Original Research

Validation and Optimization of Conditions for the Sequential Extraction of Manganese from Ash

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Abstract

Methods of sequential extraction are used to determine various chemical forms of metals in environmental samples. With the variety of different sequential extraction procedures used in environmental exploration studies, it is difficult to compare results between studies. The attempt of validation of methods of analysis of chemical fraction of Mn in ashes by FAAS method for two procedures of sequential extraction (BCR and Tessier et al.) was perfomed. It was found that both tested procedures give comparable and reproducible results. The optimal conditions of BCR methods were established, which are: parameters of ash sample (grain diameter – 0.06 mm, drying temperature – 110°C for 24 hrs, mass sample – 1.00 g) and parameters of sequential extraction process (time – 6 hrs, relation of mass of sample to the volume of extraction solution – 1:4). The optimum conditions of sequential extraction of Mn from coal fly ash can be applied in the study of chemical fraction of Mn in fly ash in different research laboratories.

Keywords: fly ash, manganese, sequential extraction, FAAS.

Introduction

Hard coal used in combustion creates considerable quantities of waste ash. The greatest quantities of industrial ashes are stored in the form of waste-heaps, which create a serious problem as sources of inorganic pollution. It is necessary to identify the physical and chemical properties of ashes, especially when analyzing pollution of the soil by trace metals, which are potentially mobile in the environment.

The availability and mobility of trace elements occurring in fly ashes depends on the physicochemical forms of the elements. The basic chemical forms of metals contained in the environmental samples can be described by using sequential extraction method [1]. The BCR procedure (proposed in 1993 by the European Community's Bureau of References – now Standards, Measurements and Testing Program) [2] and the method proposed by

Tessier et al. [3] are most often used for this purpose. The application of Tessier's procedure to samples of soils and sediments of various origin was described in [4]. The BCR scheme was widely used to analyze various samples: coal fly ashes [5-10], soils [11-15] and sediments of various origin [16-23].

The coal fly ash is chemically non-homogeneous material, which induces the problem of repeatability of analytic results and necessity of validation of practical analytical procedures. With a view to reproducibility, the important problem is optimization of sequential extraction procedures. So far, the comparative investigations and verifications of results of analysis of chemical fractions of Mn in fly ashes haven't been executed and described. There is not a recommended method to be used in practice.

The aim of this work is:

1) the study of distribution of Mn in coal fly ash by sequential extraction method (BCR and Tessier et al.);

2) the validation of methods of analysis of chemical frac-

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tion of manganese in fly ash (BCR and Tessiera et al. procedures);

3) the optimization of conditions for sequential extraction of manganese from coal fly ash according to BCR method with regard to initial parameters of ash (grain diameter, drying temperature, mass of sample) and parameters of process of extraction (time and relation of mass of sample to the volume of extraction solution).

Experimental

Reagents and Solutions

All reagents were from POCH, Gliwice, Poland, and of analytical grade or higher purity: ammonium acetate NH_4OAc; sodium acetate $NaOAc$; glacial acetic acid $HOAc$ 100%; hydrogen peroxide H_2O_2 30% (8.8 mol·dm^{-3}); magnesium chloride $MgCl_2$; perchloric acid $HClO_4$, nitric acid HNO_3; hydrofluoric acid HF hydrochloric acid HCl and hydroxylamine hydrochloride $NH_2OH·HCl$ (Sigma, Deisenhofen, Germany, 99% ± 0.01). The composition of the extraction solutions are given in Fig.1. The solutions were prepared by dissolving the listed compounds in double distilled water from a Water Purification System (Model Rel – 5, MERA – POLNA, Poland). The reagents were prepared and stored in clean polyethylene bottles. Glassware and plasticware (PE) used throughout the experimental work were previously soaked in 10% nitric acid bath overnight and washed thoroughly in double-distilled water.

Standard manganese solutions were prepared from standard solutions for atomic absorption (manganese concentration 1.000 μg·cm^{-3} in 1% of HNO_3, Aldrich).

