

Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates



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Serial parameter: CN 11-2629/X*1989*m*277*en*P*29*2014-5

Available online at www.sciencedirect.com

Journal of Environmental Sciences

www.jesc.ac.cn

In-vehicle VOCs composition of unconditioned, newly produced cars

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ARTICLE INFO

Article history:

Received 30 April 2013

revised 06 May 2013

accepted 18 September 2013

Keywords:

volatile organic compounds (VOCs)

car interior

materials emission

DOI: 10.1016/S1001-0742(13)60459-3

ABSTRACT

The in-vehicle volatile organic compounds (VOCs) concentrations gains the attention of both car producers and users. In the present study, an attempt was made to determine if analysis of air samples collected from an unconditioned car cabin can be used as a quality control measure. The VOCs composition of in-vehicle air was analyzed by means of active sampling on Carbograph 1TD and Tenax TA sorbents, followed by thermal desorption and simultaneous analysis on flame ionization and mass detector (TD-GC/FID-MS). Nine newly produced cars of the same brand and model were chosen for this study. Within these, four of the vehicles were equipped with identical interior materials and five others differed in terms of upholstery and the presence of a sunroof; one car was convertible. The sampling event took place outside of the car assembly plant and the cars tested left the assembly line no later than 24 hr before the sampling took place. More than 250 compounds were present in the samples collected; the identification of more than 160 was confirmed by comparative mass spectra analysis and 80 were confirmed by both comparison with single/multiple compounds standards and mass spectra analysis. In general, aliphatic hydrocarbons represented more than 60% of the total VOCs (TVOC) determined. Depending on the vehicle, the concentration of aromatic hydrocarbons varied from 12% to 27% of total VOCs. The very short period between car production and sampling of the in-vehicle air permits the assumption that the entire TVOC originates from off-gassing of interior materials. The results of this study expand the knowledge of in-vehicle pollution by presenting information about car cabin air quality immediately after car production.

Introduction

A variety of volatile organic compounds (VOCs) may be present inside a car's cabin, some of them being the result of off-gassing of interior materials, while the presence of the others can be a result of exterior pollution (atmospheric pollution, exhaust gases, etc.) (Chien, 2007; Fedoruk and Kerger, 2003; Yoshida et al., 2006a; Jo and Park, 1999). Yoshida and Matsunaga (Yoshida and Matsunaga, 2006) proved that the in-vehicle VOC concentration generally decreases during the first three years after delivery, and the amount of organic compounds in air is higher during the summer than during the winter. The total volatile organic compounds (TVOC) concentration level decreased

from over 10 mg/m³ right after delivery to ca. 200 µg/m³ after three years. During vehicle operation, air pollution originating from interior materials decreases as more and more of initially trapped VOCs are released from materials and eventually is removed via ventilation. The strong correlation of in-vehicle contamination levels with ambient air conditions, lower VOCs concentrations during the winter and higher concentrations during the summer, shows clearly that the efficacy of desorption of compounds increases with increasing temperature. Additionally, the presence of higher boiling point semivolatile organic compounds may lead to the deposition of a film on the windscreen's inner surface, called "fogging", which, together with dust particles, may reduce the windscreen's transparency (Wensig, 2009). Car producers are aware that air quality in the car's cabin can influence the customer's attitude towards their

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products. The odor inside the car cabin and, even more importantly, the possible negative health effects of human exposure to VOCs, are factors explaining the efforts taken to use interior materials from which emission of volatile compounds is as low as possible.

The production cycle of one car model can last for several years and during this period the air quality inside each new car can be subject to some fluctuations. One of the main reasons is changes in the interior materials used (Yoshida et al., 2006b). Changes of materials and/or colors of upholstery, roof linings or carpets, as parts of large surface area, have a significant effect on the interior air quality. Great attention is paid to the instrumental analytical methods for determining VOCs released from materials. Material emissions of organic compounds under static conditions can be measured by the application of the headspace method, for example, according to VDA 277 (VDA, 1995). Direct thermal desorption permits determination of volatile and semivolatile organic compounds under dynamic conditions, e.g. VDA 278 (VDA, 2002). Also, entire interior parts may be subjected to emission tests after conditioning in sealed compartments, e.g. VDA 276, testing of emission in a 1 m³ chamber (VDA, 2005). Car producers usually have their own testing procedures for emission testing purposes, which can be divided roughly into three groups: (a) emission testing of small material samples, (b) emission testing of entire parts, and (c) in-vehicle air analysis; most of which are similar to the ones mentioned above. However, even if all of the materials used in a vehicle cabin are subjected to emission tests and the results are acceptable, their variety and the variety of VOCs emitted from them can cause undesirable impacts on interior air quality. This is especially important while taking into account that even small changes in the air composition may lead to nuisance odor, impacting the customer's acceptance. The automotive industry tries to deal with this topic by applying the standards concerning odor determination of parts (e.g. VDA, 1992).

Precise information concerning the air quality inside car cabins can be obtained after specific air sample collection from the car's interior, which should have been previously conditioned with caution. Conditioning of the car tested under static conditions is essential as factors such as temperature, humidity and ambient air pressure influence the analysis results (You et al., 2007; Faber et al., 2012). The issue is that such conditioning demands the

usage of drive-in climatic chambers and the time necessary to stabilize the atmospheric conditions within the car. Therefore, it appears to be impractical to test a large number of cars leaving the assembly line, especially given that detailed air quality analyses are usually performed only during the implementation of a new model to the market. The assumption that the air quality inside a car does not change is accompanied by the assumption that the interior parts, once tested, (e.g. during the validation of a new product), could be characterized by the same VOC emissions characteristics as long as they are produced from the same material. However, with as any other product, car components undergo some slight changes during the long production period. Although these changes may seem to be irrelevant to the mechanical properties of the material (for example), they can influence the VOC emissions characteristic of the entire part.

