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Determination of selected trace metals (Cr, Ni, Pb and Cd) in soils by slurry sampling GF AAS

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Determination of cadmium, lead, chromium and nickel in soil samples by slurry sampling graphite furnace atomic absorption spectrometry (GFAAS) was presented. Optimization of determination conditions, stability test for slurries and metal partitioning between solid and liquid phase was investigated. The method was successfully tested by the analysis of certified reference materials.

Keywords: Cadmium, Lead, Chromium, Nickel, Slurry sampling graphite furnace atomicabsorption spectrometry, Soil.

1. INTRODUCTION

In the last decadeit has significantly increasedemission ofheavy metalsin the environment, in especially Cr, Ni, Pb and Cd. Due to the toxicity and the ability ofthe accumulationof these elements, the monitoring of the contentsin real samples is necessary [1–6].Trace metals in the environment can be converted into soluble complexes and migrated in waters and soils. The contents of elements in the soil depend mainly on the soil type, the industrial contamination,pH values and moisture content in soils [7–9].

The determination of trace metals in soils has usually been achieved by digesting them with acids or acids mixtures and further measuring the concentrationof elements by a suitable instrumental technique. The digestion procedure is a potential source of errors, and reagent, labor and time consuming processes, even if microwave accelerated digestion is applied. Additionally, this step may cause analyte losses or the sample contamination. In respect of these direct solid analysis offers a number of important advantages, e.g. the risk of contamination and an analyte loss are considerably reduced. The application of graphite furnace atomic absorption spectrometry (GF AAS) seems to be the most attractive technique for the direct analysis of solid samples, mainly because of a relatively long residence time of the sample in the atomizer, which allows all particles to be atomized independently of their size or thermal resistance [10–13]. Additionally, GF AAS method is characterized by a relatively low limit of detection and this attribute is very important in trace analysis. Determination of trace elements in a solid can be realized in two ways: by direct introduction of the solid into the graphite furnace or introduction of the solid sample in the form of a slurry. Both techniques were first applied for analytical purposes in the early 1970s [14–18].

Slurry sampling atomic absorption spectrometry is a very rapid and convenient method for determination of some trace elements in soils. This technique has several advantages compared to the solid sampling GFAAS.The main positive features of slurry sampling atomic absorption spectrometry are following:easier sample handling (because slurry aliquots are micropipetted into the graphite furnace using the standard autosampler); a smaller risk of errors due to a sample inhomogeneity (high amounts of solid can be taken for slurry preparation); partial extraction of the analyte into the acid medium used for slurry preparation.With slurry sampling, an obvious limitation is the requirement for a homogeneous distribution of particles to be achieved directly before an injection [19–21].

The goal of the presented work was the development of slurry sampling GFAAS technique for determination of chromium, cadmium, lead and nickel in agriculturePolish and reference soils. These investigations included the following steps: (i) examination of the stability and homogeneity of the suspensions and analyte partitioning between solid and liquid phase; (ii) optimization of the time-temperature programme for routine analysis of Cr, Cd, Pb and Ni in the studied soils. The studied method has been tested by the analysis of certified reference materials.

2. EXPERIMENTAL

2.1. Apparatus

Determination of Cd, Pb, Cr and Ni contained in the tested materials was carried out using AAS-3 spectrometer (Carl Zeiss Jena, Germany) with a deuterium-lamp background corrector, equipped with EA-3 electrothermal atomizer and MPE autosampler. All measurements were carried out with at least five replicates using pyrolytically coated graphite tubes equipped (with pyrolytically coated Lvov platforms in the case of Cd and Pb determination) obtained from PerkinElmer. Pure argon (99.995% pure, Air Products, Warsaw, Poland) was used as the purge gas at 280 cm^3/min, except the atomization stage. Background corrected integrated absorbance was used as the analytical signal with the integrated time of 5 s.

