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Investigation of different extraction procedures for the determination of major and trace elements in coal by ICP-AES and ion chromatography

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Abstract: This paper presents the extraction of major and trace elements from a coal sample, in deionized water, by using three different extraction techniques. Rotary mixing and ultrasonic extraction were examined for different extraction times, while the microwave-assisted extraction was performed at different temperatures. Metal concentrations (Na, K, Ca, Mg, Al, Fe, Mn, Be, Cd, Co, Cr, Hg, As, Ni, Se, Sb and Pb) in solution were determined employing inductively coupled plasma atomic emission spectrometry; whereas the results obtained for Na, K, Ca and Mg were compared employing ion chromatography. Comparing the rotary- and ultrasonic-assisted extractions, it was shown that the former technique was more efficient for the determination of Fe, Na and Pb, whereas the latter one proved more efficient for the determination of Co and Cr ions. Microwave-assisted extraction was shown to be the most efficient method for all the tested elements in coal. In addition, sequential extraction of the elements was realized using microwave digestion. The results of the sequential extraction experiments indicated associations of investigated elements with a mineral phase and organic matrix. Sequential extraction provided information on possible leaching of As, Cd, Co, Cr, Ni, Pb, Fe and Mn under environmental conditions.

Keywords: coal, extraction; microwave; ultrasonic; ICP-AES; ion chromatography.

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INTRODUCTION

Numerous studies conducted in the course of the 20th century clearly indicated that there was a direct connection between the contents of trace elements in coal and environmental pollution caused by the products of coal combustion.¹⁻³ Some of potentially toxic elements (As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, Th and U) achieve multiple concentrations both in ash and fly ash and may cause land, air, and water pollution and affect vegetation.⁴

Most methods of decomposition used in elemental analysis are based on digestion with strong acids, such as HNO₃, HCl, H₂SO₄ and HF, at elevated temperatures, which could lead to loss of easily volatile elements, such as As, Sb, Se and Sn.⁵

Determination of cation concentrations can be realized in coal and fly ash extracts obtained by single or sequential procedures of extractions. Many single or sequential procedures, mainly based on the Community Bureau of Reference (BCR) procedure or different versions thereof, have been applied to coal and fly ash to fractionate elements by using different extractants or reagents to obtain more useful information about the bioavailability and mobility of elements.⁶⁻⁹

A useful sample preparation method for solid samples, such as coal, fly ash, ash, soil, sediment, biological and environmental samples, is ultrasound-assisted digestion.¹⁰⁻¹⁵ The main benefits of ultrasonic-assisted sample pre-treatment over other methods are the speed of digestion, high sample treatment capacity and low reagent usage. Since a substantially lower pressure and temperature are used in ultrasonic-assisted digestion, it is safer than microwave digestion.¹¹

Microwave-assisted digestion can be performed in open or closed digestion systems and nowadays, the trend towards closed systems is the more dominant one.¹⁶⁻¹⁸ The main benefits of closed systems include the possibilities for controlling both temperature and pressure, and for pre-treating the sample without a significant loss of analyte elements.¹⁸

This paper presents a comparison of three techniques for the simultaneous extraction of elements using a rotary mixer, a microwave-digestion system and an ultrasonic bath. The metal concentrations in the water extracts were measured by ion chromatography (IC) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Deionized water was the agent used for all extractions. In the present study, the partitioning of the elements (Na, K, Ca, Mg, Al, Fe, Mn, Be, Cd, Co, Cr, Hg, As, Ni, Se, Sb and Pb) was investigated using a microwave sequential extraction procedure. The BCR microwave extraction protocol was modified and the fractionations of the elements found in coal were examined and discussed.

EXPERIMENTAL

Sampling and sample preparation

A composite coal sample was taken from the Kostolac coalmine, which is located approximately 90 km east of Belgrade, Serbia. Prior to use, the sample was ground, homogenized, sieved through a 250 μm mesh and oven-dried overnight at 105 °C.

Reagents

Deionized water (18.2 M Ω cm) produced by a Milli-Q reagent grade system (Millipore, USA) was used for the extractions and preparation of all solutions. Acetic acid, hydrogen peroxide, nitric acid and hydrochloric acid were of analytical grade and obtained from Merck (Germany). Hydroxylammonium chloride, oxalic acid, ammonium oxalate and ammonium acetate were of AnalaR grade and procured from Fluka (Germany).

