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The influence of pyrolysis and matrix modifiers on determination of Cr and Pb in sediment samples by GFAAS

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Abstract: The Influence of pyrolysis and matrix modifiers on determination of Cr and Pb in sediment samples using graphite furnace atomic absorption spectrometry has been investigated. The sediment samples including three certified reference materials (CRMs) are reported. Analyses were performed using microwave assisted dissolution. The matrix modifiers $Mg(NO_3)_2$, $Pd+Mg(NO_3)_2$ and $NH_4H_2PO_4$were shown to be optimazed. The recovery for Cr and Pb in CRMs in the case of sample dissolution was found to be between 81 to 91% for Cr and 94 to 98% for Pb of the certified values, respectively.

Keywords: Sediment, Pyrolysis, Matrix modifiers, Cr, Pb

Abstrak (Indonesian): Pengaruh pirolisis dan matriks pengubah pada penentuan Cr dan Pb dalam sampel sedimen menggunakan tungku grafit spektroskopi serapan atom telah diteliti. Sampel sedimen termasuk tiga bahan referensi bersertifikat (CRMs) dilaporkan dianalisis dengan menggunakan bantuan microwave ekstraktor. Matriks pengubah $Mg(NO_3)_2$, $Pd+Mg(NO_3)_2$ dan $NH_4H_2PO_4$ telah digunakan dan menghasilkan nilai temu balik untuk Cr dan Pb dalam CRMs ditemukan antara 81-91% untuk Cr dan 94-98 % untuk Pb dari nilai sertifikat masing-masing.

Katakunci: Sedimen, Pirolisis, Matrix modifiers, Cr, Pb

1. Introduction

Sediment are normally the final pathway of both natural and anthropogenic components produced or derived to the environment. Sediments form in water bodies as a result of the gravitational settling of suspended matter. In fast flowing rivers, small particles may remain suspended, while in still waters, most suspended particles will settle to the bottom. Sediment quality is a good indicator of pollution in water column, where it tends to concentrate the heavy metals and other organic pollutants [1].

As sedimentation is a continuous process, analysis of sediment cores can provide a historical record of the chemical composition of suspended particles. Since these particles originated at the surface of the water body, sediment cores can reveal chemical changes that have occurred in the environment in the past. The depth of the sediment core is proportional to time going back from the present. Toxic substances may accumulate in sediments. The analysis of environmental samples is very important to investigate the presence of contaminants and toxic elements [2,3].

Some heavy metals are pollutants with harmful influences on natural ecosystems and human health (e.g. Hg, Cd, Cr, Pb), while others are essential nutrients (e.g. Zn, Fe, Cu, Co, Mo). Various methods can be used to determine the metals in environmental samples, but often are prone to interferences. In analyses by AAS spectral interferences e.g. may occur. This type of interference may sometimes be reduced by narrowing the slit width [4]. Furthermore, physical matrix influences, resulting from variations of physical characteristics of the sample such as particle size, uniformity, homogeneity, surface condition and moisture content may influence the accuracy of the determinations.

Accurate determinations accordingly are not an easy task. Indeed, apart from interferences during the measurements, risks of sample contamination, losses of the analyte, and the presence of substances which are difficult to be dissolved among others, should be carefully considered in the preparation of the samples [5,6].

The present work aimed to investigate the pollutants levels including the accumulation of some heavy metals

Cromium and Lead in sediments samples and certified reference materials (CRMs). The optimization of the analytical lines, matrix modifier and pirolysis will be shown to be useful so as to optimize the analytical accuracy in the case of real samples.

2. Experimental Sections

2.1. Instrumentation

The analytical studies were performed with the HR-CS GFAAS series ContrAA 700 (Analytik Jena, Jena, Germany). The instrument is equipped with a xenon short-arc lamp with UV arc in hot-spot mode. High-purity inner gas Argon 5.0 was used. A CEM MARS 5 microwave assisted digestion system from CEM Corporation (Matthews, NC, USA) and a shaker machine 2400 rpm (Heidolph, Germany) were used as well.

