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APPLICATION OF THE CHROMATOGRAPHIC RETENTION INDEX SYSTEM FOR THE ESTIMATION OF THE CALIBRATION CONSTANTS OF PERMEATION PASSIVE SAMPLERS WITH PDMS MEMBRANES

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Abstract

The paper presents the results of research on the calibration of permeation passive samplers equipped with polydimethylsiloxane (PDMS) membranes using the physico-chemical properties of the analytes. Strong correlations were found between the calibration constants of the samplers and the linear temperature-programmed retention indices of the analytes determined on columns coated with pure PDMS (r^2 = 0.914). These correlations make it possible to estimate the calibration constants for unidentified analytes, which is impossible when using conventional procedures. This, in turn, enables the deployment of permeation passive samplers in the same way in which active samplers are deployed. The reproducibility of the calibration constants determined in different laboratories and retention indices determined using different chromatographic systems was very good, indicating that the calibration constants estimated using this approach should be reproducible as well. The approach proposed should lead to more widespread use of permeation passive samplers.

Key words: indoor air quality, permeation passive sampling, calibration constants, linear temperature-programmed retention index

1. Introduction

The concern about indoor air quality IAQ is on the rise recently as a result of the increasing awareness of the possible harmful effects of the numerous chemicals present in the air. One of the positive outcomes of this is the shift towards greener technologies, limiting or eliminating the use of organic solvents during manufacturing of various products, thus minimizing the emission of these compounds into the air during their use. In spite of the significant progress in this area, total elimination of questionable organic chemicals from manufacturing is practically unachievable. Consequently, it is very important to monitor the quality of indoor air, especially considering that humans spend about 80% of their lives indoors [1,2,3]. Conventional methods used for the monitoring of IAQ are based on the use of sorption tubes or evacuated canisters. They require relatively skilled personnel and/or a significant up-front investment in the equipment. As a result, large-scale deployment of IAQ monitoring is usually prohibitively expensive, therefore seldom used. Thus, there is a need for alternative methods for IAQ monitoring, which would be able to collect representative, integrated air samples and yield information on the exposure of the inhabitants to harmful organic chemicals. One such method is passive sampling.

Passive samplers collect samples of gaseous pollutants from the atmosphere at a rate controlled by physical processes such as permeation through a membrane (in the case of permeation passive samplers); they do not involve active movements of the air through the samplers. Diffusional mass transfer across a membrane can be described by Fick's first low of diffusion [4]. The amount, (M), of the analyte transported by permeation in time (t) when the concentration gradient is linear and the collection efficiency is 100 % can be described by the following relationship [4]:

$$M = U \cdot t = \frac{SA}{L_M} c_0 \cdot a \cdot t \qquad 1)$$

where: U is the transport rate (mol/s), S is the permeability coefficient of a given analyte (cm^2/min), A is the cross section of the diffusion path (cm^2), L_M is membrane thickness (cm), c_0 (kg /L) is the analyte concentration near the outer surface of the membrane, and a = RT/MW, where R is gas constant (atm L/mol•K), T is temperature (K) and MW is the molecular weight of the analyte (kg/mol). At constant temperature, S, A, a and L_M are constant, and can be replaced by:

$$\frac{1}{k} = \frac{SAa}{L_M} \qquad 2)$$

and consequently:

$$C_0 = \frac{M \cdot k}{t} \qquad 3)$$

To relate the amount of analyte collected by a passive sampler to its time-weighted average (TWA) concentration in the air, the calibration constant **k** of the sampler for a given analyte must be known. In addition, all parameters affecting the uncertainty of the final result should be defined. The uncertainty of determination of the analyte concentration by passive samplers is affected mainly by the sampling rate uncertainty. Environmental parameters, such as temperature, humidity and air velocity, might also play a significant role. Uncertainty affects method limit of detection, which is a function of the sampling rate (calibration constant), the sampling time, the blank values of the unexposed samplers, the reproducibility, the sensitivity of the applied detector, and finally, the selectivity of the column used for GC analysis.

Permeation passive samplers compare very favourably to diffusive passive samplers. They are less sensitive to air currents. With an appropriate membrane, they are immune to problems related to humidity [5]. Finally, the sampling rate of permeation passive samplers

depends very weakly on temperature [6]. Parameters affecting the determination of the analyte concentration by permeation passive samplers are illustrated as a Cause-and-Effect diagram in Figure 1 [7,8].

Taking all of the above into consideration, permeation passive samplers compare favourably not only to “classical” active methods of air sampling, but also to diffusive passive samplers. The biggest obstacle in a wider acceptance of permeation passive samplers thus far has been the need to calibrate the samplers for each individual analyte of interest. The significance of this issue is hard to overestimate. For instance, over 500 different chemicals have been identified in indoor air; about 350 of them fall within the category of volatile organic compounds (VOCs) [9,10,11]. Consequently, it would be very difficult, if not impossible, to use permeation passive samplers to monitor VOCs in indoor air, as the experimental determination of the individual calibration constants **k** of permeation passive samplers is time-consuming and costly. In fact, the need to calibrate permeation passive samplers for each individual target compound seems to be the single biggest obstacle in the widespread adoption of these samplers for air sampling.

The approach proposed in our previous paper [12] vastly simplified the calibration procedure and eliminated this fundamental limitation by making it possible to estimate the values of the calibration constants from the physico-chemical properties of the analytes. Strong correlations were found between the calibration constants of the samplers and the number of carbon atoms among families of compounds (r^2 ranging from 0.851 for alcohols to 0.999 for aromatic hydrocarbons), the molecular weights of the compounds ($r^2 = 0.874$), their boiling points ($r^2 = 0.891$) and linear temperature-programmed retention indices ($r^2 = 0.922$). The last correlation makes it possible to estimate the calibration constants even if the identity of a compound is unknown [12]. This allows the permeation passive samplers to be deployed in the same way in which active sampling is deployed.

Retention index (*I*) is a measure of the retentiveness of a compound relative to straight chain hydrocarbons under given set of chromatographic conditions. In 1958, Kovats proposed the use of the homologous series of n-alkanes as retention markers [13]. The original Kovats retention index system was applicable to isothermal separations only. Since most separations in GC are carried out these days under temperature-programmed conditions, the linear temperature-programmed retention index system (LTPRI) proposed by Van den Dool and Kratz [14] is used much more often today. LTPRI of a substance is calculated according to the following formula:

$$\mathrm{LTPRI} = 100 \cdot \left[\frac{\mathrm{t(A)} - \mathrm{t(n)}}{\mathrm{t(n+1)} - \mathrm{t(n)}} + \mathrm{n} \right] \qquad 4)$$

where t(A) is the retention time of the analyte, t(n) is the retention time of the n-alkane eluting directly before the analyte, t(n+1) is the retention time of the n-alkane eluting directly after the analyte and n is the number of carbon atoms in the n-alkane eluting directly before the analyte. Because of the great effort required when measuring the retention index (*I*) of a large number of compounds, a variety of methods have been proposed [15] to estimate or predict the retention index (*I)*, either directly from the physico-chemical properties (first approximation can be made using the empirical formula of the analyte [16]), or from quantitative structure–property relationship (QSPR) models. Complex equations with up to 20 molecular descriptors including physicochemical, geometrical, and electronic parameters are used for such QSPR and QSRR (quantitative structure–retention relationship) calculations [17,18].

This paper describes the continuation of our previous research [12] on the estimation of calibration constants of permeation passive samplers based on the physico-chemical properties of the analytes. The focus of this contribution is the relationship between the calibration constants **k** and LTPRI, since this relationship bears the most promise in

promoting a wider acceptance of permeation passive samplers by enabling the estimation of **k** values for unknown analytes.

2. Experimental

2.1. Materials and reagents

Polydimethylsiloxane membrane of 50 µm thickness (SSP-M100) was from Specialty Silicone Products (New York, USA). Active carbon (40-60 mesh, specific surface area 1500 m^2/g) was from Zakład Suchej Destylacji Drewna (Hajnówka, Poland). Standards in CS_2 were prepared freshly before use. The stock solution contained selected n-alkanes, aromatic hydrocarbons, alcohols and esters.

2.2. Generation of standard gas mixtures

Standard gas mixtures were generated dynamically using permeation sources. Separate mixtures were generated for each compound class**.** The details of the standard gas mixture generator were described previously [19,20].

2.3. Calibration of Permeation Passive Samplers

The design of the permeation passive samplers used in the study was described in detail previously [12,19]. The samplers were of badge type. The badge design was dictated by the need to have large surface area of the membrane in order to achieve high sampling rates. Six samplers were simultaneously exposed to the standard gas mixtures in the calibration chamber. The exposure time varied from one to twenty one days. Each experiment was repeated at least four times. The calibration constants (**k**) were calculated based on the amounts of the analytes trapped by the sorbent, their concentrations in the standard gas mixture and the exposure time. The details of the analytical conditions for the calibration of permeation passive samplers are given in Table 1.

2.4. Gas chromatographic analysis for the determination of calibration constants **k**

An HP 6890 gas chromatograph (Hewlett-Packard) equipped with an FID detector and a split/splitless injector was used to determine the amounts of the analytes trapped by the permeation passive samplers. Following each experiment, the carbon sorbent was transferred into PTFE-capped 2 mL glass vials. The analytes were liberated from the sorbent by desorption with CS_2. The results of gas chromatographic determination were corrected for the blank value. The details of analyte desorption and GC analysis conditions are given in Table 1.

