X-ray Fluorescence Spectrometry in Speciation Analysis of Bottom Sediments

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Abstract

This paper presents results of speciation analysis of bottom sediments. In our examinations a five-step extraction procedure was applied. Direct analysis of sediments and analysis of extracts was carried out by X-ray fluorescence spectrometry with wavelength dispersion. Examinations were carried out with the use of lake sediments CRM.

Keywords: speciation analysis, XRF, sediments, CRM

Introduction

In a widely understood analysis of the environment there exists a need to determine not only total concentrations of elements in examined samples, but also concentrations of various forms in which these element could exist. Speciation analysis gives us answers to such questions. Speciation plays a very important role in chemical analysis and in particular concerns about samples connected with environmental analysis (sediments, soils, waters).

In natural water environment elements exist in dynamic equlibrium state in system water - sediment. Mobility of these elements depends on many processes such as sedimentation, sorption, desorption, complexation, which next depend on such agents as: pH, redox potential, conent of organic matter, Fe and Mn oxides, properities of surface, influence of living organisms (bacteria, algae, water plants) **[1-7].**

Bioavailability and influenece of elements accumulated in bottom sediments depends on their physico-chemical forms. In sediments they can exist in ionic form, as organically bound, as coprecipitated with carbonates, phosphates, adsorbed on oxid surface or as ions closed in crystal stucture of minerals [8].

Examination of element distribution in sediment is very important, because in environmental conditions this material can accumulate or release them [9].

Various methods for analysis of element speciation in solid samples have been proposed. One of them is a method applying models of thermodynamic speciation equlibrium based on the knowledge of total concentrations of each element, the major complexing ligands and the thermodynamic stability constants [9, 10]. Direct methods of speciation analysis in solid samples are NMR and IR [9], applied only by a suitably high concentration of analites. Most often, indirect methods must be used, of which one of the most popular is chemical extraction, where samples are treated with various reagents to separate examined elements from the matrix.

To affirm elements which could exist in sediments involves single and sequential extraction procedures. Procedures of sequential extraction give us much more information than these single; besides, they fulfill the conditions in natural environment and could be used for estimating of the potential remobilization of elements under

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Table 1. Parameters of measurement program.

Lp.	Element	Crystal	Collimator	Detector	kV	mA
1	Sb	LiF200	150 µm	Scintillation	60	50
2*	Sn, Cd	LiF200	150 µm	Scintillation	60	50
3	Zn	LiF200	150 µm	Scintillation	60	50
4	Sr, Pb	LiF200	150 µm	Scintillation	60	50
5	Rb, Br	LiF200	150 µm	Scintillation	60	50
6	Ni, Cu	LiF200	150 µm	Flow	60	50
7	Fe, Co	LiF200	150 µm	Flow	60	50
8	Cr, Mn	LiF200	150 µm	Flow	60	50
9	V	LiF200	150 µm	Flow	60	50
10	Ca	LiF200	150 µm	Flow	40	75
11	K, S	LiF200	150 µm	Flow	40	75
12	Si, Cl	PE002	550 µm	Flow	40	75
13	Al, P	PE002	550 µm	Flow	40	75
14	Na, Mg	PX1	550 µm	Flow	40	75

* For Sn and Cd brass (300 µm) tube filter was used.

changing environmental conditions. Sequential procedures of extraction were described by many authors, but the most common was Tessier's method and many of its modification [11-25]. As extraction solvents one can use neutral electrolytes ($CaCl_2$, $MgCl_2$), buffers of weak acids, chelating agents (EDTA or DTP A), redox compounds (NH_2OH), strong acids, or bases.

Obtained extracts are examined with methods designed for mutielement analysis, like for instance AAS [26-29], ICP-OES, ICP-MS [30], DPCSV, SEM-EDX, ICP-AES [31-33]. The XRF method was used only for analysis of residue after extraction [34].

Experimental Procedures

Apparatus

In examination we used a Philips PW 2400 X-ray fluorescence spectrometer with wavelength dispersion and a Hermle centrifuge.

Materials

Bottom sediments from 3 lakes of Wielkopolski Park Narodowy: Lodzko - Dymaczewskie (sample 1-5), Witobelskie (sample 6) and Goreckie (sample 7-10) were analysed. Samples were collected from various depths: 4.2 m - (sample 1), 7 m - (sample 2), 8m- (sample 3), llm- (sample 4), 8 m - (sample 5), 3.1 m - (sample 6), 17 m - (sample 7), 6.5 m - (sample 8), 14 m - (sample 9), and 6.5 m - (sample 10), were dried and sifted (fraction 200 µm).

