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METHODOLOGY FOR TESTING CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS USING THE TD-GC-MS TECHNIQUE

Key words

Volatile organic compounds, thermal desorption, GC/MS.

Abstract

An adult spends approximately 80% of the time indoors. Building materials and the furnishings that are in the room emit volatile organic compounds (VOC – *Volatile Organic Compounds*). Many of the emitted VOC might adversely affect the human body, especially when their concentration in the air exceeds certain critical thresholds. For this reason, it is desirable and often necessary to monitor their concentrations in the air. For many VOC, the highest permitted air concentrations are set at extremely low levels. Therefore, their detection and quantitative determination requires the use of sophisticated analytical tools. Qualitative and quantitative methodology was developed for measuring VOC concentrations in the air at very low levels, which is necessary for the quality control of the equipment used in VOC testing from any source. For this purpose, gas chromatography (GC) in conjunction with mass spectrometer (MS) was used, supported by thermal desorption (TD). Using this methodology, the volume of emissions was studied for several different VOC derived from common materials in enclosed work areas. The key aspects of the applied

methodology are discussed, from the preparation stage of the apparatus through the collection and preparation of the sample for analysis, ending with the appropriate analysis with the TD-GC-MS technique and the interpretation of the result analysis. This methodology is used for testing for the presence of VOC in the membrane station and for verifying the purity of the test chambers for VOC emission from various materials.

Introduction

Volatile organic compounds (VOC) are a group of substances, which include a wide range of carbon compounds such as aldehydes, ketones, and micromolecular hydrocarbons. The number of substances classified in this group exceeds 500 [1], and they have been divided into 3 basic sub-groups: very volatile VOC (VVOC) with the boiling point (BP) in the range of 0–100°C, VOC with BP in the range of 100–240°C, and SVOC with BP in the range of 240 to 400°C [2–3]. The majority of the total VOC emissions into the environment (86%) are natural sources, called biogenic [4], the remaining emissions come from anthropogenic sources and are emitted mainly by a broadly defined industry, which is to the greatest extent associated with the production and use of plastics [5–6]. In the development of civilization, these proportions have been in a continuous flux; and although contamination is not a new phenomenon, over the recent years, their qualitative and quantitative compositions have been changing. Taking into account the fact that more than 70% of Europeans live in urban areas, the protection of air quality and continuous monitoring of pollutants (including VOC) becomes a necessity [2, 3]. There is substantial evidence that large amounts of VOC are harmful to human health [7]. For example, substances such as 1,3-butadiene and benzene have been proven to have teratogenic and carcinogenic effects [8, 9]. In addition to direct influence, the volatile organic compounds may have damaging indirect effects, contributing to the formation of secondary pollutants, including tropospheric ozone. Reducing the emissions of air pollutants, including the amount and type of VOC, is a complex, global issue. From an environmental point of view, any steps taken in this direction must be related to both the elimination of specific sources of pollution (management of specific chemicals) and the general restriction of the consumption of raw materials and energy in the industrial, residential, and transport sectors [10, 11].

Due to the harmfulness of volatile organic compounds, it has become mandatory to analyse the levels of their concentration and to establish maximum levels for contaminants in buildings, workplaces, etc. These issues are regulated by a number of national (VDI, US EPA, PN) and international (ISO) standards, for the classification of compounds, the ranges of their maximum permitted

concentrations in ambient atmosphere, as well as procedures for obtaining and analysing samples.

At present, the aim is to be able to simultaneously analyse as many VOC as possible at the lowest levels of concentrations. In the vast majority of studies, the final analysis uses the gas chromatography (GC) technique with FID detection or in combination with mass spectrometry (MS) [12]. This may be done in combination with other methods of obtaining and preparing the samples for analysis. Among them, combinations of thermal desorption with GC and MS analysis seems to offer a comprehensive approach with the most advantages despite the considerable complexity of the required apparatus.

The aim of this study was to develop a methodology for determining the presence of volatile organic compounds by the TD-GC/MS method in air samples collected by the aspiration method. For these experiments, samples of air were obtained from the laboratory premises during remodelling and construction, which included a newly purchased piece of furnishing (under-desk cabinet). The changes were analysed of the concentration of volatile organic compounds emitted from building materials in the conditions of temperature and air exchange increase. The changes of the VOC concentration were analysed in the laboratory room equipped with membrane systems.

