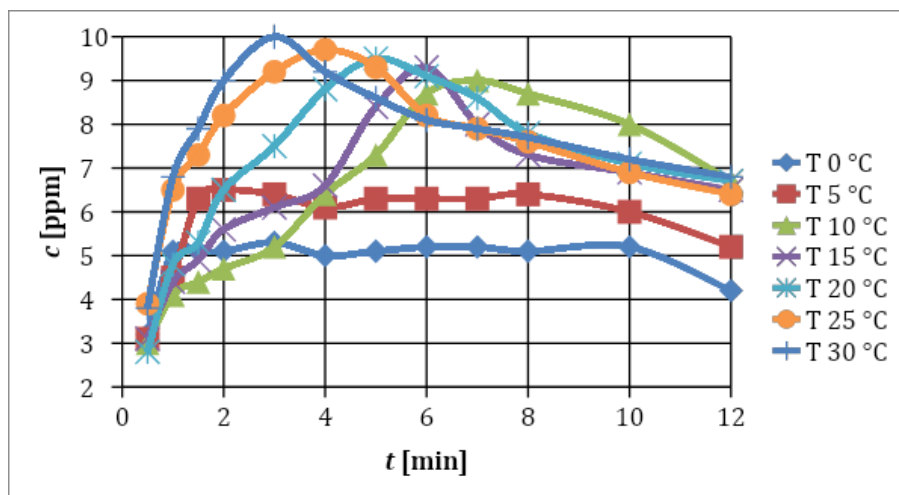
Figure 5. Dependence of amyl acetate concentration above the contaminated corduroy sample on time at varying temperatures. Only first 12 minutes of the experiments are depicted

5.3.   Amyl acetate desorption from clothes at real-life conditions

5.3.1.   Desorption in an open space

The measurements were performed on a calm day at 24°C (Figure 2). The detectors, located 20 cm and more from the test mannequin in our setup, showed no measurable concentration of amyl acetate during the experiment (from the end of sorption till 30 minutes of desorption). This means that the secondary contamination of the air is lower than the detection limit of the detector, i.e., 0.1 ppm, although in light of the experiments above, we can say that the meteorological conditions (high temperature and no wind which would further dilute the concentration) were ideal for the amyl acetate desorption.

We need to add that inhaling air containing 0.1 ppm sarin can be under normal circumstances (average volume of air inhaled 8 L/min) inhaled for 8 hours without exhibiting any sign of even the lightest, i.e., latent intoxication [14].

Contaminant desorbed from the clothes may therefore represent a certain risk for the contaminated person itself; however, this risk is quite negligible compared to the presence in the contaminated area. Under some circumstances, a person in close contact with the contaminated person could be contaminated, e.g., upon embrace. However, even this risk is significant taking into account the duration of such a close contact.

5.3.2.   Desorption in a closed space

Two sets of experiments in a closed space were conducted, both at the temperature of 19°C. The first set was performed in a 4.6×2.3 m room with a ceiling height of 2.4 m (total volume 25.4 m³), resembling a small bus the contaminated person may ride, or an emergency vehicle, emergency room or other enclosed area. The room was unventilated, with a door in the shorter wall and a double-paned window on the facing wall. The test mannequin whose clothes were contaminated at an ambient amyl acetate concentration of 40 ppm was within one minute after the contamination located in the centre

of the room, and the detectors were placed in all four corners in the height of 165 cm. The dependence of amyl acetate concentration on time is shown in Figure 6.
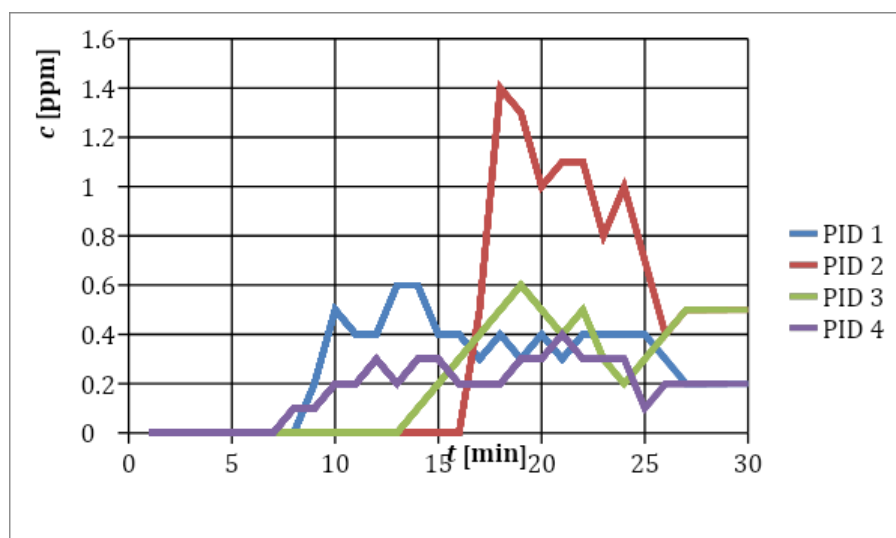

Figure 6. Dependence of amyl acetate concentration desorbed from clothes in the corners of a 4.6×2.3 m room on time

These relationships show that the distribution of amyl acetate vapours was uneven. Detectors PID 1 and 4, located in the corners close to the door, were able to detect amyl acetate within 7 minutes. Detectors PID 2 a 3, located in the corners closer to the window, could only detect amyl acetate after 15 min; however, the concentrations detected were higher than for the detectors closer to the door. This phenomenon cannot be fully explained based on the data available; however, we assume this is due to the fact that neither the door nor the window was tight, and there was a draft from the window to the door in the first half of the experiments, and in the opposite direction in the second half.

The amyl acetate concentration has reached a plateau of 0.2 ppm after ca. 27 min in the corners closer to the door, and 0.5 ppm in the corners closer to the window. These concentrations were constant until reaching 40 minutes, and then started falling.

Similar to the results of the laboratory experiments (see section 5.2), these results confirm the low rate of desorption. This contradicts and disproves previous calculation and conclusions [5,6] based on the assumption that all sarin absorbed into the passengers' clothes would desorb in the Prague subway entrance lobby.

The average value of amyl acetate in the room from the four detectors did not exceed 0.5 ppm during the experiment with the exception of the PID 2 detector which recorded the average concentration of 1.0 ppm for 10 min (17:00–26:00 in the experiment).

For sarin, the 10 min exposure at a concentration of 1 ppm would correspond to a 500 µg dose. This would lead to latent intoxication only which is basically symptom-free. Some unspecific central symptoms could occur, e.g., headache or lack of concentration; however, impaired vision (miosis), accommodation, convulsions or breathing difficulties would not be likely to occur. Persons exposed to such doses do not require medical treatment, only medical observation for 24 hours is recommended [14].

However, this poses a question whether a larger number of contaminated people in the enclosed space would represent a more significant risk of secondary air contamination. The presence of two people with contaminated clothes could after 10 min exposure translate into light intoxication and the presence of three or four people a medium intoxication [14], etc. However, even this risk should not be overestimated due to following differences between an experiment and a real setting:

- It is unlikely the exposed person would immediately assume a position in the enclosed space after leaving the contaminated area. Typically, the person has to overcome certain distance while the contaminant is already desorbing during this period
- It is unlikely a larger number of people would be all located in the enclosed space.
- It is unlikely the people with contaminated clothes would gather in an unventilated space.

Therefore, the air contamination by a toxic compound desorbing from the clothes would be lower in a real situation than in the experimental setting.

The second set of experiments was performed in a five times smaller area, in a 2.5×0.9 m room with a ceiling height of 2.4 m (total volume 5.4 m³). This resembles the cabin of a larger car. The room was unventilated, had no windows, and there were closed doors on both longer sides. The test mannequin was placed in the centre of the room. The detectors were located in all four corners at a height of 165 cm. The dependence of amyl acetate concentration on time is shown in Figure 7.
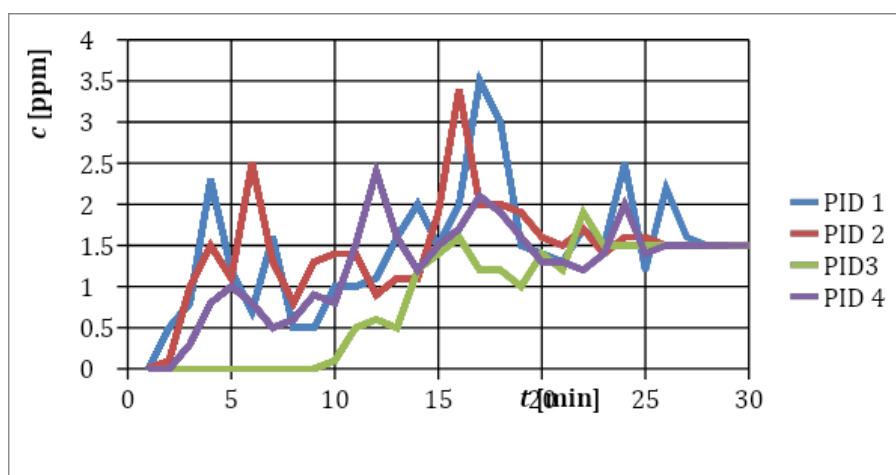

Figure 7. Dependence of amyl acetate concentration desorbed from clothes in a 2.5×0.9 m room on time

The results show that after 3 minutes, the concentration values oscillated around 1.5 ppm. The amyl acetate vapours only reached one of the corners (PID 3) after 10 minutes. The concentration in the entire space has equilibrated within ca. 28 minutes to reach the value of 1.5 ppm. This concentration remained practically constant until 60:00. Somewhat higher concentration was detected for a short period of time in two corners (PID 1 and 2) – this was in the period 15:00–18:00 in the experiment when the concentration on both detectors reached 2.7 ppm.

In case of sarin, 4 minutes' inhalation of air containing 2.7 ppm of the toxin would correspond to a 540 µg dose. As in the previous experiment, this would lead to a latent intoxication which is practically symptom-free.

In principle, four people could squeeze into the area. The short-term concentration could therefore reach 10.8 ppm, and the dose could reach 2,160 μg. Even when accepting all the reservations above, this could lead to a medium intoxication, characterised by central, muscarinic and nicotinic symptoms (with convulsions). First symptoms would occur within 10–15 min. The intoxication would be expected to fully develop within 30–40 min. The intoxicated people would be expected to salivate, perspire, experience breathing difficulties, impaired vision, nausea and vomiting, and colic-like stomach aches. Muscle convulsion and tonic-clonic constrictions of the skeletal muscles could occur. If untreated, the intoxication could lead to impaired breathing, and in the long-term impact on higher nerve functions (memory, concentration, learning) [14].

6. Conclusion

To evaluate the risks of secondary air contamination by sarin desorption from clothes of people residing in contaminated space, we have studied the sorption processes of amyl acetate as a sarin imitator on different textile materials, and its subsequent desorption. The experiments were performed in a laboratory as well as real-life settings. The results show the sorption of amyl acetate vapours from the ambient air into clothes is a rapid process, reaching equilibrium within a minute. The amount of contaminant absorbed increases with increasing ambient concentration. On the contrary, amyl acetate desorption from the textile is a slow process, and the desorption takes tens of minutes. The desorption rate depends on temperature which influences both the maximum concentration above the textile sample as well as the time required to reach the maximum concentration.

In a real-life setting in an open space, the secondary air contamination by desorption from contaminated clothes poses no risk. Even in a closed space, the risk of a secondary contamination is negligible. Dangerous concentration of sarin could only develop by desorption from clothes in case more people wearing contaminated clothes would gather in a very constrained and unventilated space, e.g., in a car with closed windows and ventilation off.

LITERATURE

[1] KOVÁŘÍK, F., OTIPKA, J. *Reakce na teroristický útok s použitím bojové chemické látky na pražské metro. (Závěrečná výzkumná zpráva)* [Reaction to a terrorist attack including a chemical warfare agent on the Prague subway (Final investigation report)] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, 2011, 26 pp.

[2] KOVÁŘÍK, F., ČAPOUN, T., OTIPKA, J. *Plán opatření „Reakce na zjištění teroristického chemického útoku na pražské metro."* (Výzkumná zpráva). [Plan of measures "Reaction to an identified terrorist chemical attach on Prague subway." (Investigation report).] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, 2011, 23 pp.

[3] ČAPOUN, T. *Dekontaminace prostoru a objektů metra. (Výzkumná zpráva).* [Subway area and object decontamination. (Investigation report).] Lázně Bohdaneč: Ministry of Interior –

Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, 2009.

