

**Dariusz WłÓKA, Marzena SMOL**

Politechnika Częstochowska, Wydział Inżynierii Środowiska i Biotechnologii  
Instytut Inżynierii Środowiska  
ul. Brzeźnicka 60a, 42-200 Częstochowa  
e-mail: d.wloka@is.pcz.czest.pl, m.smol@is.pcz.czest.pl

## **Evaluation of extraction methods of polycyclic aromatic hydrocarbons (PAHs) from soil and sewage sludge matrix**

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic contaminants with related chemical structure and properties. In natural conditions, these compounds usually are in the form of mixtures. As their main source there are given the human activities. PAHs are composed of at least two aromatic rings without any additional substituents. A direct consequence of such structure are low solubility in water and high affinity for the sorption on the solid phase materials. Due to maintained properties the biggest reservoir of these substances are: soil, sediments, sewage sludge and solid waste fractions. The presence of large amounts of PAHs in an environment is associated with numerous problems. First of all, substances belonging to this group are characterized as highly toxic in relation to living organisms, including humans. Prolonged exposure to PAHs contributes also to the induction of spontaneous genetic changes which may lead to carcinogenesis. Taking the above information into account, it can be stated that the effective monitoring of PAHs content should have a great importance from the point of view of both environmental and human safety. The basic technique used for the quantitative isolation of PAHs from solid matrices (soil, sewage sludge) is the solid-liquid extraction method. This technique relies upon the ability of non-polar organic solvents for elution of hydrophobic organic compounds from the environment in which they are located. Currently, in the scientific literature many various methods for PAHs extraction from solid matrix can be found. Each individual method is unique and depends mostly on the type of used solvent, the conditions in which the process is carried out and the number of auxiliary treatment affecting in particular the purity of the obtained extracts. The aim of the experiment was to compare the effectiveness of different techniques of extraction of PAHs from soil and sewage sludge. The scope of undertaken activities includes testing of the possibility to use four types of organic solvents (acetone, acetonitrile, methanol, and isopropanol) as PAHs extraction agents, and the study of the impact of additional treatments, such as sonification, filtration and SPE techniques on efficiency of sample preparation process. On the basis of obtained results, it can be stated that the highest efficiency of extraction of PAHs from soil can be achieved by using acetonitrile. In the case of sewage sludge the highest extraction efficiency was achieved in the methodology with use of acetone as extraction agent. The use of ultrasonic extraction technology combined with filtration and SPE methods allows to achieve high efficiency in isolation of PAHs from soil and sewage sludge.

**Keywords:** polycyclic aromatic hydrocarbons PAHs, extraction methods, soil, sewage sludge, organic pollutants

### **Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic pollutants which includes more than 200 chemical compounds. PAHs are built from at least

two aromatic rings without any substituents. They are hardly soluble in water and have high affinity for sorption on the surface of solid materials [1, 2]. Occurrence of these compounds can be observed in almost every element of the environment, however due to the physical and chemical properties of these contaminants, their largest reservoirs are in soil, solid wastes and sediments. Under natural conditions, PAHs are always in a form of mixture with composition dependent on the characteristics and properties of studied material [2, 3].

As the sources of PAHs, both the natural and anthropogenic origins are given, but from the point of view of environmental protection, human activity is considered as more important [1].

In last few years an increased attention on research related to organic pollutants such as PAHs can be observed [4-7]. Strong interest in the field of PAHs is mainly caused by the large scale of environmental contamination and the mutagenic and carcinogenic activity of these pollutants proven in many studies [3]. Compounds such as Benzo(a)pyrene have the ability to penetrate the membranes of living cells, where in result of multiple enzymatic transformations they are converted to active epoxide-form. One of products of this reaction is Benzo(a)pyren-7,8-dihydrodiol-9,10-epoxide. This compound is capable to create covalent bonds with DNA fragments, which may lead to carcinogenesis. In human organism the enzyme that plays key role in this process is cytochrome P4501A1 (CYP1A1) [8,9].

The presence of high concentrations of PAHs in the environment is also connected with ecological and economical issues. Long-term contamination may lead to permanent changes in local ecosystems, and may have influence on the reduction of the agricultural crops productivity [3, 10].

