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Aspects concerning the heavy metal analysis in samples with difficult matrix

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Abstract. The determination of the metals content in highly loaded samples with complex matrix is always difficult because of interferences affecting the results of the analysis. The present study was worked out on soil samples from steel loading berths, the metal content being determined using the FAAS technique. This type of samples is very rich in Fe, Si and Al, but it also contains heavy metals in low concentrations (Cr and Ni). Because of the presence of Si in the samples, the use of HF at digestion is compulsory; it proved to be benefic for the digestion of soil samples, in general, since the metal content was found higher in samples treated with HNO_3+HCl+HF, comparing with those treated with HNO_3+HCl in the standard method, due to the complete digestion of the sample. The heavy metals Ni and Cr were determined at concentrations close to the detection limit. Making-up a matrix with 0.2 g/L Fe and 0.02 g/L Si and 0.002 g/L Al for the standard curves of minor elements (Ni, Cr), the influence of major elements (Fe, Si, Al) on the analysis result was investigated. Also, the determination of minor elements Cr and Ni was checked by addition of 0.2 g/L of each metal to the samples, so that the concentration would be found in the middle concentration range of standard curves. The conclusions of the study confirm the modifications proposed to the standard method applied to the soil samples proceeding from steel loading berths.

Keywords: soil, heavy metals, acid digestion, FAAS

1. Introduction

The soil contains naturally some metals. The major metals in soil consists on Fe, Al and Si in compunds as iron oxides, alumina and silica[1, 2]. The usual background concentration in soils are: 48-180 mg Al/kg, 11-240 mg Fe/kg and 0.8-67 mg Si/kg. The anthropogenic activities can cause increasing of metal level in soil and more important, can lead to the pollution of soil with heavy metals.

In the recent years, a lot of research work was done for studying the distribution of heavy metals in the industrial and urban environment, drawing map with metal polution in certain areas, identifying the anthropic contributions, identifying possible sources of polution [3, 4, 5].

Because of the complexity of soil matrix, some of research aimed to find new methodes and procedures for the determination of major or minor metal elements in the soil [2, 6, 7]. Most of the works insist on the digestion method but also there were trials to find new secondary wavelength lines additional to those already known for the determination of some metals [6].

The present work has as the goal to improve the procedure for metal determination in soil samples highly loaded with metals proceeding from steel loading berths. The operators of such berths have to check the quality of the soil from time to time and take action if pollution was found. So, a reliable method for the determination of metal concentration level would be useful in this case.

2. Experimental

There were analyzed four replicas of the same sample of topsoil collected from a steel loading berth. The major elements to be analyzed were: Fe, Al and Si and it was expected to have also heavy metals as minor elements, since these elements

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appear in the composition of steel loaded in this berth. Preliminary trials proved that the heavy metals present in the sample were only Ni and Cr.

The metals content was studied on a Flame Atomic Absorption Spectrometer, ZeeNit apparatus, Analytic Jena.

The authors adapted two methods from the American standards, considering them more appropriate to this study than the existing national standard SR EN 13346/2002 [8]:

- EPA Method 3051 - Microwave assisted acid digestion of sediments, sludges, soils, and oils
- EPA Method 3052 - microwave assisted acid digestion of siliceous and organically based matrices

A representative sample of up to 0.5 g is digested in a certain combination of acids for 15 minutes using microwave heating with a suitable laboratory microwave system. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions reaching 180 ± 5 ºC in approximately less than 5.5 minutes and remaining at 180 ± 5 ºC for 9.5 minutes for the completion of specific reactions. After cooling, the vessel content is allowed to settle and then decanted, diluted to volume (100 mL), and analyzed by FAAS method. The wavelength, detection limit and concentration range are shown in Table 1.

Table 1. Specific conditions for the determination of metals by FAAS method

Element	λ[nm]	Detection limit [mg/L]	Concentration range [mg/L]
Iron	248.3	0.02	0.4 -4
Aluminium	309.3	0.1	3-30
Silicon	251.6	0.1	6 - 60
Chromium	357.9	0.005	0.3 -3
Nickel	232	0.005	0.3 -3

There were trials for the mineralization of the samples with two combinations of acids, comparatively: 2mL HF+2mL HNO_3+6mL HCl and 9 mL HNO_3+3 mL HCL. These trials were made in order to find a better combination ensuring the complete mineralization of the sample.

The make-up of a matrix containing the major elements was investigated in order to observe their influence at the determination of minor elements' concentration. So, the standard curves of Ni and Cr were drawn for water background comparatively with a make-up solution containing 0.2 mg/L Fe+0.02 mg/L Si + 0.002 mg/L Al.

Also, the determination of minor elements Cr and Ni was checked by addition of 0.2 mg/L of each metal to the solution samples, so the concentration would be found in the concentration range of standard curves.

3. Results and Discussions

The effect of acid combination used to mineralize the soil samples is shown in Table 2. As one can see, the digestion in 2mL HF+2mL HNO_3+6mL HCl leads to concentrations higher for each major element, without exception, comparing with the digestion in 9 mL HNO_3+3 mL HCl. For Si the difference is even greater since the Si can't be mineralized properly in absence of HF. The soil samples from steel loading berths would be digested in a mixture of acids: 2mL HF+2mL HNO_3+6mL HCl, in a microwave system, for the complete dissolution of mineral and organic matter.

Taking into account the major elements, a matrix was made-up for standard curves of Ni and Cr, containing 0.2 mg/L Fe+0.02 mg/L Si + 0.002 mg/L Al. The proportion of the metals in the matrix was in respect of these metals' content in the samples. The signal was compared for the standard curves with matrix and for water as background. Also, the mineralization of the samples was made with both the combination of acids. The results are shown in Table 3. It can be observed the same effect of the acid mixture used to mineralization of samples as it was in case of major elements: the use of HF leads to higher concentration of metals being determined. Speaking of the matrix effect, it was observed a decreasing of the signal when using matrix instead of water but only in case of HF+HNO_3+ HCl use at mineralization.

