



### Challenge

The quantification of cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc in aqua regia extract in accordance with the DIN ISO 11047 standard

### Solution

Quantification of metals using HR-CS-AAS contrAA 800 in flame mode

### Intended audience

Government and commercial environmental laboratories

## Quantification of Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Nickel, and Zinc in Soils in Accordance with DIN ISO 11047 Using HR-CS AAS

### Introduction

Soil composition and heavy metal analysis are two closely related aspects of environmental science that have become increasingly important in recent decades. Soil is a vital resource that provides the basis for food production and the preservation of ecosystems. However, its quality is increasingly influenced by human activities, particularly by the release of heavy metals into the environment. Heavy metals are natural elements that are mostly essential for organisms in low concentrations, but can become toxic in higher quantities. They enter the soil through various sources such as industrial emissions, agricultural fertilizers, and wastewater. The accumulation of heavy metals in soil can have serious effects on the environment and human health.

Heavy metal analysis is an important step in determining the concentrations of these elements in the soil and identifying potential hazards. Modern analytical techniques such as atomic absorption spectrometry make it possible to

accurately detect even traces of heavy metals. This data is critical for environmentalists, farmers, and governments to take appropriate action to remediate soil and prevent further contamination.

This application note describes the quantification of the metals cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc in aqua regia extracts following DIN ISO 11047 using the flame HR-CS-AAS contrAA 800 F. The aqua regia extracts of soil, sediment, and sewage sludge samples should be carried out according to ISO 11466. The AS-FD autosampler can be used for automated sample introduction and dilution.

The high-resolution flame atomic absorption spectrometer contrAA 800 F with a xenon short arc lamp as continuum source offers the possibility to measure the absorption of the eight metals (cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc) in a fast sequential order in one aspiration process. From a sample volume of

50 mL, 23 absorption lines can be measured with good precision in a single step. This special AA spectrometer offers the unique ability to observe the spectral vicinity of the analyte absorption line to detect spectral overlaps and compensate for them if necessary. In addition to the special wavelength-independent background correction, the unique design of the contrAA 800 eliminates the need to wait for a stabilization of the light source output as well as the element-specific settings of slit groups, e.g., due to secondary lines. Therefore, the best light throughput is always available and the element-independent light source is

not negatively influenced by the chemical-physical properties of the analytes. As a result, the lowest detection limits can be achieved with simultaneous precise quantification of analytes even in the smallest traces.

Using the AS-FD autosampler, fully automatic dilutions can be applied prior to the actual measurement and also if the highest calibration standard is exceeded. In addition, this autosampler can be used to automatically prepare the solutions required for the calibration function from a single stock standard and features a fully automated preparation of solutions for the standard addition procedure.

## Materials and Methods

### Reference material

- GBW07408 (NCS DC 73326), soil (Institute of Geophysical and Geochemical Exploration, Langfang China)
- GBW07306, river sediment (Institute of Geophysical and Geochemical Exploration, Langfang China)
- BCR-143R sewage sludge with enriched soil (European Commission, Institute for Reference Materials and Measurements)
- BCR-146R sewage sludge of industrial origin (European Commission, Institute for Reference Materials and Measurements)
- BAM-U110 contaminated soil (BAM, Bundesanstalt für Materialforschung und -prüfung, 2006)
- PACS-2 marine sediment (National Research Council of Canada)

### Reagents

- Concentrated  $\text{HNO}_3$  (65%, p.a.)
- Concentrated  $\text{HCl}$  (37%, p.a.)
- Cesium chloride-lanthanum chloride buffer solution (Cs/La) according to Schinkel ( $10 \text{ g L}^{-1}$   $\text{CsCl}$ ,  $100 \text{ g L}^{-1}$   $\text{LaCl}_3$ )
- Certified single element standards for Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb (concentration of the analytes  $1,000 \text{ mg L}^{-1}$ )

### Sample preparation

The samples were digested in accordance with DIN ISO 11466 using aqua regia. The sample material was weighed in at aliquots of approx. 0.3 g and the filling volume was 50 mL. The sample preparation for the flame measurement is in line with the DIN ISO 11407 norm. Even lower acid contents for standards and sample dilution than described in the norm lead to stable measuring solutions. For the measurements using the flame technique, the samples were diluted with a solution containing 21% (v/v) concentrated  $\text{HCl}$  and 7% (v/v) concentrated  $\text{HNO}_3$ . For the elements chromium and manganese, an additional 10% (v/v) of the Cs/La buffer solution was added.