1. Research method

In developing the methodology for the determination of VOC, a Perkin-Elmer TurboMatrix 650 ATD thermal desorber was used. The commercial, steel sorption tubes by Perkin-Elmer filled with 200 mg of Tenax TA were used, which were conditioned prior to use for 6 hours at a temperature of 300°C in the flow of carrier gas (helium clean N6, 0) of 100 ml/min. Air samples were collected on the sorption tubes using the layout shown in Figure 1, consisting of a membrane pump – Schwarzer Precision SP670EC – with a stabilised power supply unit, combined with a rotametre flow range 3–30 dm³/h and flow regulator.

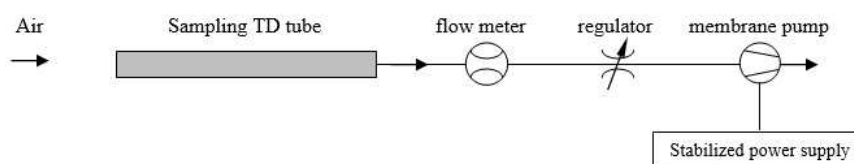


Fig. 1. Schematic diagram of the sampling system

The values of the volume and force of the airflow selected based on previous experiments (3 dm³ at a velocity of 100 ml/min.) meet the normative requirements, including ISO 16000-6: 2011, and they are safe for the stability of sorption deposits and allow for the analysis of a wide range of concentrations. The assumed volume was positively verified (by examining the second, serially attached tube) because of the lack of a “break” of the adsorptive deposit. The tube were subjected to thermal desorption at a temperature of 280°C for 10 minutes in a carrier gas flow of 30 ml/min. The original stream of desorption was routed to the cryogenic trap chamber (–20°C) from which, by means of the heated transfer line (225°C), it entered the gas chromatograph.

The tests used the GC/MS Perkin-Elmer Clarus 680/Clarus 600MS chromatographic system. The RTX-VMS Restek capillary column was used, which was 30 m in length and 0.25 mm in diameter with a stationary phase 1.4 µm thick. The temperature programme started at 40°C for 3 min, then increasing at the rate of 5°C/min. until 200°C was reached, followed by a further momentary increase to 250°C at 25°C/min. without sustaining it. Separated analytes were then routed through a heated transfer line (220°C) for the mass detector (ionization in a stream of electrons, mass range 20-400 m/z, a single scan time, and the internal between each scan of 0.2 and 0.1 s.). The carrier gas that was used had a purity of 6.0 N. The system was calibrated using commercial multicomponent standards for volatile organic compounds (VOC-Mix 18 OEKANAL[®], Fluka) by a direct jet onto the sorption tube 1 µL in a dilution series and by plotting calibration lines for all identified compounds in at least four levels of concentrations. For the quantification of substances for which the apparatus was not calibrated, the results were given as the equivalent toluene quantity. For the analysis of chromatograms, TotalChrom and TurboMass software was used, which was produced by Perkin-Elmer, and the obtained mass spectra were identified using the NIST libraries.

2. Results and discussion

New elements of an interior (construction materials, furniture, and commercial equipment) are characterized by increased emissions of VOC, which is related to the properties of materials themselves, as well as to activities related to their processing. In order to verify the assumptions of the methodology, the qualitative and quantitative composition of VOC air was examined, which was collected from the newly bought, closed under-desk cabinet with an interior volume of approximately 105 litres, and the surface area of the inside walls was approximately 2.4 m². The cabinet was made of laminated particleboard; and after being manufactured, it was tightly wrapped with stretch film. Before obtaining the sample, airflow (chromatographic lab) of 525l was run through the cabinet (5 x V of the cabinet). The chromatographic

testing identified 16 volatile organic compounds with clear the dominant signals. Then, in order to examine the changes in emissions, again the same portion of air was exchanged and the second sample was obtained. The results are presented in Table 1, and the observed changes are shown in the diagram (Fig. 3).

