

ASSESSMENT OF HEAVY METALS LEVELS IN URBAN DUSTS AND SOILS BY MICROWAVE-ASSISTED AQUA REGIA DIGESTION

Z. ANEVA^{a*}, L. CHEPANOVA^b

^a*Prof. Dr. Assen Zlatarov University, 8010 Bourgas, Bulgaria*

E-mail: analchem@btu.bg

^b*Regional Laboratory – Bourgas, Environmental Executor Agency, Ministry of Environmental and Waters, Bulgaria*

Abstract. The main aim of this work was to assess the contamination of urban dusts and soils with Cd, Cu, Pb and Zn, originated from petrol products, automobile transportation emissions and industrial activity. The study area is located near by the industrial zone of the city Bourgas, Bulgaria. For this purpose microwave-assisted aqua regia digestion procedure was validated, using certified reference materials and a comparison with standard ISO 11 466 procedure. Results show higher levels of heavy metals in the local dusts and soils than the background values and the reference earth's crust.

Keywords: heavy metals, urban dusts and soils, microwave-assisted aqua regia digestion.

AIMS AND BACKGROUND

It is well known that air particulate matter tends to pose the greatest health concern, because it can be inhaled and accumulated in the respiratory system. Sources of urban particulate matter can be all types of combustion manufacturing and industrial processes, street and car park dusts and soils¹⁻³. The latter receive potentially heavy metal elements originated from traffic (automobile exhausts), gasoline, diesel oils, lubricants and wide range of anthropogenic sources. Inhalation of toxic metal elements is associated with numerous health effects, such as inhibition of some ferments, destruction of cell systems, structure change of the live tissue and decreasing of immunity reaction⁴.

The subject of our investigation were dusts and soils from area located near by the industrial zone of Bourgas, which is characterised with very intensive automobile traffic, a number of car parks in the housing zone and also strongly windy weather conditions.

The nowadays microwave (MW)-assisted digestion of soils, sludges, sediments and particulate matter is recommended as a very effective procedure for the determination of toxic and essential elements by atomic absorption and inductively coupled plasma emission spectrometries or mass-spectrometry. The

* For correspondence.

major benefits of this digestion procedure, is a considerable reduction in the analysis total time, in the risk of a sample contamination and in losses of volatile elements⁵⁻⁸.

Different protocols have been applied using total digestion scheme involving hydrofluoric acid (HF) to completely release the elements in the aluminosilicate matrix or an acids extraction as an alternative to the total digestion. The second scheme is recently recommended for routine analysis, because it is less time-consuming, less dangerous and cumbersome procedure than the total digestion procedure.

Due to the different microwave chemical systems design and the different digestion protocols used, it is mandatory to verify the procedure used, using certified reference materials (CRM) or comparing the results with those of a standard method.

Thus, the first task of this work was to optimise and validate a MW-assisted aqua regia extraction procedure, which then can be applied for environmental samples.

EXPERIMENTAL

Sampling and preparation. The dusts were sampled from the surface (0-10 cm depth) of the parking terrenes. The soils were collected keeping the standard methods recommendations.

The samples were dried, crushed and sieved through a 2-mm sieve. Then the fraction with up to 2 mm diameter of particulate was ground until the sample passes through a 150- μ m sieve.

All samples were collected in preliminary treated with 5% HNO₃ polyethylene bags for avoiding the contamination and then were stored under refrigeration in hermetically sealed flasks.

MW-assisted aqua regia extraction procedure. About 1 g samples was weighed into a small plastic beakers and then placed into a PTFE pressure vessels, using 0.25 ml deionised water, following by addition of 7.5 ml 37% HCl (Merck Suprapur) and 2.5 ml 65% HNO₃ (Merck Suprapur). The closed vessels were introduced in the microwave chemical system (Milestone Ethos 900 with 6 vessels 100 ml, controlled by Terminac 240 computer system). The heating program used was : 1st step – 250 W for 5 min; 2nd step – 750 W for 5 min; 3rd step – 250 W for 5 min; 4th step – 0 W for 5 min. After cooling the samples were filtered through a Whatman 41 filter in 25 ml-plastic volumetric flasks and diluted with deionised water. If necessary, the samples were additionally diluted.