2.5. Determination of Linear Temperature Programmed Retention Indices (LTPRI)

Retention times of the analytes required to calculate their retention indices were determined using HP 6890 and HP 5890 gas chromatographs (from Agilent Technologies and Hewlett Packard, respectively) equipped with FID and MSD detectors, respectively. Retention indices were determined for five capillary columns coated with polydimethylsiloxane (PDMS) stationary phases of different film thicknesses. Linear oven temperature programs were used in all cases. The detailed GC conditions used in the determination of LTPRI are given in Table 2.

2.6.Indoor air measurements

The indoor air sample was collected in the living room of an apartment located in a two-storey building. The apartment was selected randomly. No complaints about indoor air quality were recorded. In addition, no restrictions were placed on indoor activities of the inhabitants during this study. Permeation passive sampler was placed centrally at a height of the breathing zone of the inhabitants (ca. 1.5 m above the floor level). Exposure time was 5 weeks.

Active sampling was based on sorption tubes filled with Tenax TA. The sample was collected by drawing air through the tube using a gas-tight syringe. The volume of the sample was 0.5 L, and the sampling time was 1 h. The final determination was carried out using a gas chromatograph equipped with a flame ionization detector, characterized by a nearly uniform response to organic compounds. For unknown analytes, response factors for toluene were used to estimate their concentrations.

3. Results and Discussion

The aim of this study was to simplify the calibration of permeation passive samplers by making it possible to estimate the value of the calibration constant **k** for any compound without the need for conventional calibration using standard gas mixtures. In our previous study [12], we have established that calibration constants **k** of permeation passive samplers equipped with PDMS membranes can be correlated with selected physico-chemical properties of the analytes, including the retention index. Other researchers utilized retention indices to estimate the values of the partition coefficients of organic compounds between air and PDMS (e.g. [21,22,23,24,25]).

While our results were promising, question remained how universal were the correlations found. We considered it particularly important to establish whether the calibration constants of the permeation passive samplers and their estimates obtained on the basis of LTPRI of the analytes could be reproduced in a different laboratory, using a different apparatus for calibration and a host of different GC conditions for LTPRI determination. To answer these questions, some of the experiments performed originally at the University of Waterloo were repeated at the Gdańsk University of Technology, and new experiments were added to better characterize the method.

To accomplish the goals of the study, the samplers were first re-calibrated using a different standard gas generator [19,20] The detailed conditions for the calibration experiments are summarized in Table 1. Calibration constants were determined for 20 volatile organics belonging to four homologous series (n-alkanes, aromatics, n-alcohols, and acetic acid esters of n-alcohols). The results are listed in Table 3. The calibration constants **k** were determined by plotting the relationships between the amounts of the analytes trapped and the exposure times for constant analyte concentrations in the calibration mixture. The reciprocals of the slopes of those lines gave the **k** values. Table 3 also includes the statistical parameters of those lines (standard deviations of the regression coefficients of the slope and the intercept (s_b and s_a) and the linear correlation coefficients (r). In addition, the standard deviations of the calibration constants (s_k) determined on the basis of the equations of the regression lines and values of the LTPRIs determined under the same conditions under which the CS_2 extracts were analyzed are also summarized in Table 3.

Table 4 presents a comparison of the calibration constants **k** determined in the two laboratories involved in the study (Department of Chemistry, University of Waterloo, Canada [12] and Department of Analytical Chemistry, Gdańsk University of Technology, Poland). The differences between the respective values were generally small. Statistical analysis using Student's *t*-test at α= 0.05 significance level and for $f=n_1+n_2-2$ degrees of freedom demonstrated that the differences were statistically insignificant in all cases ($t < t_{cr}$).

The calibration constants determined were used to re-examine the relationships between **k** and LTPRI for the individual compound classes and for all analytes. In the case of the alcohols and esters, the **k** values determined both in this study and found previously at the Department of Chemistry, University of Waterloo, Canada [12] were taken into account when plotting the relationships between **k** and LTPRI. The results are presented in Figure 2 and Figure 3. For each data point, the 95 % confidence interval of the calibration constant ($\mathbf{k}\pm ts_k$) is indicated (see Table 3). In addition, the confidence band [26,27] of the calculated calibration constants is plotted in each case to help visualize the estimated range of values that an unknown compound might have. It should be emphasized that for all the relationship

obtained, none of the 30 compounds included in the study fell outside the 95 % confidence band.

The relationships proved to be linear in all cases. The regression equations obtained, the correlation coefficients, the standard deviations of the regression coefficients and the standard deviations of the residuals ($s_{x,y}$) for all classes of compounds studied are listed in Table 5. In general, marginally higher correlation coefficients were obtained for homologous series of compounds than for broader compound classes, but the differences were not significant. Overall, the results confirmed the correlation between the calibration constants of passive samplers equipped with PDMS membranes and LTPRI of the analytes on PDMS-coated GC columns. This correlation makes it possible to estimate the calibration constant of any analyte eluting within the LTPRI range examined (500 to 1100) from the regression line obtained for all analytes or (preferably) the regression line for the class of compounds to which the analyte belongs. The latter requires the use of mass spectrometry for analyte identification.

Table 6 presents a comparison of the calibration constants determined experimentally with the values estimated using the correlations found. In all cases, the estimates obtained using the correlations for the individual compound classes were within 18% of the experimental values, with the average deviation of 5% (the modulus of the deviations was taken into account). When the correlation including all analytes examined was used, the estimates were within 34% of the experimental value, with the average deviation (modulus) of 10%. In the latter case, the estimated **k** values were generally lower than the experimental values for aliphatic hydrocarbons, aromatic hydrocarbons and most alcohols, and higher than the experimental values for esters. The differences between the experimental and the estimated values of the calibration constants were lower than 15% for 29 of the 30 compounds studied when the correlations for individual compound classes were used, and for 24 of the 30 compounds when the correlation including all analytes was used. These numbers would be acceptable in most fieldwork, where uncertainty of the measurements is usually higher than that. Thus, the data indicate that LTPRI of a compound on a PDMS-coated GC column is a useful predictor of the calibration constant of this compound for permeation passive samplers equipped with PDMS membranes.

One way to determine whether the approach proposed might affect the accuracy of the determination of analyte concentration in the air is to examine the insignificance of the difference between the experimental and the estimated calibration constant. The following relationship was used for this purpose [28]:

$$\left|k_{reg} - k_{exp}\right| < 2\sqrt{u(k_{reg})^2 + u(k_{exp})^2} \qquad 5)$$

where $\mathbf{k}_{exp}$ is the experimentally determined calibration constant, $\mathbf{k}_{reg}$ is the calibration constant estimated from the regression equation, $u(\mathbf{k}_{exp})$ is the standard uncertainty of the determination of the experimental calibration constant $\mathbf{k}_{exp}$, and $u(\mathbf{k}_{reg})$ is the standard uncertainty of the determination of the estimated calibration constant $\mathbf{k}_{reg}$. When the above condition is fulfilled, the difference between the two values is smaller than the expanded uncertainty of determination of the two values, therefore it is deemed insignificant. The results of the test are summarized in Table 6. For all compounds studied, the condition defined by equation 5 was fulfilled, which means that the differences between the experimental and the estimated **k** values were statistically insignificant at 95% probability level.

Figure 4 presents a comparison of the calibration constants obtained with the three methods (direct experimental determination, estimation from the regression line obtained for a given class of compounds and estimation from the regression line obtained for all analytes), including their expanded uncertainties (U). It is clear when examining this Figure that the **k** values obtained by any of the three methods fall within the expanded uncertainty ranges of the remaining methods.

The insignificance of the difference between $\mathbf{k}_{exp}$ and $\mathbf{k}_{reg}$ was also examined using the linear regression method [29,30,31]. Figure 5 presents the plot of $\mathbf{k}_{reg}$ vs. $\mathbf{k}_{exp}$. For the difference between the two values to be insignificant, the dependence should be linear (y = bx + a), the line should pass through the origin of the coordinate system, and the slope should be close to unity. In other words, the parameters used for the validation of the proposed approach to the estimation of the calibration constants of permeation passive samplers are the slope **b** and the intercept **a**. It was found that at the probability level P = 95% and for f = n – 2 = 28 degrees of freedom, all of the above conditions were fulfilled ($t_{\mathbf{b}calc}$ ((1-b)/s_b) = 1.767 $\leq$ t_{cr} = 2.052; $t_{\mathbf{a}\ calc}$ (a-0)/s_a) = 1.685 $\leq$ t_{cr} = 2.052). Thus, the slope **b** and the intercept **a** were not significantly different from the expected values of β_0=1 for the slope and α_0=0 for the intercept, which means that the differences between the estimated and the experimental calibration constants were statistically insignificant. It should be pointed out, however, that this approach does not take into account the uncertainties of determination of the individual values – only the overall uncertainty is considered. In general, the examination of the significance of the differences between the experimental and the estimated calibration constants indicates that the results of air analysis with the use of permeation passive samplers [32] should not differ with respect to accuracy irrespectively of the method of determination of the calibration constants of the samplers (experimentally determined or estimated from the LTPRI).

