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Spectrographic Determination of Microamount of Calcium in Magnesium with the Transient Discharge Source Unit*

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Synopsis

A spectrographic method was studied to determine microamount of calcium in magnesium metal and magnesium alloys, and it was found that calcium in magnesium could be determined by exciting sample solution in a porous-cup electrode with the transient discharge source unit. The results obtained were as follows: (1) In consideration of the viscosity of magnesium solution and the spectral intensity of calcium, 0.5 g of sample was dissolved in hydrochloric acid, afterwards diluted to 50 ml. (2) The discharge conditions were E (discharge voltage)=200V, $C=18\mu F$, $L=30\mu H$, and $R=2\Omega$. (3) Exposure was started after 15-sec preliminary discharge, as the discharge was unstable in the beginning of its start. (4) Aluminium, zinc, manganese, iron and zirconium contained in magnesium alloys had no influence on the analytical results of calcium determination, excepting the case when sample contained about 5 per cent of zinc. (5) Samples containing 0.01 to 0.3 per cent of calcium were analysed with Sr II 4215.52Å/Ca II 3933.67Å as the analytical line pair, the reproducibility being 5 to 7 per cent. (6) It was ascertained that the lower limit of the determination of calcium could be extended down to about 0.001 per cent by using magnesium of higher purity as the base material.

I. Introduction

Calcium in magnesium has been determined mainly by complexometry^{(1)~(3)} and precipitation method.⁽⁴⁾ In complexometry, however, the determination of calcium could be carried out only down to 1 per cent content, according to the recent research⁽³⁾. When the ratio of calcium to magnesium is small, accurate analytical results can not be obtained also in precipitation methods. For example, in the method in which calcium is separated by precipitating as sulfate from a solution containing magnesium, it is proposed to produce the precipitate in the solution containing 80 per cent alcohol in order to reduce the solubility of produced calcium sulfate. But calcium sulfate thus obtained is still soluble in 80 per cent alcohol solution to some extent (0.16 to 0.20 mg/100 ml at room temperature), and therefore, accurate analytical results can not be obtained, when calcium content is less than 0.5 per cent in magnesium sample.

Since in emission spectra the spectral lines of calcium are remotely separated

* The 1010th report of the Research Institute for Iron, Steel and Other Metals.

(1) V. Tichomírová and O. Simáčková, *Chem. Listy*, **50** (1956), 1925.

(2) R. W. Schmid and C. N. Reilley, *Anal. Chem.*, **29** (1957