

ASSESSMENT OF TRACE ELEMENTS CONTENT IN PRODUCTS
AND WASTES OF COAL TREATMENT FROM THE
UPPER-SILESIA BASIN

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OCENA ZAWARTOŚCI PIERWIĄTKÓW ŚLADOWYCH W PRODUKTACH
I ODPADACH Z PRZEROBU WĘGLI POCHODZĄCYCH Z GÓRNOŚLĄSKIEGO
ZAGŁĘBIA WĘGLOWEGO

Celem pracy było określenie zawartości wybranych pierwiastków śladowych w produktach i odpadach z przerobu węgla pochodzących z Górnośląskiego Zagłębia Węglowego. Zastosowano metody spektrometrii atomowej (FAAS, ETAAS) i adsorpcyjnej woltamperometrii inwersyjnej (AdSV) oraz z zateżaniem anodowym (ASV). W przypadku Zn, Cd, Pb, Ni i Mo zastosowanie dwóch metod opartych na różnych zasadach pozwoliło na sprawdzenie skuteczności roztrawiania badanych materiałów i ich homogeniczności oraz przeprowadzenie oceny błędów przypadkowych lub systematycznych. Wyniki oznaczeń analizowanych pierwiastków wykazują dobrą zgodność potwierdzając rzetelność analizy.

Summary

The aim of the study was to estimate the content of trace elements: zinc, cadmium, lead, molybdenum and nickel in products and wastes of coal treatment from Upper-Silesian Basin. Two analytical methods were applied: atomic absorption spectrometry (FAAS, ETAAS) and anodic (ASV) and adsorptive stripping voltammetry (AdSV). ASV is used to determine zinc, cadmium and lead; AdSV molybdenum and nickel, and FAAS and ETAAS to determine all elements. In the case of Zn, Ni, Mo, Pb and Cd determined by FAAS (ETAAS) the concentrations were practically the same as those obtained by ASV or AdSV.

INTRODUCTION

Coal contains numerous elements (about 60) of low concentrations of the order of 0.01 or 0.001 wt%. The contents of trace elements, connected with organic (lighter) coal matter or mineral (heavier) matter was higher in coal, than in soil of lithogenic origin [15]. There has been a growing concern regarding the potential environmental problems caused by man's activities and emission of the trace elements from coal. Knowledge of the fact is fundamental for the understanding of the behavior of trace elements in coal during mining, processing, coal combustion process or coke production [2]. As it is well known, coal is an invaluable

source of energy and fundamental raw material for the electric power generation and metallurgical fuel. But it is also the main contributor to products of combustion process (e.g. slag's, ashes, and fly ashes) which discharged to the environment may now be partitioned between flue gases and solid byproducts as well as radionuclides [1, 16, 19].

It must be pointed out here that the attention has been drawn so far to the toxicological and ecological effects of the elements in regard to the importance of coal and its wastes, which influences the conditions of plants and animals (including man). On the other hand, one may expect that they should be found among pollutants penetrating the environment if they occur in the coal subjected to the thermal decomposition of the coal process [1, 5, 17].

Jensch was the first to report on the determination of heavy metals (Zn, Pb Cd and Mn) in coals from mines situated in the Upper-Silesian (southern Poland) coal basin [7]. Pacyna [19] has reported that concentrations of most elements could be different, depending on the coal bed and basin. Parzenty et al. [20] have reported the high content of heavy metals, especially Cd, Ni, Pb and Zn in samples of coal from east-middle Upper Silesian coal basin. Additionally, a relatively high concentration of Zn, Pb and Ni was found in ashes, but the content of Cd in coals was in agreement with the values presented in the literature.

Chudek et al. [4] illustrated the fact that the content of trace elements such as Zn, Cr and As in coal fly ash may be higher than their concentrations in bituminous coal. On the basis of the results it was found that the distribution of trace elements associated with mineral or organic matter is changed upon the coal processing. The behavior of metals during processing of coal can be different [26]. Firstly, when applying coal cleaning processes, based on the difference in density, the contents of elements connected with mineral matter form may be reduced. The removal of pyrite from coal results in substantial decrease in Pb, Cd and As contents. Secondly, if trace elements connected with organic coal matter, the enrichment coal process has provided to significant changes in the coal structure. For example, according to Wang et al. [26] metals such as Ni, V and Co are believed to be associated to a large extent with the organic matter.

