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Spectrographic Determination of Microamounts of Calcium and Magnesium in Cast Iron by Porous-Cup Technique*

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Synopsis

A spectrochemical method was studied to determine simultaneously microamounts of calcium and magnesium in cast iron. Samples were dissolved with acid, iron was removed by methyl isobutyl ketone extraction, then the solution containing calcium and magnesium was put in a porous-cup electrode and the spectra were excited with a condensed spark. Strontium and beryllium were added as the internal standard elements for calcium and magnesium, respectively, and SrII 4215.52Å/CaII 3933.67Å and BeII 3130.42Å/MgII 2802.70Å were used as the analytical line pairs. This method was applicable to the determination of calcium and magnesium in contents above 0.005 per cent, and the variation coefficients were 13.5 per cent for calcium and 9.7 per cent for magnesium at a concentration level of 0.01 per cent.

I. Introduction

For the determination of microamounts of calcium in cast iron flame photometry is usually used, in which it is necessary to separate calcium from iron and phosphate ion prior to flame excitation. Microamounts of magnesium in cast iron have been determined with titan yellow, and recently, a method using xylydyl blue is proposed. But these analytical methods for magnesium likewise necessitate the complete separation of interfering substances such as iron from calcium. Accordingly, it takes plenty of time to determine both of calcium and magnesium. In the present study a spectrochemical method was investigated to determine simultaneously both of them for the purpose of the reduction of the operation time and the improvement of analytical precision.

C. Feldman proposed to use a porous-cup electrode to excite liquid sample⁽¹⁾. Being simple in operation as compared with the other solution methods, this method has been applied to analyses of various metals, and recently to the analysis of cast iron for magnesium⁽²⁾. The porous-cup method was used also in the present study on the determination of calcium and magnesium.

* The 1004th report of the Research Institute for Iron, Steel and Other Metals. Read at the 45th Meeting of the Japan Institute of Metals, in Nov., 1959.

(1) C. Feldman, *Anal. Chem.*, **21** (1949), 1041.

(2) A. C. Ottolini, *ibid.*, **31** (1959), 447.

II. Experiments and results

1. Apparatus, reagents and electrode

A Feussner spark generator was used as an excitation source, the spectra were photographed with a Carl Zeiss Qu 24 medium quartz spectrograph, and the blackness of spectral lines was measured with a Carl Zeiss spectral-line photometer.

Hydrochloric acid, nitric acid and methyl isobutyl ketone were the first grade reagents. Calcium standard solution (Ca: 1 mg/ml) was prepared by dissolving 2.5 g of calcium carbonate (special grade) in a small amount of hydrochloric acid and diluting with water to 1*l*. The solution was standardized by oxalate precipitation and potassium permanganate titration. Magnesium standard solution (Mg: 1mg/ml) was prepared by dissolving 1.66 g of magnesium oxide (special grade) in a small amount of hydrochloric acid and diluting with water to 1*l*. The solution was standardized by phosphate precipitation and ignition to the pyrophosphate. Strontium-beryllium mixed solution (Sr: 500*r*/ml, Be: 10*r*/ml) was prepared as follows: 0.5 g of metallic beryllium was dissolved in 500 ml of hydrochloric acid (1+1). 1.53 g of strontium chloride hexahydrate was dissolved in 10 ml of this solution, which was diluted to 1*l* with hydrochloric acid (1+1).

Electrode: Porous-cup electrodes were made of the Hitachi spectroscopic graphite electrode, 6 mm in diameter, of regular grade. The graphite rod was drilled with a carbon cutter and shaped in the dimensions as shown in Fig. 1.

