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ANALYSIS OF VOLATILE COMPOUNDS IN NAIL POLISH REMOVERS AS A CRITERION OF HEALTH HAZARD DETERMINATION AND COMMODITY EVALUATION

ANALIZA LOTNYCH SKŁADNIKÓW ZMYWACZY DO PAZNOKCI JAKO KRYTERIUM OCENY ZAGROŻENIA ZDROWIA I OCENY TOWAROZNAWCZEJ

Abstract: The volatile organic compounds (VOCs) content in nail polish removers available on the home market was determined. Qualitative and quantitative analyses of acetone, methanol, ethanol, isopropanol and ethyl acetate were performed. Theoretical VOCs concentrations in the standard room and time for reduction to low values were calculated. On the basis of the results the commodity evaluation of nail polish removers was carried out. The performed investigations indicate that this group of product is very often adulterated.

Keywords: nail polish removers, volatile organic compounds, indoor air quality, commodity evaluation

Nowadays discomfort and health problems affecting people more as a result of the presence of harmful factors in their close environment than they used to. According to accessible literature, people spend about 80 % of the time in the indoor areas [1–3]. The recent announcements say the time spent indoor may reach even 90 %. In those conditions the *indoor air quality* (IAQ) is important, especially for children and elder people's health [2–4]. Factors directly influencing IAQ are physical, chemical and biological pollutants [2]. High level of this kind of pollution is a reason for numbers of health problems such as headaches, dizziness, irritation of eye, nose or throat mucosa, allergic reactions on skin, concentration troubles, insomnia, tiredness or problems in breathing. Those symptoms literature describes as SBS (*Sick Building Syndrome*) [2, 4–6].

Indoor air pollutants are emitted from different sources such as combustion by-products, cooking, construction materials, office and home equipment, and consumer

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products [2–4, 7, 8]. Nitric and carbon oxides, *volatile organic compounds* (VOCs) and particulates are the most common indoor air pollutants [3]. Volatile organic compounds are defined as organic compounds with boiling points range from ca 50 to 260 ^{o}C [7]. Some studies reported correlation between symptoms of SBS and total VOCs concentration. In the majority of cases the incidence of symptoms is higher at increased total VOCs concentration [3, 9].

VOCs determined in indoor air belong to different groups of compounds. There are carbonyl compounds (aldehydes and ketones), aliphatic and aromatic hydrocarbons, terpens, alcohols, esters, halogenated hydrocarbons, ethers and others [1–4, 6, 8, 10–12].

One of sources the above of compounds are consumer products [13], such as paints, polishes, cleaning products, deodorizers, glues, sealants and cosmetics [6, 13–15]. Six compounds usually are identified in all household classes (acetone, ethanol, perchloroethylene, phenol, 1-propanol and limonene) [14].

The household products accounted about 20 % of poisoning incidents and over 80 % of those are accidental child poisonings [15]. Data presented in the available literature shows that children younger than 6 years are the most frequently endangered by substances used in cosmetics [16].

High content of VOCs is noticed in nail lacquers and polish removers. Solvents are 70–80 % of their content. The most common solvents used in polishes are acetone, ethyl acetate, butyl acetate, toluene and isopropanol [17, 18]. The mentioned above compounds are also used as components of nail polish removers [17–19].

Kwon et al identified 12 substances contained in nail polish removers available on Korean market [14]. Four of the identified substances (acetone, butyl acetate, cyclohexane, 2,2,4-trimethyl-1,3-dioxolane) are characterised by high volatility and they are significantly responsible for indoor air pollution [13]. Research on nail polish removers available on Canadian market indicated emission of toluene, 2-butoxyethanol and ethyl acetate [13].

Components of nail polish removers directly react on a nail plate. Due to this fact, in recent years producers have limited use of acetone in nail polish removers. Acetone dries a nail plate when it is often used. Other solvents, eg ethyl acetate, are more gentle [19].