This study concentrates on determining the VOC concentrations in air samples collected from cars leaving the factory assembly line not later than 24 hr before the sampling event. Qualitative and quantitative VOC determination is the starting point for comparison of air quality inside cars of the same brand and model equipped with different interior parts/materials. The usefulness of a relatively simple method of collecting and analyzing in-vehicle air samples from unconditioned cars for quality purposes is discussed.

1 Experimental methods

1.1 Vehicles under study

The vehicles under study included nine cars of the same brand and model: with three doors, four seats, and a total interior volume of ca. 2.4 m³. The main differences between them are listed in **Table 1**. The only difference between interiors of cars A–D was the presence of a sunroof, while two other pairs i.e. EF and GH differed in terms of the presence of a sunroof and different steering wheel color. Before sampling the vehicles were parked outdoors not longer than 24 hr after leaving the assembly line. The cars examined had no fuel leakages or mechanical problems.

Table 1 Interior materials detail of vehicles under study

Vehicle	Steering wheel	Upholstery	Dashboard	Other
A and B	White synthetic	Red synthetic fabric/white synthetic leather	White	–
C and D	White synthetic	Red synthetic fabric/white synthetic leather	White	Sunroof
E and F	White synthetic	Black and white synthetic fabric	White	Sunroof
G and H	Black synthetic	Black and white synthetic fabric	White	–
I	black Synthetic	Black and white synthetic fabric/black synthetic leather	White	Convertible

1.2 Air sampling

All in-vehicle air samples were collected during the same day (autumn 2012), within a 3 hr period, with vehicle's engine shut off, all doors and windows closed and AC off. Temperature, pressure and relative humidity inside the cars' cabins were: 21–25°C, 990 hPa, 48%–56% RH and were similar to ambient air conditions (a cloudy day). Two solid sorbents, Carbograph 1TD in a quartz tube and Tenax TA in a stainless steel tube (both Markes Int., UK), were used for collecting air samples. Duplicate sorbent tubes were connected to SKC PCMTX-8 pumps with the air flow rate set to 100 mL/min; the accuracy of the flow rate was provided by calibration of the sampling pumps with a DRYCAL flowmeter (BIOS, USA). Sampling systems were placed inside the car's cabin with sorbent tubes placed ca. 15 cm from the steering wheel and ca. 50 cm above the driver seat, at dashboard level. The doors were open for the ca. 10 seconds needed to place the sampling systems inside the car cabin (Chien, 2007). Field blank samples were collected alongside samples from the vehicles' interiors. Sampling lasted for 20 minutes; total sampling volumes were 2000 mL for both kinds of sorbents. After sampling, the sorbent tubes were removed, closed with brass end caps, placed in a sealed plastic box and transported to the laboratory. Analysis of all samples was performed within one week.

1.3 Samples analysis

The VOCs collected on sorbent bed were desorbed with the use of a thermal desorption system Unity2 (Markes Int., UK) equipped with a Series2 Ultra TD autosampler (Markes Int., UK). Prior to the desorption procedure an internal standard, deuterated toluene (toluene-d₈, 99.6 atom%D, Sigma-Aldrich, Poland) in methanol (Sigma-Aldrich, Poland), was injected onto each sorbent tube and flushed with helium (helium 6.0, Linde, Poland). 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 (Agilent 7890A, USA) and a mass spectrometer (Agilent MSD 5975C, USA). The GC/FID-MS system was equipped with a column splitter which permitted simultaneous analysis to be performed on both detectors. A summary of the analysis parameters, is presented in **Table 2**, which have been described in the previous work (Faber et al., 2013). Performing simultaneous detection on FID and MS detectors allowed both quantitative and qualitative analyses to be performed. Validation of the quantitative analysis method was based on an 11 point toluene calibration curve. Identification of compounds was based on analysis of retention times of 139 VOC standards (Sigma-Aldrich, Poland) from which 81 were detected in analyzed samples, and the National Institute of Standards and Technology (NIST08) spectra library. Only compounds with a quality score of 80 and above, according to the NIST library, were considered as identified if the retention time was not confirmed by standard compound analysis. Compounds with identification scores lower than 80 were reported as "other chemicals".

Quantitative analysis was based on toluene standard curves prepared with the use of both sorbents (You et al., 2007; Buters et al., 2007). A compound concentration mean value was calculated from the analysis of four samples: two samples adsorbed on Carbograph 1TD and two samples adsorbed on Tenax TA.

2 Results and Discussion

2.1 Air composition inside vehicle cabins

More than 260 volatile organic compounds were detected in the cabins of the vehicles tested and 107 of them were present in all air samples (**Table 3**). In general, there were more compounds detected in the samples collected on Carbograph 1TD than on Tenax TA. Due to the parallel

Table 2 Details of chromatographic analysis

Thermal desorber	Tube: 280°C in the case of Tenax TA, 300°C in the case of Carbograph 1TD (15 min) Purge: 1 min Cryotrap: from –30°C to 300°C at ca. 60°C/min Column pressure: 23 psi Split ratio (5:1)
Gas chromatograph (GC/FID)	Capillary column: DB-5MS UI (60 m × 1 µm × 0.32 mm) Carrier gas: helium 99.9999% Oven temperature program: from 40°C (2 min), at 3°C/min to 92°C, at 5°C/min to 160°C, 10°C/min to 290°C (12 min)
Mass spectrometer (MS)	Transfer line to MS: 300°C Ion source: electron impact (EI) Ion source temperature: 230°C Scan mode: SCAN m/z: 35–260 amu NIST08 library

Table 3 Number of compounds detected in air samples collected from vehicles' cabins

Vehicle	Number of compounds detected (Carbograph 1TD)	Number of compounds detected (Tenax TA)	Total number of compounds detected* (TVOC, $\mu\text{g}/\text{m}^3$)
A	133	126	139/934
B	133	128	142/854
C	135	143	150/1352
D	156	149	165/1426
E	183	177	202/2494
F	196	183	208/3040
G	201	194	213/6899
H	195	177	210/2933
I	194	187	205/2945

* The first value is the number of individual detected compounds on both sorbents; the second value is the total amount of VOC in $\mu\text{g}/\text{m}^3$.

sampling method, the total number of compounds detected was higher than any number for the compounds detected on a single type of sorbent, with a maximum of 19 additional compounds detected (in the case of vehicle E). The comparison of the number of compounds detected with TVOC indicates that the values were in good correlation, i.e. R^2 value was 0.97, when vehicle G was excluded from the comparison.