Standard solutions were used: Fe, Mn, Ni, Cu, Zn, Pb, Cd and Si of concentration 1 mg/ml (Merck), HNO3 cz.d.a., NaOH cz.d.a., HCl cz.d.a, NH_2OHHCl cz.d.a. and NH_4OAc cz.d.a. (POCh).
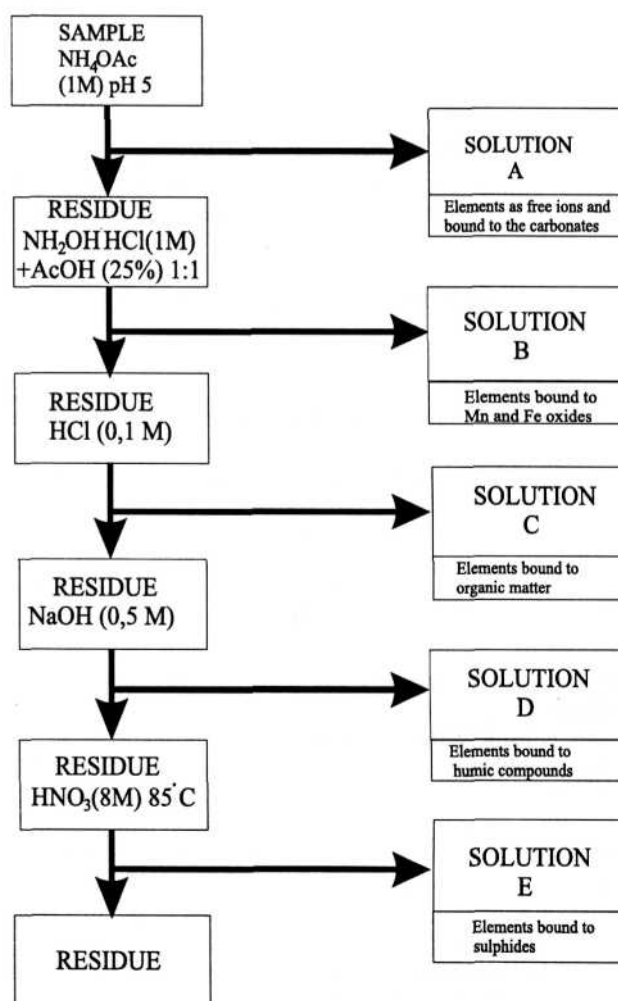

Fig. 1. Scheme of extraction procedure of bottom sediments

Methods

Samples of sediments were ground in mill with input of silicon carbide for 10 minutes at 30 rot/min, next 1 g of sample was tableted under 15 t/cm^2 pressure and direct XRF analysis was carried out.

The samples after 5 degree extraction were also examined. The scheme of this extraction procedure [13] was shown in Fig. 1.

Parallely the blank test was carried out - vessel contained only used reagents. Concentrations of elements in extracts (solutions A-E - see Fig. 1) were analysed by XRF using the hel arrangement, which is used to analyse liquid samples.

Examinations were made on the basis of measurement program, whose parameters are shown in Table 1.

Si, Al., Na, Fe, Ca, K, Mg, S, P (macroelements), Zn, Br, Rb, Mn, Pb, Sr, Cu, Cd, Ni (microelements) were analysed in examined sediments and their extracts. Examinations were carried out on the basis of calibration curves which were made with the use of certified reference materials: CRM of lake sediments LKSD-1 and LKSD-2. Correction for mutual multi-element interactions was calculated for calibration curves. For Na, Cu, Zn, Ni, Sr determination the α factor to correct the effect of Fe was introduced, for Mg determination α correction factor to correct the effect of Na, for Al., Si, Br determination α factor to correct the effect of Zn, for P, S, K α factor to correct the effect of Si, for Ca to correct the effect of K, for Fe, Rb and Pb to correct effect of Cu.

In Table 2 regression parameters of analytical curves for analysed elements are gathered.

Table 2. Regression parameters of analytical curves for liquid (a) and solid (b) standards.

	(a)	(b)
Na	y = 0.521 x + 0.038	y = 0.611 x + 0.281
Mg	y = 0.933 x – 0.146	y = 0.521 x + 0.358
Al	y = 1.441 x + 0.476	y = 0.823 x + 1.167
Si	y = 1.731 x + 0.042	y = 0.921 x + 0.998
S	y = 1.118 x + 0.426	y = 0.628 x + 2.118
K	y = 4.027 x + 0.041	y = 2.542 x – 1.321
P	y = 2.222 x + 0.683	y = 1.098 x + 0.687
Ca	y = 2.801 x – 0.042	y = 1.364 x + 1.284
Fe	y = 2.055 x – 0.492	y = 1.368 x + 0.987
Mn	y = 0.009 x + 0.021	y = 0.004 x + 0.211
Ni	y = 0.014 x + 0.229	y = 0.006 x – 0.110
Cu	y = 0.020 x + 0.257	y = 0.005 x + 0.620
Zn	y = 0.093 x + 0.037	y = 0.060 x + 0.810
Br	y = 0.191 x + 0.063	y = 0.100 x + 0.280
Rb	y = 0.273 x – 0.270	y = 0.170 x – 0.320
Sr	y = 0.232 x + 0.093	y = 0.162 x + 0.820
Cd	y = 0.009 x – 0.011	y = 0.004 x + 0.130
Pb	y = 0.061 x – 0.017	y = 0.048 x + 0.089

Results of direct analysis of sediment samples obtained by calibration curves are presented in Table 3. Statistical evaluation of results for a chosen fraction of sample 2 in Table 4 are gathered. Results of extract analysis (A, B, C, D, E) are presented in a graphic form in Figs. 2.1, 2.2., 2.3., 3, 4.1., 4.2.

A chosen X-ray spectrum of sample 1 is shown in Fig. 5.

Results and Discussion

Analysis of the data obtained in direct analysis of bottom sediments shows increased concentrations of Ca, Al, Fe, Mn and Zn with the increase of depth sampling and decrease of concentration of P, which could be connected with its uptake by water plants and microorganisms which occur in bottom sediments. Increase of concentration of Ca in sediments may be connected with accumulation of leftovers of animal skeletons, but in Lodzko-Dymaczewskie Lake we can see the decrease of concentration of Ca. There is an observed correlation between concentrations of Al, Fe, Mn and Zn.