Instrumentation

A 3540 conductivity/pH-meter (Jenway, UK) was used to measure pH values of the extracts. A 761 compact IC ion chromatography system with a conductometric detector was used, as well as a Metrosep C 2-150 separation column (all from Metrohm, Switzerland). The eluent was a 4 mmol dm⁻³ tartaric and a 0.75 mmol dm⁻³ dipicolinic acid solution, at a flow rate of 1 mL min⁻¹. The eluent was made on a daily basis, and then filtered through a 0.2 μm membrane filter (Phenomenex, USA). The injected sample volume was 20 μL for each test. For IC calibration, the certified standard solution of Na, K, Ca and Mg (primary multiion standard solution, Fluka, Switzerland) was used to prepare working solutions by serial dilutions of standard solution.

The ICP-AES measurements were performed using an iCAP-6500 DUO ICP spectrometer (Thermo Fisher Scientific, UK), with continuous wavelength coverage ranging from 166 to 847 nm, equipped with a RACID86 charge injector detector, a pneumatic cross-flow type nebulizer, a quartz torch and a quartz detector. The instrumental conditions were set to an input power of 1150 W, an auxiliary gas flow of 0.5 dm³ min⁻¹, a coolant gas flow of 12 dm³ min⁻¹ and a nebulizer flow 0.5 dm³ min⁻¹. All the concentration measurements were realized using a four-point calibration. For IC-AES calibration, multi-element plasma standard solution 4 (Specpure, Alfa Aesar, Germany) was used to prepare working solutions. Analytes were determined at the following wavelengths (nm): 308.2 (Al); 193.7 (As); 234.8 (Be); 315.8 (Ca); 226.5 (Cd); 228.6 (Co); 267.7 (Cr); 240.4 (Fe); 253.6 (Hg); 769.8 (K); 279.0 (Mg); 259.3 (Mn); 818.3 (Na); 231.6 (Ni); 217.6 (Sb); 206.3 (Se) and 220.3 (Pb).

An overhead mixer Reax 20/8 rotary mixer (Carl Roth, Germany) and a Transsonic T 760 DH ultrasonic bath (Elma, Germany), with an ultrasonic frequency of 40 kHz and an effective ultrasound power of 170 W, were used. Microwave digestion for coal sample preparation was accomplished using an ETHOS 1, advanced microwave digestion system (Milestone, Italy), equipped with 10 PTFE containers for microwave digestion. The capacity of the containers was 100 cm³ each, and the maximum pressure and temperature that could be achieved were 10 MPa and 240 °C, respectively.

Extraction procedures

Single extraction. The extraction suspension was prepared by mixing a coal sample with deionized water in the ratio 1 g:50 cm³. The extractions were realized using a rotary mixer (RE) in which the suspension was processed for the following extraction times: 30, 60, 90, 120 and 180 min by mixing at 10 rpm at room temperature (20 °C). The second extraction technique involved the use of an ultrasonic bath (UE) for the following extraction times: 10,

20, 30, 40 and 50 min. The third technique was microwave digestion (ME) at the following temperatures: 50 (M50), 100 (M100) and 150 °C (M150). Both temperature and pressure were controlled during the process; working temperature was achieved in 15 min for each cycle of extraction, while the extraction itself lasted for 15 min. After extraction, the samples were cooled to room temperature and phases were separated by centrifugation. Blank extractions were performed for each of the employed extraction techniques. The coal extracts were acidified by the addition of a nitric acid solution (2.0 mol dm⁻³) and stored at 4 °C in a laboratory refrigerator.

Microwave sequential extraction. The coal samples were subjected to the extraction scheme, suggested by the standards, measurements and testing programme (BCR, formerly) of the European Commission. In order to make a distinction between an easily reducible fraction bound to manganese oxides and a moderately and poorly reducible fraction bound to amorphous and crystalline iron oxides, the procedure was modified by adding a third extraction step. *Aqua regia* was used in the fifth stage of the extraction according to the EPA 3050B digestion method for determining the residual metal content of the analytes. The sequential extraction was investigated at three different temperatures and it was performed in triplicate. The complete scheme of the modified and applied procedure is given in Table I.