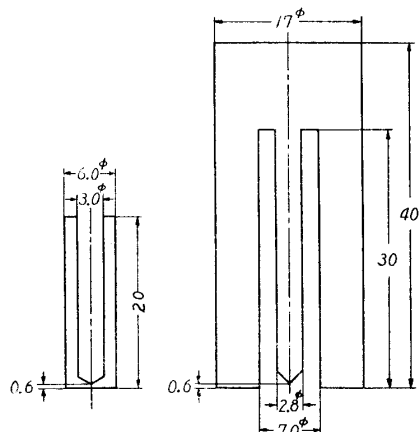


Fig. 1. Porous-cup electrode and thickness gauge. (unit in mm)

In order to keep the thickness of the bottom 0.6 mm constantly, a mechanism was devised in which the tip of the drill stops at a distance of 0.6 mm from the bottom of the graphite rod by idling of the handle of the drill. Moreover, after shaping, the thickness was inspected by inserting the electrode into a thickness gauge as shown in Fig. 1. A top of counter-electrode was sharpened to a truncated cone. The material of the porous-cup electrode had an important influence on the permeability of a solution during an excitation period. This problem will be discussed in the next report.

2. Volume of a final solution

The contents of calcium and magnesium in cast iron are generally 0.005 to 0.05 per cent and about 0.01 per cent, respectively. At first the volume of a final solution was examined which is required for the determination of these elements in contents above 0.005 per cent. Solutions containing 0.1 mg of each element to be determined, corresponding to the contents of 0.005 per cent of each element in 2 g of cast iron, were diluted to 5 to 50 ml. The solutions were put in a porous-cup electrode and the spectra were obtained under the following conditions: primary voltage=100V, secondary voltage=9.3kV, capacitance $C=0.0033\mu\text{F}$, self-

inductance $L=0.8\text{mH}$, and exposure=40 sec. In this experiment the strongest calcium line, $\text{CaII } 3933.67\text{\AA}$ and the magnesium lines, $\text{MgII } 2795.53\text{\AA}$ and $\text{MgII } 2802.70\text{\AA}$, showed sufficient intensity for the determination of these elements, unless the volume of the final solution exceeded 10 ml. Under these conditions, however, sufficient intensity was not obtained for $\text{CaII } 3968.47\text{\AA}$, the next strong line of calcium.

3. Separation of iron

In order to examine the effect of iron, the main component, 2 g of electrolytic iron* was dissolved in hydrochloric acid, to which 0.1 mg of calcium and magnesium were added, and the solution was made up to 10 ml. The spectra were photographed under the same conditions as mentioned above. From this it was found that the two spectral lines of magnesium were not detected, and that $\text{CaII } 3933.67\text{\AA}$ and $\text{CaII } 3968.47\text{\AA}$ were superimposed on $\text{FeI } 3933.61\text{\AA}$ and $\text{FeI } 3967.98\text{\AA}$, respectively. In the subsequent experiments, therefore, iron was removed by organic solvent extraction prior to photographing the spectra.

4. Internal standard

Strontium was selected as the internal standard element for calcium from the similarity of its spectroscopic properties to calcium, and $\text{SrII } 4215.52\text{\AA}$ (excitation potential 8.6 eV) and $\text{SrII } 4077.71\text{\AA}$ (e.p. 8.7 eV) were selected as possible internal standard lines because of the proximity of their wavelength and excitation potential to those of $\text{CaII } 3933.67\text{\AA}$ (e.p. 9.2 eV) and $\text{CaII } 3968.47\text{\AA}$ (e.p. 9.2 eV). From a similar point of view, beryllium was selected as the internal standard element for magnesium, and $\text{BeII } 3130.42\text{\AA}$ (e.p. 13.2 eV) and $\text{BeII } 3131.07\text{\AA}$ (e.p. 13.2 eV) were selected as possible internal standard lines for $\text{MgII } 2795.53\text{\AA}$ (e.p. 12.0 eV) and $\text{MgII } 2802.70\text{\AA}$ (e.p. 12.0 eV).

