

Differential Pulse Polarography in the Analysis of Products from Coal Treatment

I. Baranowska, A. Słaczka*, K. Srogi

Department of Analytical and General Chemistry, Silesian Technical University, ul. Strzody 7, 44-100 Gliwice, Poland
Department of Mineral Processing and Waste Utilization, Silesian Technical University, Gliwice, Poland

Received: June 15, 2000
Accepted: October 6, 2000

Abstract

The content of the heavy metals cadmium, zinc, nickel, lead and molybdenum in products and waste coming from fuel processing (originating from power plants and coal mines) was determined using DPV. Samples were digested in a microwave mineralizer in mixtures of HNO₃ + HClO₄ acids (3:2; 4:2 v/v). The following certified reference materials were used in these investigations: fly ash (CTA-FFA-1), apatite concentrate (CTA-AC-1) and coal (BCR-40).

Keywords: heavy metals, slug, ash, flotation tailings, crude coal, hard coal assortment, inversion difference pulse voltammetry

Introduction

During processing of solid fuels such as hard coal, mineral substances release so called "ballast" composed fly ash (smoke boxed ash) or slag, eliminated in the solid (granular form) or liquid state from the bottom of the furnace.

Chemical composition of ashes and slags depends on the sort of crude mineral substance existing in hard coal. During exploitation and enrichment processes other types of wastes also form, including waste rock, flotation tailings and rocks.

AAS methods are often applied to determine ecologically harmful trace elements in such materials [1-5] while volumetric methods are used to analyze of macro-components [6, 7]. In the elaboration concerning analysis of aforementioned materials CRM are rarely applied.

In the presented work the DPV method was applied in the analysis of products coming from the processing

of hard coal. The following certified reference materials were used for the calibration of apparatus and validation of methods: fly ash (CTA-FFA-1), apatite concentrate (CTA-AC-1) and coal (BCR-40).

Experimental

Apparatus

EKO-TRYBO- Polarograph (Czech Republic), with a hanging mercury electrode (HMDE) and a reference silver-silver chloride electrode was applied for the measurements. The solutions were initially bubbled for 10 min. with nitrogen for the elimination of oxygen.

Microwave oven ML MEGA 1200- Milestone (Italy) was applied for the mineralisation of samples.

Reagents and Solutions

Nitric acid (V) ($d = 1.41 \text{ g ml}^{-1}$) sp. pure (Zakłady Azotowe w Tarnowie Mościcach);
Chloric acid (VII) ($d = 1.67 \text{ g ml}^{-1}$) Suprapur (Merck, Darmstad);
Dimethylglyoxime 0.1 M solution in ethanol; 8-hydroxyquinoline (oxine) - 0.1% solution in CCl_4 ;
Acetate buffer pH=4.7 and pH=3.5; Ammonium buffer pH=10.0; 4% water solution of potassium peroxydisulfate 10% tin chloride (II) in HCl 1M disodium hydrogen phosphate (V);

Solutions of investigated elements were prepared from standard solutions (Backer) of concentration $1 \text{ mg} \cdot \text{ml}^{-1}$ (Pb, Zn, Cd, Ni and Mo);

Certified reference materials: fly ash (CTA-FFA-1), apatite concentrate (CTA-AC-1) and coal (BCR-40).

Samples of ash and slag from power plant and hard coal, rock and flotation tailings from a coal mine from Upper Silesia district were investigated.

Automatic pipettes with changeable tips made by Plastimed Poland were used.

Determination of Zn, Cd, Mo, Ni and Pb

Determination of Zn, Cd, Mo, Ni and Pb was carried out by inverse differential pulse polarography (DPASV). Measurements were taken by the triple standard addition method.

