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SIMPLIFICATION OF THE PROCEDURE OF PREPARING SAMPLES FOR PAHs AND PCBs DETERMINATION

BARTŁOMIEJ MACHERZYŃSKI[*], MARIA WŁODARCZYK-MAKUŁA, ANNA NOWACKA

Department of Chemistry, Water and Wastewater Technology
Czestochowa University of Technology,
Ul. Dąbrowskiego 69, 42-200 Częstochowa, Poland
*Corresponding author's e-mail: bmacherzynski@is.pcz.czest.pl

Abstract: The work presents examination results of the common determination of PAHs and PCBs in industrial sludge and supernatants. Sewage sludge was taken from the wastewater treatment plant, and supernatants were obtained by their centrifuging. The prepared samples of sewage sludge and supernatants were subjected to extraction with applying the mixture of organic solvents. Cyclohexane and dichloromethane were used for constant samples, and methanol, cyclohexane and dichloromethane – for liquid. Extracts, after separation from samples of sewage sludge and supernatants, were cleared on the silica gel in vacuum conditions and concentrated in the stream of nitrogen. In such prepared extracts there was conducted the qualitative-quantitative analysis of 16 PAHs using the GC-MS system. Next, the samples were evaporated and poured with water and methanol until the clear solution was obtained. Extracts were cleared on octadecyl C18 columns, and then concentrated in the nitrogen stream. In these extracts PCBs was also determined with the application of the gas chromatograph with mass spectrometer. The range of concentrations 16 PAHs in sewage sludge equalled $10-16$ mg/kg$_{d.w.}$. Summary average concentration 16 PAHs in supernatants was reached 17 µg/L. Average recovery of PAHs introduced to sewage sludge in the form of reference mixture was 78% (with consideration of naphthalene). In the case of supernatants, the average value of recovery reached 60%. Average PCBs concentration in supernatants equalled 10 ng/L. For sewage sludge the sum of marked PCBs was an average 1.23 µg/kg$_{d.w.}$. In the case of particular PCBs the percentage recovery of the reference mixture for supernatants was 86%, while for sewage sludge it was 55%.

INTRODUCTION

Procedures of preparing samples of sewage sludge for qualitative-quantitative analysis of PAHs and PCBs are not uniform. Authors often determine one group of these compounds basing on literature news and their own analytic experiences. There are used determining procedures of PAHs and PCBs different from one another in the type of solvents, method of extraction, technique and parameters of chromatographic analysis [1−4]. PAHs and PCBs belong to those micropollutants which often appear in very low concentrations. In environmental matrixes of differentiated chemical composition it is not possible to mark these relations directly in the taken sample. That is why before the quantitative determination the initial separation of organic substances is necessary followed by the

isolation of analytes and their enrichment [5]. Extraction of the organic matrix is carried out by the method of extraction in the Soxhlet's apparatus, supported with ultrasounds, microwaves or with gas in the supercritical state. This operation aims at moving analytes to matrixes of much simpler composition than the matrix of the environmental sample [6]. With the application of extraction in the liquid – liquid or solid – liquid systems, the choice of solvents giving maximal recovery with minimal co-extraction of interferents is important [6]. The application of extraction in the Soxhlet's apparatus is used most often, but it is time consuming and it requires the application of considerable amounts of solvents. This technique is used to isolate and enrich medium and hard volatile analytes and the thermally stable ones [3]. More and more often there is used the extraction under the increased pressure (100–140 bars) and in the increased temperature (100–180°C). In this process the time of extraction in comparison with other methods is shorter. The increased pressure of solvent facilitates its penetration into the matrix, what increases the efficiency of extraction [7]. In extraction supported by microwave radiation there are used teflon or quartz bombs and devices generating radiation of 2.45 GHz frequency. Using microwaves allows to reach a similar recovery like in the extraction in the Soxhlet's apparatus with the decreased amount of solvent [3, 8]. In the case of sonification, for extraction ultrasounds are used, the frequency of which oscillates between 20 kHz and 50 kHz (less often 500 kHz) and intensity – 140÷160 dB (for evoking cavitation) [9]. The next operation for preparing extracts is their enrichment and purification. Concentration of extracts is most often carried out with the help of the Kuderny-Danish's apparatus, in the vacuum evaporator or in the stream of gas. Concentration in the stream of gas (nitrogen or air) consists in the evaporating of the extract to the specific volume, what minimises the losses of analytes. The advantage is the low cost and simplicity, while the disadvantage – difficulty of evaporating solvents of high boiling temperatures. The next stage of the preparation of extracts is purification, which is led on such absorbents like alumina, silica gel or Florisil (in the presence of activated copper) [3, 5, 10]. Qualitative--quantitative identification of such micropollutants as PAHs and PCBs is carried out with chromatographic methods. Capillary gas chromatographs (GC) coupled with such detectors as electron capture detector (ECD) or mass spectrometer (MS) are used. The technique recommended most often for liquid samples is high performance liquid chromatography (HPLC) with fluorescence or UV detector [5, 11, 12]. For verification of the methodology of preparing environmental samples for determination of micropollutants there were introduced internal reference mixtures, recovery standards mixtures and syringe standards mixture, which are the analogues of the determined compounds marked with stable carbon isotopes [13]C. Introduction of the reference mixture allows us to confirm the correctness of the performed stages and to receive reliable results of the analysis [3].