Results of distribution speciation analysis (announced in % of element concentration in fraction with reference to the total concentration of element in sample):

Mg in all samples occurs mainly in carbonate fraction (20-60%) and in residue, the other fractions bound Mg to a small extent (20%). More commonly it is a fraction of oxides, sulphides and organic matter.

Phosporus in bottom sediments is mainly in residue (80-90%) and in small amounts occurs in fractions of humic compounds, carbonate and oxides (samples 3, 5, 9 - 20-30%). These fractions could be considered as a potential source of this element for plants and microorganisms. In a residue P occurs in the form of phosphates. With the increase of depth sampling small increase of P participation in fractions: carbonate, oxides, humic compounds and sulphides is observed.

Potassium was found mostly in the residue after extraction(70-90%) in the form of aluminosilicates and phosphates, to a small extent we can meet it in fraction: carbonate, oxides, sulphides and humic compounds. In Lodzko-Dymaczewskie Lake with the increase of the depth sampling increases K concentration in fraction of carbonate and decreases in fraction of oxides and sulphides. In Goreckie Lake increases K concentration in fraction of sulphides and decreases in fraction of oxides and carbonates.

Aluminium was found mostly in the residue (80-95%), but in some samples for instance 3, 4, 6, 8-10 Al occures in fraction of humic compounds and in sample 5 in fraction of organic matter too. Al included in these fractions under changing environmental conditions for instance under the influence of microorganisms, could be released in the ecosystem, but in general Al is in a form of alumininosilicates and doesn't pose potential danger.

Calcium in examined sediments occures in fractions of carbonates (40-85%), oxides (10-49%) and in the residue (5-15%). So Ca is an element which could be released as a result of changes in the environment (pH, redox potential). In Lodzko-Dymaczewskie Lake with the increase