The isothermal Kovats retention index (*I*) is a purely thermodynamic parameter, as it depends solely on solute-solvent bulk interactions [33]. Parameters like carrier gas viscosity, column geometry, column inlet and outlet pressure or phase ratio do not affect the retention index (*I*). LTPRI, on the other hand, depends to some extent on fluid dynamic parameters, therefore it cannot be directly converted to *I*. This has led to criticism of the attempts to correlate LTPRI to thermodynamic parameters like partition coefficients [33]. We found it crucial, therefore, to evaluate how different conditions of LTPRI determination might affect the estimated values of the calibration constants of the passive samplers under study. To accomplish this goal, LTPRI were determined using open tubular columns coated with PDMS of different film thickness under different chromatographic conditions. The columns were supplied by different manufactures. In addition, several different gas chromatographic systems were used to maximally differentiate the conditions of retention index determination. The details of the experiments (columns, carrier gas flow rates, initial temperature and temperature programs) were summarized in Table 2.

The repeatability and reproducibility of the LTPRI determined for selected organic compounds are presented in Table 7. In addition, Table 8 presents a comparison of the LTPRI values determined in our experiments with available literature data [34,35,36,37,38,39,40,41]. In general, the reproducibility of LTPRI obtained under very different conditions was excellent, with % RSD exceeding 1% for only one compound (methyl acetate). The differences between LTPRI found in this study and literature data were less than 1% in 29 out of 38 cases. The biggest differences (between 3% and 8.5%) were observed in some cases for n-alcohols. It should be pointed out, however, that for those same compounds other sources quoted LTPRI values within 1% of the values found in this study. Overall, the excellent repeatability and reproducibility of the LTPRI values indicates that the calibration constants **k** of permeation passive samplers equipped with PDMS membranes can be easily and reliably estimated for any unknown analyte in any laboratory dealing with air quality analysis. While in essence almost any set of chromatographic conditions could be used to determine the LTPRI of unknown analytes, it is clearly advisable to use the same set of conditions when analyzing the samples and determining the LTPRI values.

The proposed approach to the estimation of the calibration constants of PDMS-equipped permeation passive samplers was tested in the analysis of a real sample of indoor air collected in an apartment in the city of Gdansk (Poland). For a comparison, samples of air were collected in parallel using active sampling with Tenax-TA packed sorption tubes. An

example of a chromatogram obtained for a sample collected by the passive sampler is presented in Figure 6. Table 9 shows a comparison of the results obtained by the two techniques, together with the retention times of the analytes, their LTPRI and the estimated calibration constants. In general, the agreement with a few exceptions was very good. The differences between the results could be caused by many factors, including the different type of sample collected (spot vs. time-weighted average), artifacts caused by thermal desorption of Tenax, uncertainties of the calibration constant values, etc.

4. Conclusions

The excellent reproducibility of the linear temperature-programmed retention indices determined under varying chromatographic conditions (RSD < 1.5 % for all organic compounds examined) and the strong correlation found between the calibration constants (**k**) of permeation passive samplers equipped with PDMS membranes and LTPRI determined on PDMS-coated columns permit the conclusion that the calibration constants for compounds, for which experimental determination of **k** has not been carried out, can be estimated easily and reliably on the basis of the regression equations obtained. Thus, the correlation between LTPRI and the calibration constant of a permeation passive sampler makes it possible to use the latter as efficiently as sorption tubes, while preserving all the advantages of passive sampling, including low cost, simplicity, ease of deployment, etc. The concentrations of unidentified analytes collected by the passive samplers can be estimated with the use of detectors with known, uniform response factors for organic compounds (e.g. FID or atomic emission detector - AED). When the analyte identity is known, the accuracy of the result can be further improved by calibrating the response of the detector towards this particular compound. This step would not differ from what would be done for a sample collected by any active method. Thus, the correlation between LTPRI and the calibration constant of a permeation passive sampler makes it possible to use the latter as efficiently as sorption tubes.

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References

[1] M.A. Berry, Population risk assessment for indoor air pollutants. In: Pilot study on indoor quality. The implications of indoor air quality for modern society. Report on a Meeting Held in Erice, Italy, CCMS REPORT 183 (1989) 77.

[2] T.F. Cooke, Rev. Environ. Health 9 (1991) 137.

[3] B.O. Books, G.M. Utter, J.A. DeBroy, R.D. Schimke, Clin. Toxicol. 29 (1991) 315.

[4] T. Górecki, J. Namieśnik, TrAC-Trend Anal. Chem., 21 (2002) 276

[5] L.H. Nalms, K.D. Reiszner, Anal. Chem. 49 (1977) 994.

[6] E. Boscani, M.L. Alexander, P. Prazeller, T.D. Märk, Int. J. Mass Spectrom. 239 (2004) 179.

[7] K. Ishikawa, Guide to Quality Control. Asian Productivity Organization, Tokyo, 1982.

[8] K. Ishikawa, (English translation by D.J. Lu), What Is Total Quality Control? The Japanese Way. Prentice Hall, Englewood Cliffs, NJ, 1985.

[9] D.L. Heawner, W.T. Morgan, M.W. Ogden, Environ. Int. 21 (1995) 3.

[10] L. Wallace, W. Nelson, R. Ziegenfus, E. Pellizzari, L. Michael, R. Whitmore, H. Zelon, T. Hartwekk, R. Perritt, D. Westerdahl, J. Exp. Anal. Environ. Epidemiol. 1 (1991) 157.

[11] D.L. Heawner, W.T. Morgan, M.W. Ogden, Environ. Int. 22 (1996) 159.

[12] B. Zabiegała, T. Górecki, J Namieśnik, Anal. Chem. 75 (2003) 3182.

[13] E. Kovats, Helv. Chim. Acta 41 (1958) 1915.

[14] H. Van den Dool; P.D. Kratz, J Chromatogr. 11 (1963) 463.

[15] R. Kaliszan, Anal. Chem. 64 (1992) 619A

[16] H.J. Hübschmann, Handbook of GC/MS: Fundamentals and Applications, Wiley-VCH, Toronto, 2001.

[17] R. Kaliszan, Quantitative Structure-Chromatographic Retention Relationships, Wiley, New York, 1987

[18] T.C. Gerbino, G. Castello, J Chromatogr A 699 (1995) 161.

[19] B. Kozdroń-Zabiegała, J. Namieśnik, A. Przyjazny, Indoor Environ. 4 (1995) 189.

[20] B. Kozdroń-Zabiegała, B. Zygmunt, J. Namieśnik, Chem. Anal. 41 (1996) 209.

[21] P.A. Martos, J. Pawliszyn, Anal. Chem. 69 (1997) 206.

[22] E. Baltussen, H.-G. Janssen, P. Sandra, C.A. Cramers, J. High Resolut. Chromatogr. 20 (1997) 385.

[23] D. Zabaras, S.G. Wyllie, Flavour. Frag. J. 16 (2001) 411.

[24] K. Kolar, M. Ciganek, J. Malecha, J. Chromatogr. A 1029 (2004) 263.

[25] A. Kloskowski, W. Chrzanowski, M. Pilarczyk, J. Namieśnik, J Chem Thermodynamics 37 (2005) 21.

[26] J.N. Miller, Analyst 116 (1991) 3.

[27] K. Danzer, L.A. Cuurie, IUPAC, Pure Appl. Chem. 70 (1998) 993.

[28] B.W. Wenclawiak, M. Koch, E. Hadjicostas, Quality Assurance in Analytical Chemistry, Training and Teaching, Springer, NY, 2004.

[29] L. Brüggemann, R. Wennrich, Accred. Qual. Assur. 7 (2002) 269.

[30] J.V. Loco, M. Elskens, C. Croux, H. Beernaert, Accred. Qual. Assur. 7 (2002) 281.

[31] K. Heydorn, T. Anglov, Accred. Qual. Assur. 7 (2002) 153.

[32] B. Zabiegała, T. Górecki, E. Przyk, J. Namieśnik, Atmos. Environ. 36 (2002) 2907.

[33] F.R. Gonzalez, A.M. Nardillo, J. Chromatogr. A 842 (1999) 29.

[34] H. Shiota, J Agric. Food. Chem. 41 (1993) 2056.

[35] Y. Zhang, H. Chi-Tang, J Agric. Food. Chem. 39 (1991) 760.

[36] T.H. Yu, W. Chung-May, C. Shyh-Yuan, J. Agric. Food Chem. 37 (1989) 730.

[37] G.R. Binder, M.E. Benson, R.A. Flath, J. Agric. Food Chem. 38 (1990) 1245.

[38] R.G. Buttery, L.C. Ling, J. Agric. Food Chem. 43 (1995) 1878.

[39] K.H. Engel, J. Agric. Food Chem 36 (1988) 549.

[40] H.V. Izzo, H. Chi-Tang, J. Agric. Food Chem. 41 (1993) 2364.

