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Measurement of VOCs with a Portable GC/SAW Detector

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This paper describes the determination of the concentrations of volatile organic compounds (VOCs) in two Slovak buildings. Qualitative measurements were performed using an electronic nose, zNose® 4300. This device has been developed by Electronic Sensor Technology. Technology consists of a combination of gas chromatography with SAW (Surface Acoustic Wave) detector. This model was chosen for measurement because it provides a relatively fast results and full portability. Quantitative measurements were performed using a photoionization detector with UV lamp, ppbRAE 3000. Previous studies of indoor air in buildings showed that the occupant behaviour and consumer products influence indoor air quality, as well as building structures and location of the house. Our measurements were focused on VOCs, which are currently an important group of chemical pollutants. Term VOCs includes a wide range of hydrocarbons possessing a characteristic ability to vaporize at room temperature. VOCs are emitted from a large range of well-known sources. For example, from building materials, household products, human activities, cleaning, smoking, or industrial emissions, exhaust from vehicles are some of the anthropogenic sources of VOCs in the outdoor environment which contribute to indoor VOCs. Increased attention is also given to them because they can have a negative impact on human health. This study was carried out on the basis of complaints (smell, headache, nausea) of a laboratory worker, who has an office in the model house. Thus, the aim of this work was to determine what substances cause referred complaints and their possible sources.

1. Introduction

There are several reasons, which justifying the monitoring of VOCs in outdoor/indoor air. These basically respond to the two following needs:

- assessment of the exposure of the population and other vulnerable receptors to potentially toxic components released by emission sources or formed in the atmosphere and
- creation of data bases to permit the analysis of long-term trends in air pollution or for other research purposes.

In both cases, the techniques adopted are similar to those used in emission sources. However, a higher degree of sensitivity, and hence sophistication, is necessary for accurate determination of individual VOCs at the levels existing in indoor/outdoor air (ppb - ppt).

Methods for monitoring of VOCs in indoor/outdoor air can be divided into two categories, i.e. spectrometric methods and chromatographic methods. Examples for the spectrometric methods are FTIR (Fourier Transform Infrared Spectroscopy), DOAS (Differential Optical Absorption Spectroscopy) and TDLAS (Tunable Diode Laser Absorption Spectroscopy) techniques and for the chromatographic methods are gas chromatography and HPLC (High Performance Liquid Chromatography) techniques. The achievement of a high degree of sensitivity often requires that specific GC detection (e.g. flame photometry, photoionization, and electron capture) must be combined both with selective capillary columns and with highly efficient enriching procedures for sample collection (adsorption traps or cryogenic trapping on empty tubes). With optical devices, sufficient sensitivity can be obtained by accumulating signals on computer systems and processing them through dedicated software. When possible, automated systems allowing unattended operations are preferred. In this case, the monitoring unit must be interfaced with computers for data storage and statistical treatment.

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In spite of the outstanding progresses made in the selective detection of VOCs by optical methods, gas chromatography is still regarded as the most cost-effective technique for the monitoring of VOCs, because of the large number of compounds that can be determined in a single run (Siskos et al., 1997).

2. Portable electronic nose

In this study, a portable electronic nose, called the zNose® was used for qualitative determination of VOCs. The performance of this zNose® technology has been verified by the US EPA Environmental Technology Verification (ETV) program (Watson et al., 2003). This system is a small high-speed gas chromatograph (GC). It is based on a 6-port valve and oven, a pre-concentrating trap, a short GC capillary column (DB-5, 1 m length, film thickness 0.25 μm, internal diameter 0.25 mm) and a highly sensitive surface acoustic wave detector. A system controller, a laptop computer, operates the system, analyses the data and provides the user interface (Miresmailli, 2009). Accuracy of ±20% relative standard deviation is typical for GS/MS systems whereas manufacturer of zNose specifies the standard deviation <2% (Hites, 1997).