5. Concentration of hydrochloric acid in a sample solution

As hydrochloric acid was used to dissolve the residue dried up after removal of iron, the effect of the amount of hydrochloric acid on spectral intensities of calcium, magnesium, strontium and beryllium as well as their spectral intensity ratios was examined. In this experiment the change in the concentration of hydrochloric acid from 4N to 10N affected neither the intensities nor the intensity ratios. As the residue could not be completely dissolved in about 4N hydrochloric acid, 6N hydrochloric acid was used in the subsequent experiments.

6. Presparking time

Solutions containing various amounts of calcium and magnesium were dried up and the residue was dissolved in 10 ml of the strontium-beryllium mixed solution. The solutions were put in porous-cup electrodes and excited under the following conditions: primary voltage=100V, secondary voltage=9.3kV, $C=0.0017$ to $0.0033 \mu\text{F}$, $L=0.8 \text{ mH}$, and analytical gap=2 mm. The spectra were photographed at 20-sec intervals** for 80 sec, and working curves were constructed for each 20-sec period.

* Any spectral lines of calcium and magnesium could not be detected by spectroanalysis.

** A photographic plate was double exposed under the same condition.

From this experiment the working curves for the second and the third 20-sec periods were found to be linear and reproducible for both calcium and magnesium. In the first 20-sec period, however, the spectral intensities of calcium and magnesium were always varied largely and also the intensity ratios were not constant. Accordingly, reproducible working curves could not be obtained. This might be due to the fact that it takes some time for sample solution to permeate through the bottom of the porous-cup electrode, and that in the earlier discharge period the supply of the sample solution to the analytical gap is not stationary. In the subsequent experiments, therefore, the spectra were photographed after 20-sec presparking. When a porous-cup electrode was not preburned before injection of sample solution, the consumption of the sample solution was much less than when a preburned electrode was used. Moreover, the linearity of the working curves was not good. In the present study, therefore, the porous-cup electrodes were used after preburning in a direct current arc, giving 5A at 120V, for 10 sec. Another advantage in preburning the electrodes is the complete removal of the contaminants adhering to them during handling them.

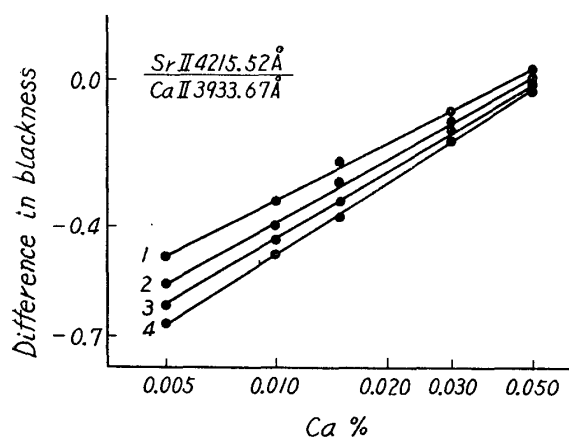


Fig. 2. Shift of the working curve of Ca with change of capacitance C :

1. $C=0.0033\mu\text{F}$ 2. $C=0.0028\mu\text{F}$
3. $C=0.0022\mu\text{F}$ 4. $C=0.0017\mu\text{F}$

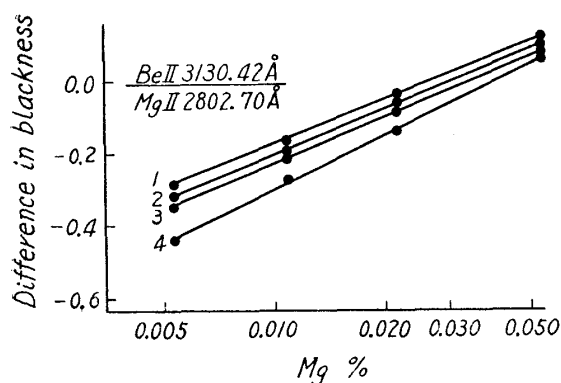


Fig. 3. Shift of the working curve of Mg with change of capacitance C :

