

# GD-MS Analysis of Trace and Ultra-trace Elements in Nickel Super Alloys

Joachim Hinrichs, Lothar Rottmann, Thermo Fisher Scientific, Bremen, Germany

## Key Words

ELEMENT GD, Nickel, Super Alloys, Trace Metals

## Introduction

Nickel alloys are used in industry due to their excellent mechanical properties. Especially on the strength of their heat-resistance in combination with long-term resistance to mechanical stress, such alloys are used for manufacturing safety-sensitive parts in the aerospace industry. Various qualities are used for turbine blades of aircrafts and rockets. Based on their complex composition and required very low contents of several trace elements deteriorating the superb properties of these alloys, the analytical task is not a simple one.

The high-resolution glow discharge mass spectrometer Thermo Scientific ELEMENT GD has been used to analyse trace element concentrations in Ni super alloys reference materials. The major focus of this application report is set on the accurate and precise measurement of trace components at or below ppm levels. The detection capability of the ELEMENT™ GD has been investigated, as specified concentrations in the sub-ppm range make detection limits in the low ppb range desirable.

## Instrumental Settings

For analysis, optimum instrumental settings were adjusted combining sensitivity with signal stability and a reasonable analysis time. Tune conditions are summarized in Table 1.

Tune conditions	
Discharge current	40 mA
Discharge voltage	~ 800 V
Discharge gas	Ar; 450 mL/min
Actual sensitivity	4 x 10 <sup>10</sup> counts per second (sum of matrix elements, Medium Resolution)
Anode material	Steel
Anode cap	Graphite
Flow tube	Graphite
Cone	Graphite

Table 1: Instrumental settings.

## Sample Material and Preparation

The reference material NIST 1249 (Inco 718) was used for this report, representing Ni alloys with a wide range of alloying components in the double and single digit percent range. The composition is listed in Table 2.

Element	[%]
Al	0.6
Ti	1
Cr	18.5
Fe	18
Ni	53
Nb	5
Mo	3

Table 2: Major elements in NIST 1249 (Inco 718).

Before every measurement, the sample surface was ground on a grit 120 diamond disc and cleaned with iso-propanole to ensure a clean and fresh surface for analysis. For highest possible precision, the sample should be as planar as possible, and existing sputter craters need to be removed. Special care should be taken to avoid the outside area of a sample due to possible pronounced curvature of the sample surface. This effect might occur especially when using SiC grinding paper and high force upon grinding, thus preferentially grinding off the outer area of the sample.

After analysis, the anode cap and the cone were replaced and afterwards cleaned in ca. 1+4 diluted nitric acid in an ultrasonic bath. After a cleaning step in DI water, the parts were dried overnight and could be used the following day. For faster drying, the parts could also be soaked in iso-propanole to remove the DI water.

## Method Development

For the Ni super alloy standards a method was developed to find the best settings for analysis in terms of resolution, isotopes and measurement duration. Whenever possible, isotopes of highest isotopic abundance were used, unless these were affected by isobaric overlaps.

The presputter time necessary was evaluated by monitoring the measured concentrations over time. When the signal had stabilized, this time was used as a presputter time in the following analyses. While elements at the ppm level gave stable concentration readings after 3-4 minutes, the presputter time for elements at the detection limits needed to be set longer. Therefore a presputter time of 8 minutes has been used, followed by ca. 4 minutes data acquisition.

The final method settings are shown in Figure 1. For the given set of elements and concentrations, only Medium Resolution ( $R = 4000$ ) was used. Overall, a sample run required less than 15 minutes, including pump-down and venting times of the GD source.