2.2. Reagents and samples

Spectral purity nitric acid – HNO_3 (Merck, Darmstadt, Germany) was used for preparing standard solutions and slurries. The calibration standards were obtained from standard solution of Cd, Pb, Cr and Ni (Merck, Darmstadt, Germany) by dilution in 5% (v/v) nitric acid. For preparation of the slurries of the tested materials twice distilled water and spectral reagents were used. The three Polish soils were collected from the agriculture experimental area of University of Live Science in Lublin (Felin, Parczew, Bezek) and two samples – 3th and 5th agriculture soil's class (Janów, Poland). Three certified reference materials (SRM) were used in this study: San Joaquin Soil 2709, Soil – 5 and Montana Soil 2711 (certificated by IAEA and NIST respectively).

2.3. Analytical procedure

For each field location (Felin, Parczew, Bezek, Janów^1, Janów^2) were collected ten randomly selected samples. These samples were distributed on a regular grid with sample spacing of 10 m and therefore each is intended to represent an area 10 m by 10 m. The depth of sampling was 20 cm. Soil samples were taken using a shovel to plastic bags. Then they were labeling and adequately prepared for further analysis. At first real soil samples were drying at 110°C to the constant weight. Then sifted through a sieve having 10 mesh size. For slurry preparation the soils were ground in a MM-2 vibrational mill (K. Retsch GmbH, Germany) equipped with the chambers and balls made of tungsten carbide. The effectivity of grinding was examined by monitoring slurries prepared in alcohol by means of an optical microscope (magnification 800 times). It was experimentally stated that after 15 min. of grinding, about 65-70% percent of the particle had the sizes below 20 µm. The slurries were prepared by the balance method in the polyethylene vessels. The weights were made by means of "Sartorius R-200 D" (Germany) balance. Then the slurries were homogenized before each measurement by UD-20 ultrasonic desintegrator (Venpan, Poland; max. output power 140 W) equipped with the concentrator made of titanium. Ultrasonic homogenization was performed in the vessels of the autosampler, directly before the sampling of the slurry, which permitted for maximal elimination of errors caused the slurries unstability.

5% nitric acid was used as a dispersion medium to obtain the slurry. During Cd and Pb determination 1% ammonium dihydrogen phosphate as the modifier and Triton X-100 were added. In the case Cr and Ni determination no modifier was used and only Triton X-100 was added.

Partitioning of Cd, Pb, Cr and Ni into the liquid phase was evaluated by preparing a slurry of soils and certified reference materials. At the beginning each slurry was analyzed, then the suspension was centrifuged and the supernatant was examined for studied elements.

The effect of slurry composition on slurry stability was also examined. The slurries were mixed once just before the series of measurements. These studies referred to the dependence of the absorbance signal of the determined element on time.

Results obtained by slurry sampling GF AAS technique were compared to those achieved by application of the conventional acid digestion GF AAS where the samples were treated by *aqua regia* using closed PTFE vessel and MARS-5 (CEM, USA) microwave system.

The basic instrumental operating conditions and temperature programmes data are presented in Table 1. In order to optimize the temperature programmes for the determination of the tested metals a precise adjustment of the temperature of the graphite tube was made. The measurements were carried out by a Ni-Cr-Ni thermocouple (in the temperature range to 1000°C) and for higher temperatures by an optical pyrometer (EP-7, made in Poland).

Table 1. Instrumental operating conditions and temperature programmes for the determination of Cd, Pb, Cr and Ni.

Element	Cd	Pb	Cr	Ni
Wavelength [nm]	228.8	283.3	357.9	232.0
Pyrolysis temp. [°C]	800	900	1400	1100
Atomization temp. [°C]	2200	2200	2650	2500
Sample volume [mm^3]	20	20	20	20
L'vov platform	Yes	Yes	No	No
Modifier	Yes	Yes	No	No

3. RESULTS AND DISCUSSION

3.1. Optimization of determination conditions

Optimal conditions for determinations of Cd, Pb, Cr and Ni are presented in the Table 1. Figure 1 shows the ashing curves ofdetermined elements.

