



Determination of VOCs in the Indoor Air of a New and a Renovated Apartment

Ludmila Meciarova, Silvia Vilcekova

Technical University of Košice
Faculty of Civil Engineering, Institute of Environmental Engineering
e-mail: silvia.vilcekova@tuke.sk, ludmila.meciarova@tuke.sk

Abstract

This study deals with the occurrence of volatile organic compounds (VOCs) in the indoor environment of a new and a renovated apartment. Qualitative determination of VOCs was carried out with a gas chromatograph with surface acoustic wave detector (GC/SAW). Concentrations of total volatile organic compounds (TVOC) were determined by a photoionization detector with UV lamp. Simultaneously, temperature and relative humidity were monitored with a data logger. The aim of this study was to determine of TVOC concentrations, to use of GC/SAW for determination of individual VOCs in indoor air as well as to predict possible sources of VOCs in these apartments. Measurements were performed after each construction work for better resolution of the contributions of individual materials to the levels of VOC. Mean concentrations of TVOC were $624 \mu\text{g}/\text{m}^3$ in the renovated apartment and $1,686 \mu\text{g}/\text{m}^3$ in the new apartment after completion of all works. The results from the renovated apartment showed that the use of new materials can lead to lower levels of organic compounds in indoor air compared to old materials that were less environmentally friendly. Many types of VOCs were found in both apartments. After reviewing the possible sources, it seems that the main sources of these substances were applied coatings and flooring materials.

Key words: indoor air, apartments, volatile organic compounds, GC/SAW, material emissions

1 Introduction

Many studies around the world focused on the occurrence of VOCs in the indoor environment have been carried out in recent decades. For example, more than 200 VOCs in indoor air were identified in Helsinki using gas chromatography-mass spectrometry (GC/MS). Most occurring compounds were alkyl benzenes, alkanes, terpenes, aliphatic aldehydes and chlorinated aliphatic hydrocarbons. Aromatic hydrocarbons; terpenes; some alkylcyclohexanes; 1,1,1-trichloroethane; and tetrachloroethane were most frequently occurring with increased concentrations in homes with symptoms of SBS and total volatile organic compounds (TVOC concentrations) ranged from 40 to $235 \mu\text{g}/\text{m}^3$ [1]. Samples were collected in 23 households and 10 workplaces in Tromsø, Norway, located in the Arctic region. TVOC concentrations

ranged from 106 to 584 $\mu\text{g}/\text{m}^3$. Interesting is that higher concentrations were measured in households than in workplaces. Most occurring compounds were terpenes (limonene) [2]. The indoor and outdoor levels of gaseous pollutants were determined during winter (from January to March) and summer (from July to September) in 602 randomly selected apartments in various regions of Japan. Almost all concentrations in the indoor environment were higher than outside, and almost all concentrations were higher in summer than in winter [3]. Benzene; toluene; xylenes; ethylbenzene; 1,3,5-trimethylbenzene; methylene chloride; chloroform; trichloroethylene; 1,4-dichlorobenzene; and tetrachloroethene were the most common VOCs in residential buildings investigated in Hong Kong [4]. 2302 samples were collected by the method of active sampling on tubes filled with Tenax-TA and analysed by gas chromatography and thermal desorption in 902 flats in the city of Hangzhou in China. Apartments studied had been furnished in the previous year. The average TVOC concentration was 650 $\mu\text{g}/\text{m}^3$ in each newly furnished room. Concentrations were determined in the bedroom, living room and laundry room. The highest average TVOC concentration of 770 $\mu\text{g}/\text{m}^3$ was measured in the living rooms [5]. As can be seen the levels of VOCs as well as the type of VOCs present in the interior are different according to the country, the region, the type of building but also between the rooms.

