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FAAS method and the extraction process applied for fractionation analysis of gravitation dust sediments and their evaluation

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Abstract: The main scope of this paper is first of all to verify the efficiency of the flame atomic absorption spectroscopy (FAAS) method for analysis of some trace elements in extracts of fractionation analysis of the gravitation dust sediments. Investigation was oriented to the analysis of some markedly toxic trace elements in the extracts of gravitation dust sediments as well as on efficiency evaluation of the individual extraction reagents. Following analytical and fractionation extraction results were deduced conclusions about toxicity of gravitation dust sediments. Three extraction reagents with different mobilization ability were applied for fractionation extraction. There was used ammonium nitrate (NH_4NO_3) whose mobilizable ability is least and practically equal to mobilizable robustness of water. The second reagent used was disodium salt of EDTA (Na_2EDTA) which is characterized by marked complexing properties. Finally, nitric acid (HNO_3) with the most marked extraction and mobilizable properties was used. In the single extracts four chosen elements (Cd, Cu, Pb, Zn) were determined by optimized FAAS method.

Keywords: Gravitation dust sediments; fractionation extraction; AAS determination; statistical evaluation of the results

1. Introduction

Fractionation analysis is an analytical procedure leading to the classification (isolation and quantification) of different element forms in the solid environmental samples. Basic stages of this

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procedure are an isolation of specific element forms (fractions) and consequential element quantification in the isolated fractions. For evaluation of the risk element mobility from the gravitation dust sediments to the soils, under specific soil conditions, it is possible to use fractionation analysis with single step extraction as an isolation method. This experimental arrangement of fractionation analysis is commonly used at evaluation of element mobility in the soils. Several procedures with application of defined extraction reagents, which simulate different soil conditions, are validated to this goal. For that reason it is necessary to optimize these procedures before their utilization.

Considering unavailability of certified reference materials for purposes of fractionation analysis of gravitation dust sediments, evaluation of repeatability of obtained results is problematic. Therefore it is useful to direct the statistical evaluation only on the evaluation of repeatability of the results. Accuracy of the final fractionation analysis result depends mainly on the accuracy of the extraction, on the accuracy of the determination of the content of elements in the extracts or on the uncertainties of these both steps, which influence final results.

It is necessary, at statistical evaluation of extraction, to put an attention to the heterogeneity of used extraction reagents with different extraction power. In accordance with Makovniková[1], no buffered solutions of salts with weakest solving extraction effect (0.01 – 0.1 mol dm^{-3} $CaCl_2$, 0.1 mol dm^{-3} $NaNO_3$, 0.1 mol dm^{-3} $Mg(NO_3)_2$, 1 mol dm^{-3} NH_4NO_3, 1 mol dm^{-3} KNO_3 ...) are used for isolation of so-called “mobile” fraction of elements. This fraction includes forms, which will be movable from the dusts to the soils under normal soil conditions. The way of their interaction with corresponding forms of elements in the sample is based on ion exchange or water dissolubility.

Extraction reagents based on organic complexes (Na_2EDTA, EDTA, DTPA, CH_3COONH_4 ...), which are used for extraction of so-called “mobilizable” fraction of elements, have stronger extraction effect. “Mobilizable” contents represent mobile fraction and potential reserve of elements, which can be mobilizable from the dusts at the soil conditions change caused by present intervention of agricultural techniques and fertilization.

2 mol dm^{-3} HNO_3 has a special position among extraction reagents; it enables an isolation of “mobilizable” fraction and these forms of elements, which can be movable in case of extreme changes of soil conditions. It is so-called “maximum potentially mobilizable“ content of elements or “environmental risk”. This fraction represents all releasable element forms except from those, which are firmly bounded to the matrix of dust particles.

2. Experimental

For purposes of fractionation analysis, sample of gravitation dust sediment sampled in the city region of Košice residential agglomeration, was used. This region belongs to the industrial areas in preference loaded by pollutants of metallurgical industry. For sampling of dust particles, the opened standard glass sedimentation vessels filled by distilled water, were used[2]. After expiration of exposition time, content of vessels was quantitatively transferred into the Pt-vessels and then evaporated to dryness. Further crushing and grinding in the agate mill homogenized the sample.

