

THE DETERMINATION OF BACKGROUND LEVELS OF VOLATILEORGANIC COMPOUNDS IN THE ATMOSPHERE

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Abstract

Volatile organic compounds (VOCs) of anthropogenic as well as biogenic origin play an important role in different photochemical processes in the troposphere. In order to evaluate their impact on ozone formation processes, a detailed knowledge about their abundance in the atmosphere is required. There are several different analytical methods available for the determination of background levels of VOC in the air. Sampling can be performed either collecting the whole sample (e.g. canister, bags) or by preconcentration on absorption tubes or cold traps. For their determination gas chromatography using different detectors (FID, ECD, MSD) is applied.

The absorption tubes filled with different adsorption materials (i.e. Tenax, Carbotrap, Carbosieve,) to collect VOC from C₂ to C₁₀ were applied and the absorption efficiency of individual adsorbents was tested. Special attention was dedicated to the sampling of biogenic compounds.

The samples were cryo-refocused after thermal desorption and injected on gas-chromatographic capillary column. Two separation methods were developed. The first one includes separation of C₂ to C₁₀ isomers using nonpolar OV-1 column. Baseline separation of C₂ isomers was obtained by cooling the chromatographic oven to -60°C. To avoid multiple overlapping of chromatographic peaks two-column system was developed. While Al₂O₃/KCl PLOT column was used for the separation of high volatile VOCs (C₂ to C₆) lower volatile VOC were separated using

nonpolar DB-5MS column. The identification of VOC was performed using several standards and MS detector, while quantitative results were obtained with FID detector.

Since unspecific fragmentations in the homologous series can hinder identification of the unknown substances during gas chromatographic separation coupled with mass spectrometry, some chemometric approaches have been introduced to solve this problem. The accuracy of the developed methods was performed by comparison of results obtained by different laboratories during field measurements.

Introduction

Although the concentrations of volatile organic compounds in the atmosphere are very low (ppbv to subppbv), they play an important role in the atmospheric chemistry and are strongly related with ozone formation. In the troposphere ozone is formed by photochemical reactions involving VOC of biogenic and anthropogenic origin in the presence of nitrogen oxides and sunlight [1-6]. Because of that, the determination of hydrocarbons in the atmosphere is of great importance and a lot of interest was focused to the investigations related to their accurate determination.

For collection of atmospheric samples two sampling techniques are commonly applied:

Sampling with absorption tubes filled with different adsorbents and whole air sampling, using stainless steel canisters and Tedlar bags [1, 7-9]. Since the use of canisters has some disadvantages (e.g., adsorption of compounds on container walls) and is also more expensive [10-12], and therefore not suitable for larger series of samples, the sampling technique with adsorption tubes is more widely applied.

Sampling of ambient air using solid sorbents is usually accompanied by problems related with humidity [8,13] and presence of reactive gases in the atmosphere [7,14-21]. Higher water vapor concentrations reduce specific surface of the adsorbent in the sampling tube [8] and can influence on the subsequent chromatographic determination [22]. At the moment there is no

universal solution for the effective elimination of water from the air sample. Additional problem involves reactions of VOCs and sorbents with ozone [7,14-18], nitrogen oxides [15,16,18-20], sulfur oxides [16,20] and halogens [16,21]. These processes lead to degradation or artifact formation. The most destructive among them and the most abundant in the troposphere is ozone. A number of different techniques and procedures for elimination of ozone were cited in the literature [7,14,16, 23]. The most common and simple technique for elimination of ozone during sampling is titration with nitrogen oxide [23], which was also applied during our sampling procedure.

For the determination of VOCs gas chromatographic techniques using flame ionization detector (FID) are most commonly applied. FID is suitable because of its unselectivity [1,24] additionally it also enables simple calculation of VOC concentrations using the effective carbon number concept [24,25]. For the qualitative identification of compounds that are separated on the chromatographic column mass spectrometric detection (MSD) is desirable [1,24,26]. To combine advantages of both detectors, we installed two equal capillary columns in a gas chromatograph. One was coupled with the FID and the other one with the MSD at the same time. Each sample was splitted between both columns. This combination made possible simultaneous qualitative compounds determination with the MS and quantitative determination with the FID for each sample.

In some cases (similarity in chemical structure), the identification of individual compounds using mass-spectrometer is hindered since all these compounds have similar mass spectra. The reliable identification of the unknown compound can be achieved in these cases by combination of mass spectra of the particular compound with its retention property. In cases where there is a lack of proper standard substances a theoretical prediction of the retention indices can also be used as an alternative method to obtain an estimate of the retention property of unknown compound. Therefore the aim of our work was to use some chemometric approaches for the theoretical prediction of gas chromatographic retention indices of organic compounds, which are usually found in the ambient air.

