Application note | 003108

GD-MS

Fast routine analysis of trace and ultra trace elements in zinc alloys by Glow Discharge Mass Spectrometry

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Introduction

Zinc is used for different applications like corrosion protection, in fertilizers, pharmaceuticals and in energy storage as alternative for lithium-based batteries. Zinc alloys are used e.g. for die casting and as galvanizing alloys[1]. Corrosion of zinc-aluminum alloys is accelerated by small amounts of impurities, especially lead, cadmium, and tin[2,3]. Lead and other impurities such as antimony influence the morphology and orientation of electrolytically deposited zinc[4]. To ensure consistently high product quality, the analysis of trace and ultra trace elements in zinc and its alloys is essential. There is an increasing demand to specify better grades of zinc and zinc alloys and therefore, better limits of detection are required. With the Thermo Scientific™ Element GD Plus™ Glow Discharge Mass Spectrometer sub-ppb levels of detection can be achieved, much lower than by Spark-OES and GD-OES. The Element GD Plus GD-MS is being used for quality control in routine production for different applications in industrial manufacturing environments. This document describes the fast direct determination of elements in zinc alloys down to ppb level.

Analytical setup

The flat zinc alloys samples (Figure 1) are analyzed directly, and no digestion is required. The instrumental conditions for the analysis with the Element GD Plus GD-MS are shown in Table 1. To remove any potential sample surface contamination, fast presputtering in continuous DC mode was applied before the data acquisition. Depending on the sample preparation (e.g. milling or grinding), the resulting degree of surface contamination, and the limits of detection required, lower presputter times can be used, leading to even higher sample throughput. Most elements are analyzed in Medium Mass Resolution (R = 4000). Gallium and Yttrium are analyzed in High Mass Resolution (R = 10000) to ensure an interference-free measurement by resolving the analytes from the ZnH and MgZn interferences.

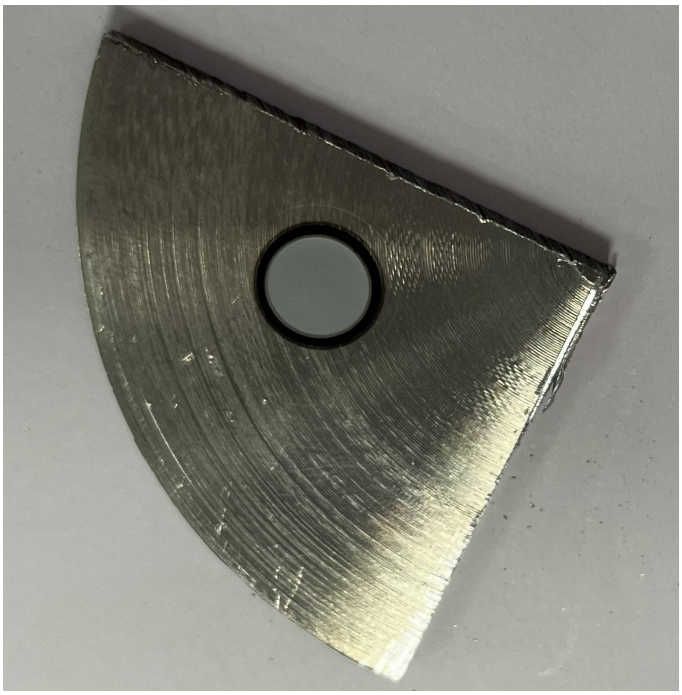

Figure 1. Zinc alloy after analysis

Table 1: Element GD Plus GD-MS conditions for analysis of zinc alloys

Discharge voltage	750 V
Discharge current	≈10 mA
Mode	Modulated DC (Pulsed)
Pulse duration	50 µs
Pulse frequency	2 kHz
Discharge gas	500 mL/min Ar
Anode parts	Steel (Basic consumables kit)
Matrix sensitivity	1.5×10^{10} cps Zn + Al in medium resolution, equivalent to ≈ 2.4 nA
Presputter time	5 min continuous DC
Integration time	≈5 min for a measurement, consisting of 3 scans, for a suite of 76 elements
Sample throughput	≈5 samples per hour