[4] KOVÁŘÍK, F., ČAPOUN, T. *Reakce na teroristický útok s použitím bojové chemicé látky na pražské metro. Řízení a organizace opatření k ochraně obyvatelstva. (Výzkumná zpráva).* [Reaction to a terrorist attack including a chemical warfare agent on Prague subway. Management and organisation of population protection measures. (Investigation report).] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, 2009, 25 pp.

[5] KLOUDA, K. et al. *Příspěvek resortu Státního úřadu pro jadernou bezpečnost k řešení úkolu Ministerstva vnitra – GŘ HZS ČR „Reakce na teroristický útok s použitím bojových otravných látek na pražské metro. [Výzkumná zpráva].* [Contribution of the State Office for Nuclear Safety to the task of the Ministry of Interior – Directorate General of the Fire Rescue Service of the Czeh Republic "Reaction to a terrorist attack including chemical warfare agent on Prague subway. (Investigation report).] Prague: State Office for Nuclear Safety, 2007.

[6] ČAPOUN, T. *Východiska pro zpracování plánu opatření k minimalizaci následků chemického teroristického útoku na pražské metro. (Výzkumná zpráva).* [Prerequisites for the elaboration of a plan of measures for the minimisation of impacts of a terrorist chemical attack on Prague subway. (Investigation report).] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, 2007, 78 pp.

[7] NAVRÁTILOVÁ, L. *Systém ochrany obyvatelstva při zneužití bojových chemických látek ve veřejných objektech. (Disertační práce).* [Population protection system for the event of chemical warfare agent used in public buildings. (Dissertation).] Brno: University of Defence, 2011, 98 pp.

[8] NAVRÁTILOVÁ, L., ČAPOUN, T. *Šíření chemické látky v Tipsport areně Pardubice. (Výzkumná zpráva).* [Distribution of a chemical agent in the Tipsport Arena Stadium in Pardubice. (Investigation report).] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, 2015, 23 pp.

[9] *Typová činnost IZS při společném zásahu. Reakce na chemický útok v metru. (Katalogový soubor typové činnosti STČ-13/IZS).* [Typical activities of the integrated rescue system in a joint intervention. Reaction to a chemical attack on the subway. (File of the typical activities catalogue STČ-13/IZS).] Prague: Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, 2013.

[10]   KLOUDA, K., BEZPALCOVÁ, K., JAŇOUR, Z. *Fyzikální modelování šíření nebezpečných látek na Staroměstském náměstí a v jeho okolí.* [Physical modelling of the distribution of a dangerous substance on the Old Town Square in Prague and its surroundings.] Proceedings of the 1st Dangerous Substances Conference 2006, Ostrava: Fire and Safety Engineering Association, 2006, p. 61.

[11]   KLOUDA, K., DUDÁČEK, A., BEZPALCOVÁ, K. *Úvahy nad zneužitím podomácku připraveného sarinu.* [Considerations on a home-made sarin abuse.] Proceedings of the 15th international conference Fire Safety 2006, Ostrava: Fire and Safety Engineering Association, 2006, p. 169.

[12]   CHUDOVÁ, D., BITALA, P., BRÁTKA, S. *Studium šíření chemické látky v objektu.* [Study of the distribution of a chemical compound in an object.] Proceedings of the 19th international conference Fire Safety 2010. Ostrava, Fire and Safety Engineering Association, 102–105. 02-105. ISBN 978-80-7385-087-6.

[13]   BINGELLI, P. *4th International Symposium Protection Against Chemical Warfare Agents.* Stockholm, June 8 –12, 1992.

[14]   KASSA, J., BAJGAR, J. *Zdravotní následky rozšíření kontaminantu v prostoru metra. (Studie).* [Health impacts of a contaminant distribution in the subway area. (Study).] Hradec Králové: University of Defence, Brno, Faculty of Military Health Sciences, 2007.

[15]   *ProRAE Guardian*. Version 1.6. San Jose: RAE Systems Inc. 2012.

[16]   *ProRAE Suite*. Version 3.32. San Jose: RAE Systems Inc. 2008.

SEPARATION OF POLLUTANTS FROM THE AIR USING A PILOT PLANT CALLED A WET SCRUBBER

Jaroslav VLASAK[*], **Petr HORVAT, Josef KALIVODA, Ondrej KRISTOF, Tomas SVERAK**

*Brno University of Technology, Faculty of Chemistry, Institute of Materials Science, Purkynova 464/118, 612 00 Brno, Czech republic, xcvlasakj@fch.vut.cz

ABSTRACT:

This work deals with the separation of polluting gaseous substances and solid particles from the air, which arise in the combustion of fossil fuels from various industrial sources, but also in the combustion of common fuels in households, or emissions from car exhaust. In all these cases, it is mainly the greenhouse gas problem where CO_2 has the largest share. Furthermore, this work also includes other harmful gases that need to be kept at low levels of concentration in the air. Separation is done using devices called "scrubbers". These devices can deprive the air of both harmful solid particles and harmful gaseous substances. In these devices, a process called chemisorption occurs during which the liquid comes into contact with the gas and, based on appropriately selected chemically reactive substances, solid particles or gaseous substances are trapped in the liquid.

KEYWORDS:

wet scrubber, liquid, gas, carbon dioxide, sodium hydroxide, efficiency, absorption, chemisorption,

1. Introduction

Today, all types of industries must meet strict emission standards for the release of various gaseous substances into the atmosphere. Basic procedures for the removal of gaseous pollutants can be ensured in various ways, such as disposal and their reduction. We must not forget the small solid particles, hereinafter referred to as PM, which are dispersed in the air. These particles are so small that they can be carried by the air. Elevated concentrations of these particles can cause serious health problems. In some cases, it is possible to reduce emissions by adapting the production process by using the right raw material or fuel with a low content of these harmful substances. In practice, the separation of harmful gaseous components from the tail gases is often used by means of a chemical catalytic process or by means of thermal decomposition of the resulting harmless substances. [1,2,3,]

Separation, adsorption, condensation, oxidation, reduction, combustion (thermal oxidation), and catalytic oxidation are most commonly used for the separation or reduction of gaseous industrial pollutants. The choice of the separation process generally depends on the chemical and

physical properties of the separated substance and on the technological conditions. An important aspect is the concentration of pollutants in the carrier gas, its total volume, and temperature, as well as the content of particles. The choice of the method is also influenced by whether the separation device will be operated continuously, discontinuously, with the possibility of using trapped substances, etc. The technology of purification of gaseous exhaust gases is still under development. However, it provides many possibilities for the separation and disposal of gaseous pollutants.[1,4,5]

One of the very effective methods is absorption. Absorption is a diffusion process in which the components of a gaseous mixture are separated due to their different solubilities in a suitable absorption liquid. The absorbent must be sufficiently selective for such a substance which is easily removed and is inert to the other components of the gaseous mixture. The absorbed gas is released by increasing or decreasing the temperature of the absorbent solution, decreasing the pressure above the liquid, or, for example, by decomposition. [1,2,4]

The devices used for absorption must provide the greatest possible interface between the phases. These devices have the most common form. The simplest are full-value cleaning towers. The washing liquid is sprayed against the gas flow and falls to the bottom of the absorber in these cylindrical or prismatic containers. Their advantages are low resistance to gas flow, simple construction, and less sensitivity to particulate matter in the gas during the cleaning process. The disadvantage of these devices is that higher flow rates cause significant abrasion of the washing liquid.[2,6,7]

More complex devices are absorbers containing cartridges, which have a higher efficiency, for example, due to Raschig rings, plastic, or other elements. The absorbent solution flows in a countercurrent or cocurrent arrangement to the gaseous component. The advantage of these absorbers is their high absorption efficiency. The disadvantage is the tendency to clog the filling and consequently strenuous cleaning. [2,6,8,9]

Other types of efficient absorption devices are tray absorbers. They consist of a cylindrical or prismatic shell in which the flowing gas passes from top to bottom through a sieve, a perforated baffle, or a grid located in a multistorey absorption unit. An absorption solution is supplied to these absorption devices, which thus comes into contact with the purified gas. With a suitably selected number of absorption trays, operating parameters and with well-soluble gases, quality results can be achieved. These quality results can be achieved even if the absorption is accompanied by a rapid chemical reaction at a low initial concentration of pollutants. In the case of a gas containing one gaseous component, an efficiency of 92 to 98% can be achieved.

The latest approach to the separation of gaseous substances from air are the so-called gaseous or even liquid "scrubbers", known worldwide as scrubbers. There are many types of scrubbers. The simplest type of scrubber is a shower scrubber, in which the flue gases are brought into contact with a liquid which is sprayed by nozzles in the opposite, direct, or vertical direction. Shower scrubbers have lower acquisition costs than other types of scrubbers. These scrubbers capture particles primarily by impact. A typical solids removal efficiency can be 90% for particles larger than 5 μm, while below 3 μm the efficiency drops to less than 50%. The efficiency of the separation of gaseous substances from air is around 80 – 90%. [2,6,5,10]

Another type of wet scrubber is a scrubber based on the Venturi tube principle. In this case, water is injected under high pressure and sprayed to improve the contact between the gas and liquid phases. The collection efficiency ranges from 70% to 99% for particles larger than 1 μm and is higher than 50% for submicron particles. Increasing the pressure drop increases the collection efficiency, but also increases energy consumption. Venturi scrubbers are therefore more expensive than washing towers in terms of operating costs, but the efficiency of removing fine solids is generally greater. [5,6,7,11]

Multistage scrubbers contain several perforated plates with different geometric shapes to achieve greater mixing of the gas and liquid phases. These washers are highly efficient (greater than 97%) for particles larger than 5 μm in diameter, but inefficiently remove particles smaller than 1 μm. Operating costs are slightly higher than for simple shower washers, but maintenance costs are higher due to clogging by large solid particles.[5,6,12,13]

Fill washers contain material that is structured or randomly arranged and provides a large wetted surface for gas-liquid contact. Filler materials are available in a variety of shapes, each with specific properties, such as surface area, pressure drop, weight, and corrosion resistance. The most interesting are bubble wet scrubber machines in combination with a Venturi scrubber machine, where this connection represents a promising and interesting alternative for collecting nanoparticles.[2,3,4]

2. Absorption and chemisorption

From a physicochemical point of view, absorption can be divided into the following main groups, based on the nature of the interaction between the absorbent and the absorbed substance. [12]

Simple physical process - the most soluble gaseous component is absorbed in the liquid phase, no chemical reaction occurs. The equilibrium concentration of the absorbed component is directly proportional to the partial pressure of the component in the gas phase. An example is the absorption of H_2S and CO_2 into a mixture of dimethyl ether and polyethylene glycol. [14]

Reversible process - there is a reversible (degradable bond) chemical reaction between the sorbed component and the absorbent. The resulting compound, increasing again with increasing temperature, reduces the saturated vapor pressure of the absorbed component. An example is the absorption of CO2 into a monoethanolamine solution. [14]

Irreversible process - there is an irreversible chemical reaction (chemisorption) between the sorbed component and the absorbent, new compounds are formed that prevent rerelease. An example is the sorption of H_2S into a solution of iron chelate, where sulfur is precipitated. [14]

Rate of physical absorption

For an explanation of the absorption rate by using the diffusion film theory, we consider a simple system with a continuous contact phase, wherein the component A is absorbed, which is located in the gas mixture with inert ingredient I assuming an interfacial phase towards the interface, the transmittance through the interphase interfaces, and the subsequent transport into the core of the liquid phase, absorbent L. [15]

Partial permeation coefficient

The partial permeation coefficients of the substance are a factor proportional to the magnitude of the diffusion driving force applicable to the general velocity equations of the substance in phase. They are defined as the quantities of matter in a phase transported by a unit area per unit time by a unit driving force. The unit area is oriented perpendicular to the direction of fabric permeation. [15]

The integral velocity equation of the permeability of a substance in a flowing gas phase with the unidirectional permeability of substance A in the environment of the inert component I can be written in the form [15]:

$$\frac{\dot{n}_A}{S} = k_{gP} \cdot \left(P_{Ag} - P_{Af}\right) \tag{1}$$

where: $\dot{n}_A$ is the mass flow of substance A

         S   is the diffusion area

    k_{gP} is the partial transmittance coefficient of substance A in the environment of inert component I

        P_{Ag} is the partial pressure of the transported component A in the gas phase core P_{Af} is the partial pressure of the transported component A at the interfacial interface

According to the film diffusion theory, at the liquid-gas phase interface, the two media are in equilibrium in each period. Thus, the interfacial interface presents no or only slight resistance to the permeation of the substance. A thin laminar film called a diffusion layer is formed at the interfacial interface, the width of which depends on the turbulence intensity of the respective phase. [15]