Production of building materials has evolved in recent years. Development of new technologies of building materials production has been reflected in the occurrence and levels of organic compounds indoors. Therefore it is necessary to deal with this issue. The most often used method for the investigation of indoor air quality (IAQ) is active sampling with Tenax TA and analysis by GC/MS. However, this method is time-consuming. Therefore, we decided to use technology of gas chromatography with surface acoustic wave detector (GC/SAW) for this purpose. The aim of this study was to determine the TVOC concentrations, the utilization of GC/SAW for determination of individual VOCs in indoor air and to predict possible sources of VOCs in two selected apartments in Kosice for further research.

2 Materials and methods

2.1 Renovated apartment

The apartment is located in a residential building built in 1960. This is an insulated building from brick blocks with central heating and with 4 floors. The two-room apartment on the 4th floor was chosen for this study. Four measurements were conducted in this apartment during the months of October and November. Measurements were conducted in the living room connected with the kitchen with a floor area of 23.1 m^2 and room height of 2.7 m. The apartment is naturally ventilated. The description of the sequence of sampling campaigns is summarized in Table 2.

2.2 New apartment

Construction of chosen residential building began in April 2013 and ended in July 2014. This building from brick blocks has 4 floors, 24 apartments, central heating and it is thermally insulated. For this research, the apartment on the 2nd floor was selected, which is oriented to

the north. Inside the apartment, three measurements (Table 3) were carried out, each at an interval of one month. The total area of the apartment including the balcony is 74.23 m². Measurements were performed in the entire apartment but for this study results from the living room with connected kitchen are important. The floor area is 32.99 m² in this room. The apartment is naturally ventilated. This new apartment has been unoccupied and unfurnished during the measurement in August (the first measurement).

Table 1: The description of the sequence of sampling campaigns in the renovated apartment

Date	Process	Materials and equipment
05-06/10/2014	initial plaster has been removed from ceiling and walls	2 plastic windows, wooden doors, floor consisting of three layers of PVC and two layers of wood flooring in thickness of approximately 10 cm bonded with resin
07/10/2014	first measurement	
14/10/2014	removal of the old floor	
15/10/2014	application of new plaster	lime cement plaster
16/10/2014	second measurement	
02/11/2014	application of levelling course	concrete course
04/11/2014	installation of new flooring	laminated flooring which does not require the use of adhesives for installation
05/11/2014	third measurement	
08/11/2014	application of bonding primer	bonding primer (max. content of VOCs in the product ready to use – 5 g/l)
09/11/2014	painting	white interior paint on base of aqueous dispersion of polymeric binders (max. content of VOCs in the product ready to use – 2 g/l) and acrylic green paint (max. content of VOCs in the product ready to use – 30 g/l)
11/11/2014	installation of kitchen unit	particleboard
13/11/2014	fourth measurement	

Table 2: The description of the sequence of sampling campaigns in the new apartment

Date	Process	Materials and equipment
05/08/2014	first measurement	lime cement plaster, basic white water-based paint, laminated flooring, plastic windows, plastic foils instead of internal doors
04/09/2014	the apartment was partially furnished	upholstered chair, small cabinet from particleboard, synthetic carpet with dimensions of 1x1 m, and kitchen unit produced from wooden pallets
08/09/2014	second measurement	
04/10/2014	painting	green acrylic copolymer emulsion (max. content of VOCs in the product ready to use – 30 g/l) and white disperse water soluble paint (max. content of VOCs in the product ready to use – 30 g/l)
07/10/2014	addition of another furniture	TV stand from particleboard and a sofa made from wooden pallets
08/10/2014	third measurement	