The compounds identified are listed in **Table 4**. The concentration of each of them was calculated in toluene equivalent with the value corresponding to the mean of four analyses performed on samples collected both on Carbograph 1TD and Tenax TA. Aliphatic (alkanes and cycloalkanes) and aromatic hydrocarbons constituted over 75% of TVOC in all cases. The majority of aromatic hydrocarbons were identified and confirmed, while identification of cycloalkanes—responsible for about one fourth of total organic compounds present in collected samples, was based mostly on the NIST 08 library. The results presented in **Tables 3** and **4** indicate that the concentration of VOCs in vehicle G's interior was actually the highest among the nine cars tested. TVOC in this vehicle was more than twofold higher than in the identically equipped cabin of vehicle H. Ten compounds present in vehicle's G cabin air were responsible for nearly half of TVOC emission (in descending order): methylcyclohexane, heptane, 3-methylhexane, toluene, 2-methylhexane, undecane, ethylcyclopentane, 2-methylheptane, m-xylene and 3-methylheptane. Taking into account that the number of compounds present in air samples collected from this vehicle's cabin was not exceptionally high in comparison with the other cars, it may indicate that some additional treatment, like painting or cleaning of the interior was carried out as the final quality control step of car assembly.

Four cars with identical upholstery, steering wheels and dashboards, differing only in terms of the presence of a sunroof (vehicles pairs AB and CD), can be characterized

by similar air composition. Undecane concentrations were the most significant, with dodecane being the second most abundant VOC in these four vehicles. The presence of undecane and dodecane may be connected with adhesives, carpets and PVC components used in the vehicles' interiors. In the case of these air samples, the ten compounds with the highest concentrations were responsible for up to 32% of TVOC. The presence of toluene and isomers of xylene is noticeable and may be also the result of emission from carpets (Brown, 2009). Benzoic acid (retention time: 35.05 min; identified with use of NIST 08 library with a probability of 97%; concentrations: (A) $8.5 \mu\text{g}/\text{m}^3$, (B) $23.1 \mu\text{g}/\text{m}^3$, (C) $32.0 \mu\text{g}/\text{m}^3$, (D) $34.9 \mu\text{g}/\text{m}^3$) and 2-ethylhexanol, which would probably be found also on the windscreen's surface due to their low volatility (Wensig, 2009), were detected along with triethylenediamine (retention time: 30.34 min; identified with use of NIST 08 library with a probability of 94%; concentrations: (A) $18.2 \mu\text{g}/\text{m}^3$, (B) $22.6 \mu\text{g}/\text{m}^3$, (C) $32.1 \mu\text{g}/\text{m}^3$, (D) $17.0 \mu\text{g}/\text{m}^3$). Their presence probably originates from the off-gassing of polyurethane foam used in production of car seats. The t-Student test ($\alpha = 0.05$) for pair AB revealed 5 results from the population of 50 to be statistically different. For the CD pair, the same test revealed only 4 significantly different results from the population of 57 confirmed organic compounds.

Vehicles equipped with black-white synthetic fabric upholstery (vehicles pairs EF and GH) and additional synthetic leather material (vehicle I) can be characterized by increased concentrations of the following aromatic compounds (in comparison with vehicles A–D): toluene and isomers of xylene. These compounds were the most abundant among all aromatic hydrocarbons collected from any air sample. Air samples collected from cars equipped with black-white fabric upholstery were richer in the number of compounds present—above 200 compounds in each case, and can be characterized by significantly higher TVOC levels than cars A–D equipped with mixed synthetic fabric/synthetic leather upholstery. The ten compounds with the highest concentrations were also responsible for a higher share in TVOC: (E) 30%, (F) 29%, (G) 47%, (H) 37% and (I) 36%. A basic comparison of the concentrations of confirmed compounds indicates that alkanes: decane, undecane and dodecane; cycloalkanes: methylcyclohexane, butylcyclopentane, 1-methyl-2-propylcyclohexane; aromatics: toluene, isomers of xylene, 1-ethyl-4-methylbenzene; ethyl acetate and 2-ethylhexanol were emitted in larger amounts from black and white synthetic fiber upholstery.

2.2 Influence of cabin equipment on air composition

The influence of the cabin's interior equipment on the organic compound composition of interior air can be estimated in various ways. One of them is to compare the presence of compounds in all air samples and