Results

The Certified Reference Materials BCR-357, BCR-359 and BCR-360 have been used to calibrate Mg, Fe, Ni, Cu, Cd, In, Sn, Tl and Pb in zinc alloys. The calibration lines are displayed in Figure 2, showing excellent linearity. This calibration was used for the quantification of elements in a zinc alloy sample. For the elements that were not calibrated, the Standard Relative Sensitivity Factors (sRSF) of the Element GD Plus GD-MS were used by the software for quantification. With the sRSFs, the semiquantitative results typically fall within ± 30 % of the true values.

Table 2 shows the mass fractions for selected elements as well as the relative standard deviation (RSD) of three replicative consecutive measurements on the same spot. Mass fractions in the single digit ppb range can be quantified with ≤ 10 % RSD. For mass fractions ≥ 0.4 ppm the RSD was ≤ 2 %. For mass fractions ≥ 30 ppm the RSD was 1 %. When the result was below the Limit of Detection (defined as 3 x standard deviation of low concentration measurements), it is stated as < Limit of Detection. With the method used, the typical Limits of Detection are in the low single digit ppb range.

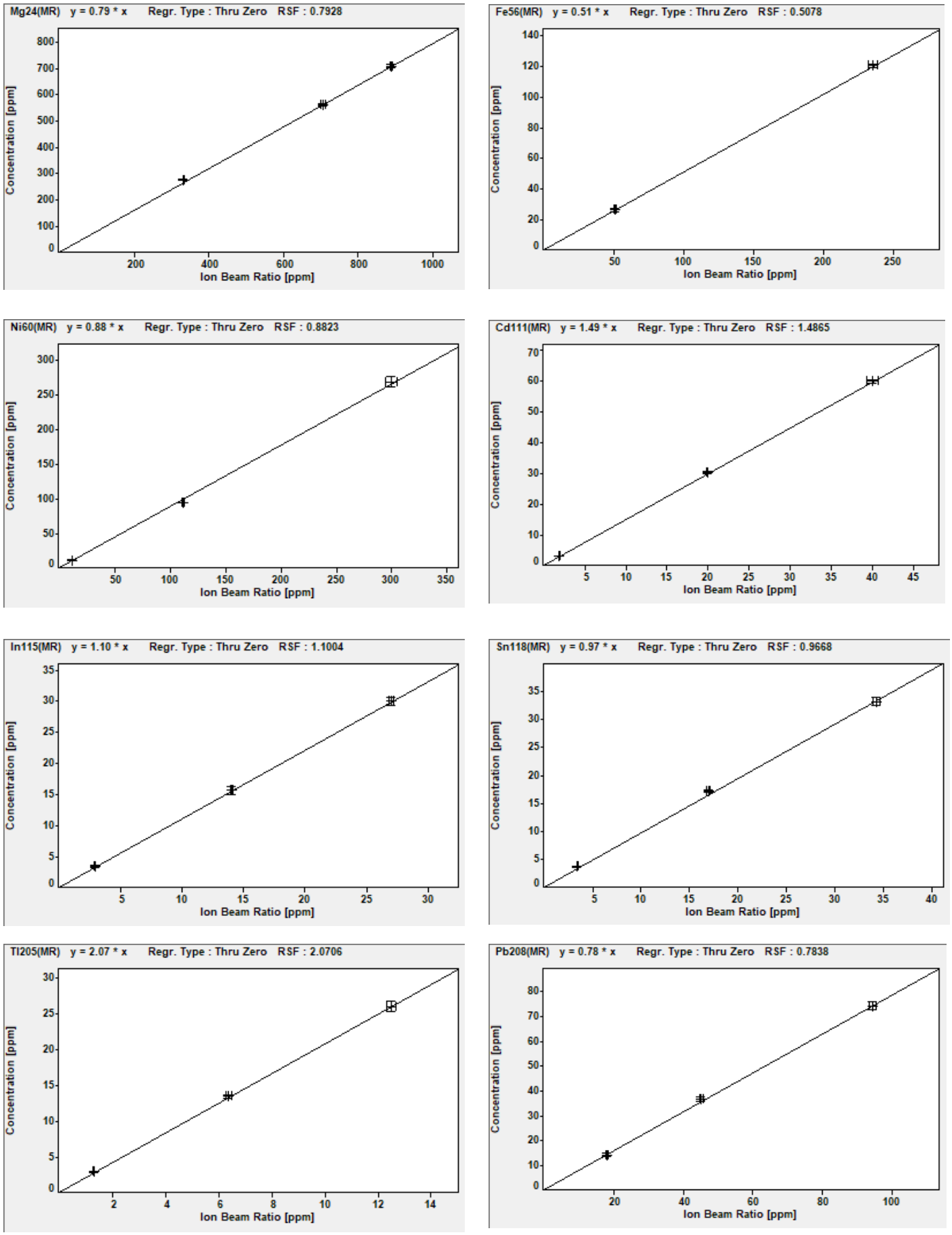

Figure 2: Calibration lines of Mg, Fe, Ni, Cd, In, Sn, Tl and Pb in zinc alloys, using BCR-357, BCR-359 and BCR-360

Table 2. Mass Fractions in ppm and RSDs of a zinc alloy sample. It is indicated whether the calibration (Cal) or the Standard RSFs (sRSF) were used for quantification.

	Mass Fraction [ppm]	RSD	Calibration
