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ANALYSIS OF VOCs IN THE INDOOR ENVIRONMENT

Volatile organic compounds have been studied over recent years in many countries. However, construction processes, building materials, building types and the methods used for the collection and analysis of VOCs vary from one country to another. At the same time constant technical and scientific progress has brought new materials that can emit completely different VOCs than older materials. Building materials represent significant source of organic compounds' emissions and we are in direct contact with these compounds at work, school or home every day. Short-term or long-term exposure to these substances can bring many health problems. Therefore, this study is focused to determine the current state of occurrence and concentrations level of VOCs. The studied building is located in eastern Slovakia. The results were compared with the guide values of other countries, because there are no guideline values for TVOC concentrations and limits are set only for a small amount of VOCs in Slovakia. The results from this study demonstrated that flooring installation together with painting caused the highest contribution to the TVOC levels in the indoor air of studied apartment. On the other hand, high levels of TVOC were not found after furnishing.

Keywords: renovation, apartment, electronic nose, indoor pollution

1. Introduction

Any chemical compound that contains at least one carbon and a hydrogen atom in its molecular structure is referred to as an organic compound. Volatile organic compounds (VOCs) are defined as compounds with boiling point ranging between 50°C and 260°C and their low boiling point means that they readily off-gas into indoor air [1]. VOCs of indoor origin are released by a variety of sources including building materials, furniture or human activities such as tobacco smoking, cleaning or cooking [2].

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Interest in VOCs in indoor environments started approximately in 1970s. This is evidenced by the large number of national studies that have been undertaken to model, quantify or identify indoor VOCs or that relate with indoor materials, indoor activities and some health and sensory effects [3]. These studies differ not only in focus but also in a way of sampling or analysis of VOCs.

The aim of this study was to perform VOCs analysis in the indoor air during renovation of an apartment. Levels of VOCs may be much higher than typical ambient levels in newly constructed buildings or those in which building work or decoration has recently taken place. This is because many of these compounds will off-gas a significant proportion of their volume in a relatively short time and their concentrations will decline exponentially and rapidly [1].

Similar study was conducted by Liang et al. who measured VOCs in a new apartment in Beijing from the beginning of interior construction to completion. The door, doorframe and cupboard released a wide variety of VOCs compared to furniture, and the wall paint (water-based) had the least number of VOCs identified. TVOC concentrations were very high and varied at each construction stage with concentrations from 1660 to 9030 $\mu\text{g}/\text{m}^3$. A slight increase of concentrations was observed after painting and huge increase occurred after installation of door and doorframe. Interesting is that concentrations decreased slowly in the cupboard and furniture stages [4]. Pang et al. measured VOCs concentrations in three households. The first was built using only conventional materials, the second used some environmentally friendly materials and the third used only environmentally friendly materials. The results showed that the living room and kitchen furniture made of particleboard and MDF emitted a large number of VOCs and the toluene concentration increased rapidly after the introduction of kitchen and living room indoor furniture [5].

2. Materials and methods

2.1. Studied object

Studied apartment is located in residential building from concrete panels built in 1988. This building has twelve floors, 48 apartments, it is not thermally insulated and it is situated in eastern Slovakia (Kosice). For this study, apartment on the ninth floor was selected. Ventilation is ensured only by natural way. Measurements were carried out in living room (72.9 m^3), bedroom (32.1 m^3) as well as in child's bedroom (32.1 m^3).