[41] G. Sun, P. Stremple, Retention Index Characterization of Flavor, Fragrance and Many Other Compounds on DB-1 and DB-XLB, J&W Scientific, Folsom, CA, 95630-4714; http://www.odour.org.uk

Table 1. Analytical conditions for the calibration of permeation passive samplers (analyte desorption and GC analysis condition)

Calibration chamber parameters	Temperature: 25°C ± 0.1°C Flow rate: 300 ml/min Chamber volume: 0.1 m^3
Desorption-solvent extraction (30 min - after transferring sorbent to a glass vial)	1 ml of CS_2 for aliphatic and aromatic hydrocarbons or 1 ml of a mixture of CS_2 + 1% isopropanol for esters and alcohols
Concentration of analytes in gas standard mixture [mg/m^3]	n-pentane 5.17 n-hexane 1.83 n-heptane 1.35 n-octane 0.60 n-nonane 0.26 n-decane 0.12 n-undecane 0.10 benzene 1.84 toluene 1.20 ethylbenzene 0.47 butylbenzene 0.08 methyl acetate 1.60 ethyl acetate 2.57 propyl acetate 2.40 buthyl acetate 5.86 n-butanol 1.02 n-pentanol 0.85 n-hexanol 0.73 n-heptanol 0.18 n-oktanol 0.06
Gas chromatograph	Hewlett Packard, GC System 6890
Detector	FID, 280°C;
Carrier gas flow rate	helium, at 1.5 ml/min
Injector	Split/Splitless, Split Mode; 200 °C
Split ratio	1:5
Injection volume	1µl
Temperature program	40°C, 7°C/min to 250°C;
Data acquisition and processing	ChemStation software
Capillary column	007-1 Quadrex, 30 m x 0.32 mm x 1 µm film thickness
Calibration method	External standard (ESTD) Multipoint calibration curve

Table 2. GC conditions used in the determination of linear temperature-programmed retention indices (LTPRI)

Gas chromatographs	Hewlett Packard, GC System 5890; Hewlett Packard, GC System 6890;
Detectors	FID, 280°C; MSD, ion source temperature: 220°C; transfer line temperature: 280°C
Carrier gas flow rates	Helium, at 1.5, 2.0 and 2.2 ml/min
Injector	Split/Splitless, Split Mode; 200 °C
Split ratio	1:5; 1:10
Injection volume	1 µl
Temperature programs	35°C, 7°C/min to 220°C; 40°C, 7°C/min to 200°C; 40°C, 10°C/min to 200°C; 50°C, 7°C/min to 200°C; 50°C, 5°C/min to 220°C; 50°C, 10°C/min to 220°C; 70°C, 7°C/min to 220°C;
Data acquisition and processing	ChemStation software
Capillary columns	DB-1, J&W, 32 m x 0.32 mm, 5.0 µm film thickness; 007-1 (Q 1), Quadrex, 30 m x 0.32 mm x 0.25 µm film thickness; 007-1 (Q 2), Quadrex, 30 m x 0.32 mm x 1 µm film thickness; Rtx-1, Restek, 30 m x 0.32 mm x 0.25 µm film thickness; HP-1, Hewlett-Packard, 32 m x 0.25 mm x 0.25 µm film thickness

Table 3. Calibration constants **k** and the statistical parameters of the calibration curves (standard deviations of the regression coefficients of the calibration constant, the slope and the intercept (s_k ,s_b and s_a) and the linear correlation coefficients R); (*y=bx+a*)

Compounds	k(=1/b) [min/ml]	Confidence interval		b [ml/min]	S_b [ml/min]	t_{cr} (P=95%; f=n-2)	Number of samplers n	a [ml]	S_a [ml]	Linear correlation coefficient r	LTPRI
		$S_k=(S_b/b)*k$	$\pm tS_k$								
n-pentane	0.217	0.008	0.017	4.61	0.17	2.12	18	-4809	2337	0.989	500
n-hexane	0.186	0.006	0.013	5.36	0.097	2.12	18	-1193	1755	0.995	600
n-heptane	0.172	0.003	0.007	5.81	0.17	2.12	18	5918	3330	0.990	700
n-octane	0.140	0.006	0.014	7.13	0.30	2.12	18	2136	5387	0.976	800
n-nonane	0.092	0.004	0.009	10.9	0.47	2.12	18	7587	7259	0.999	900
n-decane	0.056	0.003	0.007	17.7	0.66	2.12	18	-11613	11923	0.980	1000
n-undecane	0.039	0.003	0.005	25.9	1.5	2.12	18	-7451	29747	0.963	1100
benzene	0.168	0.006	0.013	5.9	0.18	2.04	36	-994	3468	0.999	649
toluene	0.145	0.004	0.009	6.90	0.31	2.04	36	14989	5963	0.978	757
ethylbenzene	0.117	0.005	0.009	8.56	0.31	2.04	36	-1347	5966	0.986	850
butylbenzene	0.068	0.003	0.006	14.7	0.83	2.04	36	-3660	16290	0.965	1051
methyl acetate	0.183	0.01	0.020	5.46	0.25	2.04	36	15864	9378	0.971	507
ethyl acetate	0.166	0.004	0.009	6.03	0.17	2.04	36	13741	6800	0.986	595
propyl acetate	0.127	0.012	0.024	7.8	0.52	2.04	36	49958	25093	0.943	695
butyl acetate	0.092	0.008	0.016	10.9	0.98	2.04	36	92411	46902	0.883	794
n-butanol	0.168	0.011	0.022	5.95	0.34	2.04	36	-7587	12427	0.947	642
n-pentanol	0.139	0.009	0.019	7.19	0.37	2.04	36	-13553	13477	0.957	747
n-hexanol	0.114	0.005	0.010	10.3	0.50	2.04	36	7878	18263	0.962	853
n-heptanol	0.098	0.009	0.018	10.2	1.1	2.04	36	97304	44443	0.848	952
n-octanol	0.054	0.004	0.009	18.5	1.6	2.04	36	143176	71468	0.888	1053

Table 4. Comparison of the calibration constants of permeation passive samplers obtained in different laboratories

Analyte	$\mathbf{k}^{*)}_{Exp}$ [min/ml]	STD (n=18)	$\mathbf{k}^{**)}_{Exp}$ [ml/min]	STD (n=12)	$t_{cal.}$	t_{cr} (P=95%).
n-pentane	0.230	0.026	0.217	0.012	1.862	2.086
n-hexane	0.184	0.02	0.186	0.025	0.235	
n-heptane	0.160	0.021	0.172	0.072	0.562	
n-octane	0.132	0.011	0.14	0.061	0.449	
n-nonane	0.100	0.021	0.092	0.054	0.490	
n-decane	0.064	0.023	0.056	0.037	0.663	
benzene	0.166	0.009	0.168	0.065	0.105	
toluene	0.142	0.011	0.145	0.100	0.103	
ethylbenzene	0.117	0.013	0.117	0.003	0.000	
butylbenzene	0.072	0.01	0.068	0.022	0.584	
methyl acetate	0.185	0.011	0.183	0.070	0.097	
ethyl acetate	0.155	0.017	0.166	0.077	0.487	
hexanol	0.110	0.018	0.114	0.020	0.561	
heptanol	0.085	0.016	0.098	0.041	1.038	

*) Determined at the Department of Chemistry, University of Waterloo, Canada
**) Determined at the Department of Analytical Chemistry, Gdansk University of Technology, Poland

Table 5. Regression equations, standard deviations of the regression coefficients S_b and S_a, correlation coefficients and standard deviations of the residuals for each individual class of compounds, as well as for all compounds tested.

Class of compounds		Regression equations (**k**= b·x +a) where x is LTPRI	S_b	S_a	Linear regression coefficient r^2	Standard deviation of the residuals $S_{x.y}$
Aliphatic hydrocarbons		-0.000313x +0.379	1.8×10^{-5}	0.015	0.983	0.0097
Aromatic hydrocarbons		-0.000253x +0.333	8.0×10^{-5}	0.0070	0.998	0.0025
Alcohols	all	-0.000247x +0.321	1.8×10^{-5}	0.015	0.943	0.0094
	n-	-0.000263x +0.334	3.6×10^{-5}	0.031	0.948	0.0016
Esters	all	-0.000315x +0.348	2.2×10^{-5}	0.015	0.980	0.0055
	n-	-0.000326x +0.353	2.9×10^{-5}	0.0061	0.985	0.0062
Summary equation		-0.000261x +0.330	1.5×10^{-5}	0.012	0.914	0.014

Table 6. Comparison of the calibration constants **k** obtained from direct calibration of permeation passive samplers and from regression line.

