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High purity aluminum analysis

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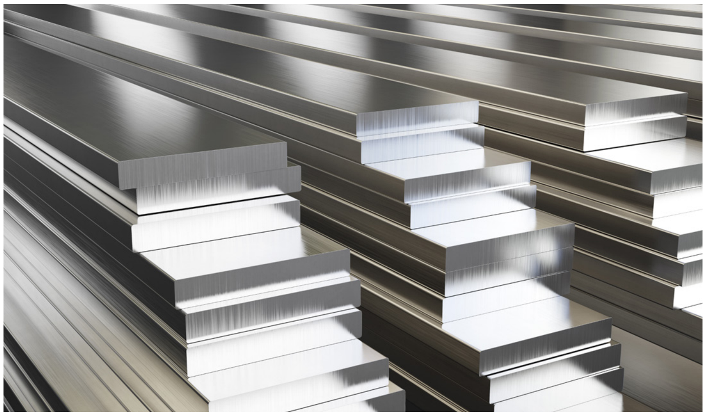

Introduction

Aluminum of 5N or 6N grade, especially with very low alpha emitters (U, Th) content, 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 aluminum is also used to coat wires, plates, and particles for use in flexible packaging of food containers.

The analytical characterization of 5N or higher aluminum is not a simple task, since very low detection limits for the majority of elements are required. The Thermo Scientific™ Element™ GD Plus GD-MS enables the analyst to routinely achieve ultra-low detection limits directly in the solid, below the parts per billion level, with a minimum of sample preparation effort. This note describes the procedures and results for GD-MS analysis of high purity aluminum.

Instrumentation

The Element GD Plus GD-MS features a 'fast flow' DC glow-discharge source. In this high power source (similar to a 'Grimm type' source) argon carrier gas flows of approximately 400 mL/min are used, providing high sputter rates and sensitivity. The sample is ablated from an 8 mm diameter area. The sector field mass analyzer used in the Element GD Plus GD-MS provides the highest mass accuracy and precision, guaranteeing highly efficient measurement of the elements of interest. Subsequently, sample throughput is about three samples per hour for the determination of 70 elements at concentrations close to the detection limit.

Sample preparation

The sample surfaces were freshly milled before analysis to obtain a flat sample surface and to remove surface contamination / oxide layers. Any lubricant other than alcohol (e.g. isopropanole) must be avoided, since otherwise severe sub-surface contaminations of the samples can occur. Directly prior to analysis, the sample surface was flushed with isopropanole and blown dry with N_2 to remove any dust and splinters that might affect the measurement.

Instrument settings

The glow discharge ion source conditions were optimized for aluminum matrix sensitivity. Compared to other metals, aluminum requires a quite high discharge current to achieve matrix signals on the order of 10^{10} cps in medium resolution. Such a level is necessary to achieve sub-ppb detection limits during analyses. At these settings the initial signal drift was observed over several minutes to make sure that stable discharge conditions could be maintained during the analysis period. Detailed instrument settings are shown in Table 1.

Table 1. Instrument conditions.

Discharge current	75 mA (continuous DC mode)
Discharge voltage	~ 750 V
Discharge gas flow	450 mL/min
Matrix sensitivity	~ 1 × 10^{10} cps (Al, MR, R = 4,000)

Calibration

Routine quantification in GD-MS is achieved through the measurement of Ion Beam Ratios (IBR) where the matrix elements are measured and the traces are normalized to the matrix ion beam. The measured IBR of several high purity aluminum certified reference materials (Alcan 115-02, Alcan 116-03, and Hydro R-02) are then plotted against the certified concentrations of each element.

The slopes of these lines give the relative sensitivity factors (RSFs) for each element. Unknowns are then referenced against these to yield concentrations from the measured IBR. Several examples are shown in Figure 1. For those elements not certified in any of the CRMs used, the Standard RSFs of the Element GD Plus were applied. The resulting semi-quantitative concentrations typically fall within ± 30% of the true value.