2.2. Reagents and samples

All chemical reagents used were of analytical grade. HNO_3 and HCl from Merck, Germany were used for the preparation of the calibration solutions and for the sample pretreatment. Bi-distilled water was further purified by sub-boiling distillation in a quartz still. Calibration solutions were prepared from standard solutions of 1000 mg L^{-1} of Cr and Pb from Merck, Germany. Chemical modifier solution was prepared from a 10 g L^{-1} as $Pd(NO_3)_2$ and a 10 g L^{-1} $Mg(NO_3)_2$ solution (Merck, Germany), which were diluted in 0.2 % (v/v) HNO_3 so as to obtain a solution with 10 µg of $Mg(NO_3)_2$ and 15 µg of Pd as $Pd(NO_3)_2$ in 10 µL of modifier solution.

The sediment certified reference materials (CRMs) used were: IMEP-14 (International Measurement Evaluation Programme, European Commission, Joint Research Centre (JRC), Institute for Reference Materials and Measurements (IRMM), Retieseweg, Geel, Belgium), CRM-320 (Trace Elements in River Sediment, Community Bureau of Reference, Geel, Belgium), and PACS-1 (Marine Sediment Reference Material for Metals and Other Constituents, National Research Council, Ottawa, Canada). Two SETOC sediment samples F1026 and F2159 from WEPAL (Wageningen Evaluating Programs for Analytical Laboratories) Wageningen, Netherlands were used as real samples.

2.3. Sample dissolution using microwave digestion

All sediment samples were digested using the microwave assisted digestion system CEM MARS 5 (Matthews, NC, USA) microwave assisted digestion system operated according to the instruction manual and safety precautions. As acid digestion reagents distilled ultrapure grade HNO_3 and HCl (Merck, Germany) were used. All CRMs and SETOC sediment samples were dried in an oven at 110 ºC for 5 h prior to weigh accurately an amount of 500 mg. The digestion process was performed in closed vessels using a mixture of $HCl:HNO_3$ (3:1) with a total volume 16 mL. The microwave digestion program shown in Table 1 was applied for sample preparation and after completion of the digestion program, the samples were filtered and diluted to 50 mL with be-distilled water. All samples were prepared in duplo and measurements for the relevant metals were made with HR-CS GFAAS under the optimum conditions with three replications. In the case of the dissolved samples an auto sampler Micropipettor unit MPE 60 was used.

Table 1. Microwave digestion program

Step	Power	Time (min.)	P (Bar)	Temp. (ºC)	Hold (min.)
1	600	30	10:00	150	10
2	600	30	15:00	175	10
3	600	30	20:00	200	10

3. Result and Discussion

3.1. Optimization

Selection of analytical lines

The ContrAA 700 has a detector with 588 pixels and 200 of those pixels are used for analytical line measurements while the rest are used for internal correction [7]. The spectral lines used for the elements Cr and Pb have to be selected in view of the samples.

The 357.9 nm line of Cr was selected due to its high is suitable for determinations of Cr by HR-CS GFAAS with in the case of aqueous solutions. For the determination of Pb, in the samples analyzed by HR-CS GFAAS the Pb 217.0 nm line was found to be too sensitive and the Pb 283.306 nm was used. It has a sensitivity which is 40% of the one of the other line in HR-CS GFAAS and gives a very good signal for the dissolved samples. The lines of analysis used are also listed in Table 2.

Table 2. Optimized operating parameters for analysis of CRMs & SETOC samples by HR-CS GFAAS

Parameters	Elements	
	Cr	Pb
Instrumental		
λ (nm)	357.868	283.306
Heating program		
Pyrolysis		
Temperature (ºC)	350/1300	350/800
Ramp (ºC s^{-1})	50/300	50/300
Hold (s)	20/10	20/10
Atomization		
Temperature (ºC)	2300	1500
Ramp (ºC s^{-1})	1500	1500
Hold (s)	4	4
Modifier	$Mg(NO_3)_2$	$Pd+Mg(NO_3)_2$, $NH_4H_2PO_4$
Linear range (µg)	0.5-6.0	5.0-40

Selection of modifiers and optimization of temperature program

To avoid any loss of analyte during pyrolysis a modifiers were used for analyte stabilization. Three modifiers were tested: 10 µg of Pd and a mixture of 10 µg of Pd+10 µg of $Mg(NO_3)_2$, and $NH_4H_2PO_4$ for Pb. The amount of $Mg(NO_3)_2$ was optimized for Cr, but it was found that no significant differences for Pb was occurred. The Pd modifier was found to lead to a high signal for Pb. The pyrolysis and atomization curves in the presence of both modifiers were recorded. The pyrolysis and atomization temperatures are different for the elements considered. The drying program before the pyrolysis for all was the same (Cr and Pb). The pyrolysis begins at 350 °C and the temperature is increased gradually according to the ramp and time program. When the atomization step starts the temperature is rapidly increased and held until the atomization is complete. After the atomization step is completed, the furnace temperature is kept high during a cleaning step so as to clean the tube from the remains of the sample that potentially could interfere with the subsequent measurement [8,9].

