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Chemical compounds emitted by main components used in interior of vehicles

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Abstract. Odors from materials used in new vehicles may cause satisfaction or dissatisfaction for people. This duality is due to a stimulation caused by receptors which act differently in each individual. It is already known that odors exhaling in a vehicles interior are caused by a gaseous mixture of the various materials which are volatilized, especially with the increase of internal temperature. The components of a newly manufactured automotive vehicles interior of high surface representativeness selected in this work are eight: air conditioner, ceiling liner, shelf package, rubber mats, door panel, carpet, instrument panel, and seats, which were analyzed by gas chromatography for the identification of volatile substances. The proportion of the peak area of each compound was calculated. Gas chromatography analysis identified the main substances from materials used in interior of vehicles which contribute to the new car odor: toluene, *p*-xylene, ethylbenzene or benzene derivatives, except in carcass of air conditioner. Polypropylene is a constituent of these components, except the rubber mats. Carbon disulfide appeared with a significant proportion of area in rubber mats and contributed in the formation of car odors.

Keywords: *material testing, automobile, volatile substances, chromatography, industrial applications*

1. Introduction

Polymeric materials are used in automobile manufacturing mainly because of low specific weight [1, 2]. The automobile interior is a complex thermal environment which continually varies during travelling on roads [3]. Wu *et al*. [3] reported that panel interior temperature increases as driving velocity increases in the evening, while the interior temperature decreases as driving velocity increases during daytime. The maximum value of automobile interior temperature registered by Wu *et al*. [3] was near to 46 °C. The volatile substances from polymers used in vehicles interior can generate odors of varying intensities and duration which may or may not please people.

Literature reports studies about the chemical analysis of the air in interior of vehicles but studies about the chemical analysis of vehicle components are scarce. Yoshida [4] analyzed organic compounds in the interior air of 101 different types of Japanese domestically produced private-use cars. Chien [5] investigated inter-brand, intra-brand and intra-model variations in volatile organic compounds (VOC) levels inside new cars and found that the intra-model variability (mean, 47%) in the VOC levels was approximately 50% that within each brand (mean, 95%). The effect of temperature on interior VOC levels was examined using model automobiles with and without the air-conditioning running [5]. VOCs have negative impacts on human health (primarily neurological), cancer (such as leukemia), neurobehavioral effects and adverse effects on the kidney [6]. Geiss [7] investigated the presence of selected volatile organic compounds (VOCs) including aromatic, aliphatic compounds and low molecular weight carbonyls in

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the interior of 23 used private cars during summer and winter. VOC concentrations often exceeded levels typically found in residential indoor air, e.g. benzene concentrations reached values of up to 149.1 $\mu g \cdot m^{-3}$. Overall VOC concentrations were 40% higher in summer, with temperatures inside the cars reaching up to 70 °C [7]. Faber *et al*. [8] examined the indoor air composition inside the cabins of five new vehicles and concluded about the influence of the materials used. Bradzik *et al*. [9] determined if analysis of air samples collected from an unconditioned car cabin can be used as a quality control measure. To analyze the influencing factors of in-car VOCS pollution concentrations, 38 taxis were investigated by Chen *et al*. [10] on the static and closed conditions. Lu *et al*. [11] identify and quantify the levels of volatile organic compounds (VOCs) and carbonyl compounds (CCs) in air samples collected from the cabins of newly produced, medium- and large-size coaches in China.

Xu *et al*. [12] published a review of the air quality of motor vehicle cabin microenvironment concluding that air recirculation with high-efficiency air filter was the most effective measure to lower air pollutant concentrations. The in-cabin pollutant concentrations are often high for newly manufactured cars, at high interior temperatures, or with low air exchange rate [12].

Literature reports the concern of researchers to develop materials for application in car interior that produce emission of low intensity of odors as the low odor-emissive polylactide/cellulose fiber biocomposites [13].

The objective of this research is to identify the compounds which can be released by materials used in vehicles and which constitute the odor of the new car, by using headspace solid phase micro extraction gas chromatographic analysis combined with mass spectrometry. A preliminary study organized the relation of components of automotive interiors and classified in two groups: high representativeness and low representativeness. Components with a higher representativeness were the materials with a higher surface area in the interior of vehicles. In this work, the chromatographic results of components with high representativeness were presented and discussed.