The first measurement was conducted to determine the initial state (before renovation) in November 2014. There were 27 years old PVC flooring, three years old wooden doors and plastic windows, and old coating on walls except the two walls in child's bedroom where coating and plaster were removed. New plaster based on gray cement and hydrated lime was applied on these walls and also on one wall in the living room. Bonding primer, gypsum as levelling

compound and white water-based paint were applied on walls and ceilings in all three rooms, but water-based blue paint from another manufacturer was also applied on two walls in the living room. Measurement was performed three days after the completion of these works. The third measurement was performed seven days after the installation of laminate flooring and plastic skirtings in all three rooms. Adhesives were used only for skirtings because this type of laminate flooring does not require use of adhesive for its installation. The water-based blue paint was applied on two walls in the living room again and water-based grey paint was applied on one wall in the child's bedroom. Paints on the walls were applied five days before measurement and synthetic white paint was applied on the radiators in each room three days before measurement. The apartment was furnished after approximately three months. Final measurement was carried out five days after these works. The apartment was not occupied during first three measurements and was not heated during all measurements. There were new cabinets, closets, coffee table, and shelves made from particleboard and MDF, sofa and beds made from combination of fabric with artificial leather, and electronic devices in the studied rooms.

2.2. Sampling and analysis

Indoor air temperature and relative humidity was measured with data logger TESTO 175-H2 with specified accuracy of $\pm 3\%$ RH and $\pm 0.5^\circ\text{C}$. Qualitative analysis was performed using gas chromatograph with surface acoustic wave detector (electronic nose) with specified precision of 5% RSD, accuracy of 10% and sensitivity at low ppb level for most compounds. The used method includes following settings: 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 ($0.5\text{ ml/s} = 30\text{ ml}$) and analysis time of 20 seconds. Used column was DB-5 with 1 m length, film thickness of $0.25\ \mu\text{m}$, and internal diameter of 0.5 mm. The device was calibrated to the alkane response with a solution of $\text{C}_6\text{-C}_{22}$ in methanol. Photoionization detector with UV lamp (ppbRAE 3000) was used for quantitative determination of concentrations of total volatile organic compound (TVOC) expressed as concentrations of toluene. This instrument has specified accuracy (isobutylene) from 10 to 2000 ppm: $\pm 3\%$ at calibration point. Two-point field calibration of zero and standard reference gases were conducted for ppbRAE. All devices were placed at the height of 1 m above the floor. All windows and doors were closed during measurements. Owner of apartment was asked not to ventilate and not to use fragrance substances twelve hours before measurements. Also construction workers were asked not to smoke in rooms minimum twelve hours before measurements. Measurements lasted thirty minutes in each room.

3. Results

Mean indoor air temperature reached 20.7°C in the living room, 22.2°C in the bedroom as well as in the child's bedroom during first day of measurement. During second day of measurement, mean indoor air temperature was 20.7°C, 21.8°C and 22.1°C, respectively. The mean air temperature was 18°C, 18.6°C and 18.1°C, respectively, after flooring installation. Indoor air temperature reached 22.5°C, 22.5°C and 22.3°C, respectively, after that rooms were furnished. Differences of temperatures after flooring installation was caused by the fact, that rooms were not heated and also the outdoor temperature was low that day.

Mean relative humidity (RH) was 47.7% in the living room, 48.1% in the bedroom and 46.5% in the child's bedroom during first day of measurement. Mean RH reached 44.1%, 42.5% and 40%, respectively, after painting. Mean RH was 38.6%, 40.8% and 39.7% after the installation of flooring, and 41.9%, 43.1% and 42.6% after that apartment was furnished. The lowest values of RH were set after the flooring installation. Significant differences between the rooms were not recorded.

Table 1 shows results from determination of TVOC concentrations. The highest mean TVOC concentrations were measured in the child's bedroom during the measurement of initial state (143 $\mu\text{g}/\text{m}^3$) and after that apartment was furnished (233 $\mu\text{g}/\text{m}^3$) and in the living room (396 $\mu\text{g}/\text{m}^3$) after painting and flooring installation (1258 $\mu\text{g}/\text{m}^3$). Painting works caused 71.5% increase in concentrations in the living room. Levels of TVOC have increased by 68.5% in the living room after the flooring installation. On the other hand, TVOC concentrations have decreased by 84% after that the apartment was furnished. But this unique phenomenon was caused by the fact that the measurement was carried out approximately three months after third measurement. In the bedroom, painting caused that concentrations increased by 54%, flooring installation caused an increase of 76.8% and concentrations decreased by 82% after that room was furnished. In the child's bedroom, painting caused 52.3% increase, flooring installation caused that concentrations increased by 66.1% and concentrations decreased by 73.7% after that room was furnished. As can be seen, installation of flooring caused the highest increases of TVOC concentrations in all cases. However, it is important to note that the applied coatings on walls and radiators can also contribute to high levels of TVOC in this step. The highest standard deviation was set during measurements after that apartment was furnished.