Table 3. Results of direct analysis of sediment samples obtained by calibration curves (for n = 6).
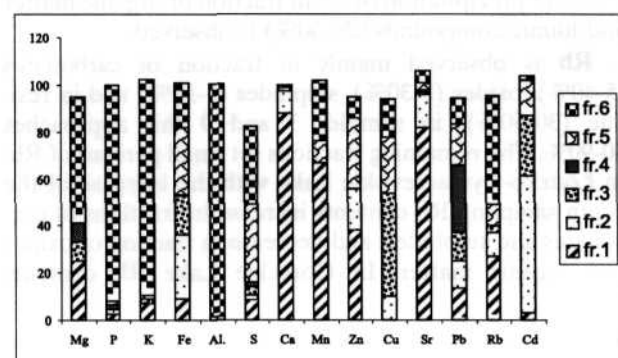
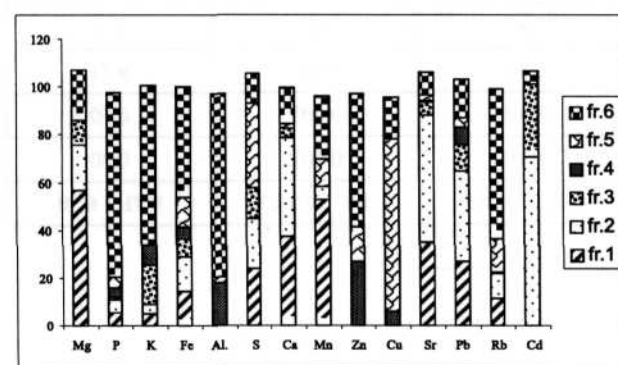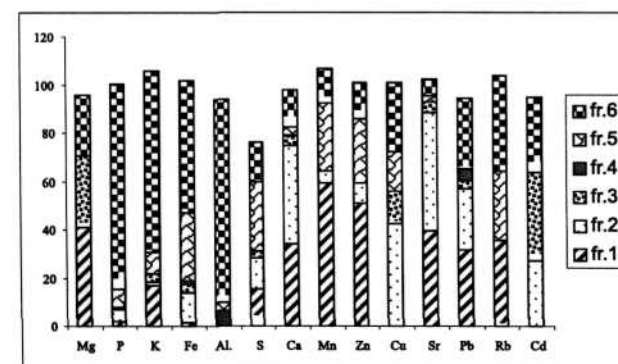| Sample	Na	Mg	Al	Si	P	S	K	Ca	Fe	Mn	Ni	Cu	Zn	Br	Rb	Sr	Pb	Cd
	mg/g										µg/g							
LKSD-1	11.41 ± 0.15	8.28 ± 0.24	35.84 ± 1.13	175.27 ± 1.05	0.79 ± 0.02	14.77 ± 0.21	8.03 ± 0.15	70.58 ± 0.08	20.97 ± 0.35	557.60 ± 7.50	11.7 ± 0.60	32.5 ± 0.80	279.8 ± 0.60	8.54 ± 0.15	19.4 ± 0.47	228.1 ± 2.5	68.9 ± 0.50	0.90 ± 0.09
Certified value	14.84	10.25	41.23	187.47	0.87	15.70	9.13	77.19	28.67	700	16	44	331	11	24	250	82	1.20
LKSD-2	13.59 ± 0.84	10.60 ± 0.1	65.17 ± 3.20	268.46 ± 2.68	1.38 ± 0.01	1.68 ± 0.07	21.29 ± 0.1	16.50 ± 0.10	38.90 ± 0.55	2068.76 ± 15.51	29.5 ± 1.45	37.2 ± 1.40	210.5 ± 3.70	11.80 ± 0.84	83.8 ± 0.71	211.6 ± 0.8	39.5 ± 1.40	0.8 ± 0.05
Certified value	14.10	10.25	65.12	275.36	1.31	1.40	21.58	15.72	43.36	2020	26	37	209	18	85	220	44	0.8
1	0.80 ± 0.08	1.65 ± 0.015	3.57 ± 0.17	22.62 ± 1.10	1.11 ± 0.09	5.99 ± 0.19	1.98 ± 0.02	165.05 ± 0.40	2.83 ± 0.03	381.01 ± 0.45	25 ± 1.20	13 ± 0.40	30 ± 1.50	8.0 ± 0.4	20 ± 0.49	236.7 ± 2.06	58 ± 1.10	9 ± 0.10
2	1.01 ± 0.10	1.77 ± 0.02	4.88 ± 0.29	41.90 ± 2.85	1.19 ± 0.06	7.87 ± 0.31	2.91 ± 0.02	157.42 ± 4.70	8.06 ± 0.09	365.36 ± 2.20	22 ± 1.10	19 ± 0.57	52 ± 1.90	6.8 ± 0.28	30 ± 0.61	229.6 ± 2.13	45 ± 1.12	10 ± 0.12
3	0.75 ± 0.08	1.57 ± 0.05	4.12 ± 0.18	49.69 ± 2.23	1.13 ± 0.06	8.18 ± 0.30	1.95 ± 0.01	151.08 ± 3.40	5.22 ± 0.08	457.35 ± 3.17	25 ± 1.20	13 ± 0.40	56 ± 2.1	9.7 ± 0.46	32 ± 0.64	292 ± 2.67	52 ± 0.97	9 ± 0.11
4	0.67 ± 0.06	1.40 ± 0.03	3.78 ± 0.23	84.42 ± 5.06	1.17 ± 0.03	8.67 ± 0.29	1.67 ± 0.07	130.19 ± 2.50	5.42 ± 0.02	442.37 ± 1.02	24 ± 1.20	14 ± 0.36	51 ± 1.80	59 ± 1.47	18.3 ± 0.43	259.3 ± 2.32	50 ± 1.10	7.5 ± 0.09
5	0.77 ± 0.07	1.58 ± 0.04	4.49 ± 0.30	58.56 ± 2.34	1.12 ± 0.07	9.08 ± 0.1	2.15 ± 0.05	145.14 ± 1.05	5.94 ± 0.11	454.19 ± 1.42	22 ± 1.10	11 ± 0.28	53 ± 1.90	41 ± 1.18	30 ± 0.67	174 ± 1.56	52 ± 0.98	7.6 ± 0.08
6	1.08 ± 0.09	1.76 ± 0.03	6.24 ± 0.35	44.53 ± 0.90	1.27 ± 0.05	7.57 ± 0.4	3.36 ± 0.02	165.88 ± 4.10	5.15 ± 0.02	328.04 ± 0.50	20 ± 1.0	20 ± 0.60	89 ± 2.40	6.5 ± 0.14	40 ± 0.45	223.8 ± 2.12	48 ± 1.56	8.5 ± 0.10
7	2.52 ± 0.17	3.85 ± 0.11	22.40 ± 1.68	136.09 ± 1.50	1.58 ± 0.03	4.71 ± 0.3	12.77 ± 0.25	115.45 ± 5.10	14.77 ± 0.22	660.68 ± 2.24	24 ± 1.20	18 ± 0.54	67 ± 2.1	70 ± 4.20	54.6 ± 0.56	133 ± 1.78	72 ± 2.12	7.5 ± 0.09
8	3.25 ± 0.17	3.46 ± 0.06	11.74 ± 0.78	142.36 ± 2.85	0.62 ± 0.02	4.65 ± 0.21	9.50 ± 0.11	82.34 ± 3.20	5.39 ± 0.04	249.90 ± 7.5	15 ± 0.08	13 ± 0.40	42 ± 1.34	103 ± 5.50	53 ± 0.53	180 ± 1.90	27 ± 1.60	4 ± 0.08
9	2.15 ± 0.14	3.84 ± 0.18	21.05 ± 1.47	134.20 ± 1.40	0.89 ± 0.1	4.19 ± 0.07	12.53 ± 0.90	107.28 ± 1.50	12.25 ± 0.09	434.94 ± 1.33	23 ± 1.15	9.8 ± 0.34	52 ± 1.70	327 ± 14.71	45 ± 0.48	108.2 ± 0.9	26 ± 1.80	5.8 ± 0.07
10	3.11 ± 0.16	1.19 ± 0.04	9.42 ± 0.60	200.70 ± 9.03	0.39 ± 0.04	1.09 ± 0.06	8.81 ± 0.34	9.10 ± 0.35	1.64 ± 0.09	84.44 ± 1.12	7.6 ± 0.05	9.8 ± 0.36	8.5 ± 0.31	71 ± 2.70	45 ± 0.49	63 ± 0.78	49 ± 1.68	2 ± 0.10
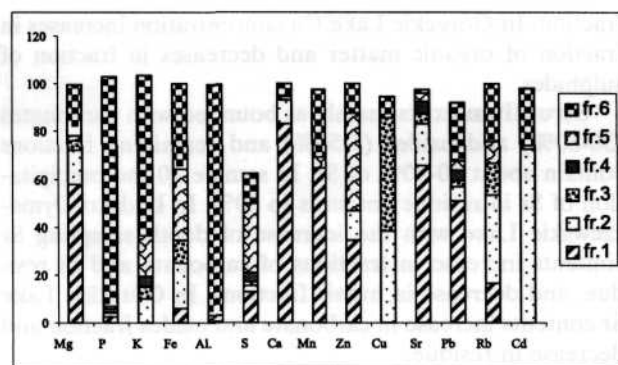
Sample 1, from the depth 4.2 m
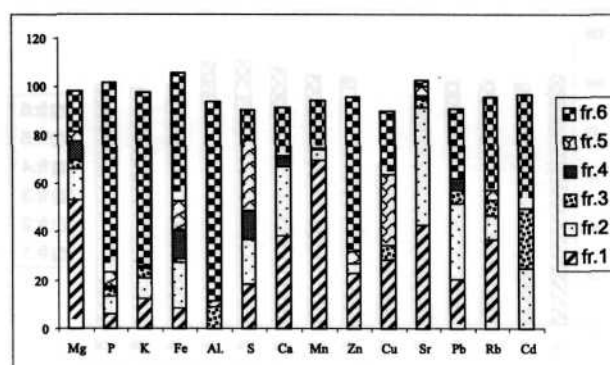
Sample 5, from the depth 8 m