On the basis of information described above, it can be stated that actions aimed to provide detailed monitoring of PAHs content in environmental samples should take an important part in modern environmental protection policy [3, 11].

At the moment in the scientific literature and various web databases many different PAHs content determination techniques can be found. The most important and most frequently used methods are chromatographic techniques such as high performance liquid chromatography with UV and fluorescent detectors (HPLC-UV and HPLC-FLD) and gas chromatography with mass detector (GC-MS). These methods allow to conduct study of PAHs content on the micro, nano and pico scales, but they also require special sample preparation procedures. The appropriate form of the chromatographic samples mainly includes strictly defined level of purity and closely defined range of expected concentration of the analyte. These requirements are necessary to ensure proper functioning of the used equipment and to ensure a high quality of the obtained results [12-15].

In the case of solid samples such as soil or sewage sludge, the sample preparation procedure for chromatographic analysis should include the following stages [16]:

- Sampling and sample validation,
- Drying and fragmentation of the test material,
- Extraction of the analyte,

- Pre-treatment of the extract,
- Densification of the extract.

Each of these steps may be carried out in several ways. The choice of the individual analytical technique depends mostly on the sample characteristics and also on available laboratory equipment. A key element of all solid sample preparation processes is the extraction of analyte from solid material matrix. The extraction methods can be distinguished into two main groups: classic and modern instrumental methods. In Table 1 an overview of currently available extraction methods that can be used in PAHs analysis is presented [12, 13, 16].

Table 1. Overview of PAHs extraction methods

Classic methods		
ID	Method	Description
1	Solid-Liquid Extraction	Use of close isolated container where both sample and solvent are added. Extraction in such systems is mainly assisted with shaking or heating.
2	Soxhlet Extraction	Samples are placed in disposable porous containers (thimbles) where they are constantly flushed with refluxed solvent. In this system dissolved analytes are continuously collected in a boiling flask.
3	Sonication	Use of ultrasonic field to create a vigorous agitation on the surface of a solid material. This technique is used as a support technique for example in solid-liquid extraction.
Modern instrumental methods		
ID	Method	Description
1	PF Extraction	Pressurized Fluid (PF) Extraction. Sample is placed in a sealed container and heated to above its boiling point, causing pressure in the vessel to rise; extracted sample is removed and transferred to vial for further treatment.
2	AS Extraction	Automatic Soxhlet (AS) Extraction. It is a combination of a hot solvent leaching and Soxhlet extraction. Samples in this system are first immersed in boiling solvent, next thimble is raised for conventional Soxhlet extraction.
3	SF Extraction	Supercritical Fluid (SF) Extraction. In this technique samples are placed in flow-through container where they are flushed with the supercritical fluid (e.g. CO <sub>2</sub> ). After depressurization, extracted analyte is collected in solvent or sorbent.

As part of the research described in this article, a comparative analysis of the possibility to use of various organic solvents for the extraction of PAHs from soil and sewage sludge was carried out.

The aim of the study was to investigate the effectiveness of the four reagents, with varying degrees of polarity, including methanol, isopropanol, acetonitrile and acetone in the process of solid-liquid extraction assisted with ultrasonic field. The second aim was to study the efficiency of used pre-treatment methods of chromatographic samples preparation such as sonication, filtration and SPE (Solid Phase Extraction).

## 1. Methodology

In the experiment, agricultural soil, taken from a crop field, located in the province of Silesia in the region of Czestochowa, Poland, was used. This material was classified as a mineral soil (loamy sand). As a sewage sludge sample, a material after mechanic stabilization, collected from the municipal wastewater treatment plant located in region of Czestochowa, was used. Both the soil and the sewage sludge were analyzed according to the methodology presented in the following research: Fijałkowski et al., Rorat et al., Placek et al., Kacprzak et al. [19-22]. Results of this analysis are presented in Table 2.

