



Challenge

Fast multi-element method for varying element concentration in complex sample matrices

Solution

Fully automated fast-sequential analysis with contrAA 800 F combined with autosampler AS-FD

Determination of the Metal Content in Mining Samples using contrAA 800 F

Introduction

The determination of main and trace elements in samples of the mining industry is of utmost importance. Thus, the composition of the extracted ores is essential to define the strategy of the further mining process. Chemical additives, required for the subsequent ore treatment, need to be analyzed in the scope of process monitoring and the generated slag also is subject to regular inspections. This leads to a high number of samples to be analyzed for a multitude of parameters.

These samples have strongly varying element concentrations in a complex sample matrix and require a robust analysis technique, which allows a fast, simple, and precise determination of a large number of elements. Therefore, the contrAA 800 F using High-Resolution Continuum Source Atomic Absorption Spectroscopy (HR-CS AAS) in combination with a sophisticated autosampler offers an efficient analysis technique for the determination of metals in samples of the mining industry. It makes it an appropriate alternative to ICP-OES.

Due to the lower numbers of occurring lines using the atomic absorption spectrometry in comparison to the ICP-OES techniques, spectral overlays and therefore the need of spectral correction methods can be minimized and matrix adaption of the used calibration standards can often be skipped. The use of a functional autosampler enables the fully automatic preparation of calibration standards from a multi-element stock solution and an automatic and customizable dilution of the samples.

Using the fast-sequential flame mode, which is described in the following application examples, the determination of the elements Ag, As, Co, Cu, Fe, Mn, Ni, Pb, and Zn can be applied in multi-element methods. The measurement time is thus three to four times faster compared to a line source AAS.

Materials and Methods

Samples and reagents

Ore reference materials of different composition, provided by GEOSTATS PTY LTD, Australia:

- GBM306-8 Oxide transition copper material
- GEM 310-15 Copper concentrate
- GBM398-4 Low grade Cu/Fe/Zn
- GBM 900-3 Sulfide ore
- S 5 Internal laboratory standard
- GBM399-5 Oxide copper ore
- GBM 398-1 Cu/Pb/Zn cap rock
- Mixed stock standard solution 100 mg/L Fe, 40 mg/L Cu, 5 mg/L Zn
- Mixed stock standard solution 20 mg/L As, Co, Mn, Ni, Pb
- Single stock standard solution 10 mg/L Ag

Approximately 0.1 g of each sample was digested with 5 mL nitric acid (65%) in a microwave digestion system. The solutions then were transferred into a volumetric flask of 25 mL and filled to volume with demineralized water.

Instrumentation

In the following, the instrument configuration, settings for analysis and method parameters are listed (see tables 1 and 2). In table 3 the applied flame settings for all determined analytes are summarized.

Table 1: Instrument configuration and material

Parameter	Specification
Device type	contrAA 800 F
Extra equipment	AS-FD, SFS 6.0
Burner type and position	50 mm, 0°
Flame type	Air/acetylene
Integration time	3 s
Evaluation pixel	5

Table 2: Method settings and evaluation parameters for method 1

Element	Wavelength [nm]	Fuel flow [L/h]	Burnerheight [mm]	Background correction
As	193.6960	80	9	IBC ¹
Co	240.7254	50	6	IBC
Mn	279.4817	60	8	IBC
Ni	232.0030	50	6	IBC
Pb	217.0005	55	5	IBC

1... Iterative background correction

Table 3: Method settings and evaluation parameters for method 2

Element	Wavelength [nm]	Fuel flow [L/h]	Burnerheight [mm]	Background correction
Ag	328.0683	70	6	IBC
Cu	327.3960	50	6	IBC
Fe	302.0639	50	6	IBC
Zn	213.8570	40	6	IBC

