Determination of Cd and Pb in sediment without sample preparation

By using direct solid sampling technique samples can be measured without time-consuming preparation. Thus, total analysis time and blank problems caused by chemicals used for sample preparation are reduced to a minimum.

Sediments act as archives, where changing conditions can be traced for heavy metal cycling in the geo- and atmosphere. Thus the increased emission of trace elements related to industrial or mining activities is known to enhance significantly the total trace element concentrations in lake sediments as compared to natural background levels. In this respect, the metal concentration profile in sediments can be followed and besides active and passive contamination studies, renaturation programs of the water bodies can be configured.

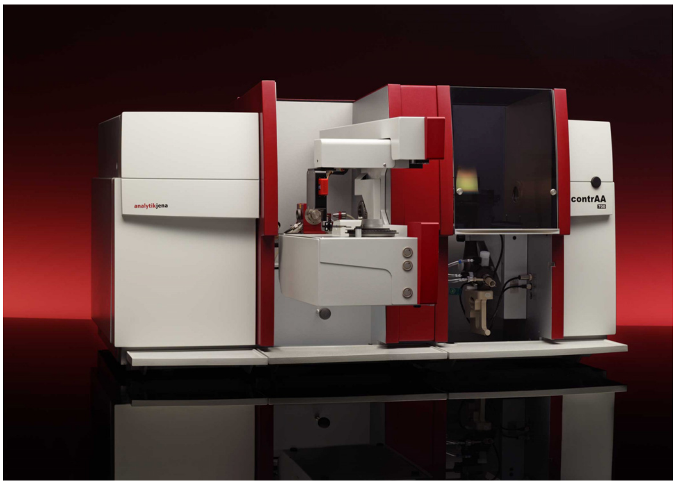
In the following, a time efficient direct solid sampling technique for complex metallic matrices is presented and the advantages of the simplified line selection in the absorption spectrum are highlighted.

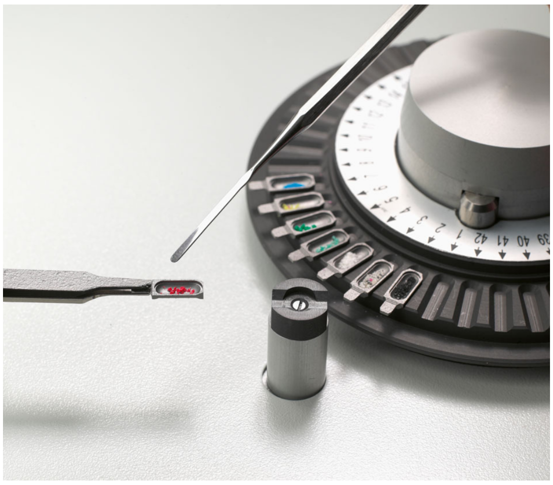
Sample preparation

The samples were analyzed directly without any further preparation.

Determination

The measurements were performed with the High-Resolution Continuum Source AAS contrAA® and the full automatic solid autosampler SSA 600.





Method parameters

Element	Wavelength [nm]	$T_{Pyr.}$ [°C]	$T_{Atom.}$ [°C]	Ramp [°C/s]	Typical weight [mg]	Modifier
Cd	228.8018	650	2000	1200	0.2 - 0.4	none
Pb	368.3462	850	2450	1400	0.2 - 0.4	5 µL 0.1 % $Pd(NO_3)_2$

Evaluation parameters

Element	Eval. pixel	Measurement time [s]	No. of spectra	Spectral range		Background correction
				[pixel]	[nm]	
Cd	3	3	90	200	0.25	dynamic, with reference
Pb	3	3	90	200	0.40	dynamic, with reference

Calibration

Cd Solid calibration with reference material MESS-2 (certif. conc.: 0.24 ± 0.01 mg/kg)

Using different weights of MESS-2 between 0.1 and 1.2 mg

Standards: 1 replicate per statistic; integration mode: area

Samples: 5 replicates per statistic; integration mode: area

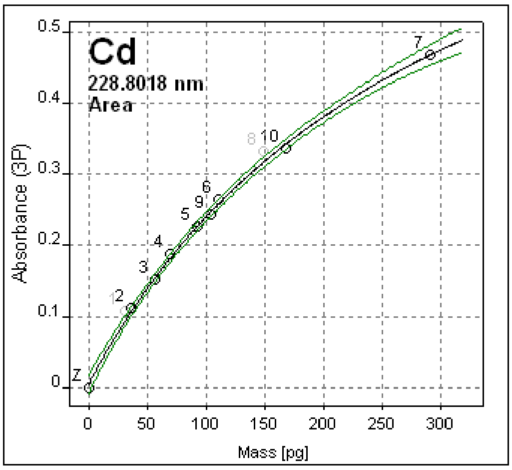
Pb Solid calibration with reference material GBW 0831 (certif. conc.: 79 ± 12 mg/kg)