Table 2. **Physical and chemical properties of used materials (soil, sewage sludge)**

Type of Analysis	Soil	Sewage Sludge
Dry matter, %	92	33
pH, in H <sub>2</sub> O	7.02	7.6
pH, in KCl	5.1	6.7
CEC, cmol(+)/kg d.m.	12.4	no data
TOC, g/kg d.m.	11.41	215
TC, g/kg d.m.	13.84	302
P, g/kg d.m.	0.20	0.31
N, g/kg d.m.	1.25	3.41

For the experiment, 8 series of soil samples and 8 series of sewage sludge samples were prepared. Each series contains 6 reps. Samples of soil and sewage sludge after drying at ambient conditions were subjected to homogenization in knife mill. Next the material was divided into test samples, soil - 10 g; sewage sludge - 1 g. Test samples, after weighting, were placed in the 100 ml extraction glass containers. To each prepared sample a close measured solvent (acetone, acetonitrile, methanol and isopropanol) amount (30 ml) was introduced. The main properties of some organic solvents are presented in Table 3 [17, 18]. The extraction procedure was held on in ambient temperature.

Table 3. **Basic physical and chemical properties of organic solvents**

Solvent name	Structure and molecular weight	T <sub>boiling</sub> °C	Density g/ml	Dielectric constant	Debye dipole moment	Viscosity 10 <sup>-3</sup> Pa·s	Surface tension 10 <sup>-3</sup> J/m <sup>2</sup>
Acetone	(CH <sub>3</sub> ) <sub>2</sub> C = O 58.08	56.3	0.7850	20.7	2.7	0.3040	22.68
Acetonitrile	CH <sub>3</sub> CN 41.05	81.6	0.7768	37.5	3.44	0.3409	28.45
Isopropanol	(CH <sub>3</sub> ) <sub>2</sub> CHOH 60.10	82.3	0.7810	19.9	1.66	2.073	18.3
Methanol	CH <sub>3</sub> OH 32.04	64.7	0.7866	32.6	1.6	0.5445	22.1

To some samples an PAHs standard (1 ml) also was introduced (16 PAH mix recommended by EPA - Restec 610 PAH calibration mix B). This procedure was performed according to the scheme shown in Table 4. Concentrations of individual compounds in used standard are presented in Table 5. After the described above procedures all samples were subjected to further treatment and final analysis.

Table 4. Scheme of the prepared sample series

ID	Description	ID	Description
1	Soil (10 g) + Acetone (30 ml)	9	Sewage sludge (10 g) + Acetone (30 ml)
2	Soil (10 g) + Acetonitrile (30 ml)	10	Sewage sludge (10 g) + Acetonitrile (30 ml)
3	Soil (10 g) + Methanol (30 ml)	11	Sewage sludge (1 g) + Methanol (30 ml)
4	Soil (10 g) + Isopropanol (30 ml)	12	Sewage sludge (1 g) + Isopropanol (30 ml)
5	Soil (10 g) + Acetone (30 ml) + PAHs standard (1 ml)	13	Sewage sludge (1 g) + Acetone (30 ml) + PAHs standard (1 ml)
6	Soil (10g) + Acetonitrile (30 ml) + PAHs standard (1 ml)	14	Sewage sludge (1 g) + Acetonitrile (30 ml) + PAHs standard (1 ml)
7	Soil (10 g) + Methanol (30 ml) + PAHs standard (1 ml)	15	Sewage sludge (1 g) + Methanol (30 ml) + PAHs standard (1 ml)
8	Soil (10 g) + Isopropanol (30 ml) + PAHs standard (1 ml)	16	Sewage sludge (1 g) + Isopropanol (30 ml) + PAHs standard (1 ml)

Table 5. Concentration of individual PAHs in used standard

ID	Compound	Number of rings	Concentration $\mu\text{g/ml}$	$\sigma$
1	Naphthalene (Naf)	2	1.021	$\pm 0.0044$
2	Acenaphthylene (Acyl)	3	2.082	$\pm 0.0023$
3	Acenaphthene (Ac)	3	1.005	$\pm 0.0038$
4	Fluorene (Fl)	3	0.201	$\pm 0.0005$
5	Phenanthrene (Fen)	3	0.208	$\pm 0.0014$
6	Anthracene (Ant)	3	0.110	$\pm 0.0031$
7	Fluoranthene (Flu)	4	0.121	$\pm 0.0025$
8	Pyrene (Pir)	4	0.106	$\pm 0.0018$
9	Benzo(a)anthracene (BaA)	4	0.113	$\pm 0.0031$
10	Chrysene (Ch)	4	0.112	$\pm 0.0011$
11	Benzo(b)fluoranthene (BbF)	5	0.241	$\pm 0.0021$
12	Benzo(k)fluoranthene (BkF)	5	0.114	$\pm 0.0018$
13	Benzo(a)pyrene (BaP)	5	0.105	$\pm 0.0004$
14	Dibenzo(a,h)anthracene (DahA)	5	0.215	$\pm 0.0007$
15	Indeno(1,2,3-c,d)pyrene (IP)	6	0.111	$\pm 0.0041$
16	Benzo(g,h,i)perylene (Bper)	6	0.221	$\pm 0.0011$