2. Experimental section

A previous study for the methodology selection and parameter optimization was performed [14–16]. The headspace solid phase micro extraction gas chromatographic analysis was performed on a Clarin 680 Perkin Elmer brand chromatograph coupled with a Clarus SQ 8T mass spectrometer, (both Perkin Elmer Instruments, Waltham, United States). Chromatographic conditions were: 30 m long WCOT HP-5 chromatographic column considering a flow rate of 5 mL/min for the entrainment gas, 0.25 mm ID, 0.25 μm film thickness, an inlet pressure of 72.4 kN/m^2, an auxiliary pressure of 69.0 kN/m^2, a heating ramp starting at 40 °C at a rate of 6 °C/min to 150 °C, final stage with a rate of 10 °/min up to 180 °C and total time of 21 minutes. The mass spectrometer used the electron ionization mode in a wide range of 45–300 m/z, with a reading start time of 1 minute.

The cars under investigation were new and analyzed at the factory. The components of vehicle under study were produced by industries near the automobile assembly plant located in Betim, Brazil, 19°58'04" S latitude, 44°11'54" W longitude. The temperature of the interior of vehicles is 24±2 °C. Air condition was in off condition. Three samples of each material were analyzed. Samples were obtained from the removal of fragments in different parts of each type of material in each component totaling a mass of 300±10 mg. Table 1 shows the list of components analyzed in this work. Each sample was conditioned in glass vials with 10 mL capacity and maintained at a temperature of 20 °C before analyses were performed. The conditioning time before analysis was 24 hours. The time of the chromatographic run was 21 minutes. However, the headspace incubation time was 1 hour. The method for the headspace was: syringe with capacity of 2.5 mL and temperature of 110 °C, filling speed of 100 μL/s, sample volume of 1 mL, incubation temperature of 100 °C, stirring speed of 500 rpm, stirring time of 30 s and stopping time between each shaking of 30 s. The identification of the main substances, based on their peak integration, was performed by using the equipment software, which has a database based on the National Institute of Standards and Technology (NIST).

2. Results and discussion

The components of vehicles interior of high representativeness selected in this work are: air conditioner, ceiling liner, shelf package, carpet, door panel, rubber mats, instrument panel, and seats. The materials of these components were analyzed using chromatographic analysis.

Table 1. Selected materials of components used in the interior of vehicles.

Component	Description	Material	Sample volume [mL]	Surface area [mm^2]
Air conditioner	Carcass	Polypropylene	5	1350
Ceiling lining	Ceiling lining	Cloth + Polypropylene + Polyurethane	7	1450
Shelf package	Shelf package	Polypropylene + Wood	6	1440
Carpet	Carpet	Expandable Polystyrene + Shredded denim + Thermoplastic + Polypropylene + Polystyrene	7	1420
Door panel	Polymer	Polypropylene	5	1340
Rubber Mats	Rubber Mats	Natural Rubber + Recycled Tire	4	1300
Instrument panel	Instrument panel	Polypropylene	5	1360
Leather seats	Synthetic leather	Polyurethane	8	1400

The air conditioner contains nine materials: pipe cover, composite foam, adhesive foam, buttons, hose, carcass, rotor, foam, and straws. Table 2 shows results of chromatography of carcass (Figure 1) which has the largest exposed area inside the vehicle. The air conditioner is an important component as the air circulation passes through the materials carrying the odors into the interior of vehicle. The main compound found was 2,3,3,4-tetramethyl cyclobutanone. Cyclobutanones, identified in irradiated food, promote cancer development and cause genetic damage in rats [17].

Table 3 presents the substances identified in the ceiling liner component and, according to the calculations of the proportion of the areas of the chromatographic peaks, toluene, ethylbenzene and *p*-xylene are the substances that stand out and have the highest relative proportions. Chromatogram of ceiling liner material is shown in Figure 2. All substances in this component have odorant characteristics. With this, and still being a component with great representation in the interior of vehicles, containing a large surface area, deserves special attention. It is noteworthy that the three substances featured in the area have odorant

Table 2. Results of chromatography of carcass of air conditioner.

Substance	Area	%	M_w	CAS number
1-bromo, 2-methyl, 2-propanol	21 560	13	153 019	38254-49-8
1,1′-oxibisheptane	16 325	10	214 387	629-64-1
3-ethyl, 3-methylheptadecane	12 263	7	282 556	11536486
2,3,3,4-tetramethyl cyclobutanone	44 389	26	126 196	53907-63-2
4,5-dimethylnonane	13 328	8	156308	17302-23-7

