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## FRACTIONATION OF HEAVY METALS IN BOTTOM SEDIMENTS AND SEWAGE SLUDGES USING SEQUENTIAL EXTRACTION

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**Abstract:** In order to determine the forms of heavy metals in bottom sediment or sewage sludge the speciation analysis is performed. The analysis is based on the sequential extraction of metals with increasingly aggressive solvents. The five steps extraction proposed by Tessier et al gained wide recognition. It extracts metals in following groups: exchangeable, associated with carbonates, with hydrated iron oxides and manganese oxides, with organic matter and metals that can be found in the residual fraction. Metals that can be found in the two first fractions (exchangeable and carbonate) are believed to be mobile. As a result of research carried out by the Standards, Measurements and Testing Programme of the European Commission, formerly the Community Bureau of Reference, a shorter, three-stage extraction procedure known as the BCR procedure was accepted.

Comparison of heavy metal (Zn, Cu, Ni, Pb, Cd, Cr) fractionation methods was done. Two different sequential extraction methods were investigated: Tessier, and BCR method. For the experiment following materials were used: certified reference material LGC6181, sewage sludge were collected from mechanical-biological municipal wastewater treatment plant located in Czestochowa, and bottom sediment from the Poraj Reservoir. After results comparison, it was stated that content of particular chemical forms of heavy metals in total amount in certified material, sewage sludge and bottom sediment vary depending on used extraction method. In case of certified material differences referred to cadmium concentrations in exchangeable-carbonate, iron and manganese oxides, and zinc in residual (insoluble compounds) fractions. Also in sewage sludge and bottom sediment cadmium concentrations measured in exchangeable-carbonate, in organic-sulfide, and in residual (insoluble compounds) fractions after extraction according to Tessier method, did not equal to values obtained after use of BCR extraction method. This also applied to zinc and lead concentrations in iron and manganese oxides fraction. The discrepancy between the results could be explained with both: used extractants, and extraction conditions (different reagents, temperature, and time). The results point out how important is the choice of a proper extraction method depending on the aim of speciation analysis but also depending on the analyzed chemical forms of heavy metals.

**Keywords:** heavy metals, sequential extraction procedures, bottom sediment, sewage sludge

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## Introduction

In order to determine heavy metal forms in soils, bottom sediments or sewage sludge, which affect mobility and bioavailability of metals, speciation analysis is performed, based on sequential extraction. It is based on gradual release of metals from soil or sludge by solutions with increasing aggressiveness [1, 2]. For each step reagents are chosen, which are able to extract a group of metal connections with known properties. Specific chemical elements in a particular fraction are not identified, only the fraction as a whole. Most often this fractions are distinguished: exchangeable, carbonate, iron and manganese oxides, organic and sulfide, residue (metals embedded in the crystalline network of primary and secondary minerals, particularly silicates). Metals found in the first two fractions are considered to be mobile, those in the two following – temporarily immobilized. The iron and manganese oxides fraction is sensitive to changes in redox potential, whereas metals bound to organic matter are released during the mineralization process of this substrate.

First complex and still utilized procedure of sequential extraction of heavy metals from bottom sediment samples taken from natural water environment (river) was developed by Tessier, Campbell and Bisson [3]. This procedure was repeatedly discussed and underwent numerous modifications. The modifications were mainly related to the used reagents and the extraction conditions. Modification of the Tessier procedure proposed by Zerbe et al [4] consisted in the introduction of different reagent for extracting metals from exchangeable fraction. It was 1 M  $\text{CH}_3\text{COONH}_4$ . The modification proposed by Perez Cid et al [5] involved the usage of microwaves to support the extraction. In this way the time of the process was reduced, with the use of the same reagents, from 17 hours and 56 minutes down to 30 minutes. Different modification was presented by Gomez Ariza et al [6] introducing higher concentration of the reducing agent – 0.4 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . A method with an entirely different procedure was proposed by Stover et al [7], a six-step extraction designed for metal fractionation in anaerobically stabilised sewage sludge, which enabled the determination of metals separately in organic and sulfide fraction. After the extraction of metals from exchangeable fraction (1 M  $\text{KNO}_3$ , pH = 7) and adsorbed (0.5 M  $\text{KF}$ , pH = 6.5) the Authors proposed extraction from organic fraction (0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$ ), carbonate (0.1 M  $\text{EDTA}$ , pH = 6.5), and then from sulfide (1 M  $\text{HNO}_3$ ) and residue ( $\text{HNO}_3 + \text{HCl}$ ). The Authors did not include the stage of oxides fraction metal separation. For a complete dissolution of resistant sulfides Rudd et al [7] performed a modification of Stover method by increasing the concentration of  $\text{HNO}_3$  acid from 1 M to 6 M.