Based on this theory, it is possible for the passage of a substance in a laminar film of a flowing gas phase in a unidirectional exchange component A in the environment of an inert component I, to state the relation [15]:

$$\frac{\dot{n}_A}{S} = \frac{D_{gA}}{R \cdot T \cdot z_{gd}} \cdot \left(\frac{P}{P_{I1s}}\right) \cdot \left(P_{Ag} - P_{Af}\right) \tag{2}$$

where: z_{gd} is the width of the diffusion film flowing in the gas phase

         P is the total pressure of the gas phase ($P = P_A + P_I$)

         P_{I1s} is the logarithmic mean of the partial pressure of the inert component I D_{gA} is the diffusion coefficient of component A in the gas phase

         R   is the universal gas constant

         T is the thermodynamic temperature

A comparison of relations (2.1) and (2.2) shows [15]:

$$k_{gP} = \frac{D_{gA}}{R \cdot T \cdot z_{gd}} \cdot \left(\frac{P}{P_{I1s}}\right) \tag{3}$$

The partial permeation coefficient of the substance k_{gP}, expressed by the difference of the transported component A in the gas phase, can also be expressed, for example, by the difference in the concentrations of the transported component. [15]

$$\frac{\dot{n}_A}{S} = k_{gC} \cdot (C_{Ag} - C_{Af}) \tag{4}$$

where: C_{Ag} is the molar concentration of transported component A in the gas phase core

C_{Af} is the molar concentration of the transported component at the interfacial interface

The partial gas permeation coefficient of substance A in k_{gC} is equal to [15]:

$$k_{gC} = \frac{D_{gA}}{z_{gd}} \cdot \left(\frac{\sum_i C_i}{C_{Ils}}\right) \tag{5}$$

where: $\sum_i C_i$ is the sum of the substance concentrations of component A and component I in the gas phase

C_{Ils} is the logarithmic mean of the substance concentration of the inert component I

The integral velocity equation of the flowing liquid phase at the unidirectional permeation of substance A in the environment of the inert component I can be written in the form using the partial coefficient of permeation of the substance [15]:

$$\frac{\dot{n}_A}{S} = k_{lC} \cdot (C_{Af} - C_{Al}) \tag{6}$$

where: C_{Al} is the molar concentration of transported component A in the mainstream liquid phase

C_{Af} is the molar concentration of the transported component A at the interfacial interface, the partial permeation coefficient of substance A in the liquid phase k_{lC} is equal to [15]:

$$k_{lC} = \frac{D_{lA}}{z_{ld}} \cdot \left(\frac{\sum_i C_i}{C_{Ils}}\right) \tag{7}$$

where: D_{lA} is the diffusion coefficient of component A in the liquid phase

z_{ld} is the width of the diffusion film in the flowing liquid phase

Aggregate permeation coefficients

In technical practice, in the description of integral rate equations, the aggregate coefficients of permeation of a substance in a phase are mainly used, because the determination of the values of the partial permeation coefficients of a substance is not easily feasible. [15]

If we express the driving force of diffusion in the liquid phase by the difference of the molar fractions of component A at the interfacial interface and in the core of the liquid phase. If we apply Henry's law, we can have an equation (1) write in the shape of [15]:

$$\frac{\dot{n}_A}{S} = \frac{1}{\left(\frac{1}{k_{gP}} + \frac{H_A}{k_{lx}}\right)} \cdot \left(P_{Ag} - P_{Al}\right) \qquad (8)$$

where: P_{Al} is the partial pressure of the transported component A in the gas phase, to which the concentration of the component corresponds in the liquid phase C_{Al}

phase

k_{lx} is the partial permeation coefficient of substance A in the liquid

k_{gP} is the partial gas permeation coefficient of substance A

H_A is Henry's constant

After introducing the aggregate coefficient of permeation of a substance in a phase, we obtain an integral equation in the form [15]:

$$\frac{\dot{n}_A}{S} = K_P \cdot \left(P_{Ag} - P_{Al}\right) \qquad (9)$$

where: K_P is the cumulative coefficient of permeation of substance A between phases belonging to the integral velocity equation of the steady transition of the substance, with the cumulative driving force expressed by the difference of the partial pressures of the diffusing component

By comparing equations (8 and 9), it is clear that the overall gas phase permeability coefficient of the component A has the form [15]:

$$K_P = \frac{1}{\left(\frac{1}{k_{gP}} + \frac{H_A}{k_{lx}}\right)} \qquad (10)$$

Aggregate permeation coefficients of a substance can be expressed by various stable aggregate driving forces. Expressed by the molar concentrations of component A, we can give the equation (2.9) rewrite into shape [8]:

$$\frac{\dot{n}_A}{S} = K_C \cdot \left(C_{Ag} - C_{Al}\right) \qquad (11)$$

where: K_C is the cumulative coefficient of permeation of the substance between the phases belonging to the integral rate equation of the steady transition of the substance, with the cumulative driving force expressed by the difference of the molar concentrations of the diffusing component. [15]

Passage of the substance through the interfacial interface

In accordance with diffusion film theory, where the interfacial interface does not resist the passage of component A gaseous into the liquid phase, the rate of diffusion of component A from the core in the gas phase toward the interfacial interface can be considered the same as the rate at which component A will diffuse into the nucleus. liquid phase after the transition of the interfacial interface. [15]

It is thus possible to lay equations (1 a 6) as equal and obtain integral integral equations of unidirectional steady transmission of component A, in the environment of inert component [15]:

$$\frac{\dot{n}_A}{S} = k_{gP} \cdot \left(P_{Ag} - P_{Af}\right) = k_{lC} \cdot (C_{Af} - C_{Al}) \tag{12}$$

By adjusting the velocity equation, we get the expression:

$$\left(P_{Ag} - P_{Af}\right) = -\frac{k_{lC}}{k_{gP}} \cdot (C_{Af} - C_{Al}) \tag{13}$$

More used aggregate mass transfer coefficients for gaseous equations 9 and the liquid phase of the equation 11 can be extended by the so-called specific interfacial surface, which is defined as the ratio of the area of the interfacial interface and the effective volume of the production equipment [15]:

$$\frac{\dot{n}_A}{V} = (K_P \cdot a) \cdot \left(P_{Ag} - P_{Al}\right) = \left(\frac{K_P \cdot S}{V}\right) \cdot (P_{Af} - P_{Al}) \tag{14}$$

$$\frac{\dot{n}_A}{V} = (K_C \cdot a) \cdot \left(C_{Ag} - C_{Al}\right) = \left(\frac{K_C \cdot S}{V}\right) \cdot (C_{Ag} - C_{Al}) \tag{15}$$

Since the area of the interfacial interface may vary depending on the operating conditions, the mass transfer coefficients are given directly, numerically, or as an equation for calculating the volumetric aggregate coefficients of the substance between the phases.($K_P \cdot a; K_C \cdot a$). [15]

In general, it can be said that the passage of the substance between the gas and liquid phases will be faster, the greater the difference in the concentration of the substance in the individual phases and at the interfacial interface, which is the farther the system is from the equilibrium state. The rate of absorption of a substance from the gaseous to the liquid phase will decrease with increasing

temperature, since a small increase in the value of the permeation coefficients of the substance in the system will never offset the current decrease in the driving forces of absorption. On the contrary, the increase in pressure has a favorable effect on the rate of absorption of the substance between the phases, since the small decrease in the value of the partial coefficient of permeation of the substance in the gas phase will almost always be exceeded by the current increase of the driving forces of absorption. [15]

Absorption accompanied by a chemical reaction

In a system in which the absorbed component enters into a chemical reaction with one or more components of the liquid absorbent, the highest possible driving force of the diffusion process can be observed. The absorbed component changes its chemical nature in the absorbent and is thus removed from the solution. In general, the concomitant chemical reaction has a beneficial effect on the rate of the reaction. In most cases, the type of absorption solution is chosen which can be easily regenerated if the purpose of the absorption is not to form the final product. [15]

The rate of absorption in a chemical reaction is affected simultaneously by the rate of physical diffusion and the rate of the chemical reaction. The acceleration of absorption due to a chemical reaction is characterized by a reaction factor. It expresses how many times the value of the mass permeation coefficient increases as a result of the concomitant chemical reaction to its value without accompanying reaction, under otherwise the same conditions. [15]

The reaction factor can be defined using the Hatt criterion [16]:

$$H_a = \frac{\sqrt{\left(r \cdot \frac{D_{lA}}{c_{Ag}}\right)}}{K_C} \qquad (16)$$

where: H_a is Hatt's criterion

r is the rate of the reaction relative to the unit volume of the reaction mixture

D_{lA} is the diffusion coefficient of component A in the liquid phase

At low values of Hatt's criterion (of the order $\leq 10^{-2}$), the rate of chemical reaction is significantly less than the rate of physical diffusion. The residence time of the absorbed component in the absorbent solution is not sufficient for its significant proportion to react. [16]

At medium chemical reaction rate and sufficient physical diffusion rate (values of Hatt's order criterion 10^{-1} to 10^0) again, the component penetrates into the entire volume of the liquid, while at the same time reacting for the most part. The rate of absorption is then proportional to the time for which the liquid remains in the space of the absorption device. [16]

At Hatt criteria values of the order of magnitude greater than 100, the rate of the chemical reaction is so high that all the absorbed component is converted to the product of the chemical reaction already near the phase interface. The absorption rate is then proportional to the size of the phase interface area. [16]

3. Materials and methods

Wet scrubber primarily created for CO₂ capture

The basic requirements for the development of experimental equipment were high efficiency of carbon dioxide removal during biogas combustion, low hydraulic resistance, low susceptibility to system clogging, and low operating and acquisition costs. Regarding these requirements, an experimental scrubber was designed, the construction of which is directly based on the previous prototype scrubber developed at the Faculty of Chemistry of the Brno University of Technology.
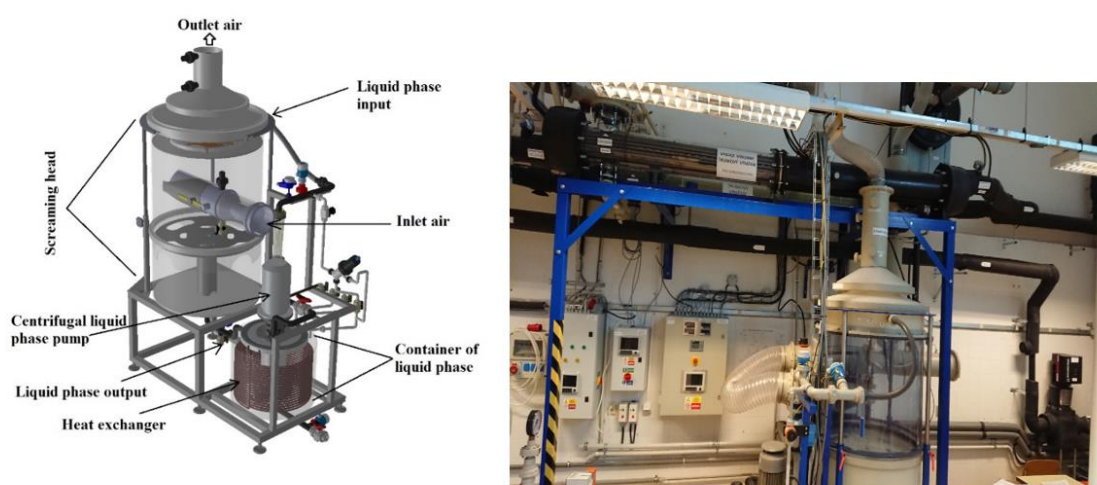

Figure 1 - Wet scrubber scheme and original photo of the scrubber with heat exchanger

The wet scrubber (Figure 1) is designed as a one-stage cleaning system for removing gaseous pollutants. The main part of the device consists of an absorption chamber, into which a spiral nozzle leads, and it is through this nozzle that the liquid phase enters the system through a cone-shaped orifice. The liquid then falls to the bottom of the absorption chamber and flows freely through a pipe into the storage tank. The purified gas enters the absorption chamber tangentially through a deflector, where it is in countercurrent contact with the liquid, and then exits through a set of control orifices to the droplet separator. The gas is pumped into the system by a vacuum fan to reduce the leakage of contaminated air into the laboratory. The liquid is pumped from the storage tank by a centrifugal pump, the liquid is tempered by a spiral tube exchanger in the storage tank, the cooling medium of which is supplied from an external thermostat.

Chemicals:

Water - The source of water was the city's drinking water regulation. The water used to prepare the solution was not analyzed in this work, as the necessary equipment was not available.

Sodium hydroxide - 50% wt. sodium hydroxide with a minimum guaranteed sodium hydroxide concentration of 47.5%, see Chapter E.