Table 1. Amounts of identified VOC before and after venting of the tested piece of furniture

Compound	RT	Initial conc. [$\mu\text{g}/\text{m}^3$]	Conc. after venting [$\mu\text{g}/\text{m}^3$]
Hexane	3.63	641.70	668.80
Acetonitrile	3.89	4.50	448.20
Methylcyclopentane	4.14	518.80	68.70
Trichloroethene	5.65	140.80	150.30
Pentanal	6.47	91.70	88.50
Toluene	7.06	160.50	132.80
Tetrachloroethene	7.46	71.80	0.00
Hexanal	8.42	210.10	185.40
Xylene	8.95	20.60	12.50
α -Pinene	9.66	230.10	216.00
Heptanal	10.28	32.60	14.80
N/A 1	10.58	74.70	79.60
3-Carene	10.99	48.60	79.80
D-Limonene	11.37	30.00	29.70
N/A 2	11.62	42.90	36.10
Octanal	12.07	31,8	33,5

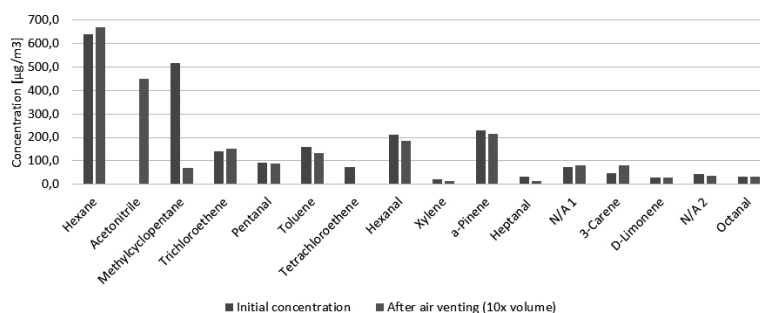


Fig. 2. Changes in concentration of the identified compounds before and after venting the container

After a 5-fold air exchange inside the test object, a decline in concentrations of most compounds was observed, including α -pinene (terpene, resin present in coniferous trees), D-Limonene (plant component of essential oils), and organic compounds related to the production processes of plastics (toluene, xylene, methylcyclopentane, pentanal, hexanal, tetrachloroethylene).

There was also a registered decrease in concentrations of two substances that had not been identified using the compound library. Furthermore, increases in concentrations of hexane and acetonitrile were noted because of the “airing” of the tested object with air from the chromatographic lab, where, among others, hexane was used as a solvent for samples in gas chromatography, and acetonitrile, as an eluent in HPLC. To confirm this, a sample of air from chromatographic laboratory was analysed, where elevated levels of these solvents were found, explaining their detection in the analysis of the air from inside the cabinet.

During construction and remodelling works, both construction and finishing materials are used, as well as secondary materials such as adhesives, silicones, varnishes, etc. In order to verify the effectiveness of the developed methodology for VOC analysis, air samples were taken from the room in which an interior door was replaced with new one made of wood-based materials. In the process of installation, the door was fitted (cut to size). In order to register potential changes of concentrations through time, another sample was obtained after 72 hours. A number of low-boiling-point organic compounds were identified, and they were analysed quantitatively (Tab. 2, Fig. 3).

Table 2. The quantities of identified VOC at the moment of new door installation and after 72 hrs

Compound	RT	Initial conc. [$\mu\text{g}/\text{m}^3$]	Conc. after 3 days [$\mu\text{g}/\text{m}^3$]
Acetone	3.55	242.60	19.06
Acetonitrile	3.90	70.50	58.30
Pentanoic acid (methyl ester)	4.78	190.70	4.70
Methyl-cyclohexane	5.69	56.40	4.70
Toluene	7.11	234.30	5.90
Acetic acid (butyl ester)	8.31	16.50	0.00
p-Xylene	9.00	41.70	2.90
a-Pinene	9.66	710.20	1.60

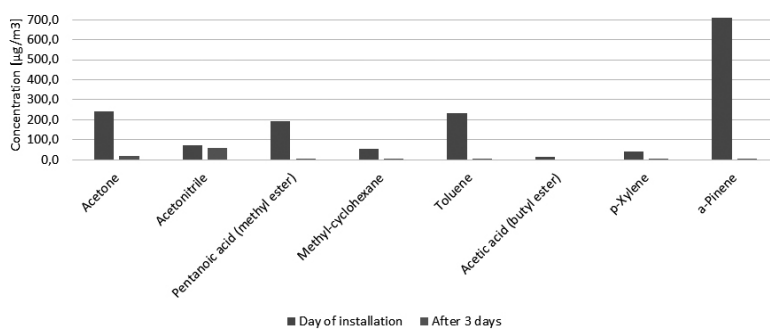


Fig. 3. Changes in concentration of the identified compounds at the moment of new door installation and after 72 hrs

On the day of the door installation, elevated concentrations of acetone, methylcyclohexane, toluene, xylene, and α -pinene were observed. It is likely that significant quantities of the last element were released into the environment while the door was being cut, while the rest is most likely the ingredients of materials used in the course of installation, i.e. adhesives, polyurethane foam, varnish, and sanitary silicon. With the exception of acetonitrile, after 72 hours, the concentrations of all compounds listed decreased below the point of detection within this method.

