EWA KRZESZOWSKA[1], MAGDALENA KOKOWSKA-PAWŁOWSKA[2], ŚWIATOSŁAW KRZESZOWSKI[3]

The role of sample preparation methods in the trace element analysis of westphalian deposits from the Lublin Coal Basin (Poland)

Introduction

Geochemical analyses, including assessing the concentrations of major and trace elements in sedimentary rocks, are increasingly being used in mining geology, exploration and stratigraphy. Geochemistry is also used in chemostratigraphy, in which the geochemical characteristics of the sediments are used to correlate between and among sequences of sedimentary rocks. The geochemical study of rocks for the purpose of correlation has been carried out since the 1970s, but in recent years, due to the availability of new analytical techniques, such studies are being performed more frequently. In the case of rock-sequence research, where precise sampling is not possible and palaeontological data is unavailable,

✉ Corresponding Author: Ewa Krzeszowska; e-mail: ewa.krzeszowska@polsl.pl

[1] Silesian University of Technology, Gliwice, Poland; ORCID iD: 0000-0002-6258-6890;
   e-mail: ewa.krzeszowska@polsl.pl
[2] Silesian University of Technology, Gliwice, Poland; ORCID iD: 0000-0003-0744-794;
   e-mail: magdalena.kokowska-pawlowska@polsl.pl
[3] Silesian University of Technology, Gliwice, Poland; ORCID iD: 0000-0003-0285-0159;
   e-mail: swiatoslaw.krzeszowski@polsl.pl

geochemistry may be the only method that allows correlation between lithologically-homogeneous rock sequences (Adams and Weaver 1958; Archard and Trice 1990; Leeder et al. 1990; Davies and McLean 1996; O'Mara and Turner 1997). Additionally, geochemistry is becoming more frequently used in the identification of the environments of deposition of marine and non-marine sediments.

Due to this growing interest in the geochemistry of sediments, there has been much comparison of published data among researchers. Interrogating the results of geochemical studies from published works involves the analysis of data obtained from different laboratories, and some papers do not provide details of the analytical methodologies used, including sample preparation and digestion methods. The selection of an appropriate sample preparation method, especially the digestion technique used, is very important for obtaining accurate results, and consequently a meaningful interpretation of the data.

Therefore, the main goals of this study were to:

◆ compare the results of geochemical analysis after using different multi-acid and aqua regia methods of digestion,
◆ determine which elements provided similar results, and thus did not depend on the method of digestion, and which gave significantly different results.

1. Methods of sample preparation for geochemical analysis

1.1. Digestion – the most common method used

Geochemical analyses, including those involving the determination of the concentration of major and trace elements in sedimentary rocks, are usually performed using spectroscopy techniques, such as atomic absorption spectrometry and inductively-coupled plasma–atomic emission spectrometry.

Each analytical procedure involves four key stages – sampling, sample transport and storage, sample preparation and sample analysis. Preparation for a geochemical analysis usually involves crushing, followed by digestion (most often using wet digestion methods). Wet digestion is used to separate trace elements from the matrix by providing thermal energy and the requisite chemical reagent, for example oxidizing (HNO_3, $HClO_4$, H_2SO_4) or non-oxidizing (HCl, HF). Such a sample preparation can take place in either open or closed systems, using convective heating and microwave-assisted or ultraviolet light. Table 1 provides an overview of wet-digestion techniques (Church et al. 1987; Isaksen and Bohacs 1995; Chen and Ma 2001; Yang et al. 2004; Melaku et al. 2005; Zhou and Jiang 2009).

Depending on the type of rock and the objective of the analysis, a suitable mixture of acids is chosen. Usually, in order to achieve whole-rock digestion, a mixture of four acids (i.e. multi-acid digestion; $HF + HClO_4 + HNO_3 + HCl$) is used. Hydrofluoric and chloric (VII) acids digest silicates; nitric acid (V) is used because of its excellent oxidative characteristics;

Table 1.   Overview of techniques for wet digestion

Tabela 1.   Przegląd metod dygestacji "na mokro"

	Wet digestion technique	Reagents	Matrix type
Open systems	Convective heating	HNO_3, HCl, HF, H_2SO_4, $HClO_4$, H_2O_2	Organic/inorganic
	Microwave-assisted heating	HNO_3, HCl, HF, H_2SO_4, $HClO_4$, H_2O_2	Organic/inorganic
	UV light heating	H_2O_2, $K_2S_2O_8$	Water, suspension
Closed systems	Convective heating	H_2O_2, HNO_3, HCl, HF	Organic/inorganic
	Microwave-assisted heating	H_2O_2, HNO_3, HCl, HF	Organic/inorganic

and hydrochloric acid dissolves carbonates, sulphates (apart from barite) and phosphates (Church et al. 1987; Chen and Ma 2001).

In order to partially digest sedimentary rocks, aqua regia – a mixture of hydrochloric and nitric (V) acids, in a volume ratio (v/v) of 3:1, are used (Church et al. 1987; Chen and Ma 2001). Aqua regia removes some of the silicate groups, including chain and layered forms (Church et al. 1987). The aqua regia method can also be assisted by microwave, although the results obtained with/without microwave power are comparable, with the main difference being the processing time and costs associated with the chosen method (Melaku et al. 2005).

Reverse aqua regia is a 2:1 v/v mixture of concentrated nitric (V) and hydrochloric acids. This mixture is used similarly to aqua regia, to partially digest the rock. The procedure for using reverse aqua regia is similar to that for aqua regia, except for the order of application of the acids, with the concentrated nitric (V) acid being applied first; the volume ratio used is also different (Yang et al. 2004; Zhou and Jiang 2009; Xu et al. 2012).

Another method for partial rock digestion involves a mixture of 1:1 v/v hydrofluoric and nitric (V) acid (Yu et al. 2009) and 1:1 v/v hydrofluoric and chloric (VII) acid (Isaksen and Bohacs 1995). Both of these methods use hydrofluoric acid, so they can be applied to silicate digestion.