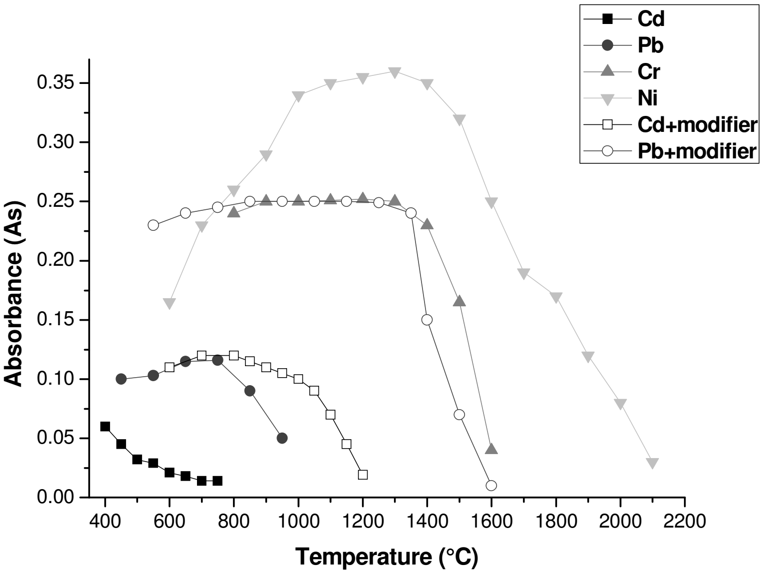

Fig. 1. Pyrolysis temperature curves for Cd, Pb, Cr and Ni for SRM San Joaquin Soil 2709 slurry prepared in 5% HNO_3 with and without chemical modifier.

Cd and Pb are lost from the graphiteatomizer at temperatures higher than 300 and 650°C, respectively. Therefore a chemical modifier should be applied for the determination of Pb and Cd in soil. The best modifier for the analyzed samples was found to be $NH_4H_2PO_4$ increasing the pyrolysis temperature to 800 and 900°C for cadmium and lead, respectively. In the case of the Cr at ashing temperatures higher than about 1400°C the absorption signal decreases significantly with increasing temperature.In applied pyrolysis temperature chlorides did not interfere with chromium. In the case of nickel determination, ~~in~~for the temperature in the range 1000–1500°C plateau of Cr signal is observed For this reason, the optimum temperature of thermal pretreatment was 1100°C.

The atomization curves ofstudied elements are presented in Figure 2. The atomizationcurves of Cd and Pb were examined in the presence of $NH_4H_2PO_4$ modifier. The operatingatomization temperatures for Cd, Pb, Cr and Ni are 2200, 2200, 2650 and 2500°C, respectively, in this work.

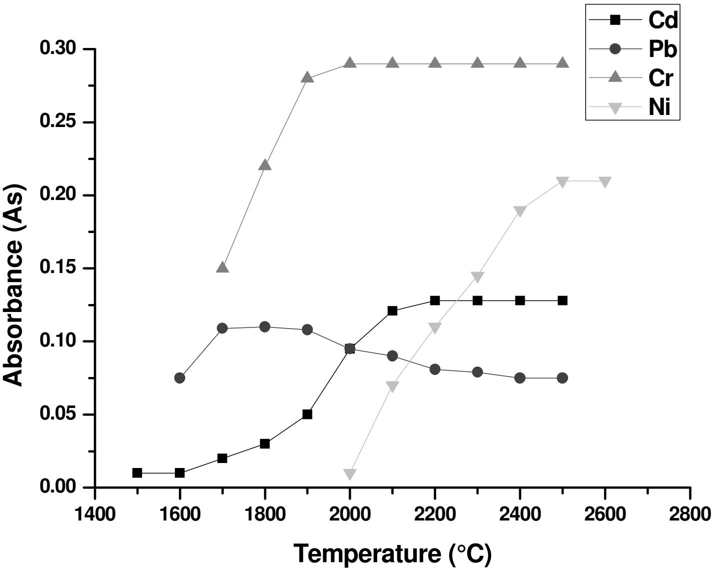

Fig. 2. Atomization temperature curves for Cd, Pb, Cr and Ni for SRM San Joaquin Soil 2709 slurry containing 5% HNO_3.