Resolution: Medium		Runs: 3	Estimated Total Time: 00:03:55									
Mode: 2		Passes: 1	[minutes]									
Method Data		Inference Correction										
Entry	Isotope	Detection Mode	Mass Window	Search Window	Integration Window	Sample Time	Samples Per Peak	Segment Duration	Index Of Matrix Element	Matrix Elements	Regression Type	Integration Type
1	B11	Triple	200	150	60	0.0200	20	0.800			Thru Zero	Average
2	C12	Triple	150	60	60	0.0500	20	1.500			Thru Zero	Average
3	Mg24	Triple	150	60	60	0.0500	20	1.500			Thru Zero	Average
4	Al27	Triple	150	60	60	0.0500	20	1.500			Thru Zero	Average
5	Si28	Triple	150	60	60	0.0200	20	0.600			Thru Zero	Average
6	P31	Triple	150	60	60	0.0200	20	0.600			Thru Zero	Average
7	S32	Triple	150	60	60	0.0200	20	0.600			Thru Zero	Average
8	Ca44	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
9	Ti48	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
10	V51	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
11	Cr52	Faraday	130	60	60	0.2000	20	5.200			Thru Zero	Average
12	Mn55	Triple	130	60	60	0.2000	20	5.200			Thru Zero	Average
13	Fe56	Faraday	130	60	60	0.2000	20	5.200			Thru Zero	Average
14	Co59	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
15	Ni60	Faraday	130	60	60	0.2000	20	5.200			Thru Zero	Average
16	Cu63	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
17	Zn66	Triple	130	30	60	0.0500	20	1.300			Thru Zero	Average
18	As75	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
19	Se82	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
20	Zr91	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
21	Nb93	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
22	Mo95	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
23	Ag107	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
24	Sn117	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
25	Sb121	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
26	Te130	Triple	130	60	60	0.0200	20	0.520			Thru Zero	Average
27	La139	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
28	Ta181	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
29	W184	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
30	Ti205	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
31	Pb208	Triple	130	60	60	0.0500	20	1.300			Thru Zero	Average
32	Bi209	Triple	130	60	60	0.1000	20	2.600			Thru Zero	Average

Figure 1: Method used for acquisition.

## Evaluation Strategy

The evaluation is based on measuring intensities of selected isotopes that are then corrected for their isotopic abundance and calculated as Ion Beam Ratios (IBR). It is necessary to include all relevant matrix components (Table 2) in the analytical method (see Figure 1) to get a good approximation of the Total Ion Beam current used for the IBR approach. The ratios of analyte to matrix signal are then transferred into concentrations by using Relative Sensitivity Factors (RSF) determined for the respective matrix and the elements of interest. For such elements where no certified concentrations are available, semiquantitative data are obtained by using the "Standard RSF" table supplied with the instrument, yielding typically accuracies of ~ 30% of the true value.

## Results and Discussion

Table 3 shows the results of repeat analyses of the CRM NIST 1249. Every data point represents a full measurement, i.e. analysis on a new spot after grinding and presputtering.

For an estimate of the repeatability of GD-MS analysis, a single point calibration of the same reference material was used for calibration. All spots analysed were then referenced against this calibration.

The data shown were selected for trace metals in the ppm range that are certified in the NIST1249. At the ppm level, very good spot-to-spot precisions of 1-4% can be achieved for the repeats on 5 spots. Some elements that were just given for information purposes show somewhat larger variability, which can be explained by poor isotopic abundance of the isotope used (e.g.  $^{44}\text{Ca}$ ) and/or lower ion yield (e.g. Se).

	Spot #1	Spot #2	Spot #3	Spot #4	Spot #5	certified value	Standard deviation [n=5 spots]	RSD
Isotope	Conc. [ppm]	Conc. [ppm]	Conc. [ppm]	Conc. [ppm]	Conc. [ppm]	Conc. [ppm]		
<sup>11</sup> B(MR)	23	22	23	23	23	23	1	3%
<sup>24</sup> Mg(MR)	12.2	12.1	12.4	12.7	12.0	12	0.3	2%
<sup>31</sup> P(MR)	135	130	140	136	132	134	4	3%
<sup>32</sup> S(MR)	6.5	6.3	6.6	6.8	6.3	6.4	0.2	3%
<sup>44</sup> Ca(MR)	4.8	5.9	6.0	6.0	5.5 info	5	0.5	10%
<sup>66</sup> Zn(MR)	6.4	6.6	6.7	6.4	6.2 info	6	0.22	4%
<sup>75</sup> As(MR)	13.0	12.9	13.4	13.1	12.9	13.0	0.21	2%
<sup>82</sup> Se(MR)	0.4	0.3	0.2	0.4	0.3 info	0.3	0.07	24%
<sup>91</sup> Zr(MR)	29.0	29.6	29.5	29.0	28.4	29	0.5	2%
<sup>117</sup> Sn(MR)	25	25	25	25	24	24	0.23	1%
<sup>121</sup> Sb (MR)	3.1	3.1	3.1	3.1	3.0	3.0	0.04	1%
<sup>208</sup> Pb (MR)	0.098	0.106	0.097	0.103	0.104 info	0.10	0.004	4%

