Determination of uranium and selected elements in Polish dictyonema shales and sandstones by ICP-MS

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Abstract Inductively coupled plasma mass spectrometry was used for characterization of Polish dictyonema shales and sandstones as a potential source of uranium and other technologically important elements. Influence of sample digestion of these materials for the determinations: U, Th, Cu, Co, Mn, Zn, La, V, Yb, Mo, Ni, Sb and Fe has been tested. The method involved two-step microwave acid digestion, followed by direct determination by ICP-MS. The instrument used for all determinations was ELAN DRC II (Perkin Elmer) with crossflow nebulizer with Scott double-pass spray chamber and Ni cones. Certified Reference Materials were used as a quality control standard to validate the applied analytical procedure. The expanded measurement uncertainty U (k = 2) ranged from 5 to 15 %, in dependence on the element. The obtained results provided information on the contents of minor and trace elements in shales and sandstones depending on their origin. At this moment, these geological deposits can be treated as a potential source of raw elements.

Keywords Uranium · Dictyonema shales · Sandstones · Microwave digestion · ICP-MS · Trace elements

Introduction

Nuclear power turns to be one of sources of energy, which apart from being CO_2 emission free, guarantees independence from the typical ways of obtaining energy sources.

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The development of a domestic nuclear power industry in Poland has been underway both at the government and several research institutions. One of scientific projects is "The possibility of uranium supply from domestic resources". Recently, there has been an increase in uranium exploration across the globe, powered by a renewed interest in nuclear energy and higher uranium prices. Application of new technology provides exploration of poor uranium sources, which were previously considered as an uneconomic. For example, application of the biotechnology, makes possible to obtain uranium from the ores containing below 0.03 % of U with the efficiency of 90–95 %. The economic benefits may be improved by the recovery of rare metals present in ores. The bioleaching processes are applied to recover such metals as copper, silver, zinc, uranium not only from the poor ores but also from different industrial wastes [1–3]. The exploration conducted by Polish Geological Institute resulted in discovery of uranium mineralization in the Ordovician dictyonema shales in the Podlasie depression and the lower and middle Triassic sediments (sandstones) in the Peribaltic Syneclise (Fig. 1). This kind of geological materials are known as uranium-bearing [4]. Uranium content in various samples taken from the same deposit differ from one another. Therefore, numerous samples have to be analyzed to fully characterize the deposit. Both dictyonema shales and sandstones are complex geological materials. The main components of the studied dictyonema shales are aluminosilicates and organic substances. The dictyonema shales contain also carbonate minerals as: siderite, dolomite and calcite, as well as sulphides as: pyrite, sphalerite, galenite, marcastine and chalcopyrite [5]. Studies of minerals of Peribaltic Syneclise showed that their main components are coffinite, nasturan, and sulphides: galenite, pyrite and clausthalite [5]. Silica is the main component of sandstones

and the organic substances content is much lower in sandstones than in shales. The content of SiO_2 and other main components calculated on the basis of the results of X-ray fluorescence spectrometry (XRF) analysis [5] are given in Table 1. In both types of ores, uranium usually was accompanied by other metals, e.g. V, Mo, Th, La, Cu or Co. Bacterial pyrite leaching is an important step of bioleaching of U from uranium-bearing materials [6]. Therefore, Fe content is essential for biotechnological application and Fe was determined in each sample.

