



# River bottom sediment from the Vistula as matrix of candidate for a new reference material



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## ABSTRACT

Bottom sediments are very important in aquatic ecosystems. The sediments accumulate heavy metals and compounds belonging to the group of persistent organic pollutants. The accelerated solvent extraction (ASE) was used for extraction of 16 compounds from PAH group from bottom sediment of Vistula. For the matrix of candidate of a new reference material, moisture content, particle size, loss on ignition, pH, and total organic carbon were determined. A gas chromatograph with a selective mass detector (GC/MS) was used for the final analysis. The obtained recoveries were from 86% (SD=6.9) for anthracene to 119% (SD=5.4) for dibenzo(ah)anthracene. For the candidate for a new reference material, homogeneity and analytes content were determined using a validated method. The results are a very important part of the development and certification of a new reference materials.

## 1. Introduction

Bottom sediments are an integral part of the aquatic environment. They deposit on the bottom of rivers, lakes, seas, dammed reservoirs and harbor canals. Chemically, the sediments are composed of solid (rock particles, minerals and organic substances), liquid (water containing a complex mixture of dissolved mineral salts, organic compounds and colloids) and gaseous (a mixture of gases and water vapor) components. Organic matter consists of humic substances (humic acids, fulvic acids, humins) and non-humic ones such as peptides, amino acid, fats, and sugars (Huang et al., 2003; Mechlińska et al., 2009; Tremolada et al., 2012). The chemical composition of sediments is closely connected to both natural and anthropogenic factors. The natural factors include: geological structure of the catchment, geomorphology of the terrain, climatic conditions, temperature, pH, pressure, and redox reactions. Economic activity of humans constitutes an anthropogenic factor (Harris et al., 2011; Ma et al., 2013; Sakulthaew et al., 2014; Sun et al., 2017).

Much of the pollution penetrating into the waters of the river, by a process of self-purification of the waters, falls to the bottom sediments. The sediments accumulate, among others, heavy metals and compounds belonging to the group of persistent organic pollutants, for example polycyclic aromatic hydrocarbons (PAHs). PAHs have carcinogenic, teratogenic, embryotoxic, mutagenic properties and are metabolized. They create derivatives, which bind covalently to DNA. They

penetrate into the human body through the gastrointestinal tract, respiratory system and skin. They can easily penetrate protein-lipid membranes. They have the ability to accumulate in fatty tissue of the body or the mammary gland. They have a negative impact on the replication of cells. PAHs in sediments not only have a negative impact on aquatic organisms, but also on higher organisms as a result of their presence in the food chain. Movement of contaminated sediments (eg. as a result of flooding, high water status, river transport and dredging) causes their movement and deposition in previously uncontaminated areas, ecosystems of open water contamination or soil pollution (Aziz et al., 2014; Countway et al., 2003; Gadzała and Buszewski, 1995; Guo et al., 2009; Kramer and Tikhonova, 2015; Semenov et al., 2016).

The compounds from PAH group can be classified by the toxic equivalency factors (TEFs). In this approach, benzo(a)pyrene (one of the most potent PAHs) is a reference compound, and TEF for it equals 1 (Nisbet and LaGoy, 1992). The toxic equivalency factors for 16 compounds from PAH group are calculated in comparison with benzo(a)pyrene. Values of TEFs are shown in Table 1.

It is important that the determination of PAHs in the sediments is carried out with appropriate precision and accuracy, for the obtained results to be considered reliable. All this ensures the application of reference materials in analytical procedures (de Boer and McGovern, 2001; Namieśnik and Zygmunt, 1999; van Leeuwen and de Boer, 2008). It is important that the materials were created from the new matrices and analytes, as similar as possible to real-life samples. The production

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**Table 1**

The toxic equivalency factors (TEFs) for various PAHs (according to Nisbet and LaGoy, 1992).

No.	Compounds	Toxic equivalency factors (TEFs)
1	Dibenzo(ah)anthracene	5
2	Benzo(a)pyrene	1
3	Benzo(a)anthracene	0.1
4	Benzo(b)fluoranthene	
5	Benzo(k)fluoranthene	
6	Indeno(1,2,3-cd)pyrene	
7	Anthracene	0.01
8	Benzo(ghi)perylene	
9	Chrysene	
10	Acenaphthene	0.001
11	Acenaphthylene	
12	Fluoranthene	
13	Fluorene	
14	Naphthalene	
15	Phenanthrene	
16	Pyrene	

and certification of new reference materials is a very long, complicated and difficult process. Reference materials must be characterized by homogeneity and stability for very specific parameters, and the reference value must be determined using validated methods, provided with the value of uncertainty. All this should be presented in the form of clear documentation that accompanies each reference material (if the material is certified) (ISO/IEC Guide 98–3:2008; ISO Guide 30, 2015; ISO Guide 31, 2015; ISO Guide 33, 2015; ISO 17034, 2016; ISO Guide 35, 2006; ISO – 5725, part 1–6; ISO – 3534, part 1–4; Dybczyński et al., 2001; Kramer and Pauwels, 1996; Kupiec et al., 2009).