Table 4 Concentrations of confirmed compounds

Compound	CAS	RT (min)	A	B	C	D	E	F	G	H	I
Alkanes											
2-Methylpentane	107-83-5	6.801				3.6	7.6	19.0		8.4	3.2
3-Methylpentane	96-14-0	7.250				2.2	6.3	7.5		14.9	
Hexane	110-54-3	7.745	2.3	1.9	1.7	2.1	7.5	10.3	13.9	6.3	10.5
2,2-Dimethylpentane	590-35-2	8.616							18.7		
3,3-Dimethylpentane	562-49-2	10.039							16.0	1.3	1.9
2-Methylhexane	591-76-4	10.390	2.5	2.1	1.8	2.0	4.8	3.6	283.7	14.3	13.7
2,3-Dimethylpentane	565-59-3	10.602		1.5			1.8	1.9	96.4	5.6	7.7
3-Methylhexane	589-34-4	10.865	7.6	5.0	3.9	5.5	11.2	9.2	421.8	30.5	27.6
3-Ethylpentane	617-78-7	11.373							35.5	2.3	2.1
Heptane	142-82-5	12.056	13.3	9.1	6.7	8.5	21.3	14.4	670.1	76.8	49.1
2,4-Dimethylhexane	589-43-5	13.803					1.3	1.5	35.6		1.9
2,3-Dimethylhexane	584-94-1	15.528							7.4	1.2	
2-Methylheptane	592-27-8	15.719				1.0	1.5	1.5	167.3	1.8	3.2
4-Methylheptane	589-53-7	15.766							57.0		
3-Methylheptane	589-81-1	16.144							141.7		
Octane	111-65-9	17.817	2.1	2.0	4.7	3.3	9.4	9.2	109.0	6.6	5.3
2,5-Dimethylheptane	2216-30-0	20.021				2.7	4.3	5.1	6.4	4.4	3.9
2,3-Dimethylheptane	3074-71-3	21.335			1.6	2.0	4.6	5.1	5.2	4.9	4.4
3,4-Dimethylheptane	922-28-1	21.513					1.2	1.6	1.9	1.4	
2-Methyloctane	3221-61-2	21.807			1.9	2.9	4.5	6.7	11.9	7.3	3.1
3-Methyloctane	2216-33-3	22.169	1.2	1.4	3.1	4.2	7.2	9.9	15.8	10.2	5.3
2,2-Dimethyloctane	15869-87-1	24.717									1.1
3,3-Dimethyloctane	4110-44-5	25.747			1.5	1.8	3.6	4.1	5.1	3.4	2.8
2,3-Dimethyloctane	7146-60-3	26.696		1.8	1.6	2.1	3.3	5.2	4.5	3.8	3.4
2-Methylnonane	871-83-0	27.124	2.9	3.9	6.7	7.8	16.3	17.6	19.4	10.0	10.7
Decane	124-18-5	28.814	16.8	22.0	33.5	34.0	74.5	74.0	84.9	43.7	74.3
Undecane	1120-21-4	33.097	60.6	73.1	93.2	83.0	150.8	194.7	219.8	272.3	163.2
Dodecane	112-40-3	36.469	40.0	40.2	43.1	40.1	63.8	76.2	60.0	48.7	55.7
Tridecane	629-50-5	39.127	7.8	8.2	7.6	6.3	9.3	12.6	10.0	10.3	7.6
Tetradecane	629-59-4	41.323	2.2	3.0	1.7	1.4	2.4	2.2	7.8	10.3	2.9
Pentadecane	629-62-9	43.208			3.2		1.9	2.4			
Other alkanes			172.5	147.8	312.5	315.8	609.4	683.1	701.9	572.3	539.6
Total alkanes			331.7	320.4	527.7	527.7	1027.5	1165.4	3219.4	1158.3	990.6
Cycloalkanes											
Methylcyclopentane	96-37-7	8.977					11.1	6.3	14.1	3.1	4.6
Cyclohexane	110-82-7	10.512		2.7	4.1	10.1	20.9	14.8	53.6	3.4	30.4
1,1-Dimethylcyclopentane	1638-26-2	10.976							6.6	3.2	4.6
cis-1,3-Dimethylcyclopentane	2532-58-3	11.470		1.4			2.3	1.9	80.9	8.6	7.3
trans-1,3-Dimethylcyclopentane	1759-58-6	11.625					2.3	2.1	69.5	8.4	7.1
trans-1,2-Dimethylcyclopentane	822-50-4	11.757					3.6	2.2	116.6	13.8	11.2
Methylcyclohexane	108-87-2	13.686	8.9	6.8	4.0	4.9	18.0	11.5	686.5	59.1	55.4
Ethylcyclopentane	1640-89-7	14.151							171.7	12.3	
ctc-1,2,4-Trimethylcyclopentane	16883-48-0	14.470							43.3	1.2	1.8
ctc-1,2,3-Trimethylcyclopentane	19374-46-0	14.913							52.7	1.5	3.8
ctt-1,2,4-Trimethylcyclopentane	4850-28-6	16.606							13.6		
trans-1,4-Dimethylcyclohexane	2207-04-7	17.082					2.1	2.3	40.9	2.5	2.9
trans-1,2-Dimethylcyclohexane	6876-23-9	18.221							20.8	2.2	2.4
Propylcyclopentane	2040-96-2	20.104							2.2	0.7	
cis-1,2-Dimethylcyclohexane	2207-01-4	20.232			1.1	1.6	2.4	3.3	6.4	2.8	1.7
ccc-1,3,5-Trimethylcyclohexane	1795-27-3	20.650				1.4	2.3	3.6	4.7	3.4	2.8
ctc-1,2,4-Trimethylcyclohexane	7667-59-6	21.609	1.5	1.9	2.4	2.2	5.3	6.3	12.6	9.2	17.1
ctt-1,2,4-Trimethylcyclohexane	7667-60-9	22.996	0.9	0.7	2.4	2.4	3.3	4.4	6.3	4.4	2.5
1,1,2-Trimethylcyclohexane	7094-26-0	23.570	1.1	1.3	3.3	4.3	6.5	9.8	13.4	8.1	4.1