Aqua regia extraction based on the ISO method 11 466. In this procedure 1.5 g of samples were paced in 250-ml Pirex digestion tubes and a pre-digestion step

was run at room temperature for 16 h with 14 ml 3:1 mixture of 37% HCl (Merck Suprapur) and 65% HNO₃ (Merck Suprapur). The suspensions were subsequently digested at 130°C for 2 h in a reflux condenser using a Gerhard apparatus. The cooled samples were filtered through a Whatman 41 filter in 25-ml plastic volumetric flasks and diluted with deionised water. If necessary, the samples were additionally diluted.

Flame atomic absorption determinations. A Shimadzu Model AA 660 flame atomic absorption spectrometer equipped with a standard air/acetylene burner was used to determine metals in acid extracts. The measurements were performed at resonance wave lengths with exception for Pb determination (283.3 nm).

Calibration standards were prepared by suitable dilution of stock multi-element standard for inductively coupled plasma atomic emission spectrometry (CertiPur (Merck Reference material)), matching the concentration of the acids to those of the samples. The dynamic ranges of the calibration curves used were as follows: Cd, Mn, Ni, Zn – up to 2 mg/l; Co, Cr, Cu, Fe – up to 5 mg/l; Pb – up to 20 mg/l.

Certified reference materials and samples. The following certified reference materials (CRM) were used to optimise and verify the digestion procedure:

- NIST-2709 San Joaquin soil from National Institute of Standards and Technology – USA;
- TILL-2 geochemical soil and till from Canadian Certified Reference Materials Project;
- BCR 142-R light sandy soil from Community Bureau of Reference Commission of the European communities.

Table 1 shows a list of the samples.

Table 1. A list of the samples

Sample	Origin
1-4	car parks dusts
5-6	car tyres park dusts
7-9	soils near-by high streets
10-12	soils near-by an industrial zone

RESULTS AND DISCUSSION

VALIDATION OF THE MW-ASSISTED DIGESTION PROCEDURE

The programs followed for the MW-assisted procedure optimisation were performed using CRM BCR 142-R. The variables of the experimental conditions were : the number of steps (3 or 4), the power applied (up to 750 W), the contact

time (up to 30 min), the sample weights (0.5; 1.0 and 1.5 g). In each experiment the acid mixture volume was 10 ml – HCl:HNO₃ = 3:1. The criterion of the applied MW-assisted extraction efficiency was the analytical recovery of each element based on the mean or mediana value for the extractable contents. The relative standard deviations (RSD%) and the combined uncertainties (U_c) were also calculated. The first term is a characteristic of the reproducibility while the second one defines the accuracy of the determinations. The U_c was calculated using the expression⁹:

$$U_c \text{ (mg/kg)} = t(0.95, f) S/n^{1/2}$$

where t is the Student criterion at 95% probability and $f = n-1$ steps of freedom; S –the standard deviation in mg/kg; n –the number of replicate samples digested in the microwave system.

Table 2 shows the results obtained for the final program applied additionally for the CRM NIST-2709 and CRM TILL-2. The program includes 3 heating steps: at 250, 750 and 250 W and one cooling step at 0 W, each step with contact time of 5 min. The recommended weight of the individual samples suitable for 10 ml acid mixture volume is about 1 g.

Based on the data in Table 2, it can be concluded that the results are acceptable, because the general formula¹⁰ (that is a criterion for the assessment of the preparation and measurement procedures trueness) is satisfied:

$$-2U_c < x_m - x_c < +2U_c$$

where x_m is the mean value of replicate measurements (mg/kg); x_c – the certified values (mg/kg).

As an exception, Cu and Pb concentration values obtained for NIST-2709 correspond to the certified total content values. The same was valid for Cu content in BCR 142-R.

RSD values acquired with the application of the final digestion procedure in most cases were lower than 10%. A contribution to the higher RSD values had the atomic absorption measurements and the low concentrations of some elements.

Because uncertainty data for certified values of the extracted with aqua regia elements in NIST-2709 and TILL-2 are not available and the uncertainty data for BSR 142-R include an allowance for systematic error among the different analytical methods used in the laboratories participating in the analysis, a comparative study of the analytical characteristics of both the proposed MW-assisted method and the ISO 11 466 conventional heating digestion method was made. Real soil sample was used for analysis and the results for Cd, Cu, Pb, Zn and Fe are presented in Table 3.

