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The presence of polycyclic aromatic hydrocarbons in disposable baby diapers: a facile determination method via salting-out assisted liquid-liquid extraction coupled with gas chromatography-mass spectrometry.

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Highlights:

- Disposable diapers contain toxic compounds as PAHs.
- There are no harmonized analytical methods for the determination of PAHs in diaper.
- A protocol for determination of PAHs using cryogenic grinding and LLE is presented.
- There was no diaper that is free of PAHs compounds.

Abstract:

In this paper we demonstrate the development of the extraction procedure of polycyclic aromatic hydrocarbons from baby diapers along with their quantification by gas chromatography-mass spectrometry. Apart from covering plastic foil, disposable baby diapers contain sorbents intended to absorb urine and feces. A hygroscopic, adsorptive, and tough-to-homogenize fibrous sorbent, represents an analytical challenge to analytical chemists. To address this issue we optimized and validated a novel extraction protocol including cryogenic homogenization, liquid-liquid extraction and further preconcentration by evaporation. By using deuterated internal standards in conjunction with matrix-matched calibration, high precision and accuracy were achieved. The limit of detection is estimated in the range of 0.041-0.221 ng/g (for fluorene and fluoranthene, respectively), which is far below the concentration currently assumed to be dangerous for children. The method was successfully applied to real samples available on the Polish market, and it was found that the amount of PAH compounds varies between manufacturers. Most diapers do not have all 15 polycyclic aromatic

hydrocarbons in their composition, but there is no diaper that is free of these compounds. The most abundant in diapers was acenaphthalene, where the concentration ranged from 1.6 ng/g diaper up to 362.4 ng/g. The lowest concentration in diapers is chrysene, which is not detected in most diapers. The article is a response to the lack of a harmonized analytical method for the determination of polycyclic aromatic hydrocarbons in disposable sanitary products for children.

Keywords: Environmental Pollutants; Toxic compounds; Gas Chromatography-Mass Spectrometry; Disposable Baby Diapers; Polycyclic Aromatic Hydrocarbons

1. Introduction

Disposable baby diapers have transformed millions lives [1]. Safe and adequate care products are necessary for a child development. It is known that baby care products contain a high variety of chemicals including polycyclic aromatic compounds (PAHs), and many other volatile organic compounds [2-3]. Many chemicals contained in the care products can pose a threat to the babies' skin-dermatitis or other health complications [1,3-5]. In order to ensure the safety of diapers products, analytical tests are carried out to confirm that the limits for the content of harmful substances have not been exceeded. The safety of these products is very critical as they can be in contact with the baby's skin throughout early childhood, such as diapers are used in direct contact with the skin, 24 h a day, 7 days a week. However, the standards do not cover all harmful substances [6]. The diaper business is a self-regulating industry. It is meaning up to the diaper companies to ensure they are compliant with safety regulations because there are no standards [6]. As a result, diaper manufacturers and parts of other consumer articles are not obligated by law to disclose the component parts of their diapers and tests of concentrations of harmful impurities. As a consequence of the above mentioned facts, the scientific discussion regarding appropriate analytical methods used to determine PAH in diapers has not started. First attempt at PAH analysis using disposable diapers as a challenging analytical matrix for compound extraction is reported in this paper.

Polycyclic aromatic hydrocarbons are a group of over 100 chemicals that occur in the environment. PAHs are widespread contaminants for the environment generated by incomplete combustion or pyrolysis of organic matter [7]. Comprise the largest class of cancer-causing chemicals and are ranked ninth among chemical compounds threatening to humans [8]. The most well-studied PAH is benzo[a]pyrene, and it is also considered as a marker compound that represents a total load of PAHs [9]. The carcinogenic properties of this molecule have been known since the 1930s [10]). PAHs are receiving global attention due to their toxicity, environmental persistence, and potential bioaccumulation. These chemical compounds are classified as organics, which are carcinogenic even in very low concentration (ppb) [11]. PAHs are highly lipid soluble and thus readily absorbed from the

gastrointestinal tract and skin tissue [12]. They present high lipophilic nature so they are rapidly distributed in a wide variety of tissues with a marked tendency for localization in body fat. Metabolism of PAHs occurs via the cytochrome P450-mediated mixed function oxidase system with oxidation or hydroxylation as the first step [13].