Experimental

Preparation of sampling tubes:

Various adsorbents are used for the collection of VOCs in the air [11,15,27-31]. Since none of these materials can fully accommodate a complete range of organic volatiles individually, the efficiency of Tenax TA (60/80 mesh, Supelco), Molecular sieve (5 Å 60/80 mesh, HP), Carbotrap (20/40 mesh, Supelco) and Carbosieve S-III (60/80 mesh, Supelco) were tested. On the basis of the results, stainless steel or glass tubes were packed with combination of three adsorbents: Tenax TA, Carbotrap and Carbosieve S-III. Before use, stainless steel tubes were cleaned with petroleter (GC, J.T.Baker), dichloromethane (GC, J.T.Baker) and acetone (GC, Aldrich) or methanol (GC, Aldrich) to avoid high blank values arising from the tubes themselves and glass tubes were silylated (Sylon-CT or dimethyldichlorosylane in toluene, Supelco). The sorbent sections and tube ends were separated with inert glass wool plugs. Conditioning of the cartridges was performed for 16 hours at 290°C or 390°C when they were filled with Tenax TA and Carbotrap or Carbosieve S-III, respectively, under a flow of helium 6.0 (35 ml/min). Conditioning was repeated for half an hour immediately before sampling. The composition of sampling tubes applied in our experiments is shown in Table 1.

Sampling procedure:

The air flow (100 ml/min) through the cartridge was controlled by mass flow controller (0-100 ml/min, Sierra Instruments Inc., model no. 840-L-11-V1-S1). Direction of sampling was Tenax TA-Carbotrap-Carbosieve S-III. In this way Tenax TA retained higher molecular volatile VOCs that would be otherwise irreversibly adsorbed mainly on Carbotrap. For ozone elimination, titration with nitrogen oxide was used. Flow (1-2 ml/min) of nitrogen oxide (flask of nitrogen oxide in nitrogen, 100 ppm) was directed through the Teflon tube (1/8 ") to a glass reaction cell (l = 14 cm, I.D. = 0,5 mm). At the same time ambient air was pumped through the glass reaction cell, where ozone was removed from the air sample. Reaction cell was linked with the Teflon connectors to the cartridge, where volatile VOCs from ozone free air sample were adsorbed.

Table 1: Cartridges for sampling of volatile VOCs

Cartridge	Cartridge type	Adsorbents in a cartridge
S1	stainless steel tube (l = 14 cm, I.D. = ¼ ")	Tenax TA (400 mg)
S2	stainless steel tube (l = 14 cm, I.D. = ¼ ")	Molecular Sieve (1598 mg)
S3	stainless steel tube (l = 14 cm, I.D. = ¼ ")	Carbotrap (800 mg)
S4	stainless steel tube (l = 14 cm, I.D. = ¼ ")	Carbosieve S-III (1200 mg)
S5	glass tube (l = 14 cm, I.D. = ¼ ")	Tenax TA (280 mg), Carbotrap (100 mg), Carbosieve III (150 mg)
S6	stainless steel tube (l = 9 cm, I.D. = ¼ ")	Tenax TA (160 mg), Carbotrap (80 mg), Carbosieve III (290 mg)

Analytical procedure:

Determination of VOCs was performed with GC and GC-MS. Two GCs were used. The first one (Varian Star 3400 CX equipped with cryogenic stainless steel trap -I.D. = 0.5 mm) was used for determination of C₂-C₁₀ volatile VOCs. Separation was performed on the capillary column OV1 (50m x 0.32mm x 1µm, Macherey-Nagel-Düred). In order to achieve baseline separation, the column was cooled with liquid carbon dioxide to - 60°C. In front of the column, an empty stainless steel pre-column (l = 40 cm, I.D. = 500 µm) was installed, to prevent plugging of separation column caused by freezing of water present in the sample. Hewlett Packard 5890 gas chromatograph equipped with six port valve (Hewlett Packard 19238A/B/C/Valve Box), and a stainless steel cryo trap (I.D. = 0.5 mm) was used for the determination of C₂-C₆ VOCs. The separation was performed using a capillary column Rt-Alumina (60 m x 0.32 mm, Restek).

The third system -GC (Varian Star 3600 CX) coupled with MSD (Varian Saturn 2000, ITD) with cryo trap, filled with silylated glass beads was applied for the determination of C₅-C₁₀ VOCs. To perform simultaneous qualitative and quantitative analysis, two capillary columns (RTX-5MS, 60 m x 0.25 mm x 0.5 µm, Restek) were installed in GC and connected to FID and MSD.

In all cases VOCs were thermally desorbed from sampling tubes by heating them in a aluminum block (250°C), and collected in a pre-concentration trap cooled with liquid nitrogen. The injection on the capillary column was performed by heating of the traps either by boiling water (manual injection) or using electric heater (automatic injection).

