

## Spectro-photometric determinations of Mn, Fe and Cu in aluminum master alloys

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**Abstract.** Highly reliable, fast and cost effective Spectro-photometric methods have been developed for the determination of Mn, Fe & Cu in aluminum master alloys, based on the development of calibration curves being prepared via laboratory standards. The calibration curves are designed so as to induce maximum sensitivity and minimum instrumental error (Mn 0.1mg/100ml-2mg/100ml, Fe 0.01mg/100ml-0.2mg/100ml and Cu 2mg/100ml-10mg/ 100ml). The developed Spectro-photometric methods produce accurate results while analyzing Mn, Fe and Cu in certified reference materials. Particularly, these methods are suitable for all types of Al-Mn, Al-Fe and Al-Cu master alloys (5%, 10%, 50% etc. master alloys). Moreover, the sampling practices suggested herein include a reasonable amount of analytical sample, which truly represent the whole lot of a particular master alloy. Successive dilution technique was utilized to meet the calibration curve range. Furthermore, the workout methods were also found suitable for the analysis of said elements in ordinary aluminum alloys. However, it was observed that Cu showed a considerable interference with Fe, the later one may not be accurately measured in the presence of Cu greater than 0.01 %.

### 1. Introduction

Aluminum master alloy is the aluminum combined with one or two other elements (e.g., Al-Cu 50 % master alloy) and is used as a CHARGE for alloying during the melting of wrought aluminum alloys. Normally aluminum master alloys are produced for such elements that are the alloying elements of Aluminum wrought alloys. Commonly used Aluminum master alloys are Al-Mn, Al- Si, Al-Ni, Al-Cu, Al-Mg, Al-V, Al-Zn, Al-Zr, Al-Ti, Al-Cr and Al-Fe and are available in 5 or 7 Kg ingots. The use of Aluminum master alloys offers distinct advantages over the addition of individual element during alloying of aluminum wrought alloys. Three major advantages are: (a) these can be calculated to become part of the initial cold charge i.e. melted with the metal at low temperature. This rapid dissolution results in a significant reduction in dross formation, minimal gas pick up and extended furnace life (b) significantly reduces the amount of energy required and shortens the length of melt time (c) gives higher accuracy to meet specified composition limits [1-2].

The above mentioned benefits can only be attained by knowing the true composition of a particular master alloy [3]. Instantly, master alloy manufacturer provides a broad range of chemical composition for a single lot of particular master alloy, for example, in Al-Cu 50 % master alloy, Cu element may varies from 47 to 52% or else as affirmed by the manufacturer. On the other hand for charge calculation one should know the nearest possible true composition of a particular master alloy so that melt could be adjusted as quickly as possible to save time, energy, and material. Also, chemical



composition analysis of master alloys is indispensable for the strict quality control of master alloys production. Spark optical emission spectroscopy (OES) is a quick and reliable tool for analysis of aluminum alloys but it does not work for master alloys because of high percentage of alloy elements (e.g., Al-Cu 50% master alloy)[6]. Other techniques such as: Gravimetric technique, Atomic Absorption Spectrometry (AAS), Atomic Emission Spectrometry (AES), and X-ray fluorescence spectroscopic (XRF) technique are also not valid for such a high concentrations [4-8].

Previously Naveed et al [3] reported a method in which Aluminum master alloys were re-melted along with Aluminum ingots of 99.9% purity in an electrical crucible furnace and subsequently analyzed by spark optical emission spectrometer (OES). However, the technique was costly. Also, the obtained analysis results were significantly dependent upon recovery of a certain element in a particular melting process.

Spectro-photometry is a technique that uses the absorbance of light by an analyte (the substance to be analyzed) at a certain wavelength to determine the analyte concentration. Spectro-photometric analysis is based on development of calibration curve: several standards containing exactly known concentrations of the analyte are introduced into instrument, and the instrumental response is recorded. Ordinarily this response is corrected for instrument output obtained with a blank. Ideally, the blank contains all of the components of the original sample except for the analyte. The resulting data are then plotted to give a graph of corrected instrument response versus analyte concentration, and this graph in turn can be used to find the concentration of an unknown [9-10].

In this contribution we presented a cost effective and reliable spectro-photometric method for the composition analysis of aluminum master alloys. Analysis of Al-Mn, Al-Fe, & Al-Cu master alloys using the calibration curve of Mn, Fe, & Cu are reported. Furthermore, the designed methods are verified by analyzing certified reference materials (CRM) containing Mn, Fe, & Cu against their calibration curves.

