

The identification of Volatile Organic Compound's emission sources in indoor air of living spaces, offices and laboratories

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Abstract. Indoor air quality is important because people spend most of their time in closed rooms. If volatile organic compounds (VOCs) are present at elevated concentrations, they may cause a deterioration in human well-being or health. The identification of indoor emission sources is carried out by comparison indoor and outdoor air composition. The aim of the study was to determinate the concentration of VOCs in indoor air, where there was a risk of elevated levels due to the kind of work type carried out or the users complained about the symptoms of a sick building followed by an appropriate interpretation of the results to determine whether the source of the emission in the tested room occurs. The air from residential, office and laboratory was tested in this study. The identification of emission sources was based on comparison of indoor and outdoor VOCs concentration and their correlation coefficients. The concentration of VOCs in all the rooms were higher or at a similar level to that of the air sampled at the same time outside the building. Human activity, in particular repair works and experiments with organic solvents, has the greatest impact on deterioration of air quality.

1 Introduction

Indoor air quality is an important issue for this reason that people spend most of the time in all kinds of rooms [1]. If the air in the room is contaminated, it can adversely affect the well-being and human health [2, 3]. The compounds that most often pose such a threat are volatile organic compounds (VOCs), which are defined as organic compounds at boiling point below 250 °C ant at the pressure 101.3 kPa [4].

The sources of indoor air pollution can be different, they may be both materials for furnishing the room and human activity or VOCs can get from the outside through ventilation or windows if the building is located near emitters such as roads or industrial plants [5-7]. The effects on well-being and human health depend on VOCs concentrations and its nature. Poor air quality due to the presence of VOCs, as well as biological or physical factors, may cause symptoms known as "sick building syndrome", that is the state of ill feeling with symptoms such as headache, nausea, eye or respiratory irritation, that

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only appear and worsen while staying in this building and disappear almost immediately after leaving the building [8].

The emission sources may occur both in the room itself and outside. Considering that, in case of high concentration of VOCs, it is essential to first identify the location of emission sources, and then to take action to improve the air quality. When investigating indoor air, outdoor air tests should be carried out simultaneously. Then the first stage of identification the presence of emission sources may be the appropriate interpretation of the results, for example comparative analysis with the concentration of compounds outside or analysis of correlation coefficients of compounds indoor and outdoor.

2 Research methodology

2.1 Scope of research

In the years 2009-2016 in Krakow concentration of VOCs was investigated in several rooms, such as student houses during renovation, private apartment, laboratories and office spaces. These rooms have been selected for testing because of the expected elevated level of VOCs or have been indicated by users because of fragrancy nuisances or syndromes of the “sick building syndrome”. The characteristics of individual rooms in which the indoor air quality was tested are given in Table 1. Part of the name marked in bold in Table 1 will be used in the further part of the work. Air samples were taken out of the building in parallel for each places.

Table 1. Place and date of research, kind of rooms and numbering the places.

The number of place	Name and location of the building	Type of rooms	Date	Number of samples
1	Student house “Żaczek” , the 3th May Avenue, Krakow	student rooms, kitchen, corridor	April 2009	9
2	Nowohucka apartment , Nowohucka 3, Krakow	private apartment	March 2014	2
3	Faculty of Chemistry of the Jagiellonian University, Ingardena 3, Krakow	laboratories, main hall, preparation room, doctoral students room,	March 2014	7
4a	The III Campus UJ: Faculty of Physics, Astronomy and Applied Computer Science of the Jagiellonian University, Łojasiewicza 11, Krakow	workshop, humidifier room	April 2015	3
4b	The III Campus UJ: Department of Environmental Chemistry, Gronostajowa 3, Krakow	office room, chromatographic lab	April 2016	3

Locations numbered 1 and 3 are situated in the centre of the city with compact building, 200 m from high traffic road - A. Mickiewicz Avenue. Private apartment (place No. 2) is located in Nowa Huta, 50 m from the crossing of Peace Avenue and Nowohucka Street. Location No. 4 are at the III Camus of the Jagiellonian University, at this place the air was investigated in two buildings (4a and 4b) located next to each other and that buildings will be described together. That buildings are located 100 m from Grota-Roweckiego Street, the road with much less traffic than in other places. This place has much better aerodynamic conditions, is more favourable for ventilation and distribution of pollutants in the atmosphere.