Table 1. TVOC concentrations in different state of renovation

Tabela 1. Stężenie TVOC w różnych stanach renowacji

State of renovation	TVOC [$\mu\text{g}/\text{m}^3$]	Living room	Bedroom	Child's bed- room
Initial state (18.11.2014)	Mean	113	133	143
	SD	4.9	6.0	7.1
	Minimum	106	122	134
	Maximum	126	143	160
After painting (26.11.2014)	Mean	396	289	300
	SD	10.7	10.4	16.0
	Minimum	375	305	273
	Maximum	416	270	325
Flooring installation (11.12.2014)	Mean	1258	1246	886
	SD	18.7	4.2	8.1
	Minimum	1197	1234	868
	Maximum	1285	1251	912
Furnishing (16.3.2015)	Mean	201	224	233
	SD	21.4	9.1	3.0
	Minimum	159	210	227
	Maximum	232	237	240

There are no WHO or Slovakian guidelines for TVOC concentrations in indoor air, therefore Table 2 shows guideline values in different countries. As can be seen guideline values vary between countries. Results from last measurement showed that guideline values of Norway, Finland (S2), Germany, Australia, Japan and China would have been met. Mølhav [6] suggested the value of $200 \mu\text{g}/\text{m}^3$ as an imaginary border which does not affect human health and does not cause of discomfort. His recommended value was not exceeded only during measurements of initial state. Thus, the owners of the apartment were instructed to increase ventilation rates after that flooring was installed and high levels of TVOCs were found.

Table 2. Recommended values for TVOC concentrations

Tabela 2. Zalecane wartości stężenia TVOC

Country	TVOC
Norway [7]	$250 \mu\text{g}/\text{m}^3$
Finland [8]	S1: best category (>90% of occupants satisfied) – $200 \mu\text{g}/\text{m}^3$ S2: $300 \mu\text{g}/\text{m}^3$ S3: minimum requirements according to building codes – $600 \mu\text{g}/\text{m}^3$
Germany [9]	$200\text{-}300 \mu\text{g}/\text{m}^3$
Australia [10]	$500 \mu\text{g}/\text{m}^3$
USA [8]	$200 \mu\text{g}/\text{m}^3$
Japan [9]	$400 \mu\text{g}/\text{m}^3$
China [11]	$500 \mu\text{g}/\text{m}^3$

Tables 3-6 show results from qualitative analysis together with possible sources of individual compounds. Naturally the smallest number of compounds has been identified during measurement of initial state and the highest number of compounds has been identified after furnishing and starting occupation of apartment.

Table 3. Identified VOCs during initial state

Tabela 3. Wyznaczone lotne związki organiczne VOCs podczas stanu wstępnego

Compound	CAS	18.11.2014			Possible source
		LR	BR	CR	
artemiseole	60485-46-3	+		+	food [12]
bis(2-chloro-1-methylethyl) ether	108-60-1	+	+	+	cleaning solutions [13]
undecane	1120-21-4	+	+	+	PVC flooring [14]
hexyl isobutyrate	2349-07-7		+	+	cosmetic products, perfuming agents [15]
carvone	99-49-0	+	+		cleaning solutions [16]
1-tridecene	2437-56-1	+	+	+	solvent [17]
methyl geranate	2349-14-6	+			cosmetic products, perfuming agents [18] [19]
(E)-2-hexenyl hexanoate	53398-86-0			+	cosmetic products, perfuming agents [20]
decanal dimethyl acetal	7779-41-1	+	+		fungi, perfuming agents, food [21] [22] [23]