TABLE I. The composition of extracting solutions and conditions of the sequential extraction procedures

Fraction No.	Elements extracted	Extraction time, min	Agitation method	Extractant volume, cm ³	Extractant
I	Water-exchangeable, weakly adsorbed	15	ME	40	0.11 mol dm ⁻³ HOAc
II	Easily reducible	15	ME	40	0.1 mol dm ⁻³ NH ₂ OH·HCl / HNO ₃ , pH 2
III	Moderately reducible	15	ME	40	0.2 mol dm ⁻³ (NH ₄) ₂ C ₂ O ₄ / 0.2 mol dm ⁻³ H ₂ C ₂ O ₄
IV	Oxidizable	180	Occasional agitation, 85 °C	2×10	30 % / 8.8 mol dm ⁻³ H ₂ O ₂ / HNO ₃ , pH 2
V	Residual	15	ME	40	1 mol dm ⁻³ NH ₄ OAc, pH 2
		15	ME	10	<i>Aqua regia</i>

RESULTS AND DISCUSSION

Single extraction

The measured pH value of the coal suspension in deionized water was 6.40.

The extraction of potassium and sodium by means of RE and UE are shown in Fig. 1a and b, respectively, while ion concentrations were measured using IC and ICP-AES. It could be seen from Fig. 1a that the amount of extracted potassium increased as the time of shaking increased. A significant increase in the concentration of extracted potassium was observed when the time of shaking was inc-

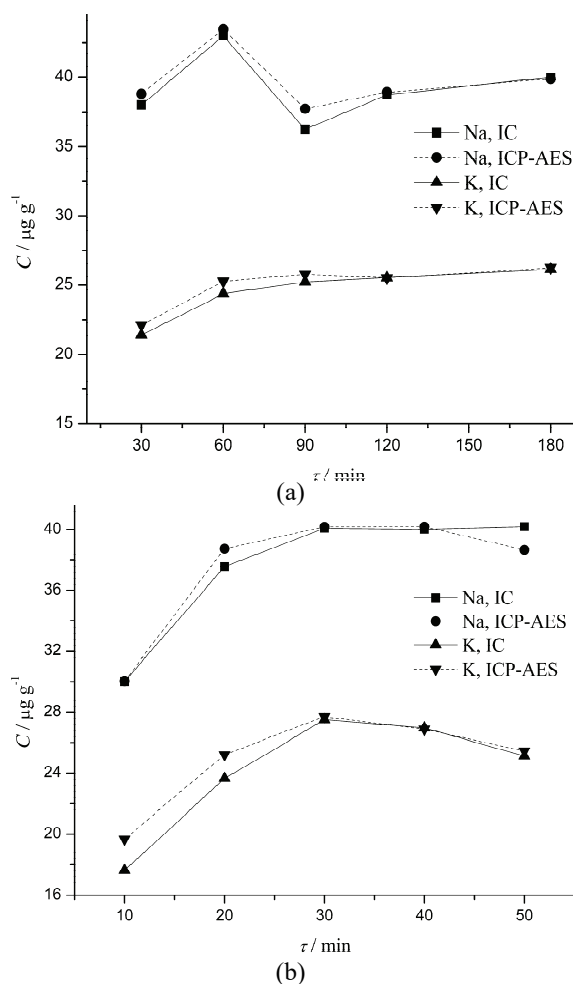


Fig. 1. The contents of Na and K obtained by means of: a) RE and b) UE at different extraction times, measured by IC and ICP-AES.

reased from 30 to 60 min. A further increase in the shaking time did not lead to any substantial increase in the quantity of extracted potassium ions and after 90 min, the concentration of potassium in the water was almost constant. The efficiency of ultrasonic-assisted extraction of potassium improved when the exposure to ultrasound was increased from 10 to 30 minutes (Fig. 1b). The quantity of extracted potassium decreased with further increase in the duration of the ultrasonic-assisted extraction. Potassium ion extraction using a rotary mixer gave almost the same results as the extraction using the ultrasonic bath. The quantity of sodium extracted by means of RE increased with the time of shaking up to 60 min. A further increase in the time of shaking led to a decrease in the quantity sodium, after which a moderate increase was observed. The quantity of sodium obtained by means of UE increased as the duration of extraction increased up to

30 min; thereafter a further increase in the time of extraction did not lead to any changes in the quantity of sodium. The quantity of sodium extracted after 30 min using an ultrasonic bath was almost the same as that obtained after 180 min using a rotary mixer.