Pre-treatment stage of sample preparation procedure was based on the solid-liquid extraction technique assisted with ultrasonic field treatment. All prepared samples were put for 30 min into ultrasonic bath, then they were shaken in automatic shaker for 24 h. Obtained extracts, after centrifugation (8000 rpm; 5 min) and filtration (membrane filtration on PP 0.45  $\mu\text{m}$  filters), were concentrated by SPE - Solid Phase Extraction technique on columns filled with C18 silica gel (C18 Chromabond 100 g/6 ml). The solvent used to flush analyte from the column was acetonitrile - 3 x 1 ml.

## 2. Determination of PAHs content

Qualitative and quantitative analyses of PAHs content in soil and sewage sludge samples were conducted using high performance liquid chromatography (HPLC) with UV and FLD detectors. Used equipment was manufactured by Thermo Scientific - Thermo Spectra SYSTEM.

For the separation of the individual PAHs the reversed phase HPLC system was prepared. Used column was Restek Principles II PAH 150 mm 5  $\mu\text{m}$  HPLC column. The column was filled with C18 silica gel. The temperature of the column during the analysis was 30°C. Elution was conducted by using a gradient technique with three solvents: water - A, acetonitrile - B and methanol - C (start 0 min - 20/20/60 A<sub>v</sub>/B<sub>v</sub>/C<sub>v</sub>; 20 min - 5/95/0 A<sub>v</sub>/B<sub>v</sub>/C<sub>v</sub>). The flow rate was 0.80 ml/min. The loop volume was 10  $\mu\text{l}$ .

Table 6. The overview of PAHs determination method

ID	Compound	Number of rings	Detection limit $\mu\text{g}/\text{kg}$	$\sigma$ %
1	Naphthalene (Naf)	2	11.24	$\pm 2.25$
2	Acenaphthylene (Acyl)	3	20.05	$\pm 7.18$
3	Acenaphthene (Ac)	3	9.89	$\pm 8.08$
4	Fluorene (Fl)	3	0.22	$\pm 4.46$
5	Phenanthrene (Fen)	3	0.21	$\pm 2.22$
6	Anthracene (Ant)	3	0.10	$\pm 11.71$
7	Fluoranthene (Flu)	4	0.11	$\pm 1.25$
8	Pyrene (Pir)	4	0.12	$\pm 3.17$
9	Benzo(a)anthracene (BaA)	4	0.11	$\pm 2.97$
10	Chrysene (Ch)	4	0.12	$\pm 1.01$
11	Benzo(b)fluoranthene (BbF)	5	0.21	$\pm 1.54$
12	Benzo(k)fluoranthene (BkF)	5	0.13	$\pm 0.69$
13	Benzo(a)pyrene (BaP)	5	0.12	$\pm 4.62$
14	Dibenzo(a,h)anthracene (DahA)	5	0.22	$\pm 2.17$
15	Indeno(1,2,3-c,d)pyrene (IP)	6	0.11	$\pm 5.71$
16	Benzo(g,h,i)perylene (Bper)	6	0.23	$\pm 2.41$

Detection of the data was carried out on both UV-Vis (UV5000) and fluorescence (FL3000) detectors. Wavelength used for UV detection was 254 nm. As an external standard, RESTEK 610 Calibration Mix B was used. Standard contains 16 compounds: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene. In Table 6 the PAHs determination method overview and standard deviations for the all analyzed compounds were presented. In Figure 1 the chromatogram of used standard is presented.

