

## PRODUCTION AND CERTIFICATION OF METALLIC CERTIFIED REFERENCE MATERIALS FOR THE ANALYSIS OF ALUMINIUM ALLOYS

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### Abstract

Rio Tinto Alcan (RTA) produces Value-Added Aluminium Products (VAP) with very tight chemical composition specifications for addition ingredients and trace elements in order to meet the final product requirements for the client. The control and the certification of the alloy chemical composition rely on the utilization of the spark atomic emission spectrometry (Spark-AES) or commonly named Optical Emission Spectroscopy (OES). This technique, used by the cast house operation personnel, must be calibrated using a combination of appropriate spectroscopic Certified Reference Materials (CRM) with very tight chemical composition which are referenced to wet chemical analysis methods. This paper presents the production and certification process applied by RTA at Arvida Research and Development Center to certify the composition of CRMs. The analytical procedures and methods from classical wet chemistry to modern instrumental techniques are used to produce global and individual certificate of analysis for every CRM disc.

### Introduction

Aluminum products are widely used in different areas like transportation, packaging, construction, aerospace, castings, sheet, foil, pharmaceutical packaging, wires and cables etc...

In order to meet the properties needed by the final application, chemical elements such as Si, Mg, Mn, Cu, and Fe are added to the molten aluminum at specific given concentrations provided by the customer. A designation system from the Aluminum Association [1,2] allows alloys classification. During production, the alloy chemical composition is measured from representative samples taken from the batch of molten metal using Spark Atomic Emission Spectroscopy (Spark-AES), also known as Optical Emission Spectroscopy (OES).[3,4] This technique, used in most production centers worldwide, can give rapidly from a single spark on a sample disc, the concentration for more than 23 chemical elements, if the configuration enables it. However, since Spark-AES is a comparative technique, it requires to be referenced to Certified Reference Materials (CRMs) with precise chemical composition that will match as close as possible the alloy produced.

CRMs [5] are defined and regulated through ISO guides 30 to 35 [6-11], and one of the most important feature for a certified reference material is its homogeneity. CRMs are accompanied by a certificate with one or more property values certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed. In addition, each certified value shall be accompanied by an uncertainty at a stated level of confidence of analysis for the chemical composition.

Due to matrix effects and spectral interferences [12], and the very large number of alloys to be covered, hundreds of CRMs are then required to produce the whole range of alloys called by the end user's applications.

For more than sixty years Rio Tinto Alcan has been producing CRMs at Arvida Research and Development Center (ARDC) to analyze aluminium alloys produced by all its production centers worldwide. RTA aluminium CRMs are designed for use with direct reading on spark atomic emission spectrometers used in production centers. More than 250 CRMs are available for optimal spark-AES analysis of alloying and trace elements. This paper describes the approach used at ARDC for the production and certification of CRMs.

### Process from the Production to the Certification of Certified Reference Materials

Figure 1 illustrates the whole production cycle of CRMs from the selection of the chemical composition to produce to the final certification delivery.

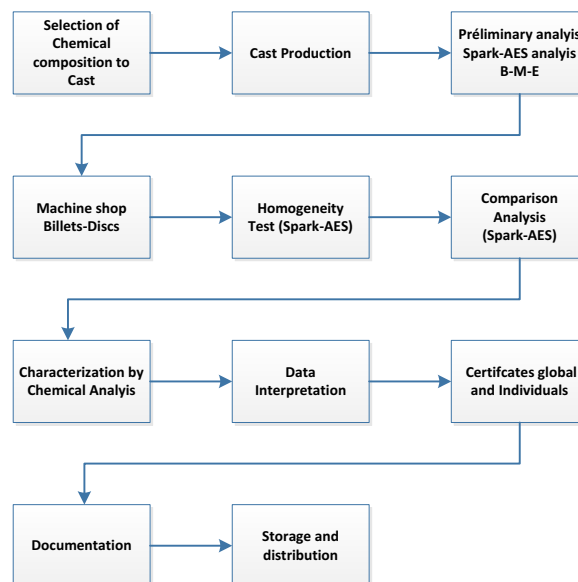


Figure 1: Production cycle steps of CRMs up to the delivery of certificates

## 1. Casting of CRM

Each CRM, produced by direct chill (DC) casting, is done using a detailed chemical composition limit based on specifications from the alloy composition needed by the client.