Citric acid - citric acid was used for food purposes to clean the circulation circuit of the liquid phase.

*Carbon dioxide* - food grade CO_2 was used to contaminate the air.

Air - air in the laboratory.

Ethylene glycol - ethylene glycol was used as a cooling medium to stabilize the temperature of the scrubbing liquid.

A set of calibration buffers - for properly calibrated pH probes was used scrubber fluid pH calibration buffer from the company Endress + Hauser pH 4.0; 7.0; 10.03.

Chemical absorption of CO_2

The simplest case of chemical absorption of CO_2 is the uptake of NaOH solution according to the following equations. The reaction rate is controlled by the slowest process in the formation of NaHCO3, which reacts almost immediately with Na_2CO_3.

$$CO_2 + NaOH \leftrightarrow NaHCO_3 \qquad\qquad (17)$$

$$CO_2 + 2NaOH \leftrightarrow Na_2CO_3 + 2H_2O \qquad\qquad (18)$$
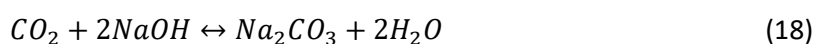
The product of chemisorption is thus CO_3^{2-} or hydrates of Na_2CO_3 in the solid phase. It is therefore necessary to take into account the clogging of the system with carbonate deposits. For simple implementation and low cost of chemisorption of carbon dioxide into sodium hydroxide solution, this reaction was used in the experimental part.

4. Results and discussions

Overview of the calculated input and output parameters of carbon dioxide at the inlet and outlet of the sprinkler head and the efficiency of the scrubber:

The drawn Figure 2 is divided into three graphs. Each graph applies to one concentration of carbon dioxide in the gas phase, and in each graph there are three series of experimental data related to three different pressures of the sodium hydroxide spray solution in the sprinkler head. The graphs have the x-axis drawn in inverse form, ie. The relative pressure, which is plotted on the x-axis, decreases to the right, which means that the vacuum increases as the flow of the gas phase is ensured by the connection to the suction line of the fan. This method of representation was chosen for better readability of experimental data. It can be read from the figure that the differences between the individual repetitions of the experiments are not more than 3 percent.
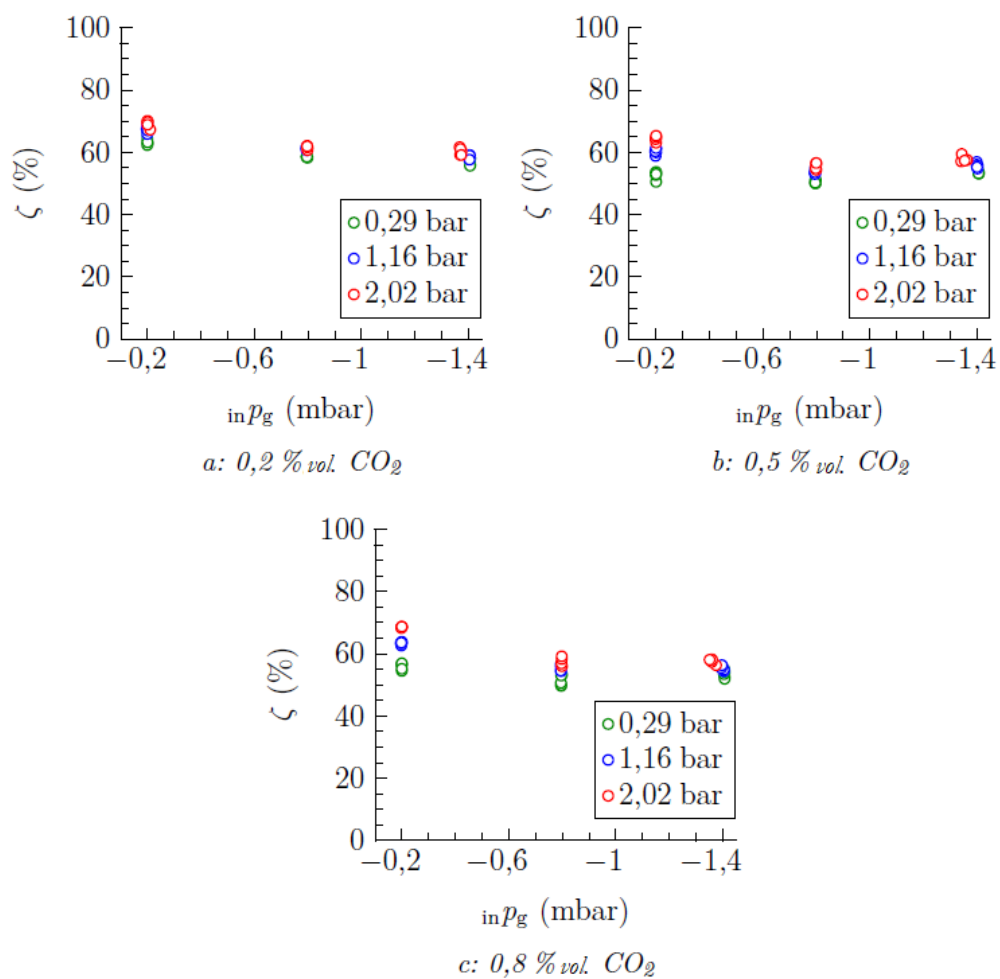
Figure 2 - Dependence of the washing efficiency on the relative air pressure at the inlet to the sprinkler head

The dependence of the washing efficiency on the pressure of the sprayed NaOH is graphically shown in Figure 3, the picture is again divided into three graphs. Each graph plots one concentration of carbon dioxide in the gas phase, and in each graph there are three series of experimental data related to three different relative pressures of contaminated air at the inlet to the sprinkler head.
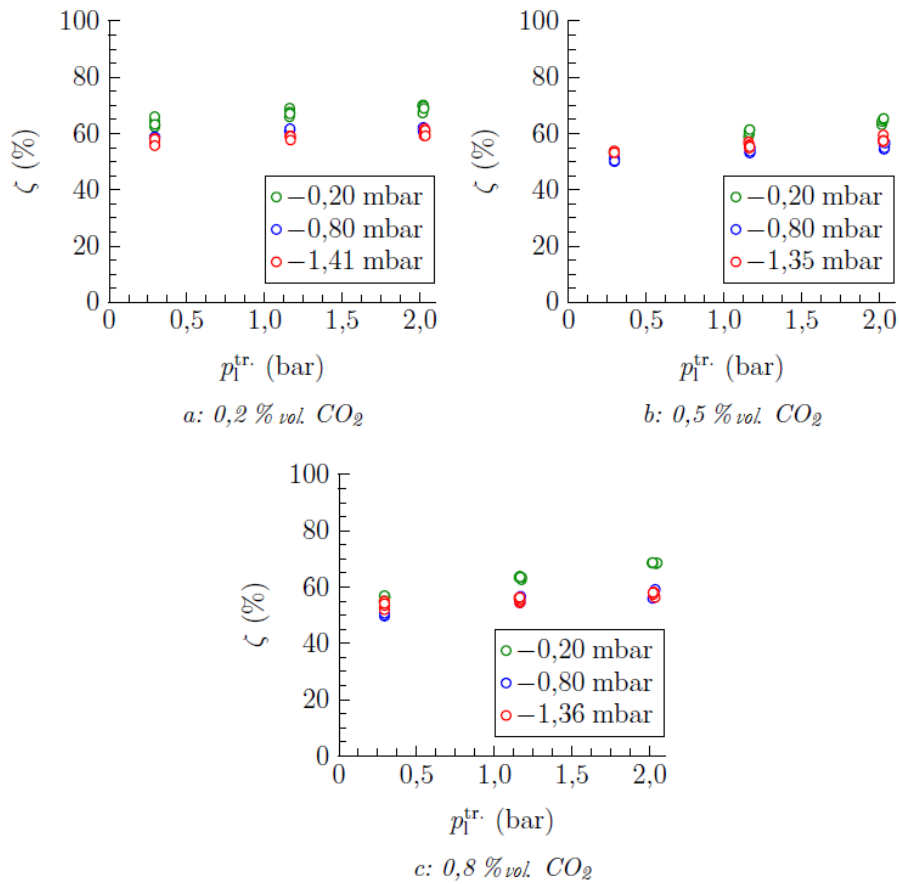
Figure 3 - Dependence of the washing efficiency on the calculated NaOH pressure at the nozzle

The obtained experimental data show that the average efficiency of carbon dioxide removal efficiency in the range of working conditions is in the range of 50.5-69.2%.

The pressure of the contaminated air at the entrance to the sprinkler head, or the air pressure inside the sprinkler head, affects the efficiency of carbon dioxide removal. At a relative pressure of 20.2 mbar (vacuum), the highest carbon dioxide removal efficiency was always achieved, depending on the pressure of the sprayed absorption solution and the carbon dioxide concentration.

Specific values of carbon dioxide removal efficiency range from 52.7-69.2% at a relative pressure of 20.2 mbar (vacuum) of air at the inlet to the sprinkler head. The lowest efficiency values were achieved at a relative pressure of 41.4 mbar (vacuum), where the absorption efficiency ranged from 53.4 to 60.4%, again depending on the pressure of the sprayed absorption solution at the nozzle and the concentration of carbon dioxide. Graphically, the dependence of the efficiency of carbon dioxide absorption on the relative pressure of the air at the entrance to the sprinkler head is shown in Figure 2. This figure shows more clearly how the absorption efficiency shows a decreasing trend with a change in the relative pressure of the contaminated air at the entrance to the sprinkler head. The pressure of the contaminated air is plotted in relative units, a negative sign indicates a lower pressure than atmospheric pressure.

As the vacuum of the inlet air increases, the absorption efficiency decreases, or as the vacuum decreases, the absorption efficiency increases. The most marked increase in absorption efficiency due to the decreasing vacuum from −1.4 mbar to −0.2 mbar is recorded at a pressure of 2.0 bar of sodium hydroxide absorption solution at the nozzle. In this case, the increase in absorption

efficiency averages 8.8%. At a pressure of 0.3 bar of sodium hydroxide absorption solution at the nozzle, the increase in absorption efficiency due to the decreasing vacuum is 3.3%.

The efficiency of carbon dioxide absorption into the sodium hydroxide solution in the scrubber varies with the inlet pressure of the contaminated air and the pressure of the sprayed sodium hydroxide absorption solution at the nozzle. As the pressure decreases (vacuum increases), the solubility of the gas in the liquid decreases, which is in accordance with Henry's law. If the fan could operate at a higher vacuum of contaminated air, which would achieve a higher air volume flow and higher steam load, it can be assumed that the efficiency of carbon dioxide absorption on the scrubber would be even lower than that achieved under experimental conditions in this work.

At a pressure of 2.0 bar of sodium hydroxide solution sprayed at the nozzle, the highest carbon dioxide removal efficiency was achieved, see Figure 3, depending on the inlet pressure of the contaminated air and the carbon dioxide concentration. In particular, the efficiency is in the range of 55.7-69.2% with 2.0 bars of sodium hydroxide solution sprayed on the nozzle. On the contrary, the lowest efficiency was achieved at a pressure of 0.3 bar of the spray solution at the nozzle, namely, 50.5-63.8%, depending on the inlet pressure of the contaminated air and the concentration of carbon dioxide. The most significant increase in absorption efficiency due to the increase in the pressure of the spray liquid at the nozzle from 0.3 bar to 2.0 bar is recorded at a relative inlet pressure of 20.2 mbar (vacuum) of contaminated air at the inlet to the spray head. In this case, the increase in absorption efficiency averages 9.9%. At a relative inlet pressure of −1.4 mbar (vacuum) of contaminated air at the inlet to the sprinkler head, the increase in absorption efficiency is 4.0%. At higher spray pressure, within the nozzle, there is a better dispersion of the liquid into the stream of contaminated air in the sprinkler head. The sprayed absorbent solution fills the sprinkler head space more efficiently, creating a larger interface between the phases. With a larger contact area between the phases, the mass transport between the phases is more efficient and a higher efficiency of CO2 absorption into the sodium hydroxide solution in the pilot plant is achieved. The optimal experimental conditions for the absorption of carbon dioxide into the sodium hydroxide solution at the pilot plant are at a pressure of 2.0 bar of NaOH solution at the nozzle and a relative pressure of 20.2 mbar of contaminated air at the inlet to the sprinkler head.

Under these conditions, 69.2% efficiency of carbon dioxide removal from contaminated air at the plant is achieved.