One of the problems with PAHs is that they can be present in many type of daily used products. The exposure to these compounds is high because of this. Consumers should be aware of the potential contaminants in each product. It is worthwhile to emphasize two reasons for this: the consumer can be directly exposed to such a pollutant, as well as the pollutant can be released into the environment. We should be careful especially on the selection of goods for the children. In spite of the fact that disposable baby diapers are a very popular product, the composition of these diapers is neither thoroughly known nor carefully regulated. There is little literature data on the occurrence of PAHs in disposable baby diapers [14], therefore the development of simple and sensitive analytical methods is crucial for the well-being of children and the environment.

PAH determination in disposable diapers represents an analytical challenge due to their potentially low concentrations (pg or ng per gram of diapers) and complexity of the matrix [14]. In addition, PAHs are compounds that occur in many analytical materials used for standard analysis and can impact on the blank problem. Therefore, sample preparation is a crucial step for accurate and precise tracing of these analytes. In fact, the procedure should help to ensure the transparency of the blank problem and it should provide methods for identifying background sources and ways to reduce or eliminate system contamination in order to design methods keeping blanks below a critical threshold.

Efficient, sensitive, and selective analytical methods are required for PAH determination. Sample preparation involves removing interfering constituents and preconcentrating target analytes. Studies have described the determination of PAHs in biological matrices, including blood [15-16], urine [17], serum [18], saliva [19] among others. It does not change the fact that no analytical methods have been developed specifically for detecting PAHs in diapers. It has been found that the diaper impose a number of limitations, including the fact that the fibrous filling inside of the matrix is difficult to homogenize and is also intended to be highly hygroscopic and absorbent. As a consequence of the above-mentioned facts, we developed a new analytical procedure that will be proposed in this paper.

Gas chromatography coupled to mass spectrometry (GC-MS) is the most widely applied technique for PAHs determination. Other techniques used in the determination of PAHs are gas chromatography coupled with flame ionization detection or liquid chromatography coupled with fluorescence detection but are less frequently used because of the sensitivity in determining low concentrations of this compound [20].

This paper describes a GC–MS method for the determination of PAHs in disposable baby diapers. A simple and quick method of sample preparation based on cryogenic grinding of diapers and salting-out assisted liquid-liquid extraction was developed and validated. Real disposable baby diaper samples available on the Polish market were tested in order to identify PAHs in them. The article is a response to the lack of a harmonized analytical method for the determination of PAH in disposable sanitary products for children. Also, it provides valuable information about the level of PAHs that newborns and infants are exposed to almost 24 hours a day through disposable diapers. On the other hand, a used diaper ends up in a landfill, where PAHs are released into the environment. **The presented article is the first step in raising awareness about carcinogenic impurities to which infants and older children are exposed.**

2 Materials and methods

2.1. Chemicals

PAHs mixture, i.e: fluorene (F), naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BgP)2[2], each at 10 µg/mL level dissolved in acetonitrile was purchased from Sigma-Aldrich (Germany). Deuterated internal standards: acenaphthene-d10, phenanthrene-d10, chrysene-d12 were also purchased from Sigma-Aldrich dissolved in acetonitrile. Acetonitrile and chloroform with GC–MS purity were provided by Merck (Darmstadt, Germany), and ultrapure water was obtained using a Milli-Q purification system (Millipore, Bedford, MA, USA). Sodium chloride was purchased from POCH (Gliwice, Poland).

2.2. Samples

Individual disposable baby diapers were purchased in Polish drugstores and grocery stores. The total number of 20 different commercial products were collected. Diapers were stored in their original packaging at room temperature. Before extraction of PAHs the diapers were immersed in liquid nitrogen for 2 minutes, then homogenized for 5 minutes under cryogenic conditions in an analytical mill (A11 basic, IKA, Germany). The powdered diapers were stored in sealed bags at room temperature until analysis. The pooled sample, used during method optimization and validation of a final analytical procedure was prepared by weighing an equal amount of each diaper followed by thorough mixing.