The extracted quantity of potassium obtained by microwave-assisted extraction at 100 °C was 2.2 times higher, while at 150 °C it was even 3.2 times higher than the one obtained using RE and UE (Fig. S-1 of the Supplementary material to this paper). The quantity of sodium ions extracted employing ME (Fig. S-1) showed a tendency for a mild increase with increasing extraction temperature.

According to results shown in Fig. 2a and b, it is clear that there were no differences for Ca and Mg extraction using RE and UE. The maximum extracted quantities of both Mg and Ca were obtained after 20 min of UE. From Fig. S-2 of the Supplementary material, it could be seen that with temperature increase, ME

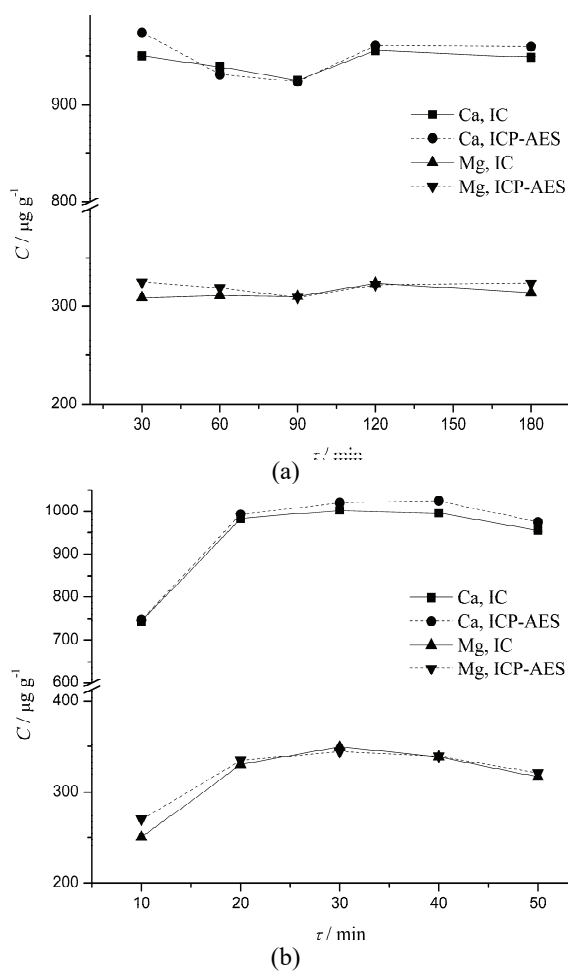


Fig. 2. The contents of Ca and Mg obtained by means of: a) RE and b) UE at different extraction times, measured by IC and ICP-AES.

became more efficient for Ca than for Mg extraction. When the ME temperature was changed from 50 to 100 °C, the extraction of Ca increased 5 times. This was expected since Ca in coal occurs as various insoluble inorganic compounds. The similarity between the results obtained in the processes of Ca and Mg extraction could be associated with the fact that the similarity of elements in terms of their chemical characteristics leads to their similar behavior in coal and similarity in the process of their association and mobility.

Every parallel measurement of the concentrations K, Na, Mg and Ca using the ICP-AES and IC methods showed an adequate level of consistency, as well as great precision and accuracy in the measurement process. In a large number of measurements, the good agreement between the results obtained by IC and ICP-AES confirmed that a readily available measurement method, such as IC, could be used effectively.

The concentrations of Be, Sb, Se and Hg, obtained using the three different coal extraction procedures were below the detection limits of ICP-AES (Be < 2; Se < 2; Sb < 5 and Hg < 10 $\mu\text{g dm}^{-3}$). Therefore, the investigated extraction methods cannot be used for the determination of these elements in coal. One of the reasons is their low concentrations, high volatility and forms of occurrence in coal.^{19,20}

The amounts of cadmium extracted using the RE and UE methods were below the detection limit (2 $\mu\text{g dm}^{-3}$). Microwave-assisted extraction at 100 °C resulted in an eleven times lower extraction amount when compared with the amount extracted at 150 °C (Table S-I of the Supplementary material).

