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 novAA 800 in flame mode

Intended audience
Government and commercial environmental laboratories

Quantification of Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Nickel, and Zinc in Soil and Sludge in Accordance with DIN ISO 11047 Using LS-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 precisely detect even traces of heavy metals. This data is crucial 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 flame AAS novAA 800 F. The aqua regia extracts of soil can be carried out according to ISO 11466. The AS FD autosampler can be used for automated sample introduction and dilution.
The novAA 800 F flame atomic absorption spectrometer is equipped with a lamp turret that has eight positions for hollow cathode lamps (HCL). This means that the eight

target elements (Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn) can be quantified without manually changing single-element HCLs. One of the advantages of single-element HCLs over multi-element HCLs is their longer lifetime.
Using the AS-FD autosampler, fully automatic dilutions can be applied prior to the actual measurement and 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)
- BAM-U110 contaminated soil (BAM, Bundesanstalt für Materialforschung und -prüfung, 2006)

Reagents

- Concentrated HNO_3 (65 %, p.a.)
- Concentrated HCl (37 %, p.a.)
- Cesium chloride-lanthanum chloride buffer solution according to Schinkel (10 g L^{-1} CsCl, 100 g L^{-1} $LaCl_3$)
- Certified single element standards for Cr, Mn, Co, Ni, Cu, Zn, Cd und Pb (concentration of the analytes 1000 mg L^{-1})

Sample preparation

The samples were digested according to 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 HCl and 7% (v/v) concentrated HNO3. 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) HCl and 7% (v/v) HNO_3. A solution with 21% (v/v) HCl and 7% (v/v) 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. Regarding 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% (w/w)).

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

Standard	Concentration [mg L^{-1}]							
	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

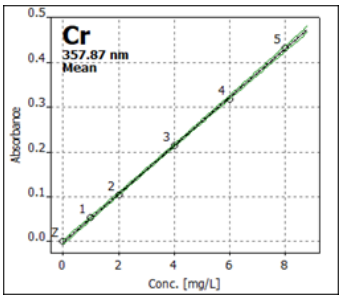
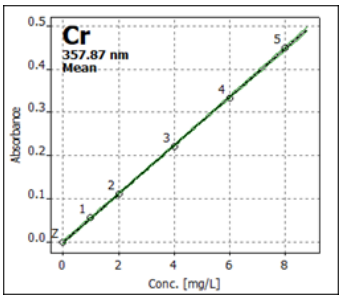
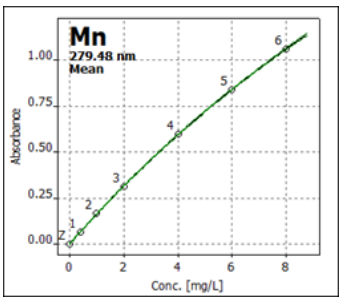
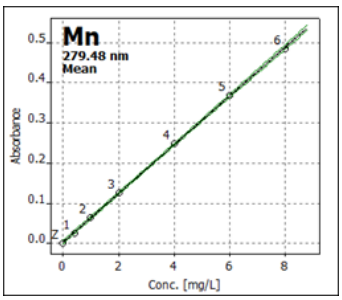
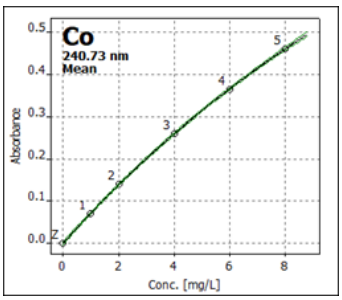
Element	Flame type	Correlation $R^2_{(adj.)}$	Graphic plot
Cr	Air-acetylene	0.9997 linear	
Cr	Nitrous oxide-acetylene	0.9998 linear	
Mn	Air-acetylene	0.99997 linear	
Mn	Nitrous oxide-acetylene	0.9996 linear	
Co	Air-acetylene	0.99991 non-linear	