As a result of the work of the Standards, Measurements and Testing Programme of the European Union Commission, a shortened, three-stage extraction was adopted, known as the BCR procedure (from previous name of this Commission – Community Bureau of Reference) [8–10]. The modification of this procedure was to increase the concentration of the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  reagent solution from 0.1 to 0.5 M for the metal extraction from reducible fraction – iron and manganese oxides. For a more complete extraction of metals from this fraction not only an increase in reagent concentration was proposed, but also lowering the pH from 2 down to 1.5 with the usage of  $\text{HNO}_3$  [11, 12].

In the literature there are also BCR procedure modifications, which include the application of microwave energy or ultrasonic waves for intensification of the extraction process [13, 14].

The course of extraction is influenced by many factors: type of examined sample, its pH, degree of fragmentation, extraction period, solid mass to solution ratio, temperature, chemical properties and selectivity of chosen extractants, order of particular extraction steps.

Table 1

Application of sequential extraction procedures to sediment and sewage sludge (selected examples)

Procedure	Matrix	Elements determined	Reference
Tessier	Sediments of the Nile River (Egypt)	Cd, Cu, Cr, Fe, Pb, Mn, Ni, Zn	[18]
BCR	Sediments of Jinjiang River (China)	Cr, Ni, Cu, Zn, Cd, Pb	[19]
BCR	Sediments of the Deule River (France)	Cd, Co, Cu, Fe, Ni, Pb, Sr, Zn	[20]
Tessier	Sediments of Bharali River (India)	Zn, Cu, Ni, Pb, Cd, Fe, Mn	[21]
BCR	Sediments of Jarama River (Spain)	Zn, Cu, Ni, Pb, Cd, Fe, Mn	[22]
BCR	Sediments of Titicaca Lake (Bolivia)	Cu, Fe, Ni, Co, Mn, Cd, Pb, Zn	[23]
BCR	Sediments of Nashina Lake (China)	Cd, Cr, Cu, Mn, Ni, Pb, Zn	[24]
Tessier	Sediments of Qarun Lake (Egypt)	Fe, Mn, Zn, and Cu	[25]
BCR	Sediments of Quanzhou Bay (China)	Cu, Zn, Cr, Co, Fe, Mn, V, Pb	[26]
BCR	Sediments of Xiamen Bay (China)	Cu, Pb, Zn, Cd, Cr	[27]
BCR	Sediments of Gowatr Bay (Iran)	Cu, Pb, Zn, Mn, Ni, Co, Cr, V	[28]
BCR	Sediments of Akyatan Lagoon (Turkey)	Cd, Cr, Cu, Mn, Ni, Pb, Zn	[29]
BCR	Six different sewage sludges (Spain)	Cu, Cr, Ni, Fe, Zn, Pb, Cd	[30]
BCR	Five different sewage sludges (Spain)	Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb	[31]
BCR	Five different sewage sludges (China)	Cu, Zn, Pb, Cd	[32]
BCR	Anaerobic sewage sludge (Turkey)	Cd, Cr, Cu, Mn, Pb, Ni, Zn, Fe	[33]
Tessier	Five different sewage sludges (Egypt)	Cd, Cu, Cr, Fe, Mn, Ni, Zn	[34]
BCR	Liquefaction residues of sludge (China)	Cu, Zn, Pb, Cd, Cr, Ni	[35]
BCR	Sewage sludge treatment wetlands (Italy)	Cr, Cu, Ni, Cd, Pb, Zn	[36]
Tessier	Composting of sewage sludge (Greece)	Cu, Ni, Pb, Zn, Mn, Fe	[37]