Concentrations of VOCs were calculated by comparing peak areas of sample and standards (1-alkenes C₁-C₆ in nitrogen, Can mix 222, Scoty II, Supelco and n-alkanes C₁-C₆ in nitrogen, Can mix 220 and Can mix 1 Scotty II, Supelco) using the effective carbon number concept [24,25]. Qualitative determination was performed with the comparison of retention times and in case of GC-MS with the comparison of the full scan mass spectra with those of reference compounds (n-alkanes C₁-C₆ in nitrogen, Can mix 1, Scotty II, Supelco; 1-alkenes C₁-C₆ in nitrogen, Can mix 222, Scoty II, Supelco; i-alkanes C₅-C₆ in nitrogen, Can mix 2, Scotty II, Supelco; alkines C₁-C₄ in nitrogen, Can mix 30, Scotty I, Supelco; standard gas mix of ethane,

ethene, ethine, propane, propene, propine and n-butane in nitrogen, Can mix 54, Scotty I; ozone precursors in nitrogen, TO-14, Supelco; biogenic HCs, Fluka: isoprene, linalool, α - and β -terpinene, α - and β -pinene, 2- and 3-carene, limonene, tricyclene, capronaldehyd, camfene, myrcene, α -phellandrene, α -terpinene, γ -terpinene; HCs p.a. quality, Aldrich: benzene, toluene ethilbenzene, o-, m- and p-xilene, n-heptane, n-octane and cyclohexane).

Results and discussion

As mentioned previously, a number of different adsorbents can be used for sampling of volatile VOCs [11,15,27-31]. In our studies different sorbents were tested to ensure quantitative collection of $C_2 - C_{10}$ VOCs. One tube at the time (S1-S4, Table 1) was inserted in a thermal desorption unit, outside of the heated stainless steel block. 0.5 ml of standard gas mixture Can mix 1 (concentration level of substances 15 ppm) was injected through the septa into the tube connected to the adsorption tubes. After the sampling tube the cryo trap was mounted to collect non-adsorbed compounds. Adsorbed, as well as no adsorbed parts were determined. From the results of the experiment performed at room temperature (21.5°C) which are presented in Table 2 it can be concluded that Tenax TA and Carbotrap are suitable for collection of VOCs with four or more carbon atoms while Molecular SI and Carbosieve S-III can be used for sampling of C_2-C_3 VOCs. On basis of these experiments the mixture of Carbosieve S-II, Carbotrap and Tenax TA was chosen and applied in further experiments (cartridge S5, Table 1). With such combination of sorbents the collection of VOCs with C_4 is quantitative, while the retention of lower VOC is approximately 60 %.

Table 2: Adsorption capacity of selected n-alkanes C₂-C₆ on different adsorbents

	ethane	Propane	n-butane	n-pentane	n-hexane
Tenax TA					
% adsorbed in the tube	98	91	0	0	0
% in the cryo trap after the tube	2	3	100	100	100
Carbotrap					
% adsorbed in the tube	81	0	0	0	0
% in the cryo trap after the tube	11	62	85	85	100

To achieve the baseline separation in simultaneous gas chromatographic determination of C₂-C₁₀ VOCs capillary column OV1 should be cooled to -60°C before each analysis. Since the bottom part of FID was cooled together with the GC oven, the effect of oven temperature on the detector signal was tested. The average calibration factor obtained for standard mixtures at four different temperatures (-60, -30, 0, 30 °C) was in an interval of one standard deviation therefore it was confirmed that the temperature of the chromatographic oven has no effect on the detector signal.

Since most of samples contain substantial amount of water, its freezing in the separation column can be a serious problem at lower temperatures that causes the deterioration of chromatograms. As a result of water freezing and column plugging some lower VOCs eluted in one large peak and the others were separated after 20 minutes. Driers such as Nafion, installed before cryo-focusing can be applied, however they can cause artifact formation [32]. To solve this problem an empty stainless steel pre-column was inserted in front of the capillary column. Water from the sample froze but not plug the stainless steel pre-column and enabled normal separation of VOCs on the column. Difference between chromatogram obtained with and without pre-column is shown in Figure 1. Steel, pre-column usage has one disadvantage. Beside water, other substances present in the sample can also freeze at -60°C. Calibration of FID was performed by injection of 0.2 ml of standard gas mixture Can mix 222 and 0.5 ml of standard gas mixture Can mix 1. Calibration factors, observed in 23 days, mainly lied in an interval of one standard deviation round its average value. Calibration factors that lied outside that interval were excluded when average calibration factor was calculated. The value of average calibration factor was 4860 area/ng (Figure 2).

