Routine Analysis of High Purity Aluminium by Glow Discharge Mass Spectrometry

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Introduction

Aluminium of 5N or 6N grade, especially with very low alpha emitters content (U, Th), is widely used in specialty electronic and chemical applications. Applications include vacuum deposition of thin films and coatings used in the manufacturing of electronic devices, integrated circuits and optical products. High purity aluminium is also used to coat wires, plates, particles for use in flexible packaging for food labelling and food containers and electrical conductors.

High purity alloys are produced for the alumina catalyst market and for electronic ceramics such as aluminium oxide and aluminium nitride. These alloys are also used for sputtering targets for semiconductors, memory industry and LCD TFT screens.

The analytical characterisation for 5N or higher aluminium purities is not a simple task, since very low detection limits for the majority of elements are required. The development of new Glow discharge mass spectrometers (GD-MS) enable an analyst to routinely achieve ultra-low detection limits, down to parts per trillion (ppt) in the solid, with a minimum of sample preparation effort. This article describes the procedures and results for GD-MS analysis of high purity aluminium.

Instrumentation

The new GD-MS instruments feature a 'fast flow' GD DC source using Argon carrier gas flows of about 400 mL/min. This is a high power source (similar to a 'Grimm type source') providing high sputter rates and sensitivity. The sample is ablated from an 8 mm sampling area.

The sector field mass analyser used in the ELEMENT GD (Thermo Fisher Scientific) enables highest mass accuracy and precision, guaranteeing highly efficient measurement of the masses of interest. Thus, the sample throughput is about three samples per hour for the analysis of elemental concentrations close to the detection limits for about 70 elements.

Method

Sample preparation:

The sample surface was milled off to remove possible surface contamination and oxide layers. The fresh surface was cleaned with isopropanole prior to analysis.

Instrument settings (ELEMENT GD):

The discharge conditions were adjusted to give best matrix sensitivity for Al: After finding the best setting for the discharge gas Argon, the discharge current was varied to reach highest Al signals. At these settings the signal drift was observed over several minutes to make sure that stable discharge conditions can be maintained during the analysis period. Details of the instrument settings are shown in Table 1.

Discharge current	65mA
Discharge voltage	~ 600V
Discharge gas flow	380 mL/min
Focus lens	950V

Table 1: Instrument conditions

Calibration

The basic principle for all quantification in GD-MS is the measurement of Ion Beam Ratios (IBR). The matrix element Al is directly measured and the trace

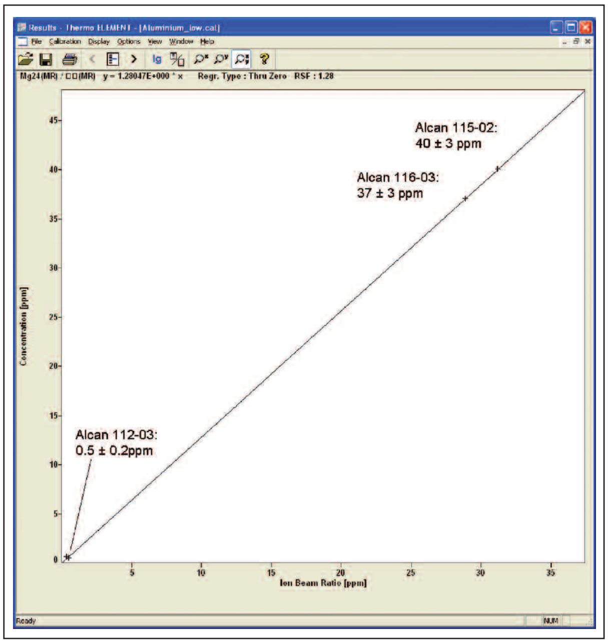

Figure 1: Magnesium at low ppm level in Aluminium CRM

metals normalised to the matrix ion beam. The measured IBR of several aluminium CRMs are plotted versus the certified concentrations of each element. The slopes of these graphs give the relative sensitivity factors (RSFs) of the instrument. These are applied to unknown samples to yield concentrations from the measured IBR. As an example, the low-level calibration graph for Mg is shown in Figure 1. For all elements not certified in any of the CRMs used, the ELEMENT GD's Standard RSFs were applied, giving semiquantitative concentrations.

