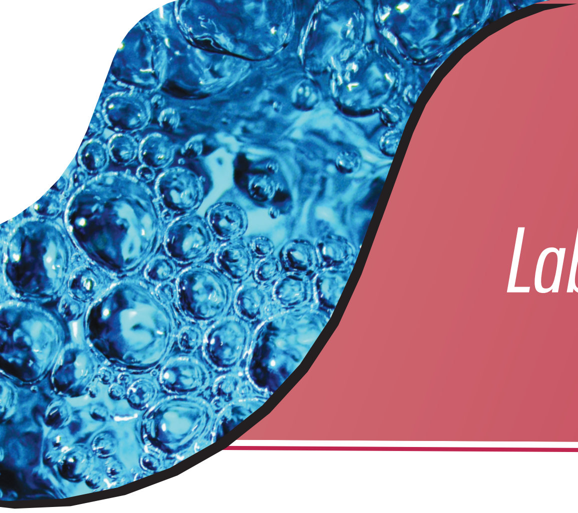

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Fast Multi-element Analysis of Heavy Metals in Soil and Sediment Samples

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Many dangerous heavy metals accumulate in the soil and sediments of our rivers, lakes and oceans if released into the environment either directly discharged by industrial plants and municipal sewage treatment plants or come from polluted agricultural areas or as a result of historical contamination. Since all these heavy metals can go into the water, the earth and the air and thus into the food chain, a proper disposal, recycling and the regulation of the application of sewage to agricultural land gain great importance. Nonetheless, not all the traces of heavy metals in soils, sediments and plants are actually the results of human activity. Some arise through absorption processes of naturally occurring soil components. Theoretically, every 1000kg of 'normal' soil contains for instance 80g nickel, 16g lead and 0.2g cadmium [1]. Therefore, it is not always easy to assign a definite cause for increased heavy metal content. Even foodstuffs produced in completely unpolluted areas are not entirely free of heavy metals. Hence, monitoring the soil and sediment especially in respect of heavy metals is of interest due to their influence on groundwater, on plants and also animals and human beings. However, the heavy metals only became a focus of public interest just after the analytical techniques had made it possible to detect them even in very small traces. The relatively uncontrolled handling of heavy metals and their compounds in the past can to a degree be explained by the fact that their effects were unknown. Today however analytical detection is possible down to very low levels. In this study a quick as well as a simple technique with great advantages will be discussed for the determination of Cd, Cu, Fe, Pb, Mn, Ni, and Zn in several soil and sediment samples collected around Thuringia Saale, Germany. The performance of the method was assessed with evaluation of standard reference material and sample spikes.

Experimental

Digestion of soil samples is performed according to EPA Method 3051A and EPA Method 3052 using the microwave digestion system, TOPwave [2,3]. The accuracy of the analysis depends on precise replications of the reaction conditions.

Therefore, the EPA methods clearly describe the microwave digestion device requirements like a defined chemistry and reaction temperature versus time. For the digestion 250-500 mg dried sample material are weighed into PM 60 microwave vessel.

PM 60 is suitable for a wide range of applications and can be handled very easily since it only consists of a few individual parts.

The Influence of digestion method is tested employing various mineral acid mixtures like only HNO3 and a mixture of HNO_3:HCl:HF (9:3:1) based on two different EPA methods, EPA 3051 A and EPA 3052. The method EPA 3051 A is not intended to accomplish total decomposition of the sample.

However, the method EPA 3052 is applied for total sample decomposition with careful choice of acid combinations.

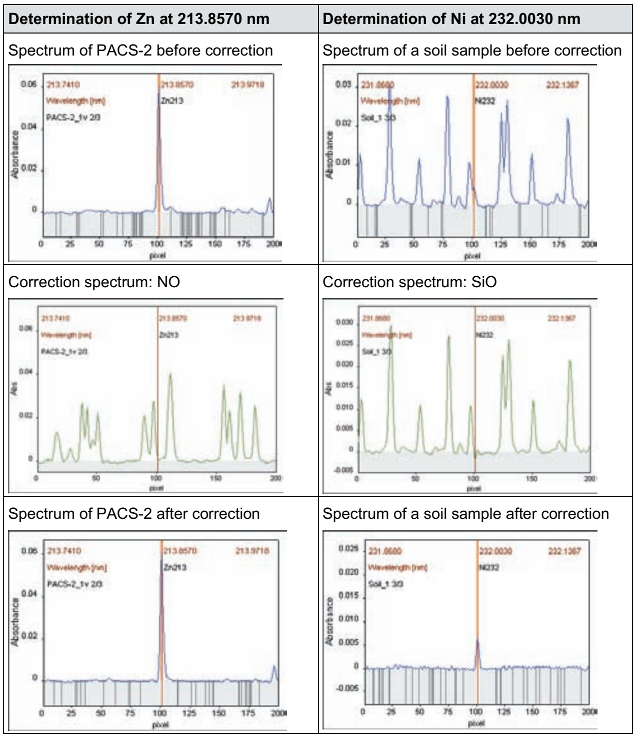
The differentiation of the sample preparation standards is given in *Table 1* for a better understanding.

After the cooling period the vessels are carefully uncapped and vented in a fume cupboard. The samples are then made up to 50mL with deionised water and analysed directly on the contrAA® 300, which is a high-resolution continuum source AAS (HR-CS AAS) for both flame and hydride techniques with simultaneous background correction [4,5]. A coded titanium 5 cm single-slot burner head is used in air-acetylene operation.