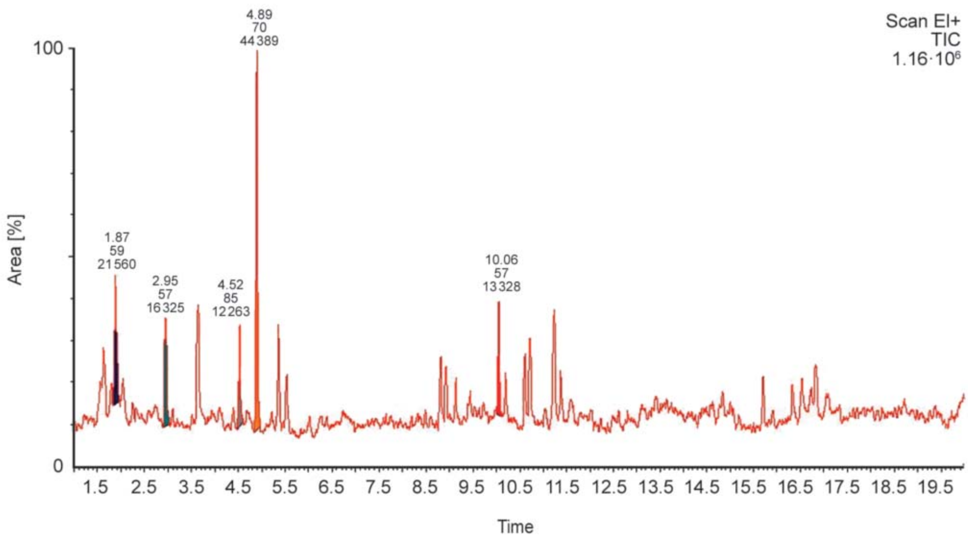

Figure 1. Chromatogram of carcass of air conditioner.

Table 3. Chromatographic analysis of ceiling lining.

Substance	Area	%	M_w	CAS number
Propylhexedrine	82048	3.07	155280	101-40-6
Toluene	379040	14.20	92138	108-88-3
Ethylbenzene	325384	12.19	1061650	100-41-4
p-xylene	780868	29.24	106165	106-42-3
1-ethyl, 2-methylbenzene	209035	7.83	120190	611-14-3
Propylbenzene	34718	1.30	120190	103-65-1
1-ethyl-4-methylbenzene	121867	4.56	370527	65104-04-3
1-ethyl-2-methylbenzene	107295	4.02	120190	611-14-3
1,2,3-trimethylbenzene	22235	0.83	160216	73905-55-3
1,2,4-trimethylbenzene	173544	6.50	252220	95-63-6

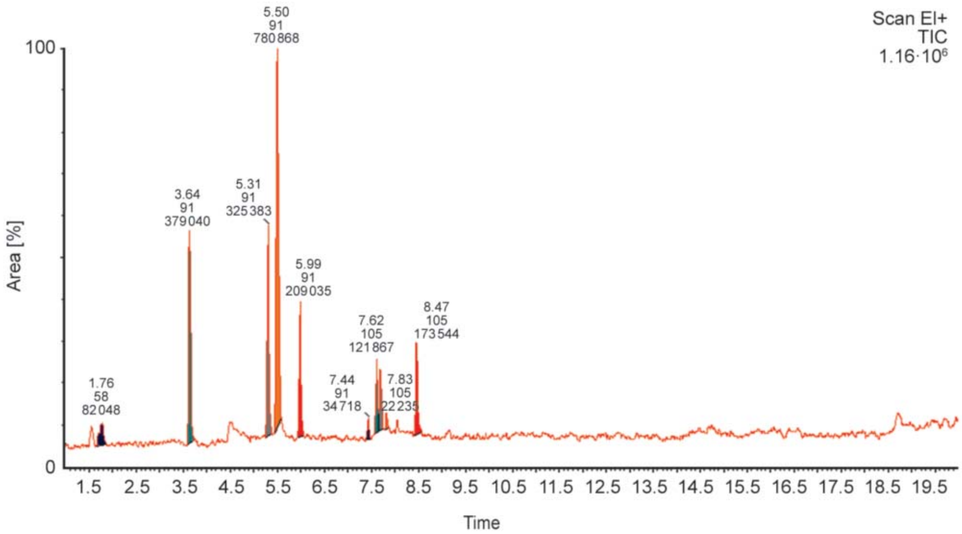

Figure 2. Chromatogram of ceiling liner.