Table 4. Identified VOCs after painting

Tabela 4. Wyznaczone lotne związki organiczne VOCs po malowaniu

Compound	CAS	26.11.2014			Possible source
		LR	BR	CR	
toluene	108-88-3	+	+	+	paints, coatings [24]
2,6-dimethyl-3-heptanone	19549-83-8	+	+	+	tobacco smoke [25]
bis(2-chloro-1-methylethyl) ether	108-60-1	+	+	+	paints, coatings [13]
undecane	1120-21-4		+		paints, coatings [24]
camphene hydrate	465-31-6		+	+	essential oil, perfuming agents [20] [26]
hexyl isobutyrate	2349-07-7	+			cosmetic products, perfuming agents [15]
2-methyl acetophenone	577-16-2		+	+	flavour and fragrance agents [27]
methyl salicylate	119-36-8	+			cosmetic products, medicinal products, flavouring agents [28]
citral	106-26-3	+	+	+	fragrances [29]
eugenol	97-53-0		+	+	plastic skirting [30]
(E)-2-hexenyl hexanoate	53398-86-0			+	flavour and fragrance agents [31]

decanal dimethyl acetal	7779-41-1		+		fungi, perfuming agents, food [21] [22] [23]
1,3-indandione	606-23-5	+			unknown

As can be seen most of identified compounds originated from cosmetic products despite the fact that use of these products was excluded twelve hours before measurements. But it is important to say that construction workers and owners were present in the apartment during these measurements, thus they were possible sources of VOCs. However, we consider that the levels of these compounds in the indoor air were very small considering that very strong odor from used materials was present in the rooms during second and third measurements. Presence of eugenol with possible source of plastic skirting may be explained by that skirting were stored in the hallway during second measurement. Emissions of compounds originating from tobacco smoke were probable present due to secondary emissions because this activity was excluded before measurements.

Table 5. Identified VOCs after installation of flooring

Tabela 5. Wyznaczone lotne związki organiczne VOCs po instalacji podłogi

Compound	CAS	11.12.2014			Possible source
		LR	BR	CR	
toluene	108-88-3	+	+	+	paints, coatings [24]
ethyl benzene	100-41-1	+	+	+	paints, coatings [24]
β -pinene	127-91-3	+	+	+	laminated flooring [32]
1,3-dichlorobenzene	541-73-1	+	+		dyes [33]
bis(2-chloro-1-methylethyl) ether	108-60-1			+	paints, coatings [13]
2,2,5,5-tetramethylhexane	1071-81-4	+	+	+	[33]
nonanal	124-19-6		+		adhesive for flooring installation [14]
undecane	1120-21-4	+		+	paints, coatings [24]
hexyl isobutyrate	2349-07-7	+	+		cosmetic products, perfuming agents [15]
methyl salicylate	119-36-8	+	+		cosmetic products, medicinal products, flavouring agents [28]
1-dodecene	112-41-4			+	exhaust of gasoline [34]
carvone	99-49-0	+	+		laminated flooring [16]
ethyl 2-phenylacetate	101-97-3			+	cosmetic products [35]
eugenol	97-53-0		+		plastic skirting [30]
4-methyltridecane	26730-12-1	+		+	unknown
α -copaene	3856-25-5		+		adhesive for flooring installation [14]
longicyclene	1137-12-8	+		+	adhesive for flooring installation [14]