### Calibration

In accordance with the DIN ISO 11047 standard, the calibration standards were prepared in a solution with 21% (v/v)  $\text{HCl}$  and 7% (v/v)  $\text{HNO}_3$ . A solution with 21% (v/v)  $\text{HCl}$  and 7% (v/v)  $\text{HNO}_3$  was used as the blank value for the calibration. Lower acid contents for standards than described in the norm also lead to stable measurement solutions. For the elements chromium and manganese, an additional 10% (v/v) of the Cs/La buffer solution was added if these analytes were measured using an air-acetylene flame. If the nitrous oxide-acetylene flame is used to determine these elements, the addition of Cs/La solution can be omitted.

Table 1: Concentrations used for calibration according to DIN ISO 11047

Standard	Concentration [mg L <sup>-1</sup> ]							
	Cd	Cr	Co	Cu	Pb	Mn	Ni	Zn
Cal. 0	0	0	0	0	0	0	0	0
Std. 1	0.2	1	1	1	1	0.4	1	0.2
Std. 2	0.4	2	2	2	2	1	2	0.4
Std. 3	0.8	4	4	4	4	2	4	0.8
Std. 4	1.2	6	6	6	6	4	6	1.2
Std. 5	1.6	8	8	8	8	6	8	1.6
Std. 6	2.0					8		2.0

Table 2: Typical calibration functions according to DIN ISO 11047

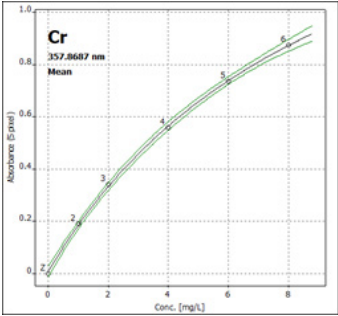
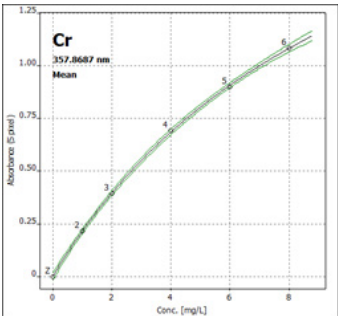
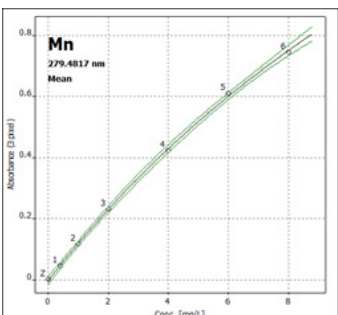
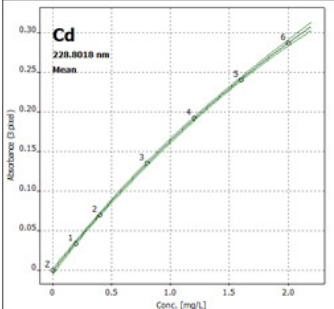
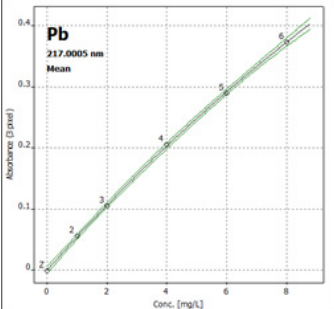
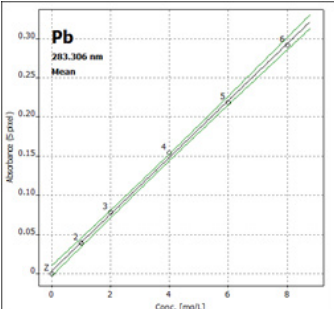
Element	Flame type	Correlation R <sup>2</sup> <sub>(adj.)</sub>	Graphic plot
Cr	Air-acetylene	0.9992 non-linear	
Cr	Nitrous oxide-acetylene	0.9997 non-linear	
Mn	Air-acetylene	0.9993 non-linear	