characteristics of pleasantness. Among the analyzed materials, the presence of toluene, a volatile organic compound (VOC) must be emphasized. Mono-aromatic hydrocarbons such as benzene, toluene and xylene, compounds found in this study, are known to be toxic [18–21]. Toluene, ethylbenzene, xylene, formaldehyde, acetaldehyde, acrolein/acetone, and isovaleraldehyde were relatively abundant in the cabins of coaches in China as reported by Lu *et al*. [11]. Brodzik *et al*. [9] measured the in-cabin pollutant compositions in several unconditioned, newly produced cars. Depending on the vehicle, the concentration of aromatic hydrocarbons varied from 12% to 27% of total VOCs [9]. The very short period between car production and sampling of the in-vehicle air permits the assumption that the entire TVOC (total VOCs) originates from off-gassing of interior materials [9]. Brodzik *et al*. [9] also concluded that the presence of a sunroof could increase the in-cabin concentrations of aliphatic hydrocarbons due to emissions from sealing materials and adhesives around the sunroof. The intentional misuse of volatile solvents, such as toluene, is a persistent public health concern. Limited clinical data suggest that chronic inhalant abusers may experience signs of withdrawal, including anxiety [22]. Propylhexedrine [23], found among compounds emitted by ceiling lining, is a cycloalkylamine that is structurally similar to methamphetamine and causes release of dopamine, and noradrenaline from presynaptic vesicles.

The shelf package is a component made from a composite of polypropylene with wood fiber. According to Table 4, the 3-carene was the substance found in a major proportion in shelf package. 3-carene is a constituent of trepentine that is obtained from the distillation of the resin of coniferous species, according to Corredor and Sarria Villa [24]. With the highest proportion of peak area (Table 4), the 3-carene represents the main substance and is justified using the wood fiber in the shelf package. With a sweet and intense characteristic, 3-carene can be considered a material that participates in a significant way

Table 4. Results of chromatography analysis of materials of shelf package.

Substance	Area	%	M_w	CAS number
Propylhexedrine	129 365	8.29	155 280	101-40-6
Chlorphenamine	61 292	3.93	274 789	113-92-8
Toluene	149 186	9.56	92 138	108-88-3
Ethylbenzene	38 176	2.45	106 165	100-41-4
p-xylene	11 2041	7.18	106 165	106-42-3
m-xylene	29 222	1.87	106 168	108-38-3
3-carene	162 971	10.45	136 238	13466-78-9
1-methylene-4-(1-methylethenyl)cyclohexane	37 814	2.42	136 234	499-97-8
2-pentylfuran	30 186	1.93	138 206	3777-69-3
1,2,4-trimethylbenzene	20 341	1.30	252 220	95-63-6
2,6,10,15-trimethylheptadecane	90 433	5.80	296 574	54833-48-6
Triacontane	35 401	2.27	422 183	638-68-6
2,6,10,15-tetramethylheptadecane	106 850	6.85	296 574	54833-48-6
2,6,10-trimethyldodecane	46 030	2.95	212 414	3891-98-3
Tritetracontane	103 051	6.60	605 158	7098-21-7

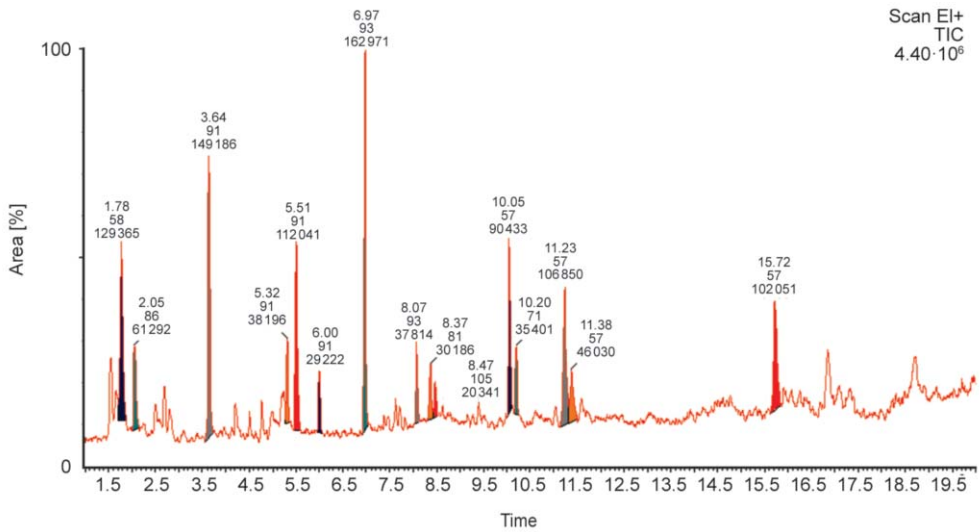

Figure 3. Chromatogram of shelf package.

in the formation of the odor. Toluene, p-xylene, and propylhexedrine are the other outstanding substances emitted from polypropylene. Heptadecane, $C_{17}H_{36}$, a solid at standard conditions and tritetracontane, $C_{43}H_{88}$, an alkane with a greater number of carbons were other substances present in high proportions. It is worth mentioning that chlorphenamine, found in the shelf package, is an anti-histamine drug [25]. Figure 3 presents the chromatogram of shelf package.