2.3 Sampling and analysis

Measurement of TVOC concentrations was performed using ppbRAE3000. This is a photoionization detector with UV lamp which allows seeing results from the measurements immediately and directly on the spot. The monitor has specified accuracy (isobutylene) from 10 to 2,000 ppm: $\pm 3\%$ at calibration point [6], measuring range is from 1 ppb to 10,000 ppm with a three-second response time [7]. Two-point field calibration of zero and standard reference gases were carried out for ppbRAE before measurements. As mentioned above, GC/SAW was used for analysis of VOCs in this research. The method used for all measurements included the inlet temperature of 200°C, valve temperature of 165°C, column temperature from 40 to 200°C, sensor temperature of 10°C, sampling time of 60 seconds (0.5 ml/s = 30 ml) and analysis time of 20 seconds. The manufacturer of GC/SAW (zNoseTM) specifies the precision of 5% RSD, 10% accuracy and sensitivity at low ppb level for most compounds [8]. The system was calibrated to the alkane response with a solution of C₆-C₂₂ in methanol before measurements. Sampling with GC/SAW was repeated 10 times, therefore, the amount of analyzed air was 300 ml for each measurement. The system can analyze hydrocarbons in the range of C₄ – C₂₅. Sensor temperature can range from 0 to 150°C. Sensitivity of detector can be increased by lowering its temperature. Simultaneously, the air temperature and relative humidity (RH) were monitored using data logger Testo 175-H2. No detergents or fragrances were used during 12 hours prior to each measurement in the apartments. The builders and owners of the apartments were also requested not to smoke at least 12 hours prior to measurements being taken in the apartment. Windows and doors were closed during each measurement. All measurements with all devices were made in the morning hours and lasted 30 minutes. The measuring time was sufficient for the purpose of this study because both devices for determining VOCs work quickly and as mentioned above allow users to see the results directly on the spot. All measuring devices were placed in the middle of the rooms approximately 1 m above the floor. Although, formaldehyde is commonly found in indoor air, it was not measured in this study.

3 Results and discussion

Outdoor air temperature during the measurements in the renovated apartment was 10°C, 14°C, 8°C and 9°C, respectively. Table 4 shows measured indoor air temperature, relative humidity (RH) and infiltration rate. As can be seen, the differences between determined temperatures were not significant. The difference between the highest and lowest value of RH was 17%. The outdoor air temperature during the measurements in the new apartment was 23°C, 20°C and 12°C, respectively. In this case, the difference between the highest and lowest value of RH was 9%. Temperatures measured in the new apartment were higher because the measurements were performed in the warmer part of the year. Air exchange was caused only by infiltration through closed windows and doors during all measurements. The results from determination of TVOC concentrations are shown in Table 5. The TVOC concentrations were highest (14,163 $\mu\text{g}/\text{m}^3$) in the renovated apartment after the removal of the old floor which resulted into the release of organic compounds from the resin. In this case, a new plaster was also applied and the lowest infiltration could also contribute to this concentration.

Table 3: Air temperature, RH and infiltration rate in the renovated apartment and new apartment

Renovated apartment	RH [%]		Temperature [°C]		Infiltration rate [m ³ /h]
	Mean	SD	Mean	SD	
1 st measurement	67	2.3	19.4	0.4	0.024
2 nd measurement	75	1.8	20.5	0.4	0.019
3 rd measurement	73	0.8	20.3	0.3	0.028
4 th measurement	58	1.1	20.5	0.2	0.024
New apartment					
1 st measurement	54	1.5	27.2	0.8	0.053
2 nd measurement	60	1.6	25.1	0.5	0.015
3 rd measurement	63	0.6	22.9	0.05	0.016

It is interesting that during the first measurement, the initial level was quite high (913 $\mu\text{g}/\text{m}^3$). This concentration was even higher than the concentration reached after the painting and installation of a new kitchen unit (624 $\mu\text{g}/\text{m}^3$). The air temperature was higher by 1.1°C, RH was lower by 9% and infiltration rate was the same, compared with the first measurement. Although these differences are negligible at first sight, the higher temperature could lead to higher concentrations of TVOC. Also it is known that after renovation, TVOC concentrations tend to reach high levels due to the installation of new materials. But in this case, new materials were better than the old ones in terms of emissions of organic compounds. Effect of air temperature and relative humidity on VOC emission from building materials has been investigated in many studies. It was found that the temperature has a major impact on the emission rate of VOCs from building materials, because the temperature affects the vapor pressure and the diffusion coefficients of the emitted VOCs. However, at present it is difficult to generalize it for all VOCs, because their emission may depend partly on the VOC polarity and material's composition [9].