1. $C=0.0033\mu\text{F}$ 2. $C=0.0028\mu\text{F}$
3. $C=0.0022\mu\text{F}$ 4. $C=0.0017\mu\text{F}$

the subsequent experiments were carried out under the following conditions: $C=$

7. Discharge conditions

In order to clarify the relation between the capacitance C and the working curve, the spectra were excited under the same conditions as used in the study on "Presparking time", and photographed for 40 sec after 20-sec prespark. Then the working curves were constructed for each value of C , as shown in Figs. 2 and 3. The gradient of the working curves of calcium and magnesium increased with decreasing C . This was caused by the fact that with decreasing C the spectral intensities of calcium and magnesium decreased and besides the decreasing tendency was more remarkable in lower concentration of these elements. In exciting these elements in concentration of 0.005 per cent with C of $0.0017\mu\text{F}$ the exposure must be continued at least for 40 sec. Between the working curves for the self-inductance of 0.8 mH and 0.08 mH no difference was observed. Consequently

0.0017 μ F, L=0.8 mH, the exposure time=40 sec, and the presparking time=20sec.

8. Analytical line pairs

Under the optimal conditions chosen by the foregoing experiments the spectra of sample solutions containing the internal standards were photographed, and working curves were constructed by pairing the calcium lines with the strontium internal standard lines and the magnesium lines with the beryllium internal standard lines, respectively, which had already been mentioned in "Internal standard".

The working curves for SrII 4077.71Å/CaII 3933.67Å and SrII 4215.52Å/CaII 3933.67Å showed a good linearity, while CaII 3968.47Å was too weak to measure in lower concentration range of calcium. Accordingly, SrII 4215.52Å/CaII 3933.67Å was selected as the analytical line pair for calcium. The working curve for this pair is shown in Fig. 2. Four analytical line pairs obtained from the two magnesium lines and the two beryllium lines all gave linear working curves. The use of MgII 2802.70Å gave more steep working curves, and BeII 3130.42Å was more intense and easy to measure as compared with BeII 3131.07Å. Accordingly, BeII 3130.42Å/MgII 2802.70Å was used as the analytical line pair for magnesium. The working curve for this line pair is shown in Fig. 3.

9. Influence of coexisting elements

An examination was carried out to find the influence of coexisting elements on the spectral line intensities of calcium, magnesium, strontium and beryllium and consequently on the analytical results of calcium and magnesium. 10 mg of iron, 12 mg of manganese, 2 mg of chromium, 1.8 mg of molybdenum, 3 mg of titanium, 1.4 mg of cobalt and 2 mg of vanadium* were added individually to the solution containing 0.10 mg of calcium and 0.12 mg of magnesium, and calcium and magnesium in each synthetic solution were determined. The deviation of observed values from the theoretical ones (Ca=0.005 per cent and Mg=0.006 per cent) were at most ± 0.001 per cent.

10. Analytical procedure

On the basis of the preliminary experiments the following analytical procedure was established.

(i) Chemical treatment prior to spectrographic determination. 2 g of sample is weighed into a beaker, dissolved by heating in 20 ml of hydrochloric acid (1+1), and ferrous iron was oxidized by adding nitric acid. Heating is continued until the solution is dried up. After cooling, the residue is dissolved in 10 ml of concentrated hydrochloric acid, diluted with 10 ml of water, and filtered. The residue on a filter paper is washed sufficiently with hot water, then ashed in a platinum crucible, next dissolved in hydrochloric acid after treatment by hydrofluoric acid,

* The amount of each element added was several times as much as the amount found usually in cast iron. When 2g of iron was extracted twice with 30 ml of methyl isobutyl ketone, 99.9 per cent of iron was removed from a water layer, and iron remaining in the water layer was 2 to 3 mg. Molybdenum more than 90 per cent was removed by this method.

and finally joined to the filtrate. (When only calcium is determined, the treatment of the residue is not necessary.) The filtrate is heated again, concentrated to 10 to 15 ml, transferred to a separatory funnel with 7N hydrochloric acid, and the volume is brought to about 30 ml. The acidic solution is shaken with 30 ml of methyl isobutyl ketone, and the extraction is repeated once more with another 30 ml of this solvent. The aqueous solution is transferred to a beaker and dried up. After cooling, 5 ml of aqua regia is added to the residue and dried up again. The residue is dissolved in 10 ml of the strontium-beryllium mixed solution. A porous-cup electrode is filled with a portion of this solution by means of a capillary before discharging a spark.