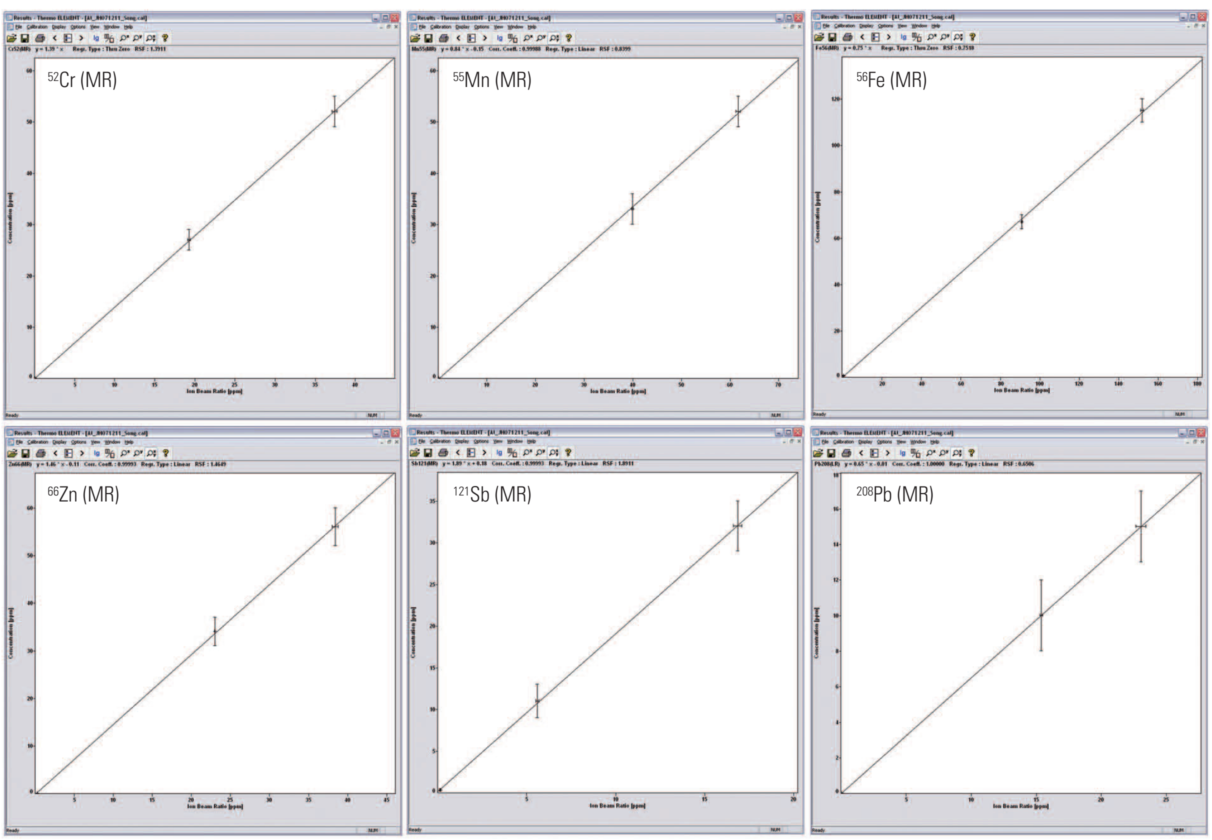

Figure 1. Calibration examples for the low level aluminum CRMs Alcan 115-02, Alcan 116-03, and Hydro R-02. For the latter CRM, the calibration points for Cr (0.02 ppm), Mn (0.04 ppm), Fe (< 0.3 ppm), Zn (0.08 ppm), Sb (< 0.01 ppm), and Pb (0.02 ppm) plot close to the origin.

Method development

The choice of isotope and resolution in the analysis method was determined from the measurement of high purity aluminum samples using analyses with wide scan windows. Polyatomic interferences originating from the sample matrix and the argon ion source can be visually identified in these analyses (examples in Figure 2) and the resolution necessary for interference free analysis taken for routine measurement. Whenever possible, the isotope of highest isotopic abundance is used, providing the highest sensitivity and therefore the lowest detection limits.

The selection of isotope and resolution for the analysis of high purity aluminum is shown together with the results obtained in Table 2.