Samples after mineralisation were diluted to 25 ml. For determining Cd^{2+} , Pb^{2+} and Zn^{2+} , 0.4 ml of the sample solution were placed in a 10 ml volumetric flask, then 8.0 ml of 0.1 M sodium acetate, pH=4.7 were added and filled to the mark with water. This solution was introduced to the polarographic vessel and bubbled for 10 min for the removal of oxygen. Then standard solution was added in a volume allowing concentration of elements to reach $1.0 \cdot 10^{-4} \text{ mg}$ and aliquots of this value.

Somer and co-authors [8] applied 0.5 M acetate buffer solution of pH=3.5 and 2.5 with the addition of EDTA as a basic electrolyte in the analysis of heavy metals, among others Mo in coal. Determination of molybdenum

in tested samples was carried out according to modified Somer's procedure. The authors applied 0.2 M acetate buffer of pH=3.5 as a basic electrolyte, 8-hydroxyquinoline as a complexing agent (ligand) and tin(II)chloride as a reducing agent.

Procedure

To 0.3 ml of sample in 10 ml measuring flask 8.0 ml of buffer solution of pH=3.5 were added and the solution was filled to the mark with distilled water. The following concentrations of the electrolyte components were applied: oxine - $1.0 \cdot 10^{-4} \text{ mmol/10 ml}$; tin(II)chloride - $1.5 \cdot 10^{-4} \text{ mol/10 ml}$ [for reducing Mo(VI) to Mo(V)]. Polarographic curve was recorded and next the standard solution of molybdenum of concentration $0.5 \cdot 10^{-4} \text{ mg/10 ml}$ was added and the curve was recorded once again.

For the determination of nickel in tested samples, conditions described in the work published by T. M. Fofonova and co-authors [9], for the analysis of nickel in water samples by stripping method, were adapted. As a basic electrolyte ammonium buffer of pH=10.0 was applied, as a ligand-dimethylglyoxime solution, and as an oxidizing agent - 4% solution of potassium peroxydisulfate (oxidation of Ni(II) to Ni(IV)).

Procedure. To 0.65 ml of a sample placed in 10 ml volumetric flask, 8.0 ml of $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer solution of pH 10.0 were added and filled to the mark with distilled water. The following final concentrations of electrolyte components were reached: H_2Dm - $1.0 \cdot 10^{-6} \text{ mol/10 ml}$; peroxydisulfate (VI) dipotassium - $0.1 \cdot 10^{-4} \text{ mol/10 ml}$. For masking of iron, 1M solution of Na_2HPO_4 was applied. The standard addition method allowed quantitative determination of nickel in examined sample. The standard nickel solution $4.0 \cdot 10^{-4} \text{ mg/10 ml}$ was added subsequently.

Conclusion and Discussion

Investigations were focused on the selection of mineralisation conditions, basic electrolytes and elimination of unfavourable influences on the shape of peaks. Possibilities of sample mineralisation by classic wet method

Table 1. Analysis of CTA-FFA-1 Coal Fly Ashes digested by microwave oven using $\text{HNO}_3 + \text{H}_2\text{O}_2$ (Method I) and $\text{HNO}_3 + \text{HClO}_4$ (Method II) by DPV, results (ppm) expressed as mean $\pm \mu$ (s).

Mineralisation programme	Elements		
	Zn	Pb	Ni
Method I $\text{HNO}_3 + \text{H}_2\text{O}_2$ (2:3) time: 20 min., power: 1400 W	586.5 \pm 16.2 (5.5)	398.3 \pm 6.9 (2.4)	95.8 \pm 6.1 (2.1)
Method II $\text{HNO}_3 + \text{HClO}_4$ (2:3) time: 33 min., power: 1700 W	563.5 \pm 3.0 (1.0)	370.5 \pm 3.1 (1.1)	94.1 \pm 2.5 (0.9)
	certified values (ppm)		
	569 \pm 58	369 \pm 46	99 \pm 5.8

μ - confidence intervals are given at 95% lever for n=6; s - standard deviation.

