

Analysis of Ni-Alloys (“Super Alloys”) Using Glow Discharge Mass Spectrometry (GD-MS) and Laser Ablation ICP-MS

Meike Hamester, Shona McSheehy, Joachim Hinrichs, Tomoko Oki and Torsten Lindemann, Thermo Fisher Scientific (Bremen) GmbH, Hanna Kunath Str. 11, 28199 Bremen, Germany
meike.hamester@thermofisher.com

Introduction

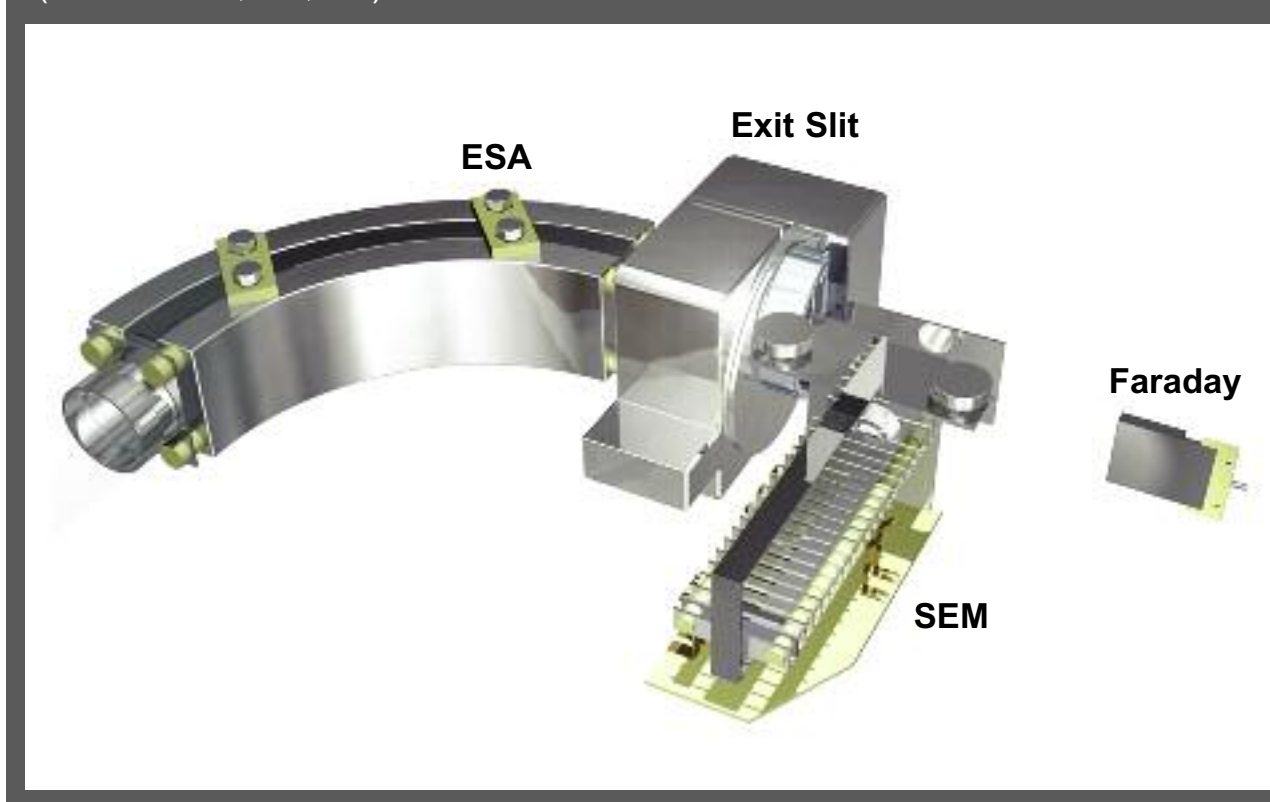
Nickel based super-alloys are used in a range of different industries where high resistance to corrosion and extreme temperature (and changes in temperature) is mandatory; for example in aerospace and aviation, as well for turbines and reactors. Between 10 and 15 elements are typically added to Nickel Alloys in order to improve their performance characteristics, mainly with regard to temperature resistance. On the other hand impurities of elements such as Bismuth and Selenium degrade their capabilities. Both Quadrupole and Sector Field ICP-MS when coupled with laser ablation can be used for the direct analysis of solid samples while GD-MS is the accepted routine tool for the direct analysis of conductive solid samples

Experimental

The mass spectrometers used in this work were the quadrupole ICP-MS (XSERIES 2) and the high resolution sector field ICP-MS (ELEMENT XR) from Thermo Fisher Scientific (Bremen, Germany) coupled to a 213 nm laser ablation system (UP213 SA, New Wave, Fremont, California, USA). Details are described elsewhere (WP14). The glow discharge mass spectrometer (GD-MS) used was the ELEMENT GD from Thermo Fisher Scientific (Bremen, Germany).