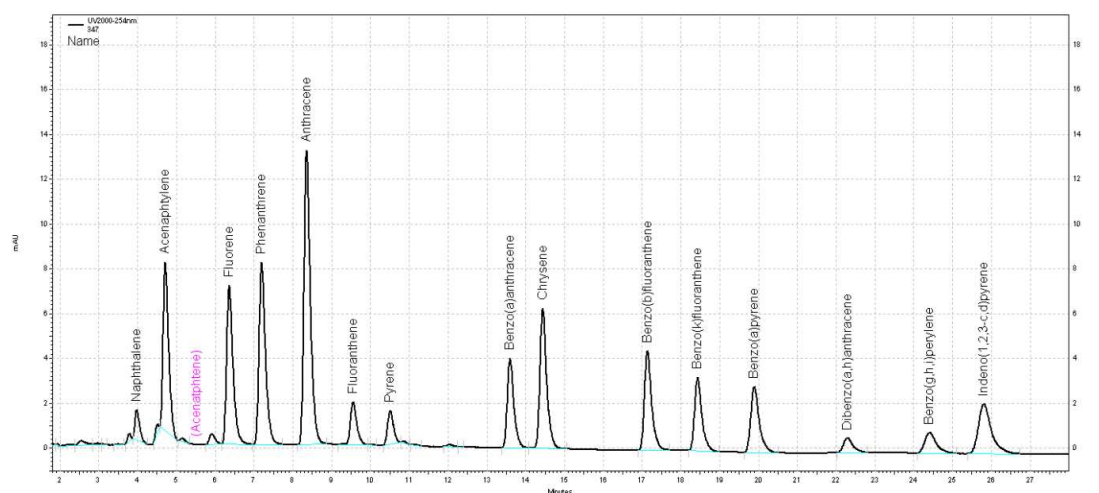


Fig. 1. Chromatogram of Restec 610 PAH calibration mix

### 3. Results

The results, obtained during the experiment, are presented in Tables 7-10. The divide of the results, for each individual table, was based on the type of solvent used for extraction. Table 7 contains the results of the series to which the acetone was introduced, Table 8 is related to series with acetonitrile, series with methanol are in Table 9 and series with isopropanol are in Table 10. Each table contains information about the efficiency of PAHs extraction both from the soil and the sewage sludge samples. This information includes measurements of all 16 PAHs content and the results of calculations of rate recovery coefficients. The calculations of rate recovery coefficients were based on the difference in PAHs content between samples with PAHs standard additive and samples into which only extraction solvent was introduced.

Table 7. Results of evaluation of PAHs extraction method with use of acetone as a solvent

Compound	Soil			Sewage sludge		
	Concentration µg/kg d.m.	$\sigma$	Recovery %	Concentration µg/kg d.m.	$\sigma$	Recovery %
Naphthalene	12	2.60	100	1143	66.99	96
Acenaphthylene	159	16.11	61	2699	95.47	93
Acenaphthene	4	0.44	67	99	7.59	101
Fluorene	53	1.72	90	956	48.98	125
Phenanthrene	138	1.91	128	2691	115.04	80
Anthracene	19	3.12	91	1204	42.85	93
Fluoranthene	146	4.97	99	6267	273.00	75
Pyrene	112	3.30	69	986	42.22	93
Benzo(a)anthracene	28	2.53	60	666	38.39	84
Chrysene	29	2.12	81	566	29.14	66
Benzo(b)fluoranthene	37	3.11	56	1013	43.67	83
Benzo(k)fluoranthene	17	1.62	39	740	49.34	77
Benzo(a)pyrene	30	0.87	34	729	22.28	57
Dibenzo(a,h)anthracene	9	0.88	36	252	8.29	58
Indeno(1,2,3-c,d)pyrene	10	0.82	29	349	15.07	64
Benzo(g,h,i)perylene	32	3.88	27	2658	147.88	49

Table 8. Results of evaluation of PAHs extraction method with use of acetonitrile as a solvent

