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GF AAS Determination of Cadmium, Lead and Copper in Environmental Materials and Food Products after Separation on Dithizone Sorbent★

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A group separation method by solid phase extraction on the dithizone sorbent for cadmium, lead and copper and their determination by GF AAS were developed. The method may be applied for a large variety of environmental materials and food products. The procedures of preliminary preparation and mineralization of various types of analytical samples were also developed. Accuracy of the method was estimated by determination of the analyzed elements in the three various certified materials. In all cases the obtained results were inside the scheduled confidence intervals. The detection limits (LOD) calculated for the samples dried to a constant weight at 70°C were estimated for cadmium, lead and copper as 2 ng g^{-1}, 20 ng g^{-1} and 2 ng g^{-1}, respectively. Relative standard deviations (RSD %, n = 5) were estimated by multiple determinations of cadmium, lead and copper in commercially available various food products and in a few collected environmental samples. Most of the estimated RSD values oscillated in the range below 2%. The highest values RSD did not exceeded 3%.

Opracowano metodę grupowego wydzielania kadmu, ołowiu i miedzi za pomocą ekstrakcji do fazy stałej oraz ich oznaczania za pomocą GF AAS. Metoda ta może być stosowana do analizy różnorodnych materiałów środowiskowych oraz produktów żywnościowych. Opracowano również procedury wstępnego przygotowania oraz mineralizacji różnego typu próbek analitycznych. Dokładność metody określono przez oznaczenie badanych pierwiastków w trzech różnych materiałach certyfikowanych. Wszystkie otrzymane wyniki znajdowały się wewnątrz przedziałów ufności podanych dla tych materiałów. Dolna granica wykrywalności (LOD) obliczona dla próbek wysuszonych do stałej masy w temperaturze 70°C

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★ Dedicated to Professor Rajmund Dybczyński on the occasion of his 75th birthday.

wyniosła dla kadmu, ołowiu i miedzi odpowiednio 2 ng g^{-1}, 20 ng g^{-1} i 2 ng g^{-1}. Względne odchylenia standardowe oznaczeń (RSD %, n = 5) określono przez wielokrotne oznaczanie kadmu, ołowiu i miedzi w dostępnych w handlu produktach spożywczych oraz w zebranych próbkach środowiskowych. Większość otrzymanych wartości oscyluje w granicach ± 2%, a wartości RSD najwyższe nie przekraczają 3%.

The effective determination of very low trace concentrations of heavy metals in environment and food products belongs to the most important toxicological investigations. It results from the fact that many chemical contaminants, including heavy metals, may be cumulated in the human body over a long period of time before the critical level of their concentration is reached in certain tissues and the clinical symptoms of the poisoning may be observed [1]. Moreover, some elements play a double role – they are essential for leaving organisms in a limited concentration and above it they became toxic. The distance between these two concentration levels is sometimes very narrow [2, 3]. The toxicity of some metals depends on their chemical form and in such cases the speciation analysis should be used [4, 5]. All mentioned problems cause that the permanent control of heavy metals concentration on the level of ng g^{-1} or ng mL^{-1} in soil, waters, plants and food products is indispensable. For such purpose the precise, accurate, relatively simple and easy for common use analytical methods should be applied. The direct instrumental methods can be used seldom only due to the insufficient detection limits or to the interferences caused by the complex matrices of the samples. Therefore, usually after the preliminary treatment and dissolution of samples the determined elements are separated from the matrix and preconcentrated before their determination. Sometimes the application of preconcentration is a way to replace a more expensive or complicated method of determination by a cheaper or simpler one, *e.g.* graphite furnace atomic absorption spectrometry (GF AAS) by flame atomic absorption spectrometry (FAAS) [6–9].

From among the various methods used for separation of elements to be determined by GF AAS the solid phase extraction (SPE) comes to the fore as a simple and very effective one [10]. For separation of heavy metals by this method the chelating sorbents are used very often since chelating reagents, particularly those with thiol groups, form stable complexes with these elements. The sorbents are prepared either by immobilization of a suitable chelating reagent on various beds (resins, silica gel, activated carbon) or by fixation of functional groups in the bed by chemical reactions during the synthesis process [11–18]. Sometimes the formation of metal complexes is carried out directly in the solution and followed with the sorption on a suitable bed [6, 9, 19, 20].