3.2. Investigation of the slurries stability and metal partitioning

The use of 5 % HNO_3 solution as a diluent leads to the partial extraction of the analytes into the slurry liquid phase. The degree of Cd, Pb, Cr and Ni extraction into the liquid phase was evaluated by preparing a slurry of analysed soils. The mixed slurry was examined for studied elements, subsequently the slurry was centrifuged and the supernatant was also analysed. The ratio of the amount of the determined metals (Cd, Pb, Cr and Ni) in the liquid fraction to the total amount of Cd, Pb, Cr and Ni in the slurry was expressed as a percentage. Table 2 shows the partitioning data for determined elements, which have been extracted to the bulk solution.

Table 2. Partitioning of Cd, Pb, Cr and Ni into the 5% nitric acid phase.

Sampling area	The extraction efficiency [%]			
	Cd	Pb	Cr	Ni
Felin	49	54	13	55
Parczew	52	57	22	57
Bezek	50	55	6	53
Janów[1]	45	50	15	61
Janów[2]	48	53	17	52

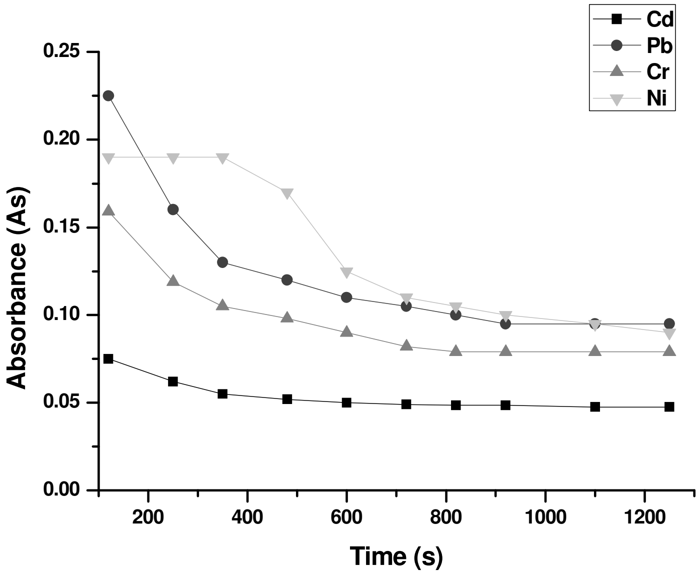

Fig. 3. Stability tests Cd, Pb, Cr and Ni for SRM San Joaquin Soil 2709 slurry containing 5 % HNO_3.

Figure 3 shows the stability tests of determined elements signals for SRM San Joaquin Soil 2709 slurry prepared in 5% HNO_3, in the cases of Cd and Pb were applied also matrix modifier $NH_4H_2PO_4$. The obtained results show the decrease of absorbance as the function of time, in the first minutes, and then the analytical signal stabilizes at the same level after 10, 12, 12 and 10 minutes for Cd, Pb, Cr and Ni, respectively. Therefore in further studies special attention was paid to shorten the time between the slurry homogenization and injection. The observed differences in the course of these curves result from different distributions of the analyte in the liquid and the solid phases. Stabilization of the signal in the stability test for longer time is a result of solid particles sedimentation and measurement of the analyte in the liquid phase of the slurry.

3.3. Application of the proposed method

After the optimization, the slurry sampling GF AAS method was tested in the determination of Cd, Pb, Cr and Ni in five samples of soils. Results are presented in Table 3.

Table 3. Results of Cd, Pb, Cr and Ni determination in soils by slurry sampling GF AAS.