Whole-rock digestion (multi-acid) is the most frequently-used method for clastic sedimentary rocks. However, many researchers have employed different, often experimental, sample preparation methodologies that have been strictly modified to serve the aim of each study.

1.2. A comparative analysis of classical sample digestion methods

Geochemical studies of sedimentary rocks generally involve identification of the environment of deposition, including palaeoredox conditions (Dill et al. 1991; Powell et al.

2001; Algeo and Maynard 2004; Cruse and Lyons 2004; Pearce et al. 2010), whilst che-mostratigraphic studies determine the stratigraphy of rock sequences and the correlation of boreholes/outcrop sections (Ehrenberg and Siring 1992; Racey et al. 1995; Pearce et al. 1999; Wray 1999, Ratcliffe et al. 2004, 2006; Pearce et al. 2005, 2010).

In geochemical analyses of sedimentary environments, the most commonly used trace elements are: U, V, Sc, Co, Ni, Mo, Re and indicators based on these elements. The trace elements in sedimentary rocks are associated with allogenic materials and their autogenic components, which are either precipitated or adsorbed directly from seawater, or are bio-genic components related to the life processes of organisms and the accumulation of their organic matter.

In most studies, the analysis of depositional environments and their palaeoredox con-ditions are based on the concentrations of trace elements in the whole rock, ignoring their autogenic and allogenic histories (Dill et al. 1991; Powell et al. 2001; Algeo and Maynard 2004; Tribovillard et al. 2006; Pearce et al. 2010). Therefore, during sample preparation, the whole-rock wet digestion method, with a mixture of four acids is used, although the diges-tion method is not always given. Xu et al. (2012) proposed that the analysis of palaeoredox conditions should only take trace elements accumulated in the authigenic component into account. They performed an analysis of the results of geochemical studies that used different sample digestion methods to estimate the concentrations of trace elements in allogenic and authigenic materials from marine deposits from the middle Triassic (Xu et al. 2009) and Permian (Georgiev et al. 2011). They applied the most common sample digestion methods (multi-acid whole-rock, aqua regia and reverse aqua regia). Based on the data from the liter-ature (Xu et al. 2009; Georgiev et al. 2011), Xu et al. (2012) compared the utility of the results in evaluating the palaeoredox conditions. Using the multi-acid whole-rock digestion method, they obtained almost complete digestion (both silicate and oxide minerals), and the results showed concentrations of trace elements in the whole rock, including both the authigenic and allogenic components. Palaeoredox indices, such as U/Th, V/Sc, V/Cr and V/(V + Ni), are usually determined on the basis of whole-rock analysis, not considering the autogenic and allogenic components.

The aqua regia and reverse aqua regia methods produced incomplete rock digestion, with the allogenic components (mainly silicate and oxide minerals) partially digested. Elements such as: P, S, Co, Ni, Cu, Zn, Mn, Mo and Pb had similar concentrations, re-gardless of the digestion method used, while the concentrations of elements such as: U, V, Cr and Sc differed significantly from each other, with their shares being up to 80% lower using the aqua regia and reverse aqua regia methods than using the multi-acid whole-rock digestion method.

The aqua regia and reverse aqua regia methods digest organic matter, sulphides and car-bonates, leaving some silicate minerals (e.g. quartz). The concentrations of trace elements obtained using these methods are similar, with the results differ by around 10%. Aqua regia is more appropriate for analyzing the authigenic component, however, with Xu et al. (2012) finding that the aqua regia and reverse aqua regia methods allowed results to be obtained

that reflected the concentration of predominantly authigenic trace elements; thus, they have value in palaeoredox proxy analysis.

As the preparation of rock samples for geochemical analysis usually involves total (multi-acid whole-rock) digestion, Tribovillard et al. (2006) proposed a mathematical method that allowed for the determination of trace element concentrations in the authigenic component.

Shares of elements in the material authigenic can be calculated using the formula (Tribovillard et al. 2006):

$$X_d = (X/Al)_{average\ shale} \cdot Al_{sample}$$

$$X_a = (X_{tot} - X_d)$$

$X_{average\ shale}$ – average share of the analyzed element in shale (Table 2),
X_d – part of the element in the analyzed detrital material,
X_{tot} – total share of the analyzed element in sample,
X_a – part of the element in the analyzed authigenic material,
Al_{sample} – total share of aluminum (Al) in sample,
$Al_{average\ shale}$ – average share of aluminum (Al) in shale (Table 2).

Table 2.   Average content of trace elements in the Earth's crust

Tabela 2.   Średnie koncentracje pierwiastków śladowych w skorupie ziemskiej

Elements	Average – the upper part of the Earth's crust [ppm][a]	Average – Post-Archean Australia shales [ppm][b]	Average – shales [ppm][c]
Mn	600	1 400	850
Ba	550	650	650
Cd	0.1	0.1	0.3
Co	17	20	19
Cr	83	100	90
Cu	25	75	45
Mo	1.5	1.0	1.3
Ni	44	60	68
U	2.80	0.91	3.00
V	107	140	130
Zn	71	80	95
Al	80 400	84 000	88 900

[a] – McLennan (2001), [b] – Taylor and McLennan (1985), [c] – Wedepohl (1991).

Chemostratigraphic correlation is widely used, particularly in the oil industry, where appropriate sampling is not possible and there is no palaeontological record (Ehrenberg and Siring 1992; Racey et al. 1995; Pearce et al. 1999; Wray 1999). This analysis uses whole-rock digestion; however, chemostratigraphy often accompanies a palaeoenvironmental analysis, for which whole-rock digestion is not the most useful method (Tribovillard et al. 2006; Abanda and Hannigan 2006).