The relatively low efficiency of the device can be explained by the insufficient coverage of the interior of the spray head with the sprayed absorbent solution. The space between individual drops can be considered as a form of gas pocket or channels through which contaminated air flows between the drops of the sprayed absorbent solution. The geometric shape of these channels or pockets is constantly changing depending on the flow of flying drops through the interior of the sprinkler head. The dimensions of these channels are many times larger than the dimensions of the sprayed drops, which leads to a reduction in the intensity of contact between the two phases. Another type of nozzle, or the addition of other nozzles of the type already used, will lead to a more efficient filling of the interior of the spray head with a stream of flying drops of absorbent. More efficient filling of the internal space of the sprinkler head will reduce the dimensions of these gas channels or pockets, which will guarantee more intensive contact between the two phases and the efficiency of the pilot scrubber will probably increase.

5. Conclusions

It has been shown that the design of the pilot scrubber is suitable for processes with higher vapor and liquid loads in absorption processes in which a rapid chemical reaction occurs between the absorbed component and the absorption solution. The design of the scrubber allows use in cases where contaminated air contains solid impurities or solid particles are formed as a result of a chemical reaction. The device is capable of operating with a final volume of absorbent solution that is circulated in the scrubber. In the case of circulating absorbent solution in a scrubber, it is necessary to prepare the concentration of the reagent in the liquid phase to guarantee a sufficient absorption capacity of the solution and thus to ensure the required efficiency of the device. In our measurements, the scrubber achieved a CO_2 capture efficiency of up to 70% in some places.

Scrubber enhancements are currently being finalized. The main emphasis is on better quality placement of various measuring devices. A heat exchanger with carbide tubes has been added to improve the cooling of both the effluent gas and the trapping liquid.

LITERATURE

[1] ALI, Hassan, Floren PLAZA a Anthony MANN. Flow visualization and modelling of scrubbing liquid flow patterns inside a centrifugal wet scrubber for improved design. *Chemical Engineering Science* [online]. 2017, **173**, 98-109 [cit. 2020-04-14]. DOI: 10.1016/j.ces.2017.06.047. ISSN 00092509. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0009250917304360

[2] ARYA, Sampurna, Joseph SOTTILE a Thomas NOVAK. Development of a flooded-bed scrubber for removing coal dust at a longwall mining section. *Safety Science* [online]. 2018, **110**, 204-213 [cit. 2020-04-14]. DOI: 10.1016/j.ssci.2018.08.003. ISSN 09257535. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0925753518304284

[3] ARYA, Sampurna, Joseph SOTTILE, James P. RIDER, Jay F. COLINET, Thomas NOVAK a Chad WEDDING. Design and experimental evaluation of a flooded-bed dust scrubber integrated into a longwall shearer. *Powder Technology* [online]. 2018, **339**, 487-496 [cit. 2020-04-14]. DOI: 10.1016/j.powtec.2018.07.072. ISSN 00325910. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0032591018305709

[4] BIANCHINI, Augusto, Francesco CENTO, Luca GOLFERA, Marco PELLEGRINI a Cesare SACCANI. Performance analysis of different scrubber systems for removal of particulate emissions from a small size biomass boiler. *Biomass and Bioenergy* [online]. 2016, **92**, 31-39 [cit. 2020-04-14]. DOI: 10.1016/j.biombioe.2016.06.005. ISSN 09619534. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0961953416301970

[5] BIANCHINI, Augusto, Marco PELLEGRINI, Jessica ROSSI a Cesare SACCANI. Theoretical model and preliminary design of an innovative wet scrubber for the separation of fine particulate matter produced by biomass combustion in small size boilers. *Biomass and Bioenergy* [online]. 2018, **116**, 60-71 [cit. 2020-08-20]. DOI: 10.1016/j.biombioe.2018.05.011. ISSN 09619534. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0961953418301235

[6] BORSARI, Vanderlei a João Vicente de ASSUNÇÃO. Ammonia emissions from a light-duty vehicle. *Transportation Research Part D: Transport and Environment* [online]. 2017, **51**, 53-61 [cit. 2020-04-14]. DOI: 10.1016/j.trd.2016.12.008. ISSN 13619209. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1361920916304151

[7] DASHLIBORUN, Amir Motamed, Faïçal LARACHI a Seyed Mohammad TAGHAVI. Gas-liquid mass-transfer behavior of packed-bed scrubbers for floating/offshore CO 2 capture. *Chemical Engineering Journal* [online]. 2018, , 11 [cit. 2020-04-14]. DOI: 10.1016/j.cej.2018.06.025. ISSN 13858947. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1385894718310611

[8] NEVALAINEN, Pauliina, Niko M. KINNUNEN, Anna KIRVESLAHTI, Kauko KALLINEN, Teuvo MAUNULA, Matthew KEENAN a Mika SUVANTO. Formation of NH 3 and N 2 O in a modern natural gas three-way catalyst designed for heavy-duty vehicles: the effects of simulated exhaust gas composition and ageing. *Applied Catalysis A: General* [online]. 2018, **552**, 30-37 [cit. 2020-04-14]. DOI: 10.1016/j.apcata.2017.12.017. ISSN 0926860X. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0926860X17305720

[9] SUN, Kang, Lei TAO, David J. MILLER, et al. *Vehicle Emissions as an Important Urban Ammonia Source in the United States and China* [online]. 2017, **51**(4), 2472-2481 [cit. 2020-04-15]. DOI: 10.1021/acs.est.6b02805. ISSN 0013-936X. Available from: http://pubs.acs.org/doi/10.1021/acs.est.6b02805

[10] VAN DER HEYDEN, Caroline, Peter DEMEYER a Eveline I.P. VOLCKE. Mitigating emissions from pig and poultry housing facilities through air scrubbers and biofilters: State-of-the-art and perspectives. *Biosystems Engineering* [online]. 2015, **134**, 74-93 [cit. 2020-04-14]. DOI: 10.1016/j.biosystemseng.2015.04.002. ISSN 15375110. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1537511015000653

[11] ÜLPRE, H. a I. EAMES. Environmental policy constraints for acidic exhaust gas scrubber discharges from ships. *Marine Pollution Bulletin* [online]. 2014, **88**(1-2), 292-301 [cit. 2020-04-14]. DOI: 10.1016/j.marpolbul.2014.08.027. ISSN 0025326X. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0025326X14005797

[12] JAFARI, Mohammad Javad, Amir Hossein MATIN, Alireza RAHMATI, Mansour Rezazadeh AZARI, Leila OMIDI, Seyed Saeed HOSSEINI a Davood PANAHI. Experimental optimization of a spray tower for ammonia removal. *Atmospheric Pollution Research* [online]. 2018, **9**(4), 783-790 [cit. 2020-04-14]. DOI: 10.1016/j.apr.2018.01.014. ISSN 13091042. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1309104217304798

[13] LI, Qing, Jingkun JIANG, Shuxiao WANG, Krassi RUMCHEV, Ryan MEAD-HUNTER, Lidia MORAWSKA a Jiming HAO. Impacts of household coal and biomass combustion on indoor and ambient air quality in China: Current status and implication. *Science of The Total Environment* [online]. 2017, **576**, 347-361 [cit. 2020-04-14]. DOI: 10.1016/j.scitotenv.2016.10.080. ISSN 00489697. Available from: https://linkinghub.elsevier.com/retrieve/pii/S004896971632246X

[14] KOHL, Arthur L. a Richard NIELSEN. *Gas purification*. 5th ed. Houston, Tex.: Gulf Pub., c1997. ISBN 978-088-4152-200.

[15] DOJČANSKÝ, Ján a Jaroslav LONGAUER. *Chemické inžinierstvo II: difúzne procesy, prestup látky, absorpcia, adsorpcia, destilácia a rektifikácia, extrakcia, úprava vzduchu a chladenie vody, sušenie, kryštalizácia, membránové procesy*. 2. Bratislava: Malé Centrum, 2000. ISBN 80-967-0648-9.

[16] MÍKA, Vladimír a Lubomír NEUŽIL. *Chemické inženýrství II*. 2., přeprac. vyd. Praha: VŠCHT, 1999. ISBN 80-708-0359-2.

DETERMINATION OF CHEMICAL WARFARE AGENTS BY THE GC/MS METHOD USING INTERNAL STANDARDS

TOMÁŠ ČAPOUN*, JANA KRYKORKOVÁ*

*Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, Na Lužci 204, 533 41 Lázně Bohdaneč, Czech Republic, jana.krykorkova@ioolb.izscr.cz ; tomas.capoun@ioolb.izscr.cz

ABSTRACT:

General conditions and requirements for an internal standard useful in the determination of chemical warfare agents (CWAs) by the method of gas chromatography coupled with mass detection (GC/MS) were defined. The determination is based on a GC/MS analysis of a mixture of a CWA with an internal standard, conversion of the TIC chromatogram to a chromatogram extracted at a particular m/z ratio, and calculation of the CWA concentration from the internal standard concentration, response factor and chromatographic peak areas. Available internal standards were identified, and they were verified for seventeen highly toxic and irritating substances. Corresponding response factors were determined as a ratio of slopes of the linear functions of peak area and compound concentration. Linearity, repeatability, and accuracy of the measurements were evaluated. The determination can be performed in the laboratories of the Fire Rescue Service of the Czech Republic (FRS), where no CWA standards are available.

KEYWORDS:

gas chromatograph with mass detector, chemical warfare agent, internal standard, response factor

1. Introduction

Chemical countermeasures of the FRS of the Czech Republic include chemical reconnaissance, detection, identification and determination of CWAs. These activities are performed by special chemical laboratories of the Fire Rescue Service (FRS). The laboratories are most commonly equipped by following gas chromatographs with mass detector (GC/MS): GC/MS 7890A/5975C (Agilent), GC/MS Intuvo 9000/5977B (same make) a EM 640 (Bruker Daltonik). Quantitative analysis is performed using the absolute calibration methods on these chromatographs, but only for analytes where a standard of appropriate purity is available.

The fundamental issue is that pure and certified CWA standards are not available in the Czech Republic. Hence, we had to turn our attention to a procedure based on an internal standard, where a known amount of a substance different than the analyte is added directly to the analysed sample.

The work has focused on the identification of an available standard, which would fulfil the requirement of equal ratio of responses to the CWA, and the internal standard on all GC/MS systems across the FRS laboratories. The goal was to develop a procedure for the FRS chemical laboratories which would not only allow for the determination of the CWAs in solution, but more importantly could be used in the laboratories for rapid and easy determination of the active ingredient in our own samples. These samples are then further used for the calibration of own implemented procedures for the determination of CWAs based on photometric and biochemical methods.

2. Requirements for the application of the internal standard technique

The internal standard method is based on the fact that within a certain concentration range, the ratio of chromatographic peak areas and concentrations is constant. This ratio is called the response or calibration factor [1]:

$$FR = \frac{A_{CWA} \, / \, c_{CWA}}{A_{ISTD} \, / \, c_{ISTD}} = \frac{ACWA.cISTD}{AISTD.cCWA} \qquad\qquad /1/$$

where F_R is the response factor, A_{CWA} the CWA chromatographic peak area, A_{ISTD} internal standard chromatographic peak area, c_{CWA} the CWA concentration in the solution, and c_{ISTD} internal standard concentration in the solution.

The internal standard method has several significant advantages. Unlike the absolute calibration and standard addition methods, pure analyte standard is not required. The absolute calibration and standard addition methods include analysis of two separate samples which often introduces significant errors into the results [1,2]. The same applies to the external standard method.

When using the internal standard method, the response factor value needs to be known in order to arrive at reliable analytical results. Additionally, the concentration range where the analyte and internal standard chromatographic peak area is a linear function must be known, as only then the constant value of the response factor is ensured [1,3]. This explains why many articles focusing on internal standard applications begin by detailed validation, especially testing linearity of the function and the limit of quantification and repeatability of the determination [4–17].

In case the sample is modified before the analysis (extraction, distillation, solvent evaporation, etc.), maximum similarity of chemical and physical characteristics of the analyte and of the internal standard should be ensured [1,3]. Close retention times of the analyte and the internal standard are also required in order to eliminate peak area discrimination at varying temperatures under temperature programmed conditions [1,3]. Additionally, the internal standard must not react or otherwise interact with the analyte, nor may the internal standard be a product of decomposition product or another admixture of the analysed substance.