Then samples taken at the beginning, middle and end of casting are analyzed by Spark-AES where the results will be used to validate if the cast respect the required specification. The billets are then machined and cut in discs of 57 mm diameter and 25 mm height. A unique ID number, which relates to the billet number and the position of the disc within that billet, will be attributed to each disc.

## 2. Spark Atomic Emission Spectrometry (Spark-AES)

Spark-AES is the standard method used in the aluminum industry to analyze the chemical compositions of alloys produced by the cast house. This multi-element method is simple, rapid and reliable. However, it must be referenced using CRMs with a chemical composition matching as closely as possible the sample to be analyzed.

As illustrated in Figure 2, the principle of Spark-AES is based on the light emitted from the spark created between a flat metallic surface and the top of a counter electrode. The atomic structure of each chemical element is unique as is the light emitted after excitation [13,14]

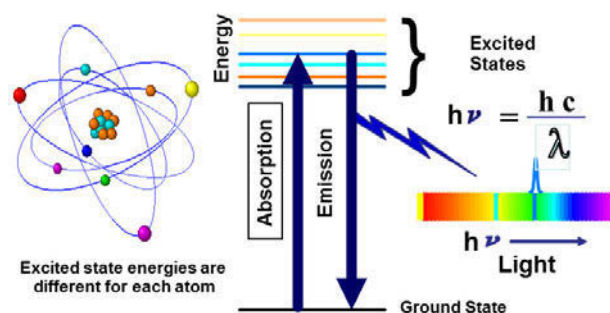


Figure 2: Principle of light emission during Spark-AES analysis

A typical spectrometer configuration as shown in figure 3, allows simultaneous multi-elements detection where photomultiplier tubes (PMT) are positioned to detect a specific wavelength range based on the resolution power of the spectrometer. Each PMT is converting the received photons into current. After calibration, the current is correlated to a concentration. Each element has its own channel which corresponds to a specific wavelength.



Figure 3: Wavelength emitted is specific for each elements present in the sample

The Spark-AES method has some limitations due to matrix effect and spectral interferences, therefore the judicious choice of interference-free spectral lines or the application of correction techniques to produce accurate analysis for a broad range of matrices by spectrometric methods are recommended.

RTA and ASTM methods [3] recommend the most frequently used spectral lines and their ionization degree for aluminum analysis based on:

- The probability of finding the interfering element in the matrix (relative concentration)
- The resolution power of the instrument as well as the order to which the observation is made
- The intensity of the interfering spectral lines
- The transition probability

Spectral interferences can be corrected through different methodologies such as using an algorithm to correct the apparent intensity, which is generally implemented within the instrument, or by using the master curve calibration methodology.

A spectrometer using a master curve calibration will require the use of a set of calibrant for each element. When used in conjunction with the 2-points standardization, this methodology has the advantage of reducing significantly any potential spectral interference and will allow correction for matrix effect.

For the analysis of real samples, the calibration curves are adjusted by using a translation and/or rotation factors that are determined through the standardization procedure. This last procedure consists in using CRMs of similar targeted sample composition so that matrix effects of alloying elements are taken into account. The resulting standardization curve will then retain the same fundamental shape as the master calibration curve.

For the analysis of trace elements, appropriate CRMs are then required. To minimize any residual effects due to macro and micro-structure on the spectral response, the CRM are analyzed on the annular band at a distance of 10 mm (Figure 4) from the edge of the sample, as specified in internal and external methods [3].

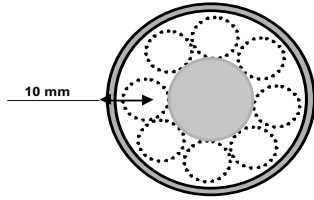


Figure 4: Spark at 10 mm from the edge

### 3. Analytical Methods

The certification of a chemical composition is determined through different techniques, analytical methods [15-17] and available quality control tools. The choice of appropriate measurement method depends on the element to be analyzed and the matrix in which the analyte is present:

- Photometric method (UV)
- Atomic Absorption Spectrometry (AAS),
- Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES )
- Inductively Coupled Plasma Mass Spectrometry ICP MS
- Spark- AES for homogeneity and variance analysis (OES)
- Spark-AES for Comparison Analysis (OES)
- Glow Discharge Mass Spectrometry (GDMS)
- Porosity test by metallographic method

As an example, the best analytical method for phosphorus analysis in aluminium alloys is the photometric method. In this method, the sample is dissolved in an acid mixture and, to avoid loss of phosphorus, a bromide saturated water is used. Ammonium molybdate solution is used to produce the phosphomolybdate complex, which is determined by UV photometric measurements at 720 nm.