Table 2. Validation of MW-assisted aqua regia digestion

Element	Content (mg/kg)	NIST-2709 ^a	TILL-2 ^b	BCR 142-R ^c
1	2	3	4	5
Fe	certified, %	3(2.5-3.3) (3.5±0.11 total)	3.86(3.20) (3.84 total)	-
	obtained, %	3.3 ± 0.3	3.85 ± 0.26	3.8 ± 0.8
	RSD, %	7.0	5.4	17.1
	R, %	110	100	-
Cd	certified	< 1	< 0.3 (<0.3)	0.25±0.01 (0.34±0.04 total)
	obtained	< 0.3	< 0.3	< 0.3
Co	certified	12(10-15)	15.5 (13)	12.1 ± 0.7 (total)
	obtained	11.2 ± 1.2	11.1 ± 0.9	9.4 ± 1.0
	RSD, %	8.6	6.6	8.7
	R, %	93	72	(78)
Cr	certified	79(60-115)	34.7 (40)	
	obtained	77.5 ± 4.4	33.5 ± 1.8	
	RSD, %	4.6	4.4	
	R, %	97	97	
Cu	certified	32(26-74)(34.6 ± 0.7 total)	176 (149)	69.7 ± 1.3 (total)
	obtained	37.0 ± 0.4	170 ± 17	71.7 ± 1.1
	RSD, %	0.9	8.3	4.4
	R, %	115	97	(108)

to be continued

1	2	3	4	5
Mn	certified obtained RSD, % R, %	470(360-600)(538±17 total) 549±46 6.5 116	588 (530) 699±57 6.6 119	970±16 (total) 846±37 3.5 (81)
Ni	certified obtained RSD, % R, %	78 (65-90) 7.2±2.4 72.5 99	29.5 (31) 26.1±7.0 21.6 88	61.1±1.5 (64.5±2.5 total) 64.7±4.7 5.8 106 (100)
Pb	certified obtained RSD, % R, %	13(12-18) (18.9±0.5 total) 17.0±1.3 6.2 130	31.5 (21) 18.9±8.9 5.5 60	25.7±1.6 (40.2±1.9 total) 25.6±1.7 5.3 100 (64)
Zn	certified obtained RSD, % R, %	100 (87-120) 101±8 6.8 101	112.7 (116) 110±151 1.3 98	93.3±2.7 92.3±0.9 0.9 99

^a Median values (extractable content range) obtained by US EPA 3050 method (HCl + HNO₃); ^b mean values obtained by US EPA 3051 method (extractable contents using conc. HCl + HNO₃); ^c mean values obtained by aqua regia extraction (complete digestion including HF); R - recoveries; RSD - relative standard deviations.

Table 3. Comparative data for MW-assisted and recommended in ISO 11 466 digestion procedures

Element	MW-assisted procedure			ISO 11 466 procedure			F-criterion* calculated		
	mean content (mg/kg) (n=9)	$U_c(0.95)$ (mg/kg)	RSD (%)	DL (μg)	mean content (mg/kg) (n=9)	$U_c(0.95)$ (mg/kg)		RSD (%)	DL (μg)
Cd	1.82 ± 0.21	0.16	11.0	0.6	1.88 ± 0.22	0.20	10.6	0.7	1.13
Cu	117 ± 3	2	2.7	10	128 ± 4	4	3.5	14	1.94
Pb	833 ± 21	16	2.5	64	612 ± 32	30	5.3	97	2.29
Zn (%)	0.62 ± 0.01	0.01	1.6	414	0.55 ± 0.02	0.02	3.6	475	1.32
Fe (%)	7.65 ± 0.15	0.11	2.0	-	4.61 ± 0.24	0.24	5.2	-	2.70

* F - criterion tabular = 3.58.

Stronger aqua regia extraction for Pb, Zn and Fe was observed for MW-assisted procedure in comparison with the standard procedure.

As regard to RSD, values lower than 5% were found for Cu, Pb and Zn and 11.5% in the case of Cd, using MW-assisted method. It was necessary to note that Cd was in very low concentration. Nevertheless the RSD values for the standard method were higher, the differences between RSD of the both methods were not significant. This statement was confirmed using the Fisher criterion for statistical assessment of difference in two dispersions of mean values. The same can be noted for the combined uncertainties calculated.