Table 2. Results of analysis of BCR-40 standard coal digested by microwave oven in differential programs - DPV, results (ppm) expressed as mean $\pm \mu$ (s).

Mineralization programme	Elements				
	Zn	Pb	Ni	Cd	Mo
time: 33 min., power: 1700 W first stage: 4 ml HNO ₃ second stage: 2 ml HClO ₄	29.8 \pm 1.4 (0.7)	23.7 \pm 2.0 (1.0)	25.8 \pm 1.6 (0.8)	0.15 \pm 0.04 (0.02)	18.2 \pm 3.6 (1.8)
	certified values (ppm)				
	30.2 \pm 1.9	24.2 \pm 1.7	25.4 \pm 1.6	0.11 \pm 0.02	—

μ - confidence intervals are given at 95% lever for n=6; s—standard deviation.

with acids or their mixtures were examined. The following acid mixtures of various ratios were applied: HNO₃, HNO₃ + HF, HNO₃ + HClO₄, HNO₃ + H₂O₂.

Mineralisation lasted many hours and peaks obtained by DPV method were badly developed with high background. Polarograms of sample solutions were difficult to interpret. Additional irradiation with UV light does not improved the effects of mineralisation. Good results were obtained using microwave digestion in acid mixture: HNO₃ + HClO₄ (3:2 v/v). To 0.1 g of samples, weighed with the accuracy 0.1 mg, 5 ml of the

mixture of acids were added. After mineralisation, solutions were transferred quantitatively to the 25 ml measuring flasks and filled with distilled water to the mark.

However, the results of analyses of fly ash certified material (CTA-FFA-1), done according to the parameters recommended by the producer of Milestone set, were satisfactory (time 20 min, power 1400 W) significant improvement of precision and repeatability was achieved using proposed new parameters: time 33 min., power 1700 W (Table 1). In a few samples, originating mainly from post-flotation wastes, obtained polarograms cannot be interpreted. In those cases the additional irradiation in quartz vessels with UV light of $\lambda=254$ nm was applied for 50 min. Obtained good shaped peaks proves the total mineralisation of organic matrix (Fig. 1). It should be underlined that only extending the time of mineralisation and increasing the current power of mineralisation does not give such good effects.

Taking into account this sort of analysed materials, the investigations were carried out to establish optimum conditions of mineralisation, using carbon as the certified reference material. The mixture of HNO₃ and HClO₄ (4:2 v/v) was applied. A double-stage mineralisation program was proposed. In the first stage the sample of reference material (0.1 g) and tested sample (0.1 g) weighed with the accuracy of 0.1 mg were introduced to the Teflon vessel, then 4 ml of HNO₃ were added. Previously established conditions were applied - time 33 min., power 1700 W. In the second stage, after passing the time, the Teflon vessel was cooled for 1 hour and the next 2 ml of HClO₄ were added and mineralisation was continued under the same parameters. After finishing mineralisation the solutions were transferred to 25 ml measuring flasks and filled with distilled water to the mark. Total mineralisation was achieved, which is proven by the statistic evaluation of the results of metal analysis in the carbon as the certified reference material (BCR-40) (Table 2).

Usefulness of various electrolytes was examined for the determination of Pb, Ni, Zn, Cd and Mo. They were: 0.3 M HNO₃, 1 M NaNO₃, 1 M HCl, acetate buffer of various pH values, 1M KSCN, 0.1 M KCl, 1M KNO₃, ammonium buffer of various pH values. Cadmium and lead were determined simultaneously in 0.3 M HNO₃ and 1M NaNO₃. Good shaped peaks of the half wave potentials: for Pb $E_{1/2} = -0.38$ V, $E_{1/2} = -0.35$ V and for Cd

