



Challenge

Direct analysis of metal alloys for trace and minor elements without sample preparation to minimize time effort and error sources.

Solution

The direct solid sampling technique (solid AA) includes the combination of the graphite furnace AAS contrAA 800 (D/G) with its unique high-resolution continuum source technique (HR-CS-AAS) by using the solid autosampler SSA 600 for a fully automated sample handling and weighing.

Determination of Trace and Minor Elements in Alloys with solid AA

Introduction

The fields of application for alloys are versatile. For example, they are applied in the automobile industry, in aircraft engines, electric home appliances, power plant generators, and waste incineration plants. During the alloy production the main component (e.g., Ni) is combined with other additives (e.g., Cu, Fe, Cr). At this point, contamination with undesirable elements result in a deterioration of the material properties. To ensure the purity and quality of alloy material, regular and reliable monitoring is mandatory.

Liquid analysis techniques usually require a time-consuming sample preparation procedure, using additional reagents and laboratory equipment. The resulting challenges, like high sample dilution, possible contamination effects, and increased error potential in general, make trace element analysis particularly difficult. Therefore, direct analysis techniques for solid samples are beneficial. Widely spread and established direct analysis techniques in the metal industry, such as XRF spectroscopy or spark emission spectroscopy, can reach their limits in terms of sensitivity for trace element analysis in the $\mu\text{g}/\text{kg}$ range and are also prone to interferences.

Using solid AA, a direct solid sampling by the autosampler SSA 600 combined with graphite furnace AAS, metal chips can be measured without time-consuming preparation. solid AA provides a direct and easy to handle technique for the determination of trace and minor elements in alloy shavings without further preparation steps. Since there is no sample dilution based on dissolution or digestion, trace elements can be determined with highest sensitivity. In addition, the analysis can be performed with a low sample material consumption in the lower milligram range. The contrAA 800 series with its unique high-resolution continuum source technique (HR-CS AAS) offers additional advantages and increases the analytical performance for complex sample matrices.

This application note is focused on the analysis of nickel-based alloys. However, other metal materials, such as copper, can be analyzed as well under comparable conditions and by using appropriate calibration material.

Materials and Methods

Samples and reagents

The sample material was submitted in the form of alloy shavings, which were directly used for the measurement without further pre-treatment. These shavings provided a sufficient homogeneity, and no further sample preparation was necessary. The shredding level of the sample material influences the reproducibility of the measurements. Only a low sample amount of approx. 0.5–3 mg was dosed on the sample boats. Additional reagents like matrix modifiers were not used for analysis.

Instrumentation

The following measurements were performed with the contrAA 800 D/G graphite furnace AAS in combination with the solid autosampler SSA 600 for a fully automated sample introduction. The samples are dosed on pyrolytically coated graphite platforms on a sample tray, the transport into the graphite furnace is fully automated. The addition of liquids, e.g., modifier solutions, can be done automatically by the included liquid dosing unit.

The instrument configuration, settings for analysis and method parameters are listed below (tables 1 and 2).

Figure 1 shows an example of a temperature program with all required heating steps. In table 3 the applied temperature program steps for all determined analytes are summarized.

Table 1: Instrument configuration and material

Parameter	Specification
Instrument	contrAA 800 D/G
Autosampler	SSA 600
Graphite tube type	Solid tube (pyrolytically coated graphite)
Sample carrier	Solid platform (pyrolytically coated graphite)

Table 2: Method settings and evaluation parameters

Element	Wavelength [nm]	Evaluation pixels	Measuring time [s]	Modifier	Background correction
Ag	206.1170	3	5	none	IBC
As	197.1970	3	8	none	IBC, CSI
Bi	223.0608	3	5	none	IBC
Cd	326.1055	3	5	none	IBC
Cu	221.4580	3	8	none	IBC
Mg	202.5850	3	6	none	IBC
Pb	283.3060	3	6	none	IBC
Sb	259.8050	3	9	none	IBC
Sn	326.2340	3	9	none	IBC
Te	225.9020	3	6	none	IBC
Tl	223.7800	3	4	none	IBC