Table 4: TVOC concentrations in the renovated apartment and new apartment

Renovated apartment	TVOC [$\mu\text{g}/\text{m}^3$]			
	Minimum	Maximum	Mean	SD
1 st measurement	580	1,065	913	144.4
2 nd measurement	10,085	17,462	14,163	2,195.2
3 rd measurement	370	463	439	26.62
4 th measurement	570	681	624	32.8
New apartment				
1 st measurement	126	201	140	14.9
2 nd measurement	261	433	311	50.1
3 rd measurement	1,587	1,806	1,686	73.7

A surprisingly low concentration (140 $\mu\text{g}/\text{m}^3$) was observed during the first measurement in the new apartment (which was carried out a month after finishing the building). It should be noted that there was the highest infiltration in the room during this measurement. The TVOC concentrations were highest (1,686 $\mu\text{g}/\text{m}^3$) in the new apartment after the painting stage. The difference between the final levels in apartments was 1,062 $\mu\text{g}/\text{m}^3$, thus the level in the new apartment was approximately three times higher than in the renovated apartment. These apartments have many similarities, such as: type of plastic windows, type of flooring, masonry made from brick, type of plaster, central heating, thermal insulation of building from

polystyrene and natural ventilation. However, it should be noted that living room in the new apartment is by 9.89 m² larger than in the renovated apartment.

Tables 6 and 7 present the results from identification of individual VOCs in apartments using GC/SAW. This device assigns each detected compound a number called Kovats index. Based on this number, individual compounds are identified using available databases. Considering the concentrations of individual VOCs were not measured in this study, the sources of identified VOCs were predicted from available literature sources and databases.

Table 5: Identified VOCs in the renovated apartment

Compound	CAS number	07/10/2014 1 st measurement	16/10/2014 2 nd measurement	05/11/2014 3 rd measurement	13/11/2014 4 th measurement
norbornane	279-23-2				*
toluene	108-88-3	*	*	*	
o-xylene	95-47-6	*	*	*	*
β-pinene	127-91-3				*
bis(2-chloro-1-methylethyl) ether	108-60-1	*	*		
limonene	138-863				*
p-cymene	99-87-6			*	
1,2-diethylbenzene	135-01-3				*
undecane	1120-21-4				*
2,6-dimethyl phenol	576-26-1		*		
nonanal	124-19-6	*			
hexyl isobutyrate	2349-07-7		*		
3-decanol	1565-81-7		*		
1-dodecene	112-41-4	*			
2,3-dimethylbenzamine	87-59-2				*
citral	5392-40-5		*		
carvone	99-49-0				*
carvotanacetone	499-71-8	*		*	
1-tridecene	2437-56-1		*		
2-phenoxyetanol	122-99-6				*
1-methylnapthalene	90-12-0	*			
tridecane	629-50-5			*	
4-allyl-2-methoxyphenol	97-53-0		*		
1,3-indandione	606-23-5				*
cis-carvyl acetate	1205-42-1	*		*	
2-chloronaphtalene	91-58-7		*		
longicyclene	1137-12-8			*	
biphenyl	92-52-4				*
1-chloronaphtalene	90-13-1	*			
terpinyl isobutyrate	7774-65-4				*

Main sources of toluene in an indoor environment are adhesives, floor coverings, paint, chipboard [10] linoleum, PVC etc. [11]. Toluene was detected during three measurements in the indoor air of the renovated apartment and during two measurements in the new apartment. Toluene was most probably released from floor coverings in the renovated apartment and from furniture or paints in the new apartment. Adhesives, floor coverings, [11] floor lacquer, paints, wallpaper, varnish, tobacco smoke etc. [10] are important sources of o-xylene, which was the most occurring compound in both apartments. Sources of this compound were floor coverings and paints in the renovated apartment and floor coverings or paints as well as varnish in the new apartment.