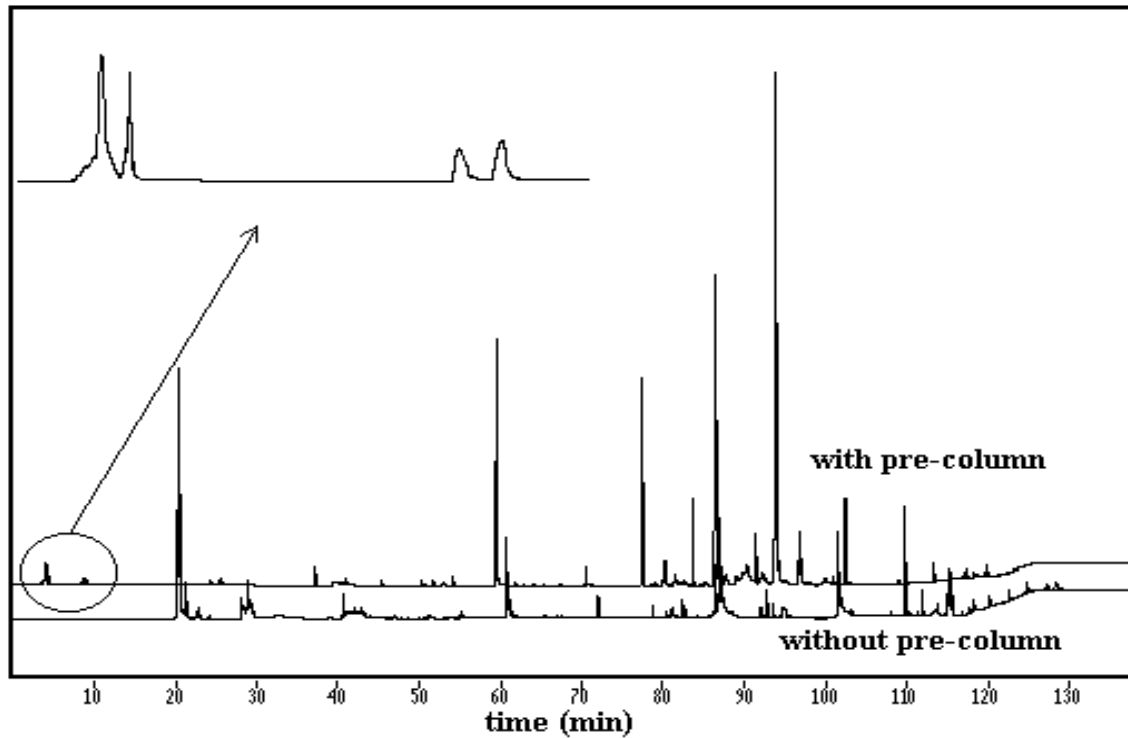


Figure 1: Chromatogram of the air sample with and without pre-column

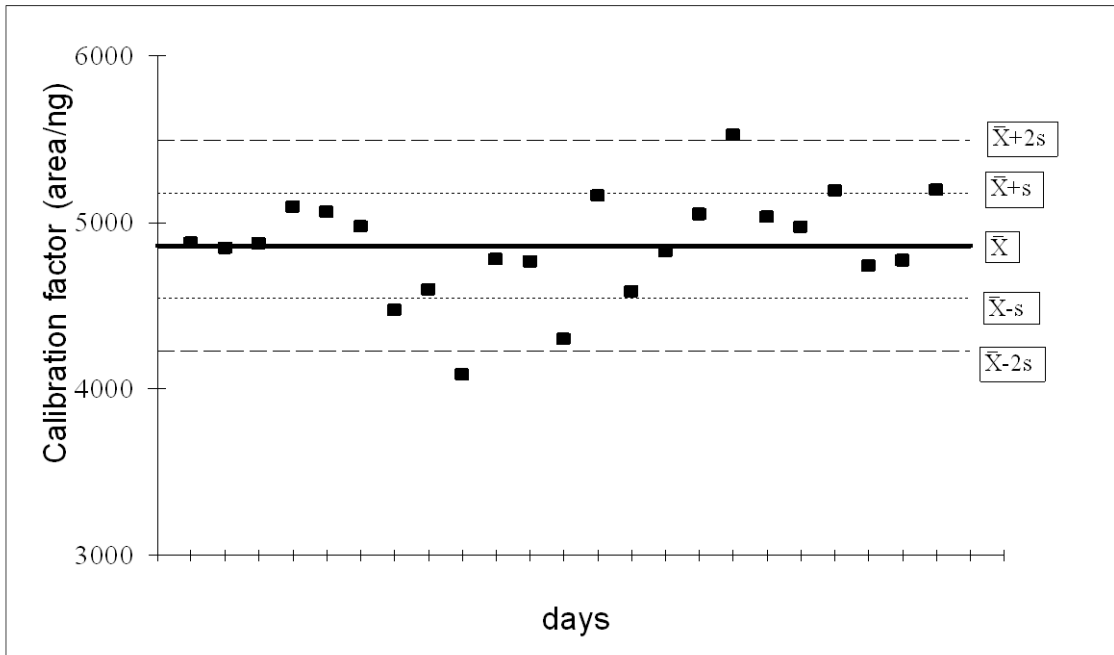


Figure 2: Fluctuations of calibration factor during several consecutive days for the system used for C₂-C₁₀ determination

The precision of analytical procedure was tested. Relative standard deviations (RSDs) for ten consecutive injections of 0.5 ml of standard gas mixture, Can mix 1, varied from 6-13%. In case of ten consecutive injections of 0.2 ml of standard gas mixture, Can mix 222, RSDs varied from 5-14%. These results (Table 3) show that the procedure is precise enough to use it for analysis of air samples.