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

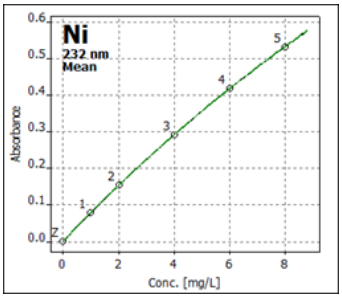
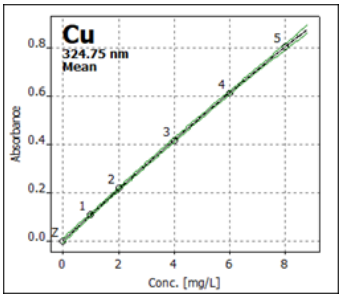
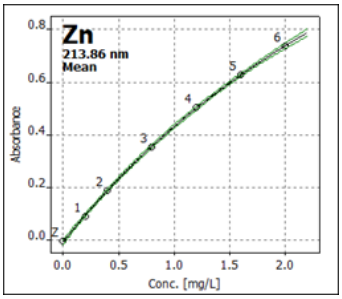
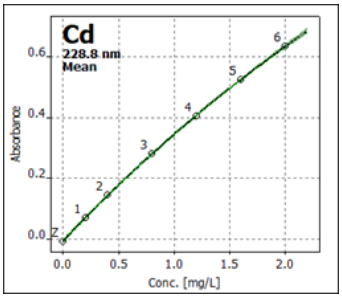
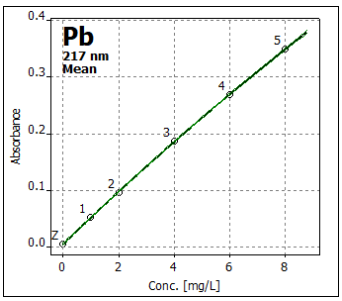
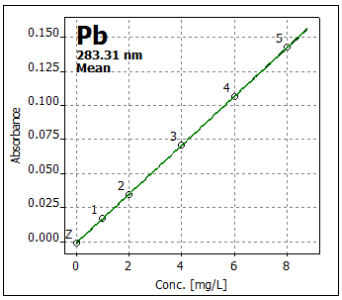
Element	Flame type	Correlation $R^2_{(adj.)}$	Graphic plot
Ni	Air-acetylene	0.999996 non-linear	
Cu	Air-acetylene	0.9998 non-linear	
Zn	Air-acetylene	0.9997 non-linear	
Cd	Air-acetylene	0.99992 non-linear	
Pb	Air-acetylene	0.99996 non-linear	

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

Element	Flame type	Correlation $R^2_{(adj.)}$	Graphic plot
Pb	Air-acetylene	0.99997 linear	

Instrument settings

The novAA 800 F a flame atomic absorption spectrometer 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 norm, 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	novAA 800 F
Burner type and position	50 mm, 0°
Flame type	air-acetylene, nitrous oxide-acetylene
Measuring time	5 s, 3 repetition
Baseline correction	D_2-HCL
Rinsing solution	1% (v/v) HNO_3

Table 4: Applied method parameters

Element	Wavelength [nm]	Slit setting [nm]	HCL-current [mA]	Flame type	Gas flow [L h^{-1}]	Burner height [mm]
Cr	357.8	0.2	5	air/C_2H_2 N_2O/C_2H_2	95 185	10 4
Mn	279.4	0.2	5	air/C_2H_2 N_2O/C_2H_2	80 180	6 4
Co	240.7	0.2	6	air/C_2H_2	65	6
Ni	232.0	0.2	5	air/C_2H_2	45	5
Cu	324.7	1.2	2	air/C_2H_2	45	5
Zn	213.8	0.5	2	air/C_2H_2	45	4
Cd	228.8	1.2	2	air/C_2H_2	45	4
Pb	217.0 283.3	1.2	4	air/C_2H_2	60	6

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 3σ or 9σ 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 the DIN ISO 11047 norm. 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 strongly reduced or non-existent in the nitrous oxide-acetylene flame. Regarding 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% (w/w)).