The atomic absorption technique is mainly used for alkaline elements such as calcium, sodium, lithium, etc....

Several elements such as magnesium, manganese, copper, iron, and others are analyzed simultaneously by ICP methods, using either an acid or caustic dissolution.

### 4. Quality Assurance Program

ARDC is accredited ISO 17025 [18] and also participates in internal cross check analysis program as well as external round robin analyses through the Proficiency Test Program for chemical analysis of aluminium [19]. These programs assure that any bias or systematic errors can be quickly identified.

Each analytical equipment is covered by a preventive maintenance program to maintain the analytical performance. High purity, trace metal reagent, and single or multiple ion reference solutions traceable to NIST are used to avoid any contamination.

The accuracy of the analyses is checked continually with statistical process control charts (SPC) using CRM from external and internal suppliers as shown in figure 5.

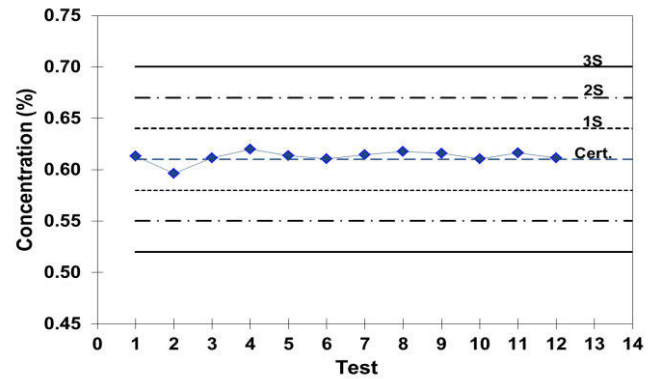


Figure 5: Results for external quality control for Fe

However analytical methods can produce different results, therefore all values outside of the control limits are flagged and investigated until the bias is solved. Corrective actions are recorded, approved and implemented. This procedure ensures continuous improvement on RTA's quality assurance program

### 5. Case Study 5182 BA Standard Certification

#### 5.1 Porosity Test for Macroscopic Defaults

Before starting the Spark-AES and chemical analysis, all the disc samples from the cast are examined for signs of physical defects such as porosity, cracks and inclusions. If, from a same billet, multiple discs are showing those defaults, the entire billet is rejected.

#### 5.2 Spark-AES for Homogeneity and Variance Analysis

This step begins with the variance analysis for each billet to determine the homogeneity for each disc. The homogeneity test depends on various parameters during the analysis such as: the standard deviation of the Spark-AES method, the instrumental drift, the variation between samples along the billet and the variance within the samples for number of sparks used. Discs showing indication of non-homogeneity are rejected.

Figure 6 and 7 show the evolution of the concentration for Mg and Na from the bottom to the top of the billet for 5182 BA standard. The concentration of Mg remains stable over the entire billet length while the concentration of Na decreases during the casting period.