Table 4 continued

Compound	CAS	RT (min)	A	B	C	D	E	F	G	H	I
Butylcyclopentane	2040-95-1	25.879	3.3	3.5	7.3	8.9	14.5	20.2	26.9	16.3	11.4
Isobutylcyclohexane	1678-98-4	28.485	4.3	5.2	8.2	9.3	17.0	19.1	15.4		
1-Methyl-2-propylcyclohexane	4291-79-6	29.178	3.1	3.7	6.5	7.6	14.0	15.2	16.8	9.2	14.8
Other cycloalkanes			252.1	183.5	359.8	402.9	582.6	792.2	737.2	395.6	458.9
Total cycloalkanes			275.2	209.8	396.7	449.1	700.3	909.6	2175.1	563.0	640.6
Aromatics											
Benzene	71-43-2	10.387	8.4	6.3	6.6	6.9	9.2	8.4	12.8	9.7	11.3
Toluene	108-88-3	16.080	28.7	19.4	21.3	35.0	95.6	111.3	315.1	110.5	118.1
Ethylbenzene	100-41-4	21.902	7.5	7.7	10.1	12.8	27.2	39.3	54.8	56.8	72.4
<i>m</i> -Xylene	108-38-3	22.404	18.9	19.2	23.0	29.6	66.6	96.6	166.0	170.3	218.7
<i>p</i> -Xylene	106-42-3	22.491	7.4	8.0	8.9	10.1	25.4	36.6	62.3	61.0	78.4
<i>o</i> -Xylene	95-47-6	23.768	12.9	15.2	21.8	23.7	55.5	77.3	130.5	124.7	128.3
Isopropylbenzene	98-82-8	25.397	1.0	1.1	2.5	3.3	5.4	7.6	10.1	6.4	6.0
1-Propylbenzene	103-65-1	26.961	3.1	2.9	4.8	6.6	11.5	13.1	16.5	10.6	10.2
1-Ethyl-3-methylbenzene	620-14-4	27.294	5.9	4.5	6.9	8.4	16.9	15.9	27.1	19.2	20.4
1-Ethyl-4-methylbenzene	622-96-8	27.471	12.4	13.3	15.6	18.3	31.3	35.5	37.4	26.6	27.8
1,3,5-Trimethylbenzene	108-67-8	27.660	2.1	2.1	1.4	2.0	3.1	3.6	6.3	9.6	6.5
1-Ethyl-2-methylbenzene	611-14-3	28.207	2.5	2.8	3.8	4.9	9.7	10.0	11.4	7.5	10.7
1,2,4-Trimethylbenzene	95-63-6	28.968	6.0	5.1	4.6	6.7	10.8	14.9	17.3	15.2	25.3
1,2,3-Trimethylbenzene	526-73-8	30.305	3.7	2.9	4.1	6.5	11.7			59.6	18.8
2-Ethyl-1,4-dimethylbenzene	1758-88-9	32.531	2.1	1.8			4.0	6.3	5.3	6.2	8.4
2-Methyl-1-phenylbutane	3968-85-2	34.334	5.4	4.1	6.9	7.6	10.2	14.4	11.9	10.8	11.9
Naphthalene	91-20-3	36.993	6.6	6.0	6.3	6.4	7.4	10.6	7.3	7.0	7.4
Other aromatic			15.5	11.3	16.2	20.0	27.9	36.0	24.5	22.5	23.2
Total aromatic			148.2	132.1	162.7	208.8	421.5	534.4	897.3	695.1	803.7
Other											
2-Butanone	78-93-3	7.641	4.3	2.4	4.9	2.9	9.7	10.6	9.7	10.0	17.5
Ethyl acetate	141-78-6	8.218	2.4	1.8	6.1	3.9	10.3	10.1	20.3	20.3	28.1
1-Butanol	71-36-3	10.252		2.5	4.1	5.3	8.7	18.4	6.6	6.3	14.0
2-Ethoxy ethanol	110-80-5	12.576					1.1				2.5
1,2-Propanediol	57-55-6	14.019	4.5	8.7	2.3		5.1	4.6	13.5	6.4	3.9
Butyl acetate	123-86-4	18.567	5.8	5.3	3.3	2.5	7.7	13.2		13.8	19.6
Cyclohexanone	108-94-1	23.870	1.3	1.3	2.7	2.8	3.1	3.9	2.7	4.1	6.2
α -Pinene	80-56-8	26.043	1.9	1.6	2.4	1.6	2.8	4.2	2.8	2.7	2.2
Phenol	108-95-2	27.586	6.0	7.1	9.3	7.5	7.2	6.2	10.0	3.5	8.3
2-Ethyl-1-hexanol	104-76-7	30.060	13.6	19.8	27.8	29.8	40.4	45.5	58.4	58.4	52.8
Acetophenone	98-86-2	32.217	5.5	5.0	7.7	6.5	9.2	10.4		40.3	18.8
Other alcohols			38.9	23.2	23.5	30.8	36.1	48.3	45.2	48.0	41.6
Other carbonyls			11.9	5.0	7.0	7.4	21.3	29.3	15.5	22.9	36.2
Alkenes			11.6	10.3	16.2	20.1	33.9	51.8	35.6	32.3	30.4
Esters			6.4	4.8	9.8	10.0	15.6	20.2	29.5	17.2	13.3
Other compounds			67.5	97.4	140.8	109.1	135.3	154.1	357.4	231.9	215.7
Total other compounds			179.3	191.8	264.9	240.3	344.8	430.9	607.1	516.4	509.7
Total VOCs			934	854	1352	1426	2494	3040	6899	2933	2945

check if there are compounds which were detected only in the case of one kind of equipment, i.e. if they are present in samples collected from vehicles with upholstery made from synthetic leather and are absent in the case of vehicles fitted with synthetic fiber upholstery. The other way is to compare the concentrations of compounds detected in differently equipped vehicles, or to combine two methods and compare both the qualitative and quantitative differences.

Table 1 presents interior equipment differences between cars tested and indicates four pairs of identical vehicles. However, only in the cases of vehicles G, H and I, which were equipped with a black synthetic steering wheel, six of 81 confirmed compounds: 2,2-dimethyl heptane, 3,3-dimethylpentane, 3-ethylpentane, 1,1-dimethylcyclopentane, 1,2,4-trimethylcyclopentane and 1,2,3-trimethylcyclopentane were exclusively present.

