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

**Dr. Mereke Alimzhanova**

**Saltanat Muratova**

**Gulyaim Sagandykova**

**Kazhybek Ashimuly**

**Dr. Michael**  **Nauryzbayev**

Center of Physical Chemical Methods of Research and Analysis, **Kazakhstan**

Al-Farabi Kazakh National University, **Kazakhstan**

**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 | Ethanol  Diethylene glycol  Butanol  Hexenol  Ethylhexanol  Octanol  Benzyl alcohol  Phenylethyl alcohol  Propylheptyl alcohol  Phenoxyethanol  Dodecanol  Dimethyl octanol | Dimethyl heptanol  Ethylhexanol  Octanol  Linalool  Dimethyl octanol  Phenoxyethanol  Ethanol  Heptanol | Ethanol  [Propylene glycol](http://chemister.ru/Database/properties-en.php?dbid=1&id=5954)  Butanol  Heptanol  Octanol  Dimethyl octanol  Benzyl alcohol  Terpinol | Propanol  Butanol  Pentenol  Hexenol  Octanol  Ethylhexanol  Dimethyloctenol  Benzyl alcohol  Hexadecanol  Phenylethyl alcohol  Ethanol | Ethanol  Methyl alcohol  Propanol  Ethylhexanol  Dimethyloctenol  Dimethyloctadienol  Phenoxyethanol |
| Aromatic compounds | Butyl hydroxy toluene  Isopropyl toluene  Durene  O-xylol  Ethyl benzene  Benzyl indole | Xylene  Styrene  Trimethyl  benzene  Toluene  p-Xylene  Diethyl benzene  Lilial | Methoxy benzene  Cymene  Ethoxy naphtalene  Butyl ethyl benzene  Butyl hydroxy toluene  2-tolylpropene | Durene  Ethenyl naphtalene  Ethyl benzene  Tolyl propene  Methyl, methyl ethyl benzene | Benzene, 4-hexenyl-  1-Butyl-2,4,6-trimethyl benzene  Methyl, methyl ethyl benzene  Durene |
| Ketones | **Ionone**  Propanone  Sulcatone  Dimetyl Cyclopropanone | Lonone  Ionon epoxide  Cyclohexanone  Undecanone  Acetyl prehnitene  Isopropyl 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 pyridone  Eucarvone  Carvotanacetone | Octen-3-one  2-Butanone  Ionon-5,6-epoxide  1,3-Dimethyl-pyrazolinone  Butyl cyclo hexanone  Hydroxy hexanone  Dioxacyclohexadecanedione  Jasmone  Carvotanacetone | Dimethyl oxetanone  β-Ionon-5,6-epoxide  Nonanone  Iso-methyl ionone  Methyl cyclopentadecanone  **Damascone**  Methylcyclohexane-1,4-dione  Damascone  Iso-methyl ionone |
| Esters | Methylpropanoic acid, dimethyl methylethyl propanediyl ester  Diethyl phtalate | Propanoic acid, ethyl ester  Acetic acid, phenylmethyl ester  Butanoic acid, methyl, ethyl ester  Acetic acid ethyl ester | Butanoic acid, methyl, ethyl ester  Hexanoic acid, ethyl ester  Hexanoic acid, propenyl ester | Octanoic acid, ethyl octyl ester  Acetic acid, butyl ester  Decanoic acid, ethyl ester  Butanoic acid, methyl ethyl ester | Propanoic acid, formyl ethyl phenyl methyl ester  Acetic acid, phenyl methyl ester |
| Aldehydes | Heptanal  Dodecanal  Benzaldehyde  Decanal  Benzene ethanal  Methyl, methylethyl phenyl ethanal | Dodecanal  Heptanal  Benzaldehyde  Acetaldehyde  Decanal  3-Furaldehyde | Methyl propenal  Butanal  Methyl butenal  Pentanal  Hexanal  Heptanal  Methyl undecanal  Citral  Acetaldehyde  Benzaldehyde | Acetaldehyde  Butanal  Heptanal  Benzaldehyde  Nonanal  Decanal  Phenylmethylene octanal | Acetaldehyde  Methyl propenal  Octanal, phenylmethylene  Pentanal  Benzaldehyde  Helional |
| Terpenes | Pinene  Limonene  Ocimene | Myrcene  Carene  Pinene | Carene  Humulene  Terpinene  Pinene | Linalool  Citronellol  Ocimene  Carene | Pinene  Acetamidofuran  Carene  Ocimene |