The experimental realization of the fractionation analysis with using of the single-step conventional extraction by shaking for isolation of element forms was in accordance with validated procedure for soil samples[2,3]. A mechanical shaker MRC TS-400D (M.R.C. Ltd., Izrael, 240 rpm) was used for sample shaking. The time of shaking was individual as follows: for NH_4NO_3 and EDTA it was 1 hour and for HNO_3 it was 6 hour. After finishing of extractions, the suspensions were passed through the filter paper with narrow pores (blue ribbon) and paper diameter of 18.5 cm at the laboratory temperature. Extraction ratio, 0.5 g of sample and 75 cm^3 of extraction reagent, was assimilated to the gravitation dust sediment samples on the basis of the optimization experiment results[4,5]. Following extraction reagents were chosen for statistical evaluation: 1 mol dm^{-3} NH_4NO_3 for isolation of “mobile” forms, 0.05 mol dm^{-3} EDTA for isolation of “mobilizable” forms and 2 mol dm^{-}

^{3} HNO_3 for isolation of "maximum potentially mobilizable" forms of elements. Atomic absorption spectrometry method with flame atomization (FAAS) was used for determination of content of elements under condition given in Table 1.

Table 1. Experimental conditions of FAAS method

Spectrometer		Varian Spectra AA 400			
Lamp		Varian HCL system			
Carrier gas		Air			
Flow rate	v / dm^3 min^{-1}	40			
Fuel gas		H_2C_2			
Flow rate	v / dm^3 min^{-1}	20			
Element		Cd	Cu	Pb	Zn
Wavelength	λ / nm	228.8	324.8	217.0	213.9
Lamp intensity	I / mA	10	15	10	15

Contribution of extraction to the total repeatability of fractionation analysis result was spotted by statistical evaluation of the measured contents of elements in the extracts in 10 repeated extractions. Efficiency of the FAAS method as well as other statistical parameters, which are important for characterization of the method, was determined from the sets of results of 10 repeated measurements in one extract. Obtained results were evaluated using the statistical software QC. Expert 2.5™ [6] and in accordance with the literature data[7].

3. Results and discussion

Content of risk elements in the extracts of fractionation analysis depends mainly on their way of occurrence in the dust particles. Total content of these elements in the samples is in the range of trace elements and their content in the different element forms will be even lower. It is necessary that directed statistical verification of availability of analytical method for determination of contents of elements in the extracts to several concentration levels and selection of measured elements adapt for it. The total percentage content of elements chosen for statistical evaluation in the studied dust sample is in the range from 0.5 % to 0.001 % and it is in the following order, from high to low: Cu, Zn, Pb, Cd. Average percentage share of elements in the appropriate forms from their total content in the sample (100 %), expressed as a percentage recovery of elements in the extracts of used extraction reagents, together with average values of measured concentrations, is given in Table 2. Obtained concentration values show that content of elements in the extracts is in four different concentration levels.

First set of experiments was focused on the statistical evaluation of results of determination of element contents in the extracts of all extraction types reagent using FAAS method. Repeatability of the method was determined and it is expressed as percentage standard deviation (RSD) together with other statistical parameters in Table 3.

Table 2. Percentage contents (c /%) of elements in the monitored forms and measured concentration values (c / mg dm^{-3}) in the extracts

Element	Isolated forms					
	1		2		3	
	c / %	c / mg dm^{-3}	c / %	c / mg dm^{-3}	c / %	c / mg dm^{-3}
Cu	17.7	0.42	44.2	16.1	92.0	34.4
Zn	20.9	0.37	27.1	3.83	76.7	10.2
Pb	N.D.	N.D.	27.4	0.81	72.9	2.09
Cd	N.D.	N.D.	21.3	0.01	36.2	0.04

N. D. – not detected

1 – “Mobile” forms, parameters of the extracted elements in 1 mol dm^{-3} NH_4NO_3;

2 – “Mobilizable” forms, parameters of the extracted elements in 0.05 mol dm^{-3} EDTA;

3 – “Maximum potentially mobilizable” forms, parameters of the extracted elements in 2 mol dm^{-3} HNO_3.