Table 6: Identified VOCs in the new apartment

Compound	CAS number	05/08/2014 1 st measurement	08/09/2014 2 nd measurement	08/10/2014 3 rd measurement
toluene	108-88-3		*	*
o-xylene	95-47-6	*	*	*
α -pinene	80-56-8	*		
pentyl propionate	624-54-4	*		
2,4,5-trimethylthiazol	13623-11-5		*	
bis(2-chloro-1-methylethyl) ether	108-60-1		*	*
p-cymene	99-87-6	*		
undecane	1120-21-4	*		*
2,6-dimethylphenol	576-26-1		*	
hexyl isobutyrate	2349-07-7		*	
undecanal	112-44-7			*
(E)-2-nonenal	18829-56-6	*		
carvone	99-49-0		*	
ethyl 2-phenylacetate	101-97-3	*		
carvotanacetone	499-71-8			*
menthyl acetate	29066-34-0		*	
2-phenoxyetanol	122-99-6	*		
tridecane	629-50-5			*
longifolene	475-20-7	*		

P-cymene is utilized in fragrances [12] but this compound was also detected in particleboard samples [13]. According to that this compound was identified in both apartments after flooring installation, the source of p-cymene could be laminate flooring. Bis(2-chloro-1-methylethyl) ether has been used extensively in paint and varnish removers, spotting agents, and cleaning solutions. This compound has also been used as an intermediate in the manufacture of resins, dyes, and pharmaceuticals and has been added to soap solutions to aid in textile cleaning [14]. Therefore, the source of this compound could be resin used in the floor construction, because after the removal of the old floor, bis(2-chloro-1-methylethyl) ether was not identified in the indoor air. On the other hand, cleaning products were most probable sources in the new apartment. Indoor sources of undecane include adhesives, paints, gasoline, combustion sources, flooring (wood, PVC) etc. [10, 11]. In this study, undecane was identified after painting in both apartments, thus it is possible to say that source of undecane were applied paints.

A delayed emission may occur in the indoor environment, that is, compounds emanating from activities or newly installed materials are adsorbed onto other materials, from which they are subsequently emitted at a much lower rate than from the original materials. A well-known example of delayed emission is the odor of environmental tobacco smoke (ETS) that may be perceived in room air several months after smoking was terminated [15]. In this case, 2,6-dimethyl phenol (both apartments) and 2,3-dimethylbenzamine (found in tobacco smoke [16]) were identified although smoking was excluded 12 hours before the measurement.

Undecanal was also detected in the study of Glas et al. [17] in the eight office buildings situated in Umeå, a town in northern Sweden. Carvone is a terpene natural product. Wood, wooden products and coatings are emission sources for terpenes in indoor rooms. Terpenes are also to be found in cleaning agents, cosmetics, air fresheners, paints, lacquers and oils.

Carvone is a very interesting compound, which, on the one hand, is a component in natural terpene balsam and, on the other hand, is also a possible oxidation product of limonene [18]. Sources of carvone were the new kitchen unit or paints in the renovated apartment and furniture in the new apartment.

A possible source of 2-phenoxyethanol in the indoor environment is carpet [19] but this compound was found in both apartments after flooring installation. Emissions of alpha-pinene and beta-pinene were identified from PVC flooring, gypsum board or chipboard by Meininghaus et al. [20]. Beta-pinene has been identified as a volatile organic ingredient of wood-based furniture with its possible source being an ecological coating system based on natural resins, nitrocellulose, and/or softwood construction [21]. The source of beta-pinene was kitchen unit in the renovated apartment and the possible source of alpha-pinene was gypsum board, which was newly installed in the bathroom.

