

# A SPECTROPHOTOMETRIC DETERMINATION OF BORON IN ALUMINIUM AND ALUMINIUM ALLOYS

## SPETROFOTOMETRIČNO DOLOČEVANJE BORA V ALUMINIJU IN ALUMINIJEVIH ZLITINAH

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A spectrophotometric method for the determination of boron in aluminium and aluminium alloys in the 5–100  $\mu\text{g g}^{-1}$  range was developed. A coloured complex between orthoboric acid and curcumin was formed in a buffered acetic medium. The calibration was performed by means of "spiked" samples. The validation was used to provide documented evidence that the selected method fulfils the requirements and that the method is "fit for purpose". The accuracy and traceability of the purposed method were tested by an analysis of closely matched matrix certified reference materials (CRMs). The limit of detection (LOD) and the limit of quantification (LOQ) were estimated to be 1.7  $\mu\text{g g}^{-1}$  and 3.4  $\mu\text{g g}^{-1}$ , respectively.

Key words: aluminium, aluminium alloys, boron, spectrophotometric method

V prispevku je opisana spektrofotometrična metoda za določevanje bora v aluminiju in aluminijevih zlitinah za koncentracijsko območje 5-100  $\mu\text{g g}^{-1}$ . Pri kontroliranih pogojih se bor nahaja v raztopini kot ortoborna kislina, ki tvori s kurkuminom obarvan kompleks.

Umeritveno krivuljo smo izdelali z dodatki standardne raztopine B aluminiju čistoče >99,98 %. Z validacijo smo dokazali, da izbrana metoda izpolnjuje zahteve in služi namenu. Pravilnost in sledljivost metode smo preverili z ustreznimi certificiranimi referenčnimi materiali. Določili smo mejo detekcije (LOD) in mejo določevanja (LOQ), ki sta 1,7  $\mu\text{g g}^{-1}$  in 3,4  $\mu\text{g g}^{-1}$ .

Ključne besede: aluminij, aluminijeve zlitine, bor, spektrofotometrična metoda

## 1 INTRODUCTION

Although the main reason for alloying aluminium is to increase its strength, alloying also has important effects on other characteristics of aluminium alloys. Most alloys produced as "fabricating ingots" for fabricating wrought products, and those in the form of foundry ingots, have small additions of titanium or boron, or combinations of these two elements in controlled proportions. Boron is used in aluminium and its alloys as a grain refiner and to improve the conductivity by precipitating vanadium, titanium, chromium, and molybdenum. All of these are detrimental to the electrical conductivity at their usual impurity levels in commercial grade aluminium. Boron can be used alone (at levels of 0.005 to 0.1 %) as a grain refiner during solidification, but it becomes more effective when used with an excess of titanium. Commercial grain refiners commonly contain titanium and boron in a 5-to-1 ratio. Boron has a high neutron-capture cross-section and is used in aluminium alloys for certain atomic energy applications, but its content has to be restricted to very low levels in alloys used in reactor areas where this property is undesirable<sup>1</sup>.

Atomic absorption spectrometry is not suitable for determining the levels of boron because of this technique's low sensitivity to boron. The detection limit is 1 mg/L, and there are refractory substances that interfere in the analysis<sup>2,3</sup>. Extraction procedures for enrichment and for separating the interfering matrix have, however,

been proposed<sup>4</sup>. Boron levels can only be determined with the graphite furnace technique using pyrolytically coated tubes. A fast heating rate for the atomisation and the addition of barium hydroxide increases the sensitivity<sup>5</sup>. Various authors have suggested the ICP-AES method for boron determination in steel and other metals<sup>6,7</sup>. High concentrations of aluminium can cause spectral interference and increase the detection limit. The separation of boron prior to spectrophotometric or ICP-AES determination has also been reported<sup>8,9</sup>, either by the distillation of boric acid methyl ester or by liquid extraction of the 2-ethyl-1, 3-hexandiol complex.