Table 3 a). Repeatability and other statistical parameters of 10 repeated measurements of Cu and Zn content in the individual extracts

Element		Cu			Zn		
Extraction reagent		1	2	3	1	2	3
Number of measurements	N	10	10	10	10	10	10
Arithmetical mean / mg dm^{-3}	$\bar{I}$ (x)	0.42	16.5	34.3	0.37	3.89	9.95
Standard deviation	s($\bar{I}$)$_x$	0.01	0.31	0.17	0.01	0.07	0.19
RSD / %	s($\bar{I}$)$_{x,r}$	1.68	1.88	0.50	2.41	1.87	1.87
Median / mg dm^{-3}	$\tilde{I}$ (x)	0.42	16.4	34.4	0.37	3.90	9.95
Standard deviation	s($\tilde{I}$)$_x$	0.01	0.13	0.11	0.01	0.03	0.07
RSD / %	s($\tilde{I}$)$_{x,r}$	0.96	0.79	0.32	1.08	0.77	0.70
Modus	$\hat{I}$ (x)	0.41	16.3	34.5	0.37	3.90	9.93
Halfsum	$\tilde{I}$ (x)$_p$	0.41	16.5	34.2	0.38	3.87	10.0

Table 3 b). Repeatability, and other statistical parameters of 10 repeated measurements of Pb and Cd content in the individual extracts

Element		Pb			Cd		
Extraction reagent		1	2	3	1	2	3
Number of measurements	N	10	10	10	—	10	10
Arithmetical mean / mg dm^{-3}	$\bar{I}$ (x)	0.05	0.81	2.08	—	0.01	0.05
Standard deviation	s($\bar{I}$)$_x$	0.01	0.03	0.02	—	0.01	0.01
RSD / %	s($\bar{I}$)$_{x,r}$	18.0	3.33	1.1	—	50.0	14.3
Median / mg dm^{-3}	$\tilde{I}$ (x)	0.05	0.81	2.09	—	0.01	0.05
Standard deviation	s($\tilde{I}$)$_x$	0.01	0.02	0.01	—	0.01	0.01
RSD / %	s($\tilde{I}$)$_{x,r}$	10.0	2.22	0.62	—	20.0	10.0
Modus	$\hat{I}$ (x)	0.04	0.81	2.09	—	0.01	0.05
Halfsum	$\tilde{I}$ (x)$_p$	0.05	0.81	2.08	—	0.01	0.05

Concentration values (1) are the highest in case of HNO_3 extraction (decomposition) reagent because it is most aggressive reagent. Values (2) are markedly lower in spite of the fact that Na_2EDTA extraction reagent has marked complexion properties. Values (3) obtained by extraction of NH_4NO_3 are lowest. Precision of the method expressed by RSD shows acceptable values for content determination of Cu and Zn in all extraction reagents. RSD values markedly exceed the acceptability in case of content determination of Pb in NH_4NO_3 and Cd in all extraction reagents. As the extraction is least effective in that case, using of this extraction reagent was canceled. Values of arithmetical mean, median, modus and half sum, as well as values of transformed arithmetical means after Box-Cox transformation are identical within the framework of the measuring errors for all tested sets. Asymmetry of the data measured for Cd changed in the range of $A(x) \in \langle -0.11, 0.46\rangle$, for Cu was $A(x) \in \langle -0.36, 0.66\rangle$, for Pb it was $A(x) \in \langle -0.58, 0.12\rangle$ and for Zn it was $A(x) \in \langle -0.64, 0.72\rangle$. Testing of these parameters showed that their values are identical with optimal zero value. Excess value for Cd was in the range $E(x) \in \langle 1.20, 2.56\rangle$; for Cu it was $E(x) \in \langle 1.55, 3.46\rangle$, for Pb $E(x) \in \langle 1,77, 2.40\rangle$ and for Zn $E(x) \in \langle 1.93, 3.77\rangle$. Testing of values for excess confirmed that these values are within the framework of measuring errors identical with optimal value 3. Summary of these data as well as testing of normality and homogeneity of the input data confirmed their normal and homogeneous distribution.