Compound	Soil			Sewage sludge		
	Concentration µg/kg d.m.	$\sigma$	Recovery %	Concentration µg/kg d.m.	$\sigma$	Recovery %
Naphthalene	19	2.27	89	1292	40.39	79
Acenaphthylene	447	13.04	95	8700	186.06	90
Acenaphthene	5	1.20	91	69	5.26	102
Fluorene	52	1.77	106	1091	163.45	108
Phenanthrene	198	2.09	93	2276	51.20	148
Anthracene	35	1.68	108	904	5.55	98
Fluoranthene	185	2.70	82	2979	53.74	82
Pyrene	123	2.55	100	1945	91.04	65
Benzo(a)anthracene	52	2.76	97	636	61.71	62
Chrysene	46	4.41	77	470	27.41	47
Benzo(b)fluoranthene	49	1.05	81	623	7.10	83
Benzo(k)fluoranthene	26	1.25	88	409	9.29	46
Benzo(a)pyrene	49	1.42	76	676	38.73	45
Dibenzo(a,h)anthracene	8	0.99	52	184	14.65	51
Indeno(1,2,3-c,d)pyrene	15	0.61	65	219	6.02	55
Benzo(g,h,i)perylene	48	7.16	48	1215	12.08	42.



Table 9. Results of evaluation of PAHs extraction method with use of methanol as a solvent

Compound	Soil			Sewage sludge		
	Concentration µg/kg d.m.	$\sigma$	Recovery %	Concentration µg/kg d.m.	$\sigma$	Recovery %
Naphthalene	8	0.19	-13	1101	166.49	86
Acenaphthylene	449	15.68	44	5653	354.24	99
Acenaphthene	1	0.36	2	76	18.05	40
Fluorene	48	6.69	67	912	90.98	42
Phenanthrene	102	18.90	64	2013	386.02	37
Anthracene	14	1.94	54	779	116.84	11
Fluoranthene	74	4.21	80	2497	234.90	15
Pyrene	49	9.13	110	1330	41.34	50
Benzo(a)anthracene	19	3.40	44	424	30.24	45
Chrysene	15	2.39	52	323	67.65	61
Benzo(b)fluoranthene	32	2.83	41	340	84.36	33
Benzo(k)fluoranthene	13	3.21	56	693	8.59	18
Benzo(a)pyrene	25	2.01	44	323	10.55	49
Dibenzo(a,h)anthracene	8	1.95	35	285	17.30	32
Indeno(1,2,3-c,d)pyrene	9	1.23	28	309	13.54	44
Benzo(g,h,i)perylene	39	1.28	28	2072	268.84	25

Table 10. Results of evaluation of PAHs extraction method with use of isopropanol as a solvent

Compound	Soil			Sewage sludge		
	Concentration µg/kg d.m.	$\sigma$	Recovery %	Concentration µg/kg d.m.	$\sigma$	Recovery %
Naphthalene	5	2.03	100	374	117.10	82
Acenaphthylene	96	40.42	137	4062	291.93	61
Acenaphthene	5	0.24	66	100	6.08	141
Fluorene	93	4.18	83	739	7.52	103
Phenanthrene	97	20.60	70	2617	26.98	85
Anthracene	17	1.81	109	654	6.76	69
Fluoranthene	94	5.71	60	2763	57.51	71
Pyrene	58	4.92	77	1208	155.57	67
Benzo(a)anthracene	19	2.94	56	396	21.82	89
Chrysene	27	5.57	72	277	26.55	71
Benzo(b)fluoranthene	23	3.60	57	425	32.02	67
Benzo(k)fluoranthene	9	2.43	47	256	27.22	51
Benzo(a)pyrene	20	0.41	41	378	14.79	27
Dibenzo(a,h)anthracene	3	0.50	53	288	12.53	32
Indeno(1,2,3-c,d)pyrene	7	0.59	28	303	63.57	48
Benzo(g,h,i)perylene	22	3.40	31	1732	52.82	30

The graphical presentation of all obtained results are presented on the graph - Figure 2.