For use in quantitative GC/MS analysis, the most efficient and reliable solution is the use of such internal standard which is identical or analogous to the analyte and labelled by a stable isotope [1]. Examples include the determination of acrylamide in wheat samples, using $[^{13}C_3]$-acrylamide [18], determination of chrysene in a foil using $[^2H_{12}]$-chrysene [19], determination of rotundone in grapes and wine by the SPME method using $[^2H_5]$-rotundone [2], determination of ethyl carbamate using $[^2H_5]$-ethyl carbamate, also in wine [9]. Additional examples include the use of $[^2H_8]$-dibenzothiophene for

the determination of dibenzothiophene in crude oil, coal and sediment extracts [20], [^{2}H$_7$]-meprobamate for the determination of meprobamate in blood [13], [^{13}C$_{12}$]-triclosane for the determination of triclosane in water [21], or [^{13}C]-dichlorodiphenyltrichloroethane for the determination of dichlorodiphenyltrichloroethane (DDT) in the air [16]. However, internal standards labelled by a stable isotope are also used for samples where compounds other than analogues of the standard are analysed. For the determination of a number of hydrocarbons and other volatile compounds in internal or external air, [^{2}H$_6$]-benzene [11], [^{2}H$_8$]-toluene [22,23] or [^{2}H$_{10}$]-ethylbenzene [24] are used as internal standards. Similarly, some deuterised components of gasoline were used for the determination of aliphatic and aromatic hydrocarbons in water by the SPME method [7]. Additional examples of the internal standard use are [^{2}H$_4$]-1,2-dichloroethane for the determination of 26 halogenated compounds in water [25], [^{2}H$_5$]-3,4-methylenedioxyamphetamine and [^{2}H$_6$]-hydromorphone for the determination of narcotics and their metabolites in biological samples [4], [^{2}H$_{14}$]-trifluarine, [^{2}H$_6$]-transpermethrine and [^{2}H$_4$]-nitrophenol for the determination of 28 pesticides in the air [26]. This makes labelled analyte analogues ideal as internal standards for the determination of compounds by the GC/MS methods; however, their disadvantage is poor availability and high price.

When the internal standard differs from the analyte, compound losses during various phases of sample preparation unavoidably differ [1]. These differences can be efficiently minimised by the use of double internal standards, when two neighbouring representatives from the homologous series are used as internal standards for determination of a specific agent [1,19]. Further examples include determination of tocopherol in plasma, where pentamethylchromanol was used as the internal standard [6], determination of 2,5-di-*tert*-butyl-3-methylphenol in chewing gums using 3,5-di-*tert*-butylphenol [27], determination of furaneol in tomatoes using maltol [28], or determination of carisoprodole in blood using benzyl carbamate [13]. Anisole was used for the determination of various air contaminants [29]. In the analysis of food industry raw materials and products, nonan-5-one was used for the determination of 34 different chemical compounds in honey by the dynamic headspace method [5,28], dinonyl phthalate for the determination of policosanol components extracted from rice bran wax [31], octyl acetate for the determination of 35 volatile compounds in essential oils obtained by steam distillation of lemon tree leaves and bark [32], and crotonic acid for the determination of volatile fatty acids in cheeses after steam distillation [33]. In water analysis, fluorobenzene was used as the internal standard for the determination of trihalomethanes by the GC/MS method using SPME [34], and benzyl benzoate for the determination of phthalates using the same method [35]. In the analysis of industrial products, diphenyl ether was used for the determination of lactide monomer in polylactic materials [36], 1,2-dichlorobenzene was used for the determination volatiles in water–oil emulsion by the SPME method [37], tetrabromodiphenyl ether was used for the analysis of fire retarders on the basis of polybrominated diphenyl ethers, organophosphates and brominated aromatic hydrocarbons [15].

This work focuses on the determination of CWAs by the GC/MS method. Only a few sources discussing internal standards for this purpose could be identified. Dipinacolyl methyl phosphonate was described as an internal standard for the determination of tabun, cyclosarin, VX agent and nitrogen mustard [8]. The TNO laboratory in Rijswijk, the Netherlands, focusing especially on the CWA analysis, uses deuterised sulfur mustard, [^{2}H$_8$]-bis-(2-chloroethyl)sulfide, as internal standard for the determination of sulfur mustard [38].

Extracts of CWAs with aqueous decontamination agents are performed in the Czech FRS laboratories are analysed using the GC/MS method in order to study their decomposition kinetics using following internal standards: tributyl phosphate for the determination of soman, tri-*n*-propylamine for the determination of the VX agent, and di-*n*-propyldisulfide for the determination of sulfur mustard. The use of some non-toxic substances as internal standards for the determination of seven nerve-

paralysing agents using the GC/MS method has been described; the determination were verified on 3 different GC/MS systems [17].

3. Experimental part

3.1 Chemicals

The quantitative analyses procedures by the GC/MS method were developed for the following CWAs: O-ethyl-N,N-dimethylphosphoramidocyanidate (tabun, GA, Military Research Institute, Brno), (RS)-propan-2-yl methylphosphonofluoridate (sarin, GB, VOZ Zemianské Kostoĺany, Slovakia), 3,3-dimethylbutan-2-yl methylphosphonofluoridate (soman, GD, Military Research Institute, Brno), cyclohexyl methylphosphonofluoridate (cyclosarin, GF, Military Research Institute, Brno), ethyl ({2-[bis(propan-2-yl)amino]ethyl}sulfanyl)(methyl)phosphinate (VX agent, VOZ Zemianské Kostoĺany, Slovakia), S-[2-(diethylamino)ethyl] O-ethyl methylphosphonothioate (Edemo, VM agent, VOZ Zemianské Kostoĺany, Slovakia), S-[2-(dimethylamino)ethyl] O-ethyl methylphosphonothioate (Medemo, VOZ Zemianské Kostoĺany, Slovakia), trichloronitromethane (chloropicrin, Military Research Institute, Brno), bis(2-chloroethyl)sulfide (sulfur mustard, HD, VOZ Zemianské Kostoĺany, Slovakia), tris-2-chloroethyl)amine hydrochloride (nitrogen mustard hydrochloride, HN3, VOZ Zemianské Kostoĺany, Slovakia), 2-chlorovinyldichloroarsine (alpha-lewisite, lewisite I) and bis(2-chlorovinyl)chloroarsine (beta-lewisite, lewisit II), technical lewisite preparation (VOZ Zemianské Kostoĺany, Slovakia), diphenylchloriarsine, (Clark I, VOZ Zemianské Kostoĺany, Slovakia), diphenylcyanoarsine (Clark II, VOZ Zemianské Kostoĺany, Slovakia), 10-chloro-5,10-dihydrophenarsazine (adamsite, VOZ Zemianské Kostoĺany, Slovakia), N-[(4-Hydroxy-3-methoxyphenyl)methyl]nonanamide (pseudocapsaicine, PAVA, > 97%, Sigma-Aldrich), ω-chloroacetophenone (CN agent, p. s., Merck), 2-(2-chlorobenzylidene)malononitrile (CS agent, min. 97%, Synthchem, Slovakia), dibenz[b,f]-1,4-oxazepine (CR agent, Chemical Institute of the Comenius University Bratislava, Slovakia).

Purity of the CWAs was determined using following procedures:

- tabun: potentiometric argentometric titration of cyanides by silver nitrate indicated by a silver electrode,
- sarin, soman and cyclosarin: potentiometric lanthanometric titration of fluorides by lanthanum(iii) chloride indicated by fluoride ion selective electrode,
- VX agent, Edemo and Medemo: potentiometric thiomercurimetric titration of thiols by silver nitrate indicated by a sulfide ion selective electrode,
- sulfur mustard, nitrogen mustard, α-lewisit, β-lewisit, chloropicrin, Clark I, Clark II, adamsite, CN agent: potentiometric argentometric titration of chlorides by silver nitrate indicated by silver electrode,
- CS agent: indirect potentiometric argentometric titration of cyanides by silver nitrate indicated by silver electode.

Triethyl phosphate (99.8+%, Sigma-Aldrich), tri-*n*-butyl phosphate (p.s., Merck), heptan-1-ol (>99%, Fluka), di-*n*-hexylamine (p.s., Merck), di-*n*-amyl ether (p.s., Merck), chlorocyclohexane, (p.s., Merck), 1,2-dichlorobenzene (ex.pur., 98%, Acros Organics), acenaphthene (p.s., Merck), 2-naphthyl acetate (BIOSYNTH, Riedel-de Haën), fluorene (p.s, Merck), benzonitrile (p.a., Fluka), ethyl 2,5-

dichlorobenzoate (Tokyo Chemical Industry), and 2,4,5-trichloroaniline (p.s., Merck) were the internal standards used.

Solutions of CWAs and internal standards were prepared in acetone or *n*-hexane (SupraSolv, for GC, Merck).

3.2 Measurement conditions and parameters

The measurements were performed on the following systems at conditions and parameters listed in Table 1: System A – GC/MS 7890A/5975C (Agilent Technologies, Inc., Wilmington, USA); System B – GC/MS Intuvo 9000/5977B same manufacturer; System C – mobile GC/MS EM 640 (Bruker Daltonik GmbH, Bremen, Germany).

Table 1: Measurement conditions and parameters

GC/MS	7890A/5975C	Intuvo 9000/5977B	EM 640
Column	HP-5MS 30 m × 0.25 mm, 0.25 μm	HP-5MS 30 m × 0.25 mm, 0.25 μm	HP-5MS 25 m × 0.35 mm, 1 μm
Carrier Gas	Helium, 147 kPa constant pressure	Helium, 1.2 mL/min constant flow	Nitrogen, 500 hPa constant pressure
Sampler	Agilent GC 80	Agilent 7693A	–
Injection Volume	1 μl	1 μl	1 μl
Inlet	290 °C, splitless mode, purge flow 100 mL/min at 2 min	290 °C, splitless mode, purge flow 100 mL/min at 2 min	230 °C, splitless mode, purge flow 30 mL/min at 1 min
Oven	40 °C (2 min), 10 °C/min to 280 °C (10 min)	40 °C (2 min), 10 °C/min to 280 °C (10 min)	40 °C (2 min), 10 °C/min to 280 °C (10 min)
Detector	Quadrupole MS, EI, scan mode, transfer line 290 °C, scan range 35– 600 amu, solvent delay 6 min	Quadrupole MS, EI, scan mode, transfer line 290 °C, scan range 35– 600 amu, solvent delay 6 min	Quadrupole MS, EI, scan mode, transfer line 280 °C, scan range 50–550 amu, solvent delay 6 min
Evaluation of chromatograms	Agilent ChemStation GC/MSD – Data Analysis, version E.02.02., Agilent Technologies, Inc., 2011	MassHunter Workstation Software, version B.07.00, Agilent Technologies, Inc., 2014	Bruker Data Analysis, version 1.1., Bruker Daltonik GmbH, 2003

Solutions of CWAs and internal standard were mixed in a 1:1 (v/v) ratio, and the mixture was introduced into the injection inlet of the GC/MS system. The linearity range of the chromatographic peak area as a function of the compound concentration was studied in parallel both for the CWA and

the corresponding internal standard. Hence, mixtures of CWAs and standards of same concentration were injected. Triplicate measurements were performed for each concentration of the compound and the standard.

3.3   Chromatogram evaluation

Peaks corresponding to the CWA and the internal standard were identified in the TIC chromatogram recorded in the scan mode. Peak area was obtained by integration using the evaluation software listed in Table 1. Generally, automatic integration was used, only tailing peaks were integrated manually. For further study, EIC chromatograms at particular *m/z* ratio were extracted from the TIC chromatograms; peak areas corresponding to the CWAs and the internal standards were obtained by an identical procedure.

In order to assess the dependency of the chromatographic peak area on concentration of the given compound in the solution, calibration curves were constructed. The linearity range was determined using a statistical software [40] based on the correlation coefficient R and coefficient QC values. Coefficient values of R_{CRIT} 0.99 and QC_{CRIT} 5.00 were considered as critical for the testing. The gradient, *y*-range, and standard deviation of the gradient and range were evaluated by software [39] in the identified linearity range.

In order to assess the accuracy of CWA determination, a series of results from parallel determinations was compared to the known concentration. The t-test was used for statistical evaluation [40], comparing the value of t criteria to the critical value. Based on the results from parallel measurement, the precision of the determination was tested. The method of concentration levels from parallel measurements and calculation of relative standard deviation was selected for the statistical evaluation [40].

3.4   Results and discussion

The primary aim of this work was to find a suitable internal standard, applicable on all GC/MS systems across the FRS chemical laboratories in a universal procedure. The procedure would be used especially for a quick and simple determination of the active ingredient of own CWA preparations which are then used for the calibration of existing determination procedures. This means a binary mixture of the CWA and the internal standard is analysed, and hence neither similarity of chemical properties of the analyte and the internal standard nor close physical characteristics are an issue here as these matter mostly in case of sample preparation before the analysis itself. On the other hand, this requires highly reliable determination which is closely related to the linearity of the chromatographic peak area as a function of the compound concentration.