IBC: Iterative baseline correction, CSI: Correction of spectral interferences

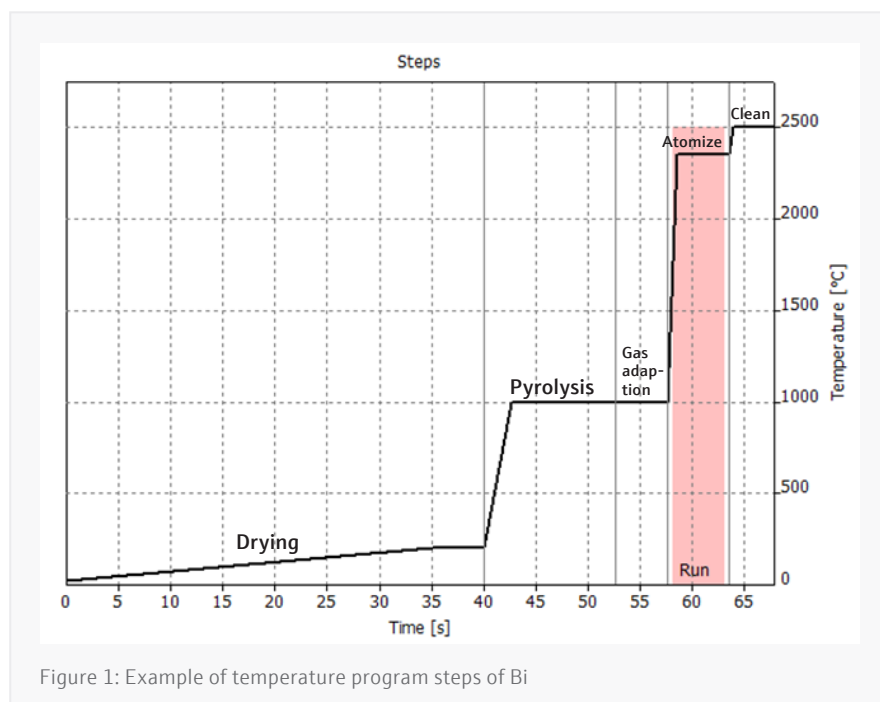


Table 3: Summary of furnace program steps for all analyzed elements

Step No.	Step name	Element	Temperature [°C]	Ramp [°C/s]	Hold time [s]	Purge gas (Argon)
1	Drying	All analytes	200	5	5	Max
2	Pyrolysis	Ag	950	300	10	Max
		As, Bi, Pb	1,000	300	10	Max
		Cd, Te	950	300	10	Max
		Cu, Sb	1,100	300	10	Max
		Mg	900	300	10	Max
		Sn	1,150	300	10	Max
		Tl	750	300	10	Max
		3	Gas adaption	Ag, Cd, Te	950	0
As	1,000			0	5	Min
As, Bi, Pb	1,000			0	5	Stop
Cu, Sb	1,100			0	5	Stop
Mg	900			0	5	Min
Sn	1,150			0	5	Stop
Tl	750			0	5	Stop

