**SCREENING ORGANIC COMPOUNDS IN WET WIPES BY SOLID-PHASE MICROEXTRACTION**

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**ABSTRACT**

The popularity of wet wipes application continues to grow, because they are an important part of skin care for millions of people around the world. Wet wipes may consist of lots of substances that can cause irritation of skin or allergy and subsequently, their composition is necessary to be identified. The aim of this study was to perform screening organic compounds in wet wipes by solid-phase microextraction (SPME) coupled with gas chromatography-mass spectrometry. Screening was carried out by analysis of six samples of wet wipes. Alcohols, esters, ketones, aldehydes, acids, aromatic compounds and terpenes were identified in the samples. Among identified alcohols, methanol and phenoxyethanol that can cause allergy was identified. Propylene glycol that can be referred to a group of preservatives was found out in 2 samples. Derivatives of benzene as ethyl benzene, methylethyl benzene and butyl ethyl benzene were also observed almost in all samples. Diethyl phthalate that is not prohibited to use in hygiene products was observed in one wet wipe sample. Applied parameters of solid-phase microextraction and gas chromatography-mass spectrometry can be used in future for development of quantitative methodology for particular compounds as phthalates, alkoxyalcohols, aromatic hydrocarbons and preservatives.

**Keywords:** gas chromatography, mass-spectrometry, solid-phase microextraction, wet wipes, organic compounds.

**INTRODUCTION**

Hygiene products are important in everyday life for people of all age categories around the world [1]. Over the last decades an increasingly diverse range of such products, including disposable wet wipes have become available.

At the same time there are more than thousand of substances in the composition of wet wipes. Wet wipes used for cleaning hands, eye make-up removing, removing dust from furniture [2-3]. Sometimes lots of organic substances are used in production of wet wipes and their composition differs from the composition marked on the packet. These compounds can cause irritation of skin and allergy to humans, particularly for babies [4]. Some cases of allergic contact dermatitis were reported in infants and adults when using cosmetics and hygiene products due to the presence of 2-phenoxyethanol in them [5]. All these compounds affect human health, as wet wipes have direct contact with human skin. Thus, it is necessary to perform screening of organic composition of wet wipes.

Modern methods as static headspace gas chromatography [6], high-performance liquid chromatography with tandem mass-spectrometry (HPLC-MS/MS) [7], and ultra-high pressure liquid chromatography [8] were used for determination of organic compounds in wet wipe samples. Methods based on HPLC with mass spectrometry are complex and requires large amount of organic solvents for mobile phase [7, 9]. The most simple method for analysis of organic compounds is gas chromatography-mass spectrometry [6]. However, determination of organic compounds in wet wipes, special sample preparation technique is required. Different extraction techniques were applied for organic compounds in wet wipes as soxhlet extraction with iso-Propanol solution [10] and pressurized liquid extraction [11]. These techniques require the use of toxic organic solvents and complex equipment for the extraction.

Solid-phase microextraction (SPME) is a preferably used technique for extraction of organic compounds from different matrixes. This method is simple, relatively inexpensive, provides compliance with green analytical chemistry and can be fully automated. SPME in headspace mode allows to extract target compounds even from solid samples compared to direct immersion mode. In addition, extraction in headspace mode allows to avoid damage and overload of the coating fiber.

Despite the wide application range of solid-phase microextraction, organic compounds of wet wipes samples were not previously analyzed by SPME and GC-MS. The aim of this study was to perform screening organic compounds of wet wipes by headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry.

**EXPERIMENTAL**

*Sample collection and preparation*

The 14 packets of wet wipes were bought from the local supermarkets in Almaty, Kazakhstan (Table 1). 1 g of one wet wipe was placed to preliminary conditioned 20-mL vials and closed by magnetic caps with silicone septa (CTC Switzerland). Then prepared samples were placed into Combi-PAL auto sampler (CTC Analytics AG, Switzerland) tray.