Table 1. Scope of sample preparation methods

	EPA 3051A	**EPA 3052**
Aim	digestion of sediments, sludges, soils and oils - not intended to accomplish total decomposition of the sample.	digestion of siliceous and organically based matrices - total sample decomposition
Reagents	10 mL HNO_3 or 9 mL HNO3 + 3 mL HCl	9 mL HNO_3 + 3 mL HF (HF may be varied from 0-5 mL). Addition of HCl, H_2O_2 or water is permitted
Conditions	Temp.: 175°C Total: 10 min	Total: 15 - 20min Temp.: 180°C

A significant advantage of this technique is the applying least squares background correction (LSBC) for the elimination of the structured background. The necessity to use the LSBC can be clearly seen by the Zn and Ni analysis example (*Figure 1*). Distinct structures of NO and SiO caused by the digestion acid and the sample matrix can be compensated by the use of LSBC. By using these correction models it is also possible to properly correct independently varying concentrations of the particular interferences. A further important advantage is the integration of correction models in the method parameter. This enables an automatic correction where the user gets the corrected spectrum directly just after the analysis.



Determination of Zn at 213.8570 nm | **Determination of Ni at 232.0030 nm**

Spectrum of PACS-2 before correction | Spectrum of a soil sample before correction

Correction spectrum: NO | Correction spectrum: SiO

Spectrum of PACS-2 after correction | Spectrum of a soil sample after correction

Figure 1. Demonstration of applying least squares background correction (LSBC) for the elimination of the structured background.

The experimental study was conducted using one soil and one sediment standard reference material. Soil (BAM-U110) and stream sediment (PACS-2) were supplied by the Federal Institute for Materials Research and Testing Germany (BAM) and the National Research Council Canada, respectively. The results are given in *Table 3*. The analytical results of the sediment certified reference material (PACS 2) were compared by two different microwave-assisted acid digestion methods indicated in *Table 1*. The observed elemental recoveries when using EPA Methods 3052 were in the same range like the certified values expect for Pb. Observed recoveries for Pb were 98% and 92% by Method 3051A and Method 3052, respectively. The value obtained by the EPA Method 3052 is lower than the other one but still in acceptable percentage range. This phenomenon can be explained by a possible precipitation of PbCl2 from solution upon addition of HCl. The EPA Method 3051 A has found to be especially for determination of Fe. The results found using the total decomposition method, EPA Method 3052, are in good agreement with the certified values. Beyond this, the recoveries of all elements of interest were between 92 – 107%. The EPA method 3052 is found to be particularly suitable for similar applications and therefore used for this present analysis of soil and sediment samples.

Soil and river sediment samples collected around Thuringia Saale were analysed. The samples were dried at 160°C for 5h in a drying oven. Subsequently they were homogenised by means of a ball mill. The results are given in *Table 4*. The calculated recovery, repeatability, and reproducibility confirm the good performance of the applied method.

Table 3. The experimental results for the standard reference material

	PACS-2 (stream sediment)			**BAM-U110 (soil)**	
	certified	found with EPA 3051A	found with EPA 3052	certified (total content)	found with EPA 3052
Cd [mg/kg]	2.11 ± 0.15	2.20 ± 0.04	2.07 ± 0.23	7.30 ± 0.60	7.21 ± 0.25
Cu [mg/kg]	310 ±12	289 ±2	294 ± 2	263 ± 12	251 ± 3
Pb [mg/kg]	183 ± 8	181 ± 2	170 ± 8	197 ± 14	185 ± 5
Mn [mg/kg]	440 ± 19	240 ± 6	422 ± 5	621 ± 20	602 ± 6
Ni [mg/kg]	39.5 ± 2.3	30.4 ± 0.3	42.2 ± 0.4	101 ± 5	94.7 ± 0.9
Fe [%]	4.09 ± 0.06	2.63 ± 0.20	3.93 ± 0.27	2.8*	2.67 ± 0.10
Zn [mg/kg]	364 ± 23	334 ± 6	360 ± 4	1000 ± 50	947 ± 5

**total content determined by X-ray fluorescence technique*

Table 4: The experimental results for soil and sediment samples using EPA Method 3052

	Soil 1	**Soil 2**	**Sediment 1**	**Sediment 2**
Cd [mg/kg]	n. d.	0.61 ± 0.10	0.39 ± 0.12	n. d.
Cu [mg/kg]	12.3 ± 0.4	26.2 ± 0.3	23.5 ± 0.3	12.4 ± 0.4
Pb [mg/kg]	31.9 ± 1.6	55.8 ± 1.6	44.6 ± 1.5	34.5 ± 1.6
Mn [mg/kg]	318 ± 4	704 ± 6	639 ± 7	291 ± 6
Ni [mg/kg]	20.8 ± 0.8	28.5 ± 0.8	27.1 ± 0.7	20.4 ± 0.8
Fe [%]	1.08 ± 0.06	1.87 ± 0.06	1.77 ± 0.05	1.10 ± 0.06
Zn [mg/kg]	107 ± 5	141 ± 5	150 ± 4	118 ± 5

Conclusion

Soil analysis test is becoming increasingly important as a result of environmental pollution. So there is a need to monitor the presence of heavy metals in soil and sediments by means of a fast routine analysis. The two certified reference materials were analysed and were found to give results in good agreement with the certified values. Satisfactory recoveries (92-107%) were obtained from both soil and sediment samples for all elements. The goal of all digestion processes is the complete dissolution of the materials being analysed and the complete decomposition of the matrix, though avoiding the loss or contamination of the analytical materials. Furthermore, it is also important that the digestion process is secure, reproducible and simple. Regarding the total decomposition it has been found out that the addition of HF is mandatory for complete digestion of the material. An appropriate digestion of soils and sediments was achieved by using an acid mixture of HNO_3, HCl and HF.

In conclusion, the experimental data indicates that today practically soil and sediment analysis can be performed using the appropriate microwave digestion followed by the latest technology HR-CS Flame AAS for quite a few number of elements very quickly, economical and very simple.

Literature:

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