

Trace element determination in contaminated sediments and soils by ultrasonic slurry sampling and Zeeman graphite furnace atomic absorption spectrometry

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Abstract. Ultrasonic suspension of powder samples in combination with graphite furnace atomic absorption spectrometry (GFAAS) has been proven to be a promising method for the analysis of the total content of As, Cd, Cr, Cu, Ni and Pb in sediments and soils. The samples have been ground to a grain size $< 63 \mu\text{m}$. The calibration has been carried out with aqueous solutions of the analytes, with the exception of Cr which requires a calibration with suspensions of a suitable reference sample. The reproducibility has been slightly lower than for measurements obtained with solutions. Advantages are the considerable simplification of the sample preparation and the reduction of blank values. Comparative analyses have shown a good agreement of the results with those obtained by other methods.

Introduction

The analytical determination of environmentally relevant elements in sediments, soils and sewage sludges is mostly carried out with solutions obtained by aqua regia digestion according to DIN 38414. Depending on the type and origin of the sample and the element in question, only parts of the total content are detected. The total content of analytes in many matrices can be determined only by direct methods or the complete analysis of a totally dissolved sample; analytical interferences are often caused by increased contents of organic matter, blank values, or the loss of elements.

The components of sediments, soils and sewage sludges mostly have small grain sizes or are easily comminuted and transformed into aqueous suspension. However, there is also a clear correlation between the contents of trace elements evaluated and the grain size so that special attention has to be paid to the preparation and preservation of the sample to keep their representativeness. Careful comminution and homogenization of

such samples presupposed the above materials are expected to be very suitable to produce slurry suspensions well suited for sample dosing. In combination with the highly sensitive GFAAS, this offers an alternative method for the determination of the total contents of trace elements in environmental materials.

Based on recent experiences on coal and fly ashes [1–3] as well as sediments and environmental samples [4–6], the potential of slurry sampling in combination with GFAAS was preferably studied for the elements As, Cd, Cu, Pb, Cr and Ni, due to their environmental relevance and their different thermal behaviour.

Experimental

Equipment. The investigations were carried out with an atomic absorption spectrometer 4100 ZL (Perkin Elmer) with a transversely heated graphite tube and background correction by longitudinal Zeeman effect, an autosampler AS-70 and the slurry sampler USS-100 [7]. Operation parameters are listed in Table 1.

Sample preparation. Preliminary investigations had shown that a suspension both visually “homogeneous” and stable over the whole time of measurement can be produced only with samples with grain sizes $< 63 \mu\text{m}$. A further reduction of the grain size to $< 30 \mu\text{m}$ does not lead to any significant improvement in the sensitivity and reproducibility in spite of a markedly higher time requirement.

Therefore, both the samples to be analyzed and the standard reference samples (Table 2) used for calibration and control were ground to a particle size $< 63 \mu\text{m}$ with a mortar mill.

Due to the sometimes very high elemental concentrations in the strongly contaminated samples, a direct introduction into the containers of the autosampler was often not possible. A suspension suitable for the working range can be produced by selecting a representative amount.

A defined amount (5–100 mg depending on the element concentration) was weighed, intensively shaken by hand for approximately 1 min with 50 ml of a mixed

Table 1. Measurement conditions

Element	As	Cd	Cu	Cr	Ni	Pb
Wavelength (nm)	193.7	228.8	324.8	357.9	232.0	283.3
Lightsource	HCL					
USS-100						
mixing time (s)	45	45	45	45	45	45
level of agitation	25	25	25	25	25	25
Furnace	transverse heated pyrolytically coated graphit tube with integrated platform					
gas	Ar					
ash (°C)	700	350	900	1100	1000	900
atomize (°C)	2100	1700	2100	2200	2100	2000
clean (°C)	2600	2600	2600	2600	2600	2600
matrix modifier	Pd/Mg(NO ₃) ₂		Mg(NO ₃) ₂		Pd/Mg(NO ₃) ₂	
sample volume	5–20 µl					
Calibration range	10–100 µg/l	0.1–1.5 µg/l	1–50 µg/l	1–50 µg/l	1–50 µg/l	1–60 µg/l