Table 1. Samples of wet wipes for screening organic compounds

|  |  |
| --- | --- |
| **Sample name/notes** | **Manufacturer country/name** |
| Clearol (lavender) | Republic of Kazakhstan, LP Albi Pharma |
| As atu | Russia, LLC Cotton Club |
| Kleenex  | Korea Republic, Wooil & Tech Corp. |
| Take a fresh | Ukraine, LLC KPD |
| Aura (exotic pineapple) | Russia, LLC Bumfa Group |
| Ola (silk sense antibacterial) | Russia, Oltex limited |

*GC-MS parameters*

Experiments were conducted using GC-MS system: 7890A/5975C (Agilent, USA) equipped with Combi-PAL autosampler (CTC Analytics AG, Switzerland). Separation was conducted using DB-35ms (30 m x 250 μm x 0.25 µm) column (Agilent, USA) at a constant flow rate of helium (> 99.995 %) of 1.0 mL/min. Oven temperature of 7890A GC was programmed from 40ºC (held for 10 min) to 240ºC (held for 10 min) at a 10ºC/min. Run time was 40 min. Temperatures of MS source, quadrupole and interface were set to 230, 150 and 280°C, respectively. Detection was performed in scan mode (m/z 34-400).

*SPME parameters*

SPME was conducted using autosampler Combi-Pal (CTC Analytics AG, Switzerland) in headspace mode. Parameters of SPME accounted for: pre-incubation time was 3 min, extraction temperature 37°C, time of extraction 5 min and desorption time 3 min. Coating fiber 85 µm CAR/PDMS were used for extraction of organic compounds from samples of wet wipes.

**RESULTS AND DISCUSSION**

The results of screening organic compounds in wet wipes have shown the presence of organic compounds as alcohols, aldehydes, esters, ketones, acids, aromatic compounds and terpenes in the studied samples. As demonstrated in figure 1, wet wipe “Clearol” contain 26 types of alcohols and “Take a fresh” contain 32 alcohols. In other wet wipes as “Kleenex” and “Ola” the number of alcohols is 2 times less than in “As Atu” and “Aura” samples. 18 aromatic compounds were identified in “Kleenex” sample, while other two samples contain 2.5 times less aromatic compounds. The greatest number of alcohols compared to other compounds were identified in all six samples (Figures 1 and 2).

Figure 1. Number of compounds in three different wet wipes samples

Figure 2 demonstrates that “Take a fresh” sample contain the highest number of alcohols, aldehydes and aromatic compounds (32, 15 and 9, respectively) comparing to other samples (1.6 and 1.3 times lower number of aldehydes). “Aura” sample contain the highest number of aldehydes comparing with “Ola” and “Take a fresh”. The samples “Take a fresh”, “Clearol” and “Ola” have a label “without alcohols” on the packets, however a large number of alcohols was identified in these samples: 32, 26 and 12, respectively (Figures 1 and 2).

Figure 2. Number of compounds in three different wet wipes samples

Organic compounds that have the highest abundance and identified in five samples of wet wipes with high number of compounds are presented in Table 2. Among identified alcohols, presence of such of them as methyl alcohol and phenoxyethanol was observed. Methyl alcohol is considered as poisonous substance, while phenoxyethanol can be a reason of skin irritation or allergy, especially for babies [4]. Also propylene glycol that may be referred to the group of preservtaives was identified in 2 wet wipes samples. According to EU Regulation No. 1223/2009, benzene is prohibited to use in cosmetics products [12]. However, benzene derivatives as trimethyl benzene, ethyl benzene and buthyl ethyl benzene were identified ialmost in all samples. Diethyl phtalate that is not forbidden to use in wet wipes and has low level of toxicity was observed in “Aura” sample [13]. Applied parameters of SPME and GC-MS can be used in future for development of methodology for quantification of particular compounds in wet wipes.

Table 2. Organic compounds with the highest abundance identified in samples of wet wipes by HS-SPME