Cadmium, copper and lead belong to these heavy metals that produce particularly harmful effects for human health affecting several organs [21]. The aim of the presented work was to prepare a versatile method for group separation, preconcen-

tration and determination of these elements on a low trace concentration level in various types of environment samples (soil, street dust, grass) and in different food products (vegetables, fishes, meat). The applied separation process bases on the dithizone sorbent that was elaborated in our laboratory and already used for separation of noble metals from environmental samples [22], speciation analysis of selenium [4] and separation of some heavy metals from highly mineralized waters [11].

EXPERIMENTAL

Apparatus

Thermo Electron Corporation Solar M6–Mk II atomic absorption spectrometer with GF 95 graphite furnace, FS95 furnace autosampler and Zeeman background correction system. Thermo Electron Corporation hollow cathode lamps and Thermo Elemental pyrolitically coated graphite tubes (extended life-time) were used for all measurement.

Mettler Delta 340 pH-meter.

Microwave mineralizer, Plazmatronika UniClever TM II was used for mineralization process of samples.

Glass columns of 4 mm in internal diameter filled with 0.2 g of sorbent conditioned with solution of pH 4.

All glassware was cleaned by soaking for 12 h in 2% solution of alkaline detergent, next rinsed with water and leached for 24 h in 10% nitric acid and finally washed with water.

Reagents

The water of resistivity 18 MΩ cm^{-1} purified by Water Purification System–Milipore, nitric and hydrochloric acids purified by sub-boiling point distillation, hydrofluoric acid 40% suprapure (Merck), dithizone (Merck), resin Diaion HP–2MG (Supelko).

Dithizone sorbent was prepared as follows: 1 g Diaion resin (polymetacrylic ester) was placed in a 50 mL separatory funnel and shaken with 25 mL of 0.04 mol L^{-1} dithizone solution in chloroform for 1 h. The sorbent was separated by filtration, allowed to dry in air for 12 h and stored in darkness in a refrigerator at 4°C.

Standard stock solutions: 1 mg L^{-1} of Cd, Pb, and Cu were prepared by dissolution of the suitable reagents in the suitable acids. Working standard solutions were obtained by dilution.

Palladium-magnesium modifier solution: 100 µg mL^{-1} of Pd and Mg in 0.5 mol L^{-1} HNO_3.

Recommended analytical procedure

Preparation of samples. Food products and plant materials containing large amount of organic matter were crumbled, homogenized in the small food mill and then dried at the temperature of 70°C to a constant weight. The samples that agglutinated during the drying process were powdered in the agate mortar. The content of water was determined in the parallel samples to enable the calculation of the obtained results for original fresh material. 0.2 g to 0.5 g of the dried samples and maximum 8 mL of mineralizing solution were put into microwave mineralizer and processed under the conditions presented in Table 1.

Table 1. Conditions for sample mineralization. Sample 0.2–0.5 g; maximum volume of solution 8 mL

Material	Active reagents	Process parameters			
		Stages:	I	II	III
Soil and street dust	HNO_3 : HF = 1 : 2	Time, min	5	5	10
Plant materials	HNO_3 : HF = 4 : 1	Power of microwave generator, %	60	80	100
Fishes	HNO_3 : H_2O_2 = 2 : 1	Pressure, atm	17–20	27–30	42–45
Poultry liver	HNO_3	Temperature, °C			~310

Separation and preconcentration. The solution after digestion was transferred to the teflon evaporating dish and evaporated to the wet salts. The residue was dissolved in 5 mL 2 mol L^{-1} HCl, transferred by water to the 50 mL beaker, adjusted to pH about 4 by ammonium hydroxide solution using pH-meter and passed through the column (previously conditioned with solution of pH = 4) at the flow rate 5 mL min^{-1}. Next the column was washed twice with solution used for conditioning and the metals were desorbed by 10 mL 2 mol L^{-1} HNO_3.The effluent was collected in 20 mL volumetric flask and fulfilled up to the mark with water.

Determination. The separated metals were determined by graphite furnace atomic absorption spectrometry. 20 μL of the effluent was injected into pyrolytic coated graphite tube. The atomization conditions for all determined elements are presented in Tables 2 and 3. Copper was atomized without modifier whereas cadmium and lead in the presence of 20 μL of palladium-magnesium modifier solution pyrolyzed preliminary in the tube at the temperature of 800°C before addition of the sample. The analytical signals were measured as the integrated absorbance and evaluated on the basis of properly diluted standard solutions in 1 mol L^{-1} nitric acid.

