Challenge

Direct elemental analysis of nickel metal alloys without acid digestion

Solution

ICP-MS coupled with Laser Ablation including comparison of wet and dry plasma performance

Analysis of Nickel Metal Alloys using LA-ICP-MS

Introduction

The coupling of ICP-MS, mass spectrometry with inductively coupled plasma and laser ablation allows the characterization of solid samples without digestion or other sample preparation procedures. This work evaluates the suitability of this technique for the characterization of trace element concentrations in metal alloys.

The quality control of metal alloys with laser ablation requires large spot sizes to quantify the average trace element concentration in the bulk sample. The aim of this analysis is the method development for the characterization of trace element concentrations in alloys using LA-ICP-MS with focus on calibration strategies.

The analysis was concentrated on elements that require lowest possible detection limits that for now cannot be ensured with complementary techniques. Main focus was put on elements like As, Se, Ag, Sb, Te, Tl, Pb, Bi as well as Ca and Mg. Additional elements were included to show the capability of the method for a simultaneous analysis of more elements.

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Instrumentation

All analyses were performed with a Teledyne CETAC LSX213 laser ablation system coupled to an Analytik Jena PlasmaQuant® MS, ICP-MS. The PlasmaQuant® MS, ICP-MS is equipped with a new solid state RF generator that creates a robust and powerful plasma for the complete ionization of laser generated particles. With a plasma gas flow of less than 10L/min stable plasma conditions are obtained. The standard sheath gas flow can be used to add Argon to the Helium carrier gas if not already mixed in the laser ablation system.

The laser ablation system was equipped with a HelEx ablation cell, a two volume cell with an open sample holder. Thus 5 to 6 samples, fusion tablet with diameter of 3 cm can be analyzed at one time. The analysis conditions are summarized in table 2. Each ablation was combined with a pre-ablation to polish/clean and to even the surface. With that a homogeneous sample removal and reproducible signals were obtained.

Table 1: PlasmaQuant® MS operating conditions

Parameter	Settings
Plasma Gas Flow	9.0 L/min
Auxiliary Gas Flow	1.35 L/min
Nebulizer Gas Flow	1.00 L/min
iCRC Gas Setting	H_2
Plasma RF Power	1.45 KW
Dwell Time	20 ms
Scans per Replicate	10 (peak hopping, 1pt/peak)
No. of replicates	4
Ion Optics	Auto-optimized

Table 2: Ablation conditions

Parameter	Preablation	Ablation & data acquisition
Energie density	7 J/cm² (80% Laser energy)	7 J/cm² (80% Laser energy)
Frequency	10 Hz	10 Hz
Spot size ø	180 µm	150 µm
Line ablation length	2 mm	2 mm
Scan speed	180 µm/sec	30 µm/sec
He carrier gas	0.7 L/min	0.7 L/min

Samples and Reagents

Sample Preparation

The certified reference materials were available in form of chips as well as compact blocks. The samples are compact fused tablets. The compact samples can be placed in the ablation chamber of the laser system without special mounting. The chips were mounted on a microscope slide (Figure 1).

Table 3: Certified reference materials for calibration and quality control

Standard	Description	Nickel concentration	Form
BAS 345 / 346	Nickel Alloy IN100	60%	chips and block
IARM 188A / 189A	High purity Nickel, low and medium levels added	99+%	compact block
NIST 1249	Ni-Cr-Fe-Nb-Mo Alloy	53.29%	compact block
NCS HC 11525 - 11529	Ni-Cr-Al-Mo-Nb-Ti Alloy	54%	chips

Method

The PlasmaQuant® MS allows a flexible sample introduction for laser ablation applications. The carrier gas that transports the sample from the laser ablation system to the ICP-MS (typically Helium) can be mixed with Argon using the default sheath gas adapter to ensure stable ionization conditions.

In addition a liquid aerosol can be added using the conventional nebulization. With this the ionization conditions in the ICP are more similar to liquid samples and are homogenized for different elements. Furthermore this setup allows the addition of liquid standards in varying concentrations for many elements. This can be used as a method for standard addition calibration for the matrix independent calibration of solid samples.

All three calibration strategies were investigated – Ionization of dry aerosol from the laser ablation, addition of liquid aerosol like ultrapure water as well as standard addition with liquid calibration standards and different concentration level.