The main purpose of this work was determination of U and selected elements in the mentioned geological samples in order to their characterization. For that purpose, several mulitelemental analytical techniques are used: instrumental neutron activation analysis [7, 8], XRF [8, 9], particle induced x-ray emission [10], and inductively coupled plasma mass spectrometry (ICP-MS) [11–14]. Each of them has advantages and weaknesses. ICP-MS is powerful analytical technique making possible the highly accurate, multielemental, ultratrace analysis of different samples. In comparison to the other analytical methods, this technique has several advantages: high sensitivity and low detection limits for big number of elements, broad linear dynamic range,

Fig. 1 Regions of samples origin and collection

Table 1 Main components of dictyonema shales and sandstones [5]

Component	Dictyonema shales	Sandstones
SiO_2	38–60 %	22–86 %
CaO	0.2–5 %	0.4–36 %
MgO	0.3–0.9 %	0.4–4.4 %
Al_2O_3	9–19 %	4–19 %
Organic matter	14–31 %	1–31 %

quickness etc. For conventional ICP-MS analysis, it is necessary to transform samples into solution form, therefore the most important stage (except collection of representative sample) is digestion of the analysed material. Depending on sample composition, different digestion procedures should be used, to ensure complete decomposition [13, 15]. In this work, digestion methods: alkali fusion [16, 17] and microwave acid digestion [18], and their influence on recovery of the determined elements were examined. The elaborated procedures have been used for ICP-MS analysis of selected geological samples: 78 dictyonema shales and 45 sandstones. The following elements were determined: U, Th, Cu, Co, Mn, Zn, La, V, Yb, Mo, Ni, Sb and Fe. These elements were chosen in terms of characterization of samples and their potential technological meaning.

Experimental

Reagents and materials

In the preparation of all solutions, 18 MΩ cm grade water from Milli-ORG Millipore Co. purification system was used. For digestion process 65 % HNO_3 (p.a. Sigma, purified by sub-boiling point distillation), 40 %HF (suprapure, MERC), H_3BO_3 (p.a., CHEMPUR), Na_2O_2 (p.a., FLUKA) were applied. Calibration standards were supplied by Perkin Elmer as stock standard solutions of 10 μg mL^{-1}. Working mixed standard solutions (2–200 ng mL^{-1}) were prepared by dilution stock standard solutions in 0.7 % nitric acid. Daily check performance solution (Perkin Elmer) was used for the spectrometer optimization.

The following Certified reference materials (CRMs) were used for validation the method: Soil 5 (IAEA), Lake sediment SL-1 (IAEA), Apatite concentrate CTA-AC-1 (INCT).

Samples of dictyonema shales were collected from Podlasie depression deposits and. samples of sandstones were collected from Peribaltic Syneclise deposits by Polish Geological Institute.

Apparatus

To prepare samples and CRMs, analytical (Sartorius MC5) and micro-analytical (BP221S) balances calibrated using national mass standards traceable to the international standards were used. Muffle furnace with temperature regulation and recorder (Nabertherm) was used for fusion. The microwave digestion system (Anton Paar Multiwave 3000, USA) equipped with temperature and pressure regulation was used for digestion of the samples. The ICP-MS instrument: ELAN DRC II (Perkin Elmer) with crossflow nebulizer with Scott double-pass spray chamber and Ni cones was used.

Analytical procedures

Sample digestion

Fusion (procedure A)   0.5 g of sample was weighed to the zirconium crucible, 2 g of Na_2O_2 was added and carefully mixed. The fusion process was carried out in an oven at temperature 550 °C during 1.5 h. The melt was washed with water (about 150 mL), then 25 mL 5 M HNO_3 was added. The mixture was heated at about 80 °C to obtain clear solution. Then the solution was transferred to a 250 mL volumetric flask and adjusted to 250 mL with water.

In the case of dictyonema shales, the sample was ashed in oven at temperature 550 °C for 4 h before fusion.

Microwave digestion (procedure B)   Digestion of the sample (c.a. 250 mg, 6 mL HNO_3 + 2 mL HF) was carried out in a microwave high-pressure system under controlled conditions. The resulting solution was transferred into 50 mL PFA volumetric flask and submitted to analysis.

To prevent losses of some elements and to remove fluoride ions, following modifications of this procedure have been introduced:

Microwave digestion (procedure C)   Procedure as described above (B), removing of fluoride ions by evaporation on a hot plate with 4 % H_3BO_3 solution.

