

Determination of Micro Amount of Iron in Aluminium Metals and Aluminium Alloys by Atomic Absorption Spectrometry

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Determination of Micro Amount of Iron in Aluminium Metals and Aluminium Alloys by Atomic Absorption Spectrometry*

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Synopsis

The method of determination of iron by atomic absorption spectrometry was applied to the analysis of aluminium metals and alloys.

The optimum conditions for the determination were as follows: the wavelength 2483 Å, the current of the hollow cathode lamp for Fe 30 mA, the slit width 0.11 mm, air pressure 1.5 kg/cm², acetylene pressure 0.5 kg/cm². In the case of the atomizing after an extraction with MIBK, the optimum acetylene pressure was 0.3 kg/cm² with water-cooling of the burner. The presence of alloying elements and acids did not interfere except nickel, the interference of which varied with the anions present.

A rapid method of the determination of 0.05~1.0% of iron in aluminium metals and alloys without any separation of main elements was established. Also, as small as 0.0005~0.01% of iron in high purity aluminium was determined after the extractive concentration of Fe with MIBK.

I. Introduction

The application of atomic absorption spectrometry to the analysis of metals has greatly progressed because of the simplicity of pretreatment of the samples and the comparatively small effect of the matrix. For example, this spectrometry has been applied to the determinations of magnesium in cast iron⁽¹⁾, of chromium in iron and steel⁽²⁾, and of iron in tungsten carbide⁽³⁾, all by Belcher and his co-worker, and to the determinations of magnesium and calcium in slag, and of magnesium in cast iron by the addition of standard substance, by the present author and others⁽⁴⁾. The limit of detection of iron by the atomic absorption spectrometry has been reported variously as 2.5 µg/ml⁽⁵⁾ and 1.0 µg/ml⁽⁶⁾, and the determination of a micro-amount of iron in high-purity aluminium metals was considered difficult.

In the present series of work, examinations were made of the determination of iron in aluminium metals and aluminium alloys by the atomic absorption

* The 1262nd report of the Research Institute for Iron, Steel and Other Metals.

(1) C.B. Belcher and H.M. Bray, *Anal. Chim. Acta*, **26** (1962), 322.

(2) K. Kinson, R.J. Hodges and C.B. Belcher, *ibid.*, **29** (1963), 134.

(3) C.B. Belcher, *ibid.*, **29** (1963), 340.

(4) H. Gotô, S. Ikeda and I. Atsuya, *Bunseki Kagaku*, **13** (1964), 111.

(5) J.W. Robinson, *Anal. Chem.*, **32** (1960), 32.

(6) K. Yasuda, S. Matsudaira, S. Sato, M. Sugawara and H. Takeuchi, *Hitachi Hyoron*, **44** (1962), 1180.

spectrometry and a method of rapid determination of iron of around 0.05~1.0% present in the sample, without separation of the main component, was established. In addition, a method of the determination of a micro-amount of iron of 0.0005~0.01% in high-purity aluminium metal was established by the application of extraction⁽⁷⁾ of iron, with methyl isobutyl ketone to remove the effect of matrix and to concentrate the component, and by spraying this solution to increase the sensitivity by the solvent effect.

II. Reagents and apparatus

1. Reagents

Standard iron solution: Electrolytic iron (99.9%) was dissolved in hydrochloric acid containing a small quantity of nitric acid, the solution was evaporated to dryness, the residue was dissolved in a small quantity of nitric acid, and diluted with distilled water to make a solution of 10 mg/ml. This solution was diluted to the desired concentration at the time of use.

Methyl isobutyl ketone: Special Grade product was shaken with 7N hydrochloric acid before use.

Acids and salts used were all Special Grades.

Magnesium solution: The metal was dissolved in hydrochloric acid to make a solution of 10 mg/ml.

2. Apparatus

Hitachi Spectrophotometer Model EPU-2A was used, with atomic absorption attachment Model RA-1, and air-acetylene mixture for the gas. Hollow cathode lamp of iron was used as the light source, and a fish-tail type burner, with an outlet of 7 cm in length was used.

III. Experimental and results

1. Investigation of working conditions

(i) Determination of wavelength for measurement

There are three resonance absorption lines for the measurement of iron, i.e., at 2483, 3719, and 3722 Å. As shown in Table 1, the line at 2483 Å is the most sensitive, being about 5 times more sensitive than that of 3719 Å and about 10 times that of 3722 Å. This order does not vary even with the use of methyl isobutyl ketone as the solvent of extraction and, therefore, 2483 Å was adopted for the measurement.