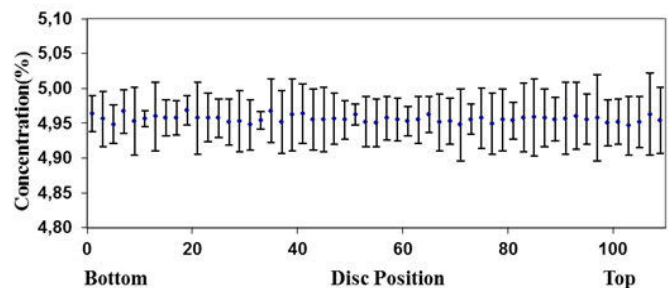


Figure 6: Homogeneity test for Mg in 5182 BA

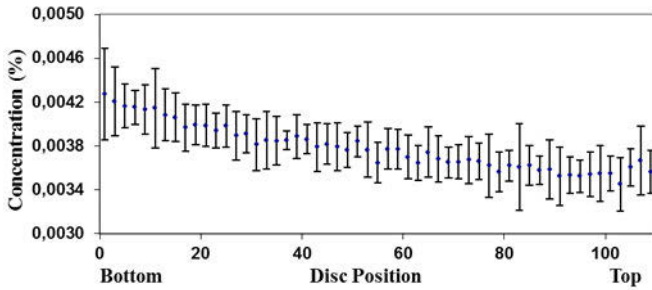


Figure 7: Homogeneity test for Na in 5182 BA

### 5.3 Spark-AES for Comparison Analysis (OES)

The Spark-AES results obtained for the new CRM 5182 BA are compared with historical data of the 9 previous 5182 series (AC, AG, AH, AM, AI, AJ, AP, AQ and AS), as shown in figure 8 for Mg, to predict the approximate certified values, which later will be confirmed by chemical analysis. This process is done for each element present in the chemical composition of the new CRM.

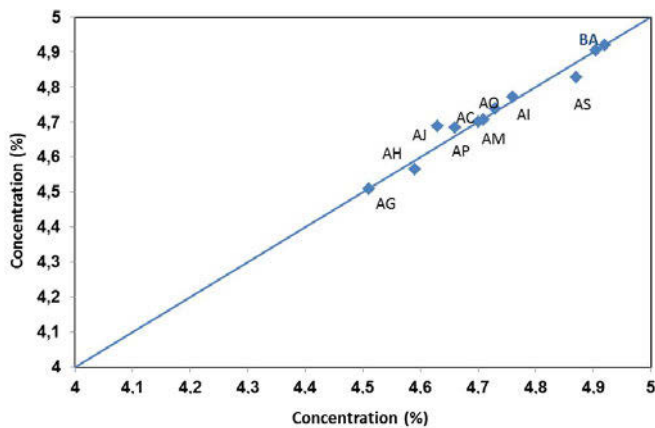


Figure 8: Comparison for Mg in 5182 BA standard with the previous series

The agreement between Spark-AES and wet chemical analysis is used to assess the accuracy of Spark-AES analytical response for the new CRM.

### 5.4 Characterization of Chemical Composition of CRM

Once the variance and comparison analysis are validated, the samples are submitted for chemical analysis.

The certification process by chemical methods is carried out in regards of the matrix alloy. Each reported value is an average of several analyses. Individual values are reported and statistically evaluated.

The mean value is compared to the value obtained from Spark-AES. If there is no disagreement, then the average value is assigned. If a disagreement is observed then each step of the analysis is checked or all of the tests are repeated.

These steps are done for each element present in the CRM.

### 5.5 Example for Mg Certification in 5182 BA

Due to the high level of Mg in 5182 alloy, the magnesium analysis requires multiple ICP methods.

As illustrated in Table I, results obtained by chemical analyses are compared to those of Spark-AES. A good correlation between the different techniques is found since the difference between the Mg values found by Spark-AES and chemical analyses is lower than relative  $\pm 1\%$ .

Table I: Comparison of Mg by wet chemical and Spark-AES analysis

Analytical Methods for Mg in 5182 BA				
Average value % (w/w)				
Spark -AES Variance	Spark -AES Comparison	ICP Multi element	ICP Bracketing	External Lab
4.99	4.92	4.96	4.96	4.98

Each analytical measurement has an uncertainty associated with it [20]. From these uncertainties, the 95 % confidence interval for Mg is estimated by the combined uncertainties derived from the Spark-AES homogeneity analysis and the average of the wet chemical analysis.

In our example the global uncertainty for Mg in 5182 BA is estimated to be 0.047%.

### 5.6 Certificate of Analysis

The certificate of analysis as shown in figure 9 and 10, report the details and the information which are essential to the use of certified reference material:

- The date of certification
- The name of the material which describe the type of reference material
- The nature of the alloy's matrix (5182)
- The code which identify the series (BA)
- The unique identifier indicating the source of the billet (E)
- The disk position within the billet (027)
- The certified value of each element with their uncertainties

As indicated in figure 9 and 10, the certified elemental composition is reported using the weight percentage unit on both global and individual certificates. Each analytical measurement has the uncertainty reported with a 95% level of confidence.

As shown in figure 9, the global certificate reports the certified values of 23 elements with their associated uncertainties.