Trace elements bound in certain inorganic matrixes may be volatilized also if these original forms decompose readily during combustion (e.g., pyrite) and subsequently they are released to the environment; trace elements in coal have been defined [22]. However, inorganic matrixes decomposition is likely to be smaller than that of organic matrixes.

Rejects, wastes and ashes deposited on heaps are a source of air and soil pollution. This may cause secondary contamination of the environment during storage and use of these ashes as recycling industrial raw materials. It should be noted that the process is associated with increasing consumption of the electric energy based on brown and bituminous coal [22].

It can also be assumed that the accumulation and concentration of elements in coal is a result of different processes, including combustion, which may be divided into three groups:

Group I – uniformly distributed among ashes: Mn, Sc and La;

Group II – enriched of fly ashes through volatilization and condensation:
As, Cd, Pb, Sb and Zn;

Group III – most strongly volatilizing elements, gaseous phases and fine particulates: Hg, Cl, Br and F [12, 13].

For this reason, it is interesting to determine trace element concentrations in slag, ashes, and fly ashes with the control of their emission during coal gasification and combustion

processes [14].

The present study has focused on the determination of trace element (Cd, Pb, Ni, Mo and Zn) concentrations in products and wastes of coal treatment, using atomic absorption spectrometry (AAS), and stripping voltammetry (SV). It has become evident that complete dissolution of metals in coal samples and tailings from coal treatments and accurate results in subsequent analysis can be obtained by means of applying pressurized digestion under microwave heating. Thus, the present works were undertaken in order to develop an optimized digestion method for coal samples and tailing from coal treatments. Our attention was focused on the optimized an analytical procedure determination of trace elements by AAS and SV.

SAMPLING AND MEASUREMENT PROCEDURES

The investigations were performed using products and wastes of coal treatments from Upper-Silesian coal basin.

These are: (i) size of coal – nut (80–25 mm), pea (31.5–8 mm), and fine coal (50–1 mm), (ii) ash and slag.

Sampling and preparation of all samples were carried out according to PN-90/G-04502 [21]. Subsamples were homogenized using a mortar and pestle and sieved to pass a 0.2 - 0.1 mm and air-dried for 24 h to a constant weight before the analysis.

Atomic Absorption Spectrometry (AAS) and Electrothermal Atomic Absorption Spectrometry (ETAAS) were used for the determination of trace element concentrations in samples after microwave digestion. All samples were subjected to pressurized digestion using a mixture HF + HClO₄ (3:2 v/v) and HNO₃ + HClO₄ (1:1 v/v) [23]. Microwave digestion was carried out in a Milestone microwave system (MLS - 1200 MEGA, Sorisole, Italy) with a Teflon vessel (MRD 1000/6/100/110), designed for pressure of up to 11×10^6 Pa.

Atomic spectroscopic determinations were carried out with a Carl Zeiss Jena AAS-3 atomic absorption spectrometer, (Germany) equipped with pneumatic nebulisation and mono-element lamps with hollow cathode made by Photron and Narva for flame atomic absorption spectrometric analysis (FAAS).

A Carl Zeiss Jena AAS 30 (Germany) equipped with an EA-30 graphite furnace and MPE autosampler was used for graphite furnace atomic absorption spectrometric analysis (ETAAS). Hollow cathode lamps were used throughout the work and D₂-background correction. The instrumental parameters are listed in Table 1. The measurement accuracy of the determination was checked by the method of standard addition and calibration curve.

Determination of Zn, Pb and Cd by Differential Pulse Anodic Stripping Voltammetry (DPASV) in samples was performed. Differential Pulse Adsorptive Stripping Voltammetry (DPAAdSV) has been proposed to determine Mo and Ni [23].