(ii) Relationship between current of hollow cathode lamp and absorbance

Examinations were made of the relationship between the current and the absorbance with various working current of the hollow cathode lamp by using aqueous solutions containing 15, 30, and 45 µg/ml of iron. As shown in Fig. 1,

(7) H. Gotô, Y. Kakita and Furukawa, *Nippon Kagaku Zasshi*, 79 (1958), 1513.

Table 1. The investigation of wavelength of iron.

Wavelength (Å)	Absorbance*		Absorbance** Iron 4 µg/ml
	Iron 15 µg/ml	Iron 30 µg/ml	
2483	0.051	0.100	0.121
3719	0.008	0.017	0.028
3722	0.005	0.009	0.014

* Aqueous solution

** Methyl isobutyl ketone

Working condition: Current of hollow cathode lamp 30A,
Slit width 0.11 mm,
Air pressure 1.5 kg/cm²,
Acetylene pressure 0.5 kg/cm².

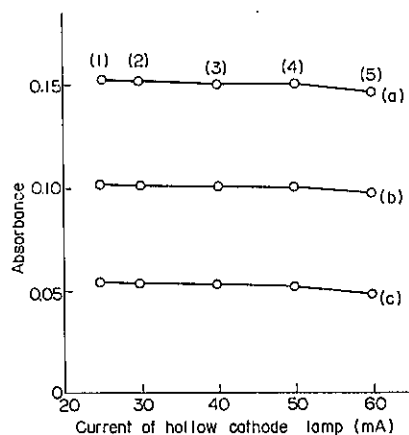


Fig. 1. The influence of hollow cathode lamp current on the atomic absorption sensitivity.

(a) iron 45 µg/ml (b) iron 30 µg/ml (c) iron 15 µg/ml

Slit width: (1) 0.13 mm (2) 0.11 mm (3) 0.09 mm (4) 0.08 mm (5) 0.07 mm

Air pressure: 1.5 kg/cm² Acetylene pressure: 0.5 kg/cm²

the absorbance increased with lowering current but below 25 mA, the intensity of the light became so weak that the slit width had to be widened. Therefore, the current density of 30 mA was adopted.

(iii) Relationship between gas pressure and absorbance

The absorbance of an aqueous solution containing 30 µg/ml of iron was measured with constant air pressure but with varying acetylene gas pressure. The result shown in Fig. 2 indicates that the absorbance does not increase at constant air pressure even if acetylene pressure is increased, but increases with increasing air pressure due to the increase in the amount of the sample solution sprayed. With consideration on the limit of the gas flow-meter used and on the stability of the flame, 1.5 kg/cm² of air pressure and 0.5 kg/cm² of acetylene pressure were adopted. However, the use of methyl isobutyl ketone as a solvent

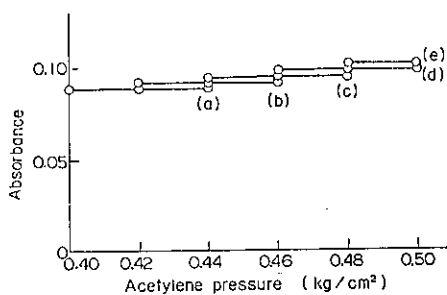


Fig. 2. The relation between gas pressure and atomic absorption sensitivity.
 Iron $30 \mu\text{g/ml}$, Slit width 0.11 mm , Current of hollow cathode lamp 30 mA
 Air pressure: (a) 1.1 kg/cm^2 (b) 1.2 kg/cm^2 (c) 1.3 kg/cm^2 (d) 1.4 kg/cm^2
 (e) 1.5 kg/cm^2

Table 2. The relation between the precision of measurement and acetylene pressure.
 (Solvent: Methyl isobutyl ketone)

Acetylene pressure (kg/cm^2)	($\Delta T/T$)	
	Air cooling of burner	Water cooling of burner
0.26	± 0.2	± 0.2
0.28	± 0.2	± 0.2
0.30	± 0.3	± 0.2
0.32	± 0.4	± 0.3
0.34	± 0.5	± 0.4

ΔT : Fluctuation of meter

T: Transmittancy

was found to make the measurement unsuitable at 0.5 kg/cm^2 pressure of acetylene due to the reducing flame, and examinations were made with lower acetylene pressure. The problem in the use of methyl isobutyl ketone as a solvent is the precision of measurement. Examination for the optimal acetylene pressure gave results shown in Table 2, indicating that the pressure of $0.28 \sim 0.30 \text{ kg/cm}^2$ is the most appropriate, and the degree of precision increased by water-cooling of the burner. The sensitivity was found to increase with lowering acetylene pressure but too low a pressure caused extinction of the flame. It was also noted that acetylene pressure should be lowered after sufficiently spraying methyl isobutyl ketone solution because, otherwise, the flame went out with explosion.