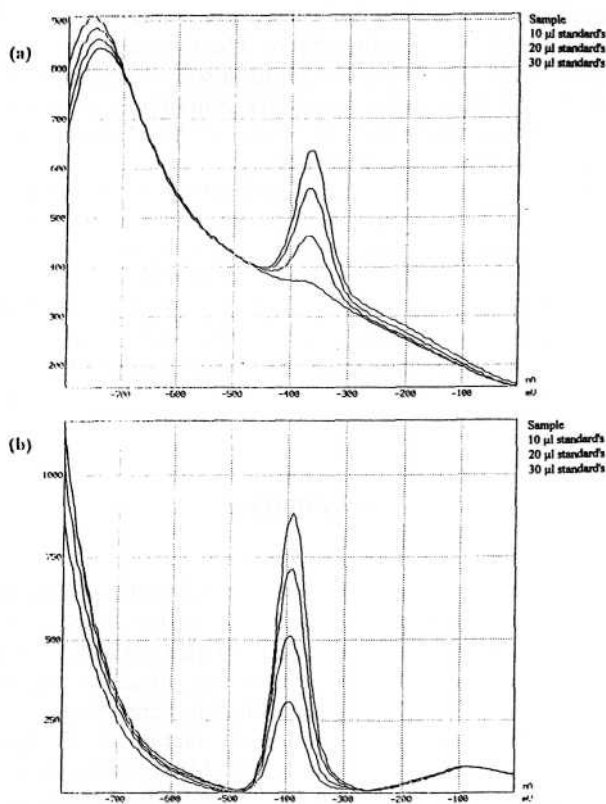


Fig. 1. Differential pulse polarogram for the determination of lead in slag sample in 0.3 M HNO₃, (a) without irradiation with UV, (b) additional irradiation with UV light of $\lambda=254$ nm.

$E_{1/2} = -0.5$ V and $E_{1/2} = -0.55$ V against Ag/AgCl were obtained. Also well separated and measurable voltammetric curves were obtained in acetate buffer of pH = 4.7 (Fig. 2), with $E_{1/2}$ values respectively Pb = -0.44 V, Cd = -0.6 V and Zn = -0.1V. This electrolyte was used for further analyses. In Fig. 2 the example of polarogram of zinc, cadmium and lead in acetate buffer in the sample of fly ash is shown.

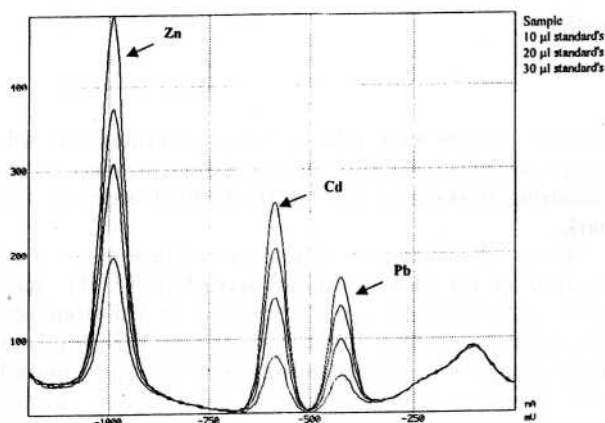


Fig. 2. Differential pulse polarogram for the determination of zinc, lead and cadmium in coal fly ash sample in acetate buffer of pH=4.7.

The well shaped peak for molybdenum of $E_{1/2} = -0.26$ V was obtained in the electrolyte containing acetate buffer of pH = 3.5 and 8-hydroxyquinoline as a ligand.

Nickel was determined by DPV method in ammonium buffer of pH = 10.0 as an electrolyte and dimethylglyoxime as a ligand. For the oxidation of Ni(II) to Ni(IV), potassium peroxydisulfate solution was used while masking iron ions Na_2HPO_4 .

Calibration of apparatus and selection of measurement conditions were done on the basis of certified reference materials - fly ash certified material (CTA-FFA-1) for slag and ashes; apatite concentrate reference material (CTA-AC-1) for waste rock and post-flotation wastes. In the case of analysis of coal assortments - coal BCR-40 was used as a reference material.