Because the preparation of samples is time-consuming and uses a relatively large amount of solvents, currently there is research in progress on simplification of the methodology of isolating micropollutants providing the determination of several groups of compounds. Research on common determination of PAHs and PCBs using a single extraction was carried out by Wolska. The examinations were conducted for bottom sediments. Organic substances were extracted with dichloromethane, and purification of extracts was performed on the silica gel in the presence of activated copper. The extracts were concentrated under a stream of nitrogen and PAHs were determined in them using the GC-MS. Then, extracts were evaporated, cleaned with pentane and again purified on

silica gel. The further operation was the evaporation, and then dissolving the dry residue in hexane. In such prepared samples PCB was determined [13]. The aim of this study was to verify the simplified procedure of preparing samples (single extraction) for determination of PAHs and PCBs in sewage sludge and supernatants by marking the concentrations of those compounds and allocating recoveries.

MATERIALS AND METHODS

Qualitative-quantitative investigation was carried out with using industrial sludge originating from the wastewater treatment plant. The selection of sewage sludge was determined by the fact that in previous research large amounts of PAHs were identified in this material. It was also predicted that sewage sludge will contain PCBs. Sludge was taken from biological wastewater treatment as an instantaneous sample. Sewage sludge was centrifuged to obtain supernatants. The content of organic compounds in supernatant measured by COD indicator was 1362 mg/L.

The successive stages of the preparation of samples for the determination of PAHs and PCBs are presented in the diagram in Figure 1.