1.3. Sequential extraction as an alternative method for preparing samples for geochemical analysis

Sequential extraction is a method that enables the separation of a rock into its individual components. It involves the use of acids and thermal energy in order to isolate these, and has been successfully used in various studies to obtain differing fractions (Tessier et al. 1979; Ohr et al. 1994; Dubinin and Strekopytov 2001; Bayon et al. 2002). Abanda and Hannigan (2006) also applied the shale extraction technique of Tait (1987) to partition trace elements into their mineral phases (Fig. 1).
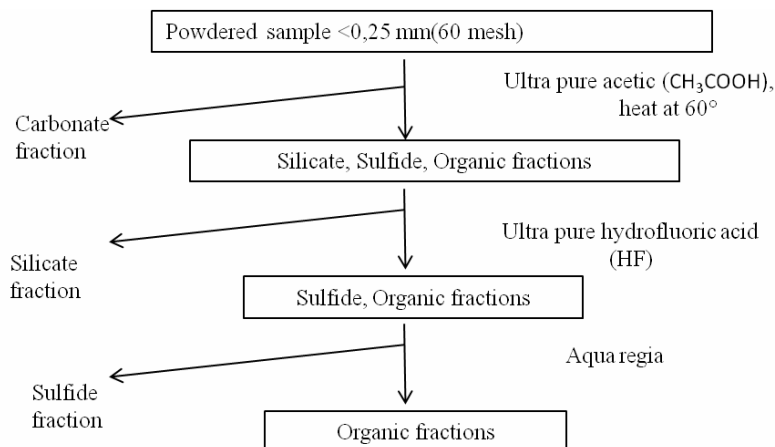

Fig. 1. Diagram showing the sequential leaching technique (Abanda and Hannigan 2006)

Rys. 1. Diagram przedstawiający ekstrakcja sekwencyjną

In the first stage of sequential extraction, concentrated acetic acid and convective heating of the sample at 60°C is used to remove the carbonates. The acetic acid can be replaced with dilute hydrochloric acid (Sondag 1981). Next, the silicates are isolated using concentrated hydrofluoric acid. Other authors have suggested that, instead of concentrated hydrofluoric acid, a mixture of concentrated hydrofluoric and perchloric acids could be used. Then, aqua regia is added to the sample to isolate the sulphides (Tessier et al. 1979; Bayon et al. 2002).

Other authors have proposed concentrated nitric (V) acid to do this (Chao and Theobald 1976). The final step involves the addition (after cooling the sample) of a few drops of hydrogen peroxide to complete the decomposition of any organic components.

Following sequential extraction, Abanda and Hannigan (2006) noted the trace element content in the carbonate, sulphide and organic fractions, respectively, using a dynamic reaction cell inductively-coupled plasma mass spectrometry, analyzing the concentrations of Ba, Th, U, La, Ce, Sr, Nd, Sm, Zr, Tb, Tm, Yb, Sc, Cr, Co and Ni. They found differences in the concentrations. In the sulphide fraction, the trace element concentrations were usually lower than in the organic or carbonate fractions. The organic fraction contained up to about 20% of the total trace element content, while the sulphide and carbonate fractions accounted for up to 10%, with the highest concentrations found in the silicates.

Abanda and Hannigan (2006) concluded that, for the analysis of sedimentary environments, the trace element results for individual fractions are more reliable than those from whole rock samples.

The share of trace elements in the silicates was calculated on the basis of the following formula:

$$X = \frac{C_{xi}^{i} \cdot W_{b}^{xi}}{C_{b}^{i}} \cdot 100$$

↳ X –   amount of particular element in a fraction [%],
C_{xi}^{i} –   concentration of element i in fraction xi,
C_{b}^{i} –   concentration of element i in whole rock,
W_{b}^{xi} –   percentage fraction xi in whole rock.

2. Study area, material and procedures

The Lublin Coal Basin (LCB) is located in south-eastern Poland. It takes the form of an extended province, trending south-east to north-west, and being 20 to 40 km wide and 180 km long (Porzycki and Zdanowski 1995). The most important part of the coal-bearing Carboniferous series of the LCB is the Lublin Formation, which contains the main multi-seam coal deposits (Porzycki and Zdanowski 1995). The Lublin Formation (upper Westphalian A and Westphalian B) comprises mainly mudstones and claystones, interbedded with sandstones. The lowest part of the formation (Westphalian A) belongs to a paralic series that ends with the highest marine faunal horizon, *Dunbarella* (Porzycki and Zdanowski 1995; Krzeszowska 2015). Above this level, the sediments are continental (Westphalian B), and belong to a limnic series (Porzycki and Zdanowski 1995).

The study material comprised core samples from four boreholes located in the central part of the LCB, drilled in 2013 and 2014, and collected from the Lublin Formation

(660–940 mbs). The data was obtained from 43 samples of gray to dark gray claystones and mudstones. For all the samples, concentrations of the main and trace elements were determined, using inductively-coupled plasma mass spectrometry at the ACME Analytical Laboratories Ltd., Canada.

These concentrations were obtained using two different methods of sample digestion – complete (multi-acid) and incomplete (aqua regia) dissolution. Whole-rock digestion was applied for the complete dissolution of the rock, multi-acid ($HF + HClO_4 + HCl + HNO_3$). The aqua regia ($HCl + HNO_3$, 3:1 v/v) method was also applied. These different dissolution methods were found to be associated with different detection levels, as shown in Table 1. The analyses were performed for the following elements: Co, Mn, Bi, Cu, Zn, Mo, Pb, Ni, Fe, P, Mg, U, Sr, Zr, K, Rb, Al, V, Ba, Cr, Na, Th and Cd.