The limits of detection (DL) based on 3 times the standard deviations of the replicate samples were also calculated and better characteristics for the MW-assisted method were achieved regardless of the greater sample weights used in the standard method.

In conclusion, MW-assisted aqua regia digestion can be considered validated for Cd, Cu, Pb, Zn and Fe determinations in soils. The proposed procedure is also applicable for determinations of Co, Cr, Mn and Ni, because the mean leach contents established for these elements in CRM correspond to the certified values and meet ISO criterion for acceptance. The extraction degree for Cu and Pb (NIST-2709 and BCR 142-R) satisfies the condition for total content assessment.

APPLICATION OF THE VALIDATED METHOD FOR DETERMINATION OF Cd, Cu, Pb, Zn AND Fe CONTENTS IN ENVIRONMENTAL SAMPLES

Figures 1-4 show the results gained for the extractable with aqua regia elements Cd, Cu, Pb and Zn in dust and soil samples from car parks, car tyres park and high streets and for industrial origin samples¹¹. For each sample and each ele-

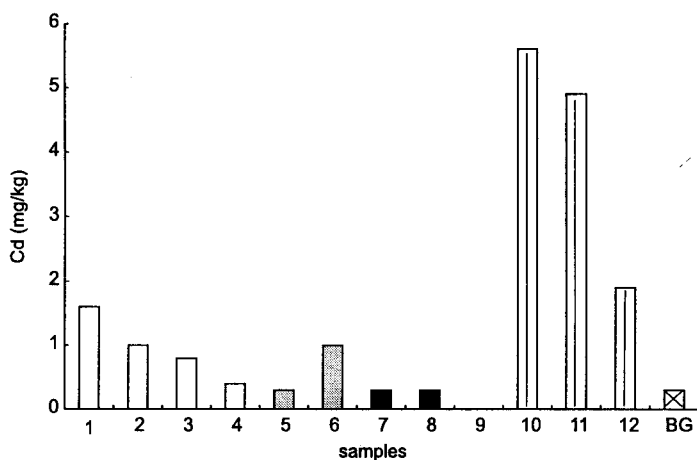


Fig. 1. Comparative data for Cd content in the samples (1-12) and the background sample (BG)

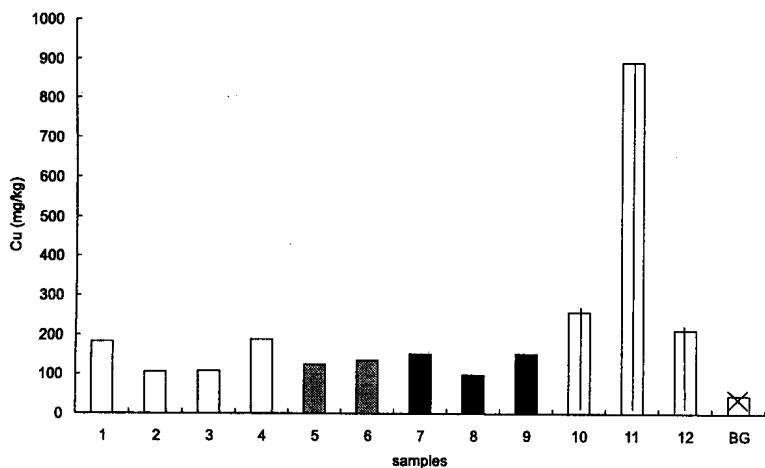


Fig. 2. Comparative data for Cu content in the samples (1-12) and the background sample (BG)