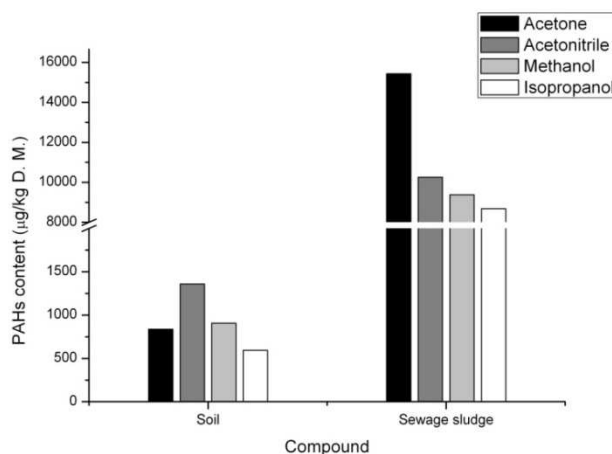


Fig. 2. Comparison of the  $\Sigma 16$  PAHs extraction efficiency in all analyzed samples (soil, sewage sludge)

The results of the PAHs content analysis in soil showed that the highest concentrations of the sum of 16 PAHs were observed in samples with acetonitrile additive (1354  $\mu\text{g}/\text{kg d.m.}$ ). In the case of sewage sludge samples, the highest concentrations were achieved in samples, where acetone was used (23 020  $\mu\text{g}/\text{kg d.m.}$ ). Both acetone and acetonitrile are classified as the organic solvents with medium level of polarity. They are very soluble in water and have a similar density, but their boiling temperatures and surface tensions are quite different [17]. Comparing the properties of acetone and acetonitrile with the other used solvents, it can be seen that these two reagents have the highest values of dipole moment (Acetone - 2.70, Acetonitrile - 3.44). These values are directly related to the relative polarity and have impact on the elution strength. From the point of view of PAHs extraction capacity, the ability to penetrate the matrix of analyzed material and to elute the desired analytes is very important. The solvent dependent, difference in the extraction efficiency between soil and sewage sludge samples, may be related to the specification of the studied material. The soil used in the experiment was classified as a mineral material, while the sewage sludge was considered as organic material.

The presence of hydrophobic organic compounds, such as PAHs, within the mineral matrix is mainly based on the physical adsorption (immobilization on the surface of the porous mineral structure). In the case of the organic materials beside the adsorption phenomenon, other PAHs immobilization effects may be observed. Occurrences of various organic substances and biological system creates a possibility to bound PAHs molecules in chemical (interactions with other organic compounds) and biological (bioaccumulation) ways. This processes often have impact on the reduction of the solvent elution ability and in result may be a reason of decreased PAHs content in extract mixture [13, 16, 17].

The rate recovery coefficients showed a similar trend as the measurements of the PAHs concentration. Highest values were obtained during the acetonitrile extraction for soil samples and acetone extraction for sewage sludge samples. On the basis of these results it can be also seen that the value of the rate recovery coefficient in most analyzed samples decreased with the increasing of the number of aromatic rings in the PAHs molecule. The lowest recovery coefficients were observed, in most all analyzed cases for pollutants such as indeno(1,2,3-c,d)pyrene (28÷65%) and benzo(g,h,i)perylene (25÷49%).

This phenomenon may result from the fact that the increase of PAHs molecule size is proportional to the decrease of solubility in the mobile fraction (solvent environment) and inversely proportional to the sorption capacity on the surface of solid matter. Therefore the potential losses of the compounds with the large particle size may occur during the filtration procedure as an effect of accumulation of insoluble matter on the surface of used membrane [3,23].

The research published by Oluseyi et al. showed that the highest extraction efficiencies of PAHs from contaminated soil were observed in methods with the methanol and acetonitrile use [26]. In other studies, solvents such as dichloromethane, hexane and acetone for the PAHs extraction from soil were used. These studies also showed high values of PAHs recovery coefficients [12, 24, 25, 27]. The large diversification in the solvent dependent, effectiveness of PAHs extraction may be caused by the different characteristics of studied material or the huge variation of used analytical equipment.

The earlier studies, published by Garcia et al. and Sun et al., showed that ultrasonic extraction yields higher or comparable quantities in extraction of hydrocarbons than other methods of extraction such as shaking or Soxhlet extraction [24, 25]. Comparing the obtained results to the results of studies described in abovementioned papers, it can be stated that methodology presented in article also showed a higher percentage recovery coefficients values than the traditional shaking and Soxhlet methods. The higher efficiency may be related to the fact that proposed method does not include any actions in increased temperature environment.