Carpet is a prominent component as it has a large surface area and thus contributes in a more representative way to the formation of the internal odors of the vehicle. Table 5 presents the substances identified by using chromatographic analysis (Figure 4) of carpet and demonstrates the marked presence of toluene, *p*-xylene and hentriacontane with the largest representations of area of chromatographic peaks. Despite a significant proportion of 11.32%, hentriacontane is not important in the formation of odors. Hentriacontane also called untriacontane, is a solid, long-chain alkane hydrocarbon with the structural formula $CH_3(CH_2)_{29}CH_3$ [23]. It is found in a variety of plants, including peas (pisum sativum), gum arabic (acacia senegal) and others [26].

With this, only toluene and *p*-xylene are outstanding. But it should be noted that ethylbenzene, which despite a small proportion, is a substance that can interfere negatively in the formation of odors. Jiang *et al*. [27] reported therapeutic effects of isothiocyanate which was found in carpet of newly manufactured automobiles.

Table 5. Results of chromatographic analysis of materials of carpet.

Substance	Arae	%	M_w	CAS number
Propylhexedrine	37365	7.06	155280	101-40-6
1,1′-oxibisheptane	18080	3.41	214387	629-64-1
Toluene	97923	18.49	92138	108-88-3
Methyl, 2-methyl, 2-methoxy, 3-hidroxyindan-1-one-3-carboxilate	28520	5.39	126153	32774-63-3
3,5-dimethylheptane	18852	3.56	128255	926-82-9
Ethylbenzene	30998	5.85	106165	100-41-4
p-xylene	99194	18.73	106165	106-42-3
1,3-dimethylbenzene	27607	5.21	106168	108-38-3
1,2,4-trimethylbenzene	20201	3.81	252220	95-63-6
Isothiocyanatecyclohexane	21741	4.11	141234	1122-82-3
1-fluorododecane	12635	2.39	188325	334-68-9
Hentriacontane	59927	11.32	605158	7098-21-7
Hexacosyl acetate	21674	4.09	424743	822-32-2

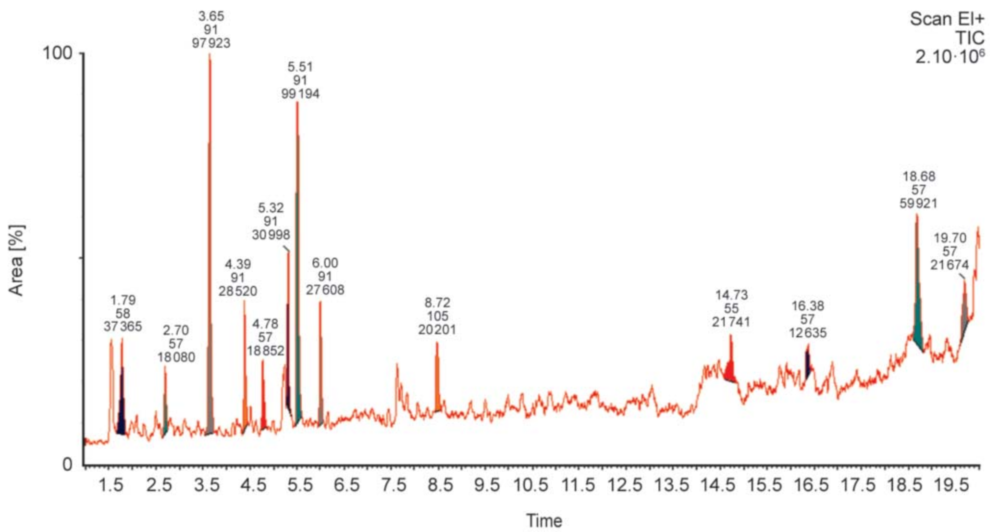

Figure 4. Chromatogram of carpet.

Of all the materials contained in the door panels such as polypropylene, polystyrene, cloth and screen, the analyzed polypropylene has significant representativeness. Table 6 presents the chromatographic analysis of door panel (polypropylene), and Figure 5 shows the chromatogram of door panel.The emitted *p*-xylene has a significant peak area and is an odor-generating substance. Other substances such as hentriacontane and tritetracontane, which also have higher peak areas, do not represent importance in the formation of odors. Hentriacontane, has various pharmacological effects including anti-inflammatory, antitumor and antimicrobial activities [26].

With high representativeness in the composition of the interior of vehicles, rubber mats deserve greater attention, especially for the highlight in the peak of carbon disulfide, as shown in Table 7. The chromatogram of rubber mats is shown in Figure 6.With a characteristic odor of ether, carbon disulfide participates in a significant way in the formation of odor of the interior of vehicles. Carbon disulfide (CS_2) is used in industry. Disulfide and (polysulfide) bonds are the crosslinking groups that result from the vulcanization of rubber; it has been shown to have neurotoxic effects [28]. *P*-xylene comes in second in the proportion of area, but much smaller than carbon disulfide. The other substances are not representative considering the area proportions.