B	0.08	9%	sRSF
Na	0.047	3%	sRSF
Mg	536	1%	Cal
Si	6.3	2%	sRSF
P	0.054	8%	sRSF
K	< 0.002	-	sRSF
Ca	0.01	10%	sRSF
Sc	< 0.001	-	sRSF
Ti	0.01	2%	sRSF
V	0.016	1%	sRSF
Cr	0.066	4%	sRSF
Mn	0.4	1%	sRSF
Fe	119	1%	Cal
Co	0.014	3%	sRSF
Ni	96	1%	Cal
Cu	9830	1%	Cal
Ga	0.18	6%	sRSF
Ge	0.008	4%	sRSF

	Mass Fraction [ppm]	RSD	Calibration
As	0.019	4%	sRSF
Se	< 0.002	-	sRSF
Y	< 0.001	-	sRSF
Ag	0.1	3%	sRSF
Cd	29.9	1%	Cal
In	15.4	2%	Cal
Sn	16.6	1%	Cal
Sb	0.032	10%	sRSF
Ba	0.004	3%	sRSF
La	0.005	5%	sRSF
Ce	0.006	8%	sRSF
Hg	< 0.001	-	sRSF
Tl	13.3	1%	Cal
Pb	35.5	1%	Cal
Bi	< 0.005	-	sRSF
Th	< 0.001	-	sRSF
U	0.002	4%	sRSF

Conclusions

The Element GD Plus GD-MS is an extremely sensitive tool for determining trace and ultra trace impurities in solid samples. The calibration lines in zinc alloy matrices show excellent linearity. Mass fractions at the ppb and ppm level are quantified precisely and reliably. Single digit ppb mass fractions can be quantified with ≤ 10 % RSD. For mass fractions ≥ 30 ppm the precision was 1 % RSD. Interferences are safely eliminated in either Medium Mass Resolution (R = 4000) or High Mass Resolution (R = 10000). Automatic resolution switching within one second enables the routine use of the optimum mass resolution. Surface contaminations are removed by fast presputtering before the data acquisition. The analysis does not require a digestion and is fast with a sample throughput of approximately five samples per hour.

Literature

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