For research 10 g of centrifuged sewage sludge and 500 mL of supernatants were collected. The separation of the organic matrix of the sludge was done via sonification for 25 min, using a solvent mixture of cyclohexane and dichloromethane (5:1, v/v). The obtained extracts were poured into centrifugal test-tubes and were centrifuged for 10 min with 9000 rev/min. Separation of organic compounds in liquid samples was carried out mechanically in the liquid–liquid system with the addition of methanol, cyclohexane and dichloromethane (20:5:1, v/v/v). In this case the separation of extracts from samples took place in the glass separatory funnel. Silica gel was used to isolate analytes from extracts from other organic substances extracted simultaneously. Before the introduction of the extracts, the columns filled with silica gel were conditioned with methanol (2 × 3 mL), and then with distilled water (2 × 3 mL). The purified extracts were concentrated in the stream of nitrogen to 2 mL. From the prepared extracts the amount of 4 µl was separated, which was allocated for the qualitative-quantitative analysis of PAHs. The measurements were performed by using the gas chromatograph coupled with mass spectrometer (model GC800/MS800). For analysis there was used the standard mixture of 16 PAHs (naphthalene, acenapthylene, acenaphthene, fluorine, phenantrene, 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 the mixture of benzene and dichloromethane (produced by AcuStandard Inc. USA). The identification was based on injecting 2 µl of extract on the column DB-5 (length 30 m, diameter 0,25 mm, thickness 0,25 µm) with use of helium as the carrier gas. Quantitative identification of PAHs was carried out at the temperature of 280ºC. The program of the oven was as follows: 40 to 120°C (heating 40ºC/min), from 120 to 280ºC (heating 5ºC/min), 280ºC for 20 minutes. After PAHs determination, extracts were concentrated to a volume of 0,5 mL, and then distilled water (30 mL) and methanol were introduced for obtaining clear solution. For further PCBs isolation, extracts were filtered through preconditioned columns of the Bakerbond SPE octadecyl C18 type. Column filled with silica gel with chemically bonded octadecyl groups, was conditioned with dichloromethane (2 × 6 mL) and distilled water (1 × 6 mL). Next polychlorinated biphenyl was eluated
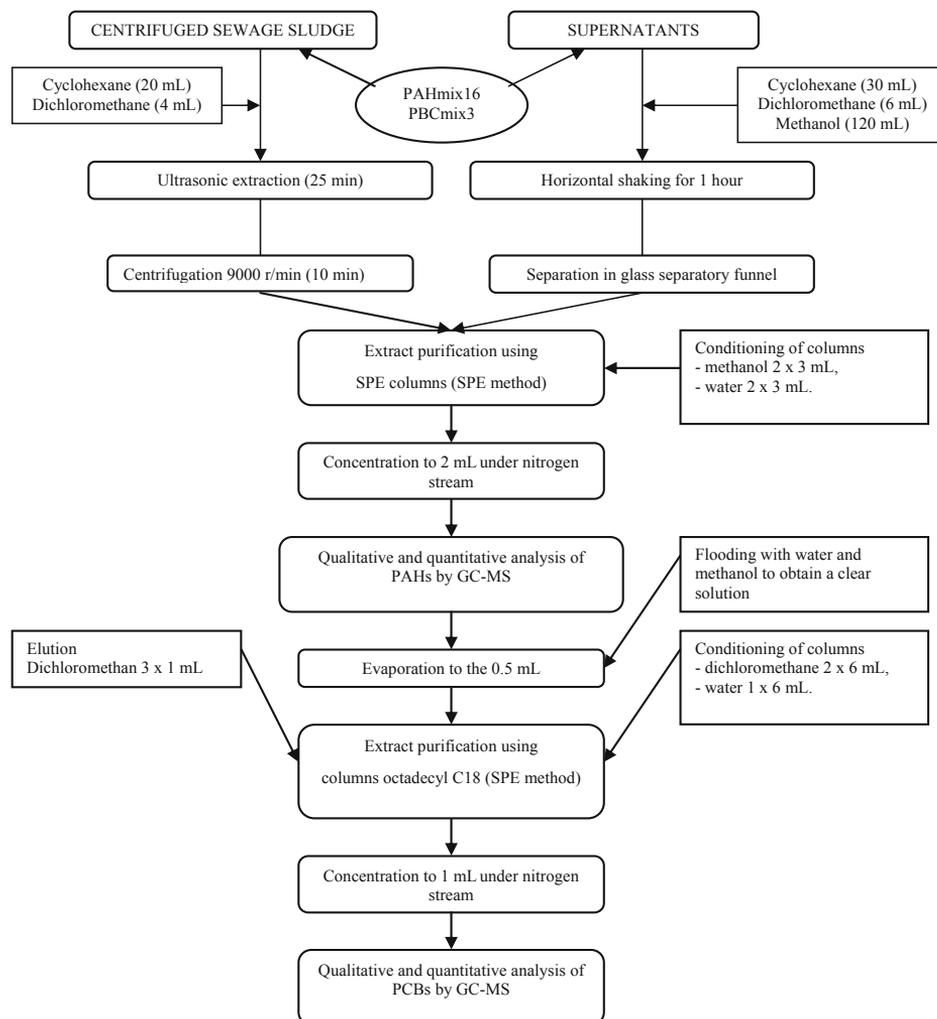
Fig. 1. Diagram of sample preparation of sewage sludge and supernatants to the common determination of PAHs and PCBs

with dichloromethane (3×1 mL). The received eluate was concentrated in the stream of nitrogen to the volume of 1 mL. Quantitative-qualitative analysis of seven congeners of PCBs was carried out by chromatography (GC-MS). Quantitative analysis was performed using a standard mixture of seven congeners of PCBs with codes 28, 52, 101, 118, 138, 153, 180. The temperature program of column oven was as follows: 40 to 120°C (heating 40°C/min), from 120 to 280°C (heating 5°C/min), 280°C for 15 minutes. Indications of PAHs and PCBs were performed in duplicate. In order to verify the adopted procedures the recoveries of PAHs and PCBs were determined.