As a last step in method development, the pre-sputter time necessary to achieve stable discharge conditions and for removal of surface contamination was established.

After a pre-sputter time of 10 minutes, data were collected over 10 minutes, giving reproducible data even at the single-digit ppb level and below as shown in Table 2.

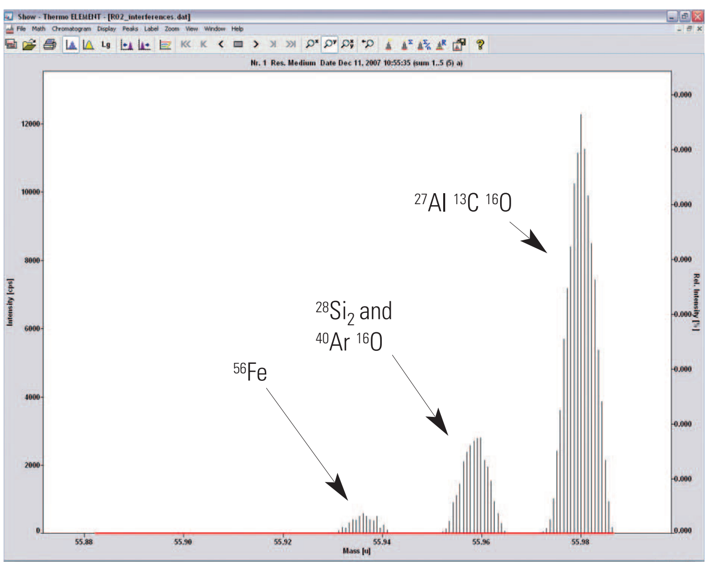

Figure 2. Example for interferences resolved from ^{56}Fe in Medium Resolution (MR, R = 4,000).

Table 2. Method details and results for the 99.999% Al Alcan 112-03 CRM (10 minutes pre-sputter + 10 minutes analysis time). LR = Low Resolution (R > 400); MR = Medium Resolution (R > 4,000); HR = High Resolution (R > 10,000).

Isotope	Calibration	Alcan 112-03 concentration [ppb]	Certified concentration in CRM [ppb]	Certified standard deviation in CRM [ppb]
^{7}Li (LR)	cal	1.1	< 100	
^{9}Be (MR)	cal	1.0	< 100	
^{11}B (MR)	cal	97	100	50
^{19}F (MR)	STD RS	77		
^{23}Na (LR)	STD RSF	11	< 100	
^{24}Mg (MR)	cal	557	500	200
^{28}Si (MR)	cal	754	700	300
^{31}P (MR)	cal	1184		
^{32}S (MR)	STD RSF	709		
^{35}Cl (MR)	STD RSF	81		
^{39}K (HR)	STD RSF	12		
^{44}Ca (MR)	STD RSF	9	< 100	
^{45}Sc (MR)	STD RSF	22	< 100	
^{48}Ti (MR)	cal	21	< 100	
^{51}V (MR)	cal	14	< 100	
^{52}Cr (MR)	cal	17		
^{55}Mn (MR)	cal	19	< 100	
^{56}Fe (MR)	cal	597	600	200
^{59}Co (MR)	cal	0.4	< 100	
^{60}Ni (MR)	cal	18	< 100	
^{63}Cu (MR)	cal	256	< 400	
^{66}Zn (MR)	cal	16	< 100	
^{69}Ga (MR)	cal	2	< 100	
^{70}Ge (MR)	STD RSF	1.0		
^{75}As (MR)	cal	107	100	50
^{82}Se (MR)	cal	12	< 100	
^{79}Br (HR)	STD RSF	2		
^{85}Rb (MR)	STD RSF	0.8		
^{88}Sr (MR)	STD RSF	0.1	< 100	
^{89}Y (MR)	STD RSF	8		
^{90}Zr (MR)	cal	4	< 100	
^{93}Nb (MR)	STD RSF	0.2		
^{95}Mo (MR)	cal	2.0	< 100	
^{102}Ru (LR)	STD RSF	0.3		
^{103}Rh (MR)	STD RSF	2		
^{106}Pd (MR)	STD RSF	1.7		
^{109}Ag (MR)	cal	1.5	< 100	
^{114}Cd (MR)	cal	4	< 100	
^{115}In (LR)	cal	0.2	< 100	
^{119}Sn (MR)	cal	6	< 100	
^{121}Sb (MR)	cal	239	300	100
^{128}Te (MR)	STD RSF	6		
^{127}I (MR)	STD RSF	3		
^{133}Cs (LR)	STD RSF	0.1		
^{138}Ba (LR)	STD RSF	0,9	< 100	
^{139}La (LR)	cal	136	100	50
^{140}Ce (LR)	cal	373	500	200
^{141}Pr (LR)	STD RSF	40		
^{146}Nd (LR)	STD RSF	118		
^{152}Sm (MR)	STD RSF	9		
^{153}Eu (MR)	STD RSF	0.3		