Fig. 2. Distribution of elements over various fractions in sediments from Lodzko - Dymaczewskie Lake.

Sample 2, from the depth 7 m

Sample 3, from the depth 8 m
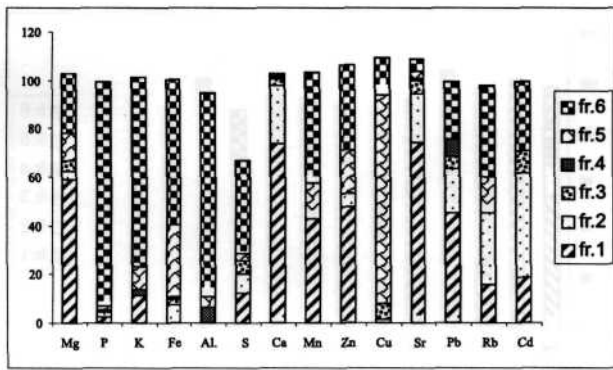

Sample 4, from the depth 11 m

of depth sampling increases Ca concentration in fractions of oxides, organic matter and sulphides, and decreases in fraction of carbonates. In Goreckie Lake Ca concentration decreases in fraction of humic compounds.

Sulphur in examined sediments occurs in residue (4-40%) and in sulphide fractions (3-35%). In Lodzko-Dymaczewskie Lake with the increase of depth sampling increases sulphur concentration in fraction of carbonates and oxides. In Goreckie Lake increases sulphur concentration in the residue and sulphide fraction, and decreases in fraction of carbonates and oxides. In samples 1, 2, 6, 7, 8, 10 we couldn't arrive at sulphur content of 100% after adding the amount of sulphur in all fractions. Connected with this is the fact that some compounds of sulphur in acid environment were undergone to H_2S and SO_2. This means that in examined sediments exists acid volatile sulphur (AVS).

Iron in sediments occured mainly in residue after extraction (30-60%), in fraction of sulphides (10-50%) and of oxides (15-30%), sometimes in fraction of organic and humic compounds (max. 10%). This element occuring mainly in fraction of sulphides and in residue is low toxic and weakly bioavailable for living organisms. In Lodzko-Dymaczewskie Lake with the increase of the depth sampling increases Fe concentration in fraction of sulphides. In Goreckie Lake increases Fe concentration in the residue and decreases in fractions of carbonates, sulphides and humic compounds.

Manganese was found mainly in fractions of carbonate (40-80%) and in residue (10-50%), in small amounts in fraction of sulphides and oxides. In Lodzko-Dymaczewskie Lake with the increase of the depth sampling increases Mn concentration in fraction of sulphides, oxides and decreases in carbonate fraction. In Goreckie Lake increases Mn concentration in fraction of carbonate and sulphides and decreases in residue.

The greatest amount of Zn was observed in residue (25-60%), in samples 3, 5, 6, 8-10. The rest is accumulated in fractions of carbonate, humic compounds and sulphides. In samples 1, 2, 4, 7 the main part of Zn is in fractions: carbonates (30-50%), sulphides (10-40%) and oxides (5-30%) as well as organic matter fraction in sample 7 (25%). In Lodzko-Dymaczewskie Lake with the increase of the depth sampling Zn concentration

Sample 6, from the depth 3.1 m

Fig. 3. Distribution of elements over various fractions in the sediment from Witobelskie Lake.

increases in fraction of carbonates and decreases in fraction of oxides.

Copper exists mainly in fraction of oxides (10-40%), organic matter (5-50%) and sulphides (15-80%). In some samples such as number 5 about 30% is in fraction of carbonates. In Lodzko-Dymaczewskie Lake with the increase of the depth sampling Cu concentration increases in sulphide fraction and decreases in organic compounds

fraction. In Goreckie Lake Cu concentration increases in fraction of organic matter and decreases in fraction of sulphides.

Strontium exists mainly as bounded with carbonates (30-80%) and oxides (5-50%) and remaining fractions contain about 10-30% of Sr. In sample 10 the precipitation of Sr in residue amounts to 60%. In Lodzko-Dymaczewskie Lake with the increase of depth sampling Sr contents increase in fractions of carbonate and in residue, and decrease in humic fractions. In Goreckie Lake Sr contents increase in carbonate and oxides fraction and decrease in residue.