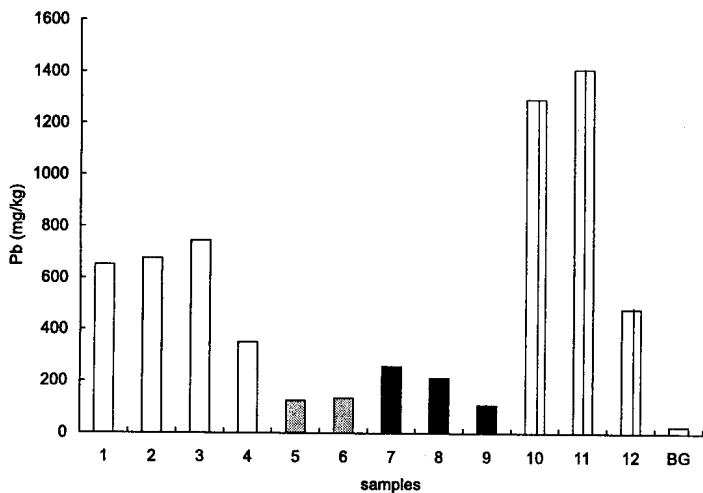


Fig. 3. Comparative data for Pb content in the samples (1-12) and the background sample (BG)

ment the contents determined were compared with those of an agricultural soil. The latter was chosen as a background sample because the content of the elements in it has corresponded to the typical soil content ranges, presented in the literature¹² (with exception of the one for Pb – up to 20 mg/kg typical content and 26 mg/kg in the background sample). As it can be ascertained from Figs 1-4, the levels of all heavy metals in the most cases are much higher than the ones in the reference sample. This is an indication of heavy metal pollution of the areas investigated. The levels of Pb in car park dusts are about 3 times higher

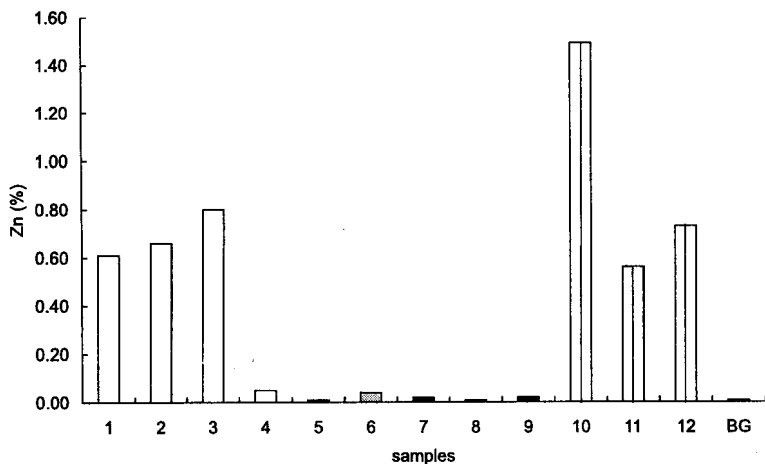


Fig. 4. Comparative data for Zn content in the samples (1-12) and the background sample (BG)

than in car tyres park dusts and in soils near by high streets and 25-28 times higher that in the background sample. The biggest Pb contaminations were got for the industrial origin samples – 18-54 times more in comparison with the reference soil. It is evident, that the investigation of the urban dusts and soils is essential for monitoring the Pb pollution originating from leaded gasoline, industrial and automobile exhausts. The Cu contents obtained by the aqua regia extraction were not so much dependable on the sampling site, but were higher than the one in the background soils well. Again, the highest contamination was stated for the industrial sample area, which indicated that Cu accumulation was mainly due to anthropogenic contributions.

Quite similar was observed for Cd levels: in the car parks samples they exceed 3-5 times the levels in the reference soil and in the industrial zone samples they were 6-19 times greater. The sources of Cd might be motor oils or stack emissions.

The dusts and soils Zn contamination was again different for the different sampling locations. Obviously, the sources of Zn are oil lubricants, fuel combustion and waste disposal from chemical activity.

On the other hand, the degree of modification of the soil chemical composition may be influenced at each location in depending on the different magnitude of a source contribution. In this reason the crustal enrichment factors (EF) for each element and sample were calculated (Table 4). These factors were figured out as a ratio of the concentration of the element determined to the one of iron in the same sample, divided to the same ratio of the elements in the earth's crust¹.