**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.

**ACKNOWLEDGEMENTS**

Authors would like to extend sincere thanks to the Center of Physical Chemical Methods of Research and Analysis.

**REFERENCES**

|  |  |
| --- | --- |
| [1] | Wiesemann F., Adam R., Absorbent products for personal health care and hygiene, Woodhead Publishing Limited, Germany, pp 316-335, 2011. |
| [2] | Rossmoore H.W., Fuel biocides, Handbook of Biocide and Preservative Use, Blackie Academic & Professional, UK, pp 211-212, 1995. |
| [3] | Siegert W., Preservative Trends in Wet Wipes, SOFW Journal, USA, issue 137, pp 44-51, 2011. |
| [4] | Roper C.S., Howes D., Blain P.G., Williams F.M., Percutaneous penetration of 2-phenoxyethanol through rat and human skin, Food Chem.Toxicol., UK, vol. 35, pp 1009-1016, 1997. |
| [5] | Scogmamiglio J., Jones L., Letizia C.S., Api A.M., Fragrance material review on 2-phenoxyethanol, Food Chem.Toxicol., USA, vol. 50, pp 244-255, 2012. |
| [6] | Lee S.J., Pyo H.S., Chung B.C., Kim H.D., Lee J., Simultaneous Determination of Alkoxyalcohols in Wet Wipes Using Static Headspace Gas Chromatography and Mass Spectrometry, Bull. Korean Chem. Soc., Korea, vol. 35/issue 11, pp 3280-3288, 2014. |
| [7] | Maeda Sh., Miwa Y., Multicomponent high-performance liquid chromatography/tandem mass spectrometry analysis of ten chemotherapeutic drugs in wipe samples, Journal of Chromatography B, Japan, vol. 921– 922, pp 43-48, 2013. |
| [8] | Willison S.A., Wipe selection for the analysis of surface materials containing chemical warfare agent nitrogen mustard degradation products by ultra-high pressure liquid chromatography–tandem mass spectrometry, Journal of Chromatography A, Journal of Chromatography A, USA, vol. 1270, pp 72-79, 2012. |
| [9] | Liao C., Kannan K., Concentrations and composition profiles of parabens in currency bills and paper products including sanitary wipes, Journal Science of the Total Environment, USA, vol. 475, pp 8-15, 2014. |
| [10] | Clifton M.S., Wargo J.P., Weathers W.S., Colуn M., Bennett D.H., Tulve N.S., Quantitative analysis of organophosphate and pyrethroid insecti cides, pyrethroid transformation products, polybrominated diphenyl ethers and bisphenol A in residential surface wipe samples, Journal of Chromatography A, USA, vol. 1273, pp 1-11, 2013. |
| [11] | Celeiro M., Lamas J.P., Garcia-Jares C., Llompart M., Pressurized liquid extraction-gas chromatography-mass spectrometry analysis of fragrance allergens, musks, phthalates and preservatives in baby wipes, Journal of Chromatography A, Spain, vol. 1384, pp 9-21, 2015. |
| [12] | EU Regulation No. 1223/2009 on cosmetic products, L.342, pp 59-209, 2009. |
| [13] | Diethyl phthalate, The Scientific Committee on Cosmetic Products and Non-Food Products intended for consumers (SCCNFP) 20th Plenary meeting, pp 2-35, 2002. |