SEQUENTIAL EXTRACTION OF MANGANESE FROM FLY ASH

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Abstract:
The four – stage sequential extraction procedure, proposed by the European Community Bureau of Reference (BCR), has applied for distribution of manganese in a fine fly ash (CTA - FFA - 1). The concentration of Mn in the solutions after extraction was determined by atomic absorption spectrometry (FAAS). The fraction of Mn were defined: (1) – acid soluble (e.g. carbonates); (2) – reducible (e.g. Fe / Mn oxides); (3) – oxidisable (e.g. organic matter); (4) – residual. On the base of results was investigated the partitioning of Mn between the individual fractions in the research material. The verification of the analytical results of the determination of Mn was carried out.

Key words: *fly ash, manganese, sequential extraction, FAAS.*

1. INTRODUCTION

The determination of total content of heavy metals in environment have been the subject of interest a several research works until recently. Total analysis may give information concerning possible enrichment of different solid samples with heavy metals, but generally, and for most elements, there are no sufficient criteria for estimating their health and ecological effects. The behaviour of the elements in the environment (e.g., bioavailability, toxicity and distribution) cannot be reliably predicted on the basis of their total concentration. At the present have been the growing interest in having available information about the mobility and bioavailability of metals present in environmental samples [14]. It has led to the widespread use of sequential extraction schemes in the research of environmental samples. These procedures have also been applied to other materials such sediments [6, 16, 17], soils [4, 5, 9, 10], incinerated sludge ash [8], municipal solid waste [7, 12], municipal solid wastes ash [2, 3, 18, 19], fly ash [1, 11, 15]. The sequential extraction procedures have been described to the fraction of trace metals, which can respond to generally occurrently the change of environmental conditions.

The aim of this work was distribution of Mn in fine fly ash samples (Polish Certified Reference Material, CTA – FFA – 1) by used the sequential extraction method, proposed by the European Community Bureau of Reference (BCR) [13]. On the base of results was investigated the partitioning of Mn among the individual fraction in fly ash. The verification of the analytical results of the determination of Mn by atomic absorption spectrometry (FAAS) was carried out.

2. EXPERIMENTAL

2.1. Reagents

All reagents were of POCH, Gliwice, Poland analytical grade or higher purity: acetic acid glacial HOAc 100 %; ammonium acetate NH_4OAc; hydroxylamine hydrochloride $NH_2OH\cdot HCl$ (Sigma, Deisenhofen, Deutschland, 99 % ± 0.01); hydrogen peroxide H_2O_2 30 % (8.8 $mol\cdot l^{-1}$); perchloric acid $HClO_4$, nitric acid HNO_3; hydrofluoric acid HF. The composition of the extractant solutions are given in Table 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). Standard manganese solutions were prepared from standard solutions for atomic absorption (Mn concentration 1.000 μg / cm^3 in 1 % of HNO_3, Aldrich).

2.2. Samples

The fine fly ash used in this study was the Polish Certified Reference Material (CTA – FFA – 1), produced and certified by: Commission of Trace Analysis of the Committee for Analytical Chemistry of the Polish Academy of Science and Institute of Nuclear Chemistry and Technology (Poland). The ash samples were only dried at 105 ° C for 24 hrs until contant weight.

2.3. Instrumentation

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/min.). A centrifuge tube - test Model WE 1 (Precision Engineering, Poland) was used for the centrifugation of the soil extracts at the speed of rotary 2500 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 by using a pH meter Model CPI-551 (Elmetron, Poland). The fine fly ash samples were dried by using a electric drier Model KBC – 65 G (Wamed, Poland).

2.4. Extraction procedure

The four-stage sequential extraction method was used here. The experimental parameters are given in Table 1. After extraction, sample solutions were first centrifuged at 3000 rpm for 15 min or filtered through a filter paper for qualitative analysis MN 616 (Macherey-Nagel GmbH & Co. KG, Germany). The supernatant was used for analysis of Mn the FAAS method. The solid phase (ash) was washed with 10 cm^3 of double – distilled water and this second supernatant was discarded. Sample blanks were prepared according to the proposed procedures and concentrations of the extracts were corrected by subtracting the corresponding blank concentrations.

Table 1. Sequential extraction procedure proposed by the European Community Bureau of Reference (BCR).

