

Metal(loids) Speciation Using HPLC-ICP-MS Technique in Klodnica River, Upper Silesia, Poland

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Abstract—The work allowed gaining knowledge about redox and speciation changes of As, Cr and Sb ionic forms in Klodnica River water. This kind of studies never has been conducted in this region of Poland. In study optimized and validated previously HPLC-ICP-MS methods for determination of As, Sb and Cr was used. Separation step was done using high-performance liquid chromatograph equipped with ion-exchange column followed by ICP-MS spectrometer detector. Preliminary studies included determination of the total concentration of As, Sb and Cr, pH, Eh, temperature and conductivity of the water samples. The study was conducted monthly from March to August 2014, at six points on the Klodnica River. The results indicate that exceeded at acceptable concentration of total Cr and Sb was observed in Klodnica River and we should qualify Klodnica River waters below the second purity class. In Klodnica River waters dominates oxidized antimony and arsenic forms, as well as the two forms of chromium Cr(VI) and Cr(III). Studies have also shown the methyl derivative of arsenic's presence.

Keywords—Antimony, arsenic, chromium, HPLC-ICP-MS, river water, speciation.

I. INTRODUCTION

THE study of trace amounts of analytes, particularly in samples with the complex matrix requires the use of complicated and sophisticated analytical methods and techniques. The latest trends in this field are hyphenated techniques in which separation methods are combined with different methods of detection. The purpose of the method validation was to determine whether the analysis process proceeded fairly and gives reliable results. In the validation study all stages of sample preparation and analysis (selection of the calibration curve, determination the method sensitivity, accuracy and precision, quantification and detection limit obtaining, identification of analyte recovery, estimation of method selectivity) are very important [1]. Chemical speciation is an important subject in the environmental protection, toxicological and analytical research, because toxicity, availability and reactivity of trace elements depend on the chemical forms in which such elements occur. Even though speciation analytics is relatively expensive, it plays an important role in the following fields: research into biochemical cycles of selected chemical compounds; determination of the toxicity and ecotoxicity of selected elements; quality control of food products and

pharmaceuticals; control of technological processes; health risk assessment; and clinical analytics [2]-[4]. Why speciation is important? The notion of speciation analysis was first used in the literature in 1993. Initially, it was defined as “movement and transformation of the element forms in the environment”. The results of toxicological tests show that (in many cases) it is not the total content of a given element but its various forms that have a decisive impact on the living organisms. A classic example of such diverse properties are such ions as Cr(III) and Cr(VI) Sb (III), Sb(V) and arsenic speciation forms: As(III), As(V), MMA, DMA, AB. For that reason, understanding different forms of the element occurrence is more important than knowing total element content in the sample. Generally, it is believed that elements in ionic forms demonstrate biological activity and toxicity to living organisms. Antimony is common in the natural environment and comes both from natural processes and human activity. Over the years, the human activity brought about the significant increase in its concentration in the environment due to its applications in the car industry (i.a. as an additive in the car tyre vulcanization process). The geochemical behaviour of antimony is similar to that of arsenic and bismuth [5]-[7]. Sb(III) is approx. 10 times more toxic than Sb(V). That is why there is such an interest in its speciation analysis [8]-[11].

Arsenic is a toxic metalloid that is common in various biological systems and the environment. The number of its speciation forms in the environment is still increasing due to the economic growth. As the industrial pollution has not been reduced in the recent decades, the arsenic emission from the industry, steelworks, animal waste, and the dust from fuel fossil combustion, is currently rising. As arsenic is very mobile, it occurs in all the environment elements. The toxicity depends on its chemical form. However, its inorganic speciation forms are 100 times more toxic than the organic ones. The contact with arsenic can cause various health effects, such as dermatologic, inhalation, cardiologic, genetic, genotoxic or mutagenic lesions [12]. Chromium is a classic example of an element whose two speciation forms differ significantly in their chemical and toxicological properties. It is believed that the Cr(III) compounds have a positive influence on the functioning of living organisms. They are responsible for the appropriate glucose metabolism in mammals. They easily undergo complexation with various substances present in the environmental samples. On the other hand, the Cr(VI) compounds are extremely toxic. The Cr(VI) toxic effect results from its strong oxidizing properties, and also from the formation of free radicals in the reduction of Cr(VI) to Cr(III), which occurs in the cells. The Cr(VI)

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MoSpeSil project (2013-2015) is supported by Small Grant Scheme 2012 the Polish-Norwegian Research Programme.

compounds are usually more easily soluble, mobile and bioavailable, which maximizes their toxic effect [13],[14]. The use of sophisticated analytical techniques in the As, Cr and Sb speciation forms study allowed for testing Klodnica River water, one of the most polluted rivers of the Upper Silesia. The central part of the Upper Silesian District is the most transformed by human Polish territory. As a result of mining activities, urbanization, and other industrial activities, irreversible changes have taken place in the rivers environment.