The amounts of extracted cobalt obtained by RE, UE and M50 were quite low, close to or even below the detection limit (Table S-I). The quantity of cobalt extracted using microwaves increased with increasing extraction temperature.

The microwave-assisted extraction at 150 °C resulted in the highest extracted amounts of aluminum, manganese and, especially, iron compared to the other employed extraction techniques (Table S-I). The results presented in the same Table showed that RE was more efficient for extraction of Al and Fe than UE. In the case of manganese, the efficiencies of the UE and RE methods were comparable. The ME at 50 °C resulted in a quantity of manganese ions that was twice as high, whereas an increase in temperature to 100 °C resulted in a ten times higher quantity of manganese and the quantity extracted at 150 °C was 30 times higher than those obtained by RE and UE.

In the case of arsenic, nickel and lead, the extraction using an ultrasonic bath or a rotary mixer proved equally efficient (Table S-I). The quantities of all extracted elements increased with increasing ME temperature. The influence of temperature on nickel extraction was more prominent than on arsenic extraction.

Considering the UE technique, the extracted amount of cations varied with the extraction time. This could be explained by the effect of ultrasonic energy on

the coal suspension that, alternately, influences the processes of ion adsorption and desorption. Studies have shown that trace elements are most commonly bound by carboxyl groups of organic macromolecules and/or fulvic acids, when hydrogen ions are exchanged by metal ions, which is consistent with previous results.²¹

In the case of As, Mn, Ni and Pb, the extracted quantities were almost constant at all RE and UE extraction times. The efficiency of RE and UE were the same for the above-mentioned elements. UE was more efficient in the case of Co and Cr, giving significantly higher extracted amounts than RE. The use of RE proved more efficient than UE for Fe and Al extraction.

Considering the ME technique, there was an obvious positive correlation between the amount of extracted elements and extraction temperature, as expected. The microwave-assisted procedures were faster than the other two techniques.

Sequential microwave extraction of major and minor elements

Sequential extraction provides useful information for risk assessment since the amount of elements mobilizable under different changes in environmental conditions can be estimated.¹⁷ The time (and hence cost) required for extraction is considerable, with the BCR and Tessier procedures requiring up to 4 and 5 days respectively.²² Microwave technology provides an opportunity to reduce extraction time and offers an attractive alternative to conventional procedures.

The average concentrations of major elements (for three measurements) in the coal sample extracted using sequential microwave extraction (SME) at three different temperatures are listed in Table II.

As expected, an increase in the temperature of the SME resulted in an increase in the total quantity of extracted elements. The highest influence of temperature increase during SME was on Al and K extraction, moderate on Fe and Mn extraction, and the lowest on Ca, Mg and Na extraction. Such results may be explained by the fact that a rise in temperature leads to the breakdown of minerals such as kaolinite, montmorillonite, illite and aluminum oxides and hydroxides.²³

In the course of the SME, calcium was extracted in fraction I and II at every temperature (Table II), which could be attributed to the breakdown of carbonates, namely calcite (CaCO_3), dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$) and siderite (FeCO_3).²⁴ Likewise, the occurrence of magnesium could be attributed to carbonates, to dolomite mainly. In addition, the fact that the highest quantities of magnesium were extracted in fraction I by means of acetic acid and in fraction II by means of a hydroxylamine solution supports the view that it is bound to carbonates.

The largest quantities of sodium, which can be found in a number of minerals, were extracted at all temperatures in fractions I and IV of the SME, an occurrence that is attributed to the breakdown of sulfide ores and the organically associated metal fraction.

TABLE II. The concentrations of major metals – Al, Ca, Fe, K, Mg, Mn and Na ($\mu\text{g g}^{-1}$), obtained by sequential microwave extraction at 50, 100 and 150 °C