Samples

In comparative investigations fine fly ash samples were applied. They were Certified Reference Material (CTA – FFA – 1) for multielement trace analysis, produced and certified by the Commission of Trace Analysis of the Committee for Analytical Chemistry of the Polish Academy of Science, and the Institute of Nuclear Chemistry and Technology (Warsaw, Poland). Prior to analysis they were dried at 105°C for 24 hrs until they were constant.

The optimization of conditions of BCR method was performed for coal fly ash. Coal fly ash samples were collected from the electric filter from the Rzeszów S.A power-plant (Rzeszów, Poland). The 0.5 kg sample was prepared from an air-dried 10 kg sample using the "quarterning" method - according to procedure BN-81/0623–01 [24]. Next, the air-dried ash was sieved initially through a laboratory sieve of 1 mm diameter, and then milled in an agate mortar to fine powder (φ ≤ 100 μm) – according to PN-77/G-04528/00 [25].

Procedures

Sequential Extraction Procedures

The composition and concentration of the extraction solutions are given in Fig.1. The sequential extraction of

fly ash (m = 1.00 g) or its total mineralization was done in glass and PTFE vessels. After extraction, sample solutions were first centrifuged at 3000 rpm for 15 min and filtered through a filter paper for quantitative analysis MN 616 (Macherey-Nagel GmbH & Co. KG, Germany). The supernatant was used for analysis of Mn by the FAAS method. Remains of ash were washed with 10 cm^3 of double–distilled water and this second supernatant was discarded. Blank samples were prepared according to the proposed procedures and concentrations of the extracts were corrected by the corresponding blank solutions.

Optimization of Conditions for BCR Method of Sequential Extraction of Mn from Fly Coal Ash

The optimization of conditions for BCR method for sequential extraction of manganese from coal fly ash were performed for parameters of the initial state of ash such as: grain diameter (0.06, 0.102, 0.12, 0.25, and 0.5 mm), drying temperature (20, 70, 80, 110°C for 24 hrs and the samples of moist ash), mass of sample (0.5, 1.0, 2.0, 5.0, 7.0, 10.0 g) and parameters of sequential extraction process such as: time of shaking (2, 4, 6, 12, 16 hrs), relation of mass of sample to the volume of extraction solution (1:2, 1:4, 1:8, 5:4, 7:4; 5:2 g/cm^3). The prepared samples were exposed to sequential extraction by BCR method (Fig. 3). In the extraction solutions, concentration of Mn by FAAS method were determined.
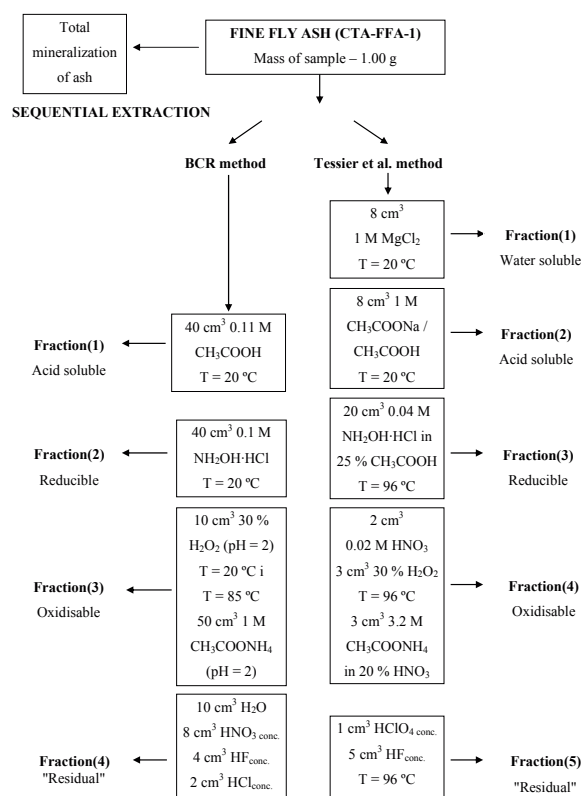

Fig. 1. Diagram of sequential extraction procedures of fine fly ash (CTA – FFA – 1).