(ii) Spectrographic procedure. The conditions for excitation and photography and the analytical line pairs are as follows:

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|------------------------|--|
| Apparatus— | Carl Zeiss Qu 24 medium quartz spectrograph |
| Optical system— | Intermediate screen irradiation |
| Analytical gap— | 2 mm. Irradiated with an ultraviolet lamp. |
| Intermediate screen— | Full open |
| Slit width— | 10 μ |
| Discharge parameters— | Primary voltage 100V, secondary voltage 9.3kV, self-inductance 0.8 mH, capacitance 0.0017 μ F. |
| Prespark— | 20 sec |
| Exposure— | 40 sec |
| Photographic plate— | Fuji, spectroscopic, process type |
| Development— | FD-31, at 20°C, for 3 min |
| Analytical line pairs— | SrII 4215.52Å/CaII 3933.67Å BeII 3130.42Å/MgII 2802.70Å |

11. Analytical results

This method was applied to analysis of practical samples. The reproducibility of the present method is shown in Table 1, and the comparison between the

Table 1. Reproducibility of the present method.

| Element | Ca | Mg |
|---------------------------|-------|-------|
| Analytical results (%) | 0.011 | 0.012 |
| | 0.012 | 0.015 |
| | 0.010 | 0.013 |
| | 0.011 | 0.014 |
| | 0.013 | 0.015 |
| | 0.010 | 0.013 |
| | 0.010 | 0.014 |
| | 0.013 | 0.013 |
| Average (%) | 0.011 | 0.014 |
| Variation coefficient (%) | 13.5 | 9.7 |

analytical results obtained by the present method and other methods is shown in Table 2. The analytical results of calcium obtained by flame photometry are generally lower than that of the present method, which might be due to the

suppression of the emission of calcium spectral lines by coexisting phosphate ion.⁽³⁾

Table 2. Analytical results obtained by the present method and other methods.

| Sample | Ca (%) | | Mg (%) | |
|--------|---------------|------------------|---------------|------------------------------------|
| | Spectrography | Flame photometry | Spectrography | Titan yellow absorption photometry |
| A | 0.008 | 0.006 | 0.017 | 0.014 |
| B | 0.012 | 0.009 | 0.028 | 0.026 |
| C | 0.008 | 0.009 | 0.020 | 0.022 |
| D | 0.015 | 0.012 | 0.021 | 0.025 |
| E | 0.012 | 0.008 | 0.003 | 0.004 |

Summary

- (1) A spectrochemical method was developed to determine simultaneously microamounts of calcium and magnesium in cast iron by a porous-cup technique.
- (2) Iron was removed by organic solvent extraction prior to the excitation of a sample solution to avoid the interference of iron in the determination of calcium and magnesium.
- (3) Sample solutions were excited with a Feussner spark generator under the following conditions: primary voltage=100V, secondary voltage=9.3 kV, C=0.0017 μ F and L=0.8 mH. The spectra were photographed for 40 sec after 20-sec prespark.
- (4) SrII 4215.52Å/CaII 3933.67Å and BeII 3130.42Å/MgII 2802.70Å were selected as the analytical line pairs.
- (5) The present method made it possible to reduce the time required for the determination and was of good reproducibility compared with the usual analytical methods.

Acknowledgement

The present author wishes to express his hearty thanks to Prof. H. Gotô for his helpful suggestions in the course of the present work.

(3) S. Ikeda, Sci. Rep. RITU, A9 (1957), 16.