In accordance with foregoing examinations, conditions for the measurement were adopted as follows: In the case of spraying an aqueous solution: Wavelength of 2483 \AA , current of the hollow cathode lamp 30 mA , slit width of 0.11 mm , air pressure of 1.5 kg/cm^2 , and acetylene pressure of 0.5 kg/cm^2 . In the case of spraying methyl isobutyl ketone solution, acetylene pressure alone was changed to 0.30 kg/cm^2 , with water-cooling the burner.

2. Effect of acid

The usual acids used for dissolving the sample, such as hydrochloric, nitric, perchloric, and sulfuric acids were examined. Effect of the acid on iron was examined on $30 \mu\text{g/ml}$ of iron with varying concentration of the acid in the range of 0.05 to 1.0 *N*. As shown in Fig. 3, a slight decrease in the absorbance was found with increasing concentration of nitric, sulfuric, and perchloric acids but their effect was slight. Hydrochloric acid was found to give a large effect and was considered to be unsuitable for use. Considering the effect of existing elements, as will be described later, perchloric or nitric acid seemed to be more suitable than sulfuric acid.

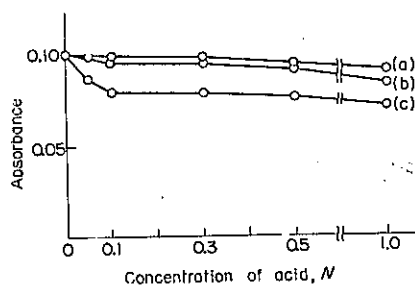


Fig. 3. Effect of acid, *N*
Fe $30 \mu\text{g/ml}$ (a) $\text{NHO}_3, \text{HClO}_4$ (b) H_2SO_4 (c) HCl

3. Effect of coexisting elements

Examinations were made of the effect of usual elements found in aluminium metals and aluminium alloys on $40 \mu\text{g/ml}$ of iron by adding 0 to $400 \mu\text{g/ml}$ of silicon, copper, sodium, zinc, manganese, magnesium, phosphorus, nickel, chromium, cadmium, and potassium. Practically none of the metals had any interfering effect but, as shown in Fig. 4, while the addition of up to $200 \mu\text{g/ml}$ of nickel as a perchlorate solution had no effect on $40 \mu\text{g/ml}$ of iron, the addition of more than $100 \mu\text{g/ml}$ of nickel as aqueous nitrate or hydrochloride solution resulted in a slight effect. When added as a sulfate solution, up to $50 \mu\text{g/ml}$ of nickel showed some effect. Above a definite quantity of nickel, the absorbance became constant irrespective of anions. From these results, it seems advisable not to use sulfuric acid considering the use of light aluminium alloys containing a small amount of nickel. This tendency was similarly observed, though in a slight degree, with cobalt.

4. Effect of aluminium

Examinations were made of the effect of the presence of a large amount of aluminium on the determination of iron in aluminium metals and alloys. In other words, the amount of the sample to be taken was examined. The standard nitric acid solution of iron (20 and $40 \mu\text{g/ml}$) was, after the addition of $0.1, 0.2, 0.3,$ or 0.4g

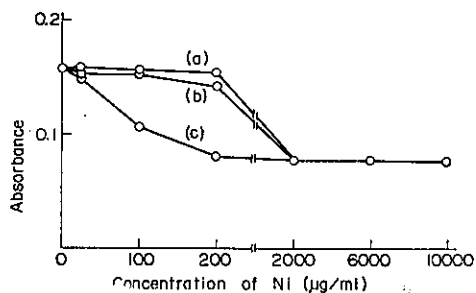


Fig. 4. Effect of nickel
Fe 40 $\mu\text{g/ml}$ (a) Nickel perchlorate (b) Nickel chloride or nickel nitrate
(c) Nickel sulfate