Isotope	Calibration	Alcan 112-03 concentration [ppb]	Certified concentration in CRM [ppb]	Certified standard deviation in CRM [ppb]
^{158}Gd (LR)	STD RSF	24		
^{159}Tb (LR)	STD RSF	4		
^{163}Dy (MR)	STD RSF	22		
^{165}Ho (LR)	STD RSF	3		
^{166}Er (LR)	STD RSF	5		
^{169}Tm (MR)	STD RSF	0.5		
^{172}Yb (LR)	STD RSF	0.18		
^{175}Lu (LR)	STD RSF	0.16		
^{177}Hf (MR)	STD RSF	0.8		
^{181}Ta (LR)	cal	5		
^{184}W (LR)	cal	1.0	< 100	
^{187}Re (LR)	STD RSF	0.04		
^{188}Os (LR)	STD RSF	0.5		
^{193}Ir (LR)	STD RSF	0.07		
^{195}Pt (LR)	STD RSF	0.13		
^{197}Au (LR)	STD RSF	0.15		
^{202}Hg (LR)	cal	0.7	< 100	
^{205}Tl (LR)	cal	1.9	< 100	
^{208}Pb (LR)	cal	4.0	< 100	
^{209}Bi (LR)	cal	32	< 100	
^{232}Th (LR)	STD RSF	51		
^{238}U (LR)	STD RSF	4		

Results

Results obtained for the low-level CRM, Alcan 112-03, are in good agreement with the certified concentrations. For quantification, this CRM was preferred over the other high-purity standard available, Hydro R-02, since no confidence intervals are provided for the latter. As for most of the CRM available at or below the ppm level the confidence intervals of the accuracies are quite large, the certified ranges for the reference material 112-03 are acceptable. Most results obtained agree very well with the certificate, thus confirming the quality of this reference material with respect to its average certified concentrations.

Figure 3 compares the measured concentrations of the CRM Alcan 112-03 with the certified values and ranges. For B, Mg, Si, P, Fe and As very good agreement was observed. Other elements like Sb, La and Ce showed a slightly larger deviation from the certified average value, but still fall well within the given ranges.

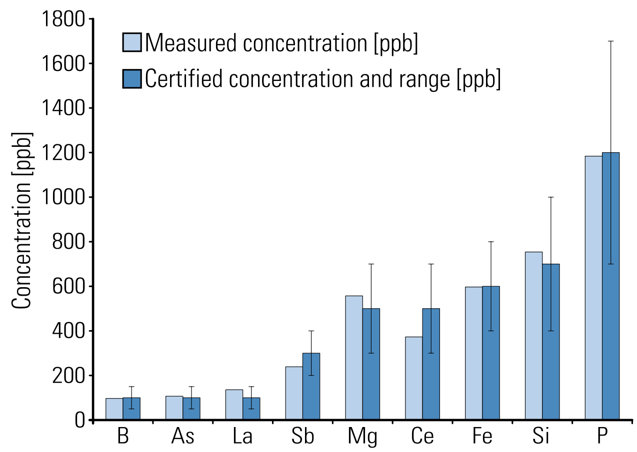

Figure 3. Comparison of the measured concentrations in the CRM Alcan 112-03 with the certified values and ranges.