Limonene was identified by Wilke et al. [11] as a substance emitted from primer (used in renovated apartment). Nonanal occurs in ambient air and is also commonly detected in indoor samples at a relative occurrence of 5%, with reported concentrations ranging from 5-10 $\mu\text{g}/\text{m}^3$ [22]. Nonanal has been identified in emissions of volatile organic compounds from furniture coatings [23] and carpet cushions [24]. Some studies showed that nonanal was also present in indoor dust [25]. 1-Tridecene is used as a solvent [26]. This compound was identified by GC/MS in plastic waste [27]. Emission of 1-tridecene was also detected from PVC shower curtain [28]. Eugenol derivatives are used in manufacturing stabilizers and antioxidants for plastics and rubbers among other things [29]. The source of these compounds was PVC flooring in the renovated apartment.

1-Methylnaphthalene is used to make chemicals such as dyes and resins. Outdoor air contains low amounts of this compound, due to the burning of wood or fossil fuels [30]. The primary use of biphenyl is in the formulation of dye carriers for textile dyeing. Biphenyl is used as an intermediate for polychlorinated biphenyls and as a paper impregnant for citrus fruit where it acts as a fungicide. In the past, a major use of biphenyl has been as a component of heat-transfer fluids [31]. Biphenyl has been also reported in diesel exhaust [32]. This compound was identified also by Otson et al. [33] during the research of indoor air of Canadian residences. Thus, it can be said that biphenyl originates from outdoor air.

Citral is used in soap, detergent, creams and perfumes [34]. Terpinyl isobutyrate [35] and ethyl 2-phenylacetate [36] are also used in cosmetics. Diethylbenzenes were detected in 8 of 10 indoor air samples from 10 publicly accessible buildings (offices, schools, elderly homes and a hospital) [37]. The median suburban atmospheric concentration of 1,2-diethylbenzene is 0.172 ppb per volume from 202 samples, according to the National Ambient Volatile Organic Compounds (VOCs) Database [38]. 1-Dodecene was reported as a compound present in the exhaust of gasoline but also was qualitatively identified as VOC released from textile floor coverings [39]. According to that textile floor coverings were not used in this apartment, it is possible that this compound originates from outdoor air.

Tridecane is a common compound emitted from building materials. A lot of sources exist for this substance and it is difficult to say, which building materials, furniture or products are the potential source in these cases. 1-chloronaphthalene and 2-chloronaphthalene are used for wood preservation [40]. Emission of 1-chloronaphthalene was identified from flooring materials [41] and also from carpets [42]. Longicyclene and longifolene were identified by Wilke et al. [11] in emissions from adhesives for flooring installation. However, adhesives were not used

during flooring installation but were used for skirting in both apartments. Sources of other compounds are unknown.

4 Conclusion

According to Mølhave [43], TVOC concentrations lower than $200 \mu\text{g}/\text{m}^3$ have no effects on health or comfort of occupants. However, this recommended concentration level was exceeded during the second and third measurement in the new apartment and also when the apartment was already occupied. Thus, the occupants of apartment were directly exposed to higher levels of VOCs. This could be avoided by moving in occupants after the concentration reached a safe level. The occupants were advised to increase the air exchange rate in the first weeks after the end of the study. The results from the renovated apartment showed that the use of new materials led to lower levels of organic compounds in indoor air compared to old materials that were less environmentally friendly. Removing the source of pollution is a way to improve indoor air quality and this method was indirectly applied in this study. Currently, most of buildings are constructed by way that they are as air-tight as possible. However, a certain degree of infiltration is also beneficial regarding the level of VOCs in the indoor environment as demonstrated in this study. The main objective of this study was to test the suitability of GC/SAW for determination of volatile organic compounds in indoor air of buildings. The method chosen for measurement with the GC/SAW was appropriate (temperatures, times...). The advantage of this method is the speed of the analysis itself, device portability and the ability to see the results immediately in the field. However, main disadvantage was the length of column which could lead to overlapping of some compounds. Therefore, in another part of research will be necessary to carry out measuring not only with the GC/SAW but also with the GC/MS and to compare the acquired results. Also, further work will be focused on detailed research of applied coating substances and flooring materials from studied apartments in an environmental chamber.

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