Table 2. Spectral parameters

Element	Cd	Pb	Cu
Wavelength, nm	228.8	217.0	324.8
Band pass, nm	0.5	0.3	0.5
Lamp current, mA	10	15	10
Background correction	Zeeman	Zeeman	Zeeman
Integration time, s	3	3	3

Table 3. Temperature-time programs

Operation	Cd			Pb			Cu		
	T °C	Ramp °C s^{-1}	Time s	T °C	Ramp °C s^{-1}	Time s	T °C	Ramp °C s^{-1}	Time s
Drying	100	10	30	100	10	30	100	10	30
Pyrolysis	800	150	20	800	150	20	850	150	20
Atomization	1700	0	3	1900	0	3	2100	0	3
Cleaning	2400	0	2	2600	0	2	2700	0	3

The blanks were processed in the identical way simultaneously with the samples and their values, if significant, were deducted from analytical signals.

RESULTS AND DISCUSSION

Sample preparation and sorption

The samples of food products and plant materials contain mostly the organic mater and many of them are very difficult to mineralizae. Moreover, some products of their disintegration can form during the mineralization volatile compounds with the metals to be determined and cause their losses. Therefore, the mineralization process should be carried out in a closed system under the severe conditions. On the other hand, the strongly oxidizing agents as perchloric or sulfuric acid must be avoided since they can interfere the separation process on the column. Organic sample evolve during mineralization a large amount of gaseous products [23] and the mass of the samples processed in a closed system is limited and must be carefully chosen. The optimum mineralization conditions selected for various types of analytical samples are presented in Table 1.

The separation and preconcentration of copper, cadmium and lead on various sorbents was investigated in our previous work [11] and on this basis the optimum separation conditions, applied in this work and presented in the section „Recommended analytical procedure", were chosen.

Evaluation of method

The accuracy of the method was tested by determination of copper, cadmium and lead in three certified materials: Tea leaves (INCT–TL–1), Mixed Polish herbs (INCT–

MPH–2) and Oriental tobacco (ICTA–OTL–1) leaves. All obtained results, presented in Table 4, are inside the confidence intervals scheduled for the reference materials and indicate unambiguously that the tested method may be considered as accurate.

Table 4. Results of analysis of certified materials; a – certified values, b – determined values (mean values of 5 determinations)

Certified material	Cu, μg g^{-1}		Cd, μg g^{-1}		Pb, μg g^{-1}	
	a	b	a	b	a	b
INCT–TL–1 Tea leaves	20.4 ± 1.5	19.5	0.030 ± 0.004	0.032	1.78 ± 0.24	1.79
INCT–MPH–2 Mixed Polish herbs	7.77 ± 0.53	7.25	0.199 ± 0.015	0.203	2.16 ± 0.23	2.28
CTA–OTL–1 Oriental tobacco leaves	14.1 ± 0.50	14.1	1.12 ± 0.12	1.12	4.91 ± 0.80	4.21

The detection limits of the method (LOD), estimated on the basis of 3s criterion for 0.5 g samples dried to a constant weight at 70°, for cadmium, lead and copper were equal to 2 ng g^{-1}, 20 ng g^{-1} and 2 ng g^{-1}, respectively.

The precision of the method was estimated as relative standard deviation (RSD) by multiple determinations (n = 5) of cadmium, lead and copper in commercially available various food products and in a few collected environmental samples. The results of these determinations are presented in Table 5. Most of the estimated RSD values oscillate in the range below 2%. The highest values, close to 3%, were estimated for very low cadmium concentration (2 ng g^{-1} and 3 ng g^{-1}) and for low lead concentration. In the last case the larger dispersion may be caused by the presence of chlorides (sorption from hydrochloric acid solution). Taking into account the low concentration level of the determined elements the precision of method may be considered as satisfactory.