3. Results and discussion

The major and trace element concentrations obtained following aqua regia and multi-acid digestion are presented in Table A1 (supplementary attachment). The different preparation methods produced significant differences in the proportions of some elements (Fig. 2). The
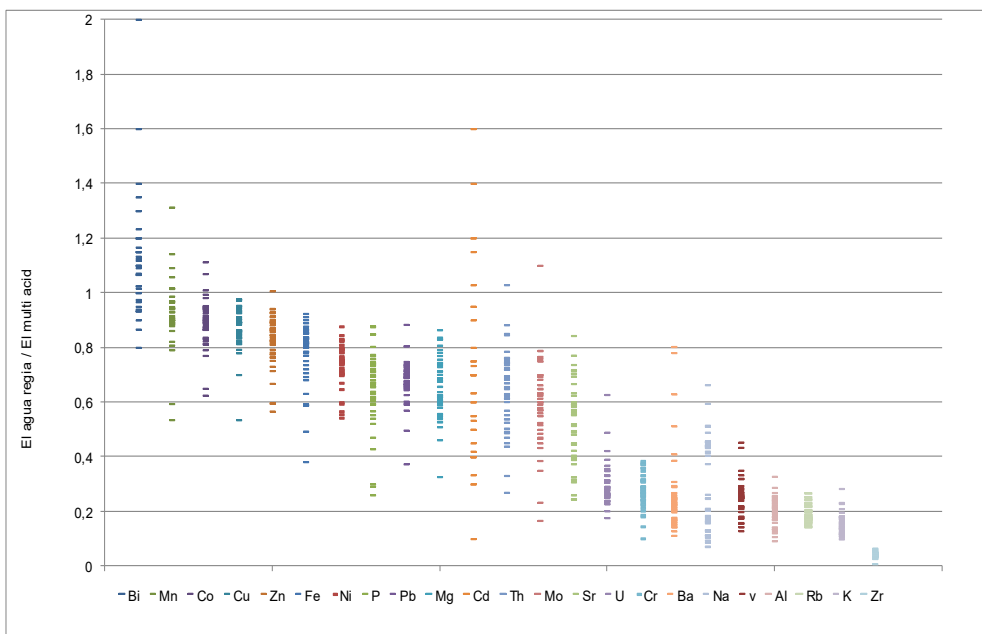

Fig. 2. Elements concentrations released by aqua regia compared to whole-rock multi-acid total digestion
for the samples from the Westphalian of the LCB

Rys. 2. Średnie koncentracje pierwiastków uzyskane z zastosowaniem metody roztwarzania
aqua regia digestion i *4 acid digestion* dla próbek skał z westfalu LZW

average, minimum and maximum concentrations of the elements in all of the 43 samples are shown in Table 3, alongside a comparison of the results obtained using the two dissolution methods (average ratio $El_{agua\text{-}regia}/El_{4\text{-}acid}$).

The concentrations of Co, Mn, Bi, Cu, Zn and Fe showed only slight differences between the digestion methods (Table 3, Fig. 2). The concentrations of Co and Mn released by aqua regia digestion were about 90% those of the multi-acid digestion (Figs 2, 3). For Bi, the aqua regia results were slightly higher, with the ratio amounting to 1.08. Similar observations were made by Xu et al. (2012) in analyzing the results of studies performed on middle Triassic (Xu et al. 2009) and Permian (Georgiev et al. 2011) marine shales. Abanda and Hannigan (2006) and Pearce et al. (2010) concluded that they are mainly associated with the clay mineral, carbonate and organic fractions.

The concentrations of the elements (including Cu, Zn and Fe) obtained using both digestion methods on all the samples are clearly different (Table 3). An analysis of the results showed that, for Cu, Zn and Fe, aqua regia digestion produced 88%, 83% and 80%, respectively, of the values for these elements obtained from multi-acid digestion. The Cu and Zn values correspond well with those found by Xu et al. (2012), while the Fe values are slightly lower than those determined by Xu et al. (2012). Cu and Zn are present in clay minerals, or can be related to sulphides and organic matter, while Fe is present mostly in carbonates (siderite, dolomite) and sulphides, which are the fraction that dissolves in aqua regia (Algeo and Maynard 2004; Pearce et al. 2010).

The concentrations of Ni, P, Pb, Mg, Cd, Th, Mo and Sr obtained from aqua regia digestion were lower, by 20–50%, than those from the multi-acid treatment, with Ni, Th, Pb and Cd from the former method accounting for 64–74% of the results from the latter; this range is slightly lower than that reported by Xu et al. (2012). Ni and Th are present in clay minerals, or can be related to sulphides and organic matter (Pearce et al. 2010; Kokowska 2018). Pb and Cd are present mostly in sulphides and silicates, and more rarely in organic substances (Algeo and Maynard 2004; Kokowska 2018). The share of P following aqua regia digestion was 69% that from multi-acid digestion. P mostly occurs in silicates, but may also be contained in carbonates (e.g. siderite) or occur as biogenic phosphate (Pearce et al. 2010). The concentration of Mo obtained from aqua regia digestion was 40% lower than for multi-acid digestion. This result might be misleading because Mo was only present in very low amounts – 0.72 ppm (aqua regia, detection level 0.1 ppm) and 0.44 ppm (multi-acid, detection level 0.01 ppm). Xu et al. (2012) reported Mo after aqua regia digestion as being 80% that found after multi-acid digestion.

Sr from the aqua regia digestion was about half (55%) that from the multi-acid digestion, confirming Xu et al. (2012) results. Sr can be connected to various fractions, such as carbonates and clay minerals, and may also be present in apatite, ilmenite, organic substances and detrital material (Jang and Naslund 2003; Xu et al. 2012).

Mg (which is mostly found in the carbonate fraction) from the aqua regia digestion was 67% that of the multi-acid digestion; this is slightly lower than determined by Xu et al. (2012).

Table 3.   Average elements concentrations released by aqua regia compared to whole-rock multi-acid total digestion for the samples of sedimentary rocks from the Westphalian of the LCB

Tabela 3.   Porównanie średnich koncentracji pierwiastków uzyskane z zastosowaniem metody roztwarzania *aqua regia digestion* i *4 acid digestion* dla próbek skał osadowych z westfalu LZW