II. OBJECT OF STUDY

Klodnica River flows through one of the most industrialized areas of Polish. Industrial plants, dense residential development and heavy industry are responsible for serious pollution of surface waters. Observed for many years a steady decline in groundwater levels and more frequent droughts in the summer cause that is often more than 90% of the flow of these rivers are different types of waste it. Adjusting the rivers in the catchment Klodnica, has led to a reduction in natural floodplains (including the elimination of wetlands in river valleys), anyway, during heavy rains often subject to inundation of coastal areas. These conditions are particularly dangerous due to the contamination of sediments by toxic elements. Along with floodwater outside the riverbed may enter the deposited sediments, which is a serious threat to thousands of people living in the immediate vicinity. Klodnica River is right tributary of Oder River. The length of the river is 84 km, and the total catchment area of 1,125.8 km². In the upper part river flows through the big cities- Katowice, Silesia Ruda, Mikołow, Swietochlowice, Bytom, Zabrze, Gliwice and many industries, including coal mines. The catchment area of the river in this section is an industrial. The lower section of the river from the dam to the mouth of Big Dzierznoand in Kedzierzyn-has an agricultural character. Klodnica from the source is contaminated with industrial waste water and municipal waste. The content of heavy metals in sediments is much higher than in river sediments from other Polish regions untreated strong anthropogenic pressure. Klodnica River is heavily contaminated with heavy metals, especially lead [15].In the literature there are no data about arsenic, antimony and chromium speciation in Klodnica River.

TABLE I
LOCATION OF THE STUDY SITES IN KLODNICA RIVER

Site	Latitude (N)	Longitude (E)
K1 Katowice origin	50°13'506"N	18°59'766"E
K2 RudaŚląska	50°14'775"N	18°47'733"E
K3 Gliwice Odrowazow St.	50°17'153"N	18°42'651"E
K4 Gliwice Zamkowa St.	50°20'604"N	18°36'785"E
K5 Ujazd	50°23'128"N	18°20'876"E
K6 Kedzierzyn-Kozle	50°19'806"N	18°09'733"E

III. SAMPLE PREPARATION AND RESEARCH METHODOLOGY

Water samples were collected monthly from March to August 2014 using a Ruttner sampler. Water samples were sampling in six points spaced on Klodnica River from source

in Katowice to the estuary of the Oder River in KedzierzynKozle (Table I). Water samples were placed in 1000 ml high-density polyethylene (HDPE) containers so as to avoid the unnecessary aeration. Directly after sampling physicochemical parameters such as: pH, redox potential, temperature, conductivity were measured. Samples were divided into two parts, directly after their arrival at the laboratory. The first part was acidified with spectral pure nitric acid (Merck, Germany). Afterwards, it was filtered through a 0.22 μm PES syringe filter and used to determine total As, Sb and Cr contents with ICP-MS. The other part of the laboratory water sample was placed into an HDPE container and kept at -22°C temperature of until the analysis was performed (no longer than a month).

The preliminary activities included quantitative analyses of total As, Sb and Cr in water samples with the ICP-MS spectrometer. The measurements of As, Sb and Cr speciation forms in water samples were performed with the HPLC-ICP-MS system.

A. Apparatus and Chromatographic Conditions

The Elan 6100 DRC-e ICP-MS spectrometer (PerkinElmer) was used for quantitative analyses of total As, Sb and Cr in water samples. The apparatus was equipped with a standard ICP quartz torch, cross-flow nebulizer and nickel cones. Samples and standards were delivered with a peristaltic pump. The spectrometer was optimized daily with a 10μg/l solution (Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U) in 1% HNO₃Elan 6100 solution. Concentrations of ⁵³Cr, ⁷⁵As and ¹²³Sb were measured with the internal ¹⁰³Rh standard. The measurements of As, Sb and Cr speciation forms in water samples were performed with the HPLC-ICP-MS system. The operating parameters of the ICP-MS spectrometer are given in Table II. To separate a speciation forms apparatus set was applied. It consisted of an HPLC chromatograph (PerkinElmer) equipped with Series 200 LC Peltier oven, Series 200 LC autosampler. Selected separation parameters are presented in Table III.