Microwave digestion (procedure D)   Procedure as described above (B), removing of fluoride ions in the microwave digestion system by means of adding 1 g solid H_3BO_3 directly to the Teflon vessel.

Microwave digestion (procedure E)   Procedure as described above (B), removing of fluoride ions in the microwave digestion system by means of adding 12 mL 4 % H_3BO_3 solution directly to the Teflon vessel.

Measurement procedure   Obtained solutions were diluted with 0.7 % HNO_3 and In was added as an internal standard prior to analysis. The following nuclides: [238]U, [232]Th, [63]Cu, [59]Co, [55]Mn, [66]Zn, [139]La, [51]V, [174]Yb, [98]Mo, [60]Ni, [121]Sb, [57]Fe were selected for quantitative measurement by ICP-MS since they are free from interference and are sufficiently abundant. The applied instrument operation conditions are summarized in Table 2. Indium-115 was selected as an internal standard, due to its absence in the analyzed samples, as well as its mass number 115 is between the lightest (51) and the heaviest (238) of determined elements.

Table 2 Operation parameters for ICP-MS analysis

Mass spectrometer ELAN DRC II	RF power: 1,000 W
	Plasma gas flow: 13.0 L min^{-1}
	Auxiliary gas flow: 1.2 L min^{-1}
	Nebulizer gas flow: 0.92 L min^{-1}
	Lens voltage: 6.75 V
	Detector mode: Dual
	Analog detector voltage: −1,650 V
	Pulse detector voltage: 800 V
	Working mode: standard Cones: Ni

Results and discussion

The optimal conditions of sample digestion

For determination of total content of elements by ICP-MS, the complete dissolution is essential to obtain accurate analytical results. One way of the total decomposition of geological samples with complex matrix, is fusion with sodium peroxide. In the case of dictyonema shales, the high content of organic substances (25–30 %) causes disturbances in the alkaline fusion. Therefore, the preliminary ashing before fusion is necessary. The widely used ashing at 800 °C for 1 h caused decreasing of the results of thorium determination of about 50 %, probably because of low soluble oxide formation. Therefore, the ashing at 550 °C for 4 h have been applied in this work. In these conditions organic substances were removed and the process was carried out in zirconium crucibles. However, it prolongs time of the analysis. In the case of sandstones, silica is a main component and the organic substances content is not so high (c.a. 5–15 %). Therefore, the digestion by alkaline fusion can be used directly.

Alternative to alkaline fusion for geological samples is microwave assisted acid digestion. Optimal amounts of nitric acid, hydrofluoric acid, hydrochloric acid and their mixture were evaluated for total digestion of selected materials. Based on the digestion procedures delivered by producer of microwave digestion system [19] and preliminary works from our laboratory, the following acid mixtures have been tested for the digestion of geological samples of 250 mg:

(a)   3 mL HNO_3 + 4.5 mL HF
(b)   6 mL HNO_3 + 2 mL HF
(c)   3 mL HNO_3 + 3 mL HF + 1 mL HCl
(d)   4 mL HNO_3 + 3 mL HCl

The mixture of 6 mL HNO_3 + 2 mL HF has been found to be sufficient to dissolution of analyzed materials. Addition of hydrofluoric acid is necessary for complete