Assuming a linear function of chromatographic peak area and concentration, the relation can be described by the following equation:

$$A = k \times c + q, \hspace{4cm} /2/$$

where A is the chromatographic peak area, k is the gradient, c is concentration and q is the intercept on the peak area axis. This equation can be combined with the response factor equation /1/:

$$FR = \frac{(kCWA.cCWA + qCWA).cISTD}{(kISTD.cISTD + qISTD).cCWA}$$

/3/

Assuming the intercept on the peak area axis is negligible compared to the product of gradient and concentration, i.e. the linear function of CWA and internal standard peak area and concentration passes through the origin, the response factor equals the ratio of gradients of the two linear functions of CWA and internal standard peak area and concentration:

$$FR = \frac{kCWA}{kISTD}$$

/4/

Use of equation /4/ for the determination of the response factor has two fundamental prerequisites. First, the intercepts on the peak area axis must be negligible compared to the product of gradient and lower limit of the linearity range both for the CWA and for the internal standard. We have set in this work that the intercept must be lower than 10% of the product of gradient and the lowest useful concentration. Second, the response factor can only be applied in the concentration range where the function of CWA and internal standard peak area is linear. Linearity of the functions is therefore a major requirement influencing the reliability of the determination. The determination method was developed for three different GC/MS systems whose linearity ranges significantly differ. Moreover, the linearity range also depends on the analyte. A typical example is illustrated in Figure 1 showing the chromatographic peak area of cyclosarin as function of its concentration in the solution.
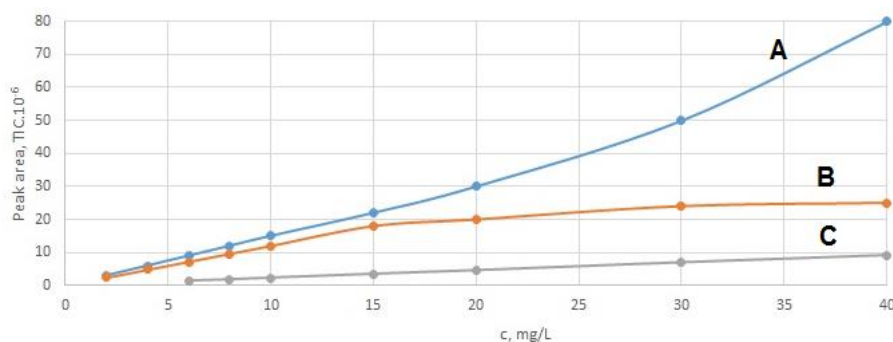

Figure 1: TIC chromatographic peak area of cyclosarin as function of its concentration in the solution, measured at the following GC/MS systems: 7890A/5975C (A), Intuvo 9000/5977B (B), EM 640 (C)

A number of potential compounds were tested during the search for suitable internal standards. Both TIC chromatograms as well as EIC chromatograms extracted for a characteristic ion *m/z* were evaluated. However, the TIC peak area is usually considered in practice [1].

Yet, more precise results can be obtained when reading the peak area of a particular ion [2,4], even though evaluation of the TIC peak area range may be more useful [5]. This is discussed in detail in the publication [4].

It was found out for particular CWAs that determination of the response factors from the TIC chromatograms recorded in the scan mode is not suitable. Only few standards with an identical

response factor across the tested systems could be found; most standards exhibited high differences between the systems. Moreover, a reproducible linear calibration curve could not be constructed at all for some of the compounds even in a narrow concentration range. In some cases, the requirement of negligible intercept on peak area axis versus the product of gradient and concentration was not met.

The use of EIC chromatogram, extracted both for the CWA and the internal standard at a particular *m/z* value, is the optimal procedure for CWAs determination using the internal standard method. This implies identification of an internal standard which exhibits an intense peak corresponding to the same ion as for the CWA mass spectrum. In turn, this allows for:

- Wider linearity range with the EIC chromatograms than with the TIC chromatograms,
- Linear functions of EIC chromatogram peak area and concentration fulfill the requirement of negligible intercept on the *y* axis against the product of gradient and concentration both for the CWA and selected standard,
- Reproducibility of the peak area readings is much higher for the EIC chromatograms than for the TIC chromatograms,
- The EIC chromatogram peak area reading is more robust with respect to compounds with similar retention times than with the use of TIC chromatograms

3.5 Useful internal standards

A large number of internal standard candidates could be identified based on the study of mass spectra during the CWA determination method development [41], and their compliance with requirements listed in section 2 was verified. Out of those, substances, which exhibited identical response factors on all GC/MS systems used in this work, were selected further. Such standard, which exhibits an intense peak corresponding to the same ion present in the CWA mass spectrum, was then selected and verified, along with the concentration range applicable for the analysis. Useful internal standards and corresponding linearity ranges are summarised in Table 2.

A simple determination procedure was developed [41]: solutions of the CWA and the internal standard whose concentration is within the linear range of chromatographic peak area as function of the concentration were prepared, mixed in a 1:1 v/v ratio, and injected into the GC/MS system. Constituents of the mixture were identified as usual, a chromatogram extracted at a particular *m/z* value was generated, integrated and peak areas of the analyte and of the internal standard were recorded.

Table 2

Internal standards, response factors, and linearity ranges for the CWA determination

CWA	Internal standard	m/z	Response factor F_R	GC/MS system	Linearity range, mg/L
Tabun	Heptan-1ol	70	0.50	Agilent 7890A/5975C	5–80
				Agilent Intuvo 9000/5977B	1–20
				Bruker EM 640	20–100
Sarin	Triethyl	99	1.99	Agilent 7890A/5975C	5–80

	phosphate			Agilent Intuvo 9000/5977B	1–20
				Bruker EM 640	10–80
Soman	Triethyl phosphate	99	1.14	Agilent 7890A/5975C	5–40
				Agilent Intuvo 9000/5977B	2–30
				Bruker EM 640	10–80
Cyklosarin	Triethyl phosphate	99	2.14	Agilent 7890A/5975C	10–60
				Agilent Intuvo 9000/5977B	2–25
				Bruker EM 640	10–100
VX Agent	Dihexylamine	114	0.55	Agilent 7890A/5975C	15–40
				Agilent Intuvo 9000/5977B	15–40
				Bruker EM 640	20–100
Edemo	Tributyl phosphate	99	0.26	Agilent 7890A/5975C	10–60
				Agilent Intuvo 9000/5977B	5–25
				Bruker EM 640	20–100
Medemo	Diamyl ether	71	0.21	Agilent 7890A/5975C	20–80
				Agilent Intuvo 9000/5977B	5–25
				Bruker EM 640	30–100
Sulfur mustard	o-Dichlorobenzene	111	0.42	Agilent 7890A/5975C	5–80
				Agilent Intuvo 9000/5977B	5–30
				Bruker EM 640	10–140
Nitrogen mustard HN3	Acenaphthene	154	0.56	Agilent 7890A/5975C	10–80
				Agilent Intuvo 9000/5977B	5–20
				Bruker EM 640	10–80
α-lewisit	2-Naphthyl acetate	145	2.15	Agilent 7890A/5975C	40–100
				Agilent Intuvo 9000/5977B	10–30
				Bruker EM 640	50–120

β-lewisit	2-Naphthyl acetate	145	2.51	Agilent 7890A/5975C	40–100
				Agilent Intuvo 9000/5977B	10–30
				Bruker EM 640	50–120
Chloropicrin	Chlorocyclo-hexane	82	0.52	Agilent 7890A/5975C	2–60
				Agilent Intuvo 9000/5977B	1–40
				Bruker EM 640	10–100
Clark I	Acenaphthene	154	0.44	Agilent 7890A/5975C	5–80
				Agilent Intuvo 9000/5977B	10–30
				Bruker EM 640	20–80
Clark II	Acenaphthene	154	0.51	Agilent 7890A/5975C	5–80
				Agilent Intuvo 9000/5977B	5–30
				Bruker EM 640	20–80
Adamsite	Fluorene	166	0.64	Agilent 7890A/5975C	10–50
				Agilent Intuvo 9000/5977B	5–30
				Bruker EM 640	20–80
PAVA	Acenaphthene	151	0.23	Agilent 7890A/5975C	40–100
				Agilent Intuvo 9000/5977B	20–40
				Bruker EM 640	50–120
CN Agent	Benzonitrile	50	0.37	Agilent 7890A/5975C	5–50
				Agilent Intuvo 9000/5977B	2–20
				Bruker EM 640	10–80
CS Agent	Ethyl 2,5-dichlorobenzoate	190	0.43	Agilent 7890A/5975C	10–30
				Agilent Intuvo 9000/5977B	1–15
				Bruker EM 640	10–60
CR Agent	2,4,5-Tri-chloroaniline	195	1.25	Agilent 7890A/5975C	20–80
				Agilent Intuvo 9000/5977B	2–20
				Bruker EM 640	10–80

3.6 Determination procedure verification

Accuracy and repeatability of the determination procedure was verified. For the verification of accuracy, solutions to be analysed were prepared from different CWA batches than those used for the determination of response factors. Five parallel determinations were performed for each solution. The obtained set of concentration determinations was then evaluated by the statistical software [40] to assess the t parameter which was compared to the critical value.

Repeatability was statistically assessed by the method of concentration levels from parallel measurements and calculation of relative standard deviations [40]. Repeatability was evaluated for the abovementioned sets of five results.

The accuracy and repeatability testing was evaluated in the research report [41]. The evaluations showed that the methods yields accurate results and that the relative standard deviation does not exceed 15% which corresponds to the accuracy of GC/MS-based determination methods. Highest relative repeatability values could be achieved with the Bruker EM 640 system. On the Agilent 7890A/8975C and Agilent Intuvo 900/5977B, relative repeatability for the determination of the CWAs reached the maximum of 7%.

Overall, it can be concluded based on the relative standard deviation obtained that the expanded uncertainty U95, i.e., the range defined by the expansion coefficient k = 2 in which the actual results lies with 95% probability, reaches:

- 14% for the Agilent 7890/5975C and Agilent Intuvo 9000/5977B GC/MS systems,
- 30% for the Bruker EM 640 GC/MS system.

3.7 Reproducibility

The studied determination method could also be verified in a multilaboratory comparison performed as part of the FRS chemical laboratories proficiency testing. The investigation was performed in 2017–2019 with five chemical laboratories equipped with three Agilent 7890A/5975C GC/MS systems, five Agilent Intuvo 9000/5977B systems, and two mobile Bruker EM 640 GC/MS systems.

Accuracy of the results was evaluated using the z-score in accordance with ČSN EN ISO/IEC 17043. Results with absolute value of z-score below or equal to 2.0 were considered as accurate. Overall expanded determination uncertainty of 25%, corresponding to relative standard deviation of 12.5% was chosen for the calculation of the z value.

Evaluation of the multilaboratory comparison is summarised in Table 3. In total, 4.4% of inaccurate results were obtained during the analysis of seven CWAs, and the relative difference of known and determined concentration between the laboratories did not exceed 8%.

Table 3

Evaluation of results from multilaboratory comparison of some CWAs using internal standard GC/MC method

Substance	Sarin	Soman	VX agent	Sulfur mustard	Nitrogen mustard	CN agent	Cr agent
Known concentration, mg/L	24.9	30.0	28.7	53.5	10.2	28.1	10.7

Number of results		24	19	22	18	27	28	20
Accurate/ inaccurate results obtained on the system	7890A/5975C	9/0	8/1	6/0	10/2	9/0	9/0	6/0
	Intuvo 9000/5977B	8/1	6/0	10/2	0/0	11/1	15/0	10/0
	Bruker EM 640	6/0	4/0	4/0	6/0	6/0	4/0	4/0
Total number of accurate results		23	18	20	16	26	28	20
Mean concentration determined by the laboratories, mg/L		23.7	28.7	29.5	54.8	11.0	27.4	11.3
Relative difference of known and determined concentration, %		−4.8	−4.3	+2.8	+2.4	+7.8	−2.5	+5.6
Relative standard deviation between laboratories, %		14.1	9.7	13.3	14.4	11.4	10.9	9.3

4. Conclusion

A gas chromatography with mass dectector (GC/MS) based procedure was studied for the determination of CWAs. Aim of the study was to select suitable internal standard which would fulfill the requirement of identical response ratios to the CWA and internal standard across GC/MS systems used by the chemical laboratories of the FRS in the Czech Republic. We found that determination of response factors from TIC chromatograms recorded in scan mode is not suitable. A standard which would have identical response factor across the systems tested could only be identified in exceptional cases; in fact, the response factor values highly differed in most cases. Optimal procedure was to use EIC chromatogram extracted for a particular ion, extracting both CWA and internal standard peaks at the same *m/z* ratio.