Adsorptive and anodic stripping voltammograms were obtained with an ECO-TRIBO Polarograph (Prague, Czech Republic). The cell was a three-electrode system with an Ag/AgCl (0.7 mol/dm³ KCl) saturated electrode as the reference electrode and a hanging mercury drop electrode – HMDE (area 1.9 mm²) as the working electrode. Table 2 shows the experimental conditions for each element: basic electrolytes and complexing agents. Quantification of heavy metals in all samples was accomplished via method of standard addition.

As it is well known, the accurate and precise methods required establishing all the analyte concentrations. Accuracy of an analytical method was evaluated in two ways: by

Table 1. Recommended conditions for the spectrometry of trace elements using FAAS and ETAAS

FAAS	Pb	Zn	Cd	Ni	Mo
Wavelength [nm]	283.3	213.9	228.8	232.0	313.3
Lamp current (Hollow Cathode Lamp–HCL [mA])	5	8	4	8	10
Slit width [nm]	0.40	0.25	0.30	0.30	0.40
Gas flow/air [dm ³ /h]	595	560	550	600	–
Gas flow/acetylene [dm ³ /h]	65	50	40	40	110
Gas flow/N ₂ O [dm ³ /h]	–	–	–	–	560
Type of burner	oxy.	oxy.	oxy.	oxy.	red.
Height of burner [mm]	9.0	10.0	9.5	11.0	9.0
ETAAS					
Drying (°C)	100	180	150	200	200
Ashing (°C)	800	1650	550	1150	1350
Atomization (°C)	2500	2200	2300	2600	2600

Table 2. Basic electrolytes used to SV determined

Analyte	Basic electrolytes
Ni	8 cm ³ 0.1 mol/dm ³ ammonium buffer (pH=9.3) + 50 µl 0.1 mol/dm ³ H ₂ Dm (dimethylglyoxime)
Pb, Cd	8 cm ³ 1.0 mol/dm ³ NaNO ₃ or 0.3 mol/dm ³ HNO ₃
Mo	or 8.0 cm ³ 1.0 mol/dm ³ HCl 8 cm ³ 0.2 mol/dm ³ octane buffer (pH=3.0)+30 µl 0.2mol/dm ³ 8-hydroxyquinoline
Zn, Pb, Cd	8 cm ³ 0.2 mol/dm ³ octane buffer (pH= 4.7)

analysis of reference materials such as: Coal fly ash (CTA-FF-1) and Coal (BCR-40) and by analyzing the samples by two independent methods: AAS and SV.

RESULTS AND DISCUSSION

Statistical evaluation of the data determination of trace elements in product and waste from coal treatments

Systematic and comprehensive monitoring of the trace elements in products and wastes of coal treatment is essential in order to provide knowledge of the state of the environment and its distribution during thermal processing and in bituminous coal (raw). The study of distribution has focused on the control of trace element concentrations in different products of the coal processing plant. From this point of view, it is very interesting to determine Cd, Pb, Zn, Ni and Mo in the coals and products coal treatments from Upper-Silesian Basin (Table 3). All of the results in Table 3 indicated that the obtained values compared with the values found in the literature did not provide significant difference for the average concentrations of trace element in coals, ashes and other product and waste from of coal treatments.

The statistical evaluation of the reported data is used to determine the trace element

Table 3. Average concentration of Pb, Cd, Ni, Zn and Mo in product and waste from coal treatments determined by FAAS method (n = 6). All concentrations given in ppm