Table 8 shows the substances identified in the instrument panel, and Figure 7 shows the chromatogram of instrument panel. As instrument panel has a large surface area, the instrument panel can contribute to the formation of odor releasing toluene and *p*-xylene, although they have little representativeness in the peak area ratio.

Table 6. Chromatographic analysis of door panel (polypropylene).

Substance	Area	%	M_w	CAS number
Toluene	66485	2.26	92138	108-88-3
2-ethylbutyl isobutyl carbonate	10512	0.36	202294	91698429
2-ethylhexyl ester pentanoic acid	123556	4.19	214344	5451-87-6
1-fluorododecane	29675	1.01	188325	334-68-9
4,5-dimethylnonane	94726	3.21	156308	17302-23-7
p-xylene	60791	2.06	106165	106-42-3
1-ethyl, 2-methylbenzene	20911	0.71	120190	611-14-3
4-nitrophenyl 3-phenylpropanoate	58453	1.98	271272	562076
1,2,4-trimethylbenzene	14950	0.51	252220	95-63-6
Butyl nonyl sulfite	50427	1.71	264425	4926348
Hentriacontane	625914	21.23	605158	7098-21-7
Triacontane	146946	4.98	422183	638-68-6
6-ethyl-3-octanyl isobutyl oxalate ester	46636	1.58	286407	4926362
2,6,10,15-tetramethylheptadecane-	290162	9.84	296574	54833-48-6
2,6,10-trimethyldodecane	127057	4.31	212414	3891-98-3
Tritetracontane	357412	12.12	605158	7098-21-7
Heneicosane	100000	3.39	296574	629-94-7
3,5,24-trimethyltetracontane	84536	2.87	605177	55162-61-3

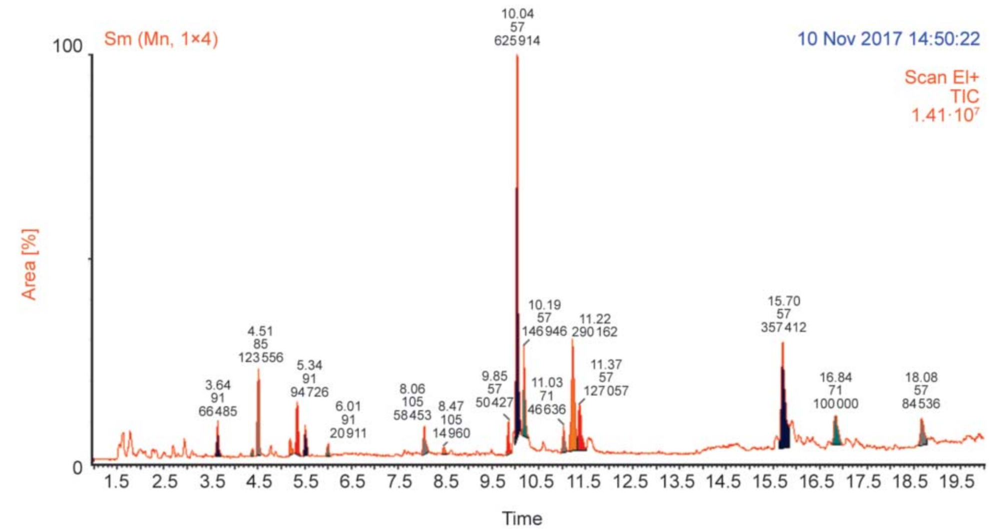

Figure 5. Chromatogram of door panel.

Seats have high representativeness, and the synthetic leather occupies a large surface area. Toluene and *p*-xylene were the substances of greatest proportions of peak area. Table 9 presents the substances identified in the seat with their percentage ratio of area of chromatographic peaks, and Figure 8 shows the chromatogram of leather seats.

Toluene and *p*-xylene were found after chromatographic analysis of ceiling lining (Table 3), shelf package (Table 4), carpet (Table 5), door panel (Table 6), rubber mats (Table 7), instrument panel (Table 8), and synthetic leather seats (Table 9). Polypropylene is a constituent of ceiling lining, shelf package, carpet, door panel, and instrument panel. The use of additives is a common way to modify polypropylene fibers to improve their properties [29]. Usually, additives such as organic pigments or flame retardants are incorporated into the polymer by physical means during fiber formation, for example [29]. Organic pigments added in polypropylene as quinacridone and phthalocyanine contain aromatic rings and thus can produce compounds such as toluene and *p*-xylene [29].