The curcumin method is considered the most sensitive spectrophotometric method for the determination of boron, and the most sensitive of all the known direct spectrophotometric methods for the determination of any element. The sensitivity of the method and the reproducibility of the results obtained depend on the quality of the curcumin reagent and on rigorous control of the reaction conditions (temperature, time, reagent quantities)<sup>10</sup>. Numerous elements (e. g., Fe, Mo, Ti, W, Ge, Be, and Ta) form coloured complexes with curcumin, and interfere with the determination of boron. Oxidants (e. g.,  $\text{HNO}_3$ ), and substances forming stable complexes with boron (e. g., HF), also interfere. In this study a procedure for determining boron levels in aluminium based on a well-established method for determining boron levels in steel<sup>11</sup> is described. The reliabil-

ity of the analytical results was proved by validation experiments that were performed in accordance with "A laboratory Guide to Method Validation and Related Topics" <sup>12</sup>, "Guidelines for Calibration in Analytical Chemistry" <sup>13</sup> and "Harmonised Guidelines for the Use of Recovery Information in Analytical Measurement" <sup>14</sup>.

## 2 EXPERIMENTAL

### 2.1 Apparatus

An OPTON PM 6 spectrophotometer was used for the measurements. The absorbance of the coloured solution was measured at a wavelength of 543 nm with a 1-cm optical cell.

The glassware was rinsed with acetic acid ( $\rho = 1.05$  g/ml), then with water, and finally dried.

### 2.2 Reagents

2.2.1 Hydrochloric acid ( $\rho = 1.19$  g/ml), p. a. (Merck)

2.2.2 Nitric acid ( $\rho = 1.40$  g/ml), p. a. (Merck)

2.2.3 Sulphuric acid ( $\rho = 1.84$  g/ml), p. a. (Merck)

2.2.4 Orthophosphoric acid ( $\rho = 1.71$  g/ml, p. a. (Merck)

2.2.5 Acetic acid ( $\rho = 1.05$  g/ml), p. a. (Merck)

2.2.6 Hydrogen peroxide (30 %), p. a. (Merck)

2.2.7 Sodium fluoride (40 g/L), p. a. quality (Kemika)

2.2.8 Mixture of acetic and sulphuric acid (1+1)

2.2.9 Acetic buffer solution: 225 g of ammonium acetate is dissolved in 400 mL of water, 300 mL of acetic acid is added. Solution is transferred in a 1000-mL volumetric flask and diluted to the mark with water.

2.2.10 Curcumin, acetic acid solution: 0.125 g of curcumin p. a. quality (Fluka),  $[\text{CH}_3\text{O}(\text{OH})\text{C}_6\text{H}_3\text{CH}:\text{CHCO}_2\text{CH}_2]$ , is dissolved in 60 mL of acetic acid ( $\rho = 1.05$  g/mL). The solution is transferred in a 100-mL volumetric flask and diluted to the mark with acetic acid.

2.2.11 Boron, standard solution, corresponding to 1000 mg/L, CertiPUR® Reference material (Merck). Boron, standard solution, corresponding 10 mg/L, should be prepared immediately before use by dilution.

2.2.12 CRM materials: HA1, HA3, HA4 and HA5 produced by ALUTERV-FKI, HUNGALU ENGINEERING AND DEVELOPMENT CENTRE

### 2.3 Procedure

#### 2.3.1 Preparation of test solution:

Carefully dissolve 1.00 g of sample in 10 mL of hydrochloric acid (1+1) and oxidise with 5 mL hydrogen peroxide. As soon as the attack is complete, boil for 10 min, transfer the solution quantitatively to a 100-mL volumetric flask, cool and dilute to the mark with water. The chemicals used for the sample preparation without

the addition of aluminium and boron standards should be prepared for a blank test with each analytical run.

#### 2.3.2 Formation of the coloured complex:

Place 1.0 mL of the test solution in a 100-mL tall beaker. Add 3.0 mL of the mixture of acetic and sulphuric acid (1+1) and 3.0 mL of the curcumin acetic acid solution. Stir the solutions and leave to stand for 2 h 30 min to complete the development of the colour. Add 0.5 mL of orthophosphoric acid to stabilize the colour. Shake and allow to stand for another 30 min. Add 15.0 mL of acetic buffer solution. The solution becomes orange. Allow to stand for exactly 15 min.

#### 2.3.3 Preparation of the compensating solution:

Take a 1.0-mL aliquot of the test solution and transfer it to a 100-mL tall beaker. Add 0.2 mL of sodium fluoride solution. Carefully swirl the small volume of solution and wait for 1 h. The reaction of the colour development proceeds as described in 2.3.2., including the addition of 3.0 mL of the mixture of acetic and sulphuric acid (1+1).