No/Sample	Pb	Cd	Ni	Zn	Mo
1 – Fly ash	270.2	11.20	100.0	189.2	12.37
2 – Fly ash	302.3	7.25	123.9	170.2	15.36
3 – Flotation concentrate	66.25	8.02	10.23	66.23	42.36
4 – Flotation concentrate	57.23	3.26	15.59	70.12	71.23
5 – Flotation concentrate	78.29	4.59	11.23	39.28	48.96
6 – Concentrate DISA	60.07	11.02	30.96	87.07	71.03
7 – Slag	50.98	3.23	55.69	133.7	12.36
8 – Slag	86.11	2.15	15.11	213.0	174.4
9 – Slag	56.89	3.65	17.89	129.1	110.1
10 – Dust from power plants	232.0	9.75	46.01	165.1	99.01
11 – Dust from power plants	233.0	6.54	39.01	505.0	105.1
12 – Stone	139.3	2.59	67.89	255.9	66.39
13 – Stone	100.3	4.69	58.96	200.6	70.12
14 – Coal	98.17	3.69	45.32	78.12	77.09
15 – Coal	86.21	1.99	20.36	88.23	55.29
16 – Coal	71.09	1.28	23.36	35.12	50.71
17 – Coal	100.1	0.99	21.28	50.18	49.89
18 – Coal	128.4	0.78	45.69	66.09	44.09
19 – Fine coal	105.3	11.25	21.55	71.29	67.12
20 – Pea (size of coal)	44.23	3.59	60.23	67.11	55.12
21 – Pea (size of coal)	96.21	18.29	32.21	49.12	41.17
22 – Cobble (size of coal)	58.96	2.28	100.7	44.02	50.19
23 – Nut (size of coal)	99.08	1.99	89.36	111.3	91.08
24 – Flotation concentrate	55.12	1.52	57.23	65.23	59.32
25 – Flotation concentrate	59.21	2.01	49.58	57.12	51.15
26 – Flotation concentrate	44.36	2.09	57.69	44.02	49.07
27 – Waste DISA	189.3	1.87	46.36	120.2	79.18
28 – Waste DISA	110.2	3.98	76.36	65.33	70.12
29 – Flotation tailings	89.23	4.59	49.32	74.08	69.11
30 – Spirale tailings	82.32	24.87	57.77	350.0	78.33
Reference [8, 11, 16]					
Coal	2–270	0.7–30	4–61	70–900	–
Coal fly ash	170±20	6.5±3.0	90±15	150±30	–

values and their uncertainties; quality indicator checks for the statistical evaluations were made: arithmetic mean, standard deviation and coefficient of variation were determined. For example, results obtained for the metals in examined sample pea are gathered in Table 4. In the present work, all of the trace elements were also analyzed by SV. Application of voltammetry as complementary to the AAS method showed satisfactory agreement of the results of two supplementary methods. For example, the result for Zn is summarized in Table 5. Precise voltammetric experimental expressed as ranges and means respectively have shown to be valid at the confidence level of 0.05, based on 6 individual determinations. In order to confirm the SV data, spectrometric metals determinations were carried out on the same digestion. The relevant data (Table 5) showed that the sample preparation is valid also in a case of spectrometric determination at the 0.05 confidence level. The data obtained by the

Table 4. Heavy metal content in pea (size of coal) by SV, $n = 6$, $\alpha = 0,05$

Element [ppm]	$\bar{x} \pm \mu$	s_r	s	s^2	v [%]	S_{dv}	Range
Cd	18.29±0.29	0.03	0.31	0.11	2.14	0.13	0.84
Mo	41.17±3.72	0.09	3.42	10.64	8.14	1.32	8.71
Pb	96.21±1.03	0.01	0.85	1.03	1.05	0.45	2.12
Ni	32.21±1.03	0.05	0.92	0.72	2.74	0.31	2.22
Zn	49.12±1.91	0.03	0.71	0.84	1.62	0.42	2.15

$\bar{x} \pm \mu$ – mean \pm confidence interval s_r – relative standard deviation, s – standard deviation, s^2 – variance, v – variability coefficient, S_{dv} – standard error [6]

two methods showed good agreement and prove that the sample digestion procedure is suitable either for voltammetric or spectrometric measurements with sufficient precision. This indicates that the methods are unbiased and they proved their validity. Additionally, the overall mean is compared with the certified values using t -Student test. The test helps us to take advantage of one specific type of design in which an important source of error could be detected. Specifically, if two groups of observations (that are to be compared) are based on the same sample of subjects which were tested twice (e.g., by two analytical methods), then a part of the within - group variation in both groups of results can be attributed to the initial individual differences between subjects (Table 5).