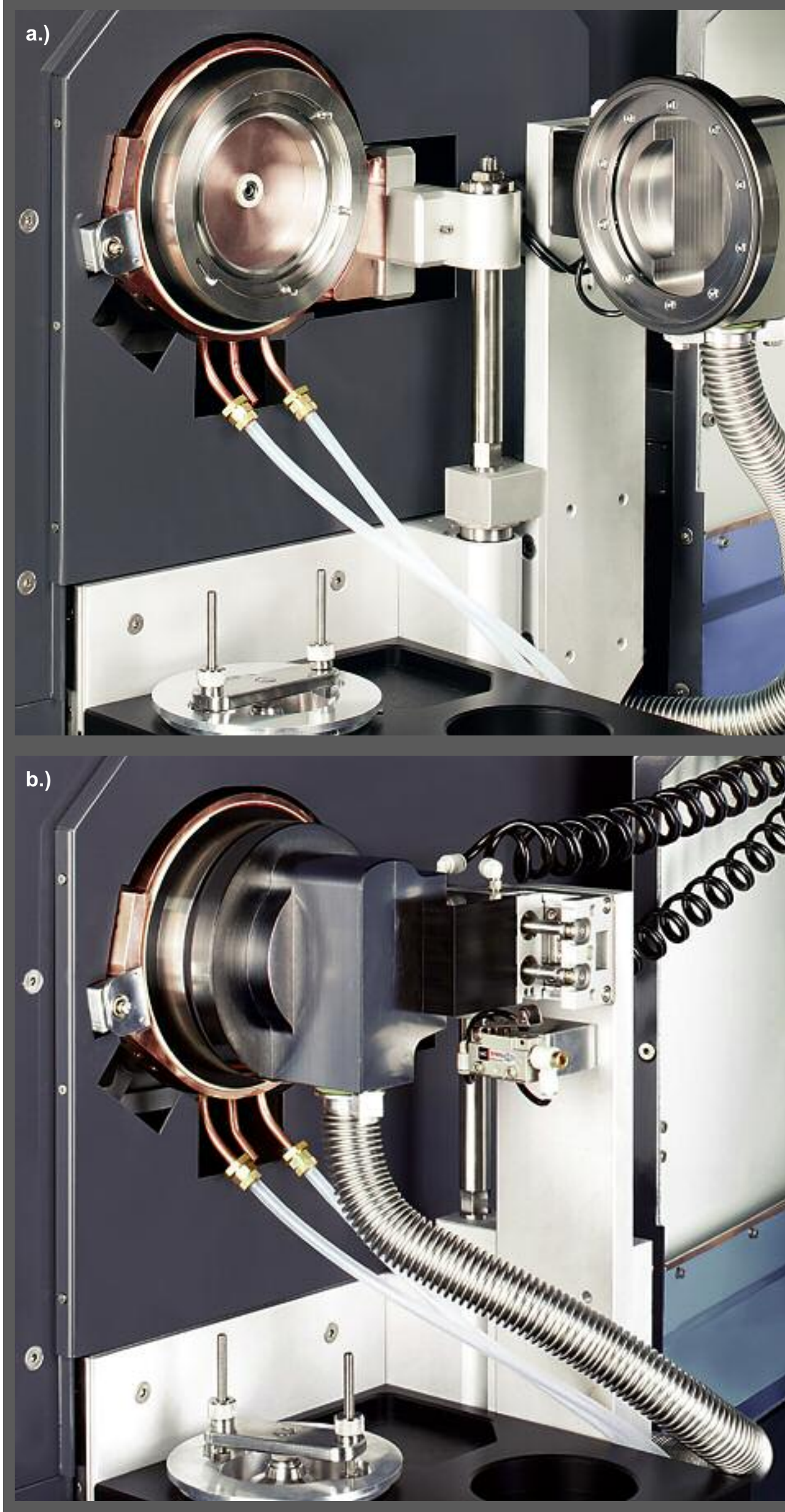
The ELEMENT GD is based on the same sector field mass spectrometer as the ELEMENT XR and is equipped with a detection system utilizing a linear dynamic range of > 12 orders of magnitude.

FIGURE 1. ELEMENT GD and ELEMENT XR Detection System; (US Patent 7,220,970).