#### 2.3.4 Preparation of calibration solution:

Weigh 1.00 g samples of Al (99.99 %) in four 250-mL beakers and add 0.5 mL, 1 mL, 3 mL, 5 mL of boron standard solution (10 mg/L). Proceed as specified in 2.3.1., 2.3.2. and 2.3.3. Carry out the measurement with a 1.00 g sample of Al (99.99 %) without the addition of the boron standard for a blank test with each analytical run.

#### 2.3.5 Validating solutions

The same procedures (2.3.1., 2.3.2. and 2.3.3.) are carried out for the 1.00 g test samples of the relevant certified reference materials (2.2.12.). The solutions were used for the validation of a calibration curve.

#### 2.3.6 Spectrophotometric measurements

After adjusting the absorbance to zero with water, carry out the spectrophotometric measurements on the calibration solutions, the test solutions, the validating solution, and the corresponding compensating solutions at a wavelength of 543 nm using 1-cm cells.

## 3 RESULTS AND DISCUSSION

The dissolution procedure was different to the standard test method. A few dissolution procedures were tested for the aluminium samples. The dissolution in 25 % NaOH was successful, but the neutralization with diluted sulphuric acid was not repeatable. The dissolution in hydrochloric acid and oxidising with nitric acid was also sufficient, but after evaporation a trace of nitric acid remained in the sample solution. The small quantity of oxidising agent interfered with the colour development.

According to the described procedure (dissolution in hydrochloric acid and oxidising with hydrogen perox-

**Table 1:** Uncertainty assessment in spectrophotometric analysis**Tabela 1:** Ocena negotovosti spektrofotometrične analize

| CRM | Certified value<br>% B | Standard uncertainty<br>$u(\text{CRM})$ | Precision study<br>$u(\text{Precision})$ | Bias t-test<br>$t(\text{crit}) = 2,57$ | Bias study<br>$u(\text{Diff})$ | Overall bias<br>$u(\text{Bias})$ | Combined std.uncert.<br>$uc$ | Expanded uncertainty<br>$U, k = 2$ |
|-----|------------------------|---|--|--|--------------------------------|----------------------------------|------------------------------|------------------------------------|
| HA1 | 0.0007                 | 0.000077                                | 0.00004                                  | -0.42                                  | 0.000017                       | 0.000078                         | 0.0000873                    | 0.0002                             |
| HA3 | 0.0023                 | 0.000189                                | 0.00007                                  | 1.87                                   | 0.000071                       | 0.000202                         | 0.000214                     | 0.0004                             |
| HA4 | 0.0065                 | 0.000302                                | 0.00033                                  | 0.87                                   | 0.0002                         | 0.000363                         | 0.000488                     | 0.001                              |
| HA5 | 0.014                  | 0.000756                                | 0.0005                                   | -0.57                                  | 0.0003                         | 0.000813                         | 0.000954                     | 0.002                              |

ide), the calibration graph was linear in the concentration range 5–100  $\mu\text{g g}^{-1}$ . The extension of the measurement range for higher boron contents is possible when the 0.5-g test sample is used.

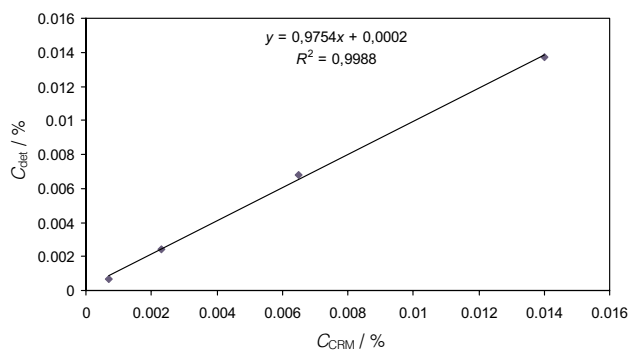
**The validation of the calibration procedure** was based on the validation function (recovery function)  $X_{\text{estim}} = f(X_{\text{true}})$ , which was estimated using normal LS regression  $Y(X_{\text{estim}}) = b + a X_{\text{true}}$ , where  $a$  and  $b$  are validation coefficients with the analytical meaning of a constant bias ( $b$ ) and a proportional bias ( $a$ ). The observed values (as a dependent variable) for the CRMs were correlated with the theoretical values (as an independent variable) by linear regression. The coefficient of correlation ( $R^2$ ) was used as an index that indicates how well the regression line represents the actual data (**Figure 1**).

**The linear range** of the spectrophotometric method was more than one decade, i.e., between three and thirty times the detection limit. The calibration curve passes through the origin.