Table 2 continued: Typical calibration functions according to DIN ISO 11047

Element	Flame type	Correlation $R^2_{(adj.)}$	Graphic plot
Mn	Nitrous oxide-acetylene	0.99990 non-linear	
Co	Air-acetylene	0.9993 non-linear	
Ni	Air-acetylene	0.9997 non-linear	
Cu	Air-acetylene	0.9996 non-linear	
Zn	Air-acetylene	0.9994 non-linear	

Table 2 continued: Typical calibration functions according to DIN ISO 11047

Element	Flame type	Correlation $R^2_{(adj.)}$	Graphic plot
Cd	Air-acetylene	0.9997 non-linear	
Pb	Air-acetylene	0.9997 non-linear	
Pb	Air-acetylene	0.9990 linear	

### Instrument settings

The contrAA 800 F, a high-resolution flame atomic absorption spectrometer with continuum emitter as the light source, was used for the determination of soil extracts in accordance with DIN ISO 11466. The 50 mm burner head is equipped with a scraper. This ensures automatic cleaning during the measurement when using the nitrous oxide-acetylene flame. An alternative is the 100 mm burner head, which provides improved sensitivity of the measurement with the air-acetylene flame. An AS-F autosampler or an AS-FD autosampler with dilution function can be used to automate the measurement. Variable sample dilutions or preparation of the standard addition procedure can be performed automatically with the AS-FD autosampler.

The instrument specifications and measurement parameters used are listed in table 3. Table 4 shows the measurement parameters and instrument settings of the method used. The iterative baseline correction (IBC) was used for background correction.

According to DIN ISO 11047, the absorption wavelength for lead is specified at 217 nm. In contrast to the main absorption wavelength at 217 nm, the absorption band at 283 nm is often selected for lead. The absorption band at 217 nm shows a reduced signal-to-noise ratio compared to the line at 283 nm for line sources (e.g., hollow cathode lamps). For HR-CS-AAS, however, the main wavelength at 217 nm can be used without significant limitations. Both lines have been used in this application note.

Table 3: General instrument parameters

Parameter	Specification
Device	contrAA 800 F
Burner type and position	50 mm, 0°
Flame type	Air/acetylene
Measuring time	5 s, 3 repetition
Baseline correction	IBC
Rinsing solution	1% (v/v) HCl

Table 4: Applied method parameters

Element	Wavelength [nm]	Number of pixels	Flame type	Gas flow [L h <sup>-1</sup> ]	Burner height [mm]
Cr	357.8687	3	air/C <sub>2</sub> H <sub>2</sub>	95	10
			N <sub>2</sub> O/C <sub>2</sub> H <sub>2</sub>	185	4
Mn	279.4817	3	air/C <sub>2</sub> H <sub>2</sub>	80	6
			N <sub>2</sub> O/C <sub>2</sub> H <sub>2</sub>	180	4
Co	240.7254	3	air/C <sub>2</sub> H <sub>2</sub>	65	6
Ni	232.0030	3	air/C <sub>2</sub> H <sub>2</sub>	45	5
Cu	324.7540	3	air/C <sub>2</sub> H <sub>2</sub>	45	5
Zn	213.8570	3	air/C <sub>2</sub> H <sub>2</sub>	45	4
Cd	228.8018	3	air/C <sub>2</sub> H <sub>2</sub>	45	4
Pb	217.0005	3	air/C <sub>2</sub> H <sub>2</sub>	60	6
	283.3060				

## Results and Discussion

Table 5 lists the typical detection and quantification limits for the instrument type and measurement settings used. The limits are determined by the blank value method, using an 11-fold blank value measurement and the 3 $\sigma$  or 9 $\sigma$  standard deviation criterion.

The elements cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc were determined in the soil and sediment samples in accordance with DIN ISO 11047. The results of the series of measurements are shown in table 6 and compared with the expected value of the reference materials.

For chromium and manganese, the air-acetylene flame may give false lower results, even when La is added in excess. Interferences of this nature are virtually non-existent in the nitrous oxide-acetylene flame. With regard to the ionization potential of the nitrous oxide flame, K or Cs should be added

in excess, e.g. in the form of KCl or CsCl solutions (Cs/K concentration of 0.1–0.2% (m/m)).