Table 4. The crustal enrichment factors of Cd, Cu, Pb and Zn (content of elements in earth crust in mg/kg: Cd - 0.2; Cu - 55; Pb - 12.5; Zn - 70; Fe - 5.6%)¹

Sample	Enrichment factors				Content of Fe (%)
	Cd	Cu	Pb	Zn	
1	7	3	46	76	6.4
2	7	3	73	126	4.2
3	4	2	58	110	5.8
4	4	7	57	14	2.8
5	2	3	4	2	3.8
6	12	6	7	16	2.2
7	1	5	34	5	3.4
8	1	3	28	3	3.4
9	1	5	3	6	3.4
10	26	4	97	196	6.0
11	27	17	121	85	5.3
12	15	6	59	156	3.7
BG	1	2	6	3	1.9

As it can be seen in Table 4, the higher EF were acquired for Cd, Pb and Zn in the car park dusts and in the soils sampled from industrial zone. In the most cases the EF for Cu were less than 10. These results were strongly dependable on the Fe content determined by using the specific digestion procedure. As the data for the abundance of the elements in the earth's crust correspond to the total content, it is mandatory to assure a complete dissolution of iron compounds in the soil. The results from validation, using CRM NIST-2709 and TILL-2 (Table 2), show that the MW-assisted procedure proposed ensures the condition given above. Soils collected near by the high streets contain a little higher extractable elements (Cd, Cu, Pb and Zn) than those in the reference soil. It was assumed¹ that EF less than 5 may not be considered significant, because such small metal accumulations may arise from some composition difference of the local soil and reference earth's crust.

CONCLUSIONS

As a result of the verification process and the validation for both MW-assisted aqua regia digestion and flame atomic absorption measuring step it was found that the method of analysis assures reliable results. The preliminary assessment of the heavy metals content in the urban dusts and soils shows high level pollution from Cd, Cu, Pb and Zn. The most contaminated samples collected from different sites of Bourgas city are those of industrial origin and from car parks. This investigation shows that the urban dusts and soils may be a source of heavy metals in particulate matter, hence they really represent a potential risk for the human health.

REFERENCES

1. S. TOKALIOGLU, S. KARTAL, G. BIROL: Comparison of Three Sequential Extraction Procedures for Partitioning of Heavy Metals in Car Park Dusts. *J. Environ. Monit.*, **5**, 486 (2003).
2. V. SANDRONI, C. M. M. SMITH, A. DONOVAN: Microwave Digestion of Sediments, Soils and Urban Particulate Matter for Trace Metal Analysis. *Talanta*, **60** (4), 715 (2003).
3. P. AVINO, D. BROCCU, S. PARETI, G. SCALISI: Description of the Carbonaceous Particulate Matter Evolution in an Urban Area. *Annali di chimica*, **93** (1-2), 21 (2003).
4. J. W. MOORE, S. RAMAMOORTHY: Heavy Metals in Natural Waters. Applied Monitoring and Impact Assessment. Springer Verlag, New York Inc., 1984.
5. K. I. MAHAN, T. A. FODERARO, T. L. GARZA, R. M. MARTINEY, G. A. MARONEY, M. TRVISONNO, E. M. WILLGING: Microwave Digestion Techniques in the Sequential Extraction of Ca, Fe, Cr, Mn, Pb and Zn in Sediments. *Anal. Chem.*, **59**, 938 (1987).
6. J. SASTRE, A. SAHUQUILLO, M. VIDAL, G. RAURET: Determination of Cd, Cu, Pb and Zn in Environmental Samples: Microwave-assisted Total Digestion Versus Aqua Regia and Nitric Acid Extraction. *Anal. Chim. Acta*, **462**, 59 (2002).
7. V. CAMEL: Microwave-assisted Solvents Extraction of Environmental Samples. *Trends in Analyt. Chem.*, **19** (4), 229 (2000).
8. Ju. IVANOVA, R. DJINGOVA, S. KORHAMMER, B. MARKERT: On the Microwave Digestion of Soils and Sediments for Determination of Lanthanides and Some Toxic and Essential Elements by Inductively Couple Plasma Source Massspectrometry. *Talanta*, **54**, 567 (2001).
9. Quantifying Uncertainty in Analytical Measurement, EURACHEM, 1999.
10. ISO Guide 33: Uses of Certified Reference Materials, 1989.
11. International Organization: Soil quality. Extraction of Trace Elements Soluble in Aqua Regia. ISO 11466, 1995.
12. H. M. GRIMSHAW, S. E. ALLEN, J. A. PARKINSON: Chemical Analysis of Ecological Materials (Ed. E. Allen). Blackwell Scientific Publications, London, 1989, p.81.

Received 27 April 2004

Revised 15 August 2004