3.2. Analytical figures of merit

The determination limits for the method showed in HR-CS GFAAS in the case of solution and based on 3σ of the blank are listed in Table 3 as are the absolute detection limits of solution samples. The measurement results for the CRMs and SETOC samples by HR-CS GFAAS with dissolved samples generally were in good agreement to the certified values of Cr and Pb. For the CRMs the recoveries for all analytes were above 81%,

Table 3. LODs for dissolution of sediment samples by HR-CS GFAAS

Element	Limits of detection	
	($\mu g\ L^{-1}$)*	($\mu g\ g^{-1}$)
Cr	0.06	60
Pb	0.008	8

With respect to the analyte concentrations in the samples to be analyzed the sample concentrations in the analysis solution had to be different from one element to another. After this optimization the LODs for work with solutions. The LOD of Cr are higher than for Pb by a factor of 1 to 7, respectively.

Determination of Cr and Pb in solution by HR-CS GFAAS made use of calibration by standard addition with aqueous standard solutions and Pd/$Mg(NO_3)_2$ was used as matrix modifier. As shown in Table 4 all analytes could be determinate with the optimum element wavelength.

The measurement results of sediments for the CRMs and SETOC samples by HR-CS GFAAS with dissolved samples, generally the concentration of Cr and Pb were in good agreement to the certified value of the CRMs in recovery. For all analytes were 81% to 98% recovery. The IMEP-14 and CRM-320 sediment samples are representing certified sediment or soil from rive's or natural water and the PACS-1 is representing marine sediment. From the analysis results, the use of pyrolisis program and $Mg(NO_3)_2$, Pd+$Mg(NO_3)_2$, $NH_4H_2PO_4$ as matrix modifier are able to produce analytical results for all analytes in the CRM were about 81% to 98% recovery. Base on the percent recovery of an analytical method, a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known or certified value, in this case the results obtained were in the range of 81 to 98 % recovery, and it can be concluded that the analysis results for Cr concentration in F1026 and F2159 of SETOC's sediment samples were 103±6 mg/kg and 94.0±0.8 mg/kg, respectively. Meanwhile the Pb concentration were 386±10 mg/kg and 116±3.6 mg/kg, respectively. The introduction of HR-CS GFAAS appears to open attractive features for sediment samples because of the significantly simplified optimization of furnace programs and the visibility of the spectral environment, which makes it easy to control spectral interferences.

Table 4. Measurement results of sediment samples by dissolution samples HR-CS GFAAS

Samples	Elements	Certified value	HR-CS GFAAS	
			Results	% rec.
IMEP-14	Cr (mg/kg)	57,4±1.6	47.8±1.6	83
	Pb (mg/kg)	87.25±1.7	82.0±3.2	94
CRM-320	Cr mg/kg)	138±7	112±8	81
	Pb mg/kg)	42.3±1.6	41.5±1.4	98
PACS-1	Cr mg/kg)	113±8	103±2	91
	Pb mg/kg)	404±20	385±2	95
F1026	Cr (mg/kg)		103±6	
	Pb (mg/kg)		386±10	
F2159	Cr (mg/kg)		94.0±0.8	
	Pb (mg/kg)		116±3.6	

4. Conclusions

The determine of heavy metal in sedemint samples using dissolution method using the microwave assisted digestion system continued analysis of Cr and Pb by HR-CS GFAAS could be shown to generally improve the recovery with respect to the certified values. The pyrolysis program and matrix modifiers (e.q. $Mg(NO_3)_2$, Pd+$Mg(NO_3)_2$ and $NH_4H_2PO_4$) were enables to overcome the interferences from samples matrix.

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