B. Chemical and Reagents

The following substances were used for analyses: ultrapure ammonium nitrate (Merck), ultrapure potassium dichromate (Merck), 1000mg/L Cr(III) standard solution (Merck), dihydro sodium arsenate heptahydrate (Sigma-Aldrich), sodium arsenite (Sigma-Aldrich), disodium methyl arsenate (Supelco), arsenobetaine (Fluka), dimethylarsinic (Supelco), potassium hexahydroantimonate(V) (Aldrich), phtalic acid (POCH, Poland). The calibration solutions were prepared each time through diluting suitable standard solutions on an analytical balance. Multi-elemental standards no. XXI and VI (Merck) were used during determinations of total As, Sb and Cr with ICP-MS. Solutions made from salt were employed for calibration during quantitative determinations of As, Sb and Cr speciation forms. All solutions and standards were prepared with Milli-Q-Gradient ultrapure deionized water (Millipore, Merck), whose electrolytic conductivity was < 0.05μS/cm.

TABLE II
THE OPERATING PARAMETERS OF THE ICP-MS SPECTROMETER

ICP-MS Parameter	Settings
Generator power RF [W]	1125
Plasma gas flow [l/min]	15
Nebulizer gas flow [l/min]	0.76-0.82
Auxiliary gas flow [l/min]	1,15-1.16
Nebulizer	cross
Torch	quartz
Scanning mode	Peak hopping
Dwell time [ms]	250
Sweeps/Reading	1
Number of replicates	830-2100

IV. RESULTS AND DISCUSSION

Table IV shows the minimum, maximum and average content of total As, Sb and Cr in water. Total analyte concentration ranged for arsenic 0.34-15.39 $\mu\text{g/L}$, chromium 0.1-63.62 $\mu\text{g/L}$ antimony 0.2-2.67 $\mu\text{g/L}$. The results indicate that, with regard to Polish legislation [16], in the case of total Cr content exceeded at acceptable concentration was observed (water class I and II purity maximum concentration - 50 $\mu\text{g/L}$). Similarly, in the case of antimony, which allowable concentration is 2 $\mu\text{g/L}$ [16], exceeding the allowable concentrations has been observed. On grounds of the total content of chromium and antimony in the Klodnica River waters, we should qualify Klodnica River waters below the second purity class. Klodnica River flows through the Upper Silesian Industrial Region. The results of the total arsenic, antimony and chromium concentration clearly indicate the anthropogenic character of these pollutants. This is particularly evident by comparing the Opolskie Province. But in the Gliwice area pollution concentration is considerably higher than in other areas. The most significant reason for this phenomenon is rainstorm and snowmelt runoff from the industrial and urban areas. The next reasons are residues which lie heavily on the bottom of the Klodnica and flows from the mining waste stockpile. There is no doubt that the quality of water in the Klodnica in the past ten years was getting better. Some poisonous substances disappeared from river and nowadays water of the Klodnica does not contain all the elements of the periodic table [20],[21]. The results show an increase of the pH in water along river course. Exceptionally, the pH was decreased in K4 sampling point. The reason for this may be its proximity to the sewage treatment plant, which is likely to affect the pH of the water in the Klodnica River. Similar results obtained previously in 2004 [20]. Tables V and VI present concentration of arsenic, antimony and chromium speciation forms. Speciation forms of As, Sb and Cr were analyzed with a low limit of detection (Cr(III)-0.19 $\mu\text{g/L}$; Cr(VI)-0.37 $\mu\text{g/L}$; Sb(III)-0.009 $\mu\text{g/L}$; Sb(V)-0.012 $\mu\text{g/L}$; As(III)-0.08 $\mu\text{g/L}$; As(V)-0.12 $\mu\text{g/L}$; AsB-0.16 $\mu\text{g/L}$; MMA-0.08 $\mu\text{g/L}$; DMA-0.09 $\mu\text{g/L}$) [22].