We were able to identify and verify a standard which exhibits a pronounced peak corresponding to the same ion present in the CWA mass spectrum, and verified the useful concentration range for all studied analytes. A simple determination procedure was developed: solutions of the CWA and the internal standard whose concentration is within the linear range of chromatographic peak area as function of the concentration were prepared, mixed in a 1:1 v/v ratio, and injected into the GC/MS system. Constituents of the mixture were identified as usual, a chromatogram extracted at a particular *m/z* value was generated, integrated and peak areas of the analyte and of the internal standard were recorded.

This procedure can be performed on the GC/MS systems used by the FRS chemical laboratories, namely on the Agilent 7890A/5975C, Agilent Intuvo 9000/5977B, and on the Bruker EM 640 GC/MS system. The response factors are identical across these systems.

The determination procedure was verified by accuracy and repeatability testing, and also by reproducibility testing in a multilaboratory comparison. This testing indicated the determination method yields accurate results and that the relative standard deviation does not exceed 15% which corresponds to the precision of GC/MS-based determinations.

During the multilaboratory comparison in which seven CWAs were determined, only 4.4% out of 158 results overall were found inaccurate. Relative difference of known and determined concentration did not exceed 8%.

LITERATURE

[1] ZENKEVICH, I. G., MAKAROV, E. D. and MAKAROVA, I. YU. Quantitative Chromatographic Analysis under Changes in the Composition of Samples in the Course of Sample Preparation: A Modification of the Double Internal Standard Method. *J. Anal. Chem.*, vol. 62, no. 8, pp. 748-755, 2007.

[2] SIEBERT, T. E., WOOD, C., ELSEY, G. M. et al. Determination of Rotundone, the Pepper Aroma Impact Compound, in Grapes and Wine. *J. Agric. Food Chem.*, vol. 56, no. 10, pp. 3745–3748, 2008.

[3] ZENKEVICH, I. G., ESHCHENKO, A. YU. and KLIMOVA, I. O. Characterization of the interlaboratory reproducibility of results in quantitative gas–chromatographic analysis using the internal normalization method. *J. Anal. Chem.,* vol. 60, no. 2, pp. 119–124, 2005.

[4] CHEN, B. G., CHANG, C. D., WANG, C. T. et al. A Novel Approach to Evaluate the Extent and the Effect of Cross-Contribution to the Intensity of Ions Designating the Analyte and the Internal Standard in Quantitative GC–MS Analysis. *Soc. Mass Spectr., v*ol. 19, no. 4, pp. 598–608, 2008.

[5] SORIA, A. C., MARTINEZ-CASTRO, I. and SANZ, J. Some aspects of dynamic headspace analysis of volatile components in honey. *Food Res. Int.*, vol. 41, pp. 838–848, 2008.

[6] VAN PELT, C. K., HAGGARTY, P. and BRENNA, T. Quantitative Subfemtomole Analysis of α-Tocopherol and Deuterated Isotopomers in Plasma Using Tabletop GC/MS/MS. *Anal. Chem.*, vol. 70, no. 20, pp. 4369–4375, 1998.

[7] LANGENFELD, J. J., HAWTHORNE, S. B. and MILLER, D. J. Quantitative Analysis of Fuel-Related Hydrocarbons in Surface Water and Wastewater Samples by Solid-Phase Microextraction. *Anal. Chem.*, vol. 68, no. 1, pp. 144–155, 1996.

[8] IWAI, T., KAKEGAWA, K., AIDA, M. et al. Development of a Gas-Cylinder-Free Plasma Desorption/Ionization System for On-Site Detection of Chemical Warfare Agents. *Anal. Chem.*, vol. 87, no. 11, pp. 5707–5715, 2015.

[9] WU, P., ZHANG, L., SHEN, X., et al. Determination of Ethyl Carbamate in Chinese Yellow Rice Wine by Diatomaceous Earth Extraction and GC/MS Method. *J. AOAC Int.*, vol. 98, no 3, pp. 79–82, 2015.

[10] WAŚ, E., SZCZESNA, T., and RYBAK-CHMIELEWSKA, H., Application of Gas Chromatography with the Mass Detector (GC–MS) Technique for Detection of Beeswax Adulteration with Paraffin. *J. Apicult. Sci.*, vol. 59, no. 1, pp. 143–152, 2015.

[11] NICOARA, S., TONINANDEL, L., TRALDI, P., et al. Determining the Levels of Volatile Organic Pollutants in Urban Air Using a Gas Chromatography-Mass Spectrometry Method. *J. Environ. Publ. Health*, pp. 148–151, 2009.

[12] SMITH, F., AUGSBURGER, M. and VARLET, V. Accuracy Profile Validation of a New Analytical Method for Propane Measurement Using Headspace-Gas Chromatography–Mass Spectrometry. *J. Anal. Toxicol.*, vol. 38, no. 2, pp. 73–79. 2014.

[13] DOWNEY, D., SIMONS, K., OTA, K. et al., Quantitative Analysis of Carisoprodol and Meprobamate in Whole Blood Using Benzylcarbamate and Deuterated Meprobamate as Internal Standards. *J. Anal. Toxicol.*, vol. 33, no. 5, pp. 278–282, 2009.

[14] MÉNDEZ, D., GONZALES, P. G., BOTELLO, A. E., et al. Solid-phase microextraction of *N*-nitrosodimethylamine in beer. *Food Chem.,* vol. 107, no. 3, pp. 1348–1352, 2008.

[15] LAZAROV, B., SVINNEN, R., SPRUYT, M., et al. Air sampling of flame retardants based on the use of mixed-bed sorption tubes – a validation study. *Environ. Sci. Pollution Res.,* vol. 22, no. 22, pp. 18221–18229, 2015.

[16] MARTIN, N., SMITH, P., BROWN, C., et al. Dichlorodiphenyltrichloroethane determination in air by thermal desorption gas chromatography-mass spectrometry. *Pest Manag. Sci.*, vol. 68, no. 10, pp. 1360–1367, 2012.

[17] ČAPOUN, T. and KRYKORKOVÁ, J. Internal Standards for Quantitative Analysis of Chemical Warfare Agents by the GC/MS Method: Nerve Agents. *Journal of Analytical Methods in Chemistry*, vol. 2020, Article ID 8857210, 11 p.

[18] LAGALANTE, A. F. and FELTER, M. A. Silylation of Acrylamide for Analysis by Solid-Phase Microextraction/Gas Chromatography/Ion-Trap Mass Spectrometry. *J. Agric. Food Chem.*, vol. 52, no. 12, pp. 3744–3748, 2004.

[19] HANKIN, M. S. Spatially Resolved Time-of-Flight Mass Spectrometry of Polycyclic Aromatic Hydrocarbons: Quantification Studies. *Anal. Chem.*, vol. 68, no. 18, pp. 3238–3243, 1996.

[20] LI, M., WANG, T. G., SIMONEIT, B. R. T. et al. Qualitative and quantitative analysis of dibenzothiophene, its methylated homologues, and benzonaphthothiophenes in crude oils, coal, and sediment extracts. *J. Chrom. A*, vol. 1233, pp. 126–136, 2012.

[21] WU, J. L., LAM, N. P., MARTENS, D. et al. Triclosan determination in water related to wastewater treatment. *Talanta,* vol. 72, no. 5, pp. 1650–1654, 2007.

[22] WALGRAEVE, C., DEMEESTERE, K., DEWULF, J. et al. Diffusive sampling of 25 volatile organic compounds in indoor air: Uptake rate determination and application in Flemish homes for the elderly. *Atmosph. Environ.*, vol. 45, no. 32, pp. 5828–5836, 2011.

[23] DUC, H. D., VAN LONGENHOVE, H., IZUKUCHWU CHIGBO, S. et al. Exposure to volatile organic compounds: Comparison among different transportation modes. *Atmosph. Environ.*, vol. 94, pp. 53–62, 2014.

[24] WALGRAEVE, C., DEMEESTERE, K., DEWULF, J. et al. Uptake rate behavior of tube-type passive samplers for volatile organic compounds under controlled atmospheric conditions. *Atmosph. Environ.*, vol. 45, no. 32, pp. 5872–5879, 2011.

[25] TOBISZEVSKI, M. and NAMIEŚNIK, J. Determination of chlorinated solvents in industrial water and wastewater by DAI–GC–ECD. *Anal. Bioanal. Chem.,* vol. 399, no. 10, pp. 3565–3572, 2011.

[26] RAEPEL, C., FABRITIUS, M., NIEF, M. et al. Analysis of airborne pesticides from different chemical classes adsorbed on Radiello® Tenax® passive tubes by thermal-desorption-GC/MS. *Environ. Sci. Pollution Res.,* vol. 22, no. 4, pp. 2726–2734, 2015.

[27] WITTER, A. E. The Quantitative Determination of Butylated Hydroxytoluene in Chewing Gum Using GC–MS. *J. Chem. Educ.*, vol. 82, no. 10, p. 1538, 2005.

[28] BUTTERY, R. G., TAKEOKA, G. R., NAIM, M. et al. Analysis of Furaneol in Tomato Using Dynamic Headspace Sampling with Sodium Sulfate. *J. Agric. Food Chem.*, vol. 49, no. 9, pp. 4349–4351, 2001.

[29] BROOKES, B. I. Gas analysis using an internal standard in adsorption tubes. *Analyst*, vol. 104, pp. 698–699, 1979.

[30] SORIA, A. C., MARTINEZ-CASTRO, I. and SANZ, J. Study of the precision in the purge-and-trap–gas chromatography–mass spectrometry analysis of volatile compounds in honey. *J. Chrom. A*, vol. 1216, no. 15, pp. 3300–3304, 2009.

[31] WANG, M. F., LIAN, H. Z., MAO, L. et al., Comparison of Various Extraction Methods for Policosanol from Rice Bran Wax and Establishment of Chromatographic Fingerprint of Policosanol. *J. Agric. Food Chem.*, vol. 55, no. 14, pp. 5552–5558, 2007.

[32] VEKIARI, S. A., PROTOPAPADAKIS, E. F., PAPADOPOULOU, P. et al., Composition and Seasonal Variation of the Essential Oil from Leaves and Peel of a Cretan Lemon Variety. *J. Agric. Food Chem.*, vol. 50, no. 1, pp. 147–153, 2002.

[33] INNOCENTE, N., CORRADINI, S. M. C. and CONTE, L. S. A Rapid Method for the Quantitative Determination of Short-Chain Free Volatile Fatty Acids from Cheese. *J. Agric. Food Chem.*, vol. 48, no. 8, pp. 3321–3323, 2000.

[34] HUANG, S. R. and PALMER, P. T. Improving Student Understanding of Qualitative and Quantitative Analysis via GC/MS using a Rapid SPME-Based Method for Determination of Trihalomethanes in Drinking Water. *J. Chem. Educ.*, vol. 94, no. 8, pp. 1129–1132, 2017.

[35] LIU, H. C., DEN, W., CHAN, S. F. et al. Analysis of trace contamination of phthalate esters in ultrapure water using a modified solid-phase extraction procedure and automated thermal desorption–gas chromatography/mass spectrometry. *J. Chrom. A.*, vol. 1188, no. 2, pp. 286–294, 2008.

[36] BIAN, X., FENG, L., LI, G. et al. Quantification of residual monomer in polylactide by gas chromatographic internal standard method. *Polymer Test.*, vol. 50, pp. 79–82, 2016.

[37] BELTRAN, G., AGUILERA, M. P. and GORDON, M. H. Solid phase microextraction of volatile oxidation compounds in oil-in-water emulsions. *Food Chem.*, vol. 92, no. 3, pp. 401–406, 2005.

[38] KONING, M. C. *Decontamination of CWAs by Hvezda – as summary of results*. Earth, Environmental and Life Sciences, Rijswijk, Netherlands, 2013.

[39] ČAPOUN, T. and KRYKORKOVÁ, J. *Testování účinnosti dekontaminačních látek a směsí v HZS ČR. Sborník přednášek z XXI. Mezinárodní konference o separační chemii a analýze toxických látek.* [Testing the efficiency of decontamination compounds and mixture in the Czech Fire Rescue Service. Proceedings from the XXI. International conference on separation chemistry and toxic compounds analysis.] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, 2015, pp. 38-51. ISBN 978-80-86466-79-8.

[40] *Statistical software EffiValidation.* Version 3.0. EffiChem: Oulehla, Czech Republic, 2002.

[41] ČAPOUN, T. and KRYKORKOVÁ, J. *Stanovení bojových chemických látek metodou GC/MS metodikou vnitřního standardu. (Výzkumná zpráva).* [The determination of chemical weapon agents by the GC/MS method using an internal standard. (Research Report)] Lázně Bohdaneč: Ministry of Interior – Directorate General of the Fire Rescue Service of the Czech Republic, Population Protection Institute, 2019. 61 pp.