Class of chemical compounds	**Analytes**	**Direct calibration**		***k* regression LTPRI*)**			***k* regression LTPRI**)**			$\|k_{exp} - k_{reg1}\|$	***A***	$\|k_{exp} - k_{reg}\|$	***A***	***U(k)***	$U(k_{reg1})$	$U(k_{reg})$	$t*u(k)$	t_{cr} (P=95% f=n-2)
		k_{Exp} [min/ml]	***u(k)***	k_{reg1}	$u(k_{reg1})$	% diff	k_{reg}	$u(k_{reg})$	% diff									
Aliphatic hydrocarbons	n-pentane	0.217	0.0080	0.223	0.0098	-2.7	0.200	0.015	7.9	0.0058	0.025	0.017	0.033	0.016	0.020	0.029	0.017	2.12
	n-hexane	0.186	0.0062	0.192	0.0098	-2.7	0.174	0.015	6.9	0.0050	0.023	0.013	0.032	0.012	0.020	0.029	0.013	2.12
	n-heptane	0.172	0.0031	0.160	0.0098	6.9	0.148	0.015	14.3	0.012	0.020	0.025	0.030	0.0062	0.020	0.029	0.0066	2.12
	n-octane	0.140	0.0064	0.129	0.0098	8.1	0.121	0.015	13.5	0.011	0.023	0.019	0.032	0.013	0.020	0.029	0.014	2.12
	n-nonane	0.092	0.0042	0.098	0.0098	-6.4	0.095	0.015	-3.8	0.0059	0.021	0.0035	0.030	0.0083	0.020	0.029	0.0088	2.12
	n-decane	0.056	0.0031	0.066	0.0098	-17.7	0.069	0.015	-22.6	0.010	0.020	0.013	0.030	0.0063	0.020	0.029	0.0067	2.12
	n-undecane	0.039	0.0025	0.035	0.0098	8.8	0.043	0.015	-11.9	0.0034	0.020	0.0046	0.030	0.0050	0.020	0.029	0.0053	2.12
Aromatic hydrocarbons	benzene	0.168	0.0062	0.169	0.0025	-0.6	0.161	0.015	4.5	0.0010	0.013	0.0076	0.032	0.012	0.0049	0.029	0.013	2.04
	toluene	0.145	0.0044	0.142	0.0025	1.9	0.133	0.015	8.4	0.0027	0.010	0.012	0.031	0.0088	0.0049	0.029	0.0089	2.04
	ethylbenzene	0.117	0.0045	0.119	0.0025	-1.6	0.108	0.015	7.2	0.0019	0.010	0.0084	0.031	0.0090	0.0049	0.029	0.0092	2.04
	butylbenzene	0.068	0.0030	0.068	0.0025	0.3	0.056	0.015	17.9	0.00022	0.008	0.012	0.030	0.0060	0.0049	0.029	0.0061	2.04
Esters	methyl acetate	0.183	0.0097	0.188	0.0056	-2.8	0.198	0.015	-8.1	0.0050	0.022	0.015	0.035	0.019	0.011	0.029	0.020	2.04
	ethyl acetate	0.166	0.0043	0.160	0.0056	3.4	0.175	0.015	-5.4	0.0056	0.014	0.0090	0.031	0.0086	0.011	0.029	0.009	2.04
	propyl acetate	0.127	0.012	0.129	0.0056	-1.2	0.149	0.015	-16.9	0.0015	0.026	0.022	0.038	0.024	0.011	0.029	0.024	2.04
	butyl acetate	0.092	0.0078	0.098	0.0056	-6.4	0.123	0.015	-34.1	0.0059	0.019	0.031	0.033	0.016	0.011	0.029	0.016	2.04
	methyl butyrate	0.131	0.0098	0.126	0.0056	4.0	0.146	0.015	-11.7	0.0052	0.038	0.015	0.046	0.036	0.011	0.029	0.037	2.04
	ethyl butyrate	0.103	0.0098	0.101	0.0056	1.6	0.126	0.015	-22.4	0.0016	0.026	0.023	0.038	0.024	0.011	0.029	0.024	2.04

Table 6. continued

Alcohols	butanol	0.168	0.011	0.162	0.0094	3.4	0.163	0.015	3.2	0.0058	0.029	0.0053	0.037	0.023	0.019	0.029	0.023	2.04	642
	pentanol	0.139	0.0092	0.136	0.0094	2.1	0.135	0.015	2.8	0.0030	0.026	0.0039	0.035	0.018	0.019	0.029	0.019	2.04	747
	hexanol	0.114	0.0051	0.110	0.0094	3.2	0.108	0.015	5.3	0.0036	0.021	0.0060	0.031	0.010	0.019	0.029	0.010	2.04	853
	heptanol	0.098	0.0088	0.085	0.0094	12.7	0.082	0.015	16.5	0.012	0.026	0.016	0.034	0.018	0.019	0.029	0.018	2.04	952
	octanol	0.054	0.0042	0.061	0.0094	-12.1	0.055	0.015	-2.7	0.0065	0.021	0.0014	0.030	0.0084	0.019	0.029	0.0085	2.04	1053
	2-methyl-1-propanol	0.185	0.0098	0.171	0.0094	7.8	0.172	0.015	7.3	0.014	0.027	0.013	0.035	0.020	0.019	0.029	0.020	2.04	608
	2-pentanol	0.160	0.0068	0.167	0.0094	-4.6	0.168	0.015	-5.1	0.0073	0.023	0.0081	0.032	0.014	0.019	0.029	0.014	2.04	621
	2.3-dimethyl-2-butanol	0.142	0.0068	0.145	0.0094	-1.9	0.144	0.015	-1.6	0.0027	0.023	0.0022	0.032	0.014	0.019	0.029	0.014	2.04	713
	3-hexanol	0.122	0.0092	0.128	0.0094	-5.2	0.127	0.015	-4.1	0.0064	0.026	0.0050	0.035	0.018	0.019	0.029	0.019	2.04	779
	2-hexanol	0.117	0.0073	0.127	0.0094	-8.7	0.126	0.015	-7.4	0.010	0.024	0.0087	0.033	0.015	0.019	0.029	0.015	2.04	784
	2.4-dimethyl-3-pentanol	0.115	0.0045	0.118	0.0094	-2.9	0.116	0.015	-1.2	0.0033	0.021	0.0014	0.031	0.0090	0.019	0.029	0.009	2.04	819
	6-methyl-2-heptanol	0.095	0.012	0.085	0.0094	10.4	0.081	0.015	14.3	0.010	0.030	0.014	0.038	0.024	0.019	0.029	0.024	2.04	953
	2-ethyl-1-hexanol	0.075	0.0058	0.070	0.0094	6.4	0.066	0.015	12.4	0.014	0.022	0.013	0.031	0.012	0.019	0.029	0.012	2.04	1014

u(k) – standard uncertainty
***k* regression LTPRI**[*)] – estimation of the calibration constants based on regression equations for each individual class of compounds (Y=-0.000313·X+0.379 for aliphatic hydrocarbons; Y=-0.000253·X+0.333 for aromatic hydrocarbons; Y=-0.000247·X+0.321 for alcohols; and Y=-0.000315·X+0.348 for esters.)
***k* regression LTPRI**[**)] – estimation of the calibration constants based on summary regression equation for all studied compounds (Y=0.000261·X+0.330)

A = $2\sqrt{u(k_{reg})^2 + u(k_{\exp})^2}$

U – expanded uncertainty

Table 7. LTPRI determined under different chromatographic conditions for selected organic compounds.

Gas chromatograph	Hewlett-Packard GC System 6890						Hewlett-Packard GC System 5890										Hewlett-Packard GC System 5890 [1]		Average LTPRI	RSD [%]
Detector	**FID**						**FID**								**MSD**		**FID**			
Capillary column	Quadrex (30 × 0.32 × 1.0)		Quadrex (30 × 0.32 × 0.25)		DB-1 (30 × 0.32 × 5.0)		Quadrex (30 × 0.32 × 1.0)		Quadrex (30 × 0.32 × 0.25)		DB-1 (30 × 0.32 × 5.0)		Rtx-1 (30 × 0.32 × 0.25)		Quadrex (30 × 0.32 × 1.0)		HP-1 (32 × 0.25 × 0.25)			
	n = 20	RSD [%]	n = 10	RSD [%]	n = 20	RSD [%]	n = 10	RSD [%]	n = 10	RSD [%]	n = 10	RSD [%]	n = 5	RSD [%]	n = 10	RSD [%]	n =5	RSD [%]		
Esters																				
methyl acetate	508.1	0.116	503.7	0.632	508.7	0.334	508.6	0.218	510.3	1.187	510.3	0.206	508.7	0.255	(-)	0	528.7	0.351	510.9	1.464
ethyl acetate	594.6	0.200	598.7	0.092	593.4	0.067	595.5	0.382	(*)	nm	594.0	0.212	587.6	0.452	(-)	0	597.8	0.212	594.5	0.611
propyl acetate	693.6	0.004	699.3	0.038	692.6	0.045	693.8	0.197	(*)	nm	692.9	0.125	693.9	0.262	698.3	1.820	nm	nm	694.9	0.395
butyl acetate	793.4	0.005	795.9	0.107	792.0	0.036	793.6	0.129	794.5	0.031	792.3	0.076	794.2	0.228	794.0	0.151	nm	nm	793.7	0.155
Alcohols																				
n-butanol	642.1	0.053	639.6	0.523	638.9	0.074	642.2	0.339	639.3	0.289	642.9	0.228	637.5	0.186	639.7	0.274	nm	nm	640.3	0.294
n-pentanol	746.4	0.140	745.9	0.354	745.9	0.016	746.7	0.278	744.7	0.427	748.1	0.124	746.7	1.243	745.1	0.331	nm	nm	746.2	0.140
n-hexanol	856.6	0.754	848.0	0.153	845.9	1.161	863.4	0.187	851.5	0.148	861.3	0.071	851.8	0.093	849.1	0.199	847.8	0.181	852.8	0.732
n-heptanol	951.3	0.055	950.9	0.208	953.4	0.118	952.4	0.101	950.6	0.222	953.1	0.081	951.3	0.189	951.8	0.122	953.2	0.541	952.0	0.113
n-octanol	1061.7	0.025	1052.2	0.132	1042.7	0.043	1060.9	0.065	1051.9	0.139	1054.7	0.092	1049.7	0.048	1052.9	0.071	nm	nm	1053.3	0.577
Aromatic hydrocarbons																				
benzene	649.9	0.015	645.8	0.388	658.6	0.002	649.3	0.242	645.1	0.476	658.4	0.262	645.5	0.672	647.5	0.249	642.5	0.215	649.2	0.887
toluene	756.6	0.004	751.2	0.266	766.3	0.001	755.9	0.182	750.7	0.240	766.1	0.236	755.8	0.143	753.9	0.202	749.6	0.054	756.2	0.816
ethylbenzene	848.8	0.027	850.4	0.226	851.6	0.361	848.3	0.186	845.3	4.130	849.8	0.244	849.6	0.334	848.5	0.194	845.8	0.201	848.7	0.240
butylbenzene	1050.3	0.001	1054.7	0.116	1052.9	0.106	1049.3	0.160	1041.8	0.135	1053.9	0.204	1052.6	0.150	1049.5	0.765	1044.8	0.195	1050.0	0.410

(*) – not separated
(-) – not determined (co-elution with solvent peak)
nm – not measured
[1] – physically different from the system in the previous column

Table 8. The comparison of the LTPRI values determined experimentally with available literature data.