Taking into account the hazardous effects of acetone, consumers, examining the declared by producers ingredients used to production, nowadays choose acetone free products more often than they used to. Considering the cost of chemical agents, production of acetone free products is obviously more cost-consuming than production of the removers containing acetone. This fact may be used by unfair producers to reduce costs. The goal of this work was studies of available on the home market nail polish removers and determination of VOCs emission to indoor air.

Materials and methods

Nail polish removers available on the home market where used as the samples. The products were grouped into two classes: A – removers with declared acetone

content and B – acetone-free removers. There were 10 removers of A class and 7 of B class.

The studies of VOCs content in nail polish removers were performed by gas chromatography method. The applied method enables a selective determination of organic solvents in consumer products.

The samples of analyzed product (5 mm^3 (μl) of nail polish removers) were injected into 1114 cm^3 glass containers, tightly closed with the screw caps containing the silicon membranes. The samples were evaporated in thermostat chamber at temperature 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 detectors* (FID).

The qualitative and quantitative analyses of polish removers components were performed using a CHROM 5 gas chromatograph with FID detectors. The chromatograph was provided with two steel chromatographic columns. Column I was 2 meter long of 3 mm inside diameter packed with 8 % SE-30 + 0.21 % Carbowax 20M on Chromosorb W NAW (60–80 mesh). Column II was 1 meter long of 3 mm inside diameter packed with Chromosorb 102 (80–100 mesh). The following temperatures were applied: column I 50 ^oC, column II 100 ^oC, injectors 120 ^oC, detectors 150 ^oC. Nitrogen (40 $cm^3 \cdot min^{-1}$) was used as the carrier gas.

Identification of removers ingredients was performed on the both columns with the aid of acetone, methanol, ethanol, isopropyl alcohol, ethyl acetate, *n*-butyl acetate standards. All standards were of analytical purity.

Quantitative analyses of ethyl acetate and *n*-butyl acetate were performed on column I. On the column I peaks of acetone and other volatile compounds such as ethyl and isopropyl alcohols were not separated very well. Analyses of acetone, methanol, ethanol and isopropyl alcohol were performed on column II. 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 limit the errors resulting from analytes adsorption on the walls of the container. In order of that 5 mm^3 of standard liquid mixtures were injected into 1114 cm^3 containers, tightly closed with the screw caps containing the silicon membrane. Two standard mixtures were used for calibration. The first mixture contained methanol, ethanol, isopropanol and acetone (1:1:2:2). In the second ethyl and butyl acetate (1:2) were used, with acetone as a solvent. The further procedure was as for the samples of the nail polish removers (evaporation at 50 ^oC, stabilization at the room temperature). After equilibration gas mixtures 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. The obtained calibration curves were rectilinear with the correlation coefficients in the range of 0.9953–0.9997.

Content of compounds *C* in the examined products was calculated from the following equation:

$$C = \frac{m \cdot V_C}{V_S \cdot V_R} \cdot 100 \text{ [g in 100 cm}^3 \text{ of product]} \quad (1)$$

where: m – mass of the substance 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 nail polish remover injected into container [µl].

Results and discussion

17 Samples of nail polish removers were examined. Results of the analyses of VOCs content in the examined samples are given in Tables 1 and 2.

Table 1

Contents of volatile organic compounds in the nail polish removers with declared acetone content

Product	Substance	Content in product [g · 100 cm^{-3}]	Coefficient of variation RSD [%]	Summary VOCs content in product [g · 100 cm^{-3}]
A1	acetone	18.62	1.00	18.62
A2	acetone	76.75	1.47	76.75
A3	acetone	58.80	0.85	70.32
	ethanol	11.52	3.53	
A4	acetone	75.88	1.27	75.88
A5	acetone	66.80	0.69	66.80
A6	acetone	70.83	0.39	70.83
A7	acetone	64.65	4.11	64.65
A8	acetone	59.17	0.68	65.82
	ethanol	6.65	4.97	
A9	acetone	71.63	1.12	71.63
A10	acetone	67.35	3.19	67.35

In products of class A there were identified volatile substances as acetone and ethanol. Composition of products in class B was more varied. In those products methanol, ethanol, isopropanol and ethyl acetate were present. Additionally, there was identified acetone content in 5 samples although producers declared their products as acetone-free ones. In examined polish removers there was not identified *n*-butyl acetate.

