Aqueous extraction of anions from coal and fly ash followed by ion-chromatographic determination

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COAL, ITS COMBUSTION AND EXTRACTION PROCESSES FOR SOLID SAMPLES

Coal is a fossil fuel and an important energy source.[1] The chemical and mineral composition of coal has a significant influence on the processing, application, and technological and environmental aspects related to this fuel.[2] During coal utilization processes, the mineral mater in coal undergoes different changes, and most important are those related to coal combustion. In combustion processes, the element are partitioned between bottom ash, fly ash and flue gases.[3]

Leaching of components from solid samples was the subject of much research, with focus on the metals leaching from coal fly ash.[4–8] Coal fly ash is a highly heterogeneous material with silicon dioxide, aluminium oxide and iron oxide as the major mineral components.[9]

The extraction of anions from various solid samples in some studies was tested using different extraction solvents. Aqueous Soxhlet extraction followed with ion chromatographic (IC) determination was used for extraction of fluoride, chloride, sulphate and some organic anions from coal.[10] Water and water solution of ammonium carbonate were used as absorbing media for halogens in the process of microwave-assisted extraction and simultaneous determination of F, Cl, Br and I by IC.[11] The microwave system was used for coal sample digestion in a mixture of nitric acid, hydrofluoric acid, and hydrogen peroxide, and then the concentrations of As, Br and I in the final solution were determined by an inductively coupled plasma–mass spectrometer.[12] Pyrohydrolysis was also successfully used to digest a coal sample and separate the halogens from the sample matrix.[13] The simultaneous extraction of bromide, chloride, fluoride and

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sulphate from soils, and waste and building materials was studied under acid and alkaline conditions.[14] The main components of the mineral matter in coal, in which fluorine, chlorine and sulphate constituents are to be found, include: muscovite ($KAl_2(OH,F)_2(AlSi_3O_{10})$), anhydrite ($CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), halite ($NaCl$), sylvite ($KCl$) and apatite ($Ca_5(PO_4)_3(F,Cl,OH)$).[15]

Microwave-assisted sample preparation in a closed system provides simultaneous treatment of multiple samples, dissolution of solids at elevated temperature and pressure with almost no loss of volatile analytes.[16,17] Some of the advantages of the ultrasound-assisted sample pre-treatment are speed of extraction, high sample treatment capacity, low reagent demand and safe analysis performance. Ultrasound-assisted digestion has been used for the elemental analysis of many solid samples, such as soil, sediment, coal fly ash and street dust.[18–20] A variety of applications of ultrasound has been explored to enhance chemical reactivity, including its employment for sequential extraction.[21] The combination of microwave or ultrasonic energy with aqueous extraction can be used for anion extraction from coal samples, in order to improve the extraction for the purpose of IC analysis.

Solid samples

The coal and coal fly ash samples were from the Kostolac coalmine located approximately 90 kilometres east of Belgrade, the Republic of Serbia, and approximately 20 km and 100 km from the Serbian borders with Romania and Bulgaria, respectively. Petrological and organic geochemical analyses showed that the lignite coal from the Kostolac Basin is a typical humic coal.[22]

REAGENTS

Deionised water from a Milli-Q system (Millipore, USA) was used for the extraction and preparation of all solutions. The resistivity of the deionised water used was 18.2 MΩ cm at 25 °C. The chemicals used for the analyses were of high analytical purity grade. The eluent for ion chromatography was prepared by dissolving Na_2CO_3 (Fluka, Switzerland), previously dried for 2 h at 105 °C, in deionised and degassed water. The eluent was made on a daily bases and then filtered through a 0.22 μm pore size membrane filter (Phenomenex, USA). A primary multi-anion standard stock solution included fluoride (100 mg dm^{-3}), chloride (200 mg dm^{-3}), bromide (400 mg dm^{-3}), nitrate (400 mg dm^{-3}), phosphate (600 mg dm^{-3}) and sulphate (400 mg dm^{-3}) (Multi-Component Anion Mix 2, IC-MAN-02-1, AccuStandard, USA) was used for calibration.

VALIDATION OF IC MEASUREMENTS

The linearity of the method was characterized by six calibration curves containing five non-zero concentrations. Each calibration curve was determined by plotting the peak area (y) of fluoride, chloride, nitrate, bromide, phosphate and sulphate *versus* the nominal concentration (x) of the measured anion in the standards. The limit of quantification (*LOQ*) was defined to be the concentration

level at which the signal-to-noise ratio was at least 10, while the limit of detection (*LOD*) was defined to be the concentration at which the signal to noise ratio was greater than 3.[23] The retention times (t_R) and calibration parameters are listed in Table S-I.

TABLE S-I. Linearity data for standard mixtures: $y = ax+b$, where x is the concentration of analyte (mg dm^{-3}), y is peak area (μS min cm^{-1}), *RRSD* is the residual relative standard deviation and *R* is the regression coefficient

Analyte	t_R min	Regression equation	*RRSD* %	*R*	*LOD* μg dm^{-3}	*LOQ* μg dm^{-3}
Fluoride	3.13	$y = 18.067x + 1.014$	0.042	1.0000	11	37
Chloride	4.88	$y = 13.010x + 1.007$	1.478	0.9999	15	50
Nitrate	7.26	$y = 5.514x + 0.936$	0.828	0.9998	26	87
Bromide	8.13	$y = 4.325x + 0.399$	1.885	0.9997	30	100
Phosphate	9.16	$y = 3.121x+0.606$	1.108	0.9999	37	125
Sulphate	13.24	$y = 9.2799x - 1.046$	1.673	0.9999	20	67

The mean values and relative standard deviation for low (up to 5 mg dm^{-3}), medium (up to 10 mg dm^{-3}), and high (up to 20 mg dm^{-3}) concentrations of the quality control samples were calculated over three validation runs that contained six replicates of each quality control level per run. The accuracy was measured *via* the percentage deviation in the quality control analysis and is expressed as the relative error (*RE*). The accuracy of the method was between 0.04 and 2.88 % for the three analyte concentrations. The repeatability of the method varied from 0.27 to 2.35 % at the three quality control levels of the analytes. The results showed that the method allowed the determination of the investigated anions with acceptable accuracy, precision, and repeatability.

Extraction recoveries of the analytes were evaluated at low, medium, and high concentrations by comparing the peak areas obtained from samples with the analytes fortified before 30-min UAE. The average recoveries were 97.86, 98.58 and 98.74 % with relative standard deviations of 0.86, 0.58 and 0.69 % for fluoride, chloride and sulphate, respectively, in coal extract. In the case of fly ash extract, the average recoveries were 96.18, 97.02 and 93.96 % with relative standard deviations of 0.76, 0.67 and 0.98% for fluoride, chloride and sulphate, respectively. These results indicated that the IC method is suitable for practical analysis of anions in coal and fly ash extracts.

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