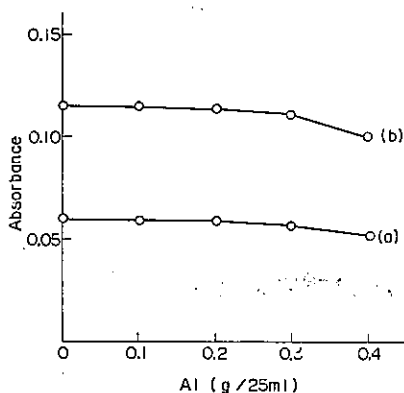


Fig. 5. Effect of aluminium
(a) Fe 20 $\mu\text{g/ml}$ (0.5 N nitric acid) (b) Fe 40 $\mu\text{g/ml}$ (0.5 N nitric acid)
Blank test aluminium absorbance
0.1–0.3 g/25 ml —
0.4 g/25 ml 0.003

of metallic aluminium (99.99%), dissolved in 6N hydrochloric acid, and the solution was evaporated to dryness. The residue was dissolved in 6 ml of 2N nitric acid, with warming, and the total volume was brought to 25 ml with distilled water. The absorbance of this aqueous solution was measured and corrected with blank value. As shown in Fig. 5, the absorbance decreased slightly with more than 0.3 g of aluminium and the amount of the sample to be taken was made below 0.3 g.

IV. Calibration curve

Based on the result of foregoing examinations, calibration curves were drawn for the cases of using water and methyl isobutyl ketone as a solvent, following the conditions set in III-1-(iii).

1. Aqueous solution

The calibration curve was obtained by varying the amount of iron from 0 to

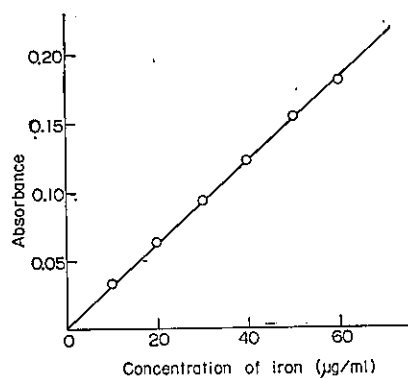


Fig. 6. Calibration curve for iron (I) 0.5 N HNO_3 aqueous solution

60 $\mu\text{g/ml}$ and a linear relationship was obtained between the concentration of iron and the absorbance as shown in Fig. 6.

2. Methyl isobutyl ketone solution

Iron (0 to 10 $\mu\text{g/ml}$) in 7N hydrochloric acid solution was extracted with 10 ml of methyl isobutyl ketone and this was sprayed to obtain the calibration curve. As shown in Fig. 7, a linear relationship was obtained between the concentration and the absorbance in the range of 0 to 10 $\mu\text{g/ml}$ of iron. In this case, the sensitivity was about 10 times higher than that obtained with aqueous solution.

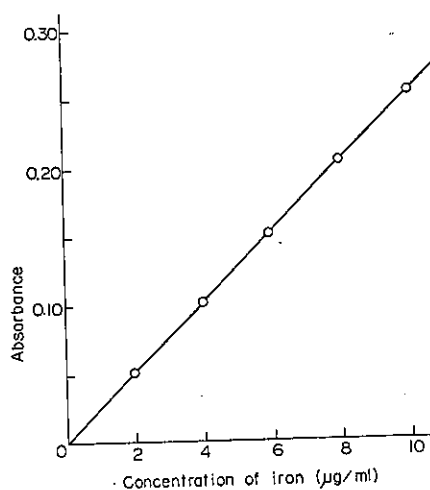


Fig. 7. Calibration curve for iron (II). Methyl isobutyl ketone used.

V. Determination of iron in aluminium metal and aluminium alloys

The purity of aluminium metal usually used in industry is 99.2~99.8% and aluminium metals of such purity and ordinary aluminium alloys dissolve easily in

6N hydrochloric acid but high-purity aluminium metals (over 99.9%) are sparingly soluble in 6N hydrochloric acid and must be dissolved with the aid of 6N sodium hydroxide solution. Since the quantity of iron in high-purity aluminium metals is very slight, it becomes necessary to carry out the extraction of iron with methyl isobutyl ketone to attenuate concentration of iron and to increase the sensitivity by the organic solvent effect. For this reason, the analytical procedure for the determination of iron in aluminium metals (Al 99.2~99.8%) and light aluminium alloys, and that for the determination of microamount of iron in high-purity aluminium metals will be described below.