It was found, that VOCs content in products of class A ranges from 64 to 77 g in 100 cm^3 of product except for the product A1, where VOCs (acetone) content was less than 20 g in 100 cm^3 of the product. VOCs content in products of class B ranged from 40 to 96 g in 100 cm^3. Coefficients of variation (RSD) for the obtained results did not exceed 5 %. Higher values of RSD (16–22 %) were obtained analysing methanol in samples B5 and B7. Methanol content in those samples was very low (less than 0.5 g in 100 cm^3).

Table 2

Contents of volatile organic compounds in the acetone-free removers

Product	Substance	Content in product [g · 100 cm^{-3}]	Coefficient of variation RSD [%]	Summary VOCs content in product [g · 100 cm^{-3}]
B1	acetone	50.42	0.59	72.21
	isopropanol	21.24	0.92	
	ethyl acetate	0.55	4.44	
B2	acetone	23.05	1.89	40.69
	methanol	17.64	4.83	
B3	methanol	5.64	1.04	71.15
	ethanol	23.76	2.65	
	ethyl acetate	41.75	2.23	
B4	acetone	17.39	3.36	84.12
	methanol	66.73	2.08	
B5	acetone	1.67	2.19	94.66
	methanol	0.30	16.37	
	ethanol	9.06	4.84	
	isopropanol	31.94	0.57	
	ethyl acetate	51.69	1.53	
B6	acetone	45.01	0.43	65.49
	isopropanol	20.48	0.72	
B7	methanol	0.07	21.53	87.39
	isopropanol	2.26	5.11	
	ethyl acetate	85.06	3.08	

Substances contained in nail polish removers may significantly affect indoor air quality. For that reason an attempt to determine concentration of those substances in indoor air was undertaken.

In order to determine the average use of nail polish removers a group of 10 women was questioned. The average use was determined to be 2.5–4 cm^3 of product. Considering very high volatility of nail polish removers ingredients it may be assumed that all the ingredients are emitted into the air in very short time being a source of VOCs emission. It was assumed that the air was well mixed and that there were no sinks in the standard room. The initial concentrations of VOCs in the standard room of volume 17.4 m^3 [12, 13] were calculated. Results are presented in the Table 3. VOCs concentrations were strongly high (> 3 mg · m^{-3}) [9] and were in the majority of cases over 100 mg · m^{-3}.

The time necessary to reduce the concentration of VOCs in the standard room to low concentration level (0.25 mg · m^{-3}) was determined [9]. To gain the aim, the following assumptions were used.

Table 3

The initial concentrations of VOCs in the standard room and the time to reduce of concentrations to low values

Product	VOCs emission [g]	Initial average concentration of VOCs [mg · m^{-3}]	Time to reduce of VOCs concentration to 0.25 mg · m^{-3} [h]
A1	0.47–0.74	34.78	7.12
A2	1.92–3.07	143.35	9.16
A3	1.76–2.81	131.34	9.04
A4	1.90–3.04	141.73	9.15
A5	1.67–2.67	124.77	8.96
A6	1.77–2.83	132.30	9.05
A7	1.62–2.59	120.75	8.92
A8	1.65–2.63	122.94	8.94
A9	1.79–2.87	133.79	9.06
A10	1.68–2.69	125.80	8.97
B1	1.81–2.89	134.88	9.08
B2	1.02–1.63	76.00	8.25
B3	1.78–2.85	132.90	9.05
B4	2.10–3.36	157.12	9.30
B5	2.37–3.79	176.81	9.47
B6	1.64–2.62	122.32	8.93
B7	2.18–3.50	163.23	9.35

Changes of VOCs concentration in the standard room may be presented in a geometric progression:

$$C_t = C_0 \cdot N^t \tag{2}$$

where: C_0 – initial concentration,
C_t – concetration at the time t,
N – air exchange rate,
t – time.