The variability of compounds confirmed was lower than

reported in other investigations (Chien, 2007), with a mean of 23%–25% in case of three identically equipped car pairs AB, CD and EF and 54% in case of the GH pair, in which vehicle G was identified as an outlier. Similarly, in the case of the *t*-Student test for pairs AB, CD and EF revealed respectively 5, 4 and 12 results which were statistically different. In the case of GH pair, the number of statistically different results was 24 from the population of 78 volatile organic compounds.

The relatively high value of TVOC detected in vehicle G, especially when compared with an identically equipped vehicle (vehicle H), indicates that probably some unusual actions were taken during assembly of the vehicle, or that the materials used for interior equipment were off-gassing differently. However, the mean concentrations of identified and confirmed compounds of vehicle pair GH are presented in **Table 4** intentionally to indicate the effect of an outlier sample. As can be seen in **Table 4**, the compound groups responsible for the high TVOC value were alkanes and cycloalkanes. The exceptionally high relative standard deviation values of identified compounds within these two groups of compounds clearly indicate that aliphatic hydrocarbons were the source of the dissimilarity between vehicles G and F. It should be also emphasized that the average relative standard deviation of identified and confirmed compounds concentrations of other three vehicle pairs (AB, CD, and EF) was low. The average RSD of all compounds groups for the AB pair was 11% with the lowest RSD being 4% in the case of total alkanes, and the highest being 15% in the case of total cycloalkanes and total other compounds. In the case of the CD and EF pairs, the average RSD values of all compound groups were 17% and 16%, respectively. In the case of these two pairs of vehicles equipped with a sunroof, the lowest accuracy was observed for determination of aromatic hydrocarbons: 22% (pair CD) and 23% (pair EF). As mentioned above, proof of aliphatic hydrocarbons' responsibility for the high TVOC value of vehicle pair GH is clearly visible, in the average RSD values of total alkanes (60%), and cycloalkanes (47%) which were more than twofold higher than in other tested samples. The *t*-Student test ($\alpha = 0.05$) for pair EF revealed 12 results from the population of 50 to be statistically different. For the GH pair, the same test revealed 24 results from the population of 57 confirmed organic compounds to be statistically different.

The average deviations of compounds groups' concentrations were higher if all cars, without the outlier G vehicle, were considered. The TVOC value deviated by 44% and the total amount of grouped compounds, i.e.: total alkanes, cycloalkanes, aromatics and other compounds, varied even more. Variation of the compounds' concentrations at a level of about 50% and above indicates that within one car brand and model, differences in interior equipment are of the highest importance. On the other hand, the very similar results obtained from analysis of air

samples collected from identically equipped cars allow for discussion on the influence of interior equipment on in-vehicle air composition.

The pair vehicles A and B was chosen as the starting point for comparison of the basic equipment's influence on in-vehicle air composition, according to the lowest pollution levels. Comparison with the CD pair indicates the influence of the presence of the sunroof. The first difference is in the number of detected compounds (**Table 3**), which is slightly larger in the case of the CD pair. The second basic difference is the absence of a few alkanes and cycloalkanes in case of the AB pair compared to the CD, among them: 2,3-dimethylheptane; 2-methyloctane; 3,3-dimethyloctane and 1,2-dimethylcyclohexane (**Table 4**). Along with these qualitative differences, quantitative differences were found, as well: over 30% of the TVOC increase was mostly a result of higher concentrations of aliphatic hydrocarbons. Interesting information was obtained from a basic comparison of compounds identified. The CD to AB ratios of concentrations of 15 compounds is presented in **Fig. 1**. The ten compounds with the highest ratio value and the five with the lowest were selected to indicate which compounds' concentrations were influenced the most by the presence (or absence) of a sunroof. This comparison confirms the large influence of aliphatic hydrocarbons on air composition in vehicles CD, as mentioned above. Only three of the ten compounds with the highest ratio values were not aliphatic hydrocarbons, namely: isopropylbenzene, ethyl acetate and cyclohexanone. Conversely, the lowest ratio, meaning a decrease of the concentration as a result of the presence of the sun-

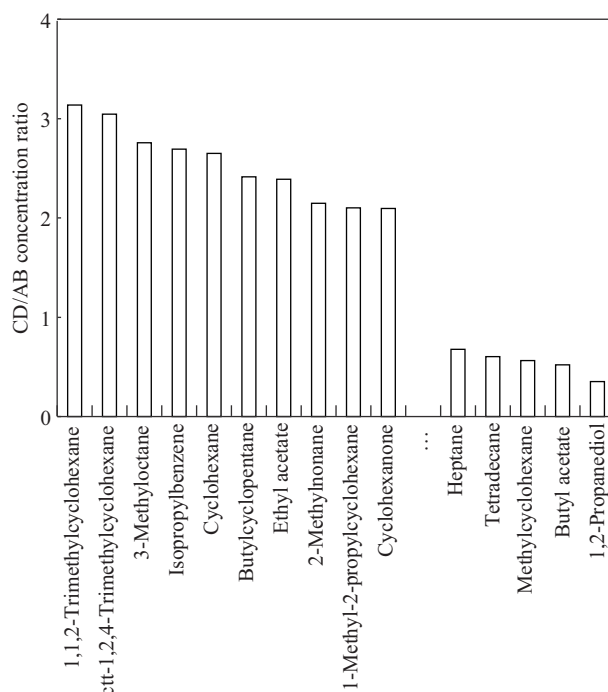


Fig. 1 Concentrations ratios of selected compounds in CD/AB vehicles pairs.

roof, was observed in the cases of 1,2-propanediol, butyl acetate and methylcyclohexane. As the assembly of the sunroof involves the use of additional sealing materials and adhesives, it can be stated that aliphatic hydrocarbons are rapidly off-gassing from these materials, thereby causing the TVOC increase.