In Table 3 the example of statistical evaluation of results of analyses obtained applying CRM (fly ash) and model solutions is presented.

Under determined conditions of mineralisation and applying aforementioned electrolytes, products of coal processing were analysed. Samples came from coal mines and power plants. The obtained results are gathered in Table 4.

On the basis of the obtained data it was found that the composition of various assortments of coal are quite similar whereas the content of investigated metals in waste coming from hard fuel treatment is diversified.

A relatively low concentration of heavy metals was found in slag and some samples of fly ashes, which proves

Table 3. Results obtained for the determination of Pb, Zn, Ni, Mo and Cd in slag (A) and coal fly ash (B) by DPV using CRM Coal Fly Ash and model solution (RM) for calibration, results (ppm) expressed as mean $\pm \mu$ (s).

Elements	A (slag)		B (coal fly ash)	
	CRM	RM	CRM	RM
Pb	55.0 \pm 0.8 (0.4)	59.5 \pm 5.2 (2.6)	76.5 \pm 1.6 (0.8)	79.2 \pm 4.2 (2.1)
Zn	131.0 \pm 1.0 (0.5)	134.5 \pm 6.4 (3.2)	70.5 \pm 1.0 (0.5)	63.2 \pm 3.0 (1.5)
Ni	33.5 \pm 1.6 (0.8)	36.7 \pm 5.2 (2.6)	60.0 \pm 1.6 (0.8)	64.5 \pm 5.8 (2.9)
Mo	11.5 \pm 4.2 (2.1)	14.0 \pm 9.0 (4.5)	72.0 \pm 6.4 (3.2)	78.6 \pm 11.4 (5.7)
Cd	3.5 \pm 0.6 (0.3)	4.4 \pm 3.8 (1.9)	20.5 \pm 1.0 (0.5)	21.1 \pm 2.2 (1.1)

μ - confidence intervals are given at 95% level for n=6;
s -standard deviation.

that processes of coal treatment (carried out at higher temperature) may result in releasing some amounts of heavy metals to the atmosphere. High content of heavy metals, especially lead, was found in some samples of fly ashes. This may cause secondary contamination of the environment during storage or use of these ashes as recycling industrial raw materials.

Summing up the results of the investigations it should be underlined that the research focused on the working out of methods useful for the analysis of raw materials and products from hard coal treatment. Obtained results suggest necessity of application of various analytical methods for the determination of toxic element content in waste from fuel treatment, which can contaminate the environment.

Summary

Carried out investigations revealed that the results of voltammetric analysis of real samples (ashes, slags, rock and flotation wastes) obtained using CRM for calibration of apparatus and examination of mineralisation conditions, perform much better precision and credibility.

Results of the content of heavy metals in samples coming from coal processing revealed that high concentrations of toxic elements in those materials could cause releasing them to the environment during improper storage or application for agricultural or building purposes.

The worked out differential pulse voltammetry procedure can be proposed as an alternative method to the commonly used AAS for this purpose.

Table 4. Results of Zn, Cd, Pb, Ni and Mo determination (ppm) in products from the coal treatment by DPV.