Using different weights of GBW 0831 between 0.1 and 0.6 mg

Standards: 1 replicate per statistic, integration mode: area

Samples: 5 replicates per statistic, integration mode: area

Calibration curves

Element	**Cd 228.8018 nm**
nonlinear R^2 = 0.998	

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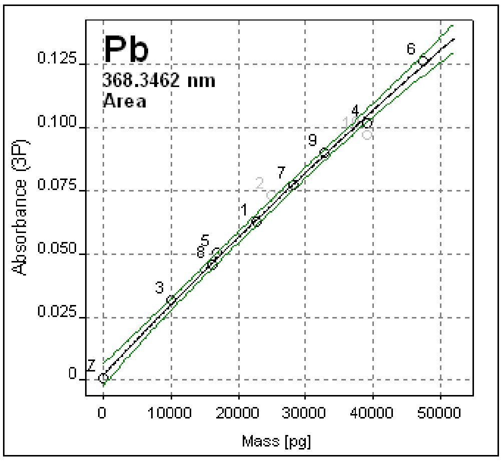
<tr><th>Element</th><th>Pb 368.3462 nm</th></tr>
<tr><td>nonlinear

R² = 0.997</td><td>
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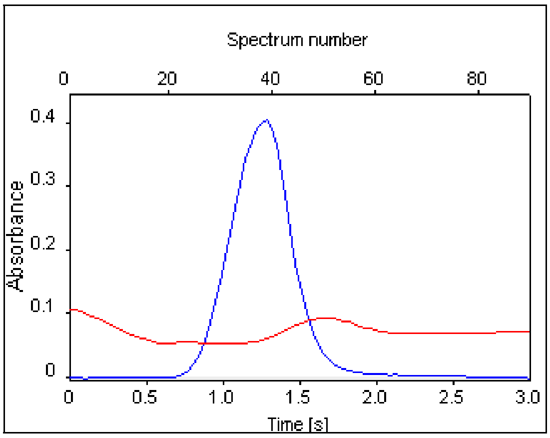
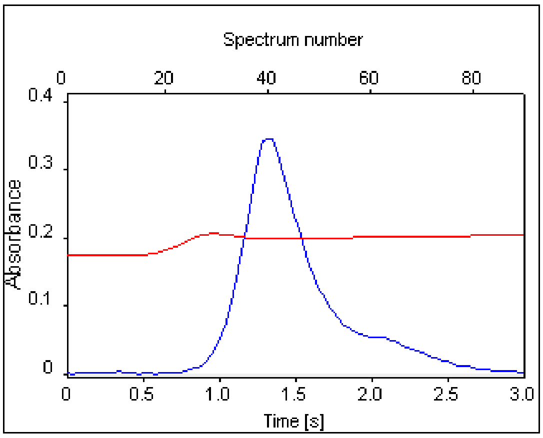
Signal profile and spectral vicinity

<table>
<tr><th>Element</th><th colspan="2">Cd 228.8018 nm</th></tr>
<tr><td rowspan="2">Signal profile</td><td>Cal. std. 4 (69.84 pg Cd)