A comparison of vehicles pairs CD and EF permits a discussion of the influence of the upholstery on in-vehicle air composition. All these cars were equipped with a sunroof and the only difference was the trim material used. In this case, both the TVOC and the number of compounds collected clearly differed between vehicle pairs. The mean TVOC value of vehicles E and F was two times higher than in the case of the CD pair. Additionally 30% more compounds were present in the samples collected from vehicles with black and white fabric upholstery. The qualitative differences, similarly to the above, referred to aliphatic hydrocarbons, especially cycloalkanes, like isomers of dimethylcyclopentane and *trans*-1,4-dimethylcyclohexane. Comparing these two pairs, aliphatic hydrocarbons concentrations were responsible for the observed quantitative differences. Both alkanes and cycloalkanes concentrations were nearly two times higher in the case of the vehicles equipped with black and white synthetic fabric than in the case of mixed fabric synthetic leather upholstery. Within the compounds identified and confirmed, undecane was the most abundant (Table 4). It is worth mentioning that in both pairs of vehicles, CD and EF, not more than 5% of total cycloalka-

nes were confirmed, and therefore their identification was based on the NIST 08 library. An attempt was made to indicate the compounds whose concentrations differed the most between two pairs of vehicles equipped with different upholstery by a simple comparison of their concentration ratios, just like in the above case (Fig. 2). In this case, aromatic hydrocarbons were the signs of the off-gassing of upholstery material: toluene, isomers of xylene and ethylbenzene were five of the ten compounds with the highest ratios; the other were alkanes and cycloalkanes, along with butyl acetate. Only phenol and pentadecane were present in collected in-vehicle air samples at a slightly lower level in the case of vehicles EF than in the case of the CD pair (Fig. 2a). A comparison of the EF and AB pairs indicates that the VOCs differentiating these two pairs were very similar to the ones differentiating pairs AB and CD. Only two of the ten compounds with the highest ratios, 1-butanol and *o*-xylene (Fig. 2b), differed from the corresponding ten compounds recognized when comparing pair AB and CD. The number of compounds detected in the case of cars AB was about 35% lower than in case of EF, where TVOC value was three times higher than for the AB pair. The similarity of compounds with the highest ratio between CD/AB and EF/AB was a result of the presence of a very large number of unconfirmed compounds, especially cycloalkanes, which were responsible for the high TVOC level. However, besides introducing new compounds to the car cabin, the use of black/white synthetic fabric upholstery and the presence of a sunroof also led to increased

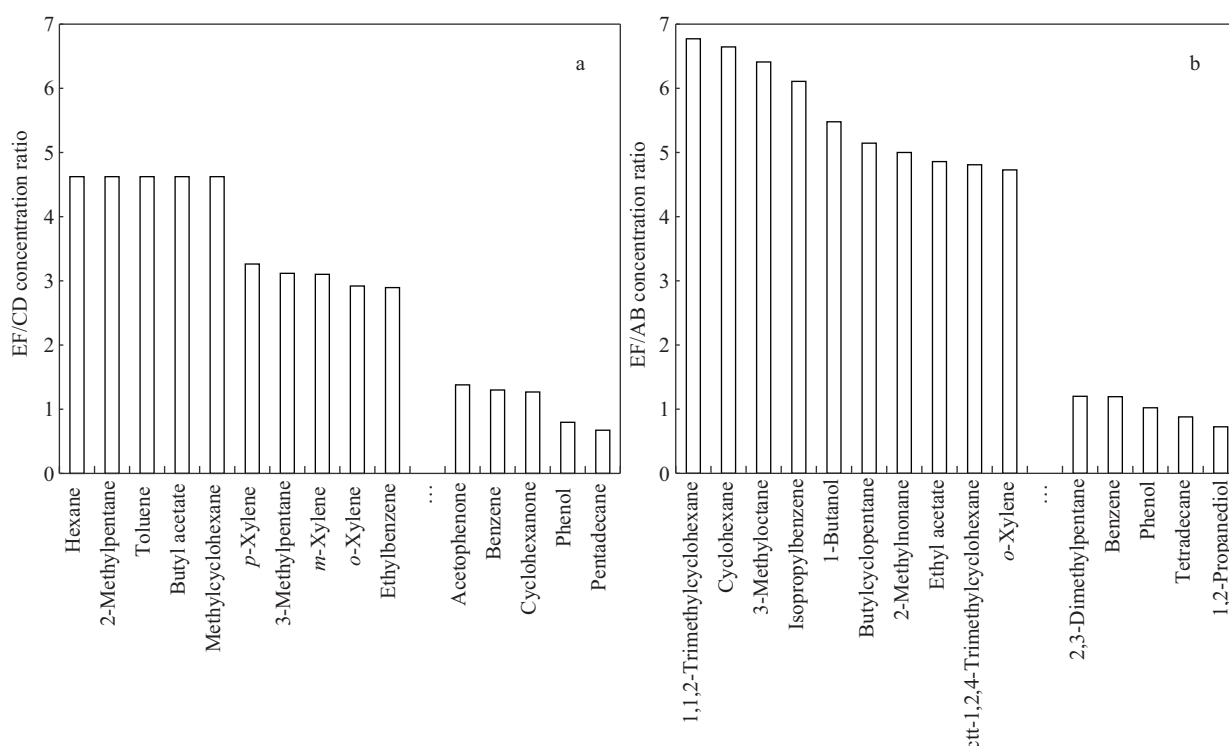


Fig. 2 Concentrations ratios of selected compounds in EF/CD (a) and EF/AB (b) vehicles pairs.