It was a different situation when the mineralization was performed with HNO_3 and HCl: an increase of the signal was observed when using matrix comparing with water as background.

Table 2. The influence of the acid mixture used at the mineralization of the samples on the major elements determnation

	Sample	Digestion in 2mL HF+2mL HNO_3+6mL HCl **[mg/kg d.m]**	Digestion in 9 mL HNO_3+3 mL HCl **[mg/kg d.m]**
Fe	1	349334	248182
	2	339830	266907
	3	361341	287716
	4	345072	302542
	Sample	Digestion in 2mL HF+2mL HNO_3+6mL HCl **[mg/kg d.m]**	Digestion in 9 mL HNO_3+3 mL HCl **[mg/kg d.m]**
Si	1	52760	688
	2	48091	4339
	3	30656	2638
	4	37787	701
	Sample	Digestion in 2mL HF+2mL HNO_3+6mL HCl **[mg/kg d.m]**	Digestion in 9 mL HNO_3+3 mL HCl **[mg/kg d.m]**
Al	1	15425	9971
	2	15367	9887
	3	16085	10679
	4	15516	9762

Table 3. The effect of acid digestion and of the matrix on minor elements determination

	Sample no.	Digestion in 2mL HF+2mL HNO_3+6mL HCl **[mg/kg d.m]**		Digestion in 9 mL HNO_3+3 mL HCl **[mg/kg d.m]**	
		a	b	a	b
Ni	1	36.47	13.3	25.25	19.5
	2	29.66	11.16	24.98	44.3
	3	24.36	23.6	27.20	52.4
	4	36.38	32.6	6.14	13.9
	Sample no.	Digestion in 2mL HF+2mL HNO_3+6mL HCl **[mg/kg d.m]**		Digestion in 9 mL HNO_3+3 mL HCl **[mg/kg d.m]**	
		a	b	a	b
Cr	1	27.8	25.69	17.8	31.43
	2	42.2	31.63	17.2	61.94
	3	32.3	46.67	18	57.24

Note: a) standard curve using water as background
b) standard curve using solution 0.2 mg/L Fe+0.02 mg/L Si + 0.002 mg/L A as matrix

Ni and Cr were determined close to the lower detection limit. Expecting the results to be affected by this, we checked by addition of 0.2 g/L of each metal to the samples, so that the concentration would be found in the middle of the standard curves. The results are shown in Table 4. Also, the same 0.2 g/L of each metal (Ni and Cr) was added to the matrix made-up of major elements (Fe, Al, Si) and the signal was compared with zero Ni and Cr in the matrix. As one can see, the effect is obvious and the added quantity can be recovered in the final result of the analysis.

Table 4. Ni and Cr determination

	Sample no.	Digestion with 2mL HF+2mL HNO_3+6mL HCl **[mg/L]**	
		Without addition	With addition 0.2
Cr	1	0.06376	0.2974
	2	0.07448	0.3056
	3	0.06749	0.3087
	4	0.07798	0.3301
	Matrix	0.06600	0.2695
	Sample no.	Digestion with 2mL HF+2mL HNO_3+6mL HCl **[mg/L]**	
		Without addition	With addition 0.2 mg/L
Ni	1	0.03229	0.2691
	2	0.02637	0.2789
	3	0.03425	0.2436
	4	0.08367	0.2895
	Matrix	-0.00840	0.1762

4. Conclusions

Following the study of metal analysis in soil samples from steel loading berths, the conclusions were:

- The analyzed samples contain three major elements: Fe, Si, Al and two minor heavy metals, at the lower detection limit of FAAS method: Ni and Cr.
- For the complete dissolution of mineral and organic matter, soil samples from steel loading berths would be digested in a mixture of acids: 2mL HF+2mL HNO_3+6mL HCl, in a microwave system.
- The make-up of a matrix containing the major elements in concentration: 0.2 g/L Fe+0.02 g/L Si + 0.002 g/L Al, proved to be inconclusive.
- The addition of Ni and Cr in solution (20 mg/L each) brings the concentration in the middle of the standard curves, so the results are expected to be more accurate; in the present samples the concentration of Ni and Cr was below the accepted limit in soil even for sensitive areas.

5. References

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[1]. P. Asokan, M. Saxena and Sh. R. Asolekar, Resources, Conservation and Recycling, **43**, 239-262 (2005)

[2]. P. Torres, E. Ballesteros and M. D.Luque de Castro, Anal. Chim. Acta, **308** (1-3), 371-377 (1995)

[3]. S. D. Manta, M. Angelone, A. Bellanca, R. Neri, and M. Sprovieri, The Science of the Total Environment, **300** (1-3), 229-243 (2002)

[4]. N. Vdovic, G. Billon, C. Gabelle, and J-L Potdevin, Environmental Pollution, **141**, 359-369 (2005)

[5]. K. Ljung, O. Selimes and E. Otabbong, Science of the Total Environment, **366**, 749-759(2006)

[6]. J. L. Raposo Jr., S. R. Oliveira, N.M. Caldas and J. A. Gomes Neto, Anal. Chim. Acta , **672** (2), 198-202 (2008)

[7]. B. Marin, E.I.B. Chopin, B. Jupinet and D. Gauthier, Talanta, **77** (1), 282-288 (2008)

[8]. *** SR EN 13346/2002 Sludge characterisation. . The determination of phosphorus and trace elements. Methods of extraction in aqua regia (in Romanian).