Table 5. Comparison of results determination of Zn by FAAS and SV, $n = 6$, $\alpha = 0,05$. All concentrations given in ppm

Sample	FAAS		SV		$t_{0,05} = 2,57^{**}$	Range between of the means Δ [%]
	range	mean	range	mean		
Pea *	36–35	35.12	32–34	33.01	Not significant	5.71
Stone	69–70	70.41	70–75	75.02	Not significant	6.31
Fly ash	50–58	57.14	69–72	70.12	Significant	22.24
Fine coal *	68–70	68.27	66–71	70.13	Not significant	4.78
Cobble *	38–40	39.89	37–41	38.34	Not significant	3.76
Coal	48–53	49.11	47–52	48.27	Not significant	3.89

* size of coal, ** $t_{0,05}$ – critical value of the Student's test at significance level 0,05

By applying the test U [24] it was found that the results (AAS and SV methods) do not differ significantly. Linear regression analysis demonstrated that the Zn content of the pea (size of coal) determination by FAAS and SV are highly correlated: $r_1 = 0.968$ ($n = 6$) and $r_2 = 0.997$ ($n = 6$). Consequently, verified of hypothesis ($r_2 > r_1$) at confidence level $\alpha = 0.05$. In such cases, the calculated and critical (tabulated) values of the test U were estimated: $U_{exp} = 0.543$ (U_{exp} – calculate the test statistic) and $U_{\alpha=0,05} = 1.78$. Because the calculated value of U_{α} is about three times U_{exp} ($U_{exp} < U_{\alpha}$) there is certainly a slowly significant difference between the observed values obtained for Zn by FAAS and SV methods. It should be noted that in all cases a good linear correlation between both groups of data (SV and FAAS methods) has been observed (Figs. 1–5).

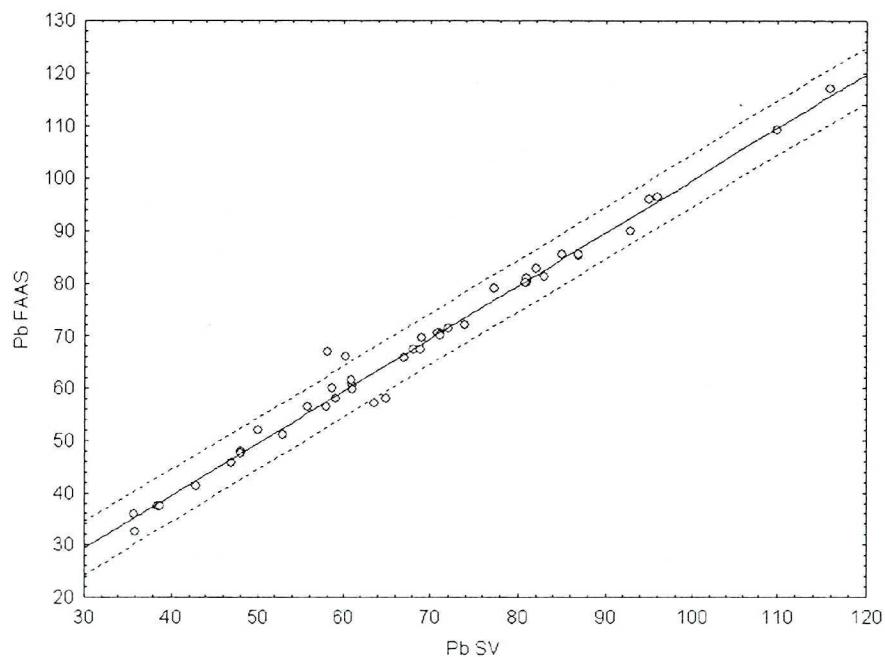


Fig. 1. The correlation between the Pb content in products and wastes from coal treatment determined by SV and FAAS methods with 95% conf. interval (dashed line)