Fig. 2 Comparison of recoveries of selected elements obtained using examined digestion methods
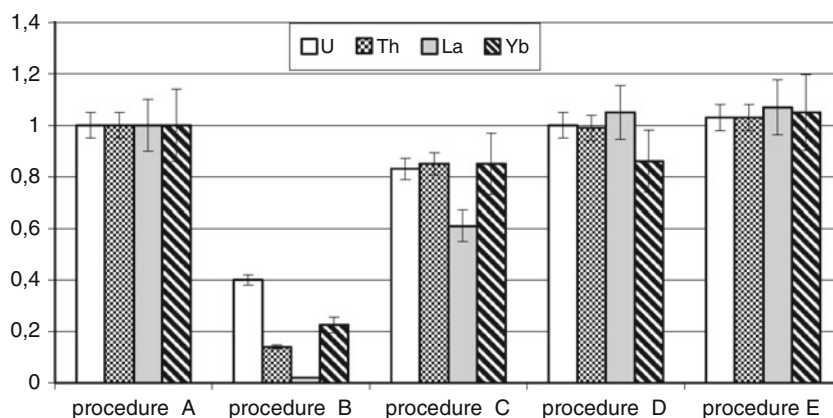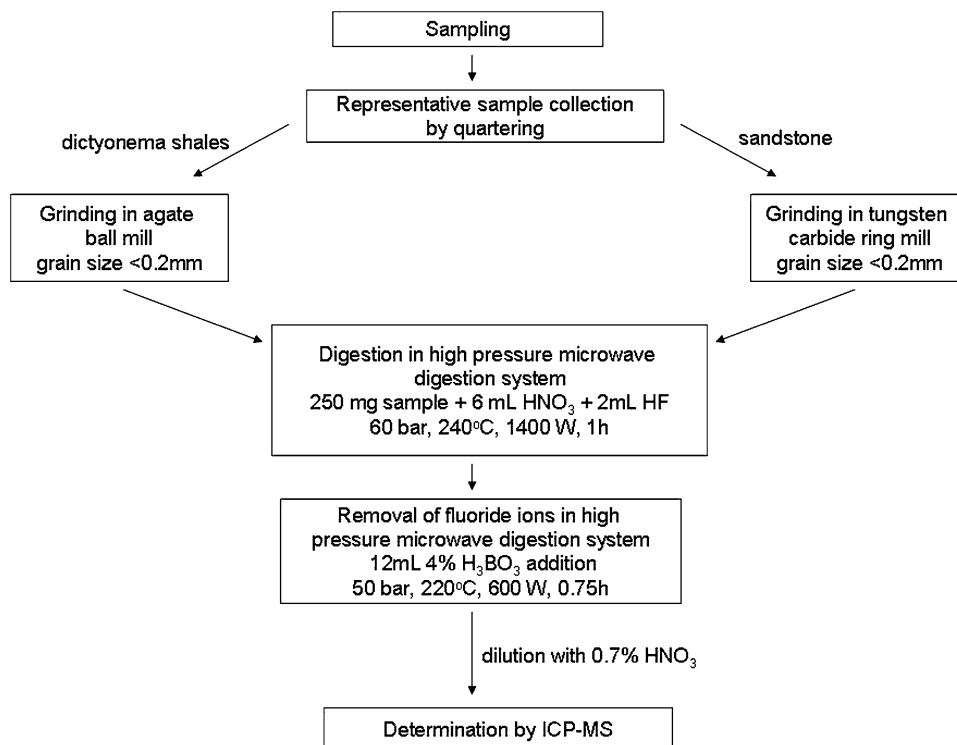

Fig. 3 Scheme of applied procedure for geological samples analysis

decomposition of the sample because of the presence of silica. However, it causes to low ion intensities (losses) of elements forming low soluble fluorides (Al, Ca, Fe) and stable fluoride complexes (U, Th, lanthanides). The dependence of recoveries of U, Th La and Yb on applied digestion procedure is shown in Fig. 2. The results were normalized with respect to the results obtained using procedure A (fusion). The obtained results show that the use of two-step process procedure E ensures the best recovery of elements which form stable fluoride complexes: U, Th, La and Yb. It reduces also the analysis time significantly comparing with fusion and can be recognized as the optimal digestion procedure.

The results of determination of remaining elements: Co, Cu, Fe, Mn, Mo, Ni, Sb, V and Zn do not depend on the

digestion methods. The final scheme of elaborated and used analytical procedure is presented in Fig. 3.