Total Manganese Determination

Fly ash samples were digested in open PTFE® vessels. 1.00 g of ash was digested with a mixture of 8 cm^3 65% HNO_3, 4 cm^3 40% HF, 2 cm^3 37% HCl and 10 cm^3 H_2O. After evaporation to dryness in a hot plane (T = 96°C) the solution was incresaed to 50 cm^3 with water, and manganese was determined by FAAS method in the conditions described in the work [26].

Apparatus

A Perkin-Elmer Model 3100 air/acetylene flame atomic absorption spectrometer (Perkin-Elmer Instruments, Shelton, CT, USA) was used for the analysis of Mn in the extraction solutions (wavelength of 279.5 nm and fuel flow rate of 0.8-1.0 $dm^3 \cdot min^{-1}$). A centrifuge tube - test Model WE 1 (Precision Engineering, Poland) was used for the centrifugation of the soil extracts at 3000 rpm. A universal shaker Model Vibramax 100 (Heidolph Instruments, Germany) and a hot plate Model HP 88720-26 (Barnstead/Thermolyne, USA) were used for the extraction. The pH of extraction solutions was determined with a pH meter Model CPI-551 (Elmetron, Poland).

Statistical Analysis

The investigations were taken at the same time for six fly ash samples with simultaneously three-times repeated manganese detection in each sample. The statistical estimation of the results of analysis of the fraction of Mn in fly ash and the content of Mn in fly ash after its total mineralization was carried out on the basis of Student's t-test (p=95%). The validation of applied sequential extraction procedures in the study of distribution of Mn in fly ash was carried out according to statistical parameters: accuracy, precision, limit of detection and limit of quantification. The accuracy was qualified based on relative error (R) of determination of Mn by FAAS method in extraction solutions after sequential extraction according to BCR and Tessier et al. methods. The precision was calculated as the standard deviation of all the measurements performed at concentration Mn by FAAS method in the solutions after sequential extraction according to BCR and Tessier et al. schemes. Detection and quantification limits were calculated 3 and 10 times, repetitions of the standard deviation of 20 measurements of the blank solutions. Analysis of the variance was performed for the system: sequential extraction procedure – fraction of Mn for comparison reproducibility of the procedures used. The F_{max} Hartley test ($n_{(1)} = n_{(2)} = n_{(3)} = 18$, p = 95%, $F_k = 2.29$) was applied using the Snedecor criterion [27, 28]. The mass balance of Mn for extraction procedures was verified by comparison of its total contents in certified ash and sum of its concentrations in chemical fractions, to get the following: $[Mn]_{total} = 1066 (\pm 41)$ $mg \cdot kg^{-1}$ ash dry mass and $\Sigma[Mn]_{F(1)-F(4)} = 983$ $mg \cdot kg^{-1}$ – BCR method and $\Sigma[Mn]_{F(1)-F(5)} = 982.5$ $mg \cdot kg^{-1}$ – Tessier et al. method.

Results and Discussion

The Study of Distribution of Mn in Coal Fly Ash

The sequential extraction of Mn from fly ash, they were Certified Reference Material (CTA – FFA – 1) according to the four-stepped BCR method the four fraction of manganese were obtained: F(1) –acid soluble, F(2) – reducible, F(3) – oxidizable, F(4) – "residual". The sequential extraction of fly ash by Tessier et al. method allowed the partitioning of Mn between the individual chemical fraction defined as: F(1) – water soluble, F(2) – acid soluble, F(3) – reducible, F(4) – oxidizable, F(5) – "residual" - Fig. 1. The last chemical fraction of Mn characterized by both extraction methods embraces the most stable forms of Mn, insoluble in water and considered immobilized and biologically inactive.