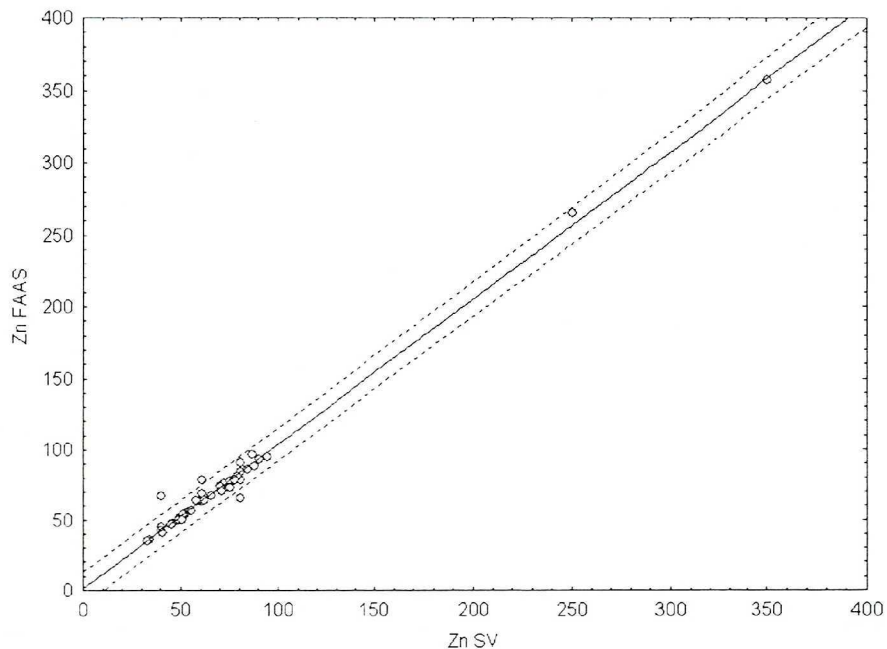


Fig. 2. The correlation between the Zn content in products and wastes from coal treatment determined by SV and FAAS methods with 95% conf. interval (dashed line)

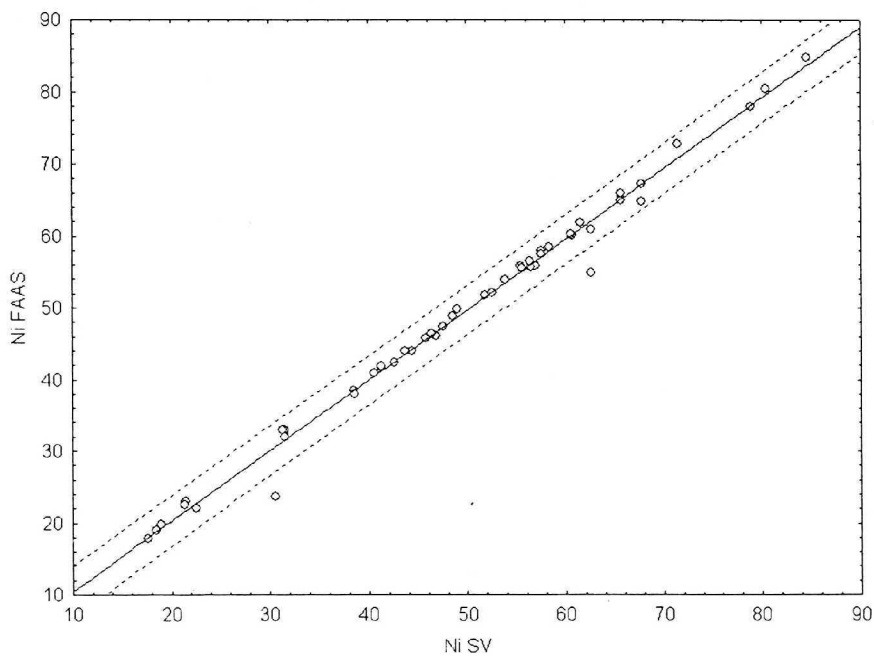


Fig. 3. The correlation between the Ni content in products and wastes from coal treatment determined by SV and FAAS methods with 95% conf. interval (dashed line)