Volatile organic compound emission by many construction materials, for obvious reasons, increases as their temperature rises. In order to examine the changes in the emissions of VOC as a function of temperature (and indirectly - time function), samples of air were taken from the premises where the tests were carried out on the microfiltration membrane system. There were many plastic components used for its construction, mainly PVC tubes and rubber. The first measurement was made before turning on of the system (temp. approximately 19°C). Another measurement was taken after an hour of operation, when the temperature increased about 10°C. As a result of analysis, 12 substances were identified whose concentration increased during the experiment of both samples. The results are presented in Table 3 and Figure 4.

For all identified substances, approximately a 90% increase of emission was observed – the greatest being for 1-chlorooctadecane by 119.3%, and the smallest for tetradecane by 79.7%. Most of these compounds are organic substances used in the plastics industry, including solvents, i.e. toluene, xylene, and 1, 3, 5-trimethylbenzene. However, in this time period, the maximum allowed concentrations (WEL – workplace exposure limit) of the listed substances were not exceeded.

Table 3. Quantities of the VOCs identified at the start and after 1 hr of operation

Compound	RT	Initial conc. [$\mu\text{g}/\text{m}^3$]	Conc. after 1 hour [$\mu\text{g}/\text{m}^3$]
Heptane	5.13	51.80	104.40
1-Dodecanol	5.69	35.20	58.60
Toluene	7.08	10.40	20.20
Xylene	9.01	28.40	49.10
1-Chlorooctadecane	10.49	25.20	60.20
1, 3, 5-trimethylbenzene	11.31	28.20	48.80
Undecane	12.18	36.30	61.20
Dodecane	13.76	24.60	48.30
Tridecane	15.24	14.70	30.50
Tetradecane	16.64	11.20	17.80
Pentadecane	18.03	6.60	13.10

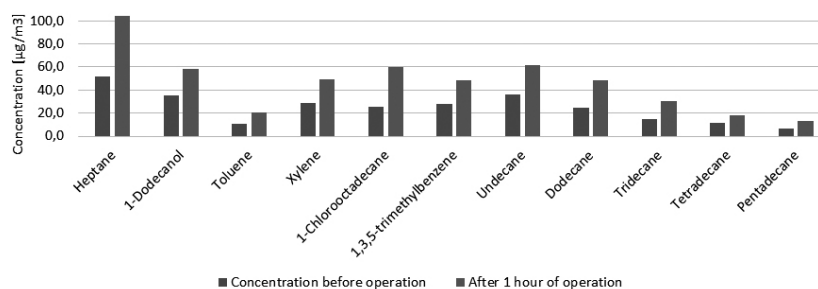


Fig. 4. Changes in concentration of the identified compounds before starting and after 1h of operation of the membrane system

Conclusions

The examples presented in this paper confirm that the TD-GC-MS technique, and the methodology designed for it, is useful in the analysis of the concentrations of VOC in the air. Despite the high degree of the complexity of the apparatus, labour consuming calibration, and somewhat high costs of materials, this method, nonetheless, has the most advantages in comparison to other methods of analysis. It allows for the simultaneous identification of the qualitative (chemical composition) and reliable quantitative assessment of VOC in the tested object. It also allows an approximate estimation of the concentrations of the substances for which no calibration has been carried out. Moreover, the compact size of both the sorption tubes and aspiration systems for sampling make the TD-GC-MS method broad in application – from miniature personal devices, and portable systems for fieldwork, to extensive stationary analysers for continuous monitoring of contamination.

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References

1. Ahn Ji-W., Pandey S.K., Kim Ki-H.: Comparison of GC-MS calibration properties of volatile organic compounds and relative quantification without calibration standards. *Journal of Chromatographic Science*, 2011, Vol. 49, pp. 19–28.
2. World Health Organization (WHO): Indoor air quality: organic pollutants. *Euro Reports and Studies*, 1989, Copenhagen, Denmark.
3. Yu C., Crump D.: A review of the emission of VOCs from polymeric materials used in buildings. *Building and Environment*, Vol. 33, pp. 357–374.