The removal of material using laser ablation is highly depending on the laser-material-interaction. Hereby parameters like energy density and laser pulse frequency need to be carefully optimized. Furthermore the interaction is influenced by the sample material itself. As a result different sample compositions lead to different sample ablation and removal of material. As a measure for the different ablation conditions and as a parameter to correct for the differences, Nickel was used as internal standard. Differences in the ablation and the amount of material removed can be seen and normalized to the calibration standards. Especially the ablation of chips can be controlled very well since differences in the sample height lead to different focus points and signal variations due to different focus/defocus of the laser beam. The simultaneous nebulization of liquid aerosol allows a sample independent calibration and the addition of external standards to control the stability of the ICP-MS.

The calibration of the method was performed using three different approaches:
1. Calibration with certified standards (BAS345/346 und NIST1249)
2. Calibration with certified standards and simultaneous addition of liquid aerosol (H_2O)
3. Calibration with liquid multi-element standards and simultaneous ablation of BAS346 – standard addition (1/10/20 µm/L)

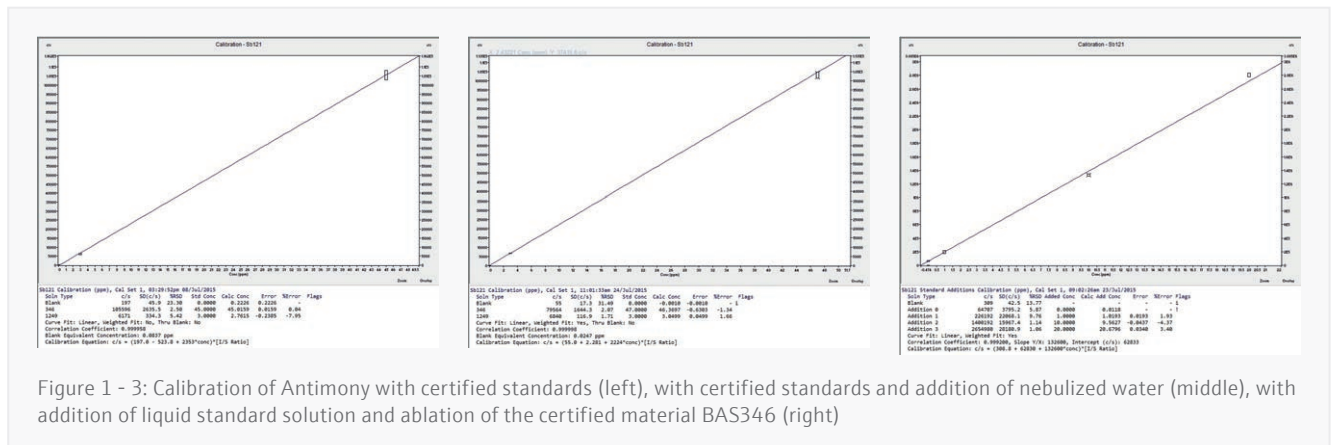**Example for the calibration of Antimony for the three different approaches**

Figure 1 - 3: Calibration of Antimony with certified standards (left), with certified standards and addition of nebulized water (middle), with addition of liquid standard solution and ablation of the certified material BAS346 (right)

1. For the calibration with sample aerosol from the laser ablation only – the carrier gas Helium was mixed with Argon prior to the ICP to ensure stable ionization conditions.
2. In the second method – nebulized water was added to this argon gas to generate a ,wet' plasma with similar conditions to the analysis of liquid samples. Recent publications found that the ionization zone for different elements is much larger in a dry plasma. This means that elements are ionized at different positions in the plasma. The addition of nebulized water minimizes this effect drastically. In addition this sample introduction allows the simultaneous nebulization of an external standard to control the stability of the ICP-MS. The ablation process can be controlled by using e.g. Nickel as internal standard for the method.
3. The nebulization of multi-element calibration standards with simultaneous ablation of a reference material can be used as a standard addition calibration. This allows the analysis of elements that are not certified in the solid standard. The calibration is performed in the following way:
    I. Blank – nebulized water + 1 %v/v HNO_3 without ablation
    II. Addition 0 – nebulized water + v/v HNO_3 and simultaneous ablation of solid calibration standard
    III. Addition 1-x – nebulized multi-element standard in different concentrations and simultaneous ablation of solid calibration standard

Results and Discussion

Good results were obtained with the direct calibration of solid reference samples and subsequent analysis of unknown samples with and without addition of nebulized aerosol. The calibration using nebulized multi-element solutions needs to be further investigated, however the results are in good agreement with certified concentrations and elements that are not certified could be quantified as well.