STAGE	FRACTION	REAGENT	SHAKING TIME AND TEMPERATURE
1	Acid soluble (e.g. carbonates)	20 cm^3 HOAc 0.11 mol / dm^3	16 hrs at 25 °C
2	Reducible (e.g. Fe-Mn oxides)	20 cm^3 $NH_2OH \cdot HCl$ 0.1 mol / dm^3 (pH = 2)	16 hrs at 25 °C
3	Oxidisable (e.g. organic matter)	5 cm^3 H_2O_2 30 % (pH = 2÷3) 5 cm^3 H_2O_2 30 % (pH = 2÷3) 25 cm^3 NH_4OAc 1 mol / dm^3	1 hrs at 25 °C and 1 hrs at 85 °C 1 hrs at 85 °C 16 hrs at 25 °C
4	Residual	1 cm^3 HCl 35 % & 2 cm^3 HF 48 % & 4 cm^3 HNO_3 70 % & 5 cm^3 H_2O	30 min.

2.5. Statistical analysis

The investigations were taken at the same time for six ash samples with simultaneous three-times of manganese detection in one sample. The typical values of R.S.D. for manganese determination on the extraction solutions by FAAS method varied from 0.3 ÷ 9.6 % respectively (Table 2). The statistical estimation of the results of analysis of Mn in the solutions and the content of Mn in the ash was carried out on the basis of a parametric test Student's t – test (p = 95 %). The analytical results of determination of Mn were to verified. The verification on results mentioned above was carried out on the basic the mass balance of total Mn in fly ash (certified value) and the sum of manganese contents in the four fractions to get appropriately: $[\mathrm{Mn}]_{\mathrm{total}} = 1066 \pm 41$and $[\mathrm{Mn}]_{\mathrm{fraction}} = 983$ mg / kg. On the basic was carried out to get the accuracy level of the sequential extraction method. The relative error was calculated for determination of Mn by FAAS method in the solutions obtained after sequential extraction by BCR procedure. Relative error is defined in percentage, between the manganese certified value and the sum of the concentrations in all the fractions of the sequential extraction procedure. It is calculated with the following formula:

$$R = \frac{|\mathrm{Mn}_{\mathrm{total}} - \sum \mathrm{Mn}_{\mathrm{fraction}}|}{\mathrm{Mn}_{\mathrm{total}}} \cdot 100 \qquad (1)$$

Table 2. Manganese partitioning in fly ash (CTA – FFA - 1).

FRACTION	CONTENT OF MANGANESE [mg / kg]	CONTENT OF MANGANESE [%]	DETECTION LIMITS [mg / kg]
F(1) acid soluble	126 ± 11	12.6	5.7
F(2) reducible	86 ± 21	8.6	9.9
F(3) oxidisable	184 ± 22	18.4	2.1
F(4) residual	587 ± 22	58.8	6.6

3. RESULTS

The four-stage extraction procedure was followed. The following Mn fractions in fly ash were investigated: F(1) – acid soluble (e.g. carbonates); F(2) – reducible (e.g. Fe / Mn oxides); F(3) – oxidisable (e.g. organic matter); F(4) – residual, which take the most durable forms of manganese, insoluble in the water. Mn include in this fraction is chemical stable and biological non-activity. We can think that, it is durably immobilize.

In Table 2, the distribution of manganese is represented in the fine fly ash samples. Sequential extraction studies of the fine fly ash samples have shown that Mn bound to all fraction. Highest proportions of Mn is found in the residual fraction F(4) – 587 ± 22 mg / kg (58.8 %). Manganese is pronouncedly present in the fraction F(1) and F(3), appropriately 126 ± 11 mg / kg (12.6 %) and 184 ± 22 mg / kg (18.4 %). Mn appers in fraction F(2) at lower percentage - 8.6 % (86 ± 21 mg / kg).