The aim of this work is to perform a candidate for a new reference material for PAHs in bottom sediment from Vistula River. In this article were described the development and validation of effective extraction methods and determination of 16 compounds of PAHs group. The number of the analyzed compounds was determined in accordance with USEPA (United States Environmental Protection Agency, 1986) standards. A candidate for a new reference material was prepared from natural matrices not from synthetic mixtures. This article shows how important the composition of the natural matrix of candidate for a new reference material is. This is a very big challenge to obtain homogeneity of a new reference material from natural bottom sediment.

## 2. Materials, equipment and methods

### 2.1. Reagents and materials

The certified standard of the sixteen PAHs (acenaphthylene, anthracene, benzo(ghi)perylene, chrysene, dibenzo(ah)anthracene, phenanthrene, fluoranthene, fluorene, naphthalene, acenaphthene, pyrene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)anthracene and indeno(1,2,3-cd)pyrene) in acetonitrile was supplied by LGC Standards. The concentration of each compound was declared as 10 ng/mL. This solution was stored at +4 °C. The certified reference materials (PAH-Sediment 1) were obtained by LGC Standards (Table 2). The water was obtained from a MilliQ system. Hexane, acetone and acetonitrile were used. They were supplied by Avantor Performance Materials Poland S.A. They were of HPLC grade. Nitrogen was of a purity higher than 99%. The sample was filtered through PTFE syringe filters with 13 mm diameter and 0.22 µm pore size.

### 2.2. Instruments and equipment

Moisture Analyzer MA – 35 (Sartorius Poland Sp. z o.o., Kostrzyn Wielkopolski, Poland) was applied for moisture analysis. Total carbon analyzer with solid sample module by Shimadzu (Kyoto, Japan) was used for carbon content determination. For pH determination, pH-

**Table 2**

Concentration of PAH in PAH-Sediment 1 (according to the certificate).

Compounds	Concentration [µg/Kg]	SD
Naphthalene	504	215
Acenaphthylene	582	169
Acenaphthene	575	195
Fluorene	270	79.1
Phenanthrene	202	58.5
Anthracene	542	171
Fluoranthene	701	175
Pyrene	375	105
Benzo(a)anthracene	146	36.2
Chrysene	347	85.2
Benzo(b)fluoranthene	283	74.2
Benzo(k)fluoranthene	296	63.5
Benzo(a)pyrene	164	52.3
Dibenzo(ah)anthracene	372	94.0
Benzo(ghi)perylene	420	83.9
Indeno(1,2,3-cd)pyrene	215	41.6

meter (Metler Toledo, Warsaw, Poland) was used. Mastersizer 2000 (Malvern, Anglia) was used for particle size determination. A muffle furnace (PWP, Wodzisław Śląski, Poland) was used for loss on ignition determination. For extraction, an accelerated solvent extraction ASE 100 (Dionex, Sunnyvale, California, United States of America) was used.

The gas chromatograph with a selective mass detector (Agilent Technologies 6890 N and 5975 Series, respectively) and a 30 m × 0.25 mm × 0.25 µm capillary column (ZB-5MS, Phenomenex) were used.

### 2.3. River bottom sediment samples and their characteristics

Bottom sediment samples were collected from bottom of the Vistula River near Włocławek (Kuyavian-Pomeranian District, Poland). It was dried, lyophilized, sifted (the mesh of the sifter = 100 µm), homogenized, and sterilized and then placed in closed dark glass bottles labeled with a lot number. Moisture, particle size, pH, total organic carbon (TOC), and loss on ignition were determined for each sediment sample. Moisture content was determined by use of the moisture analyzer. The 1.0 g sample was placed on an aluminium weighing pan. The sample was dried at 105 °C to establish a constant weight. Particle size was determined using Mastersizer 2000. pH of bottom sediment samples was determined as follows: 5 mL of a sample was placed in a polyethylene bottle with a tightly fitting cap. 25 mL of water was added, and the sample was shaken for 1 h. After at least 1 h (but no longer than 3 h) of waiting, pH was determined. TOC was determined using total carbon analyzer. Total organic carbon was determined from the difference between total carbon and inorganic carbon. A loss on ignition was determined by placing the sample in a porcelain crucible, and heating it at 550 °C in muffle furnace for at least 1 h. Next, the hot crucible was placed in the desiccator and left to cool. The difference in mass before and after the heating process is used for calculating the loss on ignition. The mass of the residue was measured at the nearest 0.1 mg. All results were presented in Fig. 1.

### 2.4. Extraction of PAHs from bottom sediment samples

The accelerated solvent extraction (ASE) was used to extract PAHs from river sediment samples. 1.0 g of the sample was mixed with roast sand and placed in an extraction cell. The extraction ran at 113 °C in three static cycles, 5 min each. The mixture of hexane and acetone (80:20, v/v) was used as the extraction solvent. After extraction, the extracts were collected and then evaporated to almost dryness in a mild stream of nitrogen at the temperature not exceeding 30 °C. Next, it was resolved in 1 mL ACN and evaporated to 500 µL. The extract was

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