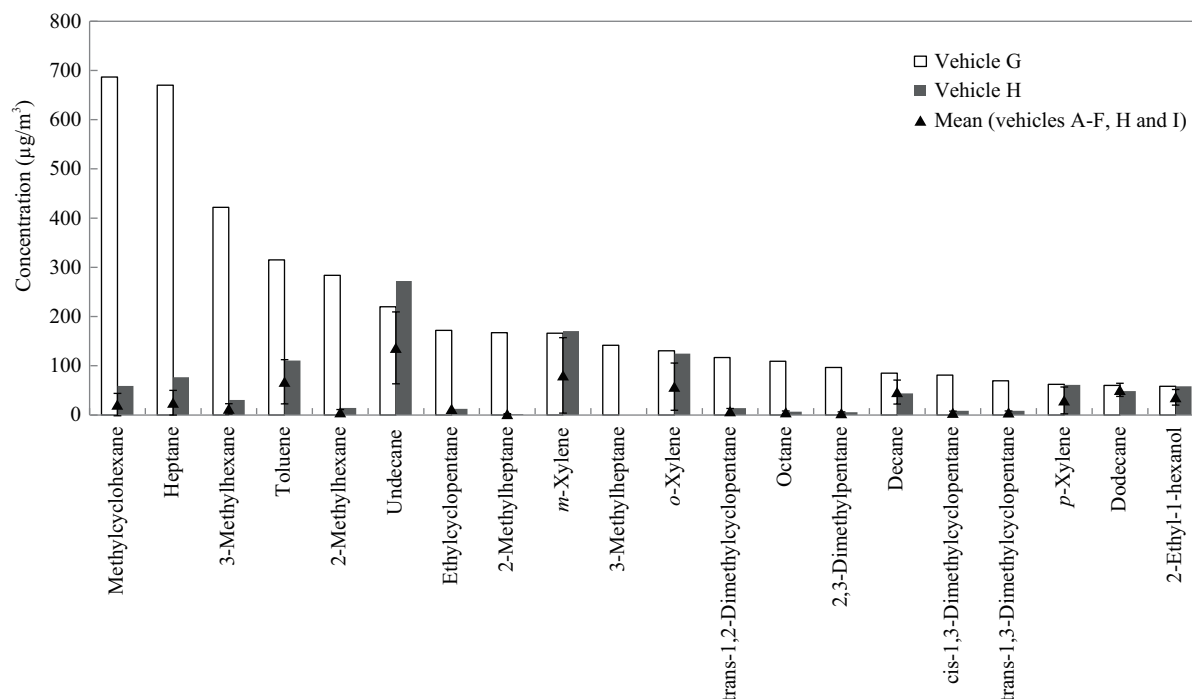


Fig. 3 Comparison of selected, confirmed compounds in vehicles G and H with the mean values (with SD indicated) corresponding for A–F, H and I cars.

concentrations of confirmed compounds.

Interesting information was gathered from a comparison of air samples collected from vehicle G, vehicle H and the mean concentration of selected compounds from vehicles A–I (excluding G). The starting point for this comparison was the selection of 20 organic compounds with the highest concentrations from the vehicle G sample, which corresponded to 60% of its TVOC. The concentrations of these compounds were compared to their concentrations in samples collected from an identical vehicle (vehicle H) and additionally to their mean values in 8 differently equipped cars (A–F, H and I) with standard deviation values plotted (**Fig. 3**). It was noticed that six of the compounds compared were present in comparable amounts both in vehicle G's and vehicle H's air: undecane, isomers of xylene, dodecane, 2-ethylhexanol; additionally, concentrations of these compounds were within (or close to) the mean values \pm SD. This proves that their presence was not an effect of any undefined change that probably took place during the assembly of vehicle G. The comparison clearly indicates that it is possible to indicate the compounds responsible for the exceptionally high VOC level in vehicle G's cabin, in descending order: methylcyclohexane, heptane, 3-methylhexane, toluene, 2-methylhexane etc.

3 Conclusions

The results presented indicate that it is possible to perform comparative analyses of air samples collected from

the cabins of unconditioned, newly produced cars, after their assembly. The interior equipment aside, in all cases aliphatic hydrocarbons, both alkanes and cycloalkanes, were the dominating group of VOCs in collected air samples. Intra-model variability in terms of TVOC levels corresponding to identically equipped cars, excluding the outlier vehicle G, was below 14%. TVOC level determination can be, therefore, the first factor of vehicles air quality investigation with applied technique. As the determined VOCs number is in good correlation with the total volatile organic compounds concentration it is possible to indicate elevated TVOC level with constant VOCs number as a result of additional operations or enhanced emission from equipment materials. Afterwards performing appropriate steps is possible to prevent increased TVOC level in other vehicles. It was shown that it is possible to indicate changes, both quantitatively and qualitatively, of in-vehicle air composition due to presence of different materials within the newly produced and unconditioned vehicle's cabin. Identification of a car as an outlier can be based on a basic comparison of TVOC concentrations. If VOCs emissions characteristics of materials or equipment parts are known, in-vehicle air composition can be useful for indicating which specific equipment parts are responsible for increased amount of selected compounds.

According to the results presented, it is possible to determine with good approximation the composition of air inside cabin of newly produced car without a need for time- and cost-consuming conditioning of car under static conditions. Characteristics of VOCs presence in vehicle cabin air once determined may be used for comparison with

differently equipped cars. Thus pointing out all the desired and undesired materials or parts can be done, as presence of some parts can lead to increased concentration's levels of some compounds and decreased concentration's levels of the others. Such a procedure should not replace the standard procedure with whole vehicle conditioning, but may be very useful for screening assessments of larger numbers of cars for quality checks right after their production.

Acknowledgments

This work was supported by the Polish Ministry of Science and Higher Education (No. N N509 480438).

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Journal of Environmental Sciences (Established in 1989)

Vol. 26 No. 5 2014

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences		Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Distributed by	
		Domestic	Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
		Foreign	Elsevier Limited http://www.elsevier.com/locate/jes
Editor-in-chief	Hongxiao Tang	Printed by	Beijing Beilin Printing House, 100083, China
CN 11-2629/X	Domestic postcode: 2-580		Domestic price per issue RMB ¥ 110.00

ISSN 1001-0742