Table 2. Concentration and confidence intervals for references samples

Reference sample	Content	Reference	As (µg/g)	Cd (µg/g)	Cu (µg/g)	Cr (µg/g)	Ni (µg/g)	Pb (µg/g)
River sediment CRM BCR 320	total content	9	76.7 ± 3.4	0.53 ± 0.026	44.1 ± 1	138 ± 7	75.2 ± 1.4	42.3 ± 1.6
	aqua regia soluble	9		0.47 ± 0.06	42 ± 2.68	70.1 ± 7.86	55 ± 4.68	30 ± 2.4
"Braunerde" BAF BHA-1 ^b	total content		[200] ^a	6.83 ± 0.19	53.8 ± 6.0	87.8 ± 15.0	21.4 ± 3.5	479 ± 25.9
	aqua regia soluble		162 ± 68.8	6.2 ± 2.46	48.3 ± 6.48	69.7 ± 10.9	15.8 ± 12.58	442 ± 60.4
Soil IAEA soil 7	total content	10	13.4 ± 0.9		11 ± 2	60 ± 14–1		60 ± 6
Basalt BCR 1	total content	8	0.64 ± 0.14	0.127 ± 0.008	19 ± 4	16 ± 4	13 ± 4	13.6 ± 0.03

^a [] = result of 1 laboratory

^b BAF BHA-1: not certified standard of the Institute of Mineralogie, TU BAF, results of a ring analysis (9 laboratories)

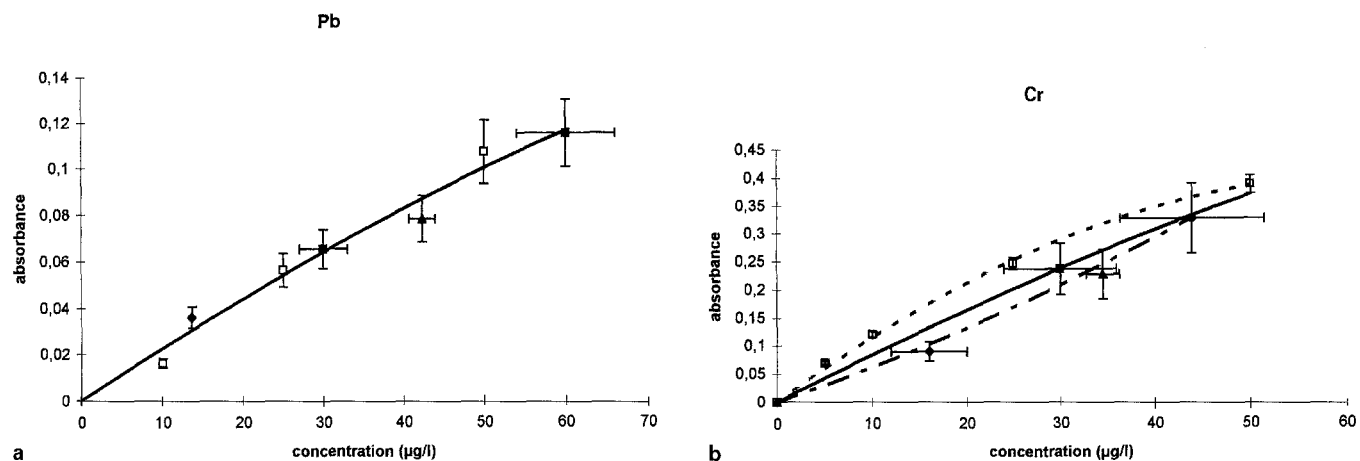


Fig. 1a, b. Calibration functions of **a** Pb and **b** Cr. □ solution standard, ■ soil "soil 7", ◆ basalt "BCR 1", ● Braunerde "BAF-BHA-1", ▲ riversediment "BCR CRM 320", I confidence range of absorbance ($n = 3$), - - - solutions, - · - · - suspensions, — solutions and suspension, |—| confidence range of reference sample ($P = 95\%$)

solution of diluted nitric acid (pH 2) and 1 droplet of wetting agent in a suitable container (e.g. a 100-ml flask), and then immediately filled into the containers (1 ml) of the autosampler.

The homogeneity of these suspensions allows to carry out repeated measurements with the same suspension so that no additional time is needed for a repeated weighing.

Calibration. The calibration was performed by both synthetic standard solutions and suspensions of reference

samples prepared as described above. The synthetic standard solutions were diluted with the same mixed solution as the suspensions.

Table 2 lists the certified and/or recommended concentrations and confidence intervals of the reference samples.

The conditions for AAS measurements (see Table 1) were evaluated in preceding tests. Conditions producing a common function for the two calibration methods were preferred. In Fig. 1 the calibration functions of Pb and Cr are shown exemplarily.