Calibration

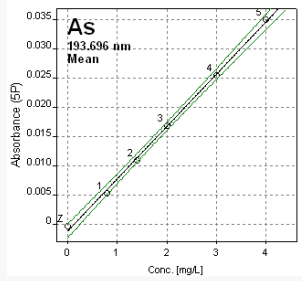
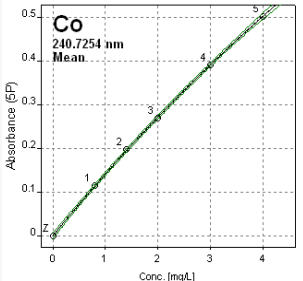
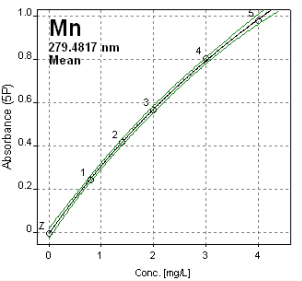
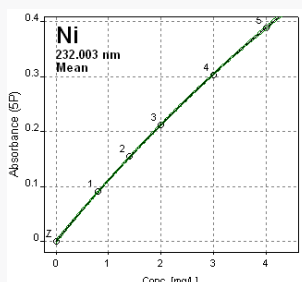
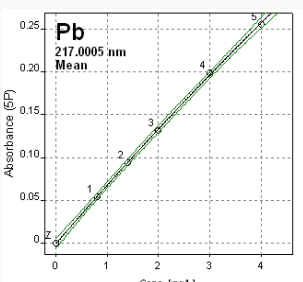
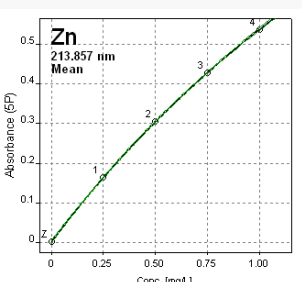
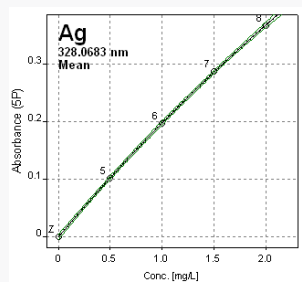
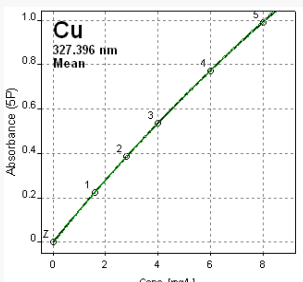
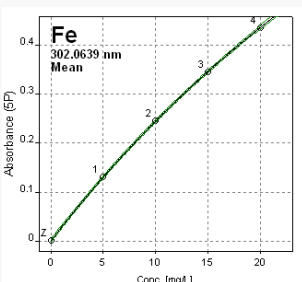
For the determination of As, Co, Mn, Ni, and Pb calibration standards of 0.8, 1.4, 2.0, 3.0, and 4 mg/L (listed in table 4) were automatically prepared by the autosampler from a multi-element solution of 20 mg/L. For the elements Cu, Fe, and Zn four standard solutions were prepared from a multi-element stock solution of 100 mg/L Fe, 40 mg/L Cu, and

5 mg/L Zn. The calibration standards for Ag were prepared from a single-element stock solution containing of 10 mg/L Ag. For all calibration standards and samples three replicate measurements were performed. The resulting calibration curves are shown in table 5.

Table 4: Concentrations of the calibration standards

Standard	Concentration standard 1	Concentration standard 2			Concentration standard 3
	As, Co, Mn, Ni, Pb [mg/L]	Cu [mg/L]	Fe [mg/L]	Zn [mg/L]	Ag [mg/L]
Cal.-Std. 0	0	0	0	0	0
Cal.-Std. 1	0.8	2	5	0.25	0.5
Cal.-Std. 2	1.4	4	10	0.5	1.0
Cal.-Std. 3	2.0	6	15	0.75	1.5
Cal.-Std. 4	3.0	8	20	1.0	2.0
Cal.-Std. 5	4.0	-	-	-	-

Table 5: Resulting calibration functions

As 193.6960 nm	Co 240.7254 nm	Mn 279.4817 nm
		
linear, R^2 (adj.) = 0.998	non-linear, R^2 (adj.) = 0.9997	non-linear, R^2 (adj.) = 0.9996
Ni 232.003 nm	Pb 217.0005 nm	Zn 213.8570 nm
		
non-linear, R^2 (adj.) = 0.9999	non-linear, R^2 (adj.) = 0.9995	non-linear, R^2 (adj.) = 0.9999
Ag 328.0683 nm	Cu 327.3960 nm	Fe 302.0639 nm
		
non-linear, R^2 (adj.) = 0.9999	non-linear, R^2 (adj.) = 0.9992	non-linear, R^2 (adj.) = 0.9999