Next it was done evaluation of the probability density functions (pdf). Typical courses for Cu and Pb are shown in Figures 1a and 1b. Similar course of pdf-line has Cd too. Arithmetical mean and median are partially or absolutely identical in these cases and the Gaussian line is always symmetrical. Symmetry of the pdf-line is admittedly element specific attribute but it is conditioned by chemical character of applied extraction reagent too. On the other hand pdf-lines of Zn show expressive skewing towards lower values (Figure 1c) as well as towards higher concentration values (Figure 1d). Objective skewing is not only element specific but also they depend on the chemical character of the used extraction reagent (different ionic power as well as complexion properties). Skewing (deformation) of the Gaussian lines caused shift of half sum towards the higher concentration values (Figure 1c) as well as ore towards lower concentration values (Figure 1d). In spite of these differences, normal and homogeneous character of the input data distribution was not disordered. Summary of the discussed statistical parameters and their interpretation justifies applying optimized analytical method for calibration.

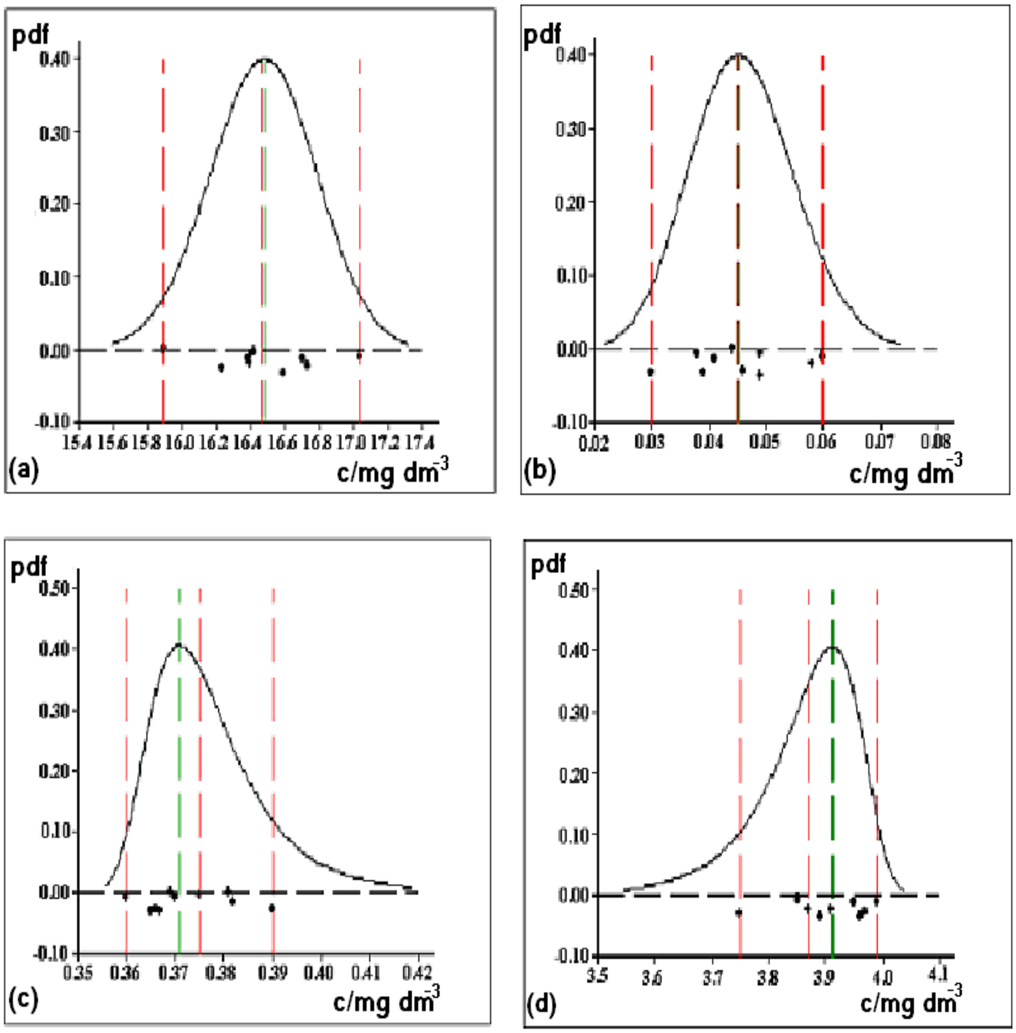

Figure 1. Probability density functions (pdf): (a) Cu in Na_2EDTA; (b) Pb in NH_4NO_3; (c) Zn in NH_4NO_3; (d) Zn in Na_2EDTA.