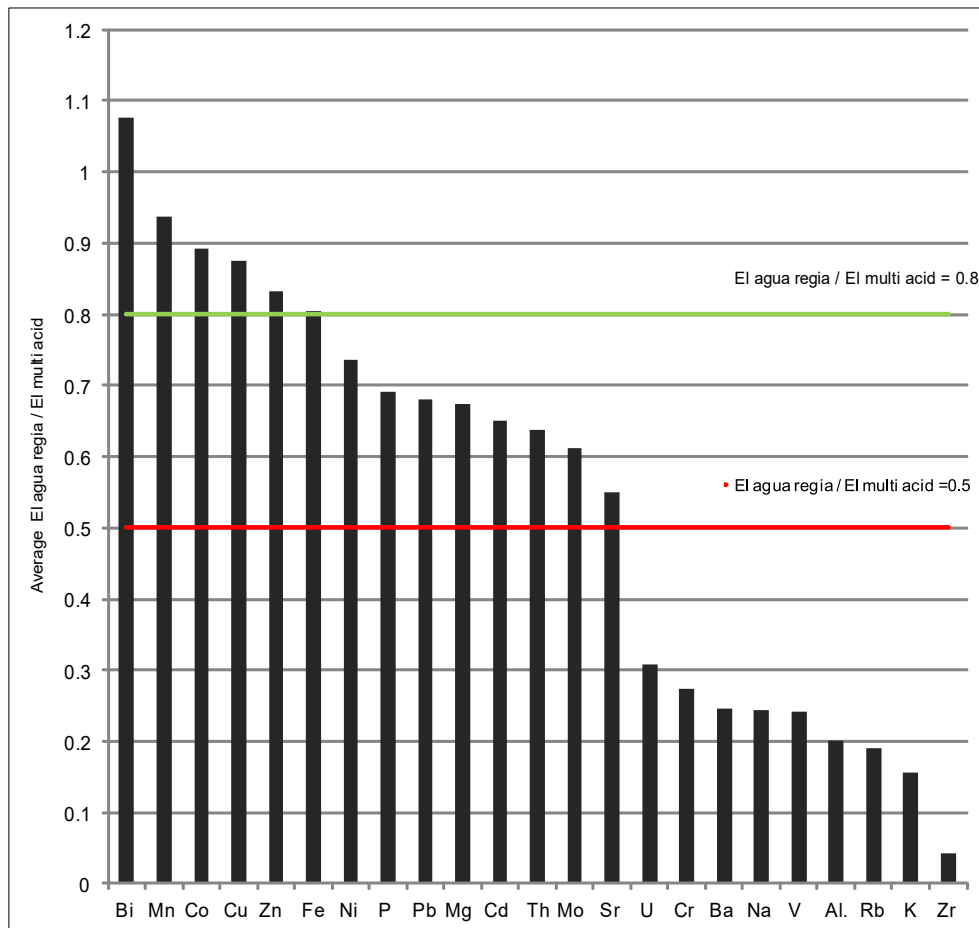| Element	Multi acid				Aqua regia				El agua regia/ /El 4 acid
	detection level	range of results		average value	detection level	range of results		average value	
		min.	max.			min.	max.		
Co (ppm)	0.2	7.2	58.5	20.4	0.1	5.7	55.1	18.2	0.89
Mn (ppm)	1.0	69.0	1715.0	604.0	1.0	41.0	1628.0	566.0	0.94
Bi (ppm)	0.1	0.1	1.1	0.4	0.02	0.16	1.26	0.4	1.08
Cu (ppm)	0.1	10.6	77.9	37.3	0.01	5.7	72.2	32.62	0.88
Zn (ppm)	1.0	42.0	181.0	111	0.1	25.1	155.1	92.4	0.83
Mo (ppm)	0.1	0.1	2.9	0.7	0.01	0.05	2.01	0.44	0.61
Pb (ppm)	0.1	13.6	52.8	30.6	0.01	5.1	35.3	20.84	0.68
Ni (ppm)	0.1	29	117.7	60.2	0.1	19.2	87.2	44.3	0.74
Fe (%)	0.01	1.31	12.15	3.9	0.01	0.5	11.08	3.11	0.80
P (%)	0.001	0.03	0.45	0.074	0.001	0.01	0.39	0.0511	0.69
Mg (%)	0.01	0.52	1.5	0.92	0.01	0.17	1.25	0.62	0.67
U (ppm)	0.1	3.6	13.4	5.1	0.05	1.1	6.56	1.58	0.31
Sr (ppm)	1.0	82.0	427.0	141.0	0.5	21.3	360.0	77.6	0.55
Zr (ppm)	0.1	106	168	135.7	0.1	0.9	8.3	5.8	0.04
K (%)	0.01	1.33	3.56	2.46	0.01	0.19	0.72	0.39	0.16
Rb (ppm)	0.1	60.6	60.6	127.9	0.1	12.7	41.4	24.5	0.19
Al (%)	0.01	6.48	12.49	9.03	0.01	0.87	3.12	1.81	0.20
V (ppm)	1.0	78.0	211.0	131.0	2.0	17.0	68.0	32.0	0.24
Ba (ppm)	1.0	103.0	955.0	501.0	0.5	65.7	589.6	122.9	0.25
Cr (ppm)	1.0	76.0	179.0	119.0	0.5	18.1	46.3	32.5	0.27
Na (%)	0.001	0.13	1.1	0.493	0.001	0.05	0.27	0.121	0.24
Th (ppm)	0.1	9.9	19.5	13.4	0.1	4.5	14.2	8.5	0.64
Cd (ppm)	0.1	0.1	0.7	0.2	0.01	0.01	0.72	0.15	0.65

Fig. 3. Comparison of the element concentration released by aqua regia and multi-acid digestion based
on the average values of the ratio $El_{agua-regia}/El_{4\ acid}$ for the samples from the Westphalian of the LCB

Rys. 3. Porównanie koncentracji pierwiastków z zastosowaniem metody roztwarzania *aqua regia digestion*
i *4 acid digestion* na podstawie średnich wartości $El_{agua-regia}/El_{4\ acid}$ dla próbek skał z westfalu LZW

A comparative analysis of the concentrations of Cu, Zn, Ni and Pb following incomplete (aqua regia) versus whole-rock (multi-acid) digestion showed that ca. 20–30% of the components came from the fraction that remained undissolved; that is, silicate minerals and oxides.