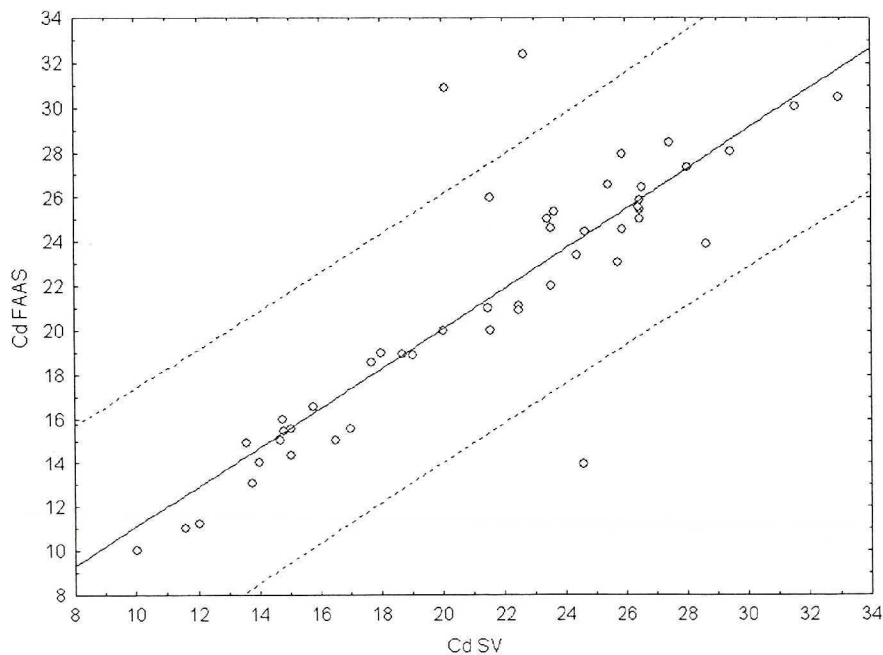


Fig. 4. The correlation between the Cd content in products and wastes from coal treatment determined by SV and FAAS methods with 95% conf. interval (dashed line)

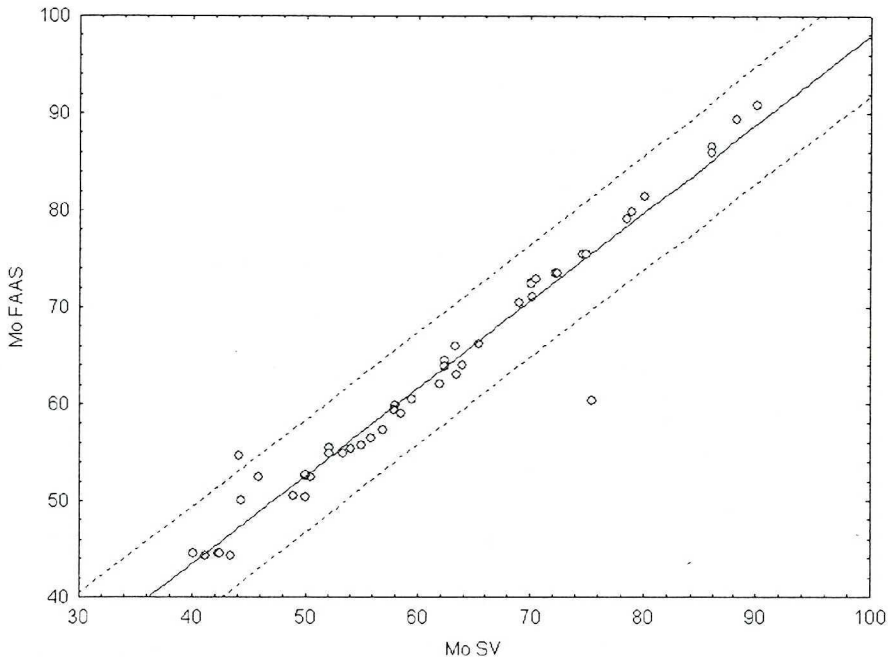


Fig. 5. The correlation between the Mo content in products and wastes from coal treatment determined by SV and FAAS methods with 95% conf. interval (dashed line)

In conclusion, the results obtained by SV and FAAS were tested for agreement and the precision and repeatability of the tests were proved. The different methods tested here showed comparatively good responses.