The distribution of Mn in fly ash obtained in the above-mentioned procedures depends on the type of procedure and the following in order (Fig. 2):

BCR method

Mn (reducible) < Mn (acid soluble) <
< Mn (oxidizable) < Mn (residual)

Tessier et al. method

Mn (acid soluble) < Mn (water soluble)<
< Mn (residual) < Mn (reducible) < Mn (oxidisable).

According to BCR method the highest content of Mn – 587($\pm$22) $mg \cdot kg^{-1}$(58.8%) – was found in fraction F(4), whereas the fractions F(1) and F(3) contained 126($\pm$11) and 184($\pm$22) $mg \cdot kg^{-1}$, respectively, which corresponds to 12.6% and 18.4% of its total contents in ash. The lowest concentration of Mn 86($\pm$21) $mg \cdot kg^{-1}$(8.6%) was obtained for fraction F(2). According to Tessier et al.
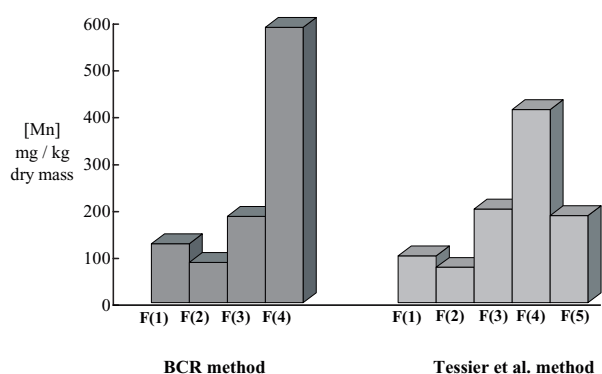

Fig. 2. Comparison of manganese distributions for various chemical fractions obtained after sequential extraction procedures by BCR and Tessier et al. (see Fig.1).
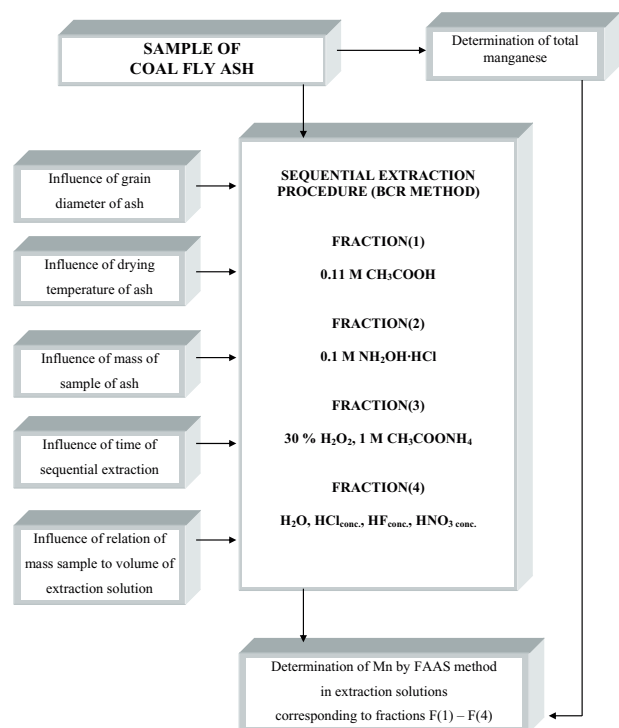
Fig. 3. Optimization of conditions of sequential extraction procedure of Mn from coal fly ash according to BCR method.

procedure the highest content of Mn was found in oxidisable fraction, F(3) – 623.3($\pm$38) mg·kg^{-1}(63.4%), and the lowest one in reducible fraction, F(2) – 15.2($\pm$3.5) mg·kg^{-1}(1.5%).