Since the development of the sequential extraction procedures, they were and still are subject to criticism, mostly for the lack of certainty as to the selectivity of the applied reagents, the possibility of metal readsorption, the utilization of different sample preparation methods, *ia* the way and time of drying, grinding, homogenising the material, as well as conditions under which the extraction is conducted [9]. Presented in the literature criticism of the procedures proves that there is no extraction scheme which could be applied to every speciation study of heavy metals. It is common to obtain different results after applying different extraction schemes [15, 16]. Studies on the extraction procedures are being continued, aiming to improve the selectivity of the eluents, and the quality and repeatability of the results. Despite numerous disadvantages, the sequential extraction method is an important source of information about activity or stability of heavy metals in fractions of examined material, which

reflects on the assessment of metal behaviour mechanisms in the environment, *ia* their mobility, moving, bioavailability [2, 17]. Examples of application of the Tessier and the BCR sequential extraction in research on heavy metal fractionation in bottom sediment and sewage sludge are shown in Table 1.

## Materials and methods

As a research material, bottom sediment and sewage sludge were used. The bottom sediment was collected from the Poraj Dam Reservoir fed by the Warta River. The sewage sludge originated from municipal wastewater treatment plant, and it was dewatered mechanically on a belt press, after being biochemically stabilized during mesophilic digestion process. The sludge and the sediment were dried in the laboratory in a dried (105°C), grinded and sieved through a 0.4 mm mesh. In the research certified reference material LGC6181 (sewage sludge) was also used.

In order to determine total heavy metal content, the sludge, the sediment and the reference material mineralization was conducted, using a mixture of concentrated acids: nitric and hydrochloric (1 + 3). The mineralization was conducted for 2 hours in the temperature of 120°C (Vario compact thermostat produced by Machery Nagel). For quantitative determination of heavy metals occurring in particular chemical forms in sludge, sediment, and certified material, sequential extraction according to the Tessier and the BCR procedures were applied – Table 2.

Table 2

Sequential extraction procedures

Chemical reagents and conditions (Tessier procedure)	Chemical reagents and conditions (BCR procedure)	Forms of metals
8 cm <sup>3</sup> 1 M MgCl <sub>2</sub> , pH = 7, temp. 22°C, shaking 1 h	40 cm <sup>3</sup> 0.11 M CH <sub>3</sub> COOH, temp. 22°C, shaking 16 h	Exchangeable
8 cm <sup>3</sup> 1 M CH <sub>3</sub> COONa, pH = 5 with CH <sub>3</sub> COOH, temp. 22°C, shaking 5 h		Bounded with carbonates
20 cm <sup>3</sup> 0.04 M NH <sub>2</sub> OH · HCl in 25% (v/v) CH <sub>3</sub> COOH, temp. 96°C, shaking 6 h	40 cm <sup>3</sup> 0.5 M NH <sub>2</sub> OH·HCl, temp. 22°C, shaking 16 h	Bounded with Fe and Mn oxides
3 cm <sup>3</sup> 0.02 M HNO <sub>3</sub> i 5 cm <sup>3</sup> 30% H <sub>2</sub> O <sub>2</sub> , pH = 2, temp. 85°C, shaking 2 h, 3 cm <sup>3</sup> 30% H <sub>2</sub> O <sub>2</sub> , temp. 85°C, shaking 3 h 5 cm <sup>3</sup> 3.2 M CH <sub>3</sub> COONH <sub>4</sub> in 20% (v/v) HNO <sub>3</sub> , temp. 22°C, shaking 0.5 h	10 cm <sup>3</sup> 8.8 M H <sub>2</sub> O <sub>2</sub> , temp. 22°C, 1 h; temp. 85°C, 1 h 10 cm <sup>3</sup> 8.8 M H <sub>2</sub> O <sub>2</sub> , temp. 85°C, 1 h 50 cm <sup>3</sup> 1 M CH <sub>3</sub> COONH <sub>4</sub> , temp. 22°C, shaking 16 h	Bounded with organic matter – sulfides
2 cm <sup>3</sup> 65% HNO <sub>3</sub> + 6 cm <sup>3</sup> 36% HCl, temp. 120°C, 2 h	2 cm <sup>3</sup> 65% HNO <sub>3</sub> + 6 cm <sup>3</sup> 36% HCl, temp. 120°C, 2 h	Residual