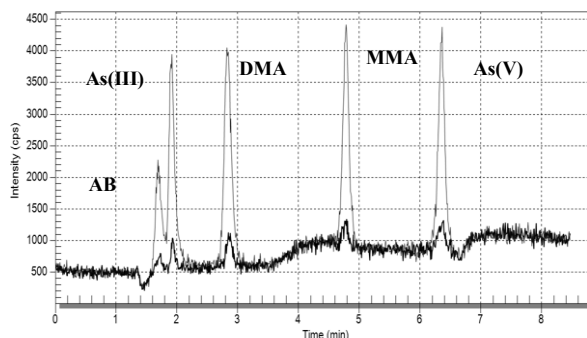


Fig. 1 Chromatograms of the real sample collected in March 2014– Klodnica River and the same sample with the 5 $\mu\text{g/L}$ standards addition

TABLE III
SEPARATION PARAMETERS

PARAMETER	VALUE
Chromium	
Separation column	Ion Pac AG-7; 50mm \times 4mm, 10 μm
Temperature	35 $^{\circ}\text{C}$
Mobile phase	A: 0.1M NH_4NO_3 pH=4; B: 0.8M HNO_3
Elution program	0-0.5min 100% A, 1.5-3.5 min 100% B Rinsing 3.5-5.0 min. 100% A
Flow rate during the analysis [mL/min]	1.7
Flow rate during the rinsing [mL/min]	2.0
Volume of sample [μL]	170
Antimony	
Separation column	Ion Pac AS-7; 200mm \times 4mm, 10 μm
Temperature	35 $^{\circ}\text{C}$
Mobile phase	1mM phthalic acid, 10mM EDTANa_2 ; pH= 4.5
Elution time	3 min
Flow rate during the analysis [mL/min]	1.2
Volume of sample [μL]	80
Arsenic	
Separation column	Hamilton PRP-X100; 100mm \times 4mm, 10 μm
Temperature	30 $^{\circ}\text{C}$
Mobile phase	A: 20mM NH_4NO_3 pH=8.7 B: 60mM NH_4NO_3 pH=8.7
Elution time	0-2.0 min. 100% A 2.0-3.0 min from 100% A to 100% B 3.0-6.5 min 100% B Rinsing 6.5-9.5 min 100% A
Flow rate during the analysis [mL/min]	1.1
Volume of sample [μL]	100

The water samples taken from the Klodnica River predominates oxidized arsenic forms: As(V), but in many sampling sites there is also a reduced form of the element. In the studied samples, there was no presence of AB and DMA. Monomethyl derivative of arsenic appeared only in the Klodnica River water at K1 sampling point, which is right at the source. The river at this point as the stream meanders among the trees, and the emergence of methyl torch also is associated with methylation processes occurring living

organisms in the Klodnica River in its initial run.

TABLE IV
MINIMUM, MAXIMUM AND AVERAGE TOTAL CONTENTS OF ANTIMONY,
ARSENIC, CHROMIUM, pH, Eh (REDOX POTENTIAL)

PARAMETERS		K1	K2	K3	K4	K5	K6
As [$\mu\text{g/L}$]	min	0.34	6.21	6.43	5.39	5.25	4.33
	max	0.81	13.49	12.16	15.39	9.59	9.67
	median	0.69	9.97	9.90	9.41	7.20	5.49
Cr [$\mu\text{g/L}$]	min	0.10	27.73	15.16	15.22	21.15	15.34
	max	6.87	63.62	44.75	55.83	43.49	44.21
	median	0.48	40.23	36.59	36.97	24.33	22.34
Sb [$\mu\text{g/L}$]	min	0.20	2.32	0.94	1.02	0.80	0.57
	max	0.56	2.67	2.44	2.56	1.22	1.12
	median	0.24	2.45	1.20	1.19	0.89	0.86
pH	min	7.59	7.05	7.42	7.31	7.42	7.58
	max	7.73	7.94	7.98	7.79	8.24	8.27
	median	7.63	7.73	7.7	7.48	7.86	7.82
T [$^{\circ}\text{C}$]	min	6.0	11.2	8.8	9.5	6.9	8.1
	max	17.4	24.4	22.2	26.4	23.4	23.3
	median	15.2	17.4	17.6	20.1	19.9	20.4
Eh [mV]	min	154	138	123	112	118	119
	max	243	220	202	195	196	204
	median	162	182	159	155	170	173
C [μS]	min	266	2920	3240	3010	4610	3580
	max	376	11430	10240	9440	5450	5640
	median	358	8690	7480	7050	4790	4930