Figure 1 Electronic nose – zNose® 4300

Three sequences control the instrument operation: sampling, injecting and analysis. During the sampling sequence, the system draws a headspace sample or ambient air into the inlet via a pump. The sample passes through the valve and onto the trap where the compounds are adsorbed. The trap consists of a metal capillary filled with approximately 1 mg of Tenax® absorbent (Miresmailli, 2009). Tenax® is a porous polymer resin based on 2.6-diphenylene oxides, which has been specifically designed for the trapping of volatiles and semi-volatiles from air or which has been purged from liquid or solid sample matrices (SIS, 1996). The valve is then rotated to put the trap in line with the column for the injection sequence. Once inline, the trap is heated quickly by a short burst of current that vaporizes the adsorbed material. The helium carrier gas then transports the material down to the capillary column. The column is heated under computer control facilitating separation of compounds. When materials sequentially exit the column, they land and stick on the SAW detector (Miresmailli, 2009).

The SAW detector has zero dead volume that maximizes its response to low levels of transient vapours. The detection area is approximately the same size as the inside diameter of a capillary column so that all the column effluent can be collected onto the sensor. The sensing crystal comprises a very high Q SAW resonator placed in contact with a small thermoelectric cooling element. A thermoelectric element provides the precise control of cooling needed for vapour adsorption and simultaneously the ability to clean the crystal using thermal desorption when needed. The crystal operates by maintaining highly focused and resonant surface acoustic waves at 500 MHz on the face of a single crystal quartz chip. Focusing the vapour through a micro-nozzle is shown in Figure 2 (Watson et al., 1999). Coatings are not used because they reduce the resonator Q, introduce instability, and require excessive time for equilibrium. Only helium gas and electrical power is required to operate the system (Staples, 2000).

According to the manufacturer, the system can analyse compounds within the range of C4 to C24 however; the system has a short column which reduces the resolution of VOCs with similar retention times. Despite this limitation, the zNose® has been successfully used in different studies. For example, it has been utilized for honey classification or on-site measurement of VOCs and odours from metal casting operations (Miresmailli, 2009). This device is fully portable and suitable for on-site measurement of VOCs and also we can see results from measurements on the spot in a short time. These facts are the main advantages in comparison with GC/MS systems.

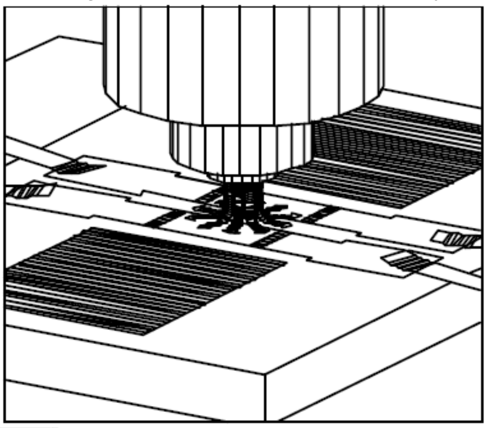

Figure 2 SAW detector (Staples et al., 1998)

3. Studied buildings

Two measurements of VOCs were carried out in this study. The first measurement was carried out in the model house and other in building of the laboratory, in which this model house was built. Both buildings are new and are located in campus of Technical University of Kosice. The model house consists from one room (the studied room), kitchen, bathroom with toilet and vestibule. In the studied room was applied laminate flooring, plastic window, ceiling from gypsum board, door fibreboard, lime-cement plaster and white interior paint. A partition is made of gypsum board; two exterior walls are made of bricks and one rear external from clay. At the time of measurement, the laboratory and even the studied room were still not fully equipped. Also the air conditioning unit in this room, which is located on the ceiling, was not functional (i.e. is ensured only natural ventilation currently) and the only furniture here were two older desks from fibreboard.