Fraction	<i>t</i> / °C	Al	Ca	Fe	K	Mg	Mn	Na
I	50	26.74	6207	51.55	50.66	1236	38.54	48.21
II		127.0	5507	2005	31.80	589.3	104.3	9.70
III		521.7	26.30	3535	11.95	72.01	51.89	17.91
IV		1462	1238	5487	38.73	192.9	22.78	77.65
V		124.8	78.34	86.05	6.62	14.94	0.52	9.13
Sum		2260	13060	11160	139.8	2105	218.0	162.6
I	100	22.99	8311	237.5	69.56	1651	111.3	51.80
II		178.9	4531	4494	26.31	407.6	132.7	10.17
III		1056	27.43	2049	11.57	72.53	15.34	12.06
IV		1253	596.6	4763	34.70	132.1	10.19	65.31
V		2213	29.95	622.0	49.03	85.05	1.69	13.57
Sum		4724	13500	12170	191.2	2348	271.2	152.9
I	150	554.3	8920	1997	86.72	1754	156.7	58.74
II		816.7	4289	4379	39.31	439.3	93.01	12.28
III		4581	36.41	2166	63.78	178.3	12.44	17.12
IV		1086	395.9	2599	27.45	71.07	6.02	70.65
V		7138	55.93	2692	240.5	271.3	5.94	24.57
Sum		14180	13700	13830	457.8	2714	274.1	183.4
ASTM D6349-13		45600	17400	31900	1878	4727	374.2	709.5

The largest quantities of potassium were extracted in the first fraction of sequential extraction at 50 and 100 °C and in the fifth fraction at 150 °C. This indicates that potassium was bound to hydrated aluminosilicate minerals.

The main components of mineral matter from many coal and clay minerals which contain aluminum include: kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), illite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), muscovite $\text{KAl}_2(\text{OH},\text{F})_2(\text{AlSi}_3\text{O}_{10})$ and montmorillonite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$). An oxalate reagent is an efficient agent to be used for the extraction of amorphous aluminum hydroxides, for which reason, a significant quantity of aluminum during was obtained in fraction III. The reason the greatest quantity of Al was extracted into fraction V is that with increasing temperature, the silicate material was decomposed.

The presence of Fe in the second extraction fraction indicates the presence of amorphous, highly mobile hydroxides of this element. It was expected that Fe would be present during fraction III due to the extraction of amorphous and crystalline oxides. In addition, a considerable amount of Fe was found in fraction IV, whereas after an increase in the temperature of the SME up to 150 °C, it became the dominant component in fraction V as well. It is known that bentonite clays found at the Kostolac Basin contain high concentrations of Fe_2O_3 (6.5–8.5 %).²¹

Manganese quantities extracted in fraction I and fraction II were considerable, due to decomposition of manganese oxides by the hydroxylamine solution.

A significantly high concentration of manganese was evident and it was most probably bound to carbonates (calcite and siderite).²¹

The average concentrations of trace elements determined by SME are presented in Table S-II of the Supplementary material.

Cobalt was released in all steps of the sequential extraction, but the easily mobilized form (easily reducible) and oxidizable were predominant at all extraction temperatures. This is in accordance with the fact that cobalt in coal is mainly associated with sulfide minerals, mostly in pyrite, or in organic associations in low-rank coals.²⁵

The highest quantities of Be extracted at 50 and 100 °C were obtained in fractions II–IV of the sequential extraction, whereas those extracted at 150 °C were the highest in fraction I and II (Table S-II).

Cadmium was released in all steps of the sequential extraction except for the residual fraction at 50 °C and presented similar percentages in the second and fourth fraction. Cadmium usually occurs in sphalerite (ZnS).²⁵

Substantial quantities of arsenic was extracted in fractions III and IV at 50 °C, in fractions II–IV at 100 °C and in fractions I and II at 150 °C. On the other hand, arsenic was almost not present in fraction V owing to its volatility.

The greatest extracted quantities chromium were found in fraction IV of sequential extraction at 50 and 100 °C, but in fractions III–V when the extraction was performed at 150 °C. Chromium is found in association with oxides, most commonly, iron oxides.²⁶ Chromium in coal is organically associated, but coal with high concentrations of chromium ($> 500 \mu\text{g g}^{-1}$) was found to contain chromite (FeCrO₄).²⁶

Considerable quantities of nickel were extracted at all temperatures in fractions II–IV. In many coals, substantial amounts of Ni may be organically bound. The inorganically bound Ni appears to be largely associated with sulfides.²⁵ The largest amounts of lead were extracted in fractions III and IV. Lead occurs predominantly as sulfides or associated with sulfide minerals. Galena (PbS) is the most common form of lead in coal, but galena can have several significantly different associations. Galena can occur as large, epigenetic crystals in cleat and fractures.²⁷