1. Determination of iron in aluminium metals and light aluminium alloys

About 0.1~0.3 g of the sample is weighed accurately, dissolved in 5~10 ml of 6N hydrochloric acid with heating, and the solution is evaporated. About 1.5 ml of nitric acid (1:1) and a small quantity of distilled water are added to the residue and the mixture is warmed to effect dissolution. The solution is transferred to a 25-ml measuring flask and diluted with distilled water to the mark. This solution is submitted to the absorption measurement under the conditions listed in III-1-(iii) and the amount of iron is calculated from the calibration curve.

2. Determination of iron in high-purity aluminium metals

About 0.5~2.0 g of the sample is weighed accurately, dissolved in 5~20 ml of 6N sodium hydroxide with heating, and 5~10ml of distilled water is added. To this solution, 1 ml of magnesium chloride solution (Mg 10 mg/ml), prepared as described in II-1, is added as a coprecipitation of iron and the precipitate formed is collected on a filter. The filter cake and the beaker are washed once or twice with a small quantity of distilled water to remove most of sodium hydroxide. The precipitate is dissolved in about 10 ml of hydrochloric acid (1:1) and the funnel is washed thoroughly with water. This whole solution is caught with original beaker, evaporated to about 1~2 ml, and transferred to a separatory funnel with 8~9 ml of 7N hydrochloric acid, so that the whole volume is brought to about 10 ml with it. This solution is extracted with 10ml of methyl isobutyl ketone preliminarily saturated with 7N hydrochloric acid. The organic layer is then submitted to the absorption measurement under the conditions listed in III-1-(iii) and the amount of iron is calculated from the calibration curve. Blank test is carried out at the same time and the measured value is corrected.

VI. Analytical results

Results of the determination of iron in aluminium metals and aluminium alloys according to the analytical procedure described in V-1 are listed in Table 3 and those of the determination of iron in high-purity aluminium metals according to the procedure described in V-2 are given in Table 4. Blank value of the absorbance in these cases was 0.041. These results are in satisfactory agreement with those

Table 3. Determination of iron in aluminium metals and aluminium alloys.

Sample	Atomic absorption		Spectrophotometric*
	Sample taken (g)	Iron found (%)	Iron found (%)
1st grade	0.2480 0.2775	0.136 0.134	0.136
2nd grade	0.1915 0.2782	0.230 0.238	0.241
3rd grade	0.2251 0.2971	0.155 0.151	0.154
Special grade	0.2294 0.3001	0.070 0.070	0.069
56 S	0.2545 0.1050	0.260 0.257	0.270
56 S	0.1821 0.1185	0.580 0.571	0.57

* Thiocyanate method used.

Table 4. Determination of iron in high purity aluminium metals.

Sample No.	Atomic absorption		Spectrophotometric	
	Sample taken (g)	Iron found (%)	Iron found (%)	
			Thiocyanate method	Phenyl 2-pyridylketoxime method
1	1.0782 1.0566	0.0025 0.0024	0.0025	0.0025
2	0.4940 0.4378	0.0089 0.0089	0.0086	0.0086
3	2.0348 2.1002	0.0006 0.0007	0.0005	0.0005

obtained by photometry (thiocyanate method and phenyl 2-pyridylketoxime method).

VII. Discussion

The determination of iron in aluminium metals by the atomic absorption spectrometry was carried out in accordance with the result of examinations described above. Nickel was found to interfere in the determination of iron and this interference of nickel was found to be affected greatly by the presence of sulfate ion. While the interference of aluminium, iron, titanium, and silicon on calcium is considered to be due to the formation of a hardly dissociable compound between two elements, the interference of nickel on iron is considered to be the

action among three elements, i.e., the formation of non-dissociable compound by the interaction of iron, sulfate, and nickel.

The thorough removal of sodium hydroxide in the analytical procedure for the determination of iron in high-purity aluminium metals was necessary because of the precipitation of sodium chloride in the subsequent solution of the residue in 7*N* hydrochloric acid, which interfered with the extraction procedure.

Precision of absorbance measurement is always a problem when organic solvent spray is used in atomic absorption spectrometry. By controlling acetylene pressure and water-cooling of the burner, spraying methyl isobutyl ketone solution gave coefficient of variation as 1.51% (Fe 4 $\mu\text{g/ml}$). The coefficient of variation was 1.58% (Fe 30 $\mu\text{g/ml}$) in the case of spraying aqueous solution.

Summary

It has been found that 0.05~1.0% of iron in aluminium metals and aluminium alloys can be determined rapidly, without separating the principal components, through atomic absorption spectrometry, and the determination of micro-amount of iron in high-purity aluminium was made possible by extracting iron with methyl isobutyl ketone.

Acknowledgement

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