For elements: U, Cr, Ba, Na, V, Al, Rb, K and Zr, the results obtained from aqua regia digestion were always significantly lower than those from multi-acid digestion (Table 3). For most of these elements, the values obtained with the former method were about 20% of those from the latter. In the case of Zr, significantly different results were obtained (Fig. 2), with aqua regia digestion producing only 4% of the value obtained from multi-acid digestion. Similar results were achieved by Xu et al. (2012). Zr almost always comes from clastic

material, and is mostly present in zircon, rutile and Fe-Ti oxides (Jang and Naslund 2003; Xu et al. 2012). Abanda and Hannigan (2006) found an increased content of Zr in the organic fraction, relative to the whole rock.

U, Cr, Ba, Na, V, Al, Rb, K and Zr are mostly related to silicates from detrital material (Pearce et al. 2010; Xu et al. 2012). V and Cr can also be connected to the organic fraction (Algeo and Maynard 2004; Abanda and Hannigan 2006).

A comparison of the elemental concentrations obtained by these two methods allowed us to distinguish three groups of elements (Fig. 3):

- ◆ those with only small differences (less than 20%) in concentrations obtained by aqua regia versus multi-acid digestion (based on average values of $El_{agua-regia}/El_{4-acid}$), which include: Co, Mn, Bi, Cu, Zn and Fe,
- ◆ elements for which the results obtained were 20–50% lower after aqua regia digestion (i.e. Ni, P, Pb, Mg, Cd, Th, Mo, Sr),
- ◆ elements for which the results obtained after aqua regia digestion were significantly lower (U, Cr, Ba, Na, V, Al, Rb, K, Zr).

Conclusions

An analysis of the concentrations of the major and trace elements in sediment samples, obtained using different sample preparation methods, showed a significant impact of this stage of the study on the obtained results, with some concentrations being present in significantly different proportions. Three groups of elemental proportions from the two preparation methods were distinguished:

- ◆ those that showed small differences between the results from the preparation methods,
- ◆ those where the elemental concentrations were 20–50% lower using aqua regia digestion,
- ◆ elemental concentrations that were significantly lower (by up to 80%) following aqua regia digestion.

Those elements with comparable concentrations following aqua regia and multi-acid digestion were closely associated with the clay-mineral, carbonate and organic matter fractions. Those elements with concentrations that were clearly underestimated after aqua regia dissolution were mainly associated with the silicate and oxide fractions, which are the components that remain undissolved following aqua regia digestion. In interpreting the results of the geochemical analyses of rocks, or comparing such results among authors, it is necessary to take the method of sample digestion used and its effect on the results into account. Unfortunately, the sample preparation methodology, despite being crucial to the results, is not always explained in detail in the literature. The selection of an appropriate methodology allows for accurate results to be obtained, which leads to better interpretation.

REFERENCES

Abanda, P.A. and Hannigan, R.E. 2006. Effect of diagenesis on trace element partitioning in shales. *Chemical Geology* 230, pp. 42–59.

Adams, J.A. and Weaver, P.A. 1958. Thorium to uranium ratios as indicators of sedimentary processes: Examples of concept of geochemical facies. *American Association of Petroleum Geologist Bulletin* 42, pp. 387–430.

Algeo, T.J. and Maynard, J.B. 2004. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chemical Geology* 206, pp. 289–318.

Archard, G. and Trice, R.A. 1990. A preliminary investigation into the spectral radiation of the Upper Carboniferous marine bands. *Newsletters on Stratigraphy* 21, pp. 167–173.

Bayon et al. 2002 – Bayon, G., German, C.R. , Boella, R.M., Milton, J.A., Taylor, R.N. and Nesbitt, R.W. 2002. An improved method for extracting marine sediment fractions and its application to Sr and Nd isotopic analysis. *Chemical Geology* 187, pp. 179–199.

Chao, T.T. and Theobald, P.K. 1976. The significance of secondary iron and manganese oxides in geochemical exploration. *Economic Geology* 71, pp. 1560–1569.

Chen, M. and Ma, L.Q. 2001. Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil Science Society of America Journal* 65, pp. 491–499.

Church et al. 1987 – Church, S.E., Mosier, E.L. and Motooka, J.M. 1987. Mineralogical basis for the interpretation of multielement (ICP-AES), oxalic-acid, and aqua regia partial digestions of stream sediments for reconnaissanceexploration geochemistry. *Journal of Geochemical Exploration* 29, pp. 207–233.

Cruse, A.M. and Lyons, T.W. 2004. Trace metal records of regional paleoenvironmental variability in Pennsylvanian (Upper Carboniferous) black shales. *Chemical Geology* 206, pp. 319–345.

Davies, S. and McLean, D. 1996. Spectral gamma ray and palynological characterisation of Kinderscoutian marine bands in the Namurian of the Pennine Basin. *Yorkshire Geological Society Proceedings* 51, pp. 103–114.

Dill et al. 1991 – Dill, H., Teschner, M. and Wehner, H. 1991. Geochemistry and lithofacies of Permo-Carboniferous carbonaceous rocks from the southwestern edge of the Bohemian Massif (Germany) A contribution to facies analysis of continental anoxic enwironments. *International Journal of Coal Geology* 18, pp. 251–291.

Dubinin, A.V. and Strekopytov, S.V. 2001. Rare earth element behaviour during leaching of oceanic sediments. *Geochemistry International* 39(7), pp. 692–701.

Ehrenberg, S.N. and Siring, E. 1992. Use of bulk chemical analysis in stratigraphic correlation of sandstones: an example from the Statfjord field, Norwegian continental shelf. *Journal of Sedimentary Petrology* 62, pp. 318–330.

Georgiev et al. 2011 – Georgiev, S., Stein, H.J., Hannah, J.L., Bingen, B., Weiss, H.M. and Piasecki, S., 2011. Hot acidic Late Permian seas stifle life in record time. *Earth and Planetary Science Letters* 310, pp. 389–400.

Isaksen, G.H. and Bohacs, K.M. 1995. *Geological controls of source rock geochemistry through relative sea level, Triassic, Barents Sea* [In:] Katz, B.J. ed., *Petroleum source rocks.* Springer-Verlag Telos Berlin, pp. 25–50.