## 2. Experimental methods

### 2.1. Development of calibration curve of Mn

A calibration curve ranging from 0.1mg/100ml to 2mg/100mlMn was obtained according to ASTM standard [11]. This was done by transferring 1.000 g of pure Mn metal powder (weighed accurately to 3<sup>rd</sup> decimal) to a 500-ml beaker and dissolved in 100 ml of H<sub>2</sub>SO<sub>4</sub> (1+9 v/v). The solution was then boiled for 5 minutes and transferred to 1 liter volumetric flask (when cool down), diluted to the volume and mixed. This 100mg/100ml solution was named as Mn standard solution-A.

From the Mn standard solution-A transferred 100 ml in 1 liter volumetric flask, diluted to the volume and mixed. This 10mg/100ml solution was named as Mn standard solution-B.

Calibration solutions were prepared by transferring 0 (reagent blank), 1.0, 2.0, 5.0, 10.0, 15.0, and 20.0 ml of Mn Standard Solution B (1 ml = 0.1mg Mn (10mg/100ml)) to 100-ml volumetric flasks. To each 15 ml of H<sub>2</sub>SO<sub>4</sub> (1+1 v/v), 10 ml of HNO<sub>3</sub>, and 5 ml of H<sub>3</sub>PO<sub>4</sub> were added and Diluted to about 70 ml. For color development, the solutions were heated to boiling in a water bath and 20 ml of KIO<sub>4</sub> (25 g/L) solution was added in each. The boiling process was continued for an hour until the characteristic color developed. The solution was then cooled to room temperature and diluted to volume with potassium iodated water (water free from reducing agents). Photometric measurements were made at approximately 525 nm against the reagent blank.

### 2.2. Development of calibration curve of Fe

A calibration curve ranging from 0.02mg/100ml to 0.2mg/100ml for Fe was obtained according to ASTM standard [11]. This was done by transferring 0.1000 g of pure Fe metal powder (weighed accurately to 3<sup>rd</sup> decimal) to a 500-ml beaker and dissolved in 50 ml of H<sub>2</sub>O, 25 ml HCL, 1ml HNO<sub>3</sub>. The solution was then heated to dissolve Fe and transferred to 1 liter volumetric flask (when cool down), diluted to the volume and mixed. This 10mg/100ml solution was named as Fe standard solution-A.

From the Fe standard solution-A transferred 100 ml in 500 ml volumetric flask, added 10 ml HCL, diluted to the volume and mixed. This 2mg/100ml solution was named as Fe standard solution-B.

Calibration solutions were prepared by transferring 0 (reagent Blank), 1.0, 2.0, 4.0, 7.0, 10.0ml of Fe Solution B (1 ml = 0.02 mg Fe) to five 100-ml volumetric flasks. Diluted to 60 ml and for color development : added 8mlNH<sub>2</sub>OH·HCl (100g/L) solution, 10ml Sodium acetate-acid (272g/L) buffer solution and 10ml of1,10-phenanthroline(2g/L) solution, diluted to volume, mixed and allowed to stand for 5 min. Photometric measurements were made at approximately 510 nm against the reagent blank.

### 2.3. Development of calibration curve of Cu

0.1g of pure Cu metal powder (weighed accurately to 3rd decimal) was dissolved in a 5ml of nitric acid and diluted to 100 ml in a volumetric flask (100mg/100mlstock Cu solution).

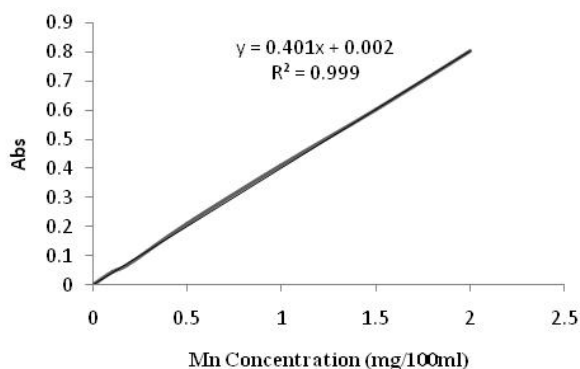
2ml, 4ml, 6ml, 8ml, and 10mlof the stock Cu solution were transferred in five different volumetric flasks of100ml. After that the ammonia solution was gradually added in each volumetric flask, resulting in a change of color(the color turns to dark blue). Adding ammonia solution was continued until a stabilized color was achieved (i.e., no further color change occurs by adding more ammonia solution). Additional 3mlof ammonia solution was added in each and diluted to the volume. Photometric measurements were made at approximately 610 nm against distilled water as a reagent blank.