Figure 3 Model house in the laboratory

4. Measurements

Both measurements were performed in one day, before noon. All measuring instruments were placed on the desk in the centre of studied premises and at the height of approximately 1 m. Measurements themselves lasted 30 minutes in the model house and also in the laboratory. Twenty-four hours before the measurements, no detergents, or fragrances, were used in the room of the model house, and it was not ventilated or smoked tobacco in it. In the laboratory, measurement was carried out under operational conditions.

Temperature and relative humidity (RH) were determined by Data Logger – Testo 175-H2. For the quantitative determination of VOCs a photoionization detector (PID) with UV lamp called ppbRAE 3000 was used. Portable electronic nose – zNose® 4300 was used for qualitative determination of individual VOCs. The method used for this device includes the following settings: sensor temperature 10°C, column temperature 40-200°C, valve temperature 165°C, inlet temperature 200°C, pump time 60 seconds (0,5 mL of air/s), analysis time 20 seconds.

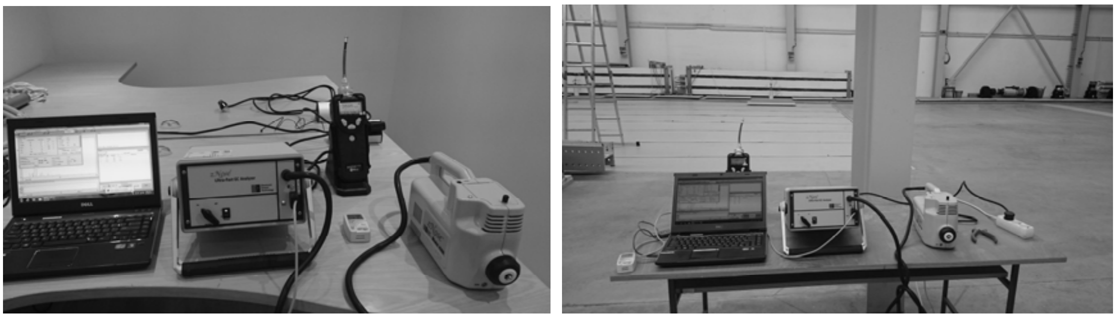

Figure 4 Measurements in the model house (left) and in the laboratory (right)

5. Results

Table 1 shows results from measurement of RH. Lowest value of RH from both measurements was 51.1 % measured in the model house and on the other hand, highest value RH was 71.1 % measured in the laboratory. Highest average value was 63.6 % measured also in the laboratory, but this value was only by 1.7 % higher than in the model house.

Table 1 Relative humidity in the model house and in the laboratory

Relative humidity	Minimum	Maximum	Average
Model house	51.1	65.0	61.7
Laboratory	61.9	71.1	63.6

Lowest value of air temperature was 20.3°C determined in the laboratory, which had highest RH and highest value was 22.1°C measured in the model house, which had lowest RH. Average temperature in the model house was by 0.8°C higher than in the laboratory. It is obvious that differences in air temperature and RH are small and therefore their impact when compared TVOC concentrations between buildings are negligible.

Table 2 Temperature in the model house and in the laboratory

Temperature	Minimum	Maximum	Average
Model house	21.3	22.1	21.6
Laboratory	20.3	21.4	20.8

Sum of VOCs - TVOC concentrations expressed as concentration of isobutylene were in the range from 3544 μg/m^3 to 3828 μg/m^3 in the model house and an average TVOC concentration was 3686.7 μg/m^3. TVOC concentrations were ranged from 1457 μg/m^3 to 1558 μg/m^3 in the laboratory. The average concentration was 1492.5 μg/m^3. The average concentration of TVOC was lower by 59.5 % in the laboratory than in the model house. Figures 4 shows course of concentrations in the model house and in the laboratory.

According to Molhave (1990) TVOC concentration < 200 μg/m^3 has no effects on health or comfort. TVOC concentrations in the range of 200-3000 μg/m^3 cause irritation and possible discomfort. Concentration determined in the laboratory belonged to this range. TVOC concentrations in the range of 3000 - 25 000 μg/m^3 cause irritation, discomfort and possible headache. Concentration achieved in the model house belonged into this discomfort range.