Table 5. Results of copper, cadmium and lead determination in selected food products and environmental materials (mean values for n = 5)

Type of sample		Cu		Cd		Pb	
		µg g^{-1}	RSD, %	µg g^{-1}	RSD, %	µg g^{-1}	RSD, %
Food products	Mixed vegetables	0.81	1.1	0.074	1.2	0.52	1.0
	Cabbage	0.23	2.5	0.003	2.9	<0.02	–
	Tomato concentrate	2.66	0.8	0.050	2.1	0.032	2.9
	Preserved sorrel	0.60	1.5	0.012	1.8	0.090	2.9
	Carp	0.82	1.2	0.002	2.9	0.14	2.1
	Salmon	0.27	0.5	0.005	0.8	0.18	1.5
	Poultry liver	3.45	0.7	0.040	1.1	<0.02	–
Environmental materials	Soil	47.6	0.8	0.43	1.0	67.6	0.9
	Street dust	33.6	1.0	0.40	1.5	21.3	2.0
	Grass	15.8	1.0	0.15	0.9	2.0	1.9

Tests for interferences showed that all cations and anions that may be present in the samples after separation of the main components of the analyzed samples do not affect the results of all tested elements.

CONCLUSIONS

The proposed method is versatile and enables determination of three toxic metals, cadmium, lead and copper, in different materials as soil, plant materials or large variety of food products. The applied dithizon sorbent is easy for preparation in the laboratory and makes possible the group separation of the determined elements from various matrices. This enables the unification of analytical methods in these laboratories that work with a large assortment of various materials.

REFERENCES

1. Cuadrado C., Kumpulainen J., Carbajal A. and Moreiras O., *J. Food Comp. Anal.,* **13**, 495 (2000).
2. Lemos V.A., Vieira D.R., Novaes C.G., Rocha M.E., Santos M.S. and Yamaki R.T., *Microchim. Acta,* **153**, 193 (2006).
3. Hussein L. and Bruggeman J., *Food Chem.*, **65,** 527 (1999).
4. Chwastowska J., Skwara W., Sterlińska E., Dudek J. and Pszonicki L., *Chem.Anal. (Warsaw),* **52,** 253 (2007).

5. Chwastowska J., Skwara W., Sterlińska E. and Pszonicki L., *Talanta,* **66,** 1345 (2005).
6. Saraçoğlu S. and Elçi L., *Anal. Chim. Acta*, **452,** 77 (2002).
7. Goswami A. and Singh A.K., *Anal. Chim. Acta,* **454,** 229 (2002).
8. Amorim F.A.C. and Ferreira S.L.C., *Talanta*, **65,** 960 (2005).
9. Tuzen M. and Soylak M., *Anal. Chim. Acta*, **504,** 325 (2004).
10. Camel V., *Spectrochim. Acta Part B,* **58,** 1177 (2003).
11. Chwastowska J., Skwara W., Sterlińska E., Dudek J., Dąbrowska M. and Pszonicki L., *Chem. Anal. (Warsaw)*, **52,** 781 (2007).
12. Pornlada Daorattanachai, Fuangfa Unob and Apichat Imyim, *Talanta,* **67,** 59 (2005).
13. Chwastowska J., Żmijewska W. and Sterlińska E., *Anal. Chim. Acta,* **276,** 265 (1993).
14. Ramesh A., Mohan K.R. and Seshaiah K., *Talanta,* **57,** 243 (2002).
15. Lemos V.A. and Baliza P.X., *Talanta,* **67,** 564 (2005).
16. Saha B., Iglesias M., Cumming I.W. and Streat M., *Solv. Extr. Ion Exch.,* **18,** 133 (2000).
17. Rahmi D., Zhu Y., Fujimori E., Umemura T. and Haraguchi H., *Talanta,* **72,** 600 (2007).
18. Ngeontae W., Aeungmaitrepirom W. and Tuntulani T., *Talanta,* **71,** 1075 (2007).
19. Soylak M. and Tuzen M., *J. Hazard. Mat.,* **B 137,** 1496 (2006).
20. Saygi K.O., Melek E., Tuzen M. and Solak M., *Talanta,* **71,** 1375 (2007).
21. Jurado J.M., Martín M.J., Pablos F., Moreda-Piñerio A. and Bermejo-Barrera P., *Food Chem.*, **101**, 1296 (2007).
22. Chwastowska J., Skwara W., Sterlińska E. and Pszonicki L., *Talanta,* **64,** 224 (2004).
23. Dolan S.P. and Capar S.G., *J. Food Comp. Anal.,* **15,** 593 (2002).

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