Impact of multisource VOC emission on in-vehicle air quality: test chamber simulation

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Abstract. Air quality inside vehicle may be strongly influenced by the presence of volatile organic compounds (VOC). The sources of these compounds may be different. In case of new vehicles VOC mainly originate from off-gassing of interior materials, while in used cars exterior pollution, like exhaust gases, starts to dominate. The aim of this work was to check the influence of multiple VOC sources on concentration of volatile organic compounds emitted from car interior parts. For this purpose material emission tests were performed in 1 m$^3$ emission testing chamber (WKE 1000, Weiss, Germany) at 65 °C, 5% RH and with air exchange. Three different car parts were studied: sun visor, headlining, and handbrake lever cover. It was stated that volatile organic compounds concentration inside test chamber during the test performed with three different parts inside was significantly lower than those being result of addition of the results obtained for parts tested separately. Presented results indicate interactions between different materials and their emissions as well as prove that some of materials acts like sorbents.

1. Introduction

Interior air quality in vehicle’s cabin is gaining an increased attention because car is frequently used mean of transport. People spend much of their time indoors, inter alia in cars, commuting to work and travelling for business or private purposes [1-4].

The presence of organic compounds, among them volatile organic compounds (VOC), very volatile organic compounds (VVOC) and semi-volatile organic compounds (SVOC), is the main factor influencing air quality and its regarding by people. Organic compounds present in air have or may have a negative impact on human health, but may also influence driving safety. Selected compounds are responsible for:

- drowsiness (e.g. saturated and unsaturated aliphatic hydrocarbons, cyclohexane, ethylbenzene, 1-butanol);
- headache and dizziness (e.g. hexane, heptane, cyclohexane, toluene, naphthalene, trimethylbenzene);
- eye irritation (e.g. 2-ethylhexanol, benzaldehyde, styrene, propylbenzene);
- respiratory problems and throat irritation (e.g. styrene, methycyclopentane, decalin);
- fatigue, nausea, skin irritation, toxic, carcinoogenic or mutagenic effect, and many others [5,6].

The other action of organic compounds, which has not direct influence on human health, but on driving safety, is a phenomenon called fogging. Semi-volatile organic compounds with boiling temperatures above 240-260°C [7], mainly phthalates, condensate on interior surface of windscreen, reducing the transparency and causing light reflections [8-10].
Some of organic compounds has also odorous character. Human nose is a very sensitive odour detector, capable to detect odour on very low concentration level [11]. On the other hand, people can recognize differently the same odour, because odour perception is a very subjective task. Moreover, even if specific odour is recognized as a pleasant, in long-term exposure may lead to odour annoyance and discomfort [12].

Organic compounds in new car cabin originate mainly from materials’ off-gassing [3,13-15], as in vehicle interior multiplicity of different materials is used [9], among them polystyrene, polyethylene, propylene, polyamide, acrylonitrile-butadiene-styrene, rubber, natural or artificial leather, polyurethane foam etc. Each of this material is a potential source of VOCs emission. It was found that ethylbenzene and styrene are specific compounds for polystyrene presence, disregarding air temperature. In ambient temperature polyurethane foam emits inter alia toluene, phenol, decane, nonanal, benzaldehyde, diethyl phthalate etc. Benzaldehyde, nonanal, tridecane, decanal, and diethyl phthalate can be emitted in 23 °C from polyethylene, while in higher temperature (70 °C) 2-ethyl-1-hexanol was additionally detected. The main compound, which is usually emitted from polypropylene, is 2,2,4,6,6-pentamethylheptane [16]. Additionally, plastics are often enriched by different additives to achieve desired properties. Among those additives plasticizers, stabilizers or flame retardants can be found. Many of this additives are regarded to be hazardous, and for that reason controlling the emission of those compounds is significant [8]. The toxicity of organic compounds mixtures in new passenger vehicles was described elsewhere [17].