Compound	Average **LTPRI**	**Literature data**	**% diff**	**Ref.**
ethyl acetate	594.5	590	-0.76	[27]
		599	0.76	[28]
		600	0.92	[29]
		600	0.92	[30]
propyl acetate	694.9	689	-0.85	[27]
butyl acetate	793.7	794	0.038	[27]
n-butanol	640.3	634	-0.98	[27]
n-pentanol	746.2	744	-0.29	[30]
		744	-0.29	[29]
		774.1	3.7	[34]
		752	0.78	[31]
n-hexanol	852.8	847	-0.68	[32]
		848	-0.56	[30]
		848	-0.56	[31]
		847.9	-0.57	[34]
		850	-0.33	[27]
		811	-4.9	[33]
n-heptanol	952.0	900	-5.4	[33]
		951.8	-0.021	[34]
n-octanol	1053.3	991	-5.9	[33]
		1053.2	-	[34]
benzene	649.2	644	-0.80	[29]
		644	-0.80	[30]
		617	-4.9	[33]
toluene	756.2	752	-0.55	[27]
ethylbenzene	848.7	850	0.15	[27]
		839.8	-1.0	[34]
		844	-0.55	[30]
butylbenzene	1050.0	1036.4	-1.3	[34]
2-methyl-1-propanol	608.0	606	-0.30	[27]
2-pentanol	621.0	674	8.5	[27]
3-hexanol	779.0	776	-0.33	[29]
		776	-0.33	[30]
2-hexanol	784.0	777	-0.86	[27]
		780	-0.45	[30]
ethyl butyrate	782.0	780	-0.25	[29]

Table 9. Comparison of the results obtained by the two techniques, together with the retention times of the analytes, their LTPRI and the estimated calibration constants.

Compound name	Retention Time (RT)	LTPRI	**k***)	c** [ng/L]	c*** [ng/L]
hexane	7.630	600	0.186	1.33	1.34
benzene	9.230	658	0.168	3.05	2.96
unknown	9.502	667	0.156	1.11	1.10
heptane	10.421	700	0.172	0.15	0.18
unknown	11.341	731	0.139	0.067	0.16
toluene	12.300	764	0.145	1.49	2.59
octane	13.291	800	0.140	0.11	0.095
ethylbenzene	14.568	844	0.117	0.12	0.18
unknown	15.254	868	0.104	0.31	0.35
unknown	15.947	892	0.097	0.27	0.22
unknown	16.072	897	0.096	0.58	0.29
unknown	16.675	919	0.090	0.23	0.46
heptanol	17.414	947	0.098	0.21	0.28
unknown	18.224	978	0.075	0.35	0.71
unknown	18.679	996	0.070	0.92	0.10
unknown	19.311	1020	0.064	0.32	0.10
unknown	19.675	1035	0.060	1.61	2.51
octanol	19.867	1042	0.054	0.051	0.07
unknown	21.126	1091	0.045	0.12	0.63
unknown	22.173	1140	0.033	0.58	1.45
C12	23.410	1200	0.017	0.011	0.30

*) equation used for **k** values calculation (Y=-0.000261·X+0.330)

) concentration obtained applying permeation passive samplers for collection of a sample of indoor air pollutants; c=k**M/t

***) concentration obtained applying sorption tubes filled with Tenax TA for collection of a sample of indoor air pollutants

Figure captions

Figure 1. The Cause-and-Effect diagram for the parameters affecting the determination of the analyte concentration by permeation passive samplers.
(**k**) - calibration constant of the permeation passive sampler; ($mass_{analyte}$) - mass of the analyte trapped on the sorption bed of the passive sampler, determined chromatographically; (t_{exp}) - sampler exposure time; ($mass_{st}$) - chromatographically determined mass of analyte standards; (flow) – flow rate of the standard gas mixture; (t_{sorpt}) - exposure time of the passive sampler in the calibration chamber; ($RSD_{results}$) - Relative Standard Deviation (RSD) of the determination of analyte mass trapped on the sorption bed (depends on the uncertainty of the injection volume (V_{inj})), uncertainty of carbon disulfide volume (V_{CS2}) and the calibration of the GC-FID system (cal) (depends on the uncertainty of the injection volume (V_{inj}), uncertainty of the volume of the standard in the calibration mixture (V_{st}), uncertainty of the dilution of the calibration mixture (V_{dill}) and Relative Standard Deviation of standard injection (RSD_{st})). Uncertainty of the mass of the analyte trapped by the passive samplers depends on the uncertainty of the calibration of the GC-FID system (cal) and the relative standard deviation of determination of the mass of the analyte trapped by the sorption bed ($RSD_{results}$).A

Figure 2. The relationship between the linear temperature-programmed retention index (LTPRI) and the calibration constant for permeation passive samplers equipped with PDMS membranes; (a) aliphatic hydrocarbons, (b) aromatic hydrocarbons, (c) esters, (d) n-acetate acid esters, (e) n-alcohols, (f) alcohols; see Table 5 for details**.**
The conditions of LTPRI determination were as follows: Capillary column: 007-1, Quadrex, 30 m x 0.32 mm, 0.25 µm; temperature program: 40°C, 7°C/min to 250°C; detector: FID, 280°C.

Figure 3. Relationships between the linear temperature-programmed retention index (LTPRI) of all studied compounds and the calibration constant for the permeation passive samplers equipped with the PDMS membrane; see Table 5 for details**.**
For the conditions of LTPRI determination, see Figure 2.

Figure 4. A comparison of the calibration constants obtained with the three methods (direct experimental determination, estimation from the regression line obtained for a given class of compounds and estimation from the regression line obtained for all analytes), including their expanded uncertainties (U).

Figure 5. The plot of $\mathbf{k}_{reg}$ vs. $\mathbf{k}_{exp}$, used to examine the significance of the differences between the experimental and the estimated calibration constants.

Figure 6. An example of a chromatogram obtained for a real sample collected by a permeation passive sampler used in the study.