CRM used for calibration

Alcan 112-03; Alcan 115-02; Alcan 116-03

Method development:

The correct choice of isotopes and resolutions has been made by measurements of the high purity samples using scans with wide scan windows. Interferences originating from mainly Argon based polyatomic interferences can be visually identified. The resolution necessary for interference free analyses is used for the routine measurement. Whenever possible, the isotope of highest isotopic abundance is used, providing highest sensitivity and thus lowest detection limits. The selection of isotopes and resolutions is shown together with the results obtained in Table 2.

As a last step for method development the presputter time necessary to achieve stable discharge conditions and for surface contamination removal was established. Typically contamination levels decreased over 10 - 12 minutes, so that a careful estimate resulted in 15 min presputter time. Data were collected over 15 minutes, giving reproducible data even at the ultra-trace level below 1 ppb.

Conclusion

All results obtained using GD-MS are in good agreement with the certified concentrations. For those few elements that could be certified with total element concentrations in this ultra-high purity standard, no confidence intervals are provided. Nevertheless, e.g. the low level Pb content of certified 20 ppb is found very closely by GD-MS, and also certified 10 ppb Ag are measured as 13 ppb.

The only element showing a larger deviation from the certified value is Zn. The measured value is significantly higher, which is likely related to sample inhomogenity: another high purity sample measured directly after the Hydro-R02 gave about 70 ppb Zn, so that contamination with Zn does not explain the too high Zn value measured in the CRM.

Element	Mass	Res.	Certified conc. [ppb]	Measured conc. [ppb]
Li	7	LR	<10	0.01
Be	9	MR	<50	0.7
B	11	MR	<500	26
Na	23	LR	<10	2.7
Mg	24	MR	600	446
Si	28	MR	<1000	898
P	31	MR	<400	11
K	39	HR	<100	27
Ca	44	MR	<200	8.5
Sc	45	MR	<20	3.7
Ti	48	MR	<100	9.3
V	51	MR	<100	2.8
Cr	52	MR	<20	2.0
Mn	55	MR	40	30
Fe	56	MR	<300	29
Ni	58	MR	<100	2.1
Co	59	MR	<10	0.8
Cu	63	MR	<400	34
Zn	64	MR	80	364
Ga	69	MR	40	38
As	75	MR	<80	0.7
Se	77	HR	<40	17
Sr	88	MR	<50	0.02
Zr	90	MR	<200	1.3
Mo	98	MR	<10	0.9
Ag	109	MR	10	13
Cd	114	MR	<10	1.6
In	115	LR	<10	0.1
Sn	119	MR	<1000	1.0
Sb	121	MR	<10	4.4
Te	128	MR	<10	2.8
Ba	138	LR	<100	0.04
La	139	LR	<10	0.02
Ce	140	LR	<10	0.01
Pr	141	LR	<20	0.02
Nd	146	LR	<10	0.05
Sm	152	LR	<10	0.2
Tb	159	LR	<10	0.06
Hf	177	MR	<10	0.1
Ta	181	LR	<10	3.1
W	184	LR	<10	3.4
Au	197	LR	<60	0.3
Hg	202	LR	<20	1.0
Tl	205	LR	<10	0.01
Pb	208	LR	20	18
Bi	209	MR	<10	0.25
Th	232	LR	<1	0.02
U	238	MR	<1	0.01

Table 2: Method details and results for Hydro R-02 CRM 99.9999% Al (15 minutes pre sputter + 15 minutes analysis time). LR = Low Resolution (R=400); MR = Medium Resolution (R=4000); HR = High Resolution (R=10000)

Most elements are certified as their maximum contents. The GD-MS results confirm these data in all cases. While for some elements the measured concentrations are only slightly below the certified values (e.g. Tl measured as 6 ppb, certified <10ppb), for most elements the measured concentrations are one or several orders of magnitude below the certified upper limit (e.g. Sn measured as 5 ppb, certified <1000ppb, or Ba measured as 0.1 ppb, certified <100ppb).

The new GD-MS instruments offer an extremely sensitive tool for determining ultra-trace impurities in the sample matrix analysed. Even at the low ppb level in the solid aluminium the technique reports accurate concentrations for all elements at minimal sample preparation effort and related risks of contamination. The sample throughput for such demanding applications is about 2-3 samples per hour, which is about five times faster than with previously available GD-MS instrumentation. **APT**

Biographies

Joachim Hinrichs is Application Specialist and Meike Hamester is Product Manager ICP-MS/GD-MS, both with Thermo Fisher Scientific in Bremen, Germany.

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