2.3. Sample preparation procedure

A quantity of 250 mg of milled disposable baby diapers was weighed and placed in a 15 mL bottle. The extraction was performed in 15 milliliter falcons from Nest (Woodbridge, USA). The tube of the falcon

is made of polypropylene and the lid is made of polyethylene. Then, 10 µL of the internal standard mixture (200 ng/mL for chrysene-d_{12}, acenaphthylene-d_{10} and 400 ng/ml for phenantrene-d_{10}, each in acetonitrile), which corresponds to 8 ng/g and 16 ng/g of diaper was added. After that, 8 mL of a 15% NaCl (w/v) solution in water was poured into the bottle, followed by 4 mL of chloroform. It was then placed in the rotator for 20 min at 40 rpm (Stuart, rotator SB3, Germany). Following this, 3 mL of chloroform (bottom fraction) was withdrawn into a 5 mL centrifuge tube. The next step was to evaporate, the sample to dryness under vacuum at 22°C (Labconco, CentriVap, USA). In the final step, 100 µL of acetonitrile were added to dissolve the extracted PAHs and briefly vortexed. The sample was transferred to GC vial and analyzed directly.

2.4. Optimization of sample preparation procedure

Two factors were considered during optimization of sample preparation stage, namely extracting solvent and salt concentration. For liquid-liquid extraction, three solvents were selected, which are chloroform, dicholoromethane and diethyl ether. The extractions were performed as described in Section 2.3.

The effect of salt concentration was examined. Sodium chloride was added to the aqueous phase in the liquid-liquid extraction. To determine the final percentage of NaCl in water, an experiment was carried out in which the extraction efficiency was compared with the use of 5%, 10% and 15% of the solution.

2.5. Gas chromatography-Mass spectrometry

The chromatographic analysis of the extract was performed using the GC-MS technique. An Agilent Technologies 7820A gas chromatograph and an Agilent Technologies 5977E MSD mass spectrometer were used. The chromatographic separation of the tested compounds was achieved using a capillary column DB-EUPAH (Agilent J&W GC Columns, USA), made of fused silica, 20 m long, internal diameter of 0.180 mm and film thickness of 0.14 µm. The above-mentioned column can operate in the temperature range of 40°C-320°C.

The splitless mode of injection was applied at temperature 320°C and the pressure was 26.935 psi. The carrier gas was helium and its flow rate was 1.3314 mL/min. The syringe of the dispenser was rinsed with acetonitrile (100 %) - six times before dosing and six times after dosing the sample. The sample was dozed in a volume of 2 µL. A GC-MS transfer line temperature of 320°C, an ion source temperature of 250°C, and a quadrupole temperature of 180°C were used. The technique of single ion monitoring (SIM) was applied. For each analyte one ion was selected for quantitative analysis and additional two signals were chosen for identification purposes (Supplementary 1)). The column temperature was

initially held at 60 °C for 0.5 min, raised to 200 °C at the rate of 8°C/min and kept for 0.5 min, then to 270 °C at the rate of 11 °C/min, and finally to 300 °C at the rate of 2 °C/min. The total analysis time is 39.86 minutes.

A solvent delay was fixed at 4 min and the analytes are divided into 8 discrete time segments: 4-10 min for Nap, 10-13 min for Acy, Ace and F D-10, 13-15.50 min for Phe, Phe D-10 and Ant, 15.50-19 min for Flu and Pyr, 19-2 3min for BaA, Chr and Chr D-10, 23-26.50 min for BbF, BkF and Bap, 26.50-32 min for InP, DBA and BgP. Table 1 shows the retention time and analyte-dependent ions.

2.6. Validation study

The method was validated in terms of linearity, range, within- and between-day precision and accuracy. Additionally, extraction recovery, matrix effect, LOD and LOQ were evaluated.

2.6.1. Calibration curve and range

The calibration curve was made on disposable diapers with the addition of analytes and an internal standard. Calibration curve was developed, consisting of 9 points in the concentration range from 1 to 800 ng/g. The value of the disposable diaper without spike was subtracted from the peak areas of the calibration curve. The highest correlation determination is and quadratic function for the weighted one $1/x^2$. The correlation determinationis in the range of 0.98-0.99.

2.6.2. Limits of quantification and detection

Limits of detection (LOD) was determined from the obtained chromatogram for the blank. For this purpose, the noise level was determined - by measuring on the chromatogram the range of signal change near the retention time for the analytes. Then, the obtained value was multiplied by 3.3 and converted into a concentration value. Limits of quantification (LOQ) obtained by multiplying by 3 LOD values.

2.6.3. Precision and accuracy

The precision and accuracy are based on three concentrations:- 10, 250 and 500 ng/g. The determination of these parameters was to be divided into two days - at the beginning of the validation, during the execution of real samples and after the completion of all analyzes. The experiment was performed in the same manner as described in Section 2.3. Each concentration was performed in three replications.