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**Certificat d'analyse  
Matériau de référence certifié  
Certificate of Analysis  
Certified Reference Material**

**5182 BA**

Certifié le / Certified : 01/31/2003

Élément	Élément	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn
% (pp)	Weight % (w/w)	0.11	0.26	0.037	0.36	4.96	0.031	0.015	0.050
Incertitude	Uncertainty	± 0.013	± 0.012	± 0.0011	± 0.010	± 0.004	± 0.0008	± 0.0013	± 0.0011

Élément	Élément	Ti	Ag	As	B	Ba	Be	Bi	Ca
% (pp)	Weight % (w/w)	0.025					0.0012	0.008	0.0031
Incertitude	Uncertainty	± 0.0013					± 0.0001	± 0.0010	± 0.00027

Élément	Élément	Cd	Co	Ga	Hg	In	Li	Mo	Na
% (pp)	Weight % (w/w)	0.0014	0.009	0.0025	0.015	0.0024	0.0028	0.0026	0.0039
Incertitude	Uncertainty	± 0.00020	± 0.0009	± 0.00047	± 0.0004	± 0.00024	± 0.00012	± 0.0008	± 0.00024

Élément	Élément	P	Pb	Sb	Sn	Sr	Tl	V	Zr
% (pp)	Weight % (w/w)	0.0014	0.009	0.0025	0.015	0.0024	0.0028	0.0026	0.0031
Incertitude	Uncertainty	± 0.00020	± 0.0009	± 0.00047	± 0.0004	± 0.00024	± 0.00012	± 0.0008	± 0.00024

(\* valeur individuelle, "L" plus petit que, "N" valeur non certifiée)  
(\* individual value, "L" less than, "N" value not certified)

Par le présent, nous certifions les analyses ci-dessus.  
We hereby certify the above analysis.

Hafida Hamoucha

Le CRMA est accrédité (SCC) 17025 par le Conseil National des Normes (CCN), laboratoire 08  
ARDC is accredited to ISO/IEC 17025 by the Standards Council of Canada (SCC), laboratory number 08

Figure 9: Global Certificate showing Na at 0.00391 % (w/w)

Elements, such as Na as presented in figure 7, showing a decrease along the length of the billets are reported using the suffix "(i)" following the certified value of the lot of that series. This means that an individual certified value for Na is assigned for each disc of this series as presented in figure 10.

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**Certificat d'analyse  
Matériau de référence certifié  
Certificate of Analysis  
Certified Reference Material**

**5182 BA - E027**

Certifié le / Certified : 01/31/2003

Élément	Élément	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn
% (pp)	Weight % (w/w)	0.11	0.26	0.037	0.36	4.96	0.031	0.015	0.050
Incertitude	Uncertainty	± 0.013	± 0.012	± 0.0011	± 0.010	± 0.004	± 0.0008	± 0.0013	± 0.0011

Élément	Élément	Ti	Ag	As	B	Ba	Be	Bi	Ca
% (pp)	Weight % (w/w)	0.051					0.0012	0.008	0.0031
Incertitude	Uncertainty	± 0.0013					± 0.0001	± 0.0010	± 0.00027

Élément	Élément	Cd	Co	Ga	Hg	In	Li	Mo	Na
% (pp)	Weight % (w/w)	0.0014	0.009	0.0025	0.015	0.0024	0.0028	0.0026	0.0040
Incertitude	Uncertainty	± 0.00020	± 0.0009	± 0.00047	± 0.0004	± 0.00024	± 0.00012	± 0.0008	± 0.00010

Élément	Élément	P	Pb	Sb	Sn	Sr	Tl	V	Zr
% (pp)	Weight % (w/w)	0.0014	0.009	0.0025	0.015	0.0024	0.0028	0.0026	0.0031
Incertitude	Uncertainty	± 0.00020	± 0.0009	± 0.00047	± 0.0004	± 0.00024	± 0.00012	± 0.0008	± 0.00024

(\* valeur individuelle, "L" plus petit que, "N" valeur non certifiée)  
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Figure 10: Individual certificate showing Na at 0.0040 % (w/w)

## Conclusion

CRMs produced and certified at the Arvida Research and Development Center of Rio Tinto Alcan are used by the production centers worldwide to calibrate the spectrometers used for the analysis of the chemical composition of alloys requested by the clients.