Sampling area	Content, [mg/kg]			
	Cd	Pb	Cr	Ni
Felin	0.206 ± 0.010	11.4 ± 0.47	8.09 ± 0.36	5.68 ± 0.26
Parczew	0.153 ± 0.007	12.0 ± 0.60	4.02 ± 0.16	3.69 ± 0.22
Bezek	0.336 ± 0.015	13.6 ± 0.82	16.3 ± 0.49	9.14 ± 0.41
Janów[1]	0.148 ± 0.007	10.4 ± 0.47	4.60 ± 0.18	4.80 ± 0.24
Janów[2]	0.079 ± 0.002	6.80 ± 0.34	2.32 ± 0.09	2.91 ± 0.16

The average of five independent determinations.

The content of studied elements in soils by the conventional acid digestion GF AAS are shown in Table 4. In the case of slurry sampling GF AAS chromium determination, the results are higher in comparison to the wet digestion of GF AAS determination. These differences seem to be due either to losses of the analyte during preparation or to incomplete decomposition of the soils while using the wet digestion method. In the other cases, the analysis results are similar.

Table 4. Results of Cd, Pb, Cr and Ni determination in soils by the conventional acid digestion GF AAS.

Sampling area	Content, [mg/kg]			
	Cd	Pb	Cr	Ni
Felin	0.218 ± 0.009	10.7 ± 0.48	7.12 ± 0.32	6.02 ± 0.30
Parczew	0.162 ± 0.007	11.3 ± 0.57	3.58 ± 0.14	3.91 ± 0.12
Bezek	0.316 ± 0.016	14.4 ± 0.65	14.3 ± 0.72	9.69 ± 0.44
Janów[1]	0.157 ± 0.007	11.0 ± 0.55	4.14 ± 0.19	5.09 ± 0.23
Janów[2]	0.084 ± 0.003	6.39 ± 0.29	2.04 ± 0.08	3.09 ± 0.14

The average of five independent determinations.

Three SRMs were assessed using the slurry sampling method. For comparison, certified values and results of Cd, Pb, Cr and Ni determination in reference materials by slurry sampling GF AAS are presented in Table 5. The results of the determination obtained by the application of the slurry technique are comparable to the certified values.

Table 5. Results of Cd, Pb, Cr and Ni in reference materials by slurry sampling GF AAS.

Certified reference material	Concentration, [mg/kg]			
	Cd	Pb	Cr	Ni
San Joaquin Soil 2709	1.90 ± 0.06 1.89 ± 0.05*	19.3 ± 0.58 18.9 ± 0.5*	127 ± 5.08 130 ± 4*	87 ± 3.92 88 ± 5*
Soil-5	1.90 ± 0.12 1.5**	127 ± 5.71 129 ± 26*	29.0 ± 1.31 28.9 ± 2.8*	11 ± 0.66 13**
Montana Soil 2711	41.48 ± 1.87 41.70 ± 0.25*	1150 ± 46 1162 ± 31*	60 ± 3.6 47**	20.9 ± 0.94 20.6 ± 1.1*

* – certified values,

** – not certified; value is given by the supplier for information purpose.

4. CONCLUSIONS

The proposed slurry sampling GF AAS method for determination of Cd, Pb, Cr and Ni in soil samples is characterized by simplicity and good sensitivity. Evident advantages of the used method areelimination of thetime-consuming sample decomposition step andthe use strong and hazardous acid mixtures. The results of Cr determination obtained by slurry sampling GF AAS technique are higher comparing to those for the wet digestion GF AAS. It seems that this effect is due to losses of the analyte during preparation or incomplete decomposition of the soils while using the wet digestion method. Cd and Pb determination in soils by studied technique requires the application of the proper modifier. Application of $NH_4H_2PO_4$ as modifier was successful. Additionally, the precision of analyzed elements determination by utilizing slurry sampling evidently depends on the slurry stability. Presented method can be used for rapid analysis traces of Cd, Pb, Cr and Ni in the soil samples.

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