Concentrations of organic compounds depend on atmospheric conditions, vehicle model, it’s age and mileage and user’s habits [14]. Within the same car model the concentration of selected compounds may differ significantly, depending on materials and equipment used in vehicle interior [4,18]. Along with the increase of vehicle age and mileage, when proper ventilation is applied, the concentration of VOCs emitted from materials usually decreases, but compounds originating from external sources may additionally appear [14]. Those sources include fuel combustion, fuel leakage and others, and concentration of pollutants depends inter alia on air exchange efficiency, season of the year, time of travelling, traffic and travelling routes [19,20]. Car exhaust gases are the main source of human exposure to particulate matter and soot [21], aldehydes, including formaldehyde and acetaldehyde [22], and naphthalene [23]. The main compounds under study in used vehicles were so called ‘emission markers’, that is: benzene, toluene, ethylbenzene and xylenes (BTEX) [14,20,24]. Interior air quality in used vehicles was widely investigated and quite great knowledge was gathered. In case of new vehicles still little is known about interior air quality, as a result of variety of models, types of equipment and materials used in vehicle interior.

The emission of VOCs from materials is affected by air temperature and relative humidity (RH), depending on type of material and type of compound. It was found that in typical ambient temperature (23-30°C) concentration of VOCs was independent on temperature, and the impact of RH was negligible [25]. Materials which are used in indoor environments are usually tested in temperature of 23°C [8]. Although in indoor environment the temperature can reach approximately 30°C in maximum, in vehicle interior in direct sunlight (i.e. in summer months) the temperature may reach an excessive maximum (over 65°C) [26]. The increased temperature in vehicle interior would result in higher emission of different organic compounds, and therefore higher human exposure to harmful pollutants [25]. For that reason materials for automotive industry are tested in temperature of 65°C.

The tendency nowadays is to reduce the use of toxic materials indoors in order to minimalize occupants’ exposure to harmful chemicals emitted from those materials [27]. Similarly, in automotive industry (in vehicle production and furnishings), producers intend to reduce harmful materials presence.

There is no clear requirements regarding interior air quality in new vehicles [15], however concentration of organic compounds may be at significantly high level. Total volatile organic compounds (TVOC) concentration inside car cabin may vary from less than 1 mg/m³ to over 10 mg/m³. Such a high VOC concentration may have effect in driver’s and passenger’s discomfort and irritation feelings. For that reason monitoring of air composition in new vehicles and measuring of VOCs emitted
from materials is essential to ensure a high quality of produced cars and to take care of human health and comfort.

The aim of this work was to compare results obtained during separate car interior parts emission testing with the results of tests performed with multiple parts. Gathered information should expand knowledge regarding in-vehicle air quality and possibility to assess quality control check based on separate parts emission testing.

2. Experimental methods

2.1. Materials under study

Three different car interior parts were chosen for this study, namely: handbrake lever cover, sun visor and headlining. All parts were made of synthetic materials and in brand new condition. Handbrake lever cover was made of only one material (polyvinyl chloride – PVC). Soft PVC was used as covering decorating layer of sun visor with some hard plastic used as inside support material while headlining was made of a wafer material of synthetic fibres/polyurethane foam/synthetic fibres (SF/PUR/SF). Emission tests were performed for separate parts as well as for all of them together.

2.2. Emission tests

Emission tests of car interior parts were performed in airtight, specially constructed emission testing chamber of ca. 1 m$^3$ internal volume (WKE 1000, Weiss, Germany). In case of handbrake lever cover and sun visor tests two pieces of each part were tested while in case of headlining only half of a part was placed inside the chamber. Each set of parts was placed into the preconditioned chamber at 65 °C supplied with humidified (5% RH) purified air (air exchange set to 0.4). After 5 h of test item conditioning air samples were collected with the use of Tenax TA sorbent in stainless steel tubes (Markes, UK) for VOC analysis and cartridges filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) on silica gel (Sigma-Aldrich, Poland) for carbonyl compounds analysis. Cartridges with sorbents were connected to heated distribution tree of WKE 1000, SKC PCMTX-8 (SKC, UK) pumps were used for sample collection with the air flow rate set to 100 cm$^3$/min in case of VOC sampling on Tenax TA and to 750 cm$^3$/min in case of carbonyl compounds sampling on 2,4-DNPH cartridges. The accuracy of flow rates was provided by calibration with DRYCAL flowmeter (BIOS, USA). Duplicate samples were collected for 20 min allowing collection of 2 dm$^3$ air sample for VOC analysis, and 15 dm$^3$ sample for analysis of carbonyl compounds. After sampling sorbent tubes were closed and stored in refrigerator prior the analysis.