Jang, Y. D. and Naslund, H.R. 2003. Major and trace element variation in ilmenite in the Skaergaard Intrusion: Petrologic implications. *Chemical geology* 193, pp. 109–125.

Kokowska-Pawłowska, M. 2018. Mineralogical and geochemical study of rocks coexisting with coal seams 405 (Zaleskie Beds) and 408 (Ruda Beds s.s.) in Upper Silesian Coal Basin (*Studium mineralogiczno-geochemiczne skał współwystępujących z węglem w pokładach 405 (warstwy załęskie) i 408 (warstwy rudzkie ss) w Górnośląskim Zagłębiu Węglowym*). *Monography* 719, p. 300 (*in Polish*).

Krzeszowska, E. 2015. New data on the development of the Dunbarella marine marker horizon in the Lublin Coal Basin (Poland). *International Jounal of Coal Geology* 150–151, pp. 170–180.

Leeder et al. 1990 – Leeder, M.R., Raiswell, R., Al-Biatty, H., McMahon, A. and Hardmann, M. 1990. Carboniferous stratigraphy, sedimentation and correlation of well 48/3-3 in the southern North Sea Basin: integrated use of palynology, natural gamma/sonic logs and carbon/sulfur geochemistry. *Geological Society of London Journal* 147, pp. 287–300.

McLennan, S.M. 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochem Geophys Geosyst* (G3) 2, (paper # 2000GC000109).

Melaku et al. 2005 – Melaku, S., Dams, R. and Moens, L. 2005. Determination of trace elements in agricultural soil samples by inductively coupled plasma-mass spectrometry: microwave acid digestion versus aqua regia extraction. *Analytica Chimica Acta* 543, pp. 117–123.

Ohr et al. 1994 – Ohr, M., Halliday, A.N. and Peacor, D.R. 1994. Mobility and fractionation of the rare earth elements in argillaceous sediments: implications for dating diagenesis and low-grade metamorphism. *Geochimica et Cosmochimica Acta* 5, pp. 289–312.

O'Mara, P.T. and Turner B.R. 1997. Westphalian B marine bands and their subsurface recognition using gamma-ray spectrometry. Yorkshire Geological Society Proceedings, pp. 307–316.

Pearce et al. 1999 – Pearce, T. J., Besly, B. M., Wray, D., Wright, D. K. 1999. Chemostratigraphy: a method to improve interwell correlation in Barren sequences—a case study using onshore Duckmantian/Stephanian sequences (West Midlands, UK). Geology 124, pp. 197–220.

Pearce et al. 2005 – Pearce, T.J., Wray, D.S., Ratcliffe, K.T., Wright, D.K. and Moscariello, A. 2005. *Chemostratigraphy of the Upper Carboniferous Schooner Formation, southern North Sea* [In:] Collinson, J.D., Evans, D.J., Holliday, D.W. and Jones, N.S. eds, *Carboniferous Hydrocarbon Geology. The Southern North Sea and Surrounding Onshore Areas: Yorkshire Geological Society. Occasional Publications Series* 7, pp. 47–164.

Pearce et al. 2010 – Pearce, T.J., McLean, D., Martin, J.H., Ratcliffe, K. and Wray, D.S. 2010. A whole-rock geochemical approach to the recognition and correlation of "Marine Bands". *SEPM Special Publications* 94, pp. 221–238.

Porzycki, J. and Zdanowski, A. 1995. Southeastern Poland (Lublin Carboniferous Basin). *Prace Państwowego Instytutu Geologicznego* 148, pp. 102–109.

Powell et al. 2001 – Powell, W.G., Johnston, P.A. and Collom, C.J. 2001. Geochemical evidence for oxygenated bottom waters during deposition of fossiliferous strata of the Burgess Shale Formation. *Palaeogeography, Palaeoclimatology, Palaeoecology* 201, pp. 249–268.

Racey et al. 1995 – Racey, A., Love, M.A., Bobolecki, R.M. and Walsh, J.N. 1995. The use of chemical element analysis in the study of biostratigraphically barren sequences: an example from the Triassic of the central North Sea (UKCS. In Dunay, R. E. and Hailwood, E. A., eds. Non-Biostratigraphical Methods of Dating and Correlation: *Geological Society of London. Special Publication* 89, pp. 69–105.

Ratcliffe et al. 2006 – Ratcliffe, K.T., Hughes, A.D., Lawton, D.E., Wray, D.S., Bessa, F., Pearce, T.J. and Martin, J. 2006. A regional chemostratigraphically-defined correlation framework for the late Triassic TAG-I in Blocks 402 and 405a. *Algeria Petroleum Geoscience* 12, pp. 3–12.

Ratcliffe et al. 2004 – Ratcliffe, K.T., Wright, A.M., Hallsworth, C., Morton, A., Zaitlin, B.A., Potocki, D. and Wray, D.S. 2004. Alternative correlation techniques in the petroleum industry: an example from the (Lower Cretaceous) Basal Quartz, Southern Alberta. *American Association of Petroleum Geologists Bulletin* 88, pp. 1419–1432.

Sondag, F. 1981. Selective extraction procedures applied to geochemical prospecting in an area contaminated by old mine workings. *Journal of Geochemical Exploration* 15, pp. 645–652

Taylor, S.R. and McLennan, S.M. 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific Publications, p. 312.

Tessier et al. 1979 – Tessier, A., Campbell, P.G.C. and Bisson, M. 1979. Sequential chemicalextraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51, pp. 844–850.

Tait, L. 1987. *Character of organic matter and the partitioning of trace element and rare earth elements in black shale, Blondeau Formation, Chibougamau*, Quebec Unpublished MS Thesis, Department des Sciences Appliques, Universite de Quebec a Chicoutimi, p. 140.

Tribovillard et al. 2006 – Tribovillard, N., Algeo, T.J., Lyons, T. and Riboulleau, A. 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chemical Geology* 232, pp. 12–32.