2.6.4. Matrix effect

A mix of diapers was used to determine the matrix effect. The samples were prepared according to the extraction precedent. The diapers with the addition of analytes, the diaper without analytes and the sample without the diaper with the addition of analytes were prepared. An identical concentration of internal standards was added to all samples. The matrix effect was determined at one concentration levels 10 ng/g. The experiment was carried out in triplicate. The matrix effect is calculated according to the formula below:

$ME = \frac{A-B}{C} \cdot 100\%$, where:

A – PAH concentration in a disposable diaper with the addition of an analytes;

B – PAH concentration in a disposable diaper without the addition of an analytes;

C – PAH concentration after extraction without disposable diaper with the addition of analytes.

3. Results and discussion

3.1. Optimization of analytical procedure

3.1.1. Sample preparation

Due to the fact that PAHs are lipophilic compounds, it is difficult to design a simple experiment that would combine solid phase extraction with a solid matrix. The extraction procedure started with ultrasound-assisted extraction of a diaper with various organic solvents was attempted, but this method, despite the optimization of many parameters, still had a low efficiency. The next step was to perform a liquid-liquid extraction. Three organic solvents were selected - dichloromethane, diethyl ether and chloroform. The highest recovery was found in the case of the use of chloroform, so this solvent was chosen as the organic phase. The ratio of the peak area of the analyte to the peak area of the internal standard are presented in Supplementary 1.

For highly volatile organic compounds such as PAHs, increasing the amount of salt in the sample typically increases the extraction yield to the organic solvent. It is related to the value of the dielectric constant of organic solvents. The recovery of three solutions of the water phase containing the appropriate 5%, 10% and 15% sodium chloride was tested experimentally. When using a 15% aqueous solution as the inorganic phase, the extraction efficiency was the most reproducible and the relative standard deviations are the smallest as shown in Supplementary 2 below.

The key step in sample preparation is evaporation. Based on the experiments it was found that evaporation at higher temperatures (above 25 °C) part of the analyte is evaporated together with the solvent. For this reason, it was decided to evaporate the samples at 23 °C. Another important step is

when the internal standard is added. In this procedure, internal standards are added to a dry diaper before starting the extraction procedure. In the case of samples with added analyte (in some trials this was done during the validation), this additive was also applied to the dry diaper.

3.1.2. Gas chromatography-mass spectrometry

Due to the fact that PAHs are volatile compounds, it was decided to analyze the samples by using GC-MS. For the highest possible separation of analytes, it was decided to use a column that is specially dedicated to PAHs compounds. The temperature gradient has been optimized to obtain the highest resolution between peaks. However, there was a problem with the separation with some pairs of compounds such as phenantrene-anthracene and benzo[b]fluoranthene-benzo[k]fluoranthene. These are compounds with a very similar chemical structure. Moreover, these pairs of compounds have identical m/z ratios and fragment ions, so separating them by mass spectrometry is impossible. Finally, after careful optination of temperature gradient full separation of all analytes was achieved. The Figure **1** below shows chromatograms for all analytes and internal standards.

3.2. Validation study

3.2.1. Linearity, range

Linearity of the method was checked at a range between 1 and 800 ng/g. Concentrations lower than 1 ng/g or higher than 800 ng/g should be considered as out of the range. The concentration points on the curve is: 1, 2, 4, 8, 16, 80, 200, 400, 800 nanograms of PAH's per gram of diaper. The calibration curve was developed on a diaper with the addition of PAH's and deuterated internal standards. The calibration curves were in the corresponding ranges with correlation determination higher than 0.94 as shown in Table 2.

3.2.2. Limit of detection and quantification

3.2.3 Accuracy and precision

The precision and accuracy of the method were evaluated by analyses of each Quality Control (QC) level sample. The data for intra- and interday precision and accuracy from QC samples are summarized in Table 3. and Table 4. respectively. The results were within acceptable limits, showing satisfactory accuracy and precision

3.2.4. Matrix effect

Matrix effect was determined on the basis of one concentrations - 10 ng/g of diaper. The results of the recovery studies are presented in the Table 5.