## Conclusions

On the basis of obtained results, following conclusions can be presented:

- The highest efficiency of extraction of PAHs from soil can be achieved by using acetonitrile and acetone as extraction agents.
- The highest efficiency of extraction of PAHs from sewage sludge can be achieved by using acetone as an extraction agent.
- The highest values of rate recovery coefficients were observed in samples where acetonitrile (soil samples) and acetone (sewage sludge) was used.
- The values of rate recovery coefficients decreased with the increasing of the number of aromatic rings in the PAHs molecule.

- The use of ultrasonic extraction technique combined with the filtration and the SPE methods allows to achieve high efficiency in isolation of PAHs from both soil and sewage sludge samples.

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## Ocena metod ekstrakcji wielopierścieniowych węglowodorów aromatycznych (WWA) z gleby i osadów ściekowych

Wielopierścieniowe węglowodory aromatyczne (WWA) stanowią liczną grupę związków organicznych o zbliżonej budowie chemicznej i podobnych właściwościach. W środowisku naturalnym występują zazwyczaj w postaci mieszanin, a ich głównym źródłem jest działalność człowieka. WWA zbudowane są z co najmniej dwóch pierścieni aromatycznych i nie posiadają dodatkowych podstawników. Bezpośrednią konsekwencją takiej budowy jest niska rozpuszczalność w wodzie oraz duże powinowactwo do sorpcji na cząstkach stałych. Właściwości te sprawiają, iż największym rezerwuarem tych substancji są: środowiska glebowe, muły i osady dennie, a także osady ściekowe i stałe frakcje odpadów. Występowanie dużych ilości WWA w środowisku związane jest z licznymi problemami. Przede wszystkim substan-

cje należące do tej grupy charakteryzują się wysoką toksycznością w odniesieniu do organizmów żywych, w tym również do człowieka. Długotrwała ekspozycja na WWA ponadto przyczynia się do indukcji spontanicznych zmian genetycznych, prowadząc wielokrotnie do kancerogenezy. Biorąc pod uwagę wymienione powyżej informacje, stwierdzić można, że prowadzenie efektywnego monitoringu substancji należących do tej grupy ma duże znaczenie z punktu widzenia zarówno ochrony środowiska, jak i bezpieczeństwa ludzi. Podstawową techniką stosowaną do ilościowej izolacji WWA z matryc stałych (gleba, osady ściekowe) jest ekstrakcja metodą ciało stałe-ciecz. Technika ta opiera się na wykorzystaniu zdolności niepolarnych rozpuszczalników organicznych do wymywania hydrofobowych związków organicznych ze środowiska, w którym się znajdują. Obecnie w literaturze naukowej opisane jest wiele metod ekstrakcji WWA z matryc stałych. Różnią się one między sobą rodzajem zastosowanych rozpuszczalników, warunkami, w których prowadzony jest proces oraz liczbą zabiegów pomocniczych, wpływających między innymi na stopień czystości uzyskiwanych ekstraktów. Celem opisywanego eksperymentu było porównanie efektywności działania różnych technik ekstrakcji WWA z gleby oraz osadów ściekowych. Zakres podjętych działań obejmował badanie możliwości zastosowania czterech odczynników (aceton, acetonitryl, metanol i izopropanol) w charakterze czynnika ekstrakcyjnego oraz badanie wpływu dodatkowych zabiegów, w tym sonifikacji, filtracji oraz zagęszczania techniką SPE, na efektywność działania badanego procesu. Na podstawie uzyskanych wyników stwierdzić można, iż najwyższą efektywność ekstrakcji WWA z gleby osiągnąć można przy użyciu acetonitrylu. W przypadku osadów ściekowych najwyższe stężenia badanych związków osiągnięte zostały w metodyce wykorzystującej aceton jako odczynnik ekstrakcyjny. Zastosowanie techniki ekstrakcji ultradźwiękowej połączonej z filtracją i zagęszczaniem metodą SPE pozwala na osiągnięcie wysokiej efektywności w izolacji WWA z gleby i osadów ściekowych.

**Słowa kluczowe:** wielopierścieniowe węglowodory aromatyczne WWA, metodyka ekstrakcji, gleba, osady ściekowe, zanieczyszczenia organiczne