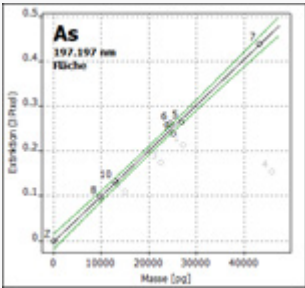
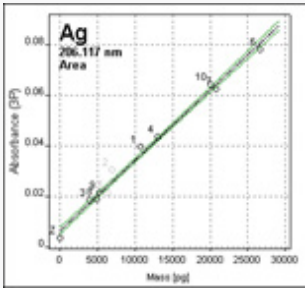
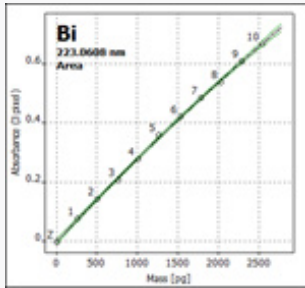
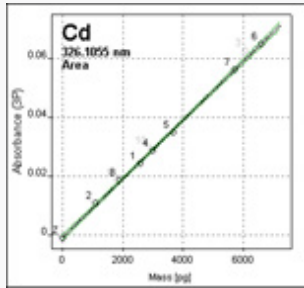
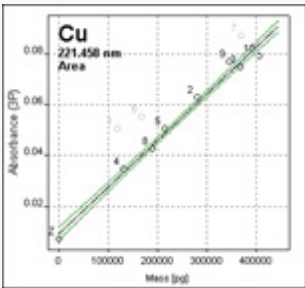
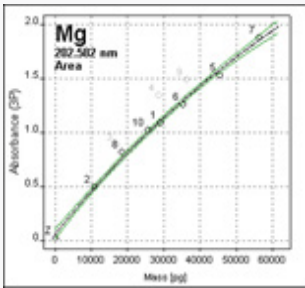
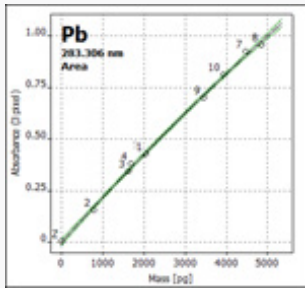
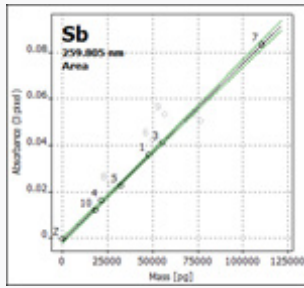
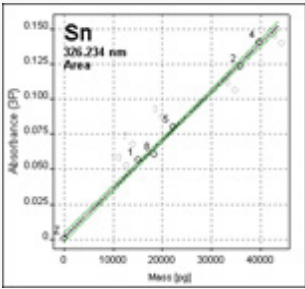
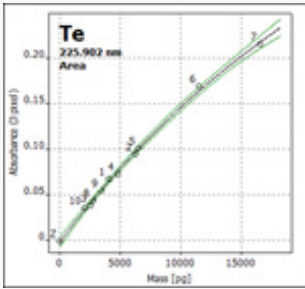
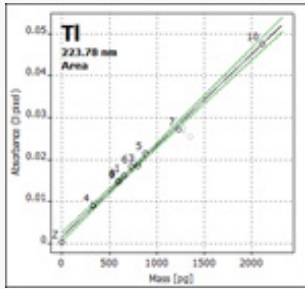
Continuation of table 3: Summary of furnace program steps for all analyzed elements

Step No.	Step name	Element	Temperature [°C]	Ramp [°C/s]	Hold time [s]	Purge gas (Argon)
4	Atomization	Ag	2,450	1,200	5	Stop
		As	2,500	1,200	8	Min
		Bi, Pb	2,350	1,500	5	Stop
		Cd	2,100	1,200	5	Stop
		Cu	2,600	1,200	8	Stop
		Mg	2,500	1,200	6	Min
		Sb	2,550	1,200	8	Stop
		Sn	2,550	1,000	9	Stop
		Te	2,300	1,200	5	Stop
		Tl	2,000	1,200	5	Stop
		5	Clean	Ag, Bi, Pb	2,500	500
Cd, Te, Tl	2,400			500	4	Max
Cu	2,650			500	4	Max
As, Mg	2,550			500	4	Max
Sb, Sn	2,600			500	4	Max

Calibration

A matrix-matched calibration was performed by measuring various weights of available solid reference materials ("Stock material", shredded nickel alloy shavings) with known.

Table 4: Calibration stock material, applied weights for calibration, and resulting calibration functions