2.2 The method of determination

Air samples were collected into stainless steel canisters, reusable containers with a capacity of 6 dm³. Canisters were evacuated to pressure 0.001 mBar before air sampling, when a cellulose filter was placed on the canister's inlet and air got into canister due to pressure difference after opening the valve. Canisters with air samples were transported to laboratory and chromatographic analysis was performed using gas chromatograph Varian Star 3600 CX equipped with flame ionization detector and sample preconcentration trap. The method of determination is based on the USA EPA method T0-14 [9]. The method detection limit was 0.2 µg/m³. Precision was determined based on five real samples and ranged between 5% and 10% relative standard deviation (RSD) for peaks that are well separated, while partially overlapping peaks have RSD of about 20%.

The analysis consisted of several steps: rinsing the supply lines, cryogenic preconcentration of a sample of 160 cm³ volume (preconcentration at -175°C for 4 minutes), thermal desorption of analytes at 120°C, separation of analytes on a capillary column DB-1. The column parameters were as follows: 60 m length, 0.32 mm diameter, stationary phase of polydimethylsiloxane 3 µm thick. The temperature column program was used: initial column temperature -60°C, when the temperature increased to 20°C at a rate of 8°C/min and 5°C/min to final temperature 250°C kept for 10 minutes. Helium was used as the carrier gas at a flow rate of 2.5 cm³/min. The temperature of detector and valves were 300 and 160°C respectively. The gas flows in the detector were as follows: hydrogen 30 cm³/min, air 300 cm³/min, make-up 27.5 cm³/min. Up to 60 compounds were identified belonging to the so-called ozone precursors, the number was the result of the standard mixture composition. Two standard mixtures have been used: the 27-component mixture manufactured by National Physical Laboratory and 25-component mixture of the Resteck catalogue. Compounds were identified by retention times and by Kovatč retention indexes and the propriety of identification was verified against the application note [10].

3 Results

The paper presents a discussion of the results of the analysis of 24 air samples collected in five different buildings. The number of identified compounds is not the same in subsequent samples, which is reflected in the charts for individual rooms. Table 2 gives the range of summary concentration of VOCs in indoor air and the summary concentrations of VOCs outdoors. In both cases total VOCs includes all concentrations of identified volatile organic compounds. A detailed discussion on identifying the presence of an emission source in a room is presented in the next subsections.

3.1 Student house “Żaczek”

The research was conducted to determine the magnitude of the impact of renovation work on air quality in the renovated rooms and in the whole building. Premises were tested before renovation, one year and two days after repairs. Rooms were closed before sampling. Four samples were taken in the new part of the student house (student rooms, common places - corridor and kitchen), three samples in the old part of the student house and two outside at the main entrance of the dorm and in the courtyard.

Concentrations in the renewed part are the highest, the mean aggregate concentration of identified compounds in the refurbished, old and outside are 2549, 763 and 224 µg/m³ respectively. The ratio of average concentration in refurbished and old rooms to concentrations in outdoor air are 11.4 and 3.4 respectively.

Table 2. Characteristics of the air condition in the each building: indoor and outdoor concentration range and compounds with the highest concentrations in relation to outdoor air.

Building	The range of concentration of total VOCs in premises [$\mu\text{g}/\text{m}^3$]	Total outdoor concentration of VOCs [$\mu\text{g}/\text{m}^3$]	Compounds in elevated concentrations with respect to outdoor air
Student house „Żaczek”	285 - 4641	162	Compounds with a short carbon chain (C2- C5): 1-butene, 1-pentene, n-butane, acetylene, ethane, propane,
Nowohucka apartment	392	351	Saturated aliphatic compounds and compounds considered to be derived from biogenic sources: n-butane, 2-methylbutane, n-hexane, isoprene, 3-methylheptane, α -pinene 3-methylheptane, trimethylbenzene
Faculty of Chemistry	318 - 11401	133	cis-pentene, 2-methylbutane, n-hexane, cyclohexane, toluene, n-pentane, 2-methylpentane, 3-methylpentane
The III Campus UJ (4a and 4b)	58 - 120	61	cyclohexane, propylbenzene, toluene, benzene, 1-pentene

Figure 1 shows average concentrations of the individual compounds outside (blue), in the refurbished part (orange) and in the old part (grey). The compounds in the graph are shown in the order as they appear on the chromatogram, compounds at the lowest boiling point are on the left. The high concentrations are mainly attributed to the fraction of the most volatile hydrocarbons, with a carbon chain of 2 to 5 carbon atoms in the molecule. The compounds that were at the highest concentrations in the restoration are: 1-butene ($943 \mu\text{g}/\text{m}^3$), n-butane ($326 \mu\text{g}/\text{m}^3$), 2-methylpropane ($197 \mu\text{g}/\text{m}^3$) and propane ($171 \mu\text{g}/\text{m}^3$). The only compounds whose outside concentrations were higher were benzene, 2,3-dimethylpentane and o-xylene. Surprisingly, there was a relatively high concentration in parts of the building where renovation works were not carried out. The same compounds occur in elevated concentrations in both the old and the renewed part of the building. This proves that the air from the refurbished part penetrates into the not renewed part [11].