Pb could be found mainly in fraction of carbonates (10-55%) and oxides (5-35%), in the case of sample 10 about 65% is found in residue. In some samples (2, 7-10) a certain precipitation of Pb in fraction of organic matter and humic compounds (20-30%) is observed.

Rb is observed mainly in fraction of carbonates (5-40%), oxides (5-30%), sulphides (5-30%) and in residue (30-50%), in samples 3 and 9 this approaches 80-90%. The remaining fractions set small percent of Rb. In Lodzko-Dymaczewskie Lake with the increase of the depth sampling Rb contents increase in fractions of carbonates and sulphides, and decrease in fraction of oxides and organic matter. In Goreckie Lake Rb contents

Table 4. Statistical evaluation of results for a first fraction of sample 2.

mg/ml					
	Mg	Al.	P	S	K	Ca
$\bar{x}$	0.157	0.03	0.03	0.10	0.02	9.71
S	0.006	0.002	0.002	0.005	0.003	0.50
S$\bar{x}$	0.002	0.001	0.001	0.002	0.001	0.20
L	0.157 ± 0.006	0.03 ± 0.002	0.03 ± 0.002	0.10 ± 0.005	0.02 ± 0.003	9.71 ± 0.50

µg/ml				
	Fe	Mn	Cu	Zn
$\bar{x}$	0.05	3.87	0.05	0.99
S	0.002	0.11	0.003	0.06
S$\bar{x}$	0.001	0.04	0.001	0.02
L	0.05 ± 0.002	3.87 ± 0.10	0.05 ± 0.003	0.99 ± 0.05

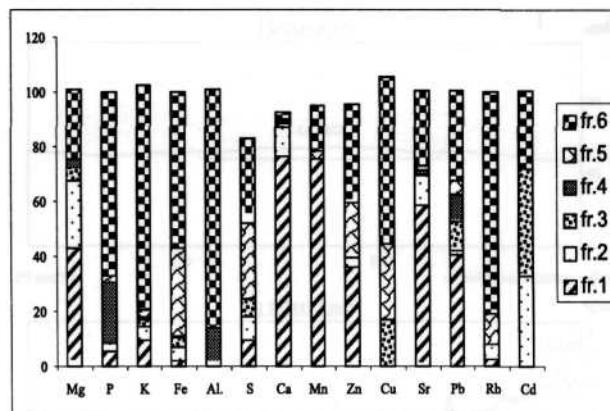| µg/ml				
	Rb	Sr	Cd	Pb
$\bar{x}$	1.15	10.36	0.16	11.14
S	0.08	0.41	0.01	0.91
S$\bar{x}$	0.03	0.17	0.004	0.37
L	1.15 ± 0.08	10.36 ± 0.40	0.16 ± 0.01	11.14 ± 0.90

x - mean value

S - standard deviation

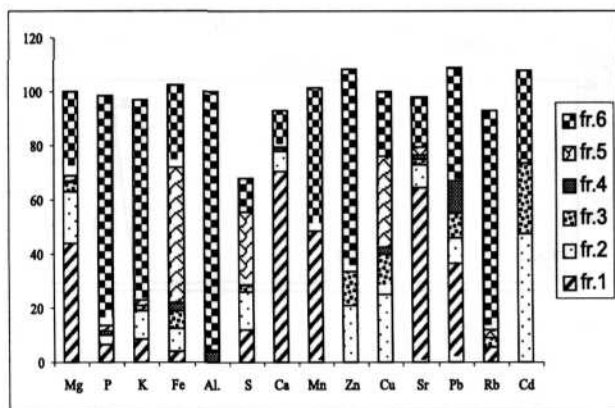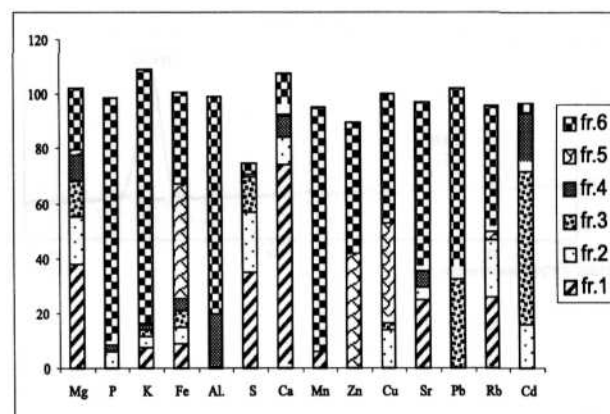Sx - standard deviation of mean value

L - confidence interval
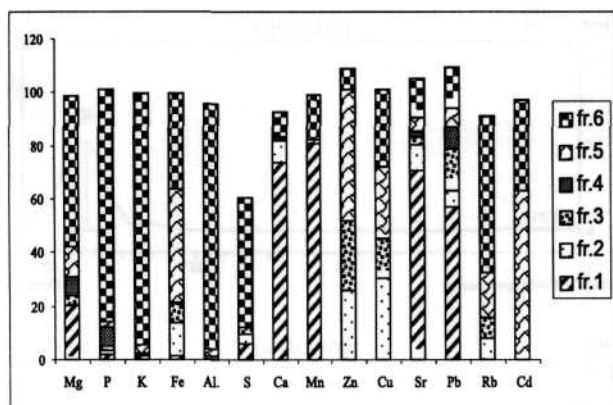
Sample 7, from the depth 17 m

Sample 9, from the depth 14 m

Sample 8, from the depth 6.5 m

Sample 10, from the depth 6.5 m

Fig. 4. Distribution of elements over various fractions in the sediments from Goreckie Lake.

increase in fraction of sulphides and decrease in carbonates fraction.