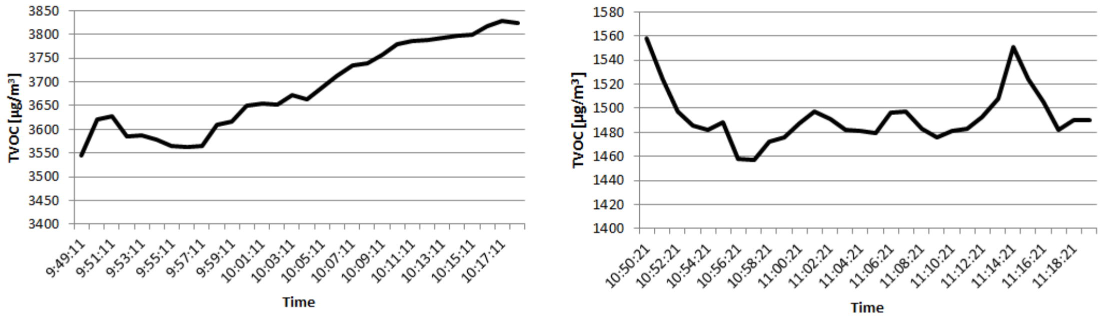

Figure 5 Course of TVOC concentrations in the model house (left) and in the laboratory (right)

From the analysis using zNose® was each detected compound expressed using a Kovats index. Compounds are identified using available databases or substances library stored in a computer based on used column (DB5) and the Kovats index. Seven VOCs and one SVOC were identified in the model house. In the laboratory six VOCs occurred, but five of them (ethyl benzene, 4- methylnonane, 2,4,5-trimethylthiazole, limonene, and nonanal) were occurred also in the model house. This can be caused by the fact that during ventilation, air is supplied only from the laboratory and not from outside.

Table 3 Identified organic compounds in the model house

Kovats index	Compounds	Formula	Odour threshold
873	Ethyl benzene	C_8H_{10}	2.3 ppm
962	4-Methylnonane	$C_{10}H_{22}$	no data available
995	2,4,5-Trimethylthiazole	C_6H_9NS	50 ppb
1036	Limonene	$C_{10}H_{16}$	1 ppm
1104	Nonanal	$C_9H_{18}O$	1 ppb
1158	4-Methyl undecane	$C_{12}H_{26}$	no data available
1410	Ethyl 2-aminobenzoate	$C_9H_{11}NO_2$	no data available
1514	(E,Z)-5,7-Dodecadien-1-ol	$C_{12}H_{22}O$	no data available

Table 4 Identified organic compounds in the laboratory

Kovats index	Compounds	Formula	Odour threshold
873	Ethyl benzene	C_8H_{10}	2.3 ppm
962	4-Methylnonane	$C_{10}H_{22}$	no data available
995	2,4,5-Trimethylthiazole	C_6H_9NS	50 ppb
1036	Limonene	$C_{10}H_{16}$	1 ppm
1104	Nonanal	$C_9H_{18}O$	1 ppb
1248	Heptyl isobutyrate	$C_{11}H_{22}O_2$	13 ppb

6. Conclusions

This study revealed that the concentrations of TVOC in the model house were in levels which may cause irritation, nausea and headaches. This means that the laboratory worker's complaints were justified. It is very likely that long-term exposure in this space will cause other health problems. Further research will be focused on accurate assessment of individual sources of VOCs occurring not only in the model building but also in the laboratory, whereas, also here the value of comfort was exceeded. Likewise it is necessary to perform measurements at the time when the air conditioning will be fully operational. Simultaneously, further research in objects will be extended to include the sensorial measurements. In the meantime it is necessary to increase the intensity of ventilation in the model house, as well as in the laboratory.

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