The recovery value was determined after the introduction of the reference mixtures to samples of sewage sludge and supernatants before extraction. The amount of introduced

reference mixture of PAHs and PCBs to the sewage sludge was respectively 2 mg/kg$_{d.w.}$ and 0.01 mg/kg$_{d.w.}$. To supernatants were added respectively 30 μg/L and 0.1 μg/L standard mixture of PAHs and PCBs.

The limit values of detection for each polycyclic aromatic hydrocarbons and polychlorinated biphenyls are shown in Table 1 and Table 2.

Table. 1. Limit of detection and recovery of PAHs from sewage sludge and supernatants

Compound	Limit of detection [μg/L]	Recovery [%]	
		Supernatant	Sewage sludge
Naphthalene	0.14	76.7	171.4
Acenaphtyhlene	0.31	50.0	10.7
Acenaphthene	0.43	60.0	46.4
Fluorene	0.46	56.7	39.3
Phenanthrene	0.59	93.3	117.9
Anthracene	0.54	53.3	42.9
Fluoranthene	0.30	23.3	103.6
Pyrene	0.22	70.0	96.4
Benzo(a)anthracene	0.28	30.0	82.1
Chrysene	0.28	36.7	82.1
Benzo(b)fluoranthene	0.28	93.3	39.3
Benzo(k) fluoranthene	0.27	83.3	71.4
Benzo(a)pyrene	0.21	96.7	64.3
Dibenzo(a,h,)anthracene	0.22	60.0	*
Indeno(1,2,3-c,d)pyrene	0.24	36.7	150.0
Benzo(g,h,i)perylene	0.20	46.7	53.6

* not detected

Table. 2. Limit of detection and recovery of PCBs from sewage sludge and supernatants

Compound	Limit of detection [μg/L]	Recovery [%]	
		Supernatant	Sewage sludge
PCB28	0.35	*	18.3
PCB 52	0.59	9.0	*
PCB 101	0.38	85.5	25.0
PCB 118	0.19	57.5	*
PCB 138	0.27	65.5	30.0
PCB 153	0.27	76.5	46.7
PCB 180	0.28	*	55.0

* not detected

RESULTS AND DISCUSSION

Summary concentration of 16 PAHs in sewage sludge equalled 13 mg/kg$_{d.w.}$. In Figure 2 average concentrations of particular hydrocarbons are presented.
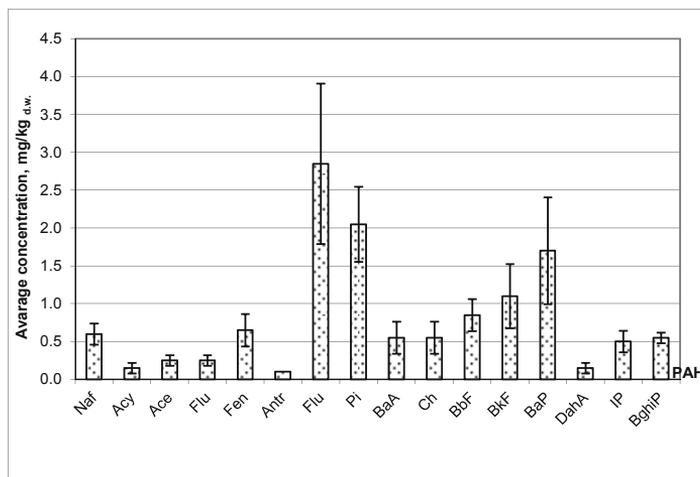

Fig. 2. PAHs concentration in coke sludge

Quantitative investigations showed that sewage sludge was dominated by fluoranthene, whose concentration constituted 22%. In the lowest concentration anthracene was marked, and its concentration did not exceed 0.1 mg/kg$_{d.w.}$. Carcinogenic compounds in sludge accounted for 47%. The highest concentration among these hydrocarbons ranging 1.7 ± 0.7 mg/kg$_{d.w.}$ showed benzo(a)pyrene. In Table 3 there are presented results of qualitative-quantitative determination of PAHs in sludge with division into the number of rings in the particle. In these matrixes dominant were hydrocarbons formed from 4-rings and accounted for more than 46%. Naphthalene was found in the lowest concentrations, which is characterized by the highest solubility in water among tested hydrocarbons. Moreover, it is classified as a volatile hydrocarbon, and that is why in open devices of wastewater treatment the losses of this compound are large.