2.3. Analytical methods

Analysis of volatile organic compounds emitted from tested car interior parts was performed as described previously [13,14,18]. The air samples collected on Tenax TA were desorbed with the use of a thermal desorption system Unity2 (Markes, UK) equipped with Series2 Ultra TD autosampler (Markes, UK). Samples were desorbed at 300 °C for 15 minutes and transferred via a heated transfer line to a gas chromatograph equipped with a flame ionization detector (7890A, Agilent, USA) and a mass spectrometer (MSD 5975C, Agilent, USA). The gas chromatograph was equipped with a column splitter allowing to perform simultaneous analysis with use of both detectors. Detailed TD-GC/FID-MS analysis parameters are presented in Table 1. Identification of volatile organic compounds was based on retention times (RT) and mass spectra of more than 140 VOCs standards (Sigma-Aldrich, Poland) and National Institute of Standards and Technology (NIST08) spectra library. The concentrations of emitted volatile organic compounds were calculated in toluene equivalent (µg/m$^3$) i.e. were calculated against the standard toluene curve.

Table 1. Details of chromatographic analysis.

| Thermal desorber | Tube: 280°C (15 min); Purge: 1 min; |
|------------------|-----------------------------------|
Carbonyl compounds collected on DNPH cartridges were extracted with 1 cm³ of acetonitrile (Sigma-Aldrich, Poland) what was followed by liquid chromatography (HPLC) analysis with use of Infinity 1260 system (Agilent, USA) equipped with Zorbax Stablebond C-18 column. In case of HPLC analysis identification and quantification of carbonyl compounds was based on retention times and calibration curves of 16 carbonyl compounds (formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, methacrolein, 2-butanone, butyraldehyde, pentanal, cyclohexanone, o-tolualdehyde, m,p-tolualdehyde, hexaldehyde, 2,5 –dimethylbenzaldehyde, all from Sigma-Aldrich, Poland).

### 3. Results and discussion

Altogether 377 volatile compounds were detected by TD-GC/FID-MS in collected air samples where: 142 compounds were detected only in samples collected from single part testing, 92 compounds were detected in samples collected from 2 separate test, 74 compounds in samples collected from 3 tests. It was stated that 69 volatile organic compounds were present in air during all the tests i.e. 3 tests of separate parts and 1 test of 3 parts together. Chromatograms of collected VOC samples are compared in Fig. 1. Even brief analysis of obtained chromatograms allows noticing that concentration of volatile organic compounds emitted during the “3 parts together” emission test is not a simple sum of VOCs emitted when parts were tested separately. There are visible differences not only in quantity, in this case signal intensity, but also in compound’s nature. Some compounds are present only in case of separate parts, however other ones were detected only while all, three parts, were tested simultaneously.
Figure 1. Comparison of chromatograms collected during the emission tests of car interior parts.