</td><td>Sample: sediment

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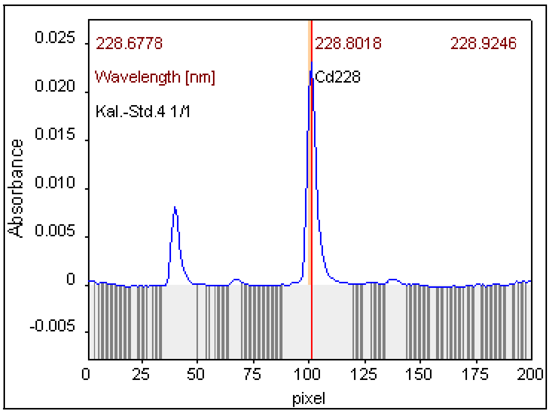
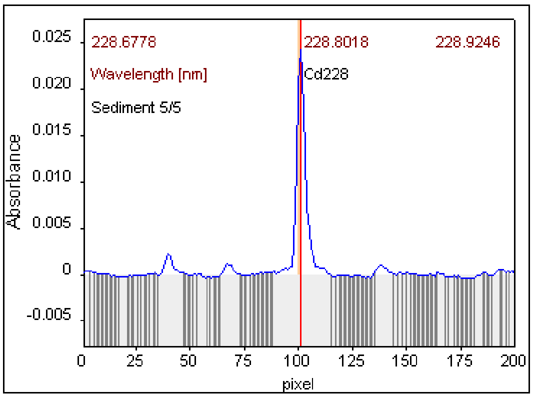
<tr><td colspan="2">Red: background signal
Blue: analyte signal</td></tr>
<tr><td>Spectral vicinity</td><td>
</td><td>
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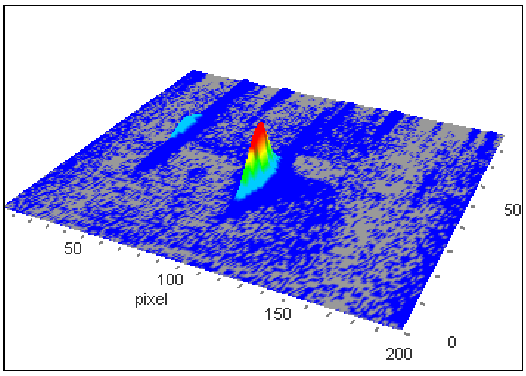
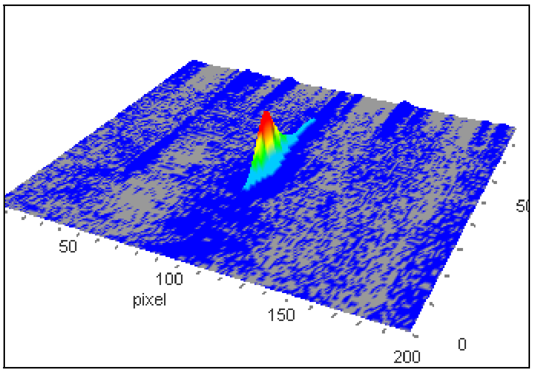
<table>
<tr><td>3D spectrum</td><td>Cal. std. 4 (69.84 pg Cd)
 </td><td>Sample: sediment
 </td></tr>
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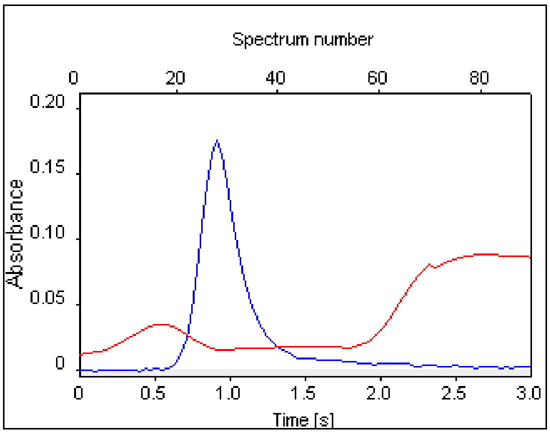
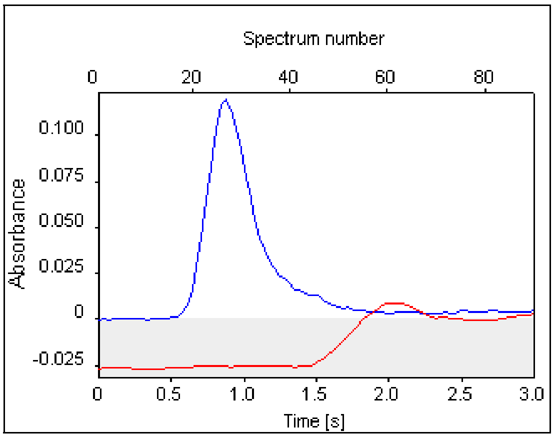
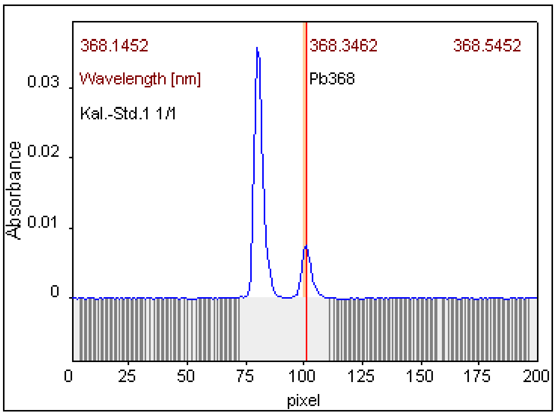
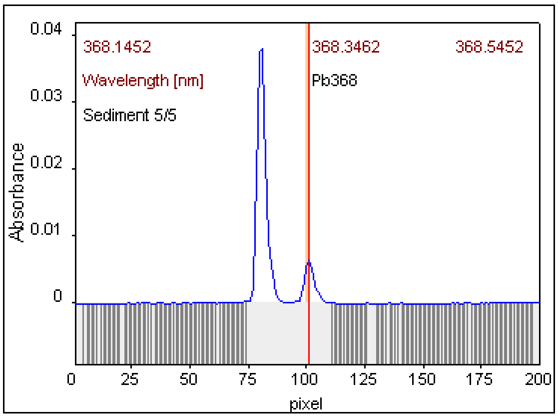
<table>
<tr><th>Element</th><th colspan="2">Pb 283.3060 nm</th></tr>
<tr><td rowspan="2">Signal profile</td><td>Cal. std. 1 (22750 pg Pb)
 </td><td>Sample: sediment
 </td></tr>
<tr><td colspan="2">Red: background signal
Blue: analyte signal</td></tr>
<tr><td>Spectral vicinity</td><td> </td><td> </td></tr>
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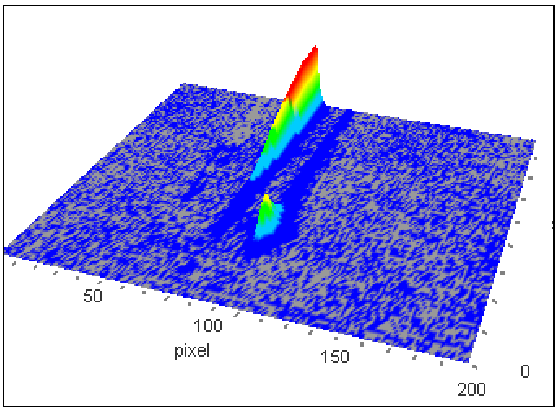
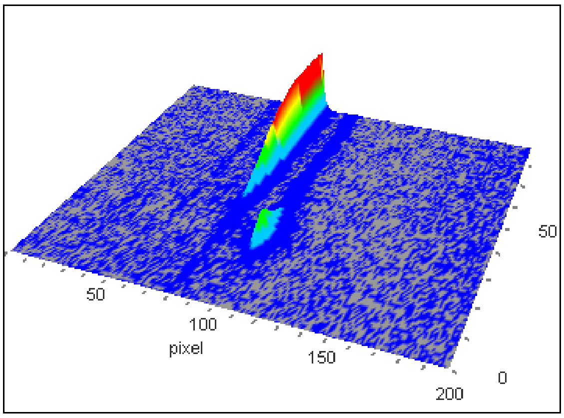
3D spectrum	**Cal. std. 1 (22750 pg Pb)**	**Sample: sediment**
		