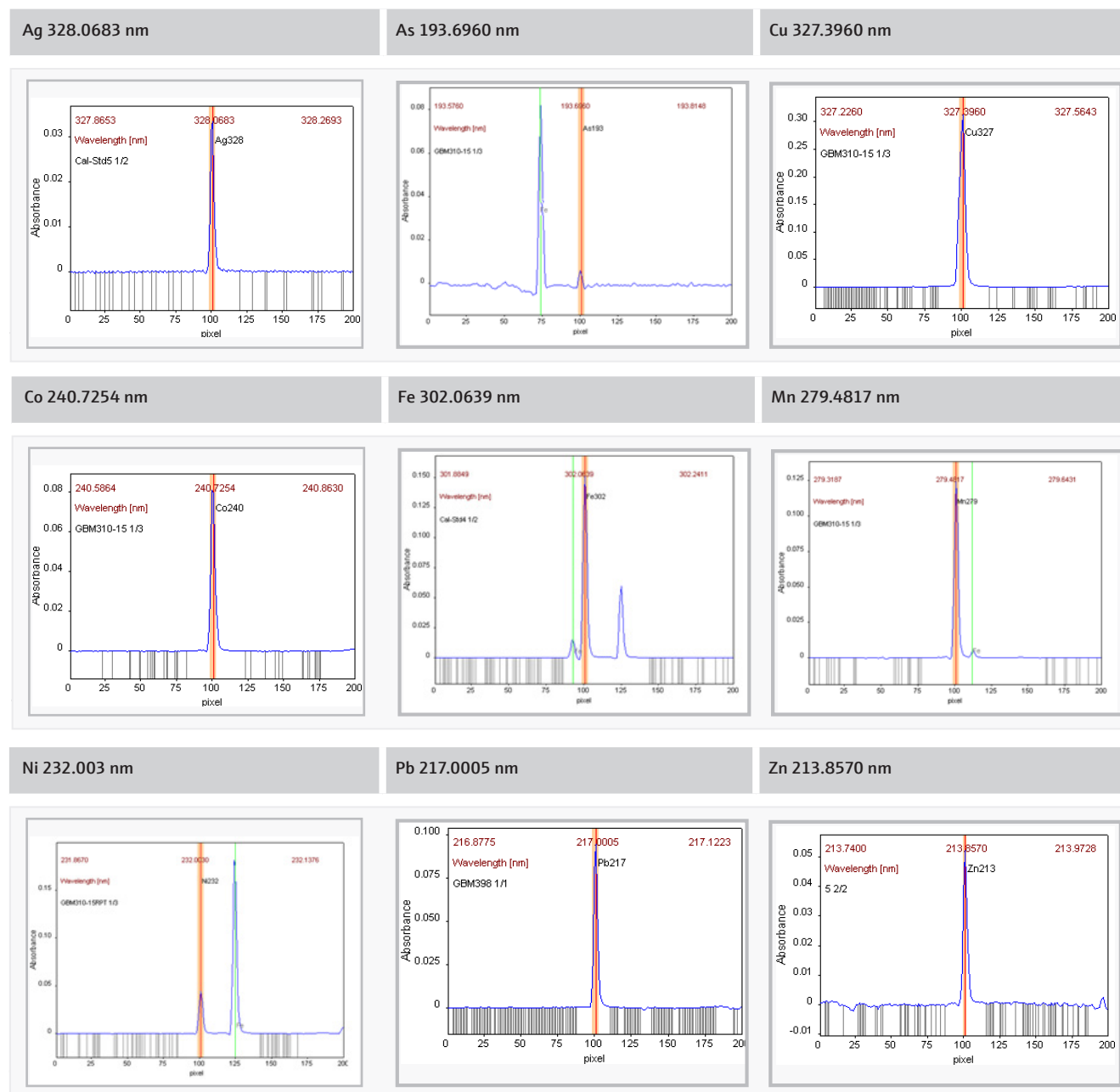
Results and Discussion

Typical signal shapes and spectral vicinity

In the following, characteristic signals and spectra are shown for the applied analysis lines (table 6).

For some of the elements, additional absorption lines are visible in the spectrum next to the resonance line of the analyte. These are mainly caused by iron. However, due to the high resolution of the system, no direct line overlay is observed. Hence the measurement is not spectrally interfered. The software additionally allows a simultaneous evaluation of several analysis lines in the measurement window.

Table 6: Characteristic signal shapes and spectral vicinity of the analyte lines (2D spectrum)



Measurement results

The measurement results for the analyzed samples are listed in table 7. Selected reference materials were quantified. The reference material was selected in terms of the typical concentration of the analytes in mining applications. As a quality control the measured content is compared to the certified value and the recovery rates, also shown in the result table. For an extra quality control of the measurement performed by the contrAA 800 F, a selected sample set was additionally quantified using the ICP-OES PlasmaQuant 9100.