Volatile organic compounds analyzed by TD-GC/FID-MS were divided into 13 groups, “RT groups”, in reference to their retention times (RT) (Fig. 1), where <C6 stands for all compounds with RT lower than RT of hexane, C6 stands for hexane and all compounds with RT lower than RT of heptane, C7 stands for heptane and all compounds with RT lower than RT of octane etc. For each compound’s group concentrations were summarized and values were compared (Fig. 2). It can be seen that for three first groups (<C6…C7) VOCs emitted during the testing of 3 parts may be close to sum of the same VOCs emitted from separate parts, however in all other cases no such dependence can be noticed. For example handbrake lever cover emitted ca. two times more C10 compounds than three parts together and even bigger differences are observed in case of sun visor. This simple approach clearly indicates that there are important differences between concentration of emitted VOCs from car interior parts when different items are in contact/proximity with one another.
Similarly, in case of comparison of different types of volatile organic compounds concentrations there are no clear dependence between substances emitted from separate parts and from test performed for parts together (Fig. 3). Large differences are observed mainly in case of ethers, aromatic hydrocarbons, phenols and alcohols. Taking into account that total concentration of volatile organic compounds (Table 2) was the highest for sun visor and the lowest for headlining, which was also the largest tested part one can assume that in case of simultaneous testing of different items some of VOCs emitted from one item may adsorb onto another’s item surface. This assumption seems to be confirmed when emission from headlining is deeper analyzed. In this case VOC lowers than C15 “RT groups” have significantly lower summary concentration than those from other separate parts. These groups emitted from 3 parts together are significantly lower than from dominating separate part, other than headlining. On the other hand when C15, C16 and >C17 RT groups are taken into account, results are in opposite to the above.
Headlining emission is larger than from two other parts and only slightly differs from emission detected from simultaneous testing of three parts.

Some additional information provides comparison of VOC type and RT (Fig. 4). Also in this case the most significant differences between concentration of emitted organic volatile compounds from separate parts and parts tested together are observed when headlining is not important source of selected VOC group. This is especially noticeable in case of hydrocarbons: RT C14 group is dominated by the emission from sun visor, while RT C16 is dominated by the emission from headlining, but similar concentrations levels are observed from 3 parts testing. However in case of RT C14 group concentration of VOCs emitted from sun visor is nearly three times higher than concentration of these compounds emitted from all parts together. On the other hand, concentration of RT C16 group emitted from headlining is only ca. 40% higher than from 3 parts. These seems to further confirm the thesis that presence of large surface headlining, which additionally is the most porous material from three tested, have the deciding effect on

Figure 4. Comparison of VOC type and RT groups, based on TD-GC/FID-MS results.
total VOC concentration in case of simultaneous testing of different parts. When separate emission test performed for headlining yield in significant concentration of VOC RT or type group the same effect is observed in case of multiple parts testing. When considered groups of compounds are not emitted in large amount by headlining their concentration in case of 3 parts testing is significantly lower than from their dominant donor. Therefore conclusion seems to be justified that parts made of different materials, which additionally differs in porosity, may as well emit and adsorb volatile organic compounds at elevated temperatures when in proximity.

Table 2. Summary of TD-GC/MS-FID and HPLC results.

|                      | Handbrake lever cover | Sun visor | Headlining | 3 parts together |
|----------------------|-----------------------|-----------|------------|------------------|
| TD-GC/FID-MS         |                       |           |            |                  |
| Total VOC concentration, µg/m³ | 4 751                 | 13 281    | 4 720      | 8 210            |
| HPLC                 |                       |           |            |                  |
| Formaldehyde, µg/m³  | 3.4                   | 63.9      | 437.0      | 497.6            |
| Acetaldehyde, µg/m³  | 40.8                  | 103.3     | 100.1      |                  |
| Acetone, µg/m³       | 2.1                   | 3.4       | 11.3       | 10.3             |
| Propionaldehyde, µg/m³ | 13.3                  | 10.5      |            |                  |
| 2-Butanone, µg/m³    | 10.8                  | 5.5       |            |                  |
| Benzaldehyde, µg/m³  | 15.6                  | 35.2      | 20.4       | 30.8             |
| Cyclohexanone, µg/m³ | 90.8                  | 1.6       | 7.6        |                  |
| Hexaldehyde, µg/m³   | 8.7                   | 8.4       |            |                  |

Results obtained with use of HPLC method are presented in Table 2. In case of carbonyl compounds analysis previously noticed dependence is confirmed. As a proof of headlining importance in multisource emission one can notice that in case of acetaldehyde theoretically possible concentration of this compound during three parts test may be ca. 140 µg/m³ (emissions from sun visor and headlining) but the real value from testing all of the parts is 100 µg/m³. On the other hand in case of cyclohexanone theoretically possible concentration for 3 parts is ca. 92 µg/m³ but the real value is only 7.6 µg/m³ probably due to previously mentioned adsorption of compound on headlining surface. Presented results confirms previously suggested interactions between VOC emitted from different materials [27, 28] what in case of our results can be noticed by differences between theoretically possible total concentration of volatile organic compounds and the real values. Deeper look at the presented results allowed conclusion that some of materials, like headlining which can be characterized by significant porosity, acts like sorbents what leads to decrease of specific compounds or group of compounds concentrations.