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

Element	Wavelength [nm]	LOD [mg L^{-1}]	LOQ [mg L^{-1}]
Cr	357	0.012	0.036
Mn	279	0.0046	0.014
Co	240	0.011	0.033
Ni	232	0.0063	0.019
Cu	324	0.0042	0.013
Zn	213	0.0019	0.0058
Cd	228	0.0045	0.014
Pb	217 283	0.063 0.036	0.19 0.11

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^{-1}]		Target value [mg kg^{-1}]	
NCSDC 73326	Cr	1	54	C_2H_2-air	36.5	±0.61	68	±6
			105	C_2H_2-N_2O	72.0	±0.36		
	Mn	2	86	C_2H_2-air	560	±2.2	650	±23
			98	C_2H_2-N_2O	637	±4		
	Co	1	89	C_2H_2-air	11.3	±0.17	12.7	±1.1
	Ni	1	97	C_2H_2-air	30.6	±0.32	31.5	±1.8
	Cu	1	90	C_2H_2-air	21.8	±0.13	24.3	±1.2
	Zn	5	92	C_2H_2-air	62.7	±0.22	68	±4
	Cd	1		C_2H_2-air	< LOQ		0.13	±0.02
	Pb	1		C_2H_2-air	< LOQ		21	±2
BAM-U110	Cr	1	97	C_2H_2-air	184	±0.73	190	±9
			109	C_2H_2-N_2O	207	±1.4		
	Mn	2	88	C_2H_2-air	512	±1	580	±19
			97	C_2H_2-N_2O	563	±1.2		
	Co	1	94	C_2H_2-air	13.6	±1.1	14.5	±0.8
	Ni	1	96	C_2H_2-air	91.7	±1.4	95.6	±4
	Cu	1	100	C_2H_2-air	262	±2.5	262	±9
	Zn	10	96	C_2H_2-air	954	±4.5	990	±40
	Cd	1	95	C_2H_2-air	6.65	±0.013	7	±0.4
	Pb	1	103	C_2H_2-air	191	±0.93	185	±8

LOQ: Limit of quantification

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 novAA 800F. Thanks to the novAA 800 F's eight-lamp changer, a fully automatic, cost-effective and convenient routine determination of the analytes can be realized. The automatic and intelligent dilution of the AS-FD autosampler make sample analysis fast and easy.

Figure 1: novAA 800 F

Recommended device configuration

Table 7: Overview of devices, accessories, and consumables

Article	Article number	Description
novAA 800 F - Flame AAS	812-08000-2	Flame atomic absorption spectrometer
AS-FD	810-60501-0	Autosampler for flame mode with dilution function
Burner head 50 mm	810-60057-0	Burner head for the air-acetylene and N_2O-acetylene flame
Scraper	812-08000-2	Automatic burner head cleaner for the N_2O acetylene flame
Cr-HCL	480-450.012C	Hollow cathode lamp chrome (Cr) equipped with RFID chip
Mn-HCL	480-450.032C	Hollow cathode lamp manganese (Mn) equipped with RFID chip
Co-HCL	480-450.013C	Hollow cathode lamp cobalt (Co) equipped with RFID chip
Ni-HCL	480-450.036C	Hollow cathode lamp nickel (Ni) equipped with RFID chip
Cu-HCL	480-450.014C	Hollow cathode lamp cupper (Cu) equipped with RFID chip
Zn-HCL	480-450.067C	Hollow cathode lamp zinc (Zn) equipped with RFID chip
Cd-HCL	480-450.008C	Hollow cathode lamp cadmium (Cd) equipped with RFID chip
Pb-HCL	480-450.028C	Hollow cathode lamp lead (Pb) equipped with RFID chip

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)

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.
Trademark notice: The brand names of the third-party products specified in the application note are usually registered trademarks of the respective companies or organizations.

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.0 · Author: HoSi
en · 08/2024
© Analytik Jena GmbH+Co. KG | Picture p. 1 ©: Unsplash/Reba Spike