The preparation of the necessary reagents and the extraction procedure was carried out according to [8]. In case of the Tessier procedure, unlike described in [3], for metal extraction from residue fraction concentrated acids HNO<sub>3</sub> and HCl were used, instead of HF and HClO<sub>4</sub>.

Concentration of heavy metals: zinc, copper, nickel, cadmium, lead, and chromium, in obtained eluents, were determined by means of atomic absorption spectrometry (novAA 400 spectrometer produced by Analytic Jena). The analyses were carried out in triplicate.

The method for result quality control is to compare the analyses results for particular elements content to the total metal content, determined independently [38]. The overall concentration of metals in the sludge (Total) determined after mineralization with aqua regia was compared with the sum of metal concentrations in the extracted fractions ( $F1 + F2 + F3 + F4$ ). Recovery in the sequential extraction procedure was calculated as follows:

$$\text{Recovery} = \frac{F1 + F2 + F3 + F4}{\text{Total}} \cdot 100\%$$

## Results and discussion

It was stated that depending on the applied extraction method, the portion of analyzed chemical forms of particular heavy metal in the total content alike in the bottom sediment, in the sewage sludge, and in the certified material differed considerably – Table 3.

The biggest disparity in results was obtained with respect to cadmium content. In case of the bottom sediment, differences were regarding the amount of this metal in exchangeable-carbonate and organic-sulfide fraction, in the certified material – in exchangeable-carbonate and iron and manganese oxides fraction, while in the sewage sludge they included content in all fractions. Applying the extraction according to Tessier, the highest cadmium content in the bottom sediment was determined in exchangeable-carbonate fraction (52% of total content), whereas using the BCR method in residue fraction (33%). In case of the sewage sludge, the highest cadmium content was observed in iron and manganese oxides fraction (39%) and organic-sulfide (49%), using the Tessier and the BCR procedure respectively.

Zinc content in exchangeable-carbonate and organic-sulfide fraction of the bottom sediment had similar values obtained using both procedures, equal respectively to 27 and 30%, and 11 and 13% of total amount, while in the sewage sludge both in those fractions and in iron and manganese oxides fraction different results were obtained. In the sewage sludge, the highest zinc content was obtained in iron and manganese oxides fraction (45% of total content) using the procedure according to Tessier, while in organic-sulfide fraction (50%) using the BCR procedure. Only in residue fraction of the sewage sludge, similar content of this metal was obtained using both procedures (17 and 18%). In the certified material, the highest correspondence occurred in exchangeable-carbonate fraction, while the largest differences in residue fraction.