Cd exists mainly in oxides fraction (20-70%), organic matter (10-55%) and in residue (5-45%). In sample 7 the large concentration of Cd in sulphide fraction - about 60% is observed. In Lodzko-Dymaczewskie Lake with the increase of the depth sampling Cd contents increase in fraction of organic matter and decrease in oxides fraction. In Goreckie Lake Cd contents decrease in fraction of oxides, organic and humic compounds.

Summarizing the obtained results we can ascertain that thanks to application of the five-step extraction procedure fractions in which elements were bounded with carbonates, oxides of Mn and Fe, organic matter, humic compounds, sulphides and residue were obtained. The above procedure permits separating fractions of organic matter from inorganic fractions - sulphides, unlike to another generally used extraction procedures of Tessier [11, 12, 17 - 25]. On the basis of sequential analysis it was proved that Si, Al, P and K exist

mainly in residue after extraction, which indicates that these elements exist in form of alumininosilicates and pohosphates, don't undergo extraction with above-mentioned extraction solvents. Mg, Ca, Mn, Sr, Pb and Rb exist in carbonate fraction, Fe, Zn in residue, Cu and Cd in oxides fraction. With the increase of the depth sampling changes in fractional distribution of elements are observed.

Taking into account the fact that sediment samples come from an area of Wielkopolski Park Narodowy (legal protection of that area limits anthropogenic pollution) examined elements exist in natural form and in concentrations typical of the geochemical conditions existing in areas of low contamination. XRF applied in examination is suitable for distribution speciation analysis of sediments. Comparing the results obtained by XRF with results obtained by AAS [25] we can come to the conclusion that results from both methods and relating to bottom sediments from Lakes of Wielkopolska are in good agreement. XRF could find an application to multielement speciation analysis of bottom sediments.
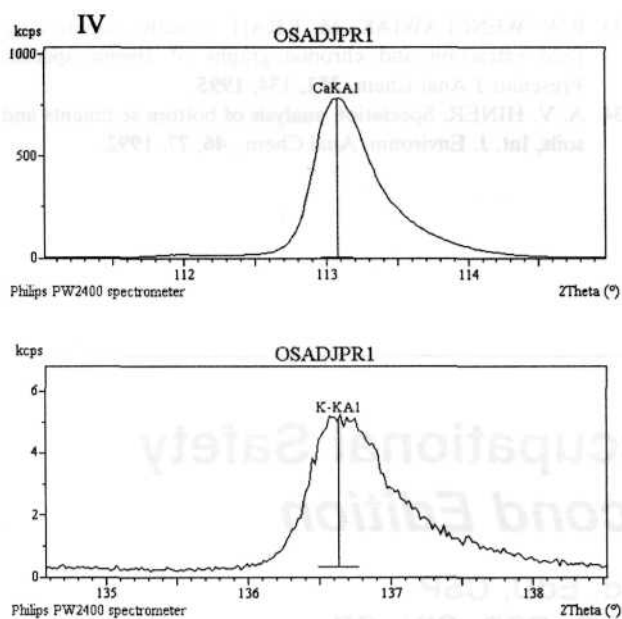
Philips PW2400 spectrometer
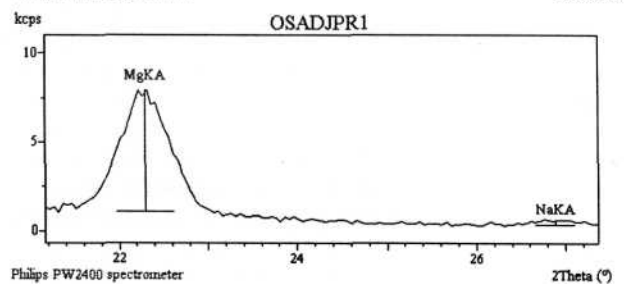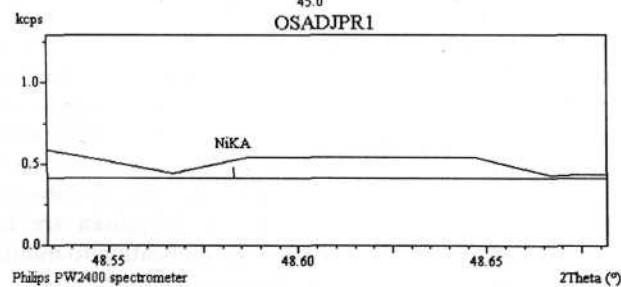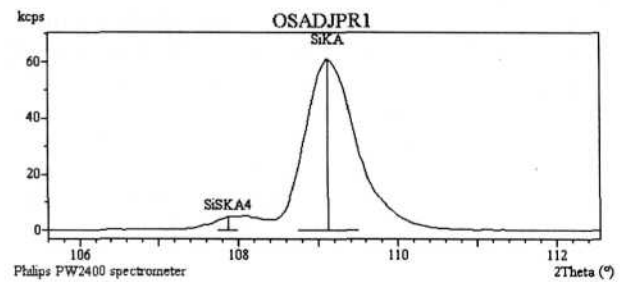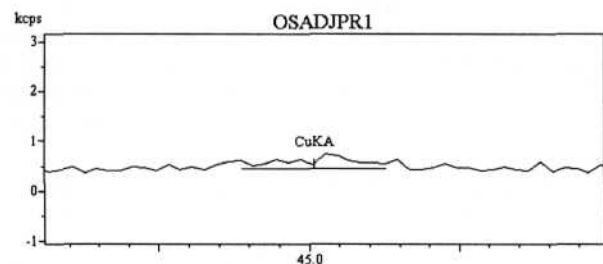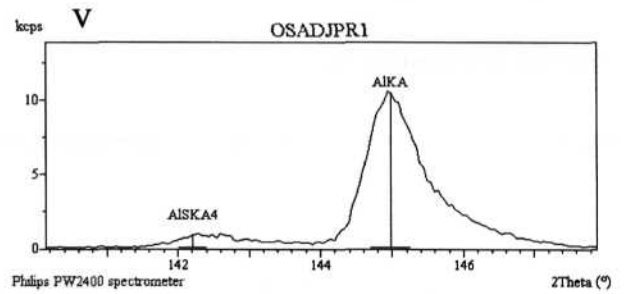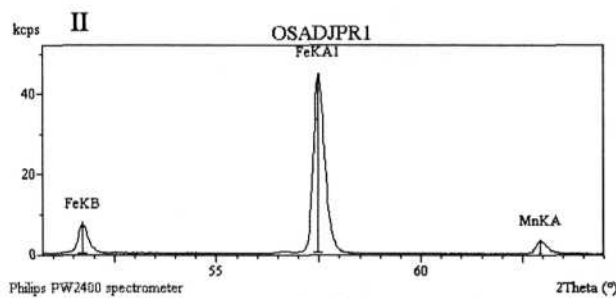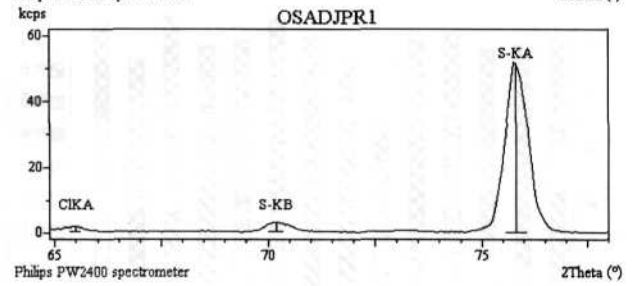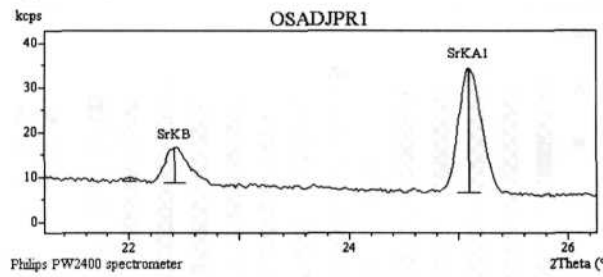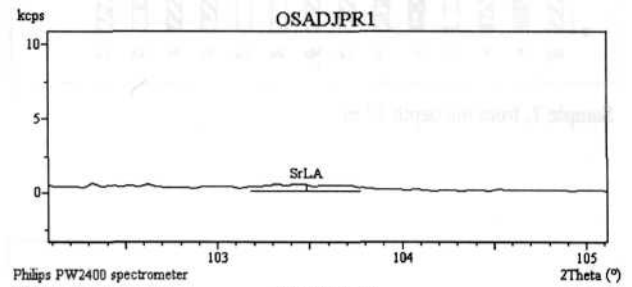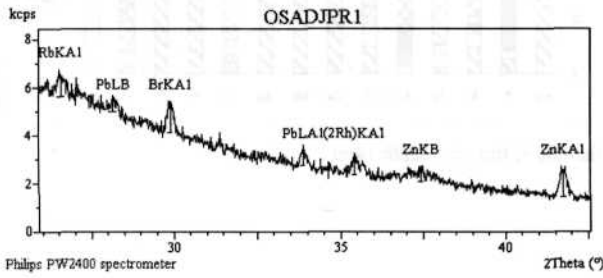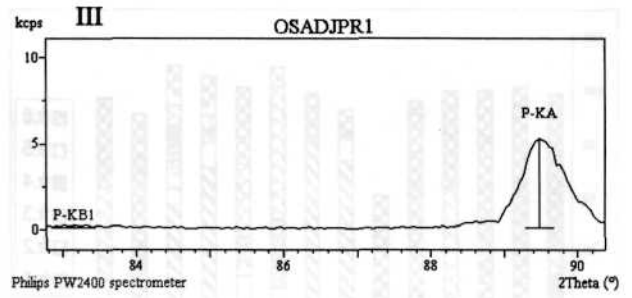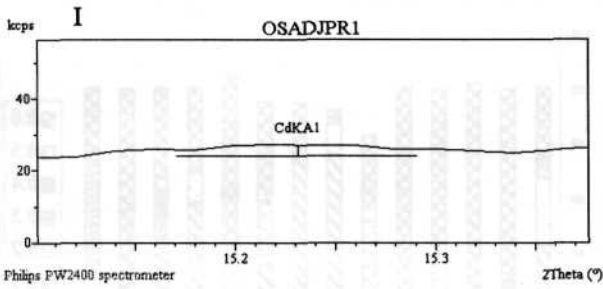
Fig. 5. X-ray spectrum for sediment sample 1 (from Lodzko-Dymaczewskie Lake) (I, II, **III**, IV, V).

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