4. Fedele R., Galbally I.E., Porter N., Weeks I.A.: Biogenic VOC emissions from fresh leaf mulch and wood chips of *Grevillea robusta* (Australian silky oak). *Atmospheric Environment*, Vol. 41, 36-87-8746.
5. Su Y.C., Chang C.C., Wang J.L.: Construction of an automated gas chromatography/mass spectrometry system for the analysis of ambient volatile organic compounds with on-line internal standard calibration. *Journal of Chromatography A*, 2008, Vol. 1201, pp. 134–140.
6. Leff J.W., Fierer N.: Volatile organic compound (VOC) emissions from soil and litter samples. *Soil Biology & Biochemistry*, 2008, Vol. 40, pp. 1629–1636.
7. Kagi N., Fujii S., Tamura H., Namiki N.: Secondary VOC emissions from flooring material surfaces exposed to ozone or UV irradiation. *Building and Environment*, 2009, Vol. 44, pp. 1199–1205.
8. Liu P.W.G., Yao Y.C., Tasi J.H., Hsu Y.C., Chang L.P, Chang K.H.: Source impacts by volatile organic compounds in an industrial city of southern Taiwan. *Science of the Total Environment*, 2008, Vol. 398, pp. 154–163.
9. Hosi J.Y., Amano S., Sasaki Y., Korenaga T.: Investigation and estimation of emission sources of 54 volatile organic compounds in ambient air in Tokyo. *Atmospheric Environment*, 2008, Vol. 42, pp. 2383–2393.
10. Brancaloneoni E., Scovaventi M., Frattoni M., Mabilia R., Ciccioli P.: Novel family of multi-layer cartridges filled with a new carbon adsorbent for the quantitative determination of volatile organic compounds in the atmosphere. *Journal of Chromatography A*, 1999, Vol. 845, pp. 317–328.
11. Atkinson R.: Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment*, 2000, Vol. 34, pp. 2063–2101.
12. Dewulf J., VanLangenhove H., Wittmann G.: Analysis of volatile organic compounds using gas chromatography. *Trends in Analytical Chemistry*, 2002, Vol. 21, pp. 637–646.

Metodyka badania stężenia lotnych związków organicznych z zastosowaniem techniki TD-GC-MS

Słowa kluczowe

Lotne związki organiczne (LZO), termiczna desorpcja, GC/MS.

Streszczenie

Dorosły człowiek spędza ok. 80% czasu w pomieszczeniach zamkniętych. Zarówno materiały budowlane, jak i sprzęty znajdujące się w pomieszczeniu emitują lotne związki organiczne (VOC – *Volatile Organic Compounds*). Wiele z emitowanych VOC może negatywnie oddziaływać na organizm ludzki,

szczególnie gdy ich stężenie w powietrzu przekroczy pewne krytyczne progi. Z tego powodu zasadne, a często nawet konieczne, jest monitorowanie ich stężenia w powietrzu. Dla wielu VOC najniższe dopuszczalne stężenia w powietrzu są ustalone na skrajnie niskim poziomie. Dlatego też wykrywanie ich i ilościowe oznaczanie wymaga zastosowania wyrafinowanych technik analitycznych. Opracowano metodykę jakościowego i ilościowego oznaczania VOC w powietrzu na bardzo niskich poziomach stężeń, niezbędnych do kontroli jakości pracy urządzeń do badania emisji VOC z dowolnego źródła. Do tego celu zastosowano chromatografię gazową (GC) w sprzężeniu ze spektrometrem mas (MS), wspomaganą termiczną desorpcją (TD). Przy zastosowaniu opracowanej metodyki zbadano wielkość emisji do otoczenia kilkudziesięciu różnych VOC, pochodzących z materiałów powszechnie występujących w zamkniętych pomieszczeniach pracy. Omówiono kluczowe aspekty realizowanej metodyki, od etapu przygotowania aparatury, poprzez pobieranie i przygotowanie próbki do analizy, właściwą analizę techniką TD-GC-MS, do interpretacji wyników analizy. Opracowana metodyka stosowana jest do badania obecności VOC na stanowisku membranowym oraz do weryfikacji czystości komór służących do badania emisji VOC z różnych materiałów użytkowych.