In case of copper and chromium content determination, in all fractions of the bottom sediment and the sewage sludge, while nickel and chromium in fractions of the certified material, consistence of the results were obtained using both procedures. However different nickel and lead content in exchangeable-carbonate fraction of the bottom

Table 3  
Content of heavy metals in chemical fractions of bottom sediment, sewage sludge and certified reference material LGC6181

Metal	Fraction	Content in bottom sediment				Content in sewage sludge				Content in reference material			
		"Tessier"		"BCR"		"Tessier"		"BCR"		"Tessier"		"BCR"	
		[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]
Zn	F1	16.0 ± 1.2	26.6	17.2 ± 0.9	29.9	432 ± 5	16.4	146 ± 4	5.4	284 ± 4	26.4	258 ± 4	24.4
	F2	17.8 ± 0.8	29.6	11.5 ± 0.5	20.1	1180 ± 12	44.7	704 ± 7	26.0	326 ± 6	30.3	390 ± 5	36.9
	F3	6.8 ± 0.6	11.3	7.7 ± 0.4	13.4	576 ± 4	21.8	1360 ± 9	50.3	165 ± 3	15.3	232 ± 2	22.0
	F4	19.6 ± 0.7	32.5	21.0 ± 1.4	36.6	452 ± 7	17.1	494 ± 6	18.3	302 ± 5	28.0	176 ± 3	16.7
Cu	F1	1.3 ± 0.2	30.9	1.1 ± 0.1	25.0	7.2 ± 0.4	2.4	5.1 ± 0.3	1.7	29.5 ± 0.5	9.2	16.2 ± 0.9	5.0
	F2	1.0 ± 0.1	23.8	1.1 ± 0.2	25.0	9.4 ± 0.7	3.1	8.2 ± 0.2	2.7	11.8 ± 0.3	3.7	7.1 ± 1.2	2.2
	F3	0.8 ± 0.1	19.1	0.9 ± 0.1	20.5	234 ± 9	78.4	248 ± 8	81.5	216 ± 5	67.6	243 ± 8	75.2
	F4	1.1 ± 0.2	26.2	1.3 ± 0.1	29.5	48.0 ± 1.1	16.1	43.1 ± 0.7	14.1	62.1 ± 1.6	19.5	56.7 ± 2.3	17.6
Ni	F1	5.3 ± 0.3	23.1	6.8 ± 0.3	29.3	66.2 ± 5.0	34.5	60.3 ± 6.2	32.3	14.4 ± 0.4	30.0	9.5 ± 0.1	22.3
	F2	9.2 ± 0.4	40.2	9.7 ± 0.3	41.8	50.7 ± 1.3	26.4	42.4 ± 0.9	22.7	7.2 ± 0.2	15.0	7.3 ± 0.2	17.1
	F3	4.4 ± 0.2	19.2	2.9 ± 0.1	12.5	49.1 ± 0.8	25.6	57.5 ± 2.3	30.7	12.6 ± 0.2	26.3	12.9 ± 0.2	30.2
	F4	4.0 ± 0.3	17.5	3.8 ± 0.2	16.4	26.0 ± 0.5	13.5	26.7 ± 0.4	14.3	13.8 ± 0.3	28.7	13.0 ± 0.3	30.4
Pb	F1	9.4 ± 0.4	45.2	8.3 ± 0.5	39.0	10.4 ± 0.3	10.3	9.8 ± 1.1	9.6	15.7 ± 0.4	14.5	9.3 ± 0.5	8.7
	F2	2.5 ± 0.2	12.0	3.4 ± 0.2	15.9	5.8 ± 0.3	5.7	7.2 ± 0.2	7.0	3.5 ± 0.3	3.3	6.1 ± 0.4	5.7
	F3	1.7 ± 0.2	8.2	2.0 ± 0.1	9.4	4.2 ± 0.2	4.2	7.4 ± 0.3	7.2	3.8 ± 0.1	3.5	14.7 ± 0.3	13.7
	F4	7.2 ± 0.4	34.6	7.6 ± 0.3	35.7	80.5 ± 1.5	79.8	78.1 ± 2.3	76.2	85.1 ± 1.1	78.7	77.2 ± 0.7	71.9

Table 3 contd.