Table 3: Precision of measurements of peak areas for C₂-C₆ n-alkanes and C₂-C₆ 1-alkenes using two standard gas mixtures

Substance	average peak area*10 ³ (10 injections)	s	RSD (%)
Can mix 1			
Ethane	47	4	8
Propane	73	6	9
n-butane	95	8	8
n-pentane	120	8	6
n-hexane	190	25	13
Can mix 222			
Ethane	123	6	5
Propene	160	22	14
1-butene	226	19	9
1-pentene	305	34	11
1-hexene	437	55	13

For the determination of the precision of real samples eight samples (0.5 l, flow was 100 ml/min) were taken with two sampling systems (four samples with each system) in an hour period. Sampling of laboratory (closed laboratory) air was performed. Precision of measurements of real air samples was slightly worse compared to the results obtained with standard mixtures, RSDs varied from 13-49%. Results are shown in Table 4. It should be mentioned that experimental conditions in the lab, where sampling took place, were not ideal.

To improve sampling as well as chromatographic determination some changes in sampling as well as in instrumental approaches were introduced. To improve effectiveness of collection of lower VOCs, the

stainless steel tubes were packed with larger amount of Carbosieve S-III. (samplers S6, Table 1). Using such combination of sorbents the blank values for preconditioned samplers were satisfactory (0.78 ng/cartridge for benzene, 0.24 ng/cartridge for toluene. For most of others VOCs blank values were below LOD of the method.

Table 4: Precision of analytical procedure for air sampling

Substance	Average peak area (measurements)		(%)
Benzene			
Toluene			
Ethylbenzene			
o-Xylene			
m-Xylene			
p-Xylene			
Styrene	8		
1,2-Dichlorobenzene			

Separation of C₂-C₁₀ VOCs was performed on two chromatographic systems with different types of capillary columns. In this case the separation was performed at temperatures higher than 3°C, the problems that resulted from water freezing were therefore avoided. For the determination of C₂-C₆ VOCs GC (Hewlett Packard), connected to FID was used. Substances from the sample were separated on the Rt-Alumina column. The second system was used for determination of C₅-C₁₀ VOCs. The system consisted of GC (Varian Star 3400 CX) with one cryo trap, lined with two equal parallel columns. One of them was connected with FID, used for quantitative determination of VOCs and the second one was MS (Varian Saturn 2000, ITD), used for qualitative evaluation of the samples.

During several consecutive days calibration factors of both systems fluctuated mainly in an interval of one standard deviation round average value (Figs 3 and 4).

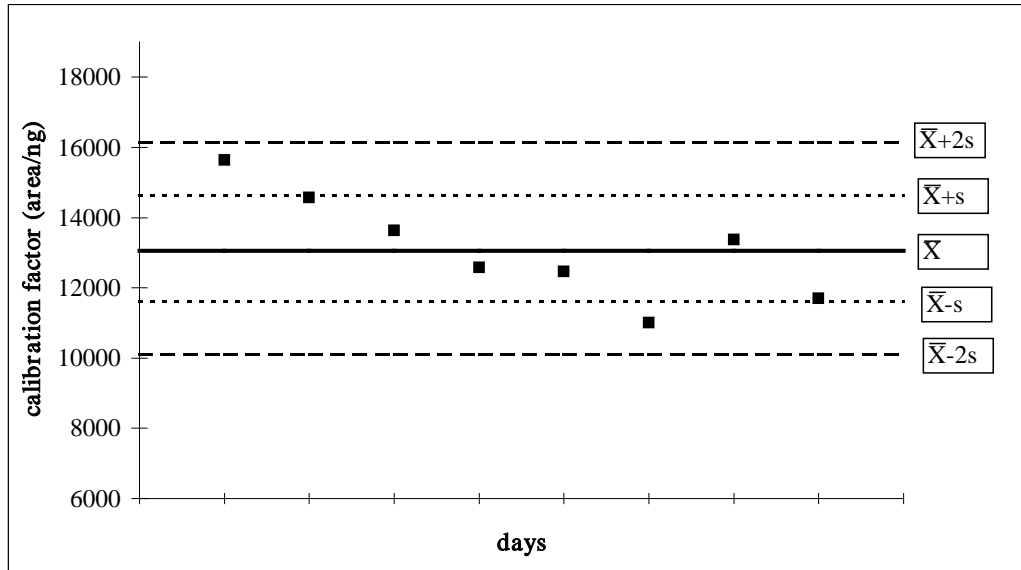


Figure 3: Fluctuations of calibration factor for the system used for determination of C₂-C₆ VOCs