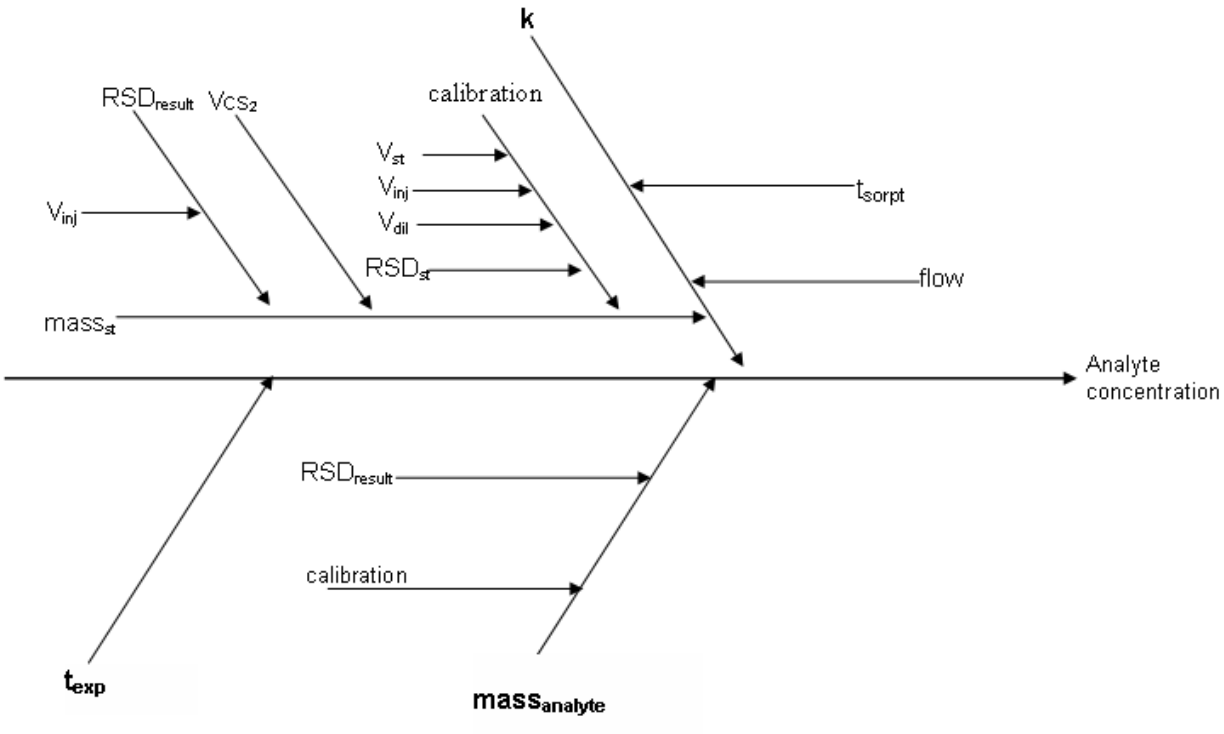
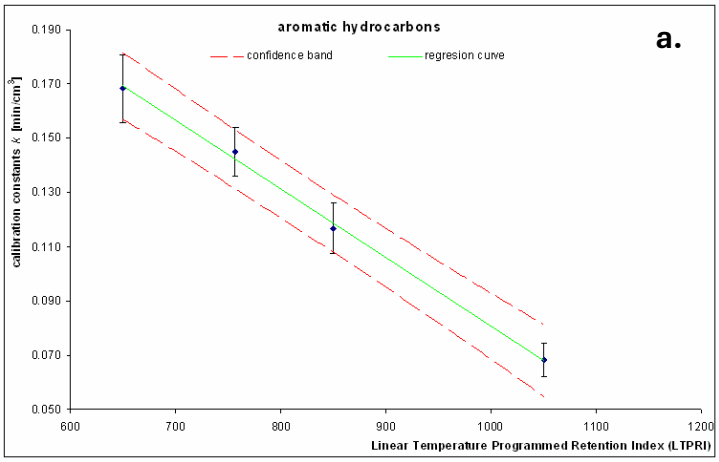
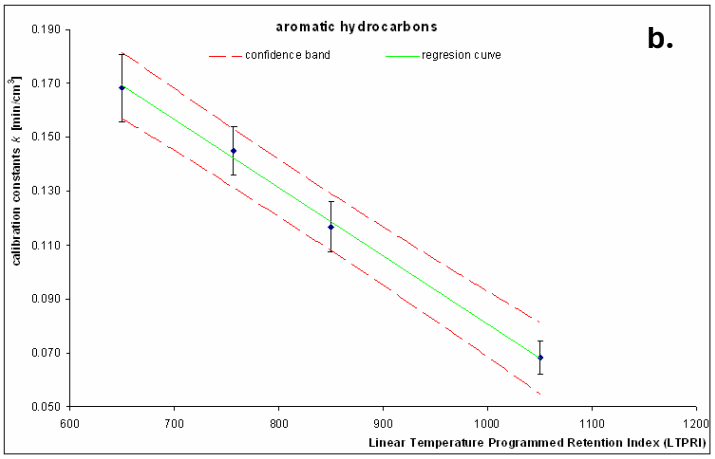
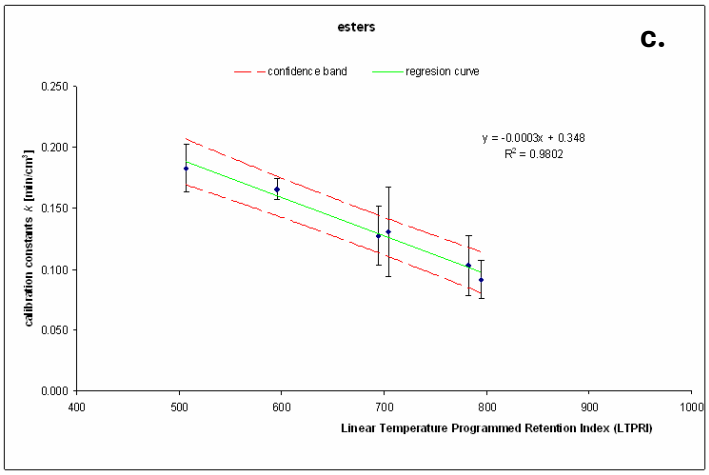
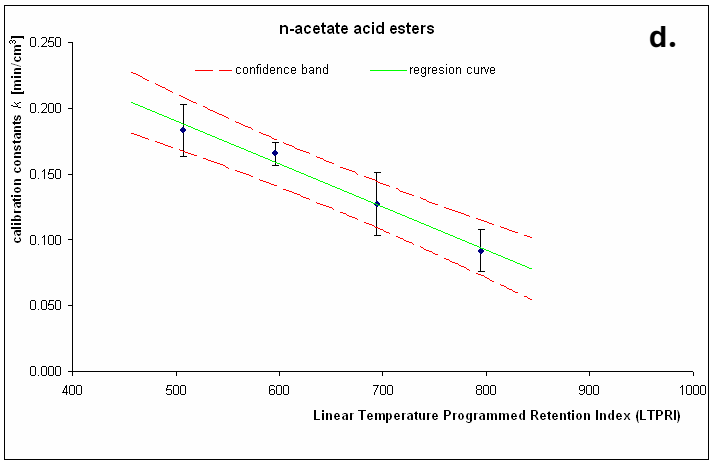


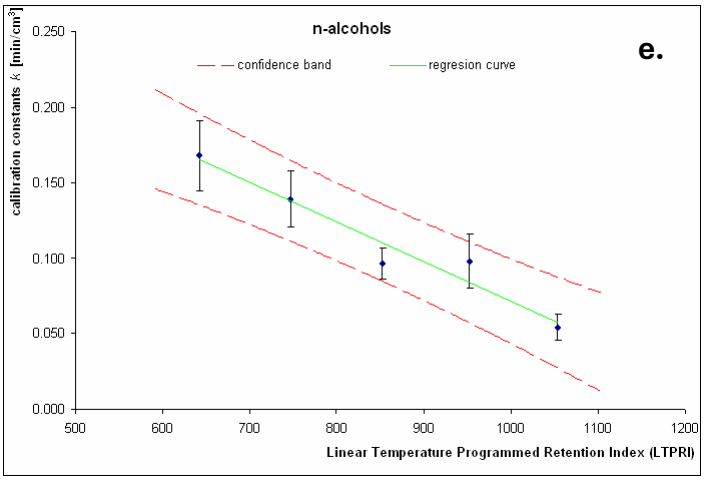
Figure 1.











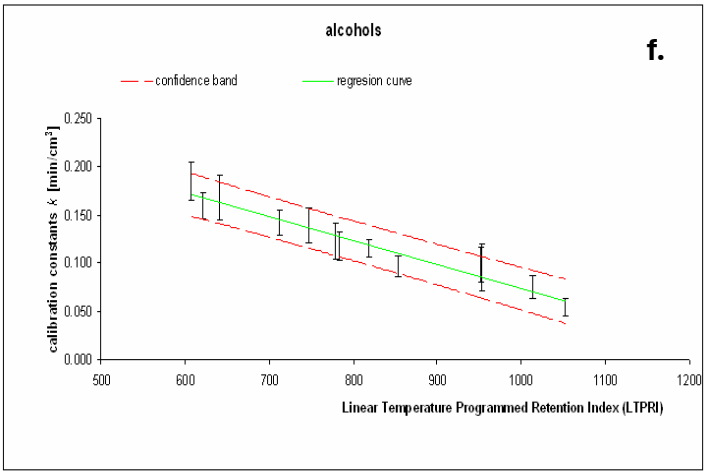


Figure 2.

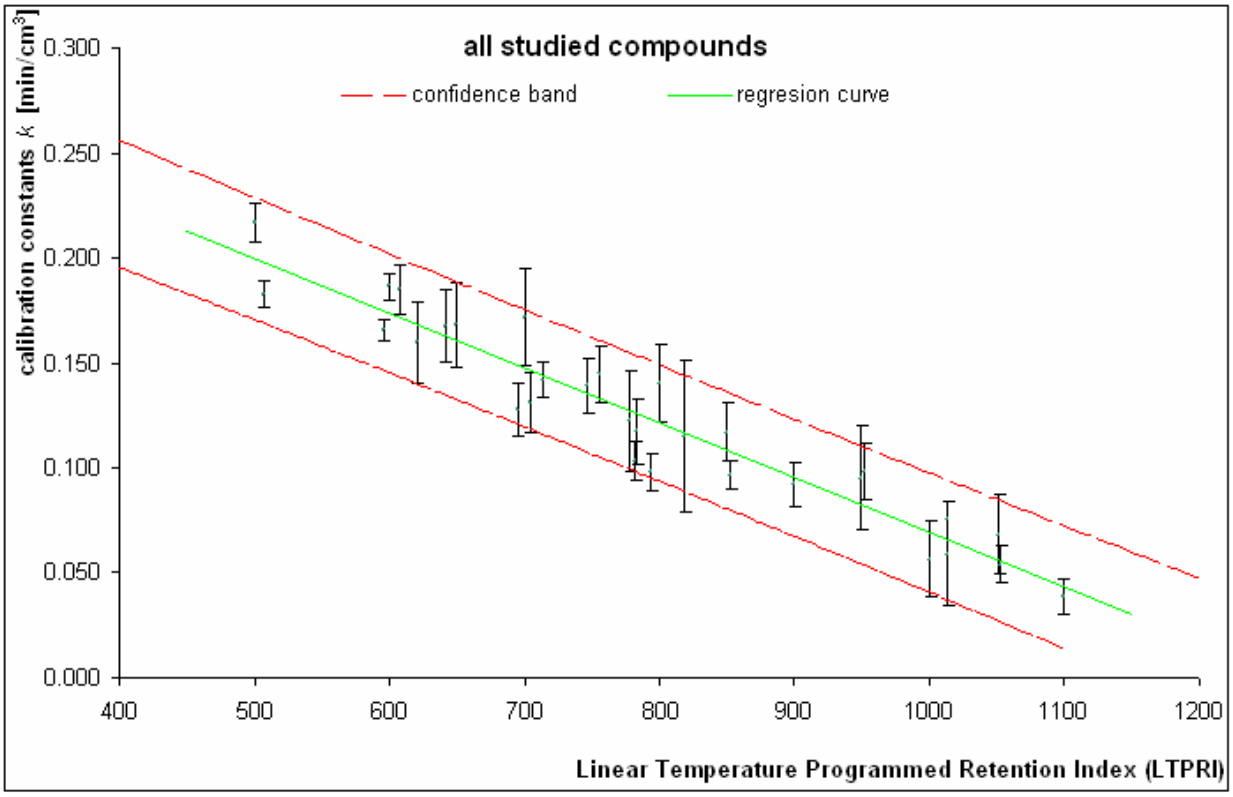


Figure 3.