Metal	Fraction	Content in bottom sediment				Content in sewage sludge				Content in reference material			
		"Tessier"		"BCR"		"Tessier"		"BCR"		"Tessier"		"BCR"	
		[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]
Cd	F1	1.3 ± 0.2	52.0	0.7 ± 0.2	29.2	1.7 ± 0.1	20.8	0.9 ± 0.1	11.8	2.7 ± 0.2	44.3	1.1 ± 0.1	18.6
	F2	0.4 ± 0.1	16.0	0.3 ± 0.1	12.5	3.2 ± 0.3	39.0	1.4 ± 0.2	18.4	1.8 ± 0.1	29.5	2.9 ± 0.2	49.2
	F3	0.3 ± 0.1	12.0	0.6 ± 0.1	25.0	1.1 ± 0.1	13.4	3.7 ± 0.3	48.7	0.7 ± 0.1	11.5	1.2 ± 0.3	20.3
	F4	0.5 ± 0.1	20.0	0.8 ± 0.2	33.3	2.2 ± 0.2	26.8	1.6 ± 0.1	21.1	0.9 ± 0.2	14.7	0.7 ± 0.1	11.9
Cr	F1	0.3 ± 0.1	14.3	0.4 ± 0.1	16.0	3.8 ± 0.2	1.0	4.2 ± 0.4	1.1	5.4 ± 0.3	7.7	3.4 ± 0.2	4.8
	F2	0.5 ± 0.1	23.8	0.4 ± 0.1	16.0	10.6 ± 0.3	2.7	9.0 ± 0.3	2.2	8.1 ± 0.2	11.5	4.5 ± 0.1	6.4
	F3	0.7 ± 0.2	33.3	0.9 ± 0.1	36.0	272 ± 4	69.8	302 ± 9	74.3	37.3 ± 0.3	53.1	42.5 ± 0.5	60.3
	F4	0.6 ± 0.1	28.6	0.8 ± 0.1	32.0	103.1 ± 5.2	26.5	91.1 ± 3.2	22.4	19.4 ± 0.4	37.7	20.1 ± 0.7	28.5

Fraction: F1 – exchangeable and carbonates-bound, F2 – Fe/Mn oxides-bound, F3 – organic matter/sulfides-bound, F4 – residual.

sediment were obtained, as well as in iron and manganese oxides and organic-sulfide fraction of the sewage sludge.

Obtainment of different results depending on the applied method is also confirmed by other research [10, 15, 39]. The reason for discrepancies in the obtained results can be both used different extractants, and conditions of conducting the extraction (temperature and time period). The characteristics of reagents used in the procedures of sequential extraction with critical justification for their utilization were presented by Gleyzes et al [9]. The Authors stated among others that due to different solubility of each metal carbonates, their release may be incomplete and continued in next step. In the procedure according to Tessier, this inconvenience can be corrected with the usage of sodium acetate solution with  $\text{pH} = 4.74$ , and ensuring the material-solution ratio 1:25, moreover by increasing the time of the extraction. In case of iron and manganese oxides fraction, with high iron content, there may occur incomplete dissolution of oxides (lowering the metal content in this fraction), or organic metal complexes may be extracted, which cover iron oxides (raising the content). Some of the sequential extraction procedures enable dividing this fraction into: easily reducible (Mn(III)/(IV) oxides), medium-reducible (amorphous Fe(III) oxides), and hardly reducible (crystalline Fe(III) oxides) [2]. The efficiency of the extractant depends on its reducing capabilities expressed by the value of redox potential ( $E_h$ ). Hydroxylamine is a preferred extractant, with  $E_h = -1.87$  V as a solution in 25% acetic acid.