Wedepohl, K.H. 1991. *The composition of the upper Earth's crust and the natural cycles of selected metals* [In:] Merian, E. ed., *Metalsand their Compounds in the Environment VCH-Verlagsgesellschaft*, Weinheim, pp. 3–17.

Wray, D.S. 1999. Identification and long-range correlation of bentonites in Turonian–Coniacian (Upper Cretaceous) chalks of northwest Europe. *Geological Magazine* 136, pp. 361–371.

Xu et al. 2009 – Xu, G., Hannah, J.L., Stein, H.J., Bingen, B., Yang, G., Zimmerman, A., Weitschat, W., Mørk, A. and Weiss, H.M. 2009. Re-Os geochronology of black shales in Arctic regions: Evaluating the Anisian-Ladinian boundary and global faunal correlations. *Earthand Planetary Science Letters* 288, pp. 581–587.

Xu et al. 2012 – Xu, G., Hannah, J.L., Bingen, B., Georgiev, S. and Stein, H.J. 2012. Digestion methods for trace element measurements in shales: Paleoredox proxies examined. *Chemical Geology* 324, pp. 132–147.

Yang et al. 2004 – Yang, J., Jiang, S., Ling, H., Feng, H., Chen, Y. and Chen, J. 2004. Paleoceangraphic significance of redox-sensitive metals of black shales in the basal Lower Cambrian Niutitang Formation in Guizhou Province, South China. *Progress in Natural Science* 14, pp. 152–157.

Yu et al. 2009 – Yu, B.S., Dong, H.L., Widom, E., Chen, J.Q. and Lin, C.S., 2009. Geochemistry of basal Cambrian black shales and cherts from the Northern Tarim Basin, Northwest China: Implications for depositional setting and tectonic history. *Journal of Asian Earth Sciences* 34, pp. 418–436.

Zhou, C. and Jiang, S.Y. 2009. Palaeoceanographic redox environments for the lower Cambrian Hetang Formation in South China: Evidence from pyrite framboids, redox sensitive trace elements, and sponge biota occurrence. *Palaeogeography, Palaeoclimatology, Palaeoecology* 271, pp. 279–286.

THE ROLE OF SAMPLE PREPARATION METHODS IN THE TRACE ELEMENT ANALYSIS OF WESTPHALIAN DEPOSITS FROM THE LUBLIN COAL BASIN (POLAND)

K e y w o r d s

trace elements, digestion methods, multi-acid method, aqua regia method

A b s t r a c t

The geochemistry of sedimentary rocks is increasingly being used in palaeoenvironmental studies, in the identification of marine versus continental stratigraphy and in chemostratigraphic correlation. The selection of an appropriate research methodology, particularly in terms of sample digestion, can have a significant impact on the accuracy of the results obtained. Depending on the type of rock being studied and the aim of the analysis, a suitable mixture of acids should be used. The most commonly used sample digestion methods are based on a mixture of four acids (multi-acid), aqua regia and inverse aqua regia. As opposed to multi-acid whole-rock digestion, the use of aqua regia and inverse aqua regia result in only the partial digestion of sedimentary rocks. Geochemical analyses using these two different methods were carried out on Carboniferous sedimentary rocks from the Lublin Coal Basin from Poland.The elemental concentrations obtained showed essentially different results for some of the elements. A comparison of the elemental concentrations allowed the distinction of three groups of elements:

- those that showed small differences between the results from the preparation methods (Co, Mn, Bi, Cu, Zn and Fe),
- those where the elemental concentrations were 20–50% lower using aqua regia digestion (i.e. Ni, P, Pb, Mg, Cd, Th, Mo, Sr),
- elemental concentrations that were significantly lower (by up to 80%) following aqua regia digestion (U, Cr, Ba, Na, V, Al, Rb, K, Zr).

WPŁYW METODY PRZYGOTOWANIA PRÓBEK NA WYNIKI ANALIZ PIERWIASTKÓW ŚLADOWYCH NA PRZYKŁADZIE OSADÓW WESTFALU LUBELSKIEGO ZAGŁĘBIA WĘGLOWEGO (POLSKA)

Słowa kluczowe

pierwiastki śladowe, metody roztwarzania, metoda czterech kwasów, metoda wody królewskiej

Streszczenie

Badania geochemiczne skał osadowych są coraz częściej wykorzystywane do badań paleośrodowiskowych, identyfikacji horyzontów morskich oraz chemokorelacji. Dobór odpowiedniej metodyki badawczej, w szczególności metod roztwarzania próbek, ma znaczący wpływ na uzyskiwane wyniki. W zależności od rodzaju skał i celu badań stosuje się, do roztwarzania próbek, odpowiednią mieszaninę kwasów. Najczęściej stosowane metody roztwarzania próbek oparte są na mieszaninie czterech kwasów, wodzie królewskiej i odwróconej wodzie królewskiej. Mieszanina czterech kwasów służy do uzyskania pełnej mineralizacji skały, natomiast woda królewska i odwrócona woda królewska są stosowane do częściowego roztwarzania skał osadowych. Analizy geochemiczne przy użyciu dwóch różnych metod roztwarzania próbek przeprowadzono dla osadów karbonu z Lubelskiego Zagłębia Węglowego (Polska). Koncentracje pierwiastków uzyskane przy użyciu dwóch różnych metod roztwarzania (mieszanina czterech kwasów oraz woda królewska) wykazały w niektórych przypadkach zasadniczo różne wartości. Porównanie wyników badań koncentracji pierwiastków uzyskanych za pomocą tych metod pozwala wyróżnić trzy grupy:

- ◆ pierwiastki, dla których wyniki wykazują małe różnice (Co, Mn, Bi, Cu, Zn i Fe),
- ◆ pierwiastki, dla których wyniki uzyskane po roztwarzaniu w wodzie królewskiej są niższe o 20–50% (m.in. Ni, P, Pb, Mg, Cd, Th, Mo, Sr),
- ◆ pierwiastki, dla których wyniki uzyskane po roztwarzaniu w wodzie królewskiej są znacznie niższe (U, Cr, Ba, Na, V, Al, Rb, K, Zr).