Calculation of the parameters of the calibration lines confirmed that value of absolute member A(x) is equals zero for all four elements that means the analytical lines go out of origin (Table 4). Notable is the fact that limit of detection value (LOD) is always lower than the lowest calibrating concentration. It apparently enables to enlarge calibration about one concentration order towards lower values. Otherwise the sensitivity for Cu, Pb, and Zn is low within the framework of measuring errors but it is mutually same. Sensitivity of Cd calibration line is higher but always low. This phenomenon is conditioned by the fact that for all four elements was confirmed only quadratic calibration model

(Figure 2) with expressive curving in the region of higher concentrations. Reached correlation values as well as determination coefficient values confirm that 98 % of calibrating concentrations are relevant in term of applied calibration by least-square method. Therefore there were obtained very soft confidence limits (Figure 2). Following obtained results it can be stated that given calibration can be applied for analysis of before - cited extracts.

Table 4 Statistical parameters of the calibration lines

Element		Cd	Cu	Pb	Zn
Wavelength	λ / nm	228.8	324.8	217.0	213.9
Number of measurements	N	20	16	20	16
Model		quadratic	quadratic	quadratic	quadratic
Suitability		+	+	+	+
Absolute member	A(x)	0.00	-0.01	0.00	0.01
Test of absolute member	$t_{A(x)} \neq 0$	-	-	-	-
Sensitivity	B(x)	0.19	0.05	0.03	0.05
Minimum concentration	c_{min} / mg dm^{-3}	0.10	2.00	1.00	2.00
Maximum concentration	c_{max} / mg dm^{-3}	2.00	20.0	20.0	20.0
Limit of detection	c_L / mg dm^{-3}	0.02	0.38	0.09	0.24
Correlation coefficient	r	0.99	0.99	0.99	0.99
Coefficient of determination	$R = r^2.100$	98.0	98.0	98.0	98.0
RSD	c / %	15.1	1.88	3.32	1.87

In the next series of experiments, an influence of the single-step conventional extraction on the total precision of the fractionation analysis result, was tested. For testing were chosen the results of extraction of the phase compounds of the above mentioned elements. Statistical evaluation of measurements of contents of elements in the extracts of repeated extractions is shown in Table 5. Extraction of elements was tested by repeating $N \in \langle 9, 10 \rangle$ extractions. It can be seen that RSD values determined in regard to extraction are higher than those obtained in regard to measurement using FAAS method. RSD values, in case of Cu, Pb, and Zn are for both extraction reagents acceptable. RSD values for Cd are significantly higher as values for Cu, Pb, and Zn. Finally it can be stated that influence of the EDTA extraction on the total precision of fractionation analysis is more expressive than influence of HNO_3 extraction. Arithmetical mean, median, modus and halfsum values as well as values of transformed arithmetical means after Box-Cox transformations are identical within the framework of measuring errors for all tested sets. Asymmetry of data measured for Cd was in the range $A(x) \in \langle 0.19, 0.46 \rangle$, for Cu it was $A(x) \in \langle 0.10, 0.66 \rangle$, for Pb was $A(x) \in \langle -0.23, -0.22 \rangle$ and for Zn it was in the range $A(x) \in \langle -0.23, 058 \rangle$. Testing of these values confirmed agreement with optimal zero value. Excess value has varied for Cd in the range $E(x) \in \langle 1.20, 1.96 \rangle$, for Cu was $E(x) \in \langle 2.29, 3.46 \rangle$, for Pb $E(x) \in \langle 1.77, 1.90 \rangle$ and for Zn $E(x) \in \langle 1.93, 2.19 \rangle$. Testing showed that these values are also identical with optimal value 3. Summary of these data as well as tests confirmed normal and homogeneous data distribution of individual elements.