As	Ag	Bi	Cd
 <p>Stock material ALLOY 2 with 42 mg/kg As Applied weights 0.2–1 mg linear, $R^2(\text{adj.}) = 0.995$</p>	 <p>Stock material ALLOY STD 2 with 2.5 mg/kg Ag Applied weights 1.5–10 mg linear, $R^2(\text{adj.}) = 0.997$</p>	 <p>Stock material ALLOY STD 4 with 0.25 mg/kg Bi Applied weights 1–10 mg non-linear, $R^2(\text{adj.}) = 0.999$</p>	 <p>Stock material ALLOY 2 with 1.9 mg/kg Cd Applied weights 0.5–3.5 mg linear, $R^2(\text{adj.}) = 0.999$</p>
Cu	Mg	Pb	Sb
 <p>Stock material ALLOY 1 with 100 mg/kg Cu Applied weights 1.1–4 mg linear, $R^2(\text{adj.}) = 0.996$</p>	 <p>Stock material ALLOY 2 with 26 mg/kg Mg Applied weights 0.4–1.7 mg non-linear, $R^2(\text{adj.}) = 0.997$</p>	 <p>Stock material 898 Tracealloy B with 2.5 mg/kg Pb Applied weights 0.3–2 mg non-linear, $R^2(\text{adj.}) = 0.997$</p>	 <p>Stock material ALLOY 3 with 45 mg/kg Sb Applied weights 0.4–2.4 mg linear, $R^2(\text{adj.}) = 0.999$</p>
Sn	Te	Tl	
 <p>Stock material ALLOY STD 3 with 12 mg/kg Sn Applied weights 1–3.7 mg linear, $R^2(\text{adj.}) = 0.997$</p>	 <p>Stock material ALLOY 1 with 4.4 mg/kg Te Applied weights 0.4–3.8 mg non-linear, $R^2(\text{adj.}) = 0.997$</p>	 <p>Stock material ALLOY STD 2 with 0.9 mg/kg Tl Applied weights 0.6–2.3 mg linear, $R^2(\text{adj.}) = 0.997$</p>	