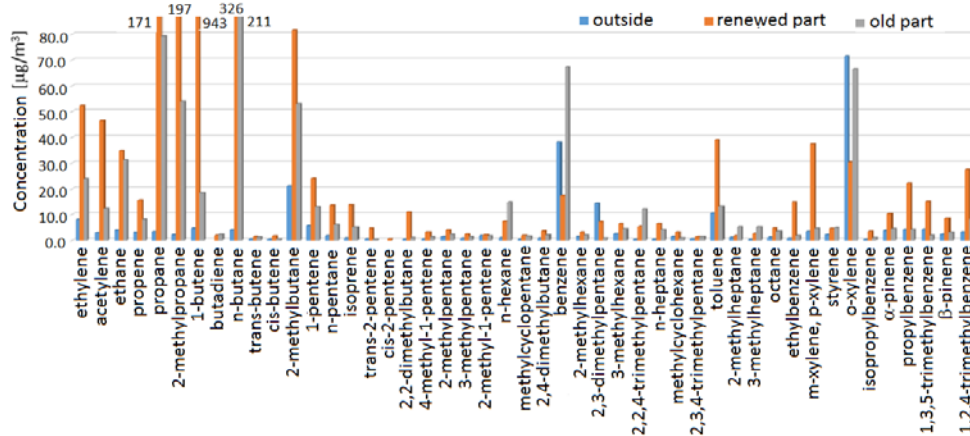


Fig. 1. Mean concentration of identified compounds in different parts of student house “Żaczek” and outside the building. Bars corresponding to the concentrations of the five compounds are shortened and the concentration values are written nearby.

3.2 Faculty of Chemistry

In 2014, the air was examined in several rooms of the Faculty of Chemistry of the Jagiellonian University, especially in the Department of Organic Chemistry: doctoral students' room, preparatory room and students' workshop during courses. Reference samples were taken at the main hall in the central part of the Faculty of Chemistry and before the main entrance to the building. All samples were taken in the morning within one hour and additionally in one of the rooms (lab 216) also in the afternoon after ventilation.

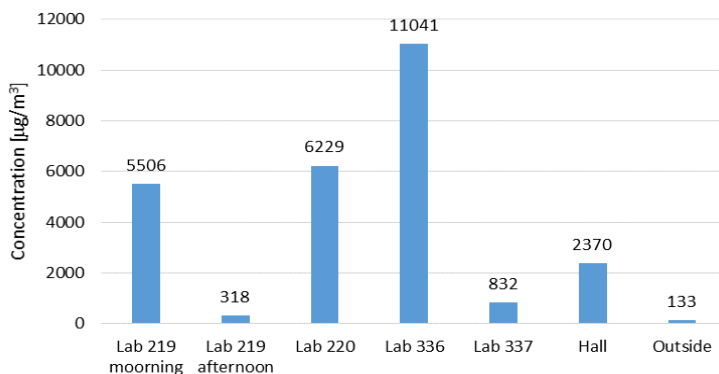


Fig. 2. Total concentration of identified compounds in different places of the Faculty of Chemistry.

The concentrations of the identified compounds in individual rooms and outside are presented in Figure 2. The concentration is higher in each room than in outdoor air (last bar). Several specific compounds are responsible for high concentration: 2-methylbutane, cis-2-pentene,, n-hexane, toluene, as illustrated in Figure 3, showing concentrations in the hall and outside the building together. The highest concentration is from the compounds identified as 2-methylbutane. But including the fact that the peak is unsymmetrical and acetone have the same retention time, it can be concluded that acetone, a compound commonly used in laboratories, is involved in high concentrations.