Validation of ICP-MS measurements

Three CRMs of different composition were analyzed to demonstrate the reliability of the used analytical procedures (Table 3). The obtained results agree well with the certified values. Elemental content of CRMs used in this work varied by 1–3 orders of magnitude, depending on the element. Therefore, it can be expected, that elaborated digestion procedure might be used for different geological materials. In the analysis, nitric acid with a concentration of 0.7–2 % was used for dilution. There were no significant differences between the obtained results and certified

Table 3 Results obtained for analyzed CRMs [mg kg^{-1}]

Element	IAEA SL-1		IAEA SOIL-5		CTA-AC-1	
	Certified value	Elaborated method (n = 5)	Certified value	Elaborated method (n = 5)	Certified value	Elaborated method (n = 5)
U	4.02 ± 0.32[a]	4.1 ± 0.2	3.15 ± 0.45	3.07 ± 0.15	4.4 ± 0.9	4.0 ± 0.2
Th	14 ± 1	13.9 ± 0.7	11.3 ± 0.7	11.5 ± 0.6	21.8 ± 2.1	21.6 ± 1.1
Cu	30 ± 6[a]	28.2 ± 2.8	77.1 ± 4.7	75.3 ± 7.5	54.0 ± 4.5	62 ± 6
Co	19.8 ± 1.6	18.4 ± 1.8	14.8 ± 0.8	14.6 ± 1.5	2.72 ± 0.28	2.80 ± 0.28
Mn	3460 ± 160	3347 ± 335	852 ± 19	901 ± 90	317 ± 50	352 ± 35
Zn	223 ± 10	212 ± 21	368 ± 8	365 ± 36	38.0 ± 7.6	44.0 ± 4.4
La	52.6 ± 3.1	53.1 ± 2.7	28.1 ± 1.5	28.3 ± 1.4	2176 ± 94	2227 ± 223
V	170 ± 15	173 ± 14	151 ± 14[a]	148 ± 12	104 ± 10	107 ± 9
Yb	3.42 ± 0.51[a]	3.14 ± 0.47	2.24 ± 0.20	2.33 ± 0.35	11.4 ± 2.0	11.9 ± 1.8
Mo	–	1.43 ± 0.14	–	1.83 ± 0.18	–	n.d.
Ni	44.9 ± 8.5[a]	42.7 ± 4.3	13.1 ± 1.8[a]	11.7 ± 1.2	9[a]	13.1 ± 1.3
Sb	1.31 ± 0.12[a]	1.32 ± 0.20	14.3 ± 1.1	11.8 ± 1.8	–	0.30 ± 0.05
Fe	67,400 ± 1700	62,100 ± 6210	44,500 ± 1900	46,174 ± 4610	50000[a]	n.d.

n.d. not determined in this material

[a] Information value

values, thus with respect to "green chemistry" principles, 0.7 % HNO$_3$ was used to all dilutions. The combined standard uncertainty was calculated according to the uncertainty propagation law [20]. The expanded measurement uncertainty U (k = 2) ranged from 5 to 15 %, in dependence on the element. The major contributor to the uncertainties was dilution of samples and standards.

For uranium, expanded uncertainty was evaluated to be 5 %, because mass 238 is free from isobaric interferences, sensitivity for U is excellent, and there is no U in analytical blank.

Detection limits

The detection limits for selected isotopes were calculated as three times the standard deviation of the intensities of the blank response at the given *m/z* position. The average values and the standard deviation were obtained by using the results of the five replicate measurements. Detection limits obtained for two different ways of sample digestion (alkali fusion and microwave digestion) are presented in Table 4. In fact, the obtained limits are similar for all elements. Probably, the difference for Fe is due to higher content of iron in acids used than in the fusion mixture.