In order to ensure precision of the analysis, content of trace element was determined by an absorption method employing the two techniques: FAAS and ETAAS, at the confidence level of 95%. Precision and accuracy, expressed as coefficient of variation were less than 4.6% for Pb and Zn; 5.1% for Ni; 3.8% for Cd and 6.4% for Mo, respectively. In order to confirm the FAAS and ETAAS experimental data for Pb and Zn in slag was carried out by the Person test [6]. The remaining values: $t_{pb} = 24.95$ and $t_{zn} = 6.45$ at confidence level 0.05 and $n = 4$ are compared with the critical value $t_{crit} = 2.77$. It is well known, if $t_{exp} > t_{crit}$ the hypothesis zero with error of 5% rejected (hypothesis zero – $H: r = 0$). However, the comparison of the analytical results obtained for the trace elements: Ni, Cd and Mo in slag using Pearson test (verification of hypothesis zero) shows that the FAAS and ETAAS have proved to be accurate techniques for trace element determinations. The results clearly indicate that results of the individual elements obtained with the two analytical techniques did not differ significantly. The analysis accuracy was been checked by simultaneous analyses of two CRMs. An excellent agreement between the found and certified values is illustrated by highly significant correlations.

The concentrations of heavy metal in product and waste from coal treatments

It should be noted that the preparation process of coal is a multi – stage process: preparation, grinding, with heavy media processing (for coarse coal sizes), spirals for the

middling sizes, and flotation for the fine coal feed [22]. Finally, we obtained “cleaned coal”. It should be noted that trace elements, such as Zn, Cd, Pb, Co, As and Hg bound in mineral matter may be volatilized if these original forms decompose readily during the enrichment coal process.

Industrial and technological development results in an ever increasing production of wastes which gradually modify environmental conditions. One of the best known sources of such wastes are thermal power plants in general and those burning coal in particular, which release vast amounts of solid particles (slag, ash, fly ash) rich in heavy metals [9, 18]. On the other hand, the absorption and assimilation of metals by living beings is known to depend on organisms the chemical form in which occurred – either their oxidation (SO_2 , CO_2 and NO_2) state which infiltrated into the environment [9, 10].

In this paper, we have examined five trace elements from the combustion and pyrolysis of Polish coals. According to the data presented in Table 3, the concentrations of heavy metals (Zn, Cd, Pb, Ni and Mo) in products and waste from coal treatments are in agreement with values reported in the literature. However, the cadmium mean values (sample 1) and nickel mean values determined in fly ashes are not substantially higher than mean values presented in literature [11]. Therefore, the values for Pb (sample 1 and 2) indicating the substantially higher values for coals and ashes reported by Marczak [16] and by Kabata-Pendias et al. [11]. However, according to Bouška [3] the content of Pb in ashes could be more than 1000 ppm.

CONCLUSION

1. From the results reported it can be concluded that use of a microwave oven digestion procedure led to complete solubility of samples resistant to mixtures: $\text{HF} + \text{HClO}_4$ (3:2 v/v) and $\text{HNO}_3 + \text{HClO}_4$ (1:1 v/v). For several elements, the two sample preparation methods give comparable results.
2. In the case of SV, as well as AAS (FAAS and ETAAS), the concentration of the trace elements was estimated by the standard additions method and calibration curve. On the basis of the obtained data it was found that both methods could be useful for the analysis of raw materials and products from hard coal treatment. No significant differences were detected between the methods. It is interesting to note that the standard addition method will be used to establish accuracy of analytical methodology.
3. The accuracy of analysis has been checked by simultaneous analyses of two CRMs. An excellent agreement between the found and certified values is illustrated by highly significant correlations.
4. A relatively low concentration of heavy metals was found in waste from fuel treatments in comparison with other samples.
5. The statistical evaluation of the results of metals analysis in all samples was satisfactory significant; improvement of precision and repeatability was achieved at confidence level $\alpha = 0.05$.

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