The HR-CS-AA spectrometer contrAA 800 provides the unique ability to record the spectral vicinity of the analytical lines. Spectral overlays can therefore be detected and compensated if necessary. Table 7 shows the corresponding spectra for the sample BAM U 110 as an example. For some analysis lines, iron absorption bands can be seen in the spectra that do not show any overlap with the analyte lines. For the analysis line of zinc at 213 nm a direct overlap occurs, origin from NO bands. This overlap leads to a false higher result if not compensated. By using the LSBC (least-squares background correction) method, overlays can be compensated to such an extent that an undisturbed detection of the analysis line is possible. The procedure is described in more detail below.

Table 5: Achievable limits of detection (LOD) and limits of quantification (LOQ) of the presented method according to the  $3\sigma$  or  $9\sigma$  criterion

Element	Wavelength [nm]	LOD [mg L <sup>-1</sup> ]	LOQ [mg L <sup>-1</sup> ]
Cr	357	0.0015	0.0045
Mn	279	0.001	0.0030
Co	240	0.0016	0.0049
Ni	232	0.0028	0.0083
Cu	324	0.00073	0.0022
Zn	213	0.0015	0.0046
Cd	228	0.00067	0.0020
Pb	217	0.0071	0.021
	283	0.0076	0.023

Table 6: Measurement results of analyte content determination in soil, sediment and sewage sludge samples

Sample	Element	Pre-dilution factor	Recovery [%]	Flame type	Measurement value [mg kg <sup>-1</sup> ]		Target value [mg kg <sup>-1</sup> ]	
NCSDC 73326	Cr	1	47	C <sub>2</sub> H <sub>2</sub> -air	32.61	±0.48	68	±6
			92	C <sub>2</sub> H <sub>2</sub> -N <sub>2</sub> O	62.31	±1.02		
	Mn	2	101	C <sub>2</sub> H <sub>2</sub> -air	659	±15	650	±23
	Co	1	97	C <sub>2</sub> H <sub>2</sub> -air	12.29	±0.087	12.7	±1.1
	Ni	1	100	C <sub>2</sub> H <sub>2</sub> -air	31.5	±0.24	31.5	±1.8
	Cu	1	92	C <sub>2</sub> H <sub>2</sub> -air	22.4	±0.13	24.3	±1.2
	Zn	5	98	C <sub>2</sub> H <sub>2</sub> -air	66.4	±0.9	68	±4
	Cd	1		C <sub>2</sub> H <sub>2</sub> -air	<LOQ		0.13	±0.02
	Pb	1	91	C <sub>2</sub> H <sub>2</sub> -air	19.15	±0.12	21	±2
BAM-U110	Cr	1	102	C <sub>2</sub> H <sub>2</sub> -air	193.5	±1.34	190	±9
	Mn	2	101	C <sub>2</sub> H <sub>2</sub> -air	585.5	±6.6	580	±19
	Co	1	104	C <sub>2</sub> H <sub>2</sub> -air	15.07	±0.091	14.5	±0.8
	Ni	1	99	C <sub>2</sub> H <sub>2</sub> -air	94.9	±0.18	95.6	±4
	Cu	1	102	C <sub>2</sub> H <sub>2</sub> -air	266	±2.4	262	±9
	Zn	10	92	C <sub>2</sub> H <sub>2</sub> -air	912.6	±5.7	990	±40
	Cd	1	103	C <sub>2</sub> H <sub>2</sub> -air	7.24	±0.095	7	±0.4
	Pb	1	100	C <sub>2</sub> H <sub>2</sub> -air	185.2	±0.93	185	±8

LOQ: Limit of quantification



Table 6 continued: Measurement results of analyte content determination in soil, sediment and sewage sludge samples