Results and Discussion

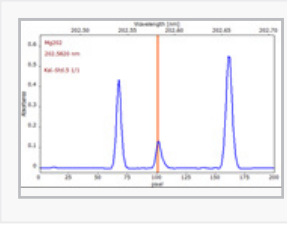
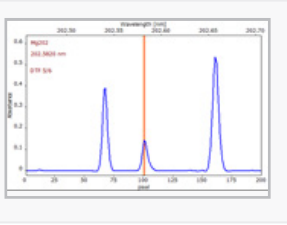
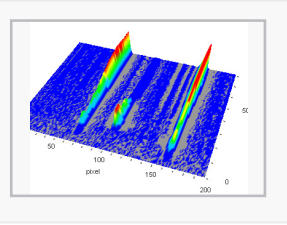
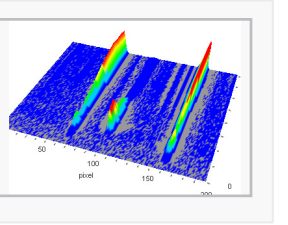
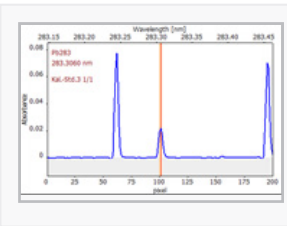
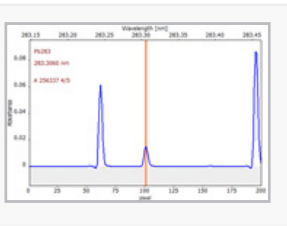
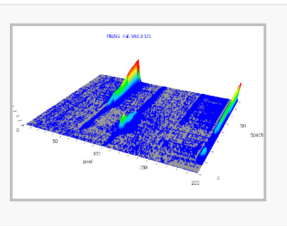
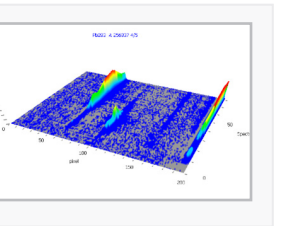
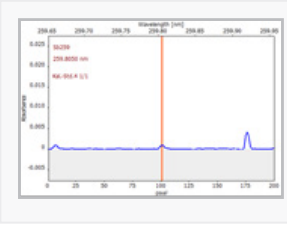
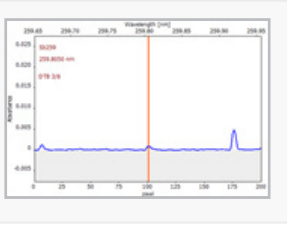
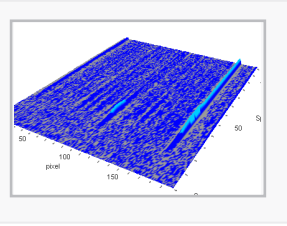
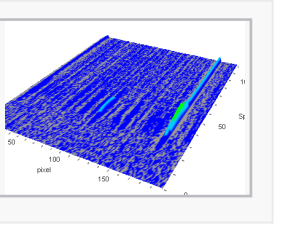
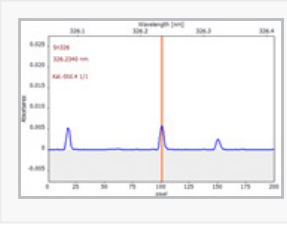
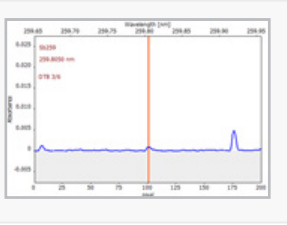
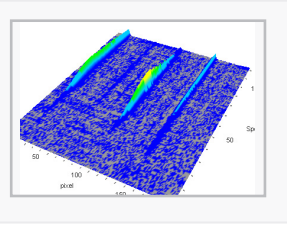
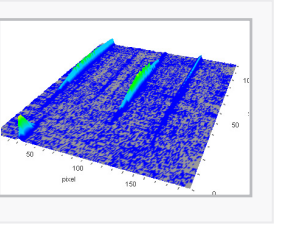
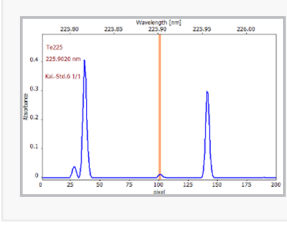
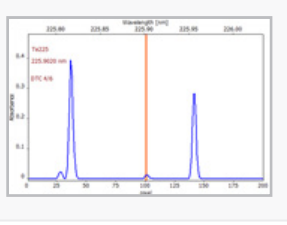
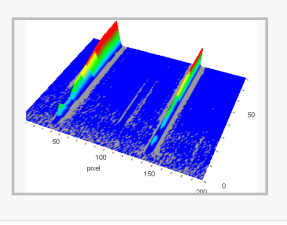
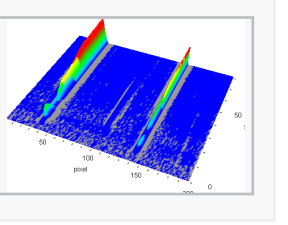
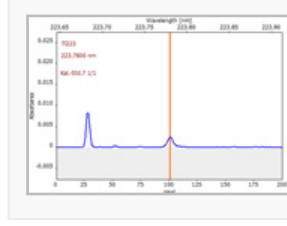
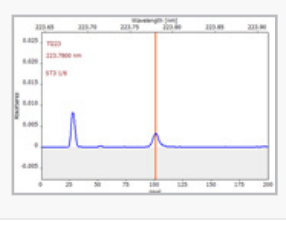
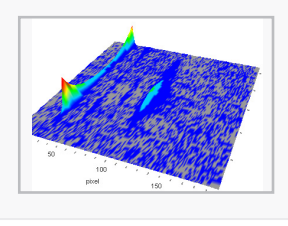
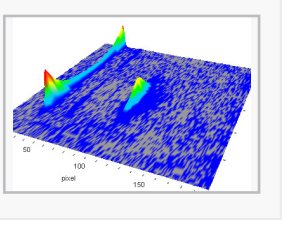
Typical signal shapes and spectral vicinity