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Clearol | Kleenex | Take a fresh | Aura | Ola |
| Alcohols | EthanolDiethylene glycolButanolHexenolEthylhexanolOctanolBenzyl alcoholPhenylethyl alcoholPropylheptyl alcohol PhenoxyethanolDodecanolDimethyl octanol | Dimethyl heptanolEthylhexanolOctanolLinaloolDimethyl octanolPhenoxyethanolEthanolHeptanol | Ethanol[Propylene glycol](http://chemister.ru/Database/properties-en.php?dbid=1&id=5954)ButanolHeptanolOctanolDimethyl octanolBenzyl alcoholTerpinol | PropanolButanolPentenolHexenolOctanolEthylhexanolDimethyloctenolBenzyl alcoholHexadecanolPhenylethyl alcoholEthanol | EthanolMethyl alcoholPropanolEthylhexanolDimethyloctenolDimethyloctadienolPhenoxyethanol |
| Aromatic compounds | Butyl hydroxy tolueneIsopropyl tolueneDureneO-xylolEthyl benzeneBenzyl indole | XyleneStyreneTrimethylbenzeneToluenep-XyleneDiethyl benzeneLilial | Methoxy benzeneCymeneEthoxy naphtaleneButyl ethyl benzeneButyl hydroxy toluene2-tolylpropene | DureneEthenyl naphtaleneEthyl benzeneTolyl propeneMethyl, methyl ethyl benzene | Benzene, 4-hexenyl-1-Butyl-2,4,6-trimethyl benzeneMethyl, methyl ethyl benzeneDurene |
| Ketones | **Ionone**PropanoneSulcatoneDimetyl Cyclopropanone | LononeIonon epoxideCyclohexanoneUndecanoneAcetyl prehniteneIsopropyl acetone | Propanone**Benzyl propyl ketone**Butyl propiophenone[Toluquinone](https://www.google.kz/url?sa=t&rct=j&q=&esrc=s&source=web&cd=3&cad=rja&uact=8&ved=0ahUKEwiz_46wks3MAhUhAZoKHQlZCXoQFggqMAI&url=https%3A%2F%2Fpubchem.ncbi.nlm.nih.gov%2Fcompound%2Fp-Toluquinone&usg=AFQjCNECASqBjaVLM6Gk2Jc8R-OpM5QyrQ&bvm=bv.121421273,d.bGs)Hydroxy methyl benzyl pyridoneEucarvoneCarvotanacetone | Octen-3-one2-ButanoneIonon-5,6-epoxide1,3-Dimethyl-pyrazolinoneButyl cyclo hexanoneHydroxy hexanoneDioxacyclohexadecanedioneJasmoneCarvotanacetone | Dimethyl oxetanoneβ-Ionon-5,6-epoxideNonanoneIso-methyl iononeMethyl cyclopentadecanone**Damascone**Methylcyclohexane-1,4-dioneDamasconeIso-methyl ionone |
| Esters | Methylpropanoic acid, dimethyl methylethyl propanediyl esterDiethyl phtalate | Propanoic acid, ethyl esterAcetic acid, phenylmethyl esterButanoic acid, methyl, ethyl esterAcetic acid ethyl ester | Butanoic acid, methyl, ethyl esterHexanoic acid, ethyl esterHexanoic acid, propenyl ester | Octanoic acid, ethyl octyl esterAcetic acid, butyl esterDecanoic acid, ethyl esterButanoic acid, methyl ethyl ester | Propanoic acid, formyl ethyl phenyl methyl esterAcetic acid, phenyl methyl ester |
| Aldehydes | HeptanalDodecanalBenzaldehydeDecanalBenzene ethanalMethyl, methylethyl phenyl ethanal | DodecanalHeptanalBenzaldehydeAcetaldehydeDecanal3-Furaldehyde | Methyl propenalButanalMethyl butenalPentanalHexanalHeptanalMethyl undecanalCitralAcetaldehydeBenzaldehyde | AcetaldehydeButanalHeptanalBenzaldehydeNonanalDecanalPhenylmethylene octanal | AcetaldehydeMethyl propenalOctanal, phenylmethylenePentanalBenzaldehydeHelional |
| Terpenes | PineneLimoneneOcimene | MyrceneCarenePinene | CareneHumuleneTerpinenePinene | LinaloolCitronellolOcimeneCarene | PineneAcetamidofuranCareneOcimene |

**CONCLUSION**

Hygiene products, including wet wipes are used by people of all age categories: from small babies to adults. However, organic composition of wet wipes in some cases can contain compounds that may be a reason of allergy or skin irritation. This paper describes the results of screening organic compounds in six samples of wet wipes by HS-SPME and GC-MS. Analyzed samples contained such classes of organic compounds as alcohols, aromatic compounds, ketones, esters, aldehydes and terpenes. All of the samples had a lot of organic compounds: the highest number of alcohols and aromatic compounds are 32 and 18 in their composition. Among identified alcohols, presence of methanol and phenoxyethanol that can cause allergy was observed. Propylene glycol that can be referred to a group of preservatives was identified in 2 samples. Derivatives of benzene as ethyl benzene, methylethyl benzene and butyl ethyl benzene were also observed almost in all samples. Diethyl phthalate that is not prohibited to use in cosmetics products was also found out in one wet wipe sample. Future directions of this research can include development of quantitative methodology based on HS-SPME for particular compounds as phthalates, alkoxyalcohols, aromatic hydrocarbons and preservatives.

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