T – temperature, C – conductivity water samples collected at six sampling points of Klodnica River (K1-Katowice, K2- Silesia Ruda, K3- Gliwice Odrowazow St., K4-Gliwice Zamkowa St., K5-Ujazd, K6-Kedzierzyn Kozle)

Also, in the case of antimony in the Klodnica River waters prevails oxidized form of the element. The average content of oxidized speciation form of $0.8\mu\text{g/L}$, reduced $0.15\mu\text{g/L}$. Taking into account that the Sb(III) is approx. 10 times more toxic than Sb(V), vantage of Sb(V) is good information. Despite the strong pollution in this heavily modified by human activity predominates the river oxidized form of antimony. Unfortunately speciation analysis of Klodnica River waters showed quite high content of the oxidized chromium form. Often, concentration of Cr(VI) and Cr(III) in water samples was comparable, there were also those samples, in which the oxidized forms were higher as reduced. This phenomenon is disadvantageous from a biological point of view. pH of the Klodnica river water from March to August 2014 showed a downward trend. The highest conductivity and redox potential was observed in May and June. Interestingly, in July saw a significant drop in these physico-chemical parameters. This may be related to heavy rainfall occurring at this time. The extraction from deep reservoirs in the preindustrial world was primarily due to volcanoes and oceanic hydrothermal inputs. However, more recently, mining activity (e.g., metal ore extraction and processing) and extraction of coal and hydrocarbon production have greatly exacerbated the inputs of metal(loid)s to aquatic ecosystems. Additionally, metal(loid)s are also reduced during the consumption of these products, especially through coal and hydrocarbon burning for energy and for transportation. The sources of metal(loid)s to freshwaters (rivers and lakes) are the erosion of surface

terrestrial material, the input of metal(loid)s associated with groundwater and runoff, and deposition of metal(loid)s from the atmosphere [17]. Taking into account the level of Silesia air pollution the effect is quite large. The metal(loid)s such as Cr, As and Sb are present in relatively high abundance compared to the trace metals, likely a function of these elements being oxyanions in natural waters. Heavy metals level in water samples from five river systems in central part of Delta State, Nigeria, varied significantly, in the case of chromium from $1\mu\text{g/L}$ to $30\mu\text{g/L}$ [18]. The Rosetta Branch of the Nile River in Egypt, studies have clearly indicated that the chromium content during and after winter period was very high, above $50\mu\text{g/L}$. The authors also found significant local water pollution problems [19]. Unfortunately, chromium concentration in Klodnica River is even higher as the Nile Delta State, can reach up to $63\mu\text{g/L}$.

TABLE V
CONCENTRATION OF ARSENIC SPECIATION FORMS IN KLODNICA RIVER
WATER [$\mu\text{g/L}$]

DATE OF COLLECTION	SAMPLING POINT	AB	As(III)	DMA	MMA	As(V)
March	K1	<0.16	0.15	<0.09	<0.08	0.65
	K2	<0.16	<0.08	<0.09	<0.08	7.95
	K3	<0.16	0.54	<0.09	<0.08	10.36
	K4	<0.16	<0.08	<0.09	<0.08	13.84
	K5	<0.16	2.02	<0.09	<0.08	7.33
	K6	<0.16	<0.08	<0.09	<0.08	8.97
April	K1	<0.16	0.34	<0.09	<0.08	0.43
	K2	<0.16	<0.08	<0.09	<0.08	10.60
	K3	<0.16	0.35	<0.09	<0.08	9.15
	K4	<0.16	<0.08	<0.09	<0.08	8.77
	K5	<0.16	2.26	<0.09	<0.08	4.44
	K6	<0.16	<0.08	<0.09	<0.08	4.68
May	K1	<0.16	<0.08	<0.09	<0.08	0.89
	K2	<0.16	<0.08	<0.09	<0.08	7.53
	K3	<0.16	<0.08	<0.09	<0.08	8.94
	K4	<0.16	<0.08	<0.09	<0.08	9.15
	K5	<0.16	1.17	<0.09	<0.08	4.21
	K6	<0.16	1.09	<0.09	<0.08	4.19
June	K1	<0.16	<0.08	<0.09	<0.08	0.32
	K2	<0.16	<0.08	<0.09	<0.08	8.21
	K3	<0.16	<0.08	<0.09	<0.08	12.79
	K4	<0.16	2.26	<0.09	<0.08	5.45
	K5	<0.16	<0.08	<0.09	<0.08	5.43
	K6	<0.16	<0.08	<0.09	<0.08	5.31
July	K1	<0.16	0.17	<0.09	0.11	0.46
	K2	<0.16	<0.08	<0.09	<0.08	8.85
	K3	<0.16	1.22	<0.09	<0.08	5.44
	K4	<0.16	0.18	<0.09	<0.08	4.08
	K5	<0.16	1.10	<0.09	<0.08	5.11
	K6	<0.16	1.56	<0.09	<0.08	3.52
August	K1	<0.16	0.12	<0.09	0.11	0.26
	K2	<0.16	1.59	<0.09	<0.08	10.36
	K3	<0.16	2.02	<0.09	<0.08	7.69
	K4	<0.16	1.26	<0.09	<0.08	8.68
	K5	<0.16	2.36	<0.09	<0.08	6.25
	K6	<0.16	1.11	<0.09	<0.08	8.65