The Validation of Methods of Analysis of Chemical Fraction of Manganese in Fly Ash

The validation of two procedures (BCR and Tessier et al.) of sequential extraction Mn from fly ash was performed. The values of the validation parameters for determination of Mn by FAAS method are summarized in Table 1. The results obtained from the application of two sequential extraction procedures showed that both used methods were accurate (relative error, R = 7.8% - BCR method; relative error, R = 7.9% - Tessier et al. method) and precision (RSD = 0.3 $\div$ 9.6% - BCR method; RSD = 0.4 $\div$ 8% - Tessier et al. method). When testing fraction F(1) in BCR method and fraction F(2) in Tessier et al. method (Mn acid soluble) by F$_{max}$ the following variances were obtained for fraction: F$_{1,2}$ = 1. 96 < F$_k$ (2.29). Identical regularities were obtained for other fractions of Mn, i.e. F(3), F(4) and F(5). This shows that the variances of both tested procedures of sequential extraction (BCR and Tessier et al.) give comparable and reproducible results in determination of Mn by FAAS method in extraction solutions.

The Optimized Conditions of Sequential Extraction of Manganese by BCR Method from Coal Fly Ash

Taking into consideration the criterion of time consumption the four-stepped BCR method can be recommended. The studies were performed on coal fly ash. The optimized conditions of sequential extraction of Mn from fly coal ash according to BCR method were embraced: parameters of the initial state of ash (grain diameter, drying temperature, mass of sample) and parameters of process of extraction (time of shaking and volume of extraction solution in relation to mass sample) - Fig. 3. The obtained results showed that in conditions of conducting sequential extraction of Mn from coal fly ash (according to BCR procedure) the highest concentration of Mn was determined for samples with the following parameters of initial state of ash, such as: grain diameter φ = 0.06 mm (Table 2), temperature of drying T = 110°C for 24 hrs (Table 3), mass of sample m = 1.00 g (Table 4) and parameters of process of extraction, such as: time of shaking t = 6 hrs (Table 5), relation of mass of sample to the volume of extraction solution 1:4 (Table 6). Simultaneously the concrete influence of these parameters on determined content of Mn in each fraction of coal fly ash after the BCR sequential extraction procedure was not obtained.

Table 1. Validation parameters for determination of chemical fractions of Mn in coal fly ash using the FAAS method in the BCR procedure and Tessier et al. scheme see Fig.1).

	Limit of detection [mg·kg^{-1}]	Limit of quantification [mg·kg^{-1}]	Relative error R [%]	Precision [% RSD]
BCR PROCEDURE	F(1) – 5.7 F(2) –9.9 F(3) – 2.1 F(4) – 6.6	F(1) – 19 F(2) –33 F(3) – 7 F(4) – 22	7.8	0.3 $\div$ 9.6
TESSIER SCHEME	F(1) – 2.5 F(2) – 2.1 F(3) – 17.1 F(4) – 5.4 F(5) – 2.7	F(1) – 8.3 F(2) – 7 F(3) – 57 F(4) – 18 F(5) – 9	7.9	0.4 $\div$ 8

Table 2. Influence of grain diameter of ash on Mn determination in F(1) - F(4) fractions obtained after BCR sequential extraction procedure by FAAS method; m = 1.00 g, V = 40 cm³ (see Fig.1).

Content of Mn [mg·kg⁻¹]	Grain diameter [mm]				
	0.06	0.102	0.12	0.25	0.5
F(1)	115.0	116.7	120.0	119.6	118.0
F(2)	83.3	83.3	85.0	85.0	83.3
F(3)	60.3	63.5	61.7	62.5	60.5
F(4)	59.7	53.5	50.0	50.5	53.3
$\sum$ Mn $_{F(1)-F(4)}$	318.3	317.0	316.7	317.6	315.1

Table 3. Influence of drying temperature of ash on Mn determination in F(1) - F(4) fractions obtained after BCR sequential extraction procedure by FAAS method; m = 1.00 g, V = 40 cm³, $\varphi \leq 100$ μm (see Fig.1).

Content of Mn [mg·kg⁻¹]	Temperature of drying [°C]				
	20	70	80	110	moist ash
F(1)	115.0	111.0	113.5	113.5	112.5
F(2)	81.5	83.5	83.5	80.5	83.3
F(3)	67.5	68.5	61.5	64.8	67.5
F(4)	50.0	55.7	60.0	60.0	52.5
$\sum$ Mn $_{F(1)-F(4)}$	314.0	318.7	318.5	318.8	315.8

Table 4. Influence of mass of sample of ash on Mn determination in fractions F(1) - F(4) obtained after BCR sequential extraction procedure by FAAS method; T = 110 °C, V = 40 cm³, $\varphi \leq 100$ μm (see of Fig.1).