Sample	Element	Pre-dilution factor	Recovery [%]	Flame type	Measurement value [mg kg <sup>-1</sup> ]		Target value [mg kg <sup>-1</sup> ]	
BCR 143R	Cr	1	98	C <sub>2</sub> H <sub>2</sub> -air	417	±2.0	426	±12
	Mn	2	98	C <sub>2</sub> H <sub>2</sub> -air	840.3	±3.4	858	±11
	Co	1	107	C <sub>2</sub> H <sub>2</sub> -air	12.67	±0.076	11.8	±1
	Ni	1	96	C <sub>2</sub> H <sub>2</sub> -air	285.2	±7.0	296	±4
	Cu	1	100	C <sub>2</sub> H <sub>2</sub> -air	128.8	±0.92	128	±7
	Zn	10	94	C <sub>2</sub> H <sub>2</sub> -air	999.5	±2.4	1063	±16
	Cd	2	98	C <sub>2</sub> H <sub>2</sub> -air	70.86	±0.53	72	±1.8
	Pb	1	100	C <sub>2</sub> H <sub>2</sub> -air	173.7	±2.3	174	±4
BCR 146R	Cr	1	105	C <sub>2</sub> H <sub>2</sub> -air	182.7	±3.6	174	±7
	Mn	2	100	C <sub>2</sub> H <sub>2</sub> -air	298.6	±1.8	298	±9
	Co	1	107	C <sub>2</sub> H <sub>2</sub> -air	6.96	±0.071	6.5	±0.4
	Ni	1	100	C <sub>2</sub> H <sub>2</sub> -air	65.4	±0.66	65	±3
	Cu	1	98	C <sub>2</sub> H <sub>2</sub> -air	815.2	±3.6	831	±16
	Zn	30	95	C <sub>2</sub> H <sub>2</sub> -air	2892	±50	3040	±60
	Cd	2	100	C <sub>2</sub> H <sub>2</sub> -air	18.43	±0.17	18.4	±0.4
	Pb	1	101	C <sub>2</sub> H <sub>2</sub> -air	588	±2.3	583	±17
PACS 2	Cr	1	79	C <sub>2</sub> H <sub>2</sub> -air	71.74	±0.69	90.7	±4.6
			99	C <sub>2</sub> H <sub>2</sub> -N <sub>2</sub> O	91.94	±0.96		
	Mn	2	70	C <sub>2</sub> H <sub>2</sub> -air	306	±3.6	440	±19
			94	C <sub>2</sub> H <sub>2</sub> -N <sub>2</sub> O	412	±7.2		
	Co	1	89	C <sub>2</sub> H <sub>2</sub> -air	10.21	±0.05	11.5	±0.3
	Ni	1	90	C <sub>2</sub> H <sub>2</sub> -air	35.74	±0.39	39.5	±2.3
	Cu	1	101	C <sub>2</sub> H <sub>2</sub> -air	310.9	±0.59	310	±12
	Zn	1	96	C <sub>2</sub> H <sub>2</sub> -air	352.5	±6.5	364	±23
	Cd	1	104	C <sub>2</sub> H <sub>2</sub> -air	2.2	±0.046	2.11	±0.15
	Pb	1	95	C <sub>2</sub> H <sub>2</sub> -air	173.1	±0.53	183	±8
GBW0 7306	Cr	1	50	C <sub>2</sub> H <sub>2</sub> -air	94.3	±1.6	190	±24
			89	C <sub>2</sub> H <sub>2</sub> -N <sub>2</sub> O	168.3	±4.3		
	Mn	2	97	C <sub>2</sub> H <sub>2</sub> -air	943.8	±5.8	970	±60
	Co	1	93	C <sub>2</sub> H <sub>2</sub> -air	22.6	±0.11	24.4	±3
	Ni	1	89	C <sub>2</sub> H <sub>2</sub> -air	69.75	±0.40	78	±7
	Cu	1	100	C <sub>2</sub> H <sub>2</sub> -air	383.1	±3.4	383	±18
	Zn	2	101	C <sub>2</sub> H <sub>2</sub> -air	146.3	±2.9	144	±10
	Cd	1		C <sub>2</sub> H <sub>2</sub> -air	<LOQ		0.43	±0.04
	Pb	1	92	C <sub>2</sub> H <sub>2</sub> -air	24.95	±0.081	27	±5