Table 7. Chromatographic analysis of rubber mats.

Substance	Area	%	M_w	CAS number
Trisylane	124615	5.11	92320	7783-26-8
Carbon disulfide	1147204	47.06	76141	75-15-0
2-cyclopenten-1-one	39944	1.64	82100	930-30-3
Etilefrin-propionyl	37966	1.56	349427	547106
Toluene	42123	1.73	92138	108-88-3
Ethylbenzene	37669	1.55	106165	100-41-4
p-xylene	163290	6.70	106165	106-42-3
1-ethyl, 2-methylbenzene	65296	2.68	120190	611-14-3
1-ethyl-4-methylbenzene	21572	0.88	370527	65104-04-3
1,2,3-trimethylbenzene	24528	1.01	160216	73905-55-3
1,2,4-trimethylbenzene	11820	0.48	252220	95-63-6
4-nitrophenyl-β-phenyl propionate	12953	0.53	271268	17895-71-5
1,2,4-trimethylbenzene	55304	2.27	252220	95-63-6

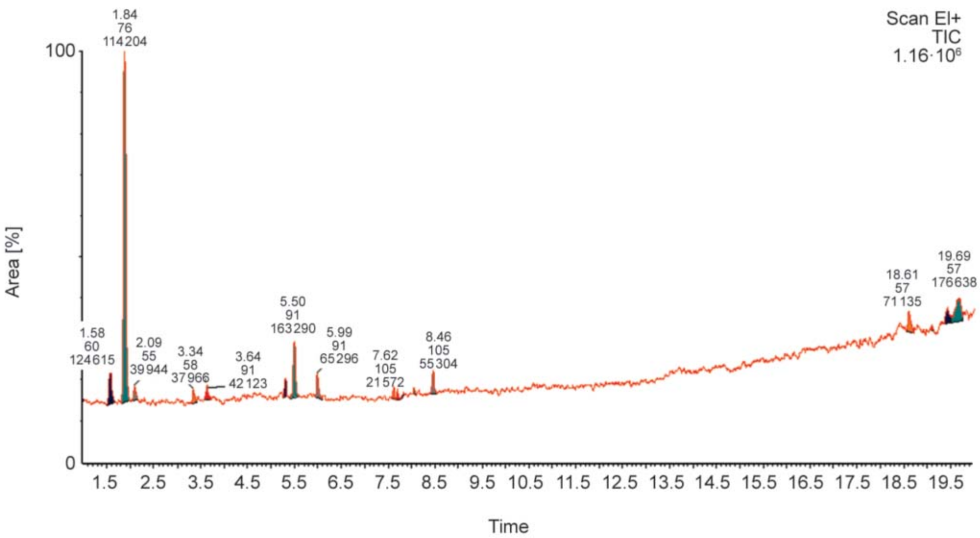

Figure 6. Chromatogram of rubber mats.

Table 8. Chromatography results of materials of instrument panel.

Substance	Area	%	M_w	CAS number
1,1′-oxybisheptane	50988	2.06	214387	629-64-1
Toluene	80997	3.26	92138	108-88-3
3-etyl, 3-methylheptadecane	47191	1.90	282556	11536486
p-xylene	58242	2.35	106165	106-42-3
1-ethyl, 2-methylbenzene	14002	0.56	120190	611-14-3
1,2,4-trimethylbenzene	12007	0.48	252220	95-63-6
2,6,10,15-tetramethylheptadecane	478762	19.30	296574	54833-48-6
2-ethylhexyl tridecyl sulfite	106411	4.29	376640	6740778
2,6,10,15-tetramethylheptadecane	252470	10.18	296574	54833-48-6
3,8-dimethyldecane	94610	3.81	170334	17312-55-9
Tritetracontane	450048	18.14	605158	7098-21-7
Heneicosane	257686	10.39	296574	629-94-7

3. Conclusions

The components of vehicles interior of high representativeness due to the higher exposed area selected in this work are: air conditioner, ceiling liner, shelf package, rubber mats, door panel, carpet, instrument panel, and seats. The materials of the selected components were analyzed by using chromatographic analysis.