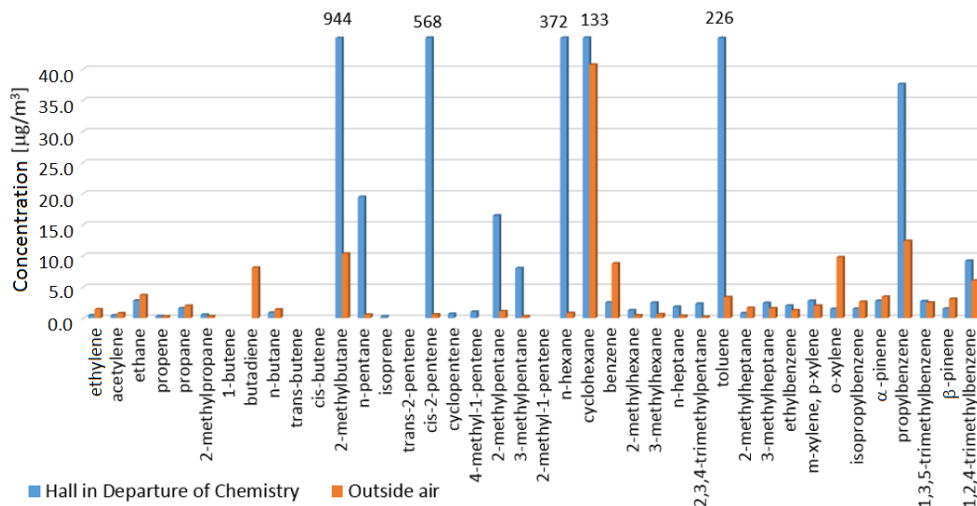


Fig. 3. Concentration of compounds in the main hall in the Faculty of Chemistry (■) and outside the building (■). Bars corresponding to the concentrations of the five compounds are shortened and the concentration values as written above.

It was noted that there is a correlation between concentrations in laboratories (Figure 4a) and also between concentrations in laboratories on the third floor and the hall on the second floor (Figure 4b). This demonstrates the penetration of pollutants from laboratories into other parts of the building. At the same time there is no correlation between indoor and outdoor air (Figure 4c). Only a similar profile of concentrations with outdoor air occurred in room 219 in the afternoon, where a few hours of airing of the room occurred (Figure 4d). Room ventilation caused a 17-fold decrease in concentration.

The results obtained in this part of the study show a strong influence of the way the room is used on the condition of air, the possibility of contaminating the rooms due to the movement of pollutants within the building [11].

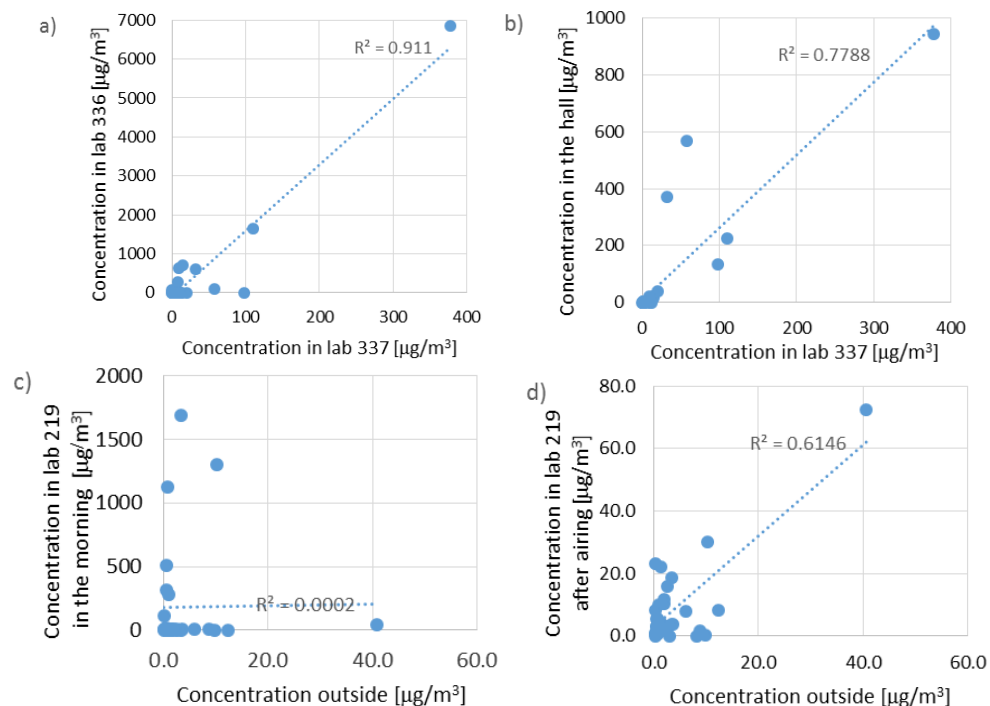


Fig. 4. Correlation between concentrations in: a) lab 336 and 337, b) hall and lab 337, c) lab 219 in the morning and outside, d) lab 219 in the afternoon and outside.

3.3 Nowohucka apartment

Research was conducted in a private apartment in a block at Nowohucka Street, a road with high traffic. Cleaners and air fresheners are used in the apartment; one of the rooms was repaired 3 years before the test. In this case, the total concentration of the identified compounds in the apartment is slightly higher than the concentration in the outdoor air, these values are 392 and 351 $\mu\text{g}/\text{m}^3$ respectively. Compounds that have a higher concentration in the room are most of all iso-pentane, n-butane and some aromatic hydrocarbons. On the other hand, compounds that have higher concentrations outside are cyclohexane, 1-butene, o-xylene, ethylene and propane.