Table. 3. PAHs concentration in sewage sludge and supernatants with division to the number of rings

PAHs	Sewage sludge	Supernatant
	µg/kg$_{d.w.}$	µg/L
Naphthalene	0.6 ± 0.1	3.0 ± 0.2
3-ring	1.4 ± 0.4	3.8 ± 0.7
4-ring	6.0 ± 2.0	6.5 ± 3.0
5-ring	3.8 ± 1.4	2.4 ± 1.0
6-ring	1.1 ± 0.2	1.4 ± 0.2

The occurrence of PAHs in sewage sludge has been confirmed in the Polish and worldwide literature. Most of the research, however, is concerned with urban sewage sludge, which flows a mixture of domestic and industrial sewage. The results of PAHs concentrations in these matrixes show significant discrepancies, what results from the differentiated characteristics of sewage and hence the heterogeneity of sludge. In previous studies of authors of this publication, PAHs concentrations depended on the applied solvents, the method of extraction and the way of purification the extracts. An average concentration of 16 PAHs in industrial sludge reached 740 mg/kg$_{d.w.}$ [14]. In research conducted by Hua and others, PAHs concentrations fluctuated from 33.7 to 87.5 mg/kg$_{d.w.}$ [15]. While in research conducted by Bernal-Martinez the concentration of 13 PAHs did not exceed 14.4 mg/kg$_{d.w.}$ [16]. These discrepancies result from a different characteristics of sewage, different type and share of industrial sewage, from which sludge was extracted and from heterogeneous analytic procedures.

An average summary concentration in liquids extracted from sewage sludge was 17 µg/L. Concentrations of particular hydrocarbons are presented in Figure 3.
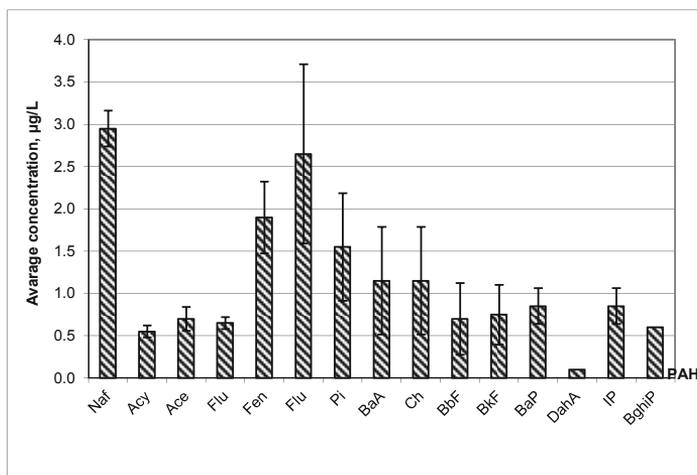