The total contents of analyzed elements were determined by the standard ASTM method and the results are presented in Tables II and S-II.²⁸ The results of applied standard method were compared with results obtained for SME at 150 °C. The highest investigated temperature was selected, since, for most of the investigated elements, the extracted concentrations increased with temperature increase. According to the results listed in Tables II and S-II, it could be seen that for all analyzed elements, less than 80 % of total content was determined by SME. Considering the major elements (Table II), the lowest recovery (according to total content) was for Al, K and Na, moderate recovery was achieved for Fe

and Mg, while the highest recovery was obtained for Ca and Mn. The reason for this is that in applied SME, aggressive reagents, such as concentrated mineral acids, were not used. In addition, Al and K in coal are usually bonded to silica matter, and in this study HF, as proven reagent for silica decomposition, was not used. On the other hand, coal from the Kostolac mine has a high silica content (up to 9 %). The results listed in Table S-II indicated that for the trace elements, lowest recoveries were for As and Co, while moderate recoveries were achieved for Cr, Ni and Pb. Total contents for Be and Cd were below the detection limit, contrary to SME when these elements were detected. Although, *aqua regia* was used in the fifth step of SME to determine the residual metal content, it is evident that some further investigations should be conducted in order to improve the precision and accuracy of the method.

From a practical point of view, it is very important to evaluate the migration of the investigated major and, especially, trace elements to the environment. The mobility of elements from coal under environmental conditions depends on the pH of the rain and/or ground water, the pH values of which are lower than 7. The analyzed elements that are mobile under environmental conditions are bound to the water-exchangeable and weakly adsorbed fractions (the first step of the SME). The SME experiments of were conducted at raised temperatures, but from results presented in Tables II and S-II, it is obviously that elements such as As, Cd, Co, Cr, Ni, Pb, Fe and Mn from coal could influence environmental pollution. The element found in the other fractions could migrate to the environment under specific conditions, *i.e.* aggressive (fractions II and IV) and/or in the presence of microorganisms (fractions II–V).²⁹

Validation of extraction methods

Calibration curves were established for all investigated elements using aqueous standards. For this purpose, the certified reference solution multi-element standard solution 4 (Specpure, Alfa Aesar) and diluted solutions were used. The parameters of the calibration lines, *i.e.*, slopes, intercepts and correlation coefficients (r), as well as limits of detection (LOD) and limits of quantifications (LOQ) are presented in Table III. The LOD and LOQ values were calculated as 3 and 10 times the ratio of the relative standard deviation to the slope, respectively.³⁰ The LOD and LOQ values for investigated elements in coal sample ($\mu\text{g kg}^{-1}$) are 10-times the corresponding values presented in Table III.

It was found that the linear range is at least up to 3 orders of magnitude in relation to the LOQ s.

The accuracy of the complete method, starting from the extraction (rotary, ultrasonic-assisted and microwave-assisted) to ICP-AES measurements was checked using the standard addition method.³⁰ Different small amounts of aqueous CRM were added to a real coal sample, which was air dried, at room tem-

perature, before the extraction procedure. The obtained extracts were analyzed in triplicate, the standard deviations and the recoveries (R) were calculated for each element. The results are given in Table S-III of the Supplementary material. The accuracy of the extraction methods were investigated under the optimal analytical conditions, as can be seen from Figs. 1, 2 and S-1 and Table S-I: RE for 120 min, UE for 30 min, and ME at 150 °C.

TABLE III. Calibration data, LOD and LOQ for ICP-AES measurement of the investigated elements

Element	Intercept, cps	Slope, cps dm ³ µg ⁻¹	r	LOD / µg dm ⁻³	LOQ / µg dm ⁻³
Al	298.6	5.01	0.9970	2.51	8.36
As	-0.87	1.11	0.9999	1.24	4.14
Ca	150.53	20.05	0.9993	0.72	2.4
Cd	15.39	37.84	0.9999	0.06	0.22
Co	2.31	15.88	0.9999	0.13	0.45
Cr	10.07	28.07	0.9999	0.33	1.09
Fe	20.58	10.15	0.9988	0.67	2.24
K	736.3	68.09	0.9993	0.50	1.66
Mg	34.72	4.52	0.9998	2.22	7.39
Mn	87.89	139.47	0.9997	0.06	0.20
Na	-144.85	4.82	0.9999	7.62	25.39
Ni	10.64	12.22	0.9998	0.20	0.65
Pb	-1.04	2.73	0.9892	0.81	2.71