4. Summary

The results presented highlight the issues in predicting air composition on the basis of single emission source measurements, thus make car quality control based on in-vehicle VOC concentration very difficult to achieve while only single parts results are available. Taking into account that in new car VOCs emitted from interior materials are main source of air contamination [13], and may have negative effect on users comfort, health and safety, interaction of emitted substances with other materials may lead to elongation of exposure, due to their adsorption and expected desorption in future.

References
[1] WHO 2006 Development of WHO Guidelines for Indoor Air Quality
[2] WHO 2010 Selected pollutants. Guidelines for Indoor Air Quality
[3] Yoshida T and Matsunaga I 2006 Environ. Int. 32 58-79
[4] Zhang G-S, Li T-T, Luo M, Liu J-F, Liu Z-R and Bai Y-H 2008 Build. Environ. 43 315-19
[5] Salthammer T and Uhde E 2009 Organic indoor air pollutants (Weinheim: Wiley-VCH Verlag GmbH)
[6] Sarbu I and Sebarchievici C 2011 Olfactory comfort assurance in buildings Chemistry, emission control, radioactive pollution and indoor air quality (InTech)
[7] ISO 16000-6:2011 Indoor air. Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID
[8] Wensing M, Uhde E and Salthammer T 2005 Sci. Total Environ. 339 19-40
[9] Loock F, Lampe T and Bahadir M 1993 Fresenius J. Anal. Chem. 347 280-85
[10] Kalman E-L, Löfvendahl, Winquist F and Lundström I 2000 Anal. Chim. Acta403 31-38
[11] Delahunty C M, Eyres G and Dufour J-P 2006 J. Sep. Sci. 29 2107-25
[12] Bartsch J, Uhde E and Salthammer T 2016 Anal. Chim. Acta904 98-106
[13] Faber J, Brodzik K, Golda-Kopek A and Łomankiewicz D 2013 Pol J. Environ. Stud. 22 (6) 1701-09
[14] Faber J, Brodzik K, Golda-Kopek A and Łomankiewicz D 2013 J. Environ. Sci.25 (11) 2324-30
[15] Buters J T M et al. 2007 Environ. Sci. Technol.41 2622-29
[16] Mitchell G, Higgit C and Gibson L T 2014 Polym. Degrad. Stabil. 107 328-40
[17] Janicka A 2013 Proc. ECOpole7 (1) 93-99
[18] Brodzik K, Faber J, Łomankiewicz D and Golda-Kopek A 2014 J. Environ. Sci.26 (5) 1052-61
[19] Jo W-K and Park K-H 1999 Atmos. Environ. 33 397-404
[20] Rahman Md M and Kim K-H 2012 J. Hazard. Mater. 241-242 267-78
[21] Lee K, Sohn H and Putti K 2010 J. Air Waste Manage. 60 130-36
[22] Jo W-K and Lee J-W 2002 Environ. Res. A 88 44-51
[23] Jo W K and Lee J H 2011 Int. J. Environ. An. Ch. 91 1412-24
[24] Som D, Dutta C, Chatterjee A, Mallick D, Jana T K and Sen S 2007 Sci. Total Environ. 372 426-32
[25] Lin Ch-Ch, Yu K-P, Zhao P and Lee G W-M 2009 Build. Environ. 44 525-33
[26] Mandalakis M, Stephanou E G, Horii Y and Kannan K 2008 Environ. Sci. Technol. 42 6431-36
[27] Setnikova I 2014 Mat. Sci. Eng. C 36 1-6
[28] Guo H, Murray F and Wilkinson S 2000 J. Air Waste Manage. Assoc. 50 199-206