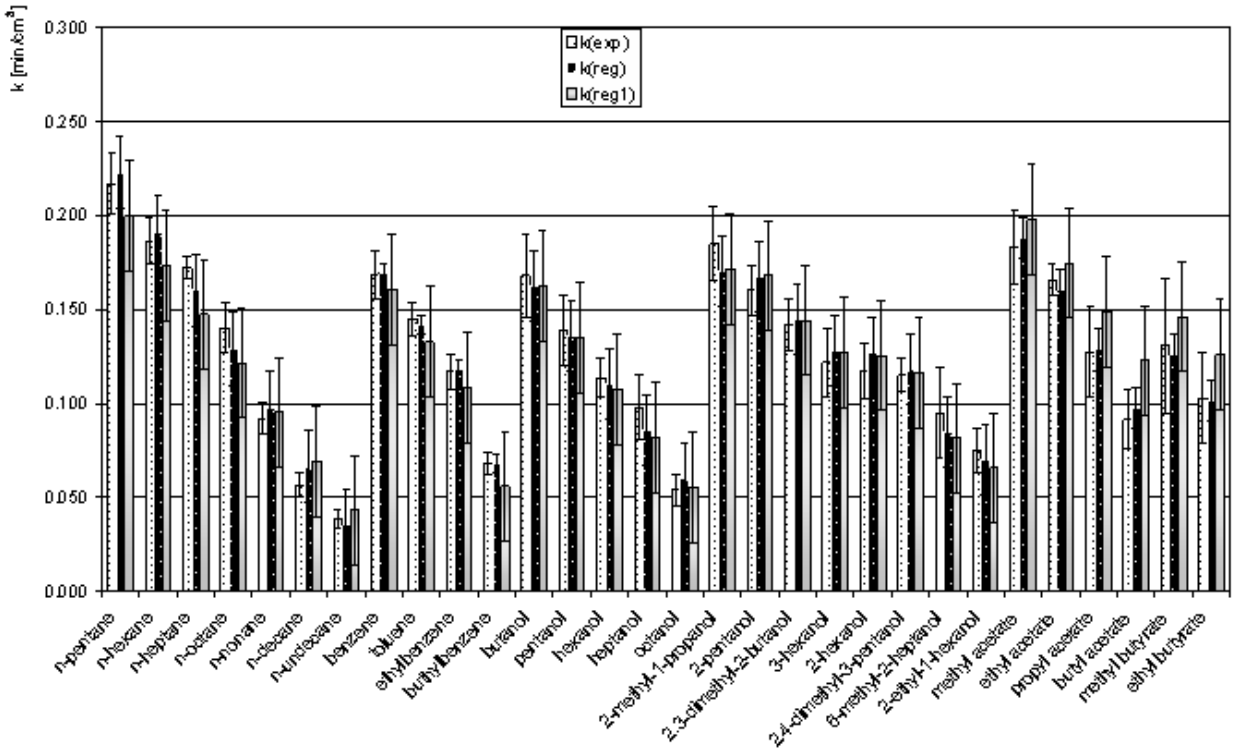


Figure 4.

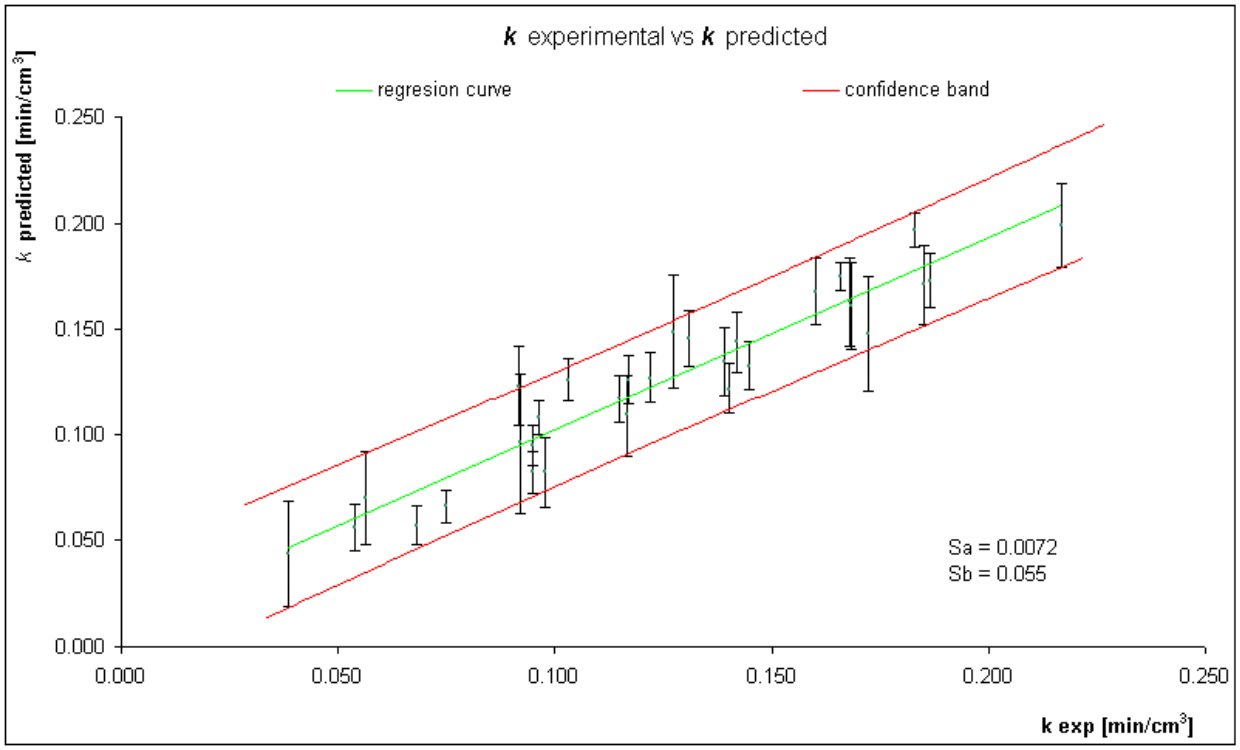


Figure 5.

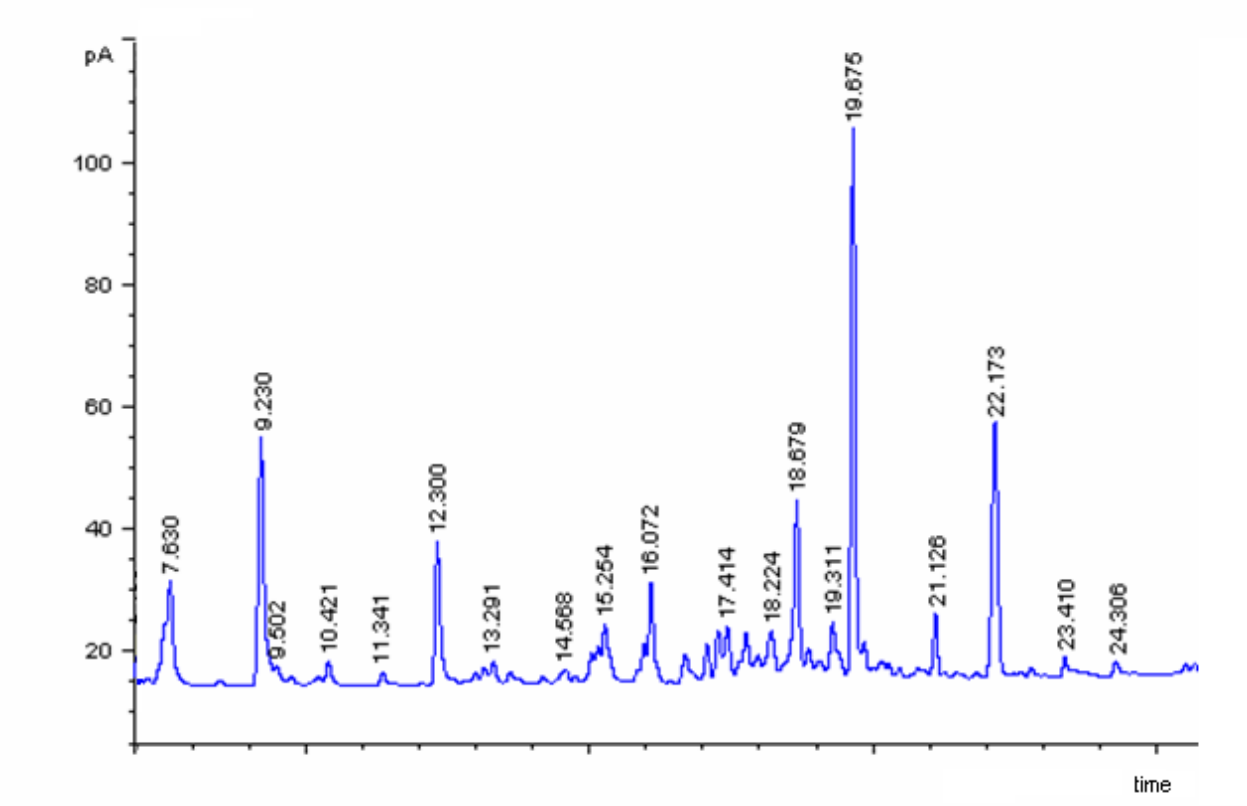


Figure 6.