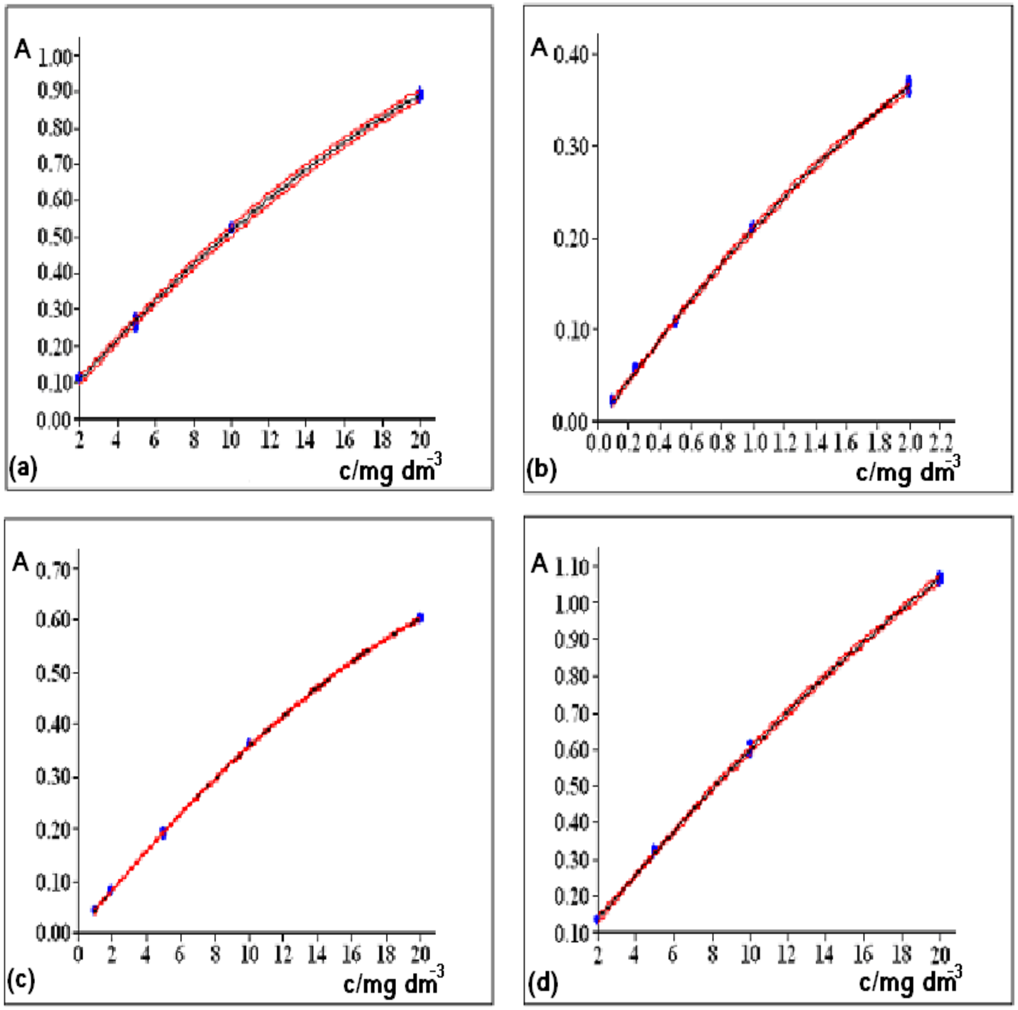

Figure 2. Calibration lines with confidence limits for (a) Cu; (b) Cd; (c) Pb; (d) Zn.

Table 5. Repeatability and other statistical parameters determinations of Cu, Zn, Pb, and Cd in extracts of 10 repeated extractions

Element		Cu		Zn		Pb		Cd	
Extraction reagent		1	2	1	2	1	2	1	2
Number of measurements	N	9	10	10	9	10	9	9	10
Arithmetical mean / mg dm^{-3}	$\bar{I}$ (x)	15.7	34.4	3.77	10.52	0.81	2.09	0.01	0.03
Standard deviation	$s(\bar{I})_x$	0.37	0.47	0.18	0.59	0.03	0.02	0.01	0.01
RSD / %	$s(\bar{I})_{x,r}$	2.36	1.37	4.77	5.61	3.70	0.96	53.9	48.3
Median	$\tilde{I}$ (x)	15.6	34.3	3.76	10.38	0.81	2.09	0.01	0.03
Standard deviation	$s(\tilde{I})_x$	0.35	0.38	0.14	0.44	0.02	0.01	0.01	0.01
RSD / %	$s(\tilde{I})_{x,r}$	2.24	1.11	3.72	4.24	2.47	0.50	40.0	40.0
Modus	$\hat{I}$ (x)	15.6	34.1	3.72	10.2	0.81	2.09	0.01	0.02
Halfsum	$\tilde{I}$ (x)$_p$	15.7	34.6	3.74	10.7	0.81	2.09	0.01	0.03