The instrument is equipped with a “Grimm type” fast flow glow discharge cell for fast sputtering enabling sample turn-around times of ~ 10 minutes.

FIGURE 2. ELEMENT GD Source a.) open and b.) closed.



Sample preparation

The Ni-Alloy samples were ground using a wet grinding machine (STUERS, LaboPol-2 at 500 rpm, MD Piano 80, finished with grid 120).

TABLE 1. ELEMENT GD instrumental settings.

Discharge current	35 mA
Discharge voltage	800 V
Discharge gas	425 ml/min
Pre-sputter time	4 min
Total analysis time	10 min

Calibration

All mass spectrometers were calibrated using Ni Alloy reference materials: CRM 345 and CRM 346a (BCS, British Chemical Standard). The results presented in Table 2 compare the elemental concentrations obtained from the 3 mass instrumental techniques considered.

TABLE 2. Comparison of results in Ni-Alloy.

Element	XSERIES 2	ELEMENT XR	ELEMENT GD
Fe	219000	165469	157335
Cr	193500	188722	184173
Mo	35000	32092	33210
Ti	11800	10549	10076
Al	5600	5885	5324
Co	1400	1369	1071
C	1100	823	590
Mn	400	341	219
Cu	not cal	185	192
V	200	26.9	23.0
W	60	not cal	160
P	40	54.6	51.9
S	40	3.9	6.2
B	40	35.7	34.7
Sn	12	7.3	7.1
Se	3	0.5	0.02
Pb	0.6	0.013	0.07
Ag	0.17	0.37	0.03
Bi	0.16	0.11	0.002

All results are shown in ppm.

For concentrations in the percent and higher ppm range there is good agreement between all three techniques. In the lower ppm range the ELEMENT XR and ELEMENT GD show still a good agreement.

At lower concentrations (in the ppb range) the higher sensitivity of the ELEMENT GD results in high accuracy data even in the single digit ppb range (e.g. Bismuth).

TABLE 3. Sensitivity Comparison between the ELEMENT XR and ELEMENT GD (BAS 345, Ni-Alloy).

	ELEMENT XR [cps]	ELEMENT GD [cps]	GD-MS/ICP-MS
P	4527	199487	44
Co	194322891	13100000000	67
Cu	9648	766537	79
Ta	64270	775730	12
Pb	337	3369	10

A comparison of elemental sensitivities of the high resolution ICP-MS ELEMENT XR and high resolution GD-MS ELEMENT GD shows a clear advantage of the ELEMENT GD. This is especially noticeable in the lower mass range.

The significantly higher sensitivity of GD-MS in comparison to ICP-MS is combined with high reproducibility, resulting in single digit ppb detection limits.

Table 4 demonstrates the reproducibility for BAS 346a when comparing results from 3 different spots.

TABLE 4. ELEMENT GD reproducibility.

Element	BAS346A #1 Conc. [ppm]	BAS346A #2 Conc. [ppm]	BAS346A #3 Conc. [ppm]	Average Conc. [ppm]	RSD [%]
Cd	0.37	0.36	0.37	0.37	0.8%
Tl	1.90	1.84	1.85	1.86	1.6%
Se	5.69	5.73	5.85	5.76	1.5%
Bi	9.80	9.62	9.51	9.64	1.5%
Ca	20.5	21.0	20.8	20.8	1.2%
Pb	21.8	21.1	21.1	21.3	1.8%
Zn	28.8	28.4	28.7	28.6	0.6%
Ag	42.4	41.7	41.5	41.9	1.2%
Ga	48.0	47.4	47.7	47.7	0.6%
As	50.3	49.7	49.6	49.9	0.8%
B	256	257	268	260	2.5%
Zr	430	420	423	424	1.2%
C	1645	1623	1780	1683	5.1%
V	9757	9632	9656	9682	0.7%
Al	55642	55526	56313	55827	0.8%
Cr	99141	99140	99515	99265	0.2%
Co	146468	147963	147817	147416	0.6%
Ni	605329	605472	604592	605131	0.08%

FIGURE 3. Turbine.



Conclusion

ICP-MS - both quadrupole and high resolution - when coupled with laser ablation can be used to directly quantify trace elements in Ni-Alloys. At higher concentrations good agreements with GD-MS can be demonstrated. However, towards the lower ppm and ppb range, GD-MS shows significantly higher sensitivity and reproducibility resulting in single digit ppb detection limits in Ni-Alloys. Furthermore, the ELEMENT GD convinces with its ease of operation and high throughput, with the advantage of using one instrument instead of two (ICP-MS plus laser ablation).