Sample	Pb	Cd	Zn	Ni	Mo
	ppm/RSD				
coal fly ash	240.0 ± 2.2	20.5 ± 4.5	165.0 ± 1.5	60.5 ± 1.4	13.5 ± 2.7
coal fly ash	226.5 ± 3.0	16.0 ± 3.0	124.5 ± 3.0	92.0 ± 1.5	18.5 ± 3.6
coal fly ash	67.0 ± 3.0	23.0 ± 1.5	62.0 ± 2.0	48.0 ± 2.0	44.0 ± 8.0
coal fly ash	70.5 ± 3.5	20.0 ± 2.8	76.5 ± 1.5	60.0 ± 3.0	72.0 ± 5.5
slag	56.0 ± 3.0	3.7 ± 1.0	130.0 ± 3.5	33.5 ± 2.5	11.0 ± 2.7
slag	76.0 ± 3.0	20.0 ± 2.5	56.0 ± 3.0	50.0 ± 1.5	76.0 ± 9.0
slag	47.5 ± 2.5	26.0 ± 2.0	52.5 ± 2.0	54.0 ± 3.0	50.5 ± 5.0
stone	62.0 ± 4.0	14.0 ± 1.0	250.5 ± 3.5	50.0 ± 1.0	62.5 ± 2.5
stone	120.0 ± 2.0	10.5 ± 1.5	46.0 ± 2.0	51.0 ± 1.0	74.5 ± 2.5
flotation tailings	58.0 ± 2.5	19.0 ± 2.0	63.5 ± 3.0	60.4 ± 1.0	55.6 ± 2.8
flotation tailings	40.1 ± 0.7	17.4 ± 1.3	95.7 ± 2.6	36.3 ± 1.0	29.3 ± 3.0
pea (size of coal)	65.0 ± 0.8	14.0 ± 2.2	60.0 ± 2.8	80.0 ± 2.5	50.0 ± 5.6
nut (size of coal)	50.5 ± 2.1	18.2 ± 0.9	100.5 ± 2.0	78.0 ± 2.8	81.0 ± 4.5
cobble (size of coal)	82.0 ± 0.5	25.0 ± 1.5	42.0 ± 1.5	22.3 ± 3.0	52.0 ± 3.0
fine coal	41.0 ± 0.3	24.0 ± 0.5	69.0 ± 1.5	62.0 ± 2.0	51.0 ± 4.0
apatite concentrate	32.0 ± 0.8	13.0 ± 0.4	70.0 ± 0.9	54.0 ± 1.5	72.0 ± 3.5
apatite concentrate	55.0 ± 1.2	22.0 ± 0.9	61.0 ± 0.8	38.5 ± 3.0	42.0 ± 2.0
coal	81.0 ± 0.7	26.0 ± 1.0	86.0 ± 2.0	54.0 ± 3.0	56.0 ± 4.5
pcoal	70.0 ± 1.2	10.0 ± 2.0	48.2 ± 1.7	58.5 ± 1.5	70.0 ± 5.0

Acknowledgements

Investigations were supported by the PBU 88/RG5/96 grant of the Committee of the Scientific Research.

References

1. TROJANOWSKI J. Oczyszczanie paliw kotłowych, Fundacja Ochrony Powietrza Atmosferycznego, Warszawa, **1996**.
2. FRANZEL W. Microanalytical concept for multicomponent analysis of airborne particulate matter. *Fresenius J. Anal. Chem.* **340**, 525 **1991**.
3. BRADSHAW D. SLAVIN W. Rapid slurry analysis of solid coal and fly ash samples. *Spectrochim. Acta* **44B**, 1245 **1989**.
4. OTTMERS D.M, EKLUND A.G.: "Coal in Environment" - Proces of the World Coal Institute Conference and Exhibition, London **1991**.
5. ŚLĄCZKA A., BARANOWSKI R, SZMYD E., SROGI K., KOT B. Distribution of harmful trace elements among coal preparation products. *Polish Journal Environmental Studies* **7**, 185 **1998**.
6. GABZDYL W. Petrografia węgla, Politechnika Śląska, Gliwice, **1987**.
7. DUBIEL K. Ochrona i kształtowanie środowiska, Instytut Podstaw Inżynierii Środowiska PAN, Zabrze, **1996**.
8. SOMER G., ÇAKIR O., SOLAK A.O. Differential-pulse polarographic determination of trace heavy elements in coal samples. *Analyst*, **109**, 135, **1984**.
9. FOFONOWA T.M., BULANTSEVA V.N, KARBAINOW YU.A. Determination of nickel in ammonium-ammonia media by stripping voltammetry. *Zh.-Anal.Khim.* **3**, 50 **1995**.