Table 7: Measurement results and recovery rates

Sample	Element	Automatically applied dilution factor	Measured concentration [mg/kg]	RSD [%]	Recovery of certified concentration [%]
GBM306-8* Oxide transition copper material	Co	-	73	0.1	97
	Cu	50	5.58	4.0	95
	Mn	-	552	0.5	not certified
	Ni	3.3	1.08	0.4	98
	Pb	-	399	0.7	102
	Fe	50	70.9	1.5	97
	Zn	50	805	1.1	102
	As	3.3	1.40	0.4	100
GEM 310-15* Copper concentrate	Co	10	614	0.9	not certified
	Cu	166	218	0.5	92
	Mn	-	295	0.1	not certified
	Ni	-	272	0.1	93
	Pb	4.4	3.22	0.5	97
	Fe	50	223	0.4	not certified
	Zn	50	11.3	0.7	99
	Ag	-	75	0.2	98
GBM398-4* Low grade Cu/Pb/Zn From surface with laterite	As	-	646	2.2	not certified
	Co	9.7	1.95	0.2	99
	Cu	50	36.6	0.6	94
	Ni	10	3.97	1.8	98
	Pb	18.9	11.4	0.1	98
	Fe	50	46.3	1.3	97
	Zn	50	5.15	1.0	101
	Ag	-	47	0.5	96
GBM 900-3* Sulfide ore	Co	-	137	0.7	91
	Cu	50	15.1	0.1	91
	Mn	-	458	0.7	not certified
	Ni	39.8	32.9	0.7	96
	Pb	-	857	0.4	98
	Fe	50	56.6	1.4	96
	Zn	50	742	1.6	104
	Ag	-	8.5	0.9	106

Continuation of table 7: Measurement results and recovery rates

Sample	Element	Automatically applied dilution factor	Measured concentration [mg/kg]	RSD [%]	Recovery of certified concentration [%]
S 5 (Values measured by ICP-OES)	Co	25.6	6.45	0.4	96*
	Cu	50	6.18	0.4	95*
	Mn	-	31	0.2	105*
	Ni	66.7	47.8	0.4	97*
	Fe	125	453	0.4	91*
	Ag	-	81.5	1.3	101*
	As	25.4	19.6	1.1	107*
GBM399-5* Oxide copper ore	Co	-	45	1.4	95
	Cu	50	26.3	0.4	89
	Mn	-	270	1.2	-
	Ni	33.6	22.8	0.7	93
	Pb	33.6	21.3	0.5	101
	Fe	50	42.6	0.9	95
	Zn	50	9.21	0.2	97
	Ag	-	24.3	1.0	101
	As	-	302	1.0	94
GBM 398-1* Cu/Pb/Zn cap rock	Co	-	23	1.3	96
	Cu	50	14.0	0.7	95
	Mn	41	18.6	2.3	-
	Ni	15.2	9.00	1.8	95
	Pb	41	26.4	0.2	99
	Fe	50	34.2	2.0	91
	Zn	112	19.8	1.4	98
	Ag	-	6.8	2.2	105

* Reference materials from GEOSTATS PTY LTD, 0A Marsh Close, O'Connor, Western Australia 6163
RSD: Relative standard deviation of 6 measurement replicates

Summary

The accuracy of the measurement using the contrAA 800 F was shown by the quantification of the reference material. A good agreement of the measured values and the target values was reached, also for the additionally performed quality check using ICP-OES for sample S-5. The recovery rates for all reference materials were calculated within a range of 91 to 107%.

The high-resolution continuum source AAS is an easy to use and robust analytical technique for the determination of metals in samples of the mining industry and thus offers an appropriate alternative to classic ICP-OES. Thanks to the absorption spectrometric determination with fewer lines, but excellent optical resolution, spectral interferences are minimized and the effort of spectral corrections is significantly reduced. As flame AAS is far less influenced by high matrix contents than ICP-OES, for most applications a matrix adaption of the calibration standards is not required. The use of an intelligent autosampler allows the individual predilution of the samples as well as an automatic over-range dilution and provides a high degree of automation for routine analysis.



Figure 1: contrAA 800 F

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.

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 · 11/2022

© Analytik Jena | Picture © p.1: Adobe Stock/JT Jeeraphun