1 – Quantity of the extracted elements in 0.05 mol dm^{-3} EDTA;
2 – Quantity of the extracted elements in 2 mol dm^{-3} HNO_3.

4. Conclusion

Amount and toxicity of determined elements Cd, Cu, Pb, and Zn is markedly different. Thanks to heavy traffic jam, mainly in the residential city agglomeration, dust sediment whirls and crumbles, and so it raises amount portion of fly ash. The most effective extraction reagent is HNO_3. It dissolves a part from SiO_2 and some silicates all phase components of dust sediments too. EDTA has only cca 40 % efficiency in comparison with HNO_3. Following obtained results of statistical evaluation it can be stated that: availability of utilization of FAAS method for the analysis of extracts as well as applicability of extraction for isolation of fractions is possible to deduce on the base of RSD values; FAAS method is suitable for Cu, and Zn determination in the all used extraction reagents, and for Pb determination in HNO_3, and EDTA; neither FAAS method nor mentioned extraction reagents are suitable for Cd determination; high RSD values of measurements in extracts of 10 repeated extractions show that conventional extraction is not suitable method for isolation of element forms of Cd. Influence of extraction on total result of fractionation analysis is least marked in case of isolation of Cu and Pb forms. RSD values for Zn were higher but acceptable yet. Different content of Zn in single extracts could be caused by their contamination because of biogenic character of Zn. Cd determination in extracts is influenced by its low content (below LOD) therefore it is necessary to find a new way of its determination. The most expressive influence of the total precision of result of fractionation analysis has the isolation method (extraction), which burden analysis with the highest uncertain.

As alternative ways of the determination of Cd contents in the fractionation analysis extracts (instead of direct determination by FAAS method) is possible to use the direct determination of contents using method with lower limit of detection (e.g. ETAAS). It is suggested to extract Cd from the extract on the solid phase (SPE extraction) and its content may be determined in the solid phase (e.g. XRF method), eventually its elution into the less volume, preconcentration and determination by FAAS method may be used.

Disadvantage of the conventional extraction by shaking is possibility of creation of aggregates of particles and their deposition on the walls of extraction vessels. It leads to the interruption of the contact of extraction reagent with sample. This fact increases uncertainty of the extraction. There are several techniques (e.g. ultrasound, microwave, supercritical extraction), which are able to prevent negative effects of conventional extractions.

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References

[1] J. Makovniková (2000). Distribution of Cd, Cu, Pb, and Zn in soils, and its evaluation considering on potentials and barriers of metal transposrt to plants. Research report. Research institute of soil science and soil conservation, Bratislava.

[2] VDI/DIN Handbuch (1991). Reinhaltung der luft. Beuth Verlag, Berlin.

[3] A. M. Ure, C. M. Davidson and R. P. Thomas (1995). Single and sequential extraction schemes for trace metal speciation in soil and sediment, In: (Quality assurance for environmental analysis), ed: Elsevier Science B. V. pp. 505-523.

[4] D. Remeteiová, E. Krakovská, J. Tomko, E. Sminčáková and V. Vojteková (2002). Extraction of gravitation dust sediment samples by EDTA. *Book of conference "Mikroelementy 2002"*, 2 Theta, Český Těšín, 124-128.

[5] J. Tomko, E. Krakovská, D. Remeteiová and E. Sminčáková (2002). Determination of mobilizible content of some metals in the grawitation dust by 2M HNO_3. *Book of conference "Mikroelementy 2002"*, 2 Theta, Český Těšín, 129 - 133.

[6] K. Kupka (2002). QC Expert 2.5^{TM} statistical software. TriloByte, Pardubice.

[7] M. Meloun, J. Militký and M. Forina (1992).Chemometrics for Analytical Chemist.Ellis Howard, Chichester.