Oxidizing reagents used for heavy metal extraction from organic fraction may also lead to sulfide oxidation, which is why this fraction is also often called organic-sulfide (introduction of ammonium acetate prevents readsorption of released metal ions). However oxidation of organic matter resistant to high temperatures may not occur. As the oxidant, 30%  $\text{H}_2\text{O}_2$  is the most often used, acidified to  $\text{pH} = 2.0$  with nitric acid. This reagent additionally causes the oxidation of metal sulfides. Elevated temperature favours the decomposition of organic matter. Solution of sodium chlorate (I)  $\text{NaClO}$  ( $\text{pH} = 8.5-9.5$ ) or potassium pyrophosphate  $\text{K}_4\text{P}_2\text{O}_7$  ( $\text{pH} = 10$ ) is less commonly used.

The fraction of residue metals includes mainly metals embedded into the crystal lattice of primary and secondary minerals included in sludge. There are mainly metals of silicate and aluminosilicate minerals, as well as metals which have not been extracted in earlier stages of the sequential extraction. Under natural conditions, this metals can be considered as permanently immobilized.

In order to extract the metals, the crystal lattice of stable minerals must be destroyed by means of concentrated solutions of inorganic acids ( $\text{HClO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ) or their mixtures at elevated temperature, however the decomposition of silicate minerals takes place in the presence of  $\text{HF}$  acid.

Total heavy metal content determined after mineralization of the analysed bottom sediment and sewage sludge using a mixture of concentrated acids: nitric and hydrochloric, and the total calculated based on determined quantities in each chemical fractions are presented in Table 4.

The heavy metal content obtained by adding their amount in each chemical fractions of the bottom sediment, the sewage sludge and the certified material, determined both after the extraction with the procedure according to the Tessier, and the BCR procedure,



Table 4

Total content of heavy metals in sewage sludge, bottom sediment and certified reference material

Material	Metal	Total content [mg/kg]	$\Sigma F1 + F2 + F3 + F4$ (extraction "Tessier")		$\Sigma F1 + F2 + F3 + F4$ (extraction "BCR")	
			Content [mg/kg]	Recovery [%]	Content [mg/kg]	Recovery [%]
Bottom sediment	Zn	55.9 ± 2.1	60.2	107.7	57.4	102.7
	Cu	4.6 ± 0.5	4.2	91.3	4.4	95.6
	Ni	21.4 ± 0.3	22.9	107.0	23.2	108.4
	Pb	22.2 ± 0.4	20.8	93.7	21.3	95.9
	Cd	2.1 ± 0.2	2.5	119.0	2.4	114.3
	Cr	2.2 ± 0.3	2.1	95.5	2.5	113.6
Sewage sludge	Zn	2863 ± 22	2640	92.2	2704	94.4
	Cu	309.0 ± 8.1	298.6	96.6	304.4	98.5
	Ni	204.0 ± 7.4	192.0	94.1	186.9	91.6
	Pb	109.1 ± 5.2	100.9	92.5	102.5	94.0
	Cd	7.7 ± 0.5	8.2	106.5	7.6	98.7
	Cr	431.0 ± 11.2	389.5	90.4	406.3	94.3
Certified reference material LGC6181	Zn	1100 ± 50	1077	97.9	1056	96.0
	Cu	354.0 ± 18.0	319.4	90.2	323.0	91.2
	Ni	45.0 ± 3.0	48.0	106.7	42.7	94.9
	Pb	105.0 ± 8.0	108.1	102.9	107.3	102.2
	Cd	5.8 ± 0.3	6.1	105.2	5.9	101.7
	Cr	78.0 ± 8.0	70.2	90.0	70.5	90.4

did not differ significantly from content determined after direct mineralization with a mixture of concentrated acids  $\text{HNO}_3$  and  $\text{HCl}$ . Total content of zinc, copper, nickel and lead in four analyzed fractions amounted to 91–108%, whereas cadmium and chromium 90–119% of their total quantity. This proves the correctness of applied research methodology and the credibility of the obtained results [32, 40]. The best compatibility of total metal content and the sum in individual fractions was obtained for lead in the bottom sediment, copper in the sewage sludge, and zinc and lead in the certified material.