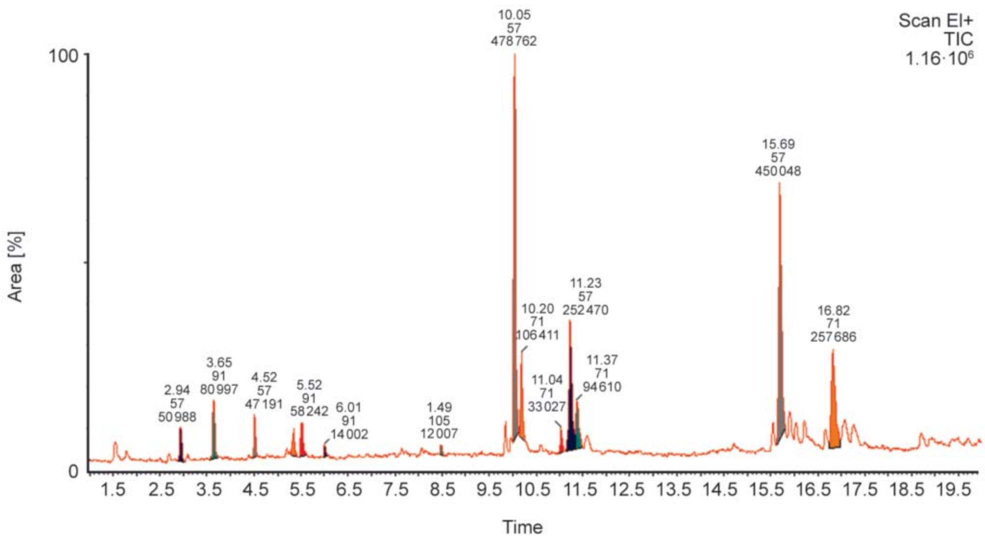

Figure 7. Chromatogram of instrument panel.

Table 9. Chromatographic analysis of leather seat (synthetic leather).

Substance	Area	%	M_w	CAS number
N,*N'*-dimethyl-*N*,*N'*-dinitroethanediamide	147 808	19.48	206 114	14760-99-7
Toluene	163 991	21.61	92 138	108-88-3
Ethylbenzene	30 114	3.97	106 165	100-41-4
p-xylene	113 578	14.97	106 165	106-42-3
1-ethyl, 2-methylbenzene	41 864	5.52	120 190	611-14-3
1,2,4-trimethylbenzene	24 492	3.23	252 220	95-63-6
3,5,24-trimethyltetracontane	61 607	8.12	605 159	55162-61-3

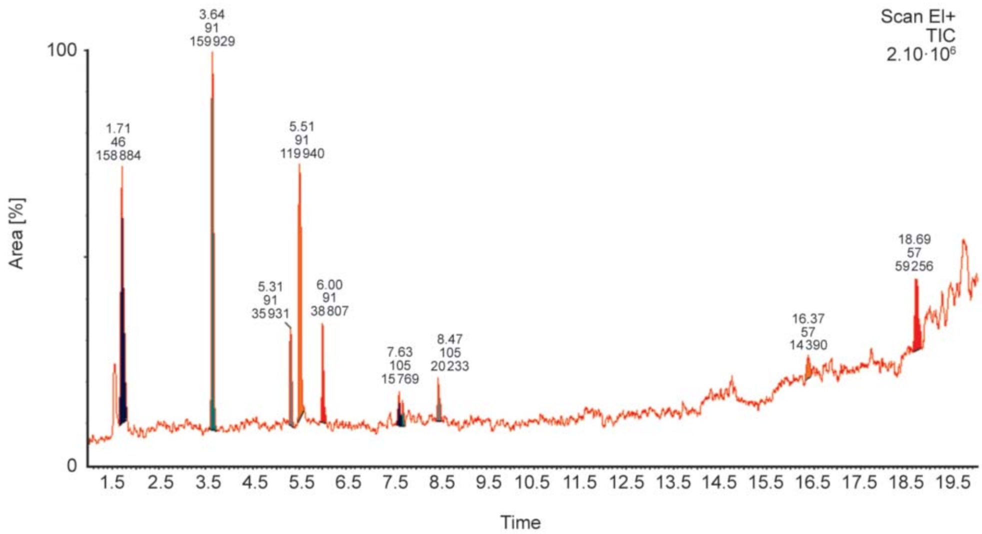

Figure 8. Chromatogram of leather seats.

Gas chromatography analysis identified the main substances from materials used in interior of vehicles which contribute to the new car odor: toluene, *p*-xylene, ethylbenzene or benzene derivatives, except in carcass of air conditioner. Polypropylene is a constituent of these components, except the rubber mats. Carbon disulfide appeared with a significant proportion of area in rubber mats and contributed in the formation of car odors.

The ceiling liner has great representation in the interior of vehicles, containing a large surface area, and deserves special attention. It is noteworthy that toluene, ethylbenzene and *p*-xylene featured in the peak area have odorant characteristics of pleasantness.

The 3-carene was the substance found in a major proportion in shelf package, made from a composite of polypropylene and wood fiber. With a sweet and intense characteristic, 3-carene can be considered a material that participates in a significant way in the formation of the odor.

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