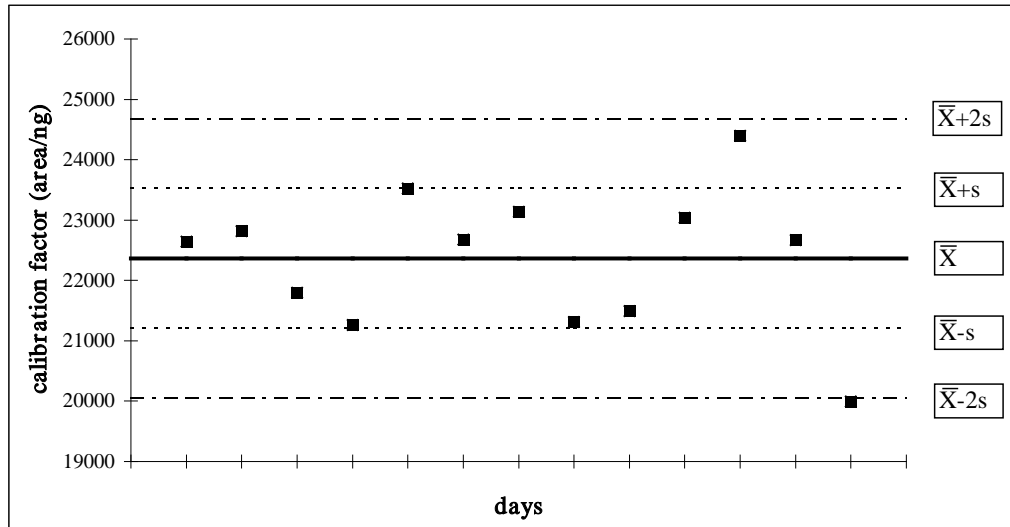


Figure 4: Fluctuations of calibration factor for the system used for determination of C₅-C₁₀ VOCs

Precision of the analytical procedure (RSDs), varied between 6-13%. (Tables 5 and 6)

Table 5: Precision of signal areas on the FID for alkanes and alkenes using standard gas mixture with the system for determination of C₂-C₆ VOCs

	average area*10 ³ (10 injections)	s	RSD (%)
Can mix 220			
Ethane	572	37	6
Propane	912	14	2
n-butane	1154	21	2
n-pentane	1447	19	1
n-hexane	1672	39	2
Can mix 222			
Ethane	581	32	5
Propene	886	18	2
1-butene	1167	24	2
1-pentene	1487	20	1
1-hexene	1559	23	1

Table 6: Precision of signal areas on the FID for alkanes and alkenes using standard gas mixture with the system for determination of C₅-C₁₀ VOCs

	average area*10 ³ (10 injections)	s	RSD (%)
Can mix 220			
Ethane	572	37	6
Propane	912	14	2
n-butane	1155	21	2
n-pentane	1447	19	1
n-hexane	1672	39	2
Can mix 222			
Ethane	581	32	5
Propene	886	18	2
1-butene	1167	24	2
1-pentene	1487	20	1
1-hexene	1559	23	1

Precision of the results for air samples (Table 7), using the same procedure as described above, was slightly worse than the one for standards but it was also significantly better than the precision of the of the previous method.

Table 7: Precision of measurements of VOCs for collected samples

	Average (4 measurements) Concentration ($\mu\text{g}/\text{m}^3$)	S	RSD (%)
First series			
Benzene	5.30	0.31	6
Toluene	9.60	0.44	5
Ethilbenzene	1.50	0.09	6
M/p-xilene	4.91	0.31	6
o-xilene	1.91	0.20	11
Second series			
Benzene	5.82	0.54	9
Toluene	12.13	0.39	3
Ethilbenzene	2.02	0.17	8
M/p-xilene	6.27	0.14	2
o-xilene	2.41	0.10	4
Third series			
Benzene	5.42	0.63	12
Toluene	12.28	0.30	2
Ethilbenzene	2.00	0.09	4
m/p-xilene	6.27	0.19	3
o-xilene	2.40	0.20	8

For qualitative determination retention times of reference substances ($\text{C}_2\text{-C}_5$) or mass spectrometric data were used. For this purpose our own library of mass spectra for reference substances, scanned under same conditions as mass spectra of substances in the air samples were elaborated. The distinction between our mass spectra and mass spectra of the same substance from NIST 92 library was in slight difference of intensity of some mass fragments and in mass fragments arising from the background. For identification NIST 92 as well as our own libraries were used.

The accuracy of the method was checked with intercomparison studies performed during during VOTAL/LOOP campaign (May- June 1998). The results shown in Table 8 indicate good agreement of results of both groups.