## Conclusions

Analysis of heavy metal chemical forms in an examined material depends on the amount of stages of used method, type and concentration of reagents, extraction conditions (temperature, time period, pH). Used sequential extraction procedures refer to group metal discharge and not always are selective with regard to particular heavy metals. The choice of suitable extraction method is important, depending on the purpose of conducted speciation analysis and analyzed chemical forms of heavy metals. It is also

crucial to strictly follow the extraction conditions and to compare the results obtained with the same extraction procedure for heavy metal fractionation.

During the conducted research, different proportion of certain chemical forms of heavy metals in their total content in the bottom sediment, the sewage sludge and the certified material, was obtained, depending on the applied extraction procedure (Tessier, BCR). The discrepancy of the obtained results referred mainly to zinc and cadmium, to a lesser extent to copper and chromium. While a high correspondence of the total metal content in particular fractions with total content determined after direct mineralization was observed.

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### FRAKCJONOWANIE METALI CIĘŻKICH W OSADACH DENNYCH I ŚCIEKOWYCH Z UŻYCIEM EKSTRAKCJI SEKWENCYJNEJ

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**Abstrakt:** W celu określenia form chemicznych metali ciężkich w osadach dennych, czy też w osadach ściekowych wykonuje się analizę specjacyjną opartą na ekstrakcji sekwencyjnej, która polega na stopniowym wydzielaniu metali z osadów roztworami o wzrastającej agresywności. Szerokie uznanie zdobyła pięciostopniowa ekstrakcja zaproponowana przez Tessiera i współpracowników, której zastosowanie umożliwia wydzielenie metali wymiennalnych, związanych z węglanami, z uwodnionymi tlenkami żelaza i manganu, z materią organiczną oraz pozostałych. Za mobilne uważa się metale występujące w dwóch pierwszych frakcjach (wymiennej i węglanowej). W wyniku prowadzonych prac w ramach Programu Pomiarów i Testowania w Komisji Unii Europejskiej przyjęto skróconą, trzy etapową ekstrakcję, znaną jako procedura BCR.

Przeprowadzono porównawcze badania frakcjonowania metali ciężkich (Zn, Cu, Ni, Pb, Cd, Cr), wykorzystując ekstrakcję sekwencyjną stosowaną przez Tessiera oraz procedurę BCR. Materiałem badawczym były: materiał certyfikowany LGC 6181, osad ściekowy pochodzący z mechaniczno-biologicznej oczyszczalni ścieków komunalnych w Częstochowie oraz osad denny pobrany ze zbiornika zaporowego Poraj. Porównując wyniki, stwierdzono różny udział określonych form chemicznych metali ciężkich w całkowitej ich zawartości w badanych próbkach w zależności od zastosowanej procedury ekstrakcji. Dla materiału certyfikowanego rozbieżności dotyczyły głównie zawartości kadmu we frakcji wymiennie-węglanowej oraz tlenków żelaza i manganu, cynku we frakcji pozostałościowej (związków praktycznie nierozpuszczalnych). Również w osadzie ściekowym i osadzie dennym zawartość kadmu oznaczona we frakcjach wymiennie-

-węglanowej, organiczno-siarczkowej oraz związków praktycznie nierozpuszczalnych po ekstrakcji metodą Tessiera nie pokryła się z wartościami uzyskanymi po ekstrakcji metodą BCR. Dotyczyło to także zawartości cynku i ołowiu we frakcji tlenków żelaza i manganu. Przyczynami rozbieżności uzyskanych wyników mogły być zarówno użyte ekstrahenty, jak i warunki prowadzenia ekstrakcji (różne reagenty, temperatura i czas). Potwierdza to, jak ważny jest dobór odpowiedniej metody ekstrakcji w zależności od celu prowadzonej analizy specjacyjnej i analizowanych form chemicznych metali ciężkich.

**Słowa kluczowe:** metale ciężkie, procedury ekstrakcji sekwencyjnej, osad denny, osad ściekowy

