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WINTER WINDSCREEN WASHING LIQUIDS AS A SOURCE OF HUMAN EXPOSURE TO ALCOHOLS

ZIMOWE PŁYNY DO SPRYSKIWACZY JAKO ŹRÓDŁO NARAŻENIA CZŁOWIEKA NA DZIAŁANIE ALKOHOLI

Abstract: Analyses of 12 winter windscreen washing liquids available on the home market were performed. Ethanol, methanol and 2-propanol were determined. Results of the investigations indicated that in the all samples ethanol was present. Its content in the majority of tested winter windscreen washing liquids was about 30–50 %. In four samples methanol was determined. Methanol content in one sample was very high and achieved nearly 40 %. One sample contained about 11 % of 2-propanol. The total alcohols content in all samples was calculated. Alcohols content in winter windscreen washing liquids was between 30–50 %.

Keywords: windscreen washing liquids, cabin air quality, methanol, ethanol, 2-propanol

Indoor air quality is more and more important due to the time people spend indoors. People generally spend more than 80 % of their time in an indoor environment such as residential and office buildings, shopping centers, etc [1–3]. As well as indoor air quality in various buildings, air quality in mobile cabins (CAQ – *Cabin Air Quality*) including cars, trains, buses, aircrafts and subway is also important [3, 4].

In big city agglomerations people have spent more time in their cars. It is a result of the increase in numbers of vehicles as well as a bad road organization. Hence, the main roads in cities in the rush hours are full of cars stuck in a traffic jam.

The air pollution accumulated inside a car cabin very often consists of gasoline and diesel exhaust. This toxic mixture of gases, aerosols, and microscopic particles includes carbon monoxide, nitrogen oxides, particulate matter, and a host of other hazardous chemicals, such as formaldehyde, 1,3-butadiene, and aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes, BTEX) [5]. All the substances may influence harmfully the environment and human health. According to accessible literature, in car's cabin the other volatile substances such as acetone, ethanol, limonene, 2-propanol,

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2-butanone are present very often [3, 5]. Ethanol and limonene are those, whose content in cabin air is the biggest. They are often ingredients of car cosmetics such as waxes, air-freshners, cleaning and conditioning agents. Windscreen washing liquids rank among this group of products. They may contain ethanol, 2-propanol and methanol.

During intensive use of these liquids the concentrations of alcohols inside a car cabin may reach high values. The above compounds have harmful impact on a human body that may give the symptoms such as sickness, irritation of an eye, nose or throat mucosa. Ethyl alcohol decreases the motor and muscle coordination and reaction time becomes slower, what may endangers the road safety. Both ethyl and methyl alcohols badly affect the eyesight and methyl alcohol may lead to irreversible damage of the eyesight [6].

Materials and methods

The studies of alcohols contents in the windscreen washing liquids were performed by using gas chromatography method. The subject of examinations was 12 of winter windscreen washing liquids available on the home market.

The samples of analyzed product (5 mm^3) were injected into 1114 cm^3 containers, tightly closed with the screw caps containing the silicon membranes. The samples were evaporated in thermostat chamber at the temperature of 50 ^oC. Next, they were stabilized at the room temperature for 30 minutes. After equilibration, the gas samples of 1 cm^3 volume were drawn with a Hamilton gas-tight syringe and analyzed on a gas chromatograph equipped with a *flame-ionization detector* (FID). The qualitative and quantitative analyses of windscreen washing liquids components were performed using a CHROM 5 gas chromatograph with a FID detector. The chromatograph was provided with a steel chromatographic column of 1 meter long of 3 mm inside diameter packed with Chromosorb 102, (80–100 mesh). The following temperatures were applied: column 100 ^oC, injector 120 ^oC, detector 150 ^oC. Nitrogen (40 $cm^3 \cdot min^{-1}$) was used as the carrier gas.

Identification was performed with the aid of methanol, ethanol and 2-propanol standards (standards for GC, ≥ 99.9 %). The identification of the alcohols was confirmed using an Agilent 6890N gas chromatograph with a 5973N mass selective detector, equipped with a 7683 series injector. In order to prepare samples for the GC-MS analyses, the windscreen washing liquids were dissolved in butyl acetate. A HP-5MS capillary column with 5 % phenylmethylpolysiloxane, 30 m × 0.25 mm I.D. and 0.25 μm film thickness was used with the following temperature program: 50 ^oC (hold 5 min), 10 $^oC\ min^{-1}$ to 280 ^oC (hold 2 min). Helium was used as carrier gas at a constant flow rate of 1.2 $cm^3\ min^{-1}$. The injection port temperature was 250 ^oC, 2 mm^3 of solutions was injected via split (1:10) injection. The mass selective detector conditions were as follows: electron impact ionization, full scan mode (10–200 m/z), MSD transfer line temperature: 280 ^oC, MS quad: 150 ^oC; MS source: 230 ^oC. The chromatographic data of the windscreen washing liquids components are shown in Table 1.