Table 3: Results for CRM NIST 1249: only for certified elements or at least those with info values the concentrations are shown. Calibration was carried out with the same reference material measured on an additional spot.

Especially soft metals deteriorate the longterm flexibility of the alloys, causing enhanced risk of micro-cracks in the turbine blades. Therefore the required concentrations of several trace metals are in the sub-ppm range. E.g. Bi is usually required to be <0.3 ppm in the alloy, thus demanding a LoD well below this values. Although no certified material is available at this level, the analysis of several non-certified elements can be used to get an estimate of the detection capabilities of the ELEMENT GD (Table 4).

Although the concentrations measured are semiquantitative and thus accuracy might suffer, the detection limits still can be calculated from these values. As an example a spectrum of the Bismuth peak contained in the reference sample is shown in Figure 2. About 13 ppb Bi in the reference sample show up as a peak of several hundred cps, and still giving an “on-peak” detection limit of ca. 1 ppb. When considering the standard deviation of the 5 repeats for itself, the stability of the Bi data is again in the range given for ppm level analytes, although here the concentrations are 100-fold less. For Bismuth, the integration times have been increased from typical 20 ms to 100 ms integration time to improve low-level precision. The off-peak detection limit (i.e. the signal to noise ratio) will be about two orders of magnitude lower, considering the typical background noise of ca. 1 cps during analysis.

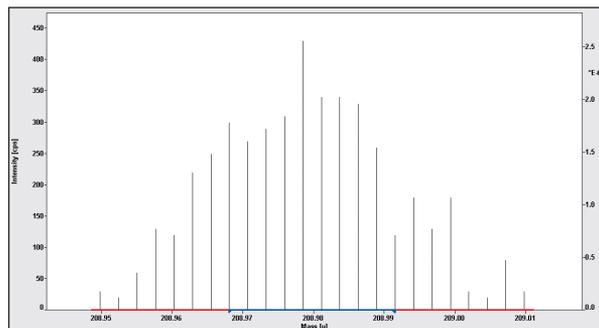


Figure 2: Peak of ca. 13 ppb Bismuth analysed in Medium Resolution. (<sup>209</sup>Bi, MR, R = 4000); integration time per channel: 0.1 seconds.

	Spot #1	Spot #2	Spot #3	Spot #4	Spot #5	Average semiquant Conc. [ppm]	Standard deviation [n=5 spots]	LOD (3s from n=5 spots)
Isotope	Conc. [ppm]	Conc. [ppm]	Conc. [ppm]	Conc. [ppm]	Conc. [ppm]	Conc. [ppm]		
<sup>130</sup> Te(MR)	0.012	0.013	0.009	0.013	0.009	0.011	0.002	0.006
<sup>205</sup> Tl(MR)	0.0024	0.0026	0.0025	0.0023	0.0020	0.0024	0.0002	0.0007
<sup>209</sup> Bi(MR)	0.013	0.012	0.013	0.013	0.012	0.013	0.0003	0.0010

Table 4: On-peak detection limits calculated as 3 times the standard deviations of 5 repeat analyses of several low-level analytes. These have no certified values and were therefore quantified semiquantitatively.

## Conclusions

The Thermo Scientific ELEMENT GD glow discharge MS enables high precision determination of trace metals at or below the ppm level in Nickel super alloys. With the appropriate sample preparation, very good precisions in the range 1-4% RSD can be achieved at the ppm level for repeat analyses, and with 100 ms integration time even at the ppb level. Sample turnaround is about 4 samples per hour for this application.

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