In the Alcan 112-03 CRM, most elements are certified at < 100 ppb. The results shown here confirm these concentrations in all cases, but the maximum value of 100 ppb appears to be too high for many important elements. For example, the levels of the actinides Th and U should be more accurate since the radiation formed during their decay will cause failures in electronic products. As can be seen, the extreme sensitivity of the Element GD Plus GD-MS shows that these elements can be specified at < 1 ppb. Table 3 shows data for selected elements that are significantly lower in Hydro R-02 than in the Alcan 112-03. In addition to several lanthanides (La, Ce, Pr, Nd), concentrations of the heavy elements Bi, Th, and U are obtained. In Figure 4, spectra for Bi (measured at 0.5 ppb) and Th (measured at 0.02 ppb) demonstrate the capabilities of the Element GD Plus GD-MS for ultra-trace metal analyses at the ppt level directly in the solid.

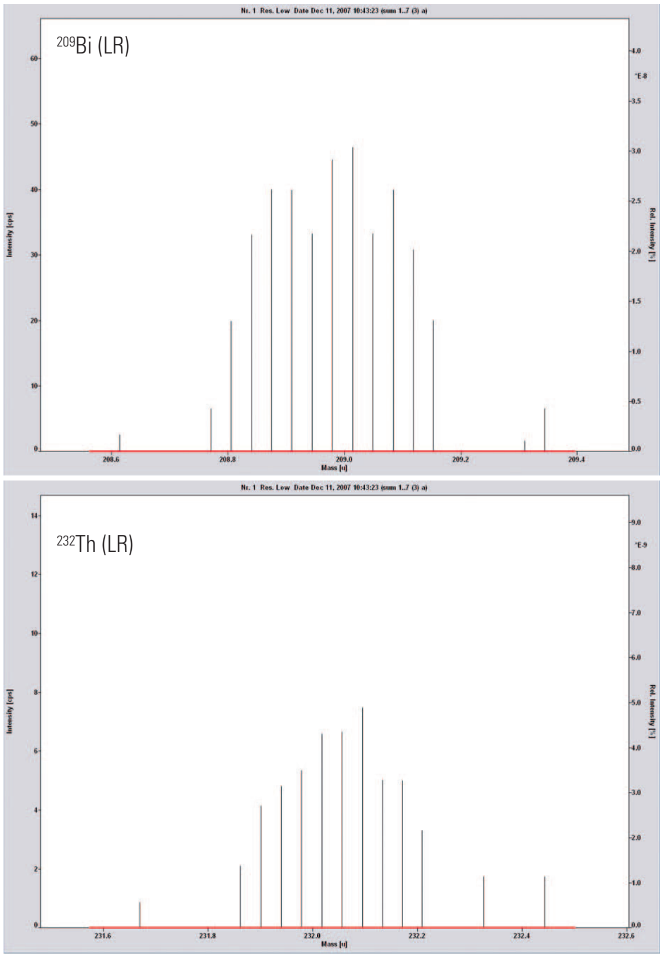

Figure 4. Example spectra for low level measurements of ^{209}Bi and ^{232}Th at ppt level in Low Resolution (LR).

Conclusions

The Thermo Scientific Element GD Plus Glow Discharge Mass Spectrometer is an extremely sensitive tool for determining ultra-trace impurities in solid samples. Even at low ppb levels in aluminum, the technique delivers accurate concentrations for all elements after minimal sample preparation and related risks of contamination. The sample throughput for such demanding applications is about three samples per hour, which is about five times faster than with previously available GD-MS instrumentation.

Table 3. Results for selected ultra-trace elements in 99.9999% Al Hydro R-02 CRM.

Isotope	Calibration	Hydro R-02 Concentration [ppb]	Certified in CRM [ppb]
^{139}La (LR)	cal	0.08	< 10
^{140}Ce (LR)	cal	0.08	< 10
^{141}Pr (LR)	RSF	0.05	< 20
^{146}Nd (LR)	STD RSF	0.12	< 10
^{209}Bi (LR)	cal	0.54	< 10
^{232}Th (LR)	STD RSF	0.017	< 1
^{238}U (LR)	STD RSF	0.029	< 1

Find out more at **thermofisher.com/GD-MS**

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