Table 4: Results for the CRM after 20 samples, calibrated with solid reference materials (approach 1)

µg/g	As	Se	Ag	Sb	Te	Tl	Pb	Bi	Ga	Sn
IARM 188A	<0.2	1.08	0.79	1.3	1.07	1.2	2.01	1.25	0.3	0.8
IARM 189A	<0.2	1.27	1.19	1.8	1.6	1.8	3.6	3.08	0.47	1.7
BAS 345	0.29	1.33	0.38	0.94	<0.1	<0.1	0.23	<0.1	-	-
BAS 346	42.8	2.6	53.1	35.1	2.61	1.8	20.2	8.5	-	-

The Table 4 summarizes the results obtained for the CRM after 20 real samples calibrated with solid reference materials. Nickel was used as internal standard to correct for differences in the ablation behavior.
Most elements show a good match within 10 % of the certified mean. Only Ag, Se and Sb show a difference of more than 10 %. Especially the IARM standards show more deviation from the certified numbers. This is related to the matrix difference. The IARM standards are made of pure Nickel – the calibration was performed with materials that contain 54 – 60 % Nickel. Here the correction with Ni as internal standard is limited.

Table 5: Results for the CRM from 3 analyses of the series, calibrated with solid reference materials in wet plasma (approach 2)

µg/g	As	Se	Ag	Sb	Te	Tl	Pb	Bi
IARM 188A	<0.1	<0.5	0.8 ± 0.36	0.7 ± 0.07	0.2 ± 0.1	0.5 ± 0.09	1.6 ± 0.09	0.3 ± 0.02
IARM 189A	<0.1	<0.5	2.0 ± 0.64	2.3 ± 0.26	0.9 ± 0.53	1.5 ± 0.53	2.3 ± 0.7	0.9 ± 0.16
BAS 345	3.5 ± 0.18	3.4 ± 0.45	0.2 ± 0.03	2.3 ± 0.53	0.2 ± 0.01	0.02 ±0.01	0.3 ±0.02	< 0.1
BAS 346	52.3 ± 2.66	13.2 ± 2.1	37.3 ± 1.69	52.6 ± 1.14	14.1 ± 0.73	1.8 ± 0.7	26.6 ± 3.53	11.9 ± 0.78
NIST 1249	15.5 ± 0.22	0.4 ± 0.1	0.2 ± 0.02	3.3 ± 0.18	0.2 ± 0.04	<0.1	0.2 ±0.01	<0.1

µg/g	Ga	Sn
IARM 188A	<0.1	0.6 ± 0.29
IARM 189A	<0.1	1.4 ± 0.52
BAS 345	7.8 ± 0.44	6.1 ±1.23
BAS 346	53.2 ± 1.75	95.2 ± 3.43
NIST 1249	23.9 ± 0.45	26.7 ± 0.4

After a calibration with solid reference materials and parallel injection of nebulized water, a set of CRM was analyzed 3 times. The results are summarized in table 5. The IARM reference samples show again 40 % lower quantitative results than certified. The BAS 345/346 and the NIST1249 show good agreement within 10 % of the certified range.
As a second set of samples the NCS CRM's were analyzed 3 times. The results in table 6 show good agreement to the certified numbers. The standard deviations typically reflect the certified ranges. Inhomogeneous concentrations between different chips of the same sample were found especially for Se and Sb.