Table 1

Retention time and mass fragmentation patterns of the windscreen washing liquids components

Substance	Retention time [min]		Mass/charge (relative intensity)
	GC-FID	GC-MS	
Methanol	2.50	1.38	32 (M^+, 72), 31 (100), 29 (60), 15 (12)
Ethanol	6.10	1.44	46 (M^+, 24), 45 (67), 43 (15), 31 (100), 29 (31), 27 (22)
2-Propanol	12.50	1.50	59 (M^+–1, 5), 45 (100), 43 (23), 41 (9), 39 (8), 29 (9), 27 (9)

Quantitative analyses of the windscreen washing liquids components were performed on the CHROM 5 gas chromatograph with a FID detector. The apparatus was calibrated using the standard gas mixtures prepared in the same containers and conditions in which the tested samples were prepared. The aim of this was to eliminate the errors resulting from adsorption on the walls of the container. In order of that, 5 mm^3 of liquid mixture containing methanol, ethanol, 2-propanol (0.13, 0.13, and 0.26 $g \cdot cm^{-3}$, respectively) was injected into 1114 cm^3 container, tightly closed with the screw cap containing the silicon membrane. The further procedure was as for the samples of the windscreen washing liquids (evaporation at 50 ^oC, stabilization at the room temperature). After equilibration the gas mixture of 0.4; 0.8; 1.2 and 1.6 cm^3 volume were drawn with a Hamilton gas-tight syringe and analyzed on a gas chromatograph. Correlation coefficients of calibration curves for determined compounds were in the range of 0.9953–0.9967.

Alcohols content C in the examined products was calculated from the following equation:

$$C = \frac{m \cdot V_C}{V_S \cdot V_R \cdot d} \cdot 100 \text{ [\% vol.]}$$

where: m – mass of alcohol calculated from calibration curve [mg],
V_C – volume of the container [cm^3],
V_S – volume of gas sample injected to the chromatographic column [cm^3],
V_R – volume of windscreen washing liquid injected into container [mm^3],
d – density of alcohol [$g \cdot cm^{-3}$].

Results and discussion

The analyses of 12 winter windscreen washing liquids available on home market were performed. Results of the quantitative analyses of alcohols content in the examined samples are given in Table 2.

Results of the investigations indicated that in the all samples ethanol was present. Its content in the majority of tested winter windscreen washing liquids was about 30–50 %. Only in two samples ethanol content was lower and averaged 6.00 % for the sample WL3 and 12.37 % for the sample WL7. Application of windscreen washing liquids with high ethanol content may influence the cabin air quality. High ethanol concentration in

air may have an effect on decrease of concentration and reaction time extension of drivers.

Table 2

Results of the determination of alcohols content in products

Product	Substance	Content [% vol.]	Standard deviation SD	Coefficient of variation RSD [%]
WL1	ethanol	34.90	0.97	2.79
WL2	methanol	4.57	0.14	3.15
	ethanol	34.41	0.21	0.62
WL3	methanol	38.66	1.30	3.35
	ethanol	6.00	0.21	3.53
WL4	ethanol	37.09	1.39	3.75
WL5	methanol	3.92	0.16	4.06
	ethanol	31.53	1.08	3.42
WL6	ethanol	48.61	1.74	3.57
WL7	methanol	8.87	0.12	1.35
	ethanol	12.37	0.21	1.71
	2-propanol	11.34	0.43	3.77
WL8	ethanol	35.02	0.92	2.64
WL9	ethanol	35.14	0.56	1.60
WL10	ethanol	40.41	0.37	0.91
WL11	ethanol	42.61	0.37	0.86
WL12	ethanol	41.75	0.42	1.02

In four samples methanol was determined. Methanol content in sample WL3 was very high and achieved nearly 40 %. In our opinion using of this product is dangerous. The large amount of methanol has harmful effect on human health, especially on sight. In the three other samples (WL2, WL5 and WL7) methanol content was considerably lower. Additionally in the WL7 sample, 2-propanol was identified. Its content in this product was about 11 %.

The summary alcohols content in the samples was calculated. Results are presented in Fig. 1. Alcohols content in winter windscreen washing liquids was between 30–50 %. In the majority of products this value varied from 30 to 40 %. The maximum alcohols content was found in samples WL3 (44.66 %) and WL6 (48.61 %). WL6 sample was a concentrate to mix with water, which helps to prevent windscreen washer freeze. Without water addition, it protects to temperature –70 ^{o}C. All remaining winter windscreen washing liquids can be used to temperatures –20, –22 and –25 ^{o}C.