### 2.4. Determination of Mn, Fe, and Cu in aluminum master alloys

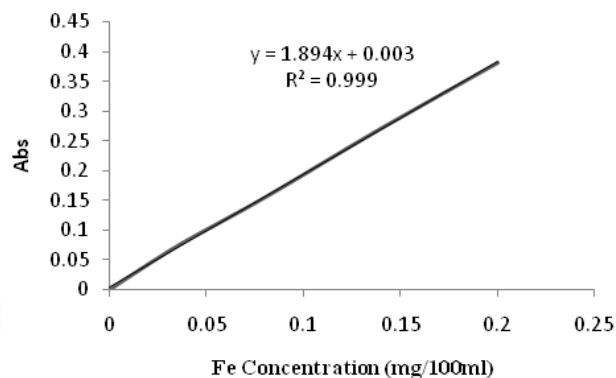
After the development of calibration curves, some test runs were conducted to characterize the calibration curves. This was done by testing Mn, Fe and Cu in certified reference materials (CRM's). Sample preparation was started with the chipsformation ofCRM's using lathe machine. Similarly, master alloy samples were collected in chips form by drilling several master alloy ingots of a single lot (e.g., Al-Mn 10 % master alloy lot) and mixed them.The test and master alloy solutions were prepared in the same way as that of calibration solutions but using successive dilutions to meet with the ranges of Mn, Fe and Cu calibration curves.

## 3. Results and discussion

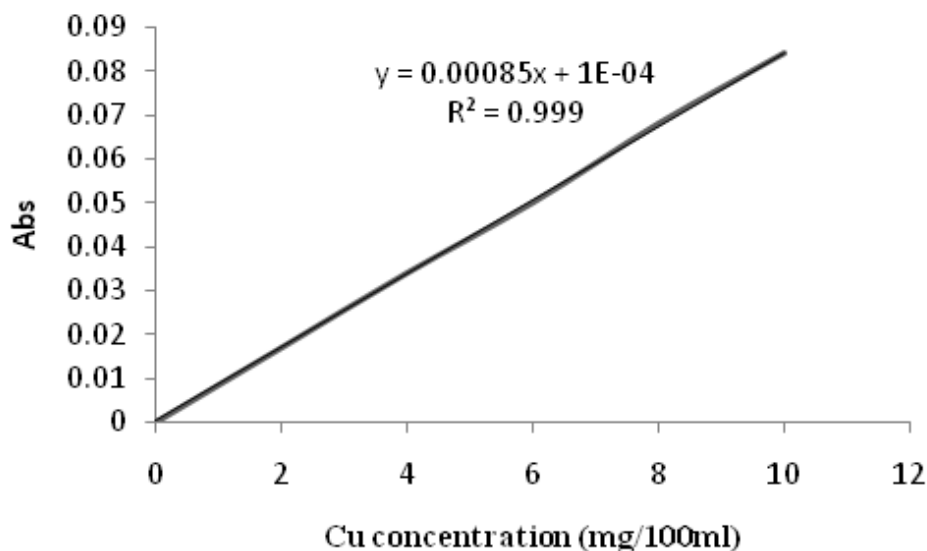
Calibration standards for Mn, Fe and Cu were prepared and their response in the visible region of electromagnetic spectrum was recorded. Figures 1-3 represent the corresponding calibration curves.



**Figure 1.**Calibration curve of Mn. Photometric measurements were made at 525 nm



**Figure 2.**Calibration curve of Fe. Photometric measurements were made at 510 nm



**Figure 3.** Calibration curve of Cu. Photometric measurements were made at 610 nm

At the outset the test run analysis is carried out in order to characterize the calibration curves. This is done by testing Mn (wt. %) in Certified Reference Materials (CRM's) against the calibration curve prepared for Mn. The photometric calculations and analysis results of Mn are shown in Table 1. It may be seen from Table 1 that the results of photometric analysis of Mn in CRM's (49712b-4 & A333.O AE) are in well agreement with certified values. Also the spectro-photometric results of Mn matches good with spark OES results. These results standardize the characteristic calibration curve of Mn. Table-1 also enlists the spectro-photometric calculations and analysis results of 5%, 10% and 20% Al-Mn master alloys. The Mn % is within the prescribed range for all types of master alloys.