Table 8: Comparison of results for VOC's obtained by FKKT and ETH – Zurich during VOTAL/LOOP campaign (concentrations are in ppbv)

Starting time	10:30	11:00	11:30	12:00	13:00	13:30	14:00	14:30
Benzene								
UL-FKKT	0.29	0.36	0.28	0.33	0.35	0.34	0.32	0.57
ETH Zurich	0.41	0.30	0.23	0.28	0.32	0.29	0.23	0.23
Toluene								
UL-FKKT	3.40	3.02	3.03	1.18	1.07	0.86	0.69	0.76
ETH Zurich	3.77	3.19	3.48	1.51	1.23	0.95	0.84	0.88
Ethylbenzene								
UL-FKKT	0.21	0.22	0.10	0.13	0.14	0.10	0.11	0.12
ETH Zurich	0.24	0.28	0.13	0.16	0.16	0.13	0.13	0.14
m/p-Xylene								
UL-FKKT	0.74	0.77	0.32	0.38	0.37	0.26	0.28	0.32
ETH Zurich	0.73	0.86	0.39	0.45	0.38	0.31	0.31	0.37
o-Xylene								
UL-FKKT	0.24	0.22	0.16	0.18	0.20	0.12	0.10	0.13
ETH Zurich	0.32	0.34	0.21	0.22	0.19	0.16	0.17	0.18

In some cases the identification of individual compounds using mass-spectrometer is hindered because of similarity in their chemical structure (several groups of VOCs have the same molecular formula). In such cases the reliable identification of the unknown compound can be achieved by combination of mass spectra of the particular compound with its retention property. Sometimes it may not be possible to obtain experimental information about the retention property of the unknown compound due to the lack of available standard material. A theoretical prediction of the retention indices can be used as an alternative method to obtain an estimate of the retention property of unknown compound.

An approach that tries to establish a correlation between the chemical structure and the retention property of the particular compound is called quantitative structure retention relationship (QSRR) research. QSRR study involves two main stages. At the beginning the chemical structure must be translated to the computer readable form, and afterward the quantitative correlation between a chemical structure and its property can be obtained using different statistical and learning procedures like multiple linear regression (MLR) model or different types of artificial neural networks (ANNs). The major problem in QSRR studies remains a mathematical representation of chemical compounds, that is, transformation of molecular structure to the computer-readable form. The structural code should be uniform, that is, it should have the same number of components regardless of the type of the molecule, should correlate well with the property value measured experimentally and, if possible, should give some physical insight to the molecular behaviour.

In our work the theoretical prediction of gas chromatographic retention indices for the group of organic compounds which are usually found in the ambient air was investigated. Gas chromatographic retention indices were obtained on nonpolar stationary phase. The retention indices were predicted from different types of molecular descriptors using multilinear regression model as well as different types of artificial neural networks (ANNs). The most appropriate subset of descriptors for MLR model was selected by minimising an error in prediction during stepwise selection procedure using CODESSA software.

We have investigated the coding capabilities of topological description indices for QSRR studies. The topological indices were selected for the representation of the chemical structures because of their simplicity and effectiveness. They are easy to calculate and therefore could be used also by chromatographers who are not expert in structural representation. A very heterogeneous data set was selected to test whether our description vector is capable of encoding different types of interactions that are responsible for the retention properties.

Of 57 topological descriptors, 16 were selected on the basis of prediction results of the MLR model. A complete selectivity of the description vector was achieved. The same set of structural descriptors was used also for the creation of back propagation of error (BPE) and counterpropagation (CP) ANNs Table 9.

The worst results were obtained by the CP ANN model. The MLR model gave better results than, to our best knowledge, any previous similar study without the use of complicated electrotopological and quantum-chemical descriptors or even physical properties such as the boiling points of the molecule. Although the description vector was optimized for the MLR model, the BPE ANN model improved the prediction results. The average RMS value in a 10-fold cross-validation procedure was 19.2 retention time units. The proposed system for the prediction of gas-chromatographic retention indices on a nonpolar stationary phase is robust. Because of its simplicity it is suitable also for routine work. It can solve identification problems where unspecific fragmentation in homologous series occurs in a MS detector and hinders identification of organic compounds during GC-MS analysis.

Table 9: Prediction results using ten-fold crossvalidation procedure

	MLR				BPE ANN				CP ANN			
	RMS	r²	b₁	b₀	RMS	r²	b₁	b₀	RMS	r²	b₁	b₀
AVG	22.5	0.974	0.978	10	19.2	0.981	0.993	5	36.1	0.938	0.938	29
S	6.0	0.016	0.032	17	3.3	0.008	0.033	16	8.8	0.027	0.034	18
RSD[%]} (%)	26.6	1.6	3.3	180	17.1	0.9	3.3	325	24.5	2.9	3.6	64

AVG - average value of ten-fold cross-validation procedure

s - standard deviation of ten-fold cross-validation procedure

RSD - relative standard deviation of ten-fold cross-validation procedure

The method for simultaneous determination of C2-C10 volatile HCs was used during the VOTALP project (Vertical Ozone Transports in the Alps). More than 100 samples obtained within two measuring campaigns were analyzed in which 24 anthropogenic and 10 biogenic VOCs were determined. In the second VOTAP campaign over two hundred of samples were analyzed and 16 anthropogenic and 4 biogenic HCs were evaluated.