Table 7: Spectral vicinity of the analysis lines

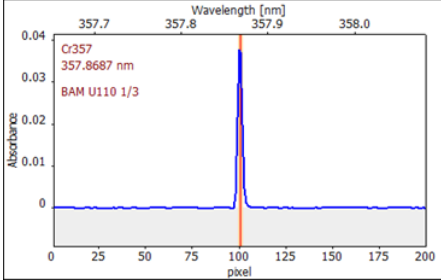
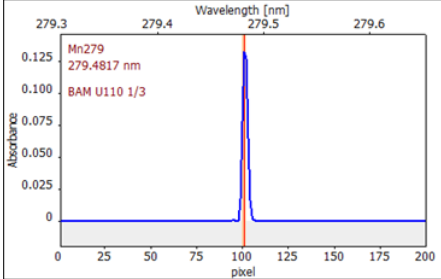
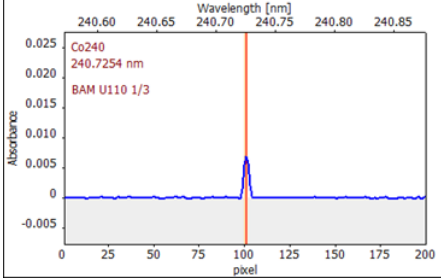
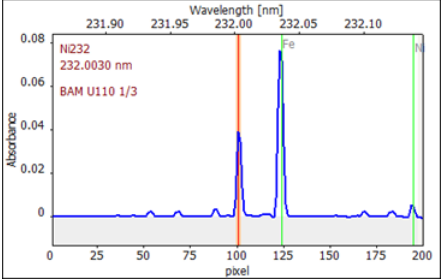
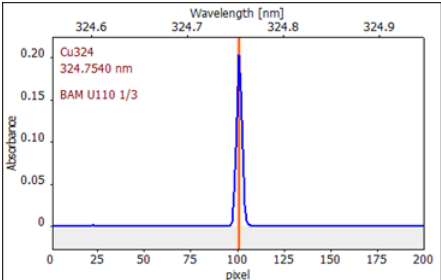
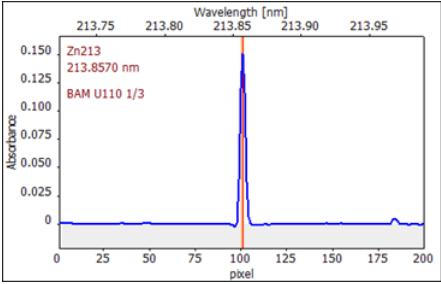
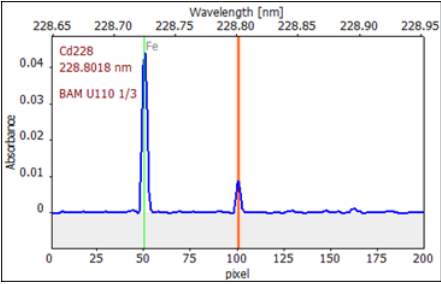
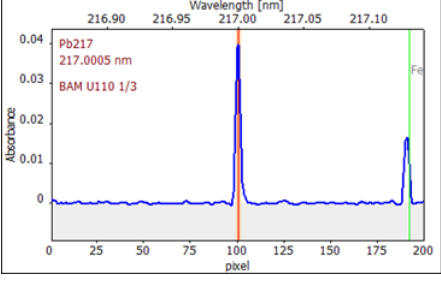
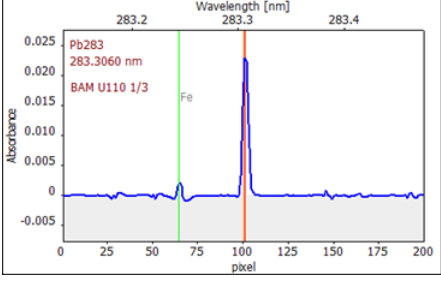
Element	Spectral vicinity	Remarks
Cr (sample BAM U110)		
Mn (sample BAM U110)		
Co (sample BAM U110)		
Ni (sample BAM U110)		
Cu (sample BAM U110)		