**Table 1.** Spectro-photometric data for analysis of Mn

Sample Identity	Known Value, Mn Wt. %	Sample weight/Dilution for photometry	Concentration found by photometry (mg/100ml)	Result, Mn Wt. %
Alcan International Ltd. CRM ALC-A 333.0-AE	0.32	0.1g/100ml	0.333	0.333
Bureau of Analysed Samples (BAS) Ltd. CRM NCS HS 49712b-4	1.93	0.05g/100ml	0.967	1.934
AA 2024	0.601	0.1g/100ml	0.609	0.609
Mn 10% MA	9-11	0.1g/20x100ml	0.507	10.14
Mn 20% MA	18-22	0.1g/20x100ml	1.024	20.48

Where, CRM=certified reference material, MA=master alloy, x=multiplication

The photometric calculations and analysis results of Fe are represented in Table 2. It may be seen from Table 2 that the results of photometric analysis of Fe in CRM (49712b-4) are close to the certified value. However for CRM (A333.O AE) there is a large deviation in spectro-photometric analysis results as compared to certified value. This happens because CRM (A333.O AE) contains high % of

Cu (3.5%) that interferes with Fe [11]. Also the spectro-photometric results of Fe for AA1050 are closed to OES value because of low % of Cu. These results standardize the characteristic calibration curve of Fe and express that the Fe can only be determined accurately in the absence of Cu. The spectro-photometric calculations and analysis results for 10% Al-Fe master alloy are also shown in Table 2. The Fe % is within the prescribed range.

**Table 2.**Spectro-photometric data for analysis of Fe

Sample Identity	known value, Fe Wt. %	Sample weight /Dilution for photometry	Concentration found by photometry (mg/100ml)	Result, Fe Wt. %
Bureau of Analysed Samples (BAS) Ltd. CRM NCS HS 49712b-4	0.242	0.1g/2x100ml	0.111	0.222(Cu=0.057)
Alcan International Ltd. CRM ALC-A 333.0-AE	0.78	0.1g/5x100ml	0.051	0.255*
AA 1050	0.37	0.1g/10x100ml	0.033	0.33 (Cu= 0.02)
Fe 10% MA	9-11	0.1g/100x100ml	0.101	10.1

Where, CRM=certified reference material, MA=master alloy, \*low reading due to Cu (3.53%) interferes, x=multiplication

First the Cu (wt. %) is determined in CRM against the calibration curve prepared for Cu. The photometric calculations and analysis results of Cu are shown in Table 3. It may be seen from Table 3 that the results of photometric analysis of Cu in CRM (A333.O AE) are just close to the certified value. Also the spectro-photometric results of Cu for AA2219 do not match well with OES results. This variation as compared to the Certified or OES value is due to the reason that the absorption coefficient for copper tetra amine complex is very small (Figure 3. calibration curve of Cu). The spectro-photometric calculations and analysis results for 10% and 50% Al-Cu master alloys are also shown in Table 3. The Cu % is within the prescribed range but lies away from central value. Again this is because the absorption coefficient for copper tetra amine complex is very small which probably increases the instrumental error.

**Table 3.**Spectro-photometric data for analysis of Cu

Sample Identity	Known value, Cu Wt. %	Sample weight /Dilution for photometry	Concentration found by photometry (mg/100ml)	Result, Cu Wt. %
Alcan International Ltd. CRM ALC-A 333.0-AE	3.53	0.5g/5x100ml	3.3	3.3
AA 2219	6	0.5g/5x100ml	6.23	6.23
Cu 10% MA	9-11	0.5g/5x100ml	9.5	9.5
Cu 50% MA	47.5-52.5	0.1g/5x100ml	9.42	47.1

Where, CRM=certified reference material, MA=master alloy, x=multiplication

#### 4. Conclusions

Chemical compositional analysis of Al-Mn, Al-Fe, and Al-Cu master alloys are necessary to adjust the melt chemistry quickly. Also, it is indispensable for the strict quality control of master alloys production. The presented spectro-photometric methods are reliable and cost effective. Particularly, these spectro-photometric methods cover all the ranges for Mn, Fe and Cu determinations in aluminum master alloys. Also, the sampling practices (chips formation and mixing) suggested here easily include a large number of master alloy ingots, whose average results are the true representatives of the whole lot.

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