The accuracy of the described method was determined on the basis of calculation of alcohols recovery from winter windscreen washing liquids of strictly determined composition. For this purpose composed four types of model washing liquids with different content of methanol, ethanol and 2-propanol. Alcohols content and composi-

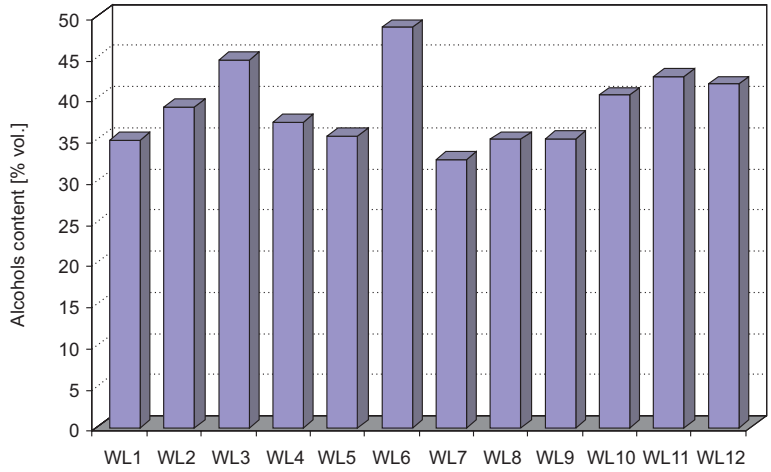

Fig. 1. Summary alcohols (methanol, ethanol and 2-propanol) content in winter windscreen washing liquids

tion of the model windscreen washing liquids were selected in the way to respond to the commercial product composition. Their characteristics and alcohols recoveries are given in Table 3.

Table 3

Data of accuracy and precision of determination method of alcohols content in windscreen washing liquids

Model windscreen liquid	Substance	Content [% vol.]	Recovery [%]	Standard deviation SD	Coefficient of variation RSD [%]
TWL1	methanol	10	101.86	1.91	1.87
	ethanol	10	94.13	3.10	3.30
	2-propanol	10	94.76	2.38	2.55
TWL2	methanol	40	111.00	0.62	0.56
	ethanol	5	96.85	2.50	2.59
TWL3	methanol	5	106.43	2.88	2.71
	ethanol	40	103.36	0.63	0.61
TWL4	ethanol	50	103.50	0.50	0.48

The mean alcohols recovery for the analysed products was 101.49 %. The lowest recovery was obtained for 2-propanol (94.76 %). The average recoveries of methanol and ethanol were a bit higher and achieved respectively 106.43 and 99.46 %. It may be caused by higher boiling temperature of 2-propanol than boiling temperatures of methanol and ethanol. Another cause of the lowest 2-propanol recovery may be its low content in a sample.

Precision of the method was determined by evaluation of repeatability of the results calculating the standard deviation and a coefficient of variation. The coefficients of variation for the obtained results were below 5 %.

Conclusions

The analyses of 12 winter windscreen washing liquids available on the home market were performed.

Summary alcohols content in winter windscreen washing liquids was between 30–50 %. In the tested products three alcohols (methanol, ethanol and 2-propanol) were identified. Ethanol was present in the all samples. In four samples methanol was determined. Its content was very high (39 %) in one product. One sample contained about 11 % of 2-propanol.

The described methodology may be used to control the quality of windscreen washing liquids and may be used to evaluation of cabin air quality. The method is repeatable and accurate. The mean alcohols recovery was 101.49 %.

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ZIMOWE PŁYNY DO SPRYSKIWACZY JAKO ŹRÓDŁO NARAŻENIA CZŁOWIEKA NA DZIAŁANIE ALKOHOLI

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Abstrakt: Przedmiotem badań było 12 zimowych płynów do spryskiwaczy dostępnych na rynku krajowym. W badanych produktach zidentyfikowano i oznaczono ilościowo etanol, metanol i 2-propanol. Wyniki badań wskazują, że we wszystkich badanych produktach obecny jest etanol. Jego zawartość w większości zimowych płynów do spryskiwaczy wynosiła 30–50 %. Metanol zidentyfikowano w czterech próbkach, przy czym w jednej z próbek jego zawartość była bardzo duża i wynosiła prawie 40 %. Jeden z produktów zawierał około 11 % 2-propanolu. Obliczono sumaryczną zawartość alkoholi w próbkach. Mieściła się ona w granicach 30–50 %.

Słowa kluczowe: płyny do spryskiwaczy, jakość powietrza w kabinach, metanol, etanol, 2-propanol