**The trueness** was determined by means of four certified reference materials (2.2.12.). The bias  $t$ -test values were compared with the  $t_{\text{critical}}$  value ( $t_{(6)} = 2,57$ ). As long as the  $t$ -test value is smaller than  $t_{\text{critical}}$  we concluded that there is no statistically significant bias (**Table 1**).

**The limit of detection (LOD)** was determined as three times the random variation in the blank.

It was 1.7  $\mu\text{g g}^{-1}$ , and the **limit of quantification (LOQ)** for B was 3.4  $\mu\text{g g}^{-1}$ .

**Figure 1:** Validation of calibration curve by means of certified reference materials ( $C_{\text{CRM}}$  – certified value,  $C_{\text{det}}$  – determined value)**Slika 1:** Validacija umeritvene krivulje s certificiranimi referenčnimi materiali

**The uncertainty estimation** of the method was based on the best available estimation of the overall precision and the best available estimation of the overall bias and its uncertainty. The uncertainty of the instrument operation was estimated from a series of repeated observations by calculating the standard deviation as the overall precision of the method. The calibration uncertainty was contained in an overall bias study. The data for the measurement uncertainty evaluation is given in **Table 1**.

The overall precision was estimated under a repeatability condition that gives a fair indication of the in-house variability normally encountered. It was performed with four different CRMs (2.2.12.), marked as HA1, HA3, HA4 and HA5. The standard uncertainty  $u(\text{precision})$  for a single determination was estimated by dividing standard deviation by  $\sqrt{6}$ .

The overall bias was estimated by an analysis of the relevant CRMs (**Table 1**) that cover the analysed concentration range using the complete measurement procedure. The bias estimated in this way combines the bias in the laboratory performance with any bias intrinsic to the method in use. The mean difference ( $\text{Diff}$ ), defined as the average difference of the certified value ( $C_{\text{CRM}}$ ) and the determined value ( $C_{\text{det}}$ ), and the standard deviation of these differences  $s(\text{Diff})$  for all four CRMs were determined. The standard uncertainty was calculated as a standard deviation of the mean difference, using the equation:  $u(\text{Diff}) = s(\text{Diff}) / \sqrt{n}$ , where  $n$  is the number of repeated analyses ( $n = 6$ ). A significance test was used to establish whether the measurements differ significantly from the assumed correct values (**Table 1**). The test statistic  $t$  was calculated using equation (1). This value was compared with the two-tailed critical value  $t_{\text{crit}}$ , for  $n-1$  degrees of freedom at 95 % confidence ( $n = 6$ ,  $t_{\text{crit}} = 2,57$ ).

$$t = \frac{|\overline{\text{Diff}}|}{u(\text{Diff})} \quad (1)$$

The overall bias was insignificant ( $t < t_{\text{crit}}$ ), the uncertainty associated with the bias could be calculated as a combination of independent variables (Equation 2): the standard uncertainty of the CRM value (type B) with the standard uncertainty associated with the bias (type A).

$$u(\text{Bias}) = \sqrt{u(\text{CRM})^2 + u(\overline{Diff})^2}$$

The combined standard uncertainty  $u_c$  and expanded uncertainty  $U$  were also calculated.

In this study, all the important uncertainty sources were included in the calculation of the combined measurement uncertainty. The magnitudes of the uncertainty components vary with the concentration level of the measurand and the combined standard uncertainties were similar to the standard uncertainties on the certified reference materials. It was proved for the concentration range that boron was added as grain refiner.

#### 4 CONCLUSIONS

Boron can be determined in aluminium and aluminium alloys without preconcentration and separation when the sensitive curcumin spectrophotometric method is used. The absence of bias demonstrates that the analytical method is capable of measuring the investigated component accurately in CRMs. An extrapolation of this observation to real test samples is only warranted as long as the test sample resembles the CRM very closely in terms of both matrix and homogeneity.

The uncertainty components were included in the calculation of the combined standard uncertainty  $u_c$ . The contributions of individual uncertainty sources were comparable. The expanded uncertainty  $U$  was calculated

by multiplying the combined standard uncertainty with a coverage factor of 2. Laboratories should know the uncertainty associated with a test result, whether it is reported or not. ISO/IEC 17025 requires that uncertainty estimates must be reported when the client requires them, when it is relevant to the validity or application of the test result, or when the uncertainty affects the compliance with a specification limit.

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