Table 3. Homogeneity test for suspensions of different grain sizes, element Cu (sediment sample from the river Zwickauer Mulde)

Sample preparation	Cup-number	\bar{x} (n = 4) [$\mu\text{g/g}$]	RSD
30 μm suspension	1	181	6.49
	2	178	5.16
	3	175	4.32
	4	183	4.08
30 μm suspension	total procedure	179	4.74
63 μm suspension	5	181	3.24
	6	182	2.66
	7	181	4.16
	8	181	3.69
63 μm suspension	total procedure	181	3.13
Digestion	total procedure	187	5.57

Results

Values obtained with the suspension demonstrate a satisfactory reproducibility of this procedure. Table 3 lists the mean values and standard deviations for Cu of repeated measurements of one container and the complete procedure of four containers with one suspension prepared with a sediment sample of a particle size < 30 μm (container No. 1–4) and < 63 μm (No. 5–8). The standard deviations for repeated measurements of one container are comparable with the standard deviation of the complete procedure.

The total content of Cu in the sample is indicated for comparison.

The calibration functions for solutions and suspension obtained for As, Cd, Cu, Pb and Ni do not show any systematic differences between both calibration types. In some cases slight deviations were observed from the linearity in the investigated concentration ranges. The use of a Pd/Mg(NO₃)₂ matrix modifier was necessary in the case of As and Pb. No evaluable peaks were obtained for Pb employing the phosphate modifier, which is frequently used for liquids.

Marked differences between the calibration functions for solutions and suspensions were observed only for Cr so that the calibration with suspension and modifier has to be used for this element. Based on these results a combined calibration with suspensions of reference samples and synthetic standard solutions is used for the elements As, Cd, Cu, Ni and Pb. The calibration of Cr is performed only with suspensions of reference samples. The most pronounced increase of the relative standard deviation was found for Cr (Table 4). These results can be related to the solubility of the elements in acidic suspensions (pH 2). In the given case of the analysis of a polluted river sediment, Cr was dissolved at 26%, Cu at 62%, Pb at 62%, Ni at 63%, As at 79% and Cd at 82%. The deviation of As from the trend between standard deviation and solubility is due to its concentration close to the detection limit which leads to a poorer reproducibility. Epstein [5] has indicated this relationship between the proportion dissolved in the suspension and the reproducibility.

No general influence of the different matrices (sediment, soil, basalt) on the absorption signals was found. Larger deviations are possible for very high solid contents in the suspensions, which may become necessary for very low concentrations while staying in the selected calibration range (e.g. Cr in Basalt BCR, Cu in Soil 7).

The recovery for the addition of a standard solution to the suspensions was $100 \pm 10\%$. A second homogenization by ultrasonic is necessary, if a standard suspension is added, otherwise low results (70–80% recovery) will be registered.

Apart from the analysis of certified samples, a comparison with other methods and the results of ring analyses was carried out to check the accuracy of the obtained results.

Table 5 compares the results for a river sediment obtained by slurry sampling with results obtained by the analysis of a solution of the complete digested sample as well as results of a ring analysis based on dissolution in aqua regia. The results of slurry sampling and total sample digestion show an acceptable agreement. As expected, however, differences were revealed in comparison with the results obtained from the digestion in aqua regia;

Table 4. Standard deviation of AAS values (n = 10) of the suspension of a sediment sample (river Zwickauer Mulde) and a synthetic solution obtained by the slurry system

Sample	As		Cd		Cu		Cr		Ni		Pb	
	conc. ($\mu\text{g/l}$)	RSD	conc. ($\mu\text{g/l}$)	RSD	conc. ($\mu\text{g/l}$)	RSD	conc. ($\mu\text{g/l}$)	RSD	conc. ($\mu\text{g/l}$)	RSD	conc. ($\mu\text{g/l}$)	RSD
Suspension	11.2	13.6	0.75	2.21	31.1	2.88	13.3	4.5	16.7	3.92	26.5	4.24
Synthetic solution	50	3.6	0.5	1.51	10	2.47	20	0.91	10	2.91	50	3.57

Table 5. Comparison of results obtained by different methods (sample: sediment from storage reservoir Glauchau)

Sample preparation/measurement	n	As ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Pg ($\mu\text{g/g}$)
Suspension/Slurry System-AAS	4	87	11.9	241	99	130	205
Total digestion/Slurry System-AAS	6		10.7	240	96	115	200
Aqua regia digestion/ring analysis	28–40	91.1	11.1	232	65.4	86.8	174

these were smallest for elements best soluble in the acidic suspensions.

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