3.2.5. Recovery

In addition to validation parameters, recovery was calculated. A mix of diapers was used to determine this parameter. An internal standard of the same concentration was added to each sample. Recovery test at one concentration level of 10 ng/g. In this experiment, an analyte-free diaper, and a sample containing no diaper were used. In the sample without the diaper, the analyte was added after sample evaporation in the proportion of 0.75 relative to the samples that contained the analyte. The procedure is so constructed because after extraction 3 of 4 mL of the organic phase was withdrawn and evaporated. The recovery is calculated according to the formula below:

$RE = \frac{A-B}{D} \cdot 100\%$, where:

A – PAH concentration in a disposable diaper with the addition of an analytes;

B – PAH concentration in a disposable diaper without the addition of an analytes;

D – acetonitrile with the addition of PAH standard in the amount of 0.75 against the sample A or B.

The results of the recovery studies are presented in the Table 5table .

3.3 Real sample analysis

The guiding purpose of this study was to develop a precise method for the determination of PAHs in disposable baby diapers. In twenty tested disposable diapers PAHs were found, but the amount of individual analytes varied between manufacturers. There were also diapers with only some analytes in their composition.[Phe], [Chr], [BbF], [BkF] were found in only some diapers, while there was no diaper that was free from all PAHs. The schematic representation of the concentration level for each analyte found in disposable baby diaper are presented in Figure 2.

One of the worrying issues arising from the presented research is the presence of acenaphthene in several diapers at relatively high concentration levels. The highest concentration for this analyte was cc. 362 ng/g. Please, remember that Acy may be poisonous if inhaled or absorbed through skin. There is evidence that acenaphthene is photomutagenic, therefore skin exposure to acenaphthene at the same time as exposure to sunlight is ill-advised. Looking at the environmental problems, Acy should biodegrade rapidly in the environment (biodegradation half-lives for in aerobic soil and surface waters range from 10 to 60 and from 1 to 25 days, respectively). From the other site, it may persist under anaerobic conditions or at high concentration due to toxicity to microorganisms[21].

The next compound that occurs at quite high concentration level (cc. 60 ng/g) in few samples is dibenz[a,h]anthracene which is not a good news as this compound can irritate the skin. In fact, prolonged or repeated contact can cause a skin rash, dryness, and redness, especially, when it is expose to sunlight because it can greatly aggravate these effects. There are many other effects when the

human is exposed to this compound as well. It also need to be remember, that after usage of diaper, it is through out and finish at landfill. There, DBA is released into the environment what is very danger especially to the aquatic organisms as it may case long-term and toxic effects [22]. Moreover, bioaccumulation of this compound may occur along the food chain, why it is strongly recommended not to let the chemical enter into the environment.

Another compound which occurs in few samples at quite high concentration and is worth to notice, is benzo[g,h,i]pyrelene what is obvious as this compound is used to make for example dyes and plastics. Although, there is no much information available from studies on humans to tell what effects can result from being exposed to [BgP] at certain level, by analogy to other PAHs, in particular benzo[*a*]pyrene, it would be expected to be absorbed from the gastrointestinal tract, lungs, and skin. When BgP was administered together with [BaP] to the mice skin, an increased frequency of occurrence of skin tumours was observed in comparison to the tumour incidence in mice exposed to BaP alone, what can give a signal that possible cocarcinogenic activity of [BgP] can exist.

Although other compounds occur at lower concentration level in disposable baby diaper, it needs to be notice, that contact with any PAHs is not good for little ones. The disposable baby diaper is changed in cc. 3 hours or even more often if required. Over the course of two years each baby using disposable diapers generates about 2000 pounds of harmful garbage. Please, realize how many toxic compounds are realised into the environmental.

4. Conclusion

In today's world, the possibility of using disposable diapers is associated with a significant improvement in family life. There is very little research into the content of xenobiotics in disposable baby products such as diapers. Due to the presence of toxic compounds as a PAHs in diapers and their possible negative effect on babies' health, it is necessary to control the content of individual compounds in diapers. In a document issued by a European Chemical Agency (ECHA) on March 7, 2018, it can be read that childcare articles the corresponding concentration limit is 0.5 mg/kg (0.00005%). The proposed analytical method is a response to the lack harmonized method for the determination of PAHs in childcare products in the European Union zone. However, the available national or international methods can be used, but their regulation does not cover the entire European zone. In the tested diapers, the concentrations of the selected 15 analytes are significantly lower than the standards proposed by ECHA. However, this does not change the fact that monitoring PAH levels is a key aspect as it is directly related to children's health as well as environment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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