Table 6: Results for CRM from NCS, results are the mean of 3 analyses of the series, calibrated with solid reference materials in wet plasma (approach 2)

µg/g	As	Se	Ag	Sb	Te	Tl	Pb	Bi
NCS HC 11525	6.4± 0.4	18.9 ± 4.9	0.7 ± 0.1	1.2 ± 0.03	21.5 ± 0.4	<0.1	4.9 ± 0.5	0.1 ± 0.02
NCS HC 11526	14.9 ± 1.3	21.6 ± 0.1	0.7 ± 0.1	3.4 ± 0.4	30.9 ± 5.7	0.15 ± 0.02	6.7 ± 1.0	0.2 ± 0.01
NCS HC 11527	96.2 ± 2.5	6.0 ± 2.3	2.4 ± 0.2	15.1 ± 3.3	5.8 ± 1.2	4.3 ± 0.3	7.1 ± 1.6	1.1 ± 0.4
NCS HC 11528	43.5 ± 3.4	3.5 ± 1.1	3.8 ± 0.5	44.2 ± 10.7	2.3 ± 0.6	4.6 ± 0.8	12.4 ± 2.7	1.6 ± 0.4
NCS HC 11529	27.7 ± 2.1	2.9 ± 0.8	5.2 ± 0.4	32.8 ± 4.7	1.6 ± 0.2	1.4 ± 0.4	21.9 ± 6.7	1.6 ± 0.5

µg/g	Ga	Sn
NCS HC 11525	33.6 ± 2.4	4.4 ± 1.0
NCS HC 11526	36.6 ± 0.7	9.5 ± 0.9
NCS HC 11527	40.0 ± 1.5	18.6 ± 3.3
NCS HC 11528	57.6 ± 1.6	39.7 ± 9.7
NCS HC 11529	55.5 ± 1.0	42.4 ± 5.0

A third calibration method was tested where a parallel ablation and calibration with liquid standards was applied. A response factor was calculated to normalize the liquid calibration to the solid reference materials. For the alloys, water was added to ensure stable and constant plasma performance.

Results for CRM after 25 sample analyses are summarized in table 7. Additional elements like Indium, Hafnium and Uranium could be added since the liquid calibration allows for more flexibility and is not limited by the elements certified in the CRM.

Table 7: Results for CRM from NCS, results are the mean of 3 analyses of the series, calibrated with solid reference materials in wet plasma (approach 2)

µg/g	As	Se	Ag	Sb	Te	Tl	Pb	Bi
BAS 346	46.2 ± 1.4	10.3 ± 0.8	31.5 ± 1	46.8 ± 0.7	11.2 ± 0.8	2.2 ± 0.18	23.3 ± 1	9.9 ± 1
NIST 1249	10.4 ± 0.3	< 0.5	3.6 ± 0.2	2.5 ± 0.3	<0.1	0.24 ± 0.03	0.3 ± 0.1	0.12 ± 0.01

µg/g	Ga	Sn	Mg	Zn	In	Hf	U
BAS 346	48.3 ± 0.4	93.4 ± 0.3	139 ± 6	26 ± 1	18 ± 0.2	1.9 ± 0.1	0.24 ± 0.01
NIST 1249	22 ± 0.2	25.8 ± 1	15 ± 2	3.9 ± 0.7	<0.1	0.59 ± 0.1	<0.1

The results for the certified elements are in good agreement with the specified ranges. The results for Indium and Uranium are in the range of the limit of quantification, the concentrations of Hafnium are in the µg/kg (ppb) range.

The analysis of the reference materials at the end of the sequence shows that the replacement of samples with subsequent evacuation and conditioning of the sample chamber with helium had no influence on the stability of the mass spectrometer. This proves furthermore the good long term stability of the ICP-MS.

Many samples were analyzed multiple times at different positions on the sample to avoid a misinterpretation of the results due to inhomogeneous element distribution. The results show that the real samples as well as the reference materials are very homogeneous.

Conclusion

The coupling of laser ablation to ICP-MS is a sensitive and timesaving approach for the characterization of trace element contaminations in alloys.

The high sensitivity and flexible ion optic system allowed for a specific optimization of the PlasmaQuant® MS, ICP-MS for this application. A careful optimization of the method included the evaluation of different calibration strategies. All three strategies tested resulted in good performance and correct results that matched with the certified concentrations of reference materials. Beyond that it was shown that a matrix matched calibration is crucial for correct results. The calibration standards and samples contained 53 to 60 % Nickel. The reference material with 99 % Nickel (IARM188A, 189A) showed a systematic difference for the quantitative results.

The excellent recovery for the CRM after several hours of sample analysis underlines the outstanding plasma robustness and stable performance of the PlasmaQuant® MS.

The experiments show the need for reference materials that are characterized for more elements and contain different concentration ranges. This would lead to further improvements in data quality and validation of the method.