Characterization of analyzed samples

Dictyonema shales from the Podlasie depressions

Dictyonema shales are one of the Ordovician dictyonema shales, with the highest U content. Table 5 shows the mean

Table 4 Detection limits [pg mL^{-1}]

Element	Alkali fusion	Microwave digestion
U	42	23
Th	73	70
Cu	77	165
Co	45	10
Mn	168	232
Zn	180	140
La	36	15
V	65	35
Yb	44	19
Mo	1,800	1,085
Ni	68	55
Sb	86	245
Fe	2,000	11,500

values and the range of determined elements concentration for dictyonema shales coming from 5 geological boreholes, located around Rajsk region (Fig. 1). Presented data show the high variability of determined elements. Within the dictyonema shale vanadium and molybdenum have been found in relatively high concentration. In the case of V, the differences in content between the various boreholes and at different depths are relatively small (only for five samples analyzed, the concentration of V was below 500 mg kg^{-1}). Molybdenum is an element dispersed in the earth's crust and occurs at an average level of 1.5 mg kg^{-1} [21]. Obtained values for Mo in dictyonema shales (0.74–674 mg kg^{-1}), make them a hyphotetical source of this element. Iron—element important from chemical and

Table 5 Elemental analysis of dictyonema shales

Element	Mean content from 78 samples [mg kg^{-1}]	Range [mg kg^{-1}]	Expanded uncertainty U (k = 2) of measurements (%)
U	94.1	15–1,480	5
Th	14.7	2.7–27	5
Cu	212	8–927	10
Co	32.2	9.4–137	10
Mn	218	24–2,493	10
Zn	4,028	69–19,981	10
La	44.5	22–91	10
V	1,250	256–2,374	10
Yb	3.72	1.5–9.6	15
Mo	83.6	0.75–674	10
Ni	183	55–1370	10
Sb	8.0	2.1–21	15
Fe	29,369	10,908–91,792	10

Table 6 Elemental analysis of sandstones

Element	Mean content from 45 samples [mg kg^{-1}]	Range [mg kg^{-1}]	Expanded uncertainty U (k = 2) of measurements (%)
U	256	3.3–1,316	5
Th	5.91	2–16	5
Cu	42.1	14–111	10
Co	68.8	3.6–176	10
Mn	970	105–3,050	10
Zn	38.6	10–100	10
La	29.1	4–53	10
V	220	37–770	10
Yb	2.17	0.5–3.2	15
Mo	4.81	0.6–9	10
Ni	33.3	6.3–100	10
Sb	0.42	0.1–4.1	15
Fe	22,390	2,930–180,000	10

biochemical point of view [1–3, 6], was determined in the range 1.1–9.2 %.

Sandstones from the Triassic of the Peribaltic Syneclise

Characterisation of analysed sandstones is presented in Table 6. As can be seen, the calculated mean value for uranium content is three times higher than that in dictyonema shales. However, the contents of the other elements are generally lower than in the shales except for Mn and Co. Diversity of element contents in sandstone samples is bigger comparing with dictyonema shales. Fe concentration varied between 0.3 and 18 %.

Conclusions

The procedure consisting of two-step microwave digestion and direct ICP-MS measurement was used for accurate and precise determination of U and Th, Cu, Co, Mn, Zn, La, V, Yb, Mo, Ni, Sb and Fe in geological materials. The different conditions of digestion of geological samples—dictyonema shales and sandstones have been examined. The digestion process in microwave oven was found as optimal: dissolution in acid mixture 6 mL HNO_3 + 2 ml HF and removing of fluoride ions by 4 % H_3BO_3 solution. The second step is necessary to ensure complete recovery of such elements as uranium, thorium, lanthanides, which form stable fluoride complexes. The digestion method applied in the presented studies is faster and more efficient than alkali fusion and conventional acid digestion. The accuracy of the applied method was confirmed by analysis of geological CRMs. The results obtained showed good agreement with the certified values. The expanded measurement uncertainty U (k = 2) ranged from 5 to 15 %, in dependence on the element.

Obtained results show, that the analyzed materials contain uranium and numerous metals in considerable dispersion. At this moment these Polish geological deposits can be treated as a potential source of raw elements.

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