TABLE VI
CONCENTRATION OF ANTIMONY AND CHROMIUM SPECIATION FORMS IN
KŁODNICA RIVER WATER [$\mu\text{g/L}$]

DATE OF COLLECTION	SAMPLING POINT	Sb(V)	Sb(III)	Cr(VI)	Cr(III)
March	K1	0.18	0.09	0.71	2.67
	K2	0.95	0.19	0.98	0.84
	K3	0.97	0.1	0.53	1.25
	K4	0.98	0.09	0.87	1.34
	K5	0.68	0.14	0.96	0.87
	K6	0.69	0.09	0.65	0.82
April	K1	0.39	0.06	0.63	1.48
	K2	0.62	0.10	0.77	0.81
	K3	0.80	0.21	0.61	1.14
	K4	0.88	0.16	0.67	1.01
	K5	0.80	0.11	0.86	0.65
	K6	0.84	0.10	0.74	0.98
May	K1	0.26	0.05	<0.37	3.58
	K2	0.89	0.15	0.68	3.88
	K3	0.86	0.17	0.86	7.28
	K4	0.79	0.08	1.07	6.17
	K5	0.83	0.05	1.01	6.09
	K6	0.78	0.05	0.57	3.96
June	K1	0.13	0.16	<0.37	2.73
	K2	0.73	0.28	0.58	3.12
	K3	0.67	0.17	0.47	1.54
	K4	0.98	0.27	<0.37	1.31
	K5	0.75	0.38	0.55	2.50
	K6	0.86	0.36	<0.37	1.59
July	K1	0.39	0.11	0.82	2.43
	K2	1.44	0.14	1.15	1.75
	K3	1.28	0.08	1.07	2.18
	K4	1.36	0.19	0.82	1.97
	K5	0.95	0.06	0.79	3.10
	K6	0.90	0.14	0.94	3.04
August	K1	0.32	0.14	0.83	2.50
	K2	0.76	0.16	1.26	1.97
	K3	0.99	0.28	1.54	3.00
	K4	1.34	0.09	0.98	3.02
	K5	0.95	0.17	0.86	2.63
	K6	0.91	0.12	0.91	3.12

V. CONCLUSION

The research allowed determining the total content of As, Sb and Cr as well as their speciation forms in six points located on the Kłodnica River. Despite low concentrations of arsenic, chromium and antimony in water, the methodology applied HPLC-ICP-MS is able to provide reliable analysis results. Such studies have not been conducted in Silesia and allow to supplement the information gap, mobility, and investigate the seasonal changes in the concentration speciation forms of metals and metalloids in the Upper Silesian rivers. Studies on the speciation of arsenic, antimony and chromium continue to be carried out within the framework of the Polish-Norwegian Research Programme MoSpeSil (2013-2015).

ACKNOWLEDGMENT

The work is a part of the MoSpeSil project (2013-2015)

supported by Small Grant Scheme 2012 the Polish-Norwegian Research Programme. The author would like to thank for the possibility project implementation in the framework of Polish-Norwegian cooperation.

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