The production and certification of CRMs involve multiple steps from the casting to the final delivery of certificate of analysis. Numerous analytical methods, quality controls and statistical process control analysis are applied along the certification process to guarantee the final results.

The certified reference material used as calibration samples can either be made in house or purchased. The advantage to produce CRM allows the producer to be more flexible, and also independent from external producers. Producing CRMs offers the opportunity to increase the CRM Library which enables evaluation and determination of matrix effects. However, the disadvantage is the cost and the infrastructure required to produce and certify such CRM.

The main characteristic of RTA's CRM is the chemical composition of the reference material produced to match as closely as possible the aluminium alloy to analyze in the cast house. RTA's CRM are certified for 23 alloying and trace elements which will contribute to improve accuracy of analytical results by minimizing bias and matrix effect.

The RTA methodology on Spark-AES provides not only accuracy on alloying element for alloys with tight chemical composition but also on the determination and accuracy of trace element determination. This methodology could also be transferred to other fields than the aluminum industry.

## References

1. The Aluminum Association, International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys, 1525 Wilson Boulevard, Arlington, VA, 22209, Supersedes April 2006; Revised February 2009
2. The Aluminum Association, Designations and Chemical Composition Limits for Aluminum Alloys in the Form of Casting and Ingot; 1525 Wilson Boulevard, Arlington, VA, 22209; Supersedes February 2008, Revised November 2009
3. ASTM-E1251-11, Standard Test Method for Analysis of Aluminum and Aluminum Alloys by Spark Atomic Emission Spectrometry, p. 1-10
4. ASTM-E716-10, Standard Practices for Sampling and Sample Preparation of Aluminum and Aluminum Alloys for Determination of Chemical Composition by Spectrochemical Analysis, p. 1-5

5. Markus Stoeppler, Wayne R. Wolf, Peter J. Jenks, Reference Materials for Chemical Analysis; Certification, Availability and Proper Usage, Wiley-VCH Verlag GmbH 69469 Weinheim, 2001
6. ISO Guide 30-1992, Terms and definitions used in connection with reference materials. Second Edition 1992 International Organization for Standardization 1992 (Switzerland)
7. ISO Guide 31-2000, Reference Materials- Contents of Certificates and Labels, Second Edition 2000 ISO 2000 (Switzerland)
8. ISO Guide 32-1997, Calibration in Analytical Chemistry and Use of Certified Reference Materials, First Edition 1997 International Organization for Standardization 1997 (Switzerland)
9. ISO Guide 33-2000, Uses of Certified Reference Materials Second Edition 2000, ISO 2000 (Switzerland)
10. ISO Guide 34-2000, General Requirements for the Competence of Reference Material Producers Second Edition, ISO 2000 (Switzerland)
11. ISO Guide 35-2006, Reference Materials –General and Statistical Principles for Certification- Third Edition ISO 2006 (Switzerland)
12. Archambault, J.F. Selection of Spectrographic Certified Reference Material for the Analysis of Aluminum Alloys, INALCO, 12th International Aluminum Conference, October 21-22, 2013, Montréal, Québec.
13. James D. Ingle, Jr. and Stanley R. Crouch, Spectrochemical Analysis, , Prentice-Hall Inc, 1988 - Englewood Cliffs, New Jersey 07632
14. Douglas A. Skoog and James J. Leary, Principles of Instrumental Analysis, 4th edition, Chapter 11, Saunders College Publishing, 1992
15. EN14242-CEN-2004 Aluminum and Aluminum Alloys - Chemical Analysis -Inductively Coupled Plasma Optical Emission Spectral Analysis. European Committee for Standardization, 2004 CEN
16. ASTM-E34-11e1, Standard Test Methods for Chemical Analysis of Aluminum and Aluminum-Base Alloys
17. ASTM-1479-99 (2011), Standard Practice for Describing and Specifying Inductively-Coupled Plasma Atomic Emission Spectrometers
18. ISO/IEC 17025, General Requirements for the competence of Testing and Calibration laboratories
19. ASTM- Proficiency Test Program- Chemical Analysis of Aluminum
20. Guide to the Expression of Uncertainty in Measurement First Edition 1995- International Organization for Standardization (Switzerland)