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References

- [1] C. Nicholas Hewitt, Xu-Liang Cao, Christophe Boissard, S. Craig Duckham (1995) *Volatile Organic Compounds in the Atmosphere*, Ed. R. E. Hester and R. M. Harrison, The Royal Society of Chemistry, Cambridge, 17-36.
- [2] F. J. Fehsenfeld, J. Calvert, R. Fall, P. Goldan, A. B. Guenther (1992) *Global Biogeochemical Cycles* 6: 389-430.
- [3] G. P. Brasseur and R. B. Chatfield (1991) *Trace gas emissions by plants*, Ed. T.D. Sharkey, E.A. Holland and H. A. Mooney, San Diego, London, Academic Press, Inc. p.p. 1-27.
- [4] W. P. Carter and R. Atkinson (1989) *J. Atmos. Chem.* 8: 165-173.
- [5] R. S. Martin, H. Westberg, E. Allwine, L. Ashman, J. C. Farmer (1991) *J. Atmos. Chem.* 13: 1-32.
- [6] R. Atkinson, S. M. Aschmann and J. Arey (1990) *Atmos. Environ.* 24A: 2647-2654.
- [7] T. Hoffman (1995) *Fresenius J. Anal. Chem* 351: 41-47.
- [8] J. Rudolph, K. P. Müller, R. Koppmann (1990) *Anal. Chim. Acta* 236: 197-211.
- [9] J. B. Clements, R. G. Lewis (1988) *Principles of Environmental Sampling*, Ed. Lawrence H. Keith, American Chemical Society, United States of America, 287-296.
- [10] P. Leinster, R. Perry, R. J. Young (1977) *Talanta* 24: 205 - 213.

- [11] K. Figge, A. M. Dommrose, W. Rabel, W. Zerhau (1987) *Fresenius J. Anal. Chem.* 327: 279 - 292.
- [12] Th. Class, K. Ballschmiter (1986) *Fresenius Z. Anal. Chem.* 325: 1 - 7.
- [13] D. Helmig, L. (1995) *Anal. Chem.* 67: 4380 - 4386.
- [14] A. Calogirou, B. R. Larsen, C. Brussol, M. Duane, D. Kotzias (1996) *Anal. Chem.* 68: 1499 - 1506.
- [15] R. J. B. Peters, J. A. D. V. Renesse V. Duivenbode, J. H. Duyzer, H. L. M. Verhagen (1994) *Atmos. Environ.* 28: 2413 - 2419.
- [16] E. Pellizzari, B. Demian, K. Krost (1984) *Anal. Chem.* 56: 793-798.
- [17] X. - L. Cao, C. N. Hewitt (1994) *Environ. Sci. Technol.* 28: 757 - 762.
- [18] P. A. Clausen, P. Wolkoff (1997) *Atmos. Environ.* 31: 715 - 725.
- [19] D. P. Rounbehler, J. W. Reisch, J. R. Coombs, D. H. Fine (1980) *Anal. Chem.* 52: 273 - 276.
- [20] M. B. Neher, P. W. Jones (1977) *Anal. Chem.* 49: 512 - 513.
- [21] E. D. Pellizzari, K. J. Krost (1984) *Anal. Chem.* 56: 1813 - 1819.
- [22] X. - L. Cao, C. N. Hewitt (1994) *J. Chromatogr. A* 688: 368 - 374.
- [23] D. Helmig (1997) *Atmos. Environ.* 31: 3635 - 3651.
- [24] J. Begerow, E. Jermann, T. Keles, T. Koch, L. Dunemann (1996) *J. Chromatogr. A* 749: 181 - 191.
- [25] J.T. Scanlon, D.E. Willis (1985) *J. Chromatogr. Sci.* 23: 333-340.
- [26] J.L. Esteban, I. Martinez-Castro, R. Morales, B. Fabrellas, J. Sanz (1996) *Chromatographia* 43: 63-72.
- [27] V. Simon, M.-L. Riba, A. Waldhart, L. Torres (1995) *J. Chromatogr. A* 704: 465 - 471.
- [28] H. Rothweiler, P. A. Wäger, C. Schlatter (1991) *Atmos. Environ.* 25B: 231 - 235.
- [29] D. Helmig, L. Vierling (1995) *Anal. Chem.* 67: 4380 - 4386.
- [30] C. Prado, J. F. Periago, A. Sepúlveda-Escribano (1996) *J. Chromatogr. A* 719: 87 - 93.
- [31] C. Coeur, V. Jacob, I. Denis, P. Foster (1997) *J. Chromatogr. A* 786: 185 - 187.
- [32] Q. Gong, K. L. Demerjian (1995) *Air & Waste Manage. Assoc.* 45: 490 - 493.