The distribution of Mn over the different forms follows the order (Fig. 1):

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

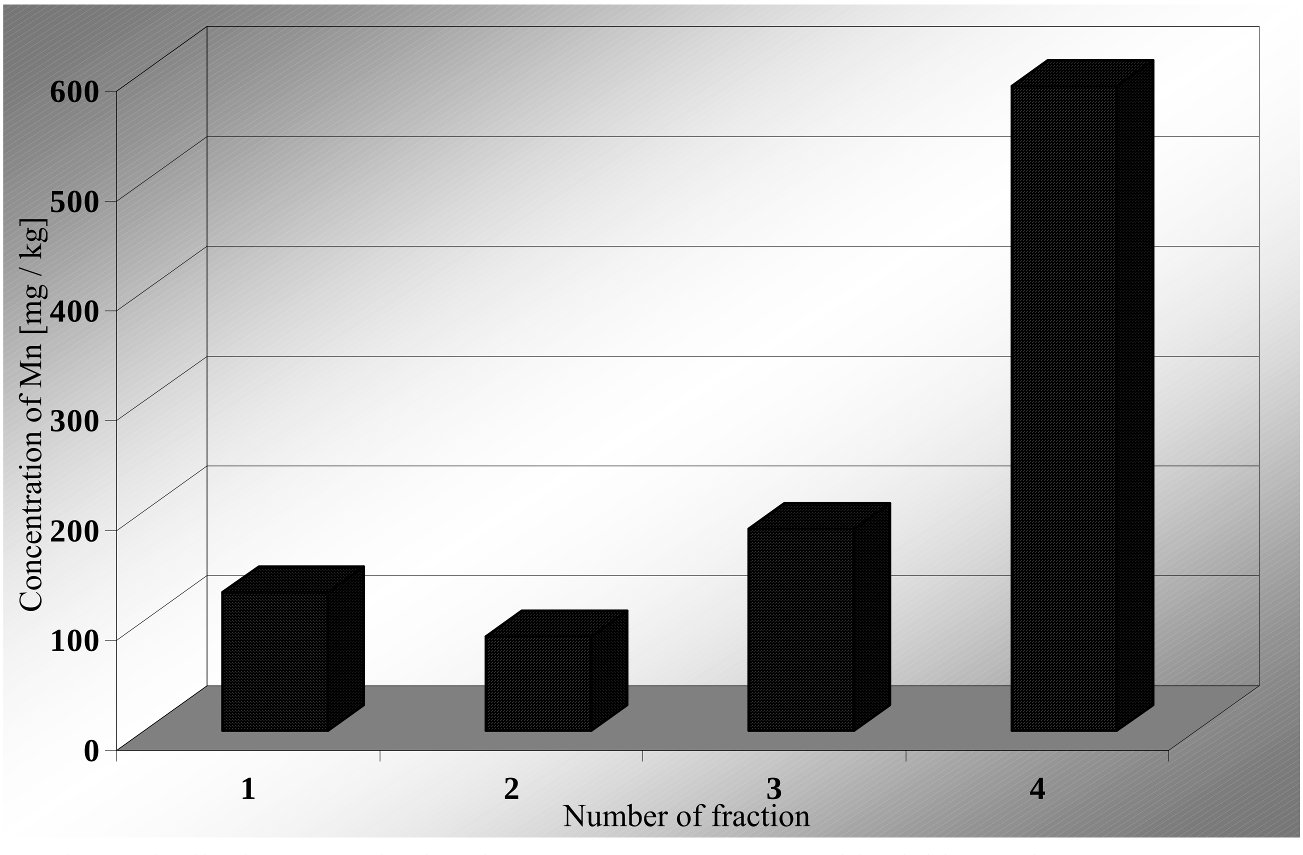

Fig.1. Distribution of Mn in fly ash (CTA – FFA - 1); (1) – acid soluble fraction, (2) – reducible fraction, (3) – oxidisable fraction, (4) - residual.

For sequential extraction method used (BCR) was obtained the accuracy manganese determination 92.2 %. The sum of the Mn present in the individual fractions shows a good agreement with the certified value of total manganese content. The proposed method has the detection limits for Mn determination by FAAS method for each fraction were: F(1) – 5.7, F(2) – 9.9, F(3) – 2.1, F(4) – 6.6 mg / kg; detection limits were calculated on the basis of 3 SD (blank solution). The relative error of determination of Mn by FAAS method was obtained 7.8 %. A method proposed by the European Community Bureau of Reference (BCR) to determine the distribution of manganese in different fractions in fine fly ash has been applied to the environmental fly ash samples.

4. CONCLUSION

The sequential extraction procedure can help in under standing which fractions of manganese take in the fine fly ash (Polish Certified Reference Material, CTA – FFA – 1). The accuracy of the method is high enough to use the results to a quantitative partitioning of Mn into the fractions described. The sequential extraction method, proposed by the European Community Bureau of Reference (BCR) to determine the forms of manganese in environmental fly ash samples has been applied.

5. REFERENCES

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