Take it for granted that concentration of volatiles in indoor air is regarded as a low, when its values is below 0.25 mg · m^{-3} [9], we obtain:

$$0.25 > C_0 \cdot N^t \tag{3}$$

Transforming the above relation we obtain relation (4) from which we may calculate the time necessary to reach the assumed concentration:

$$t > \frac{\log 0.25 - \log C_0}{\log N} \tag{4}$$

To estimate the necessary time to obtain concentrations below 0.25 mg · m^{-3}, an average air exchange rate N of 0.5 h^{-1} was applied [13]. Results of calculations are presented in Table 3. The time to reduce of VOCs concentrations to low values appear to be in the range of 7–9.5 hours.

The described methodology together with gas chromatography may be used to commodity evaluation of nail polish removers. Results of investigation indicated that this group of product is very often adulterated.

There were examined 17 samples of nail polish removers. Producers declared acetone content in 10 of them but acetone was found in 15 samples. For declared acetone-free removers (class B) the factual state was according with producer's declaration about acetone absence only in two samples. In one sample of B class product (B5) acetone content was low and it was about 2 g in 100 cm^3. In four „acetone-free" removers (B1, B2, B4, B6) acetone content was significantly higher and it ranged from 17 to 50 g in 100 cm^3 of product.

In products of class A in two cases (A3 and A8) some content of ethanol was found. Although producers declared ethyl acetate content, it was not identified in the A1 and A3 products.

Analysing polish removers of class B none of the examined samples contained *n*-butyl acetate. Its content was declared by four producers (B1, B2, B4, B6). Additionally declared content of products B2 and B4 was not in agreement with the factual state. In those products high contents of methanol and acetone were found, whereas producers declared butyl acetate (B4) or butyl acetate and isopropanol (B2). Very low content of methanol in products B3, B5 and B7 may result from pollution of alcohols used for nail polish removers production.

Conclusions

Analyses of 17 nail polish removers available on the home market were performed. In the products there were identified very volatile organic compounds such as acetone, methanol, ethanol, isopropyl alcohol and ethyl acetate. The composition of tested products often differs from declared by producers.

Calculated VOCs concentrations in the standard room during application of the tested products are strongly increased. Nail polish removers are a significant source of VOCs emission into the indoor air. The time to reduce of VOCs concentrations to low values appear to be in the range of 7–9.5 hours.

The described methodology may be used to control the quality of nail polish removers and evaluation of indoor air quality. The method is repeatable. Its advantage is low costs of analysis and undemanding apparatus requirements.

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ANALIZA LOTNYCH SKŁADNIKÓW ZMYWACZY DO PAZNOKCI JAKO KRYTERIUM OCENY ZAGROŻENIA ZDROWIA I OCENY TOWAROZNAWCZEJ

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Abstrakt: Przeprowadzono badania zawartości lotnych składników zmywaczy do paznokci dostępnych na rynku krajowym. W badanych produktach zidentyfikowano i oznaczono ilościowo: aceton, metanol, etanol, izopropanol i octan etylu. Określono teoretyczne stężenia lotnych związków organicznych wydzielających się ze zmywaczy do paznokci w pomieszczeniu standardowym i wyznaczono czas niezbędny do uzyskania niskich wartości tych stężeń. Na podstawie tych wyników dokonano oceny towaroznawczej zmywaczy do paznokci. Wyniki badań wskazują, że skład większości produktów nie jest zgodny ze składem deklarowanym przez producentów.

Słowa kluczowe: zmywacze do paznokci, lotne związki organiczne (VOCs), jakość powietrza wewnętrznego, ocena towaroznawcza