In the following, characteristic spectra in 2D and 3D are shown for the applied analysis lines (table 5).

Table 5: Characteristic signal shapes and spectral vicinity of the analyte lines

Element	2D spectrum		3D spectrum	
	Calibration Stock	Sample	Calibration Stock	Sample
As	24.6 ng As	"ALLOY 3"	24.6 ng As	"ALLOY 3"
Ag	3,893 pg Ag	"ALLOY 3"	3,893 pg Ag	"ALLOY 3"
Bi	1,012 pg Bi	"ALLOY 6"	1,012 pg Bi	"ALLOY 6"
Cd	3,648 pg Cd	"ALLOY 3"	3,648 pg Cd	"ALLOY 3"
Cu	214.9 ng Cu	"ALLOY 2"	214.9 ng Cu	"ALLOY 2"

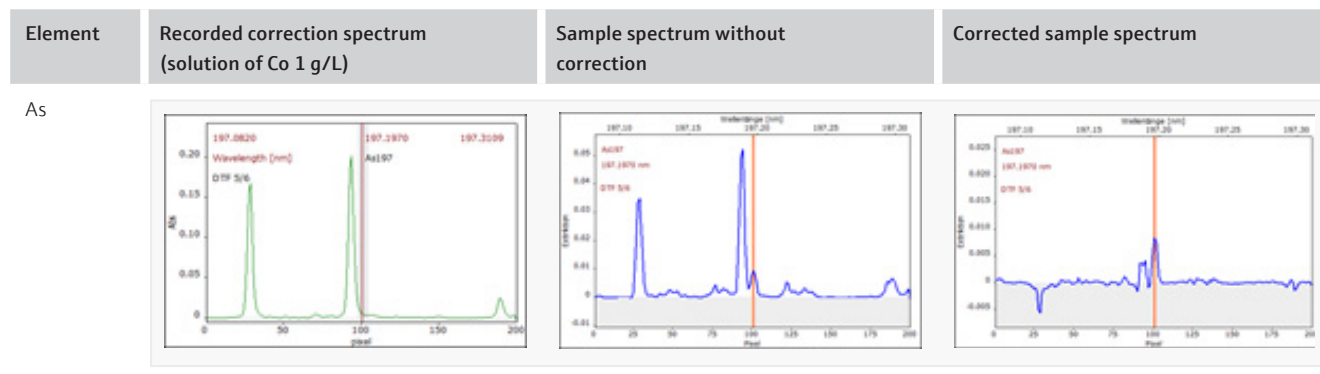
Continuation of table 5: Characteristic signal shapes and spectral vicinity of the analyte lines

Element	2D spectrum		3D spectrum	
	Calibration Stock	Sample	Calibration Stock	Sample
Mg	45.2 ng Mg	"ALLOY 3"	45.2 ng Mg	"ALLOY 3"
				
Pb	1,620 pg Pb	"ALLOY 6"	1,620 pg Pb	"ALLOY 6"
				
Sb	21.5 ng Sb	"ALLOY 1"	21.5 ng Sb	"ALLOY 1"
				
Sn	39.8 ng Sn	"ALLOY 2"	39.8 ng Sn	"ALLOY 2"
				
Te	11.5 ng Te	"ALLOY 2"	11.5 ng Te	"ALLOY 2"
				
Tl	1,230 pg Tl	"ST 3"	1,230 pg Tl	"ST 3"
				

CSI – Correction of spectral interferences

Matrix related molecule bands or distinct atomic absorption peaks can lead to a partial or direct overlap of the analyte line and falsely high results. These spectral interferences can be minimized or compensated using the software integrated CSI tool (Correction of Spectral Interferences), which works with a mathematical algorithm called LSBC (“Least Squares Background Correction”). For this purpose, one or more reference spectra of interfering matrix compounds are recorded. Subsequently, the reference spectra are subtracted from the sample spectrum (correction model). Thus, the structured background is reduced. Once created, the correction model can be implemented into the method and is applied automatically when needed. Table 6 shows the correction model and its effect on the analyte peak of the arsenic line at 197.1970 nm, which is partially overlapped by an adjacent atomic line of cobalt.

Table 6: Spectral correction of As197 with cobalt (CSI correction model)



Green: correction spectrum of interferent (Co 1 g/L), Blue: analyte spectrum

Measurement results

The measurement results of the analyzed samples are listed in table 7. Reference material with a given analyte concentration (target value) was measured as a quality control.

Table 7: Measurement results

Sample	Element	Target value (Ref. material) [mg/kg]	Measured concentration [mg/kg]	RSD (n=6) [%]	Sample	Element	Target value (Ref. material) [mg/kg]	Measured concentration [mg/kg]	RSD (n=6) [%]
	As	23	26.7	18.9		Cu	-	129	11.2
	Ag	-	2.0	7.3	ALLOY 3	Mg	-	39.2	13.1
	Cd	-	0.94	3.7		Sn	-	35.2	21.5
ALLOY 1	Mg	-	16.8	10.5	ALLOY 4	Bi	-	< LOQ	-
	Sb	10	15.8	18.9		Pb	-	0.079	19.8
	Sn	-	13.9	20.5	ALLOY 5	Bi	-	1.07	9.0
	Te	8	8.97	6.1		Pb	-	1.33	8.8
	Ag	-	3.44	11.4	ALLOY 6	Bi	-	0.344	4.8
	Cu	-	121	12.0		Pb	-	0.443	3.4
ALLOY 2	Sb	20	26.3	15.5		Bi	1.0	1.02	16.3
	Sn	-	22.2	13.7	ALLOY STD 1	Pb	1.0	1.15	4.5
	Te	18	18.1	6.4		Sn	8.0	7.79	19.9
	As	70	66.7	15.5	ALLOY STD 2	Pb	2.5	2.74	2.7
ALLOY 3	Ag	-	8.78	8.1		Ag	1.0	1.13	12.4
	Cd	-	1.91	2.6	ALLOY STD 3	Tl	2	2.72	4.0