Fig. 3. PAHs concentration in supernatants

Naphthalene and fluoranthene dominated in liquids and these hydrocarbons constituted relatively 18 and 16% in total of 16 compounds. Carcinogen carbohydrates constituted 36%. Table 3 presents the results of PAHs concentrations with the division into the number of rings. The highest share in the summary concentration of PAHs had the 4-ring hydrocarbons, and the lowest − 6-ring ones. The results obtained in these examinations were close to the results from previous examinations of the authors, in which the concentration of 10 PAHs reached 13.6 µg/L with the application of the same procedure of sample preparation. In the literature several papers written by other authors deal with the contents of PAHs in supernatants [17]. Typically these compounds are marked in reference to the dry mass (in sewage sludge) without supernatants [13]. In Table 1 there are presented the average values of recovery of particular hydrocarbons introduced to the samples before extraction (parallel to sludge and to supernatants). In the case of liquids, the recovery of
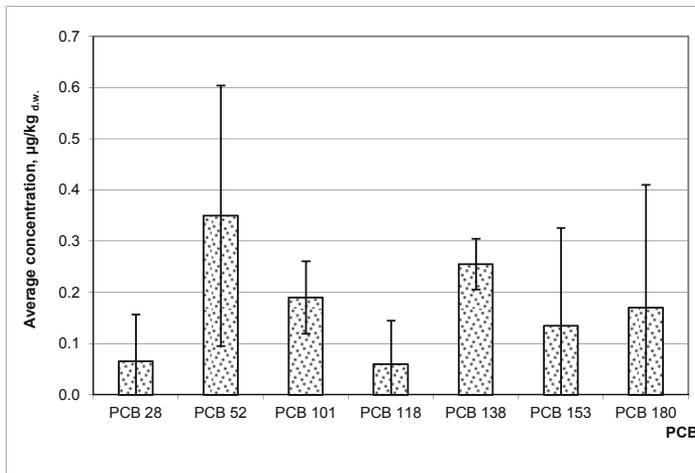
Fig. 4. The average concentration of PCBs in sewage sludge
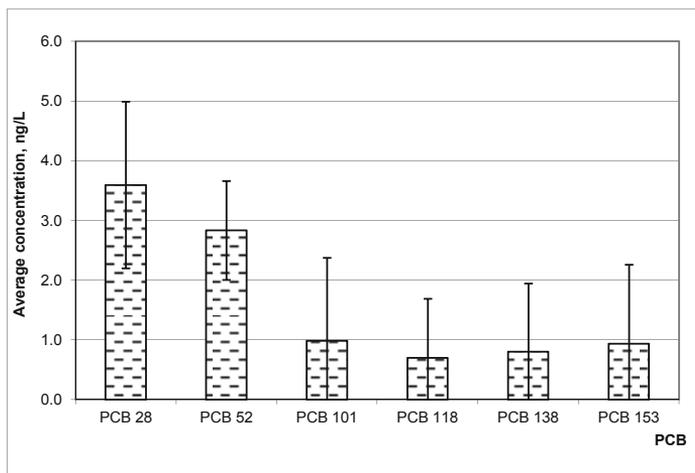

Fig. 5. The average concentration of PCBs in supernatants

particular PAHs was in the range from 23.3 to 96.7%. The lowest recovery was obtained for fluoranthene, while the highest for benzo(a)pyrene. The scope of recovery values for sludge was wide and average recovery for particular hydrocarbons was in the range from 10.7 to 171.4%. Recovery values determined by other authors are different depending on the kind of the matrix examined. For example, for supernatants isolated from municipal wastewater recoveries equalled from 35.8% for naphthalene to 75.5% for pyrene. For sewage sludge recoveries were in the range from 23.3 to 62.4% [18]. In a different work, the average degree of PAHs recovery for sludge reached 60%, and the highest, more than 70%, was reached for anthracene and benzo(k)fluoranthene [2, 15, 19].

In extracts of coke wastewater PCBs congeners was determined with codes 28, 52, 101, 118, 138, 153 of the seven analyzed compounds. Total concentration of PCBs was 1.23 µg/kg$_{d.w.}$. In the highest concentration there was tetrachlorobiphenyle with code number 52. In the lowest concentration there were congeners with code numbers 118 (0.06µg/kg$_{d.w.}$) and 28 (0.07 µg/kg$_{d.w.}$) belonging to penta- and trichlorobiphenyles. In research conducted by Rosińska and others, which was carried out for sludge separated from municipal wastewater treatment, the concentration of seven PCB congeners was 52.33 µg/kg$_{d.w.}$ [20]. In supernatants there were identified and marked six PCB congeners. Summary concentration of PCBs was in the scope from 8 to 11.7 ng/L. The highest concentrations were found for biphenyls, lower for chlorinated congeners (PCB 28 and PCB 52), whose summary concentration equalled 65%. In the literature the content of PCB in supernatants extracted from urban sludge is omitted, and available information say that these compounds occur in concentrations below the boundary of determination [21]. In Table 2 average recoveries of PCBs are presented. In the case of supernatants, recoveries of particular relations were in the range from 9 to 86%, and for sludge the percentage recovery was in the range from 18 to 55%. In research carried out by Wolska and co-workers, the recovery of PCBs from bottom sediments was in the range from 92 to 119%. However, it should be noted that research was conducted on bottom sediments of different chemical characteristics than that for sewage sludge. Moreover, concentrations of PAHs and PCBs, which were determined in research, were expressed in micrograms and equalled, respectively, 309 and 9.1 µg/kg$_{d.w.}$ [2]. In the present investigation, PAHs concentrations were about two orders of magnitude higher (13 mg/kg$_{d.w.}$) and PCBs − about one order smaller (1.23 µg/kg$_{d.w.}$). Thus, the concentration range of studied micropollutants determined in research was significant, indicating the diversity of the organic matrix in the sewage sludge and probably had an impact on the recovery of individual compounds.