Content of Mn [mg·kg⁻¹]	Mass of sample [g]					
	0.5	1.0	2.0	5.0	7.0	10.0
F(1)	114.5	117.0	118.5	112.3	114.7	113.5
F(2)	82.5	85.0	96.0	86.0	85.5	82.5
F(3)	62.7	60.4	61.0	61.5	62.5	63.3
F(4)	55.0	55.5	52.0	54.2	54.7	60.0
$\sum$ Mn $_{F(1)-F(4)}$	314.7	318.9	317.5	314.5	317.4	319.3

Analysis of Chemical Fraction of Mn in Coal Fly Ash and Determination of Total Mn

In the settled optimum conditions of sequential extraction by BCR method the chemical fractions of manganese in coal fly ash were determined. In summary, the partitioning of Mn between individual fractions was the following: F(1) - Mn acid soluble: 120(±4.3), F(2) - Mn reducible: 85(±2.5), F(3) - Mn oxidisable: 62.5(±1.9) and F(4) - Mn "residual": 57.5(±1.7) mg·kg⁻¹ ash dry mass. The total content of Mn in coal fly ash was on the level of 325(±27) mg·kg⁻¹ ash dry mass.

Conclusions

In conclusion, the applied sequential extraction procedures (BCR and Tessier et al.) are extremely suitable for studies of chemical fraction of Mn in fly ash. Considering time-consumption of analytical procedure the study of partitioning of manganese from coal fly ashes ought to be carried out according to BCR method in the following optimum conditions: grain diameter of ash − 0.06 mm, drying temperature of ash − 110°C for 24 hrs, mass of coal fly ash sample − 1.00 g, time of sequential extraction − 6 hrs, relation of mass of sample to the volume

Table 5. Influence of time of shaking on Mn determination in the fractions F(1) - F(4) obtained after BCR sequential extraction procedure by FAAS method; m = 1.00 g, T = 110 °C, V = 40 cm^3, $\varphi \leq 100$ µm (see Fig.1).

Content of Mn [mg·kg^{-1}]	Time of extraction [hrs]				
	2	4	6	12	16
F(1)	115.8	120.0	113.0	112.5	124.0
F(2)	80.5	82.5	85.5	87.5	81.2
F(3)	62.5	62.5	64.5	65.0	60.5
F(4)	55.0	52.5	55.5	53.0	51.5
$\sum$ Mn $_{F(1)-F(4)}$	313.8	317.5	318.5	318.0	317.0

Table 6. Influence of relation of mass of sample to the volume of extraction solution on Mn determination in the fractions F(1) - F(4) obtained after BCR sequential extraction procedure by FAAS method; m = 1.00 g, T = 110 °C, $\varphi \leq 100$ µm (see Fig.1).

Content of Mn [mg·kg^{-1}]	Relation of mass of sample to the volume of extraction solution [g/cm^3]					
	1 : 8	1 : 4	1 : 2	5 : 4	7 : 4	5 : 2
F(1)	115.0	120.0	118.5	115.5	117.4	113.5
F(2)	82.0	82.0	84.0	84.0	85.7	85.5
F(3)	65.5	60.5	60.0	60.5	59.5	57.2
F(4)	55.0	55.4	53.0	54.2	54.8	53.8
$\sum$ Mn $_{F(1)-F(4)}$	317.5	318.9	316.5	314.2	317.4	310.0

of extraction solution – 1:4. The optimum conditions of sequential extraction Mn from fly coal ash according to BCR procedure can be employed for study of chemical fraction of Mn in ash in different research laboratories. The results obtained from these studies can be interesting for those laboratories, that apply sequential extraction procedures and concentrate on the results of optimization of the method.

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