RSD: Relative standard deviation of six measurement replicates

In table 8 the limits of detection (LOD) and limits of quantification (LOQ), which were determined by using the blank method (3- or 9-fold standard deviation of 11 measurement replicates of an empty sample boat), are listed for the applied analytical lines and measurement conditions. The values are given in total mass (ng) and calculated for an average sample weight of 1.0 mg ($\mu\text{g}/\text{kg}$). For Ag, Cd, Cu, Mg, Sb, Sn, Te, and Tl insensitive lines have been selected due to the high analyte concentration in the samples. By using sensitive primary lines, LOD/LOQ values in the low $\mu\text{g}/\text{kg}$ range can be achieved.

Table 8: Limits of detection and limits of quantification for the applied wavelengths

Element	Analyte line [nm]	Total mass [ng]		Mass fraction for 1 mg sample weight [$\mu\text{g}/\text{kg}$]	
		LOD	LOQ	LOD	LOQ
As	197.1970	0.056	0.17	56	170
Ag	206.1170	0.46	1.38	460	1,380
Bi	223.0608	0.37	1.11	370	1,110
Cd	326.1055	0.13	0.39	130	390
Cu	221.4580	4.9	14.7	4,900	14,700
Mg	202.5850	1.3	3.9	1,300	3,900
Pb	283.3060	0.03	0.09	30	90
Sb	259.8050	2.6	7.8	2,600	7,800
Sn	326.2340	0.64	1.9	640	1,900
Te	225.9020	0.43	1.3	430	1,300
Tl	223.7800	0.08	0.24	80	240

Conclusion

Direct analysis techniques are preferred for analysis of solid samples, since they have significant advantages in terms of time efficiency and use of additional chemicals.

By using the high-resolution atomic absorption spectrometer (HR-CS AAS) contrAA 800 D/G all absorption lines of an element in the spectral range of 185–900 nm are accessible due to a xenon short-arc lamp as a continuum light source. The spectral background is corrected directly on the analysis line, simultaneously and independently of the applied wavelength, thus simplifying the development of the method and selection of suitable lines.

In combination with the solid AA option, elements can be determined by running a fast and short furnace program, using a matrix-matched calibration with reference material similar to the sample matrix. For the measurements carried out for this application note, additional reference materials with given target concentrations of the analytes were analyzed to verify the accuracy of the methodology.

The measurement results of the reference samples are in the range of the target values. Thus, the suitability and analytical possibilities of using the solid AA technique for analysis of the observed elements in nickel-based alloys could be demonstrated. The high detection performance of the solid AA technique allows for using insensitive absorption lines for some elements. The spectral vicinity of the analytical lines shows further atomic absorption peaks, caused by other matrix components (see table 5). Due to the high resolution of the spectrometer these peaks are separated from the analysis line. Thus, there are no significant spectral interferences detectable for the performed measurements. A partial spectral overlapping of the applied arsenic line by cobalt could be compensated by using the CSI software tool.

The low sample amount (approx. 0.5–3 mg), dosed on the sample boats, places high demands on the homogeneity of the sample material. For this reason, the RSD values using solid AA are usually higher compared to liquid techniques. Hence, a higher number of measurement replicates (at least five) for each sample is recommended. The reproducibility can be improved by a finer shredding of the metal shavings.

The solid AA technique is recommended for an analysis task with moderate sample throughput of up to four or five elements with up to 15 samples per day. With its high sensitivity for trace element impurities solid AA can be seen as a proven method complementary to the already established direct analysis techniques.



Figure 2: Automatic solid sampler SSA 600

Headquarters