Table 7 continued: Spectral vicinity of the analysis lines

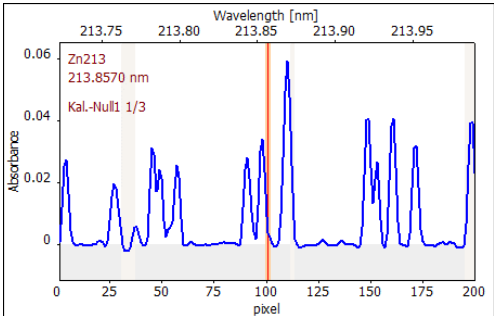
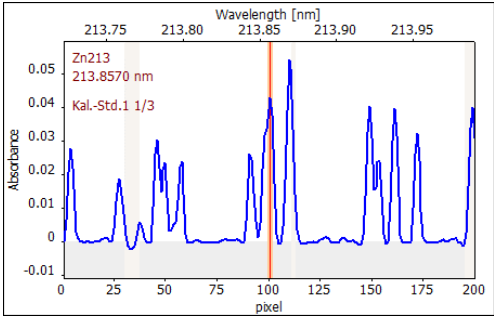
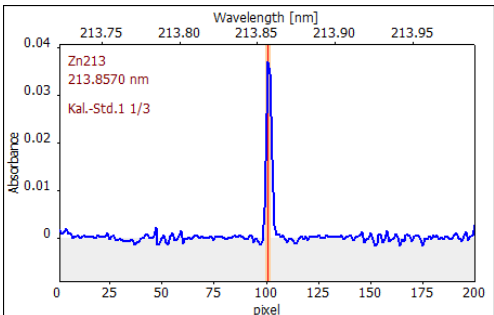
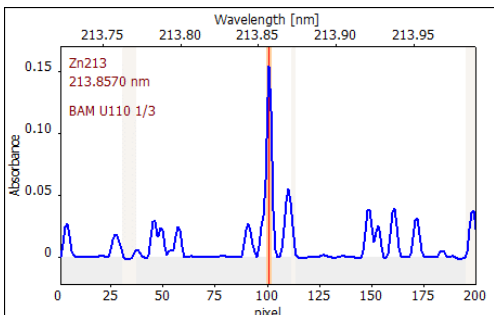
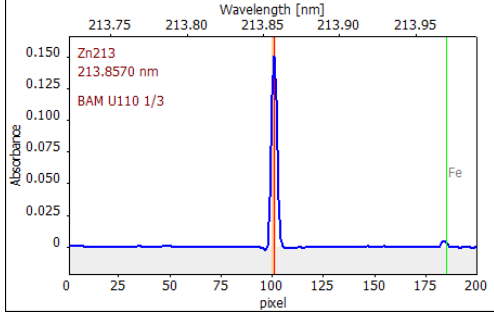
Element	Spectral vicinity	Remarks
Zn (sample BAM U110)		*LSBC applied
Cd (sample BAM U110)		
Pb (sample BAM U110)		
Pb (sample BAM U110)		*LSBC applied

LSBC: Least-squares background correction

### Correction spectra

Spectral overlap of the analyte wavelength due to molecular or other atomic absorption bands can falsify the analysis result. These overlaps can be compensated for by a spectral correction. A suitable correction spectrum can be recorded in the ASpect CS software to minimize or eliminate the overlap of the analysis line using the LSBC algorithm. In this series of measurements, the LSBC was used for the NO molecule bands adjacent to the zinc analysis line. The reagent blank value (no detectable Zn contamination present) was used to generate the correction spectrum. The effects of the LSBC on the analyte absorption line of zinc at 213.9 nm are shown in table 8.

Table 8: Spectral vicinity of the analytic lines used

Sample	Spectral vicinity
Blank	
Std. 1 without correction model	
Std. 1 using correction model	
sample BAM U110 without correction model	
sample BAM U110 using correction model	

## Summary

Fast and cost-effective analysis of the metals cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc in soil and sewage sludge extracts in accordance with DIN ISO 11047 is easy and user-friendly with the contrAA 800 F. The method presented in this application note shows the necessary procedure from sample preparation of the acid extracts to analysis using a flame atomic absorption spectrometer. The fast sequential analysis of the contrAA 800 F, which enables the detection of all necessary analysis lines to be detected in a single aspiration process and without changing lamps, and the automatic and intelligent dilution of the AS-FD autosampler make sample analysis fast and easy. This analytical performance capability of an AA spectrometer is unmatched and takes AA analysis to a new level.



## Recommended device configuration

Table 9: Overview of devices, accessories, and consumables

Article	Article number	Description
contrAA 800 F - HR-CS	815-08000-2	HR-CS AAS flame mode
AS-FD	810-60501-0	Autosampler for flame analysis with dilution function
Burner head 50 mm	810-60057-0	Burner head for the air-acetylene and N2O-acetylene flame
Scraper	812-08000-2	Automatic burner head cleaner for the N2O acetylene flame

## References

- [1] DIN ISO 11047:2003-05, Soil quality - Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc in aqua regia extracts of soil - Flame and electrothermal atomic absorption spectrometric methods (ISO 11047:1998)
- [2] DIN ISO 11466:1997-06 Soil quality - Extraction of trace elements soluble in aqua regia (ISO 11466:1995)

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