As can be seen from Table S-III, the used extraction methods provided good recoveries of all elements, ranging from 91 to 105 %. This means that the proposed methods are of good accuracy. The relative standard deviations (RSD) of the measured elements were in all cases, except Na and K, less than 10 %, leading to the conclusion that the precision of the methods is satisfactory. The RSD values for Na and K determination in spiked coal sample (Table S-III) were between 15 and 20 %. The RSD values for Na and K were 12.24 and 11.30 %, respectively, for the calibration measurements with ICP-AES. In these cases, the use of IC is more appropriate because the RSD for Na and K were 0.35 and 0.29 %, respectively, and the contents of these metals in coal were in the range of the sensitivity of IC.

CONCLUSIONS

Three different extraction methods for the extraction and determination of elements in coal were investigated. The results of ion measurements in an extraction solution by IC and ICP-AES indicated that IC could be successfully applied for the determination of the investigated alkali and earth alkali elements. The ICP-AES method is very applicable in the study of a multi-element extraction process and metal partitioning in coal. The metal contents extracted using a rotary mixer and an ultrasonic bath were very similar and much lower than

quantities extracted by a single microwave-assisted extraction. With respect to the extractions in which a rotary mixer or an ultrasonic bath was used, there were no positive correlations between the amount of extracted elements and the extraction time. In addition, the most efficient extraction technique for Fe, Na and Pb ions was the RE, while the UE was the most efficient method for Co and Cr extraction.

The proposed microwave-assisted methods significantly reduced the time required for a conventional sequential extraction. With dependence on the analyte and temperature, the proposed microwave-assisted sequential procedure for coal digestion was considered suitable for the determination of the elements by ICP-AES. The extracted amounts for each of the elements analyzed using the microwave-assisted digestion system correlated positively with increasing extraction temperature. Additional research on microwave extraction at a constant temperature should be conducted in order to optimize the conditions for the total determination of the elements.

Results of sequential microwave extraction indicated possible leaching of As, Cd, Co, Cr, Ni, Pb, Fe and Mn from coal under environmental conditions. Among these elements, As, Cd, Cr, Ni and Pb are toxicologically the most important and they were present in the first phase fractions (the water-exchangeable and weakly adsorbed fractions).

SUPPLEMENTARY MATERIAL

The contents of Na, K, Ca and Mg obtained by microwave assisted extraction at different temperatures, the concentrations of trace elements and the data of the determination of elements in a spiked coal sample are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

ИСПИТИВАЊЕ РАЗЛИЧИТИХ ПРОЦЕДУРА ЕКСТРАКЦИЈЕ ЗА ОДРЕЂИВАЊЕ МАКРО-И МИКРО-ЕЛЕМЕНАТА У УГЉУ ПОМОЋУ ИСП-АЕС И ЈОНСКЕ ХРОМАТОГРАФИЈЕ

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У раду је представљен поступак екстракције метала и неметала из угља дејонизованом водом применом три екстракционе технике: помоћу ротационе мућкалице, ултразвучне екстракције уз различито време трајања процеса, и микроталасну дигестију на различитим температурама. Концентрације елемената (Na, K, Ca, Mg, Al, Fe, Mn, Be, Cd, Co, Cr, Hg, As, Ni, Se, Sb и Pb) у раствору одређиване су применом атомске емисионе спектрометрије са индуковано спрегнутим плазмом, док су вредности за Na, K, Ca

и Mg утврђене и применом јонске хроматографије. Поређење ротационе и ултразвучне екстракције показује већу ефикасност ротационе екстракције за одређивање Fe, Na и Pb, док је ултразвучна екстракција ефикаснија за одређивање Co и Cr. Утврђено је да је микроталасна екстракција најефикаснија техника за екстракцију и одређивање садржаја испитиваних елемената у угљу. Будући да се микроталасна екстракција показала бржом и ефикаснијом од друге две технике, спроведене су додатне секвенцијалне екстракције применом микроталаса: резултати указују да су испитивани елементи везани делом за минералну и делом за органску фазу. Резултати секвенцијалне екстракције омогућавају процену излуживања As, Cd, Co, Cr, Ni, Pb, Fe и Mn из угља у животну средину.

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