Results and Discussion

The spectral vicinity of Cd and Pb shows additional Fe lines at 228.7262 nm and 368.304 nm. Due to the high resolution of the spectrometer those signals could be separated from the analyte signal. High concentrations of Pb could be measured on an insensitive absorption line.

By measuring of reference materials recovery rates of about 92 and 95 % could be reached, proofing the analytical performance of the method employed.

Element	Sample	Concentration [mg/kg]	RSD [%]	Recovery rate [%]
Cd	Sediment	0.26 ± 0.06	7.6	-
	CRM 280 (*)	1.48 ± 0.11	8.2	92.5
Pb	Sediment	47.1 ± 2.5	6.5	-
	CRM 277 (**)	139 ± 4	4.3	95.2

(*) Reference material, certif. concentration of Cd: 1.6 ± 0.1 mg/kg

(**) Reference material, certif. concentration of Pb: 146 ± 3 mg/kg

Conclusion

All absorption lines of an element in the spectral range of 185–900 nm can be analytically evaluated by using a Xe short-arc lamp as a continuum lamp in the HR-CS AAS. The spectral background of the samples in the HR-CS AAS is always corrected directly on the analysis line, simultaneously and independently of the wavelength used, thus simplifying the development of the method and selection of lines.

By using direct solid sampling technique samples can be measured without time-consuming preparation. Thus, total analysis time and blank problems caused by chemicals used for sample preparation are reduced to a minimum. Due to the availability of certified reference materials, same or similar calibration standards to the sample matrix could be applied.