According to literature data, average concentration in homes is in the order of 200-500 $\mu\text{g}/\text{m}^3$ and is usually two or several times greater than in outdoor air [5, 12, 13]. The value 392 $\mu\text{g}/\text{m}^3$ is within the given range, however, after adding the concentration from unidentified compounds, the number 500 is exceeded. There is a fairly high correlation

between indoor and outdoor concentrations (Figure 5), so it can be concluded that in this case air quality is more dominated by outside air than by endogenous emission [14].

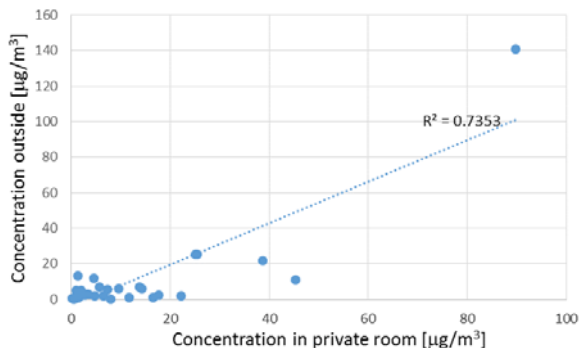


Fig. 5. Correlation between concentrations of identified compounds in private apartments and outdoor.

3.4 The III Campus UJ

The air in two buildings at the III Jagiellonian University Campus was examined in years 2015-2016: Faculty of Physics, Astronomy and Applied Computer Science (4a) and Department of Environmental Chemistry (4b). Tests in the first of the buildings was run about 1 year after completion of the finishing work, in two rooms: workshop and a room with air humidification equipment. The building of Department of Environmental Chemistry was commissioned in 1999.

The total concentration of the identified compounds in place “4a” was 98-120 µg/m³. Also it was stated the presence of many unidentified compounds giving a total concentration of more than 500 µg/m³. In both rooms, the concentrations of compounds are lower than in the previously tested rooms and lower than the average concentration of hydrocarbons in Krakow, but they are almost twice as high as in atmospheric air in that part of Krakow (60 µg/m³). An important factor affecting the air condition in this part of the city is the fact that the III Campus UJ is in a well-ventilated area, there are no traffic jams and in this situation the pollution from car communication is much less affected the air than in the city centre. There are only several compounds responsible for higher concentrations: mainly cyclohexane, toluene, propylbenzene.

A clear answer to the question whether emission sources are present in the examined rooms, give correlation graphs of concentrations in rooms with outdoor air. The correlation coefficient of concentration in both rooms, located in the separate wings of the building and at a different level, ie in the basement and on the second floor, and have different destinies, is about 0.77 while the correlation coefficient of indoor and outdoor concentrations is only 0.10. At the same time, there is another concentration profile for compounds above 5 carbon atoms in the molecule for the air in the rooms compared with outside. Hydrocarbons having a carbon chain of 2 to 4 carbon atoms in the molecule are at a very similar concentration. The final conclusion is that the emissions from finishing materials occur but are rather low and do not cause significant deterioration to indoor air quality.

The air from chromatography laboratory and office room in Department of Environmental Chemistry (place “4b”) was also examined. The average concentration of the total identified compounds is 58 µg/m³. This value does not differ significantly from the concentration in atmospheric air in this part of the city and at the same time, the concentration profile is similar and the correlation coefficient is 0.81. In this case, there are no sources of emission in the room.

4 Conclusion

It is essential to conduct indoor and outdoor air research simultaneously. However, to find out if the sources of emissions are inside the building, it is necessary to compare the concentrations of individual compounds, not just the total concentration of VOCs. Very helpful in identification the presence of endogenous emission sources is the analysis of the correlation coefficient between indoor and outdoor concentrations of compounds as well as between rooms in one building. Appropriate interpretation of the results allows us to say whether there are or are no sources of emission in the examined room, but they do not indicate what the source is.

The VOCs concentration in the rooms were higher or at a similar level to that of the air sampled at the same time outside in all tested rooms. Most of the study areas found endogenous sources of emissions, but their impact on air quality was very differential. Human activity, in particular repair works (the use of paints and varnishes) and experiments with organic solvents have the greatest impact on the deterioration of the air quality in the examined premises. Significant improvement in air condition was achieved after room ventilation. The only room where the endogenous source did not exist was the chromatographic laboratory on the III Jagiellonian University Campus.

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