The obtained values of recovery for PAHs and PCBs, were in the range of values obtained by other authors [2, 15, 18, 19, 20, 22]. In the literature, there is no data for the determination of PAHs and PCBs in coke sludge and liquids separated from them, except for author's own research. Therefore, further studies are planned using other solvents, extraction methods and including the use of deuterated and C^{13} isotope-labelled standards.

CONCLUSIONS

On the basis of research and received results, it can be concluded that:

1. The proposed procedure of preparing samples of sewage sludge and supernatants involving the common extraction may be used for the determination of PAHs and PCBs. However, each time preliminary research should be carried our consisting of marking out the value of recoveries of the reference mixture introduced to the samples before the process of extraction.

2. Summary concentration of 16 PAHs in industrial sludge equalled 13 mg/kg$_{d.w.}$, and the average value of recovery for hydrocarbons introduced to the sludge in the form of reference mixture reached 78%.

3. In liquids separated from sewage sludge, the average summary concentration of 16 PAHs equalled 17 µg/L, and the average value of the recovery of the examined hydrocarbons was determined on the level of 60%.

4. In sewage sludge there were quantitatively determined six PCBs in the summary concentration equal 1.2 μg/kg$_{d.w.}$, while in liquids obtained from concentration of sewage sludge the concentration of seven congeners reached 10 ng/L.

5. The percentage value of recovery of the reference mixture for PCBs introduced to sewage sludge before extraction reached 55%, while in the case of supernatants – 86%.

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UPROSZCZENIE PROCEDURY PRZYGOTOWANIA PRÓBEK DO OZNACZANIA WWA I PCB

W pracy przedstawiono wyniki badań wspólnego oznaczania WWA i PCB w osadach przemysłowych oraz cieczach nadosadowych. Osady pobrano z zakładowej oczyszczalni, a ciecze nadosadowe uzyskano poprzez ich odwirowanie. Przygotowane próbki osadów i cieczy poddawano ekstrakcji z wykorzystaniem mieszaniny organicznych rozpuszczalników. Stosowano cykloheksan i dichlorometan do próbek stałych, a metanol, cykloheksan i dichlorometan – do ciekłych. Ekstrakty, po oddzieleniu od próbek osadów i cieczy, oczyszczano na żelu krzemionkowym w warunkach próżniowych i zatężano w strumieniu azotu. W tak przygotowywanych ekstraktach prowadzono analizę jakościowo-ilościową 16 WWA z wykorzystaniem układu GC-MS. Następnie próbki odparowywano i zalewano wodą oraz metanolem do uzyskania klarownego roztworu. Ekstrakty oczyszczano na kolumienkach octadecylowych C18, a następnie zatężano w strumieniu azotu. W tych ekstraktach oznaczano PCB również z wykorzystaniem chromatografu gazowego ze spektrometrem mas. Zakres stężeń 16 WWA w osadach ściekowych wynosił od 10–16 mg/kg$_{s.m.}$. Sumaryczne średnie stężenie 16 WWA w cieczach nadosadowych wynosiło 17 μg/L. Średni odzysk WWA wprowadzonych do osadów w postaci mieszaniny wzorcowej wynosił 78% (z uwzględnieniem naftalenu). W przypadku cieczy nadosadowych średnia wartość odzysku to 60%. Średnie stężenie PCB w cieczach nadosadowych wynosiło 10 ng/L. Dla osadów suma oznaczonych PCB wyniosła średnio 1,23 μg/kg$_{s.m.}$. W przypadku poszczególnych PCB procentowy odzysk mieszaniny wzorcowej dla cieczy nadosadowych sięgał do 86%, natomiast dla osadów do 55%.