Table 6. Identified VOCs after furnishing

Tabela 6. Wyznaczone lotne związki organiczne VOCs po umeblowaniu

Compound	CAS	16.03.2015			Possible source
		LR	BR	CR	
octane	111-65-9	+	+	+	adhesives [24]
o-xylene		+		+	adhesives [24]
alpha-thujene	2867-05-2	+	+	+	essential oil, tobacco smoke [25]
2,6-dimethyl-3-heptanone	19549-83-8	+			tobacco smoke [25]
3-propylthiopene	1518-75-8	+	+	+	food [12]
gamma-terpinene	99-85-4	+	+	+	cleaning agent, air freshener [36] [37]
nonanal	124-19-6	+	+	+	adhesives [14]
camphene hydrate	465-31-6	+	+		essential oil, Perfume [20] [26]
1-dodecene	112-41-4	+		+	exhaust of gasoline [24]
citral	106-26-3	+			fragrances [29]
thymol	89-83-8	+	+	+	tobacco smoke, repellent, insecticide [38]
citronellol acetate	150-84-5	+			cleaning products [37]
undecan-1-ol	112-42-5	+			unknown
cyperene	2387-78-2	+			food [12]
alloarmadendrene	25246-27-9	+			electronic products [39]
alpha-citral	141-27-5		+	+	cleaning products [40]
orcinol	504-15-4		+	+	fragrance and flavour materials [41]
Ionene	8013-90-9		+		perfuming agents, masking agents [42]
bis (2-chloroethoxy) methane	111-91-1			+	unknown
hexyl 2-methylbutaroate	10032-15-2			+	food, beverages [23]
cis-jasmone	488-10-8			+	cosmetic products [43]

Presence of 1-dodecene from exhaust of gasoline can be explained by the fact that the apartment is oriented to side of the street with road and parking. This VOCs analysis showed that emissions from furniture were already released. Identified were only octane and o-xylene which the possible sources are adhesives commonly used in furniture industry. Most important sources from used materials were flooring (adhesives for skirting) and coatings.

4. Conclusion

The current “green” trend affects also sector of building materials production. Nevertheless, these products still emit significant amounts of VOCs to indoor environment. Whereas these compounds may have a significant impact on our health, it is important to carry out monitoring focused on their identification and quantification. The results from this study showed that TVOC concen-

trations slightly increased after painting and much more increased after floor installation. But relatively high levels of these concentrations decreased on permissible levels after three months. Equipment with furniture surprisingly did not cause a big contribution to indoor air pollution. The many of identified VOCs originated from coatings and also from adhesives used during installation of skirting. The assumption of higher emissions from new furniture was not confirmed. The results from analysis of VOCs also showed the presence of many compounds originating from food, beverages or cosmetic products indicating a slight disadvantage of a very high sensitivity of GC/SAW system. Considering this, it is necessary to change measurement methodology and although this is not always possible to exclude the presence of construction workers in studied rooms minimum one hour before measurement.

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ANALIZA LOTNYCH ZWIĄZKÓW ORGANICZNYCH VOCs W ŚRODOWISKU WEWNĘTRZNYM

Streszczenie

Ostatnimi laty, lotne związki organiczne VOCs były studiowane badane w wielu krajach. Jednakże, procesy budowlane, materiały budowlane, typy budów i metody wykorzystane przy pobieraniu i analizie VOCs w zależności od kraju różniły się od siebie. W tym samym czasie ciągle postęp naukowy i techniczny przyniósł nowe materiały, które mogą emitować całkowicie inne VOCs niż starsze materiały. Materiały budowlane stanowią znaczące źródło emisji związków organicznych, a my jesteśmy codziennie w bezpośrednim kontakcie z tymi związkami chemicznymi w pracy, szkole czy w domu. Krótko- lub długoterminowe działanie tych substancji może powodować wiele problemów zdrowotnych, dlatego, badania skupione są na ustaleniu bieżącego stanu występowania i poziomu stężenia VOCs. Analizowany w artykule budynek znajduje się we wschodniej Słowacji. Skutki Wyniki były porównywane z wartościami wyszczególnionymi w innych państwach, ponieważ na Słowacji nie ma żadnych wytycznych co do wartości całkowitego stężenia VOCs a limity stężenia są podane jedynie dla niektórych związków VOCs. Wyniki analizy wykazały, że instalacja podłogi wraz z malowaniem ma najwyższy udział na poziom TVOC w powietrzu wewnętrznym badanego mieszkania. Z drugiej strony, nie odnotowano wysokich poziomów TVOC po meblowaniu.

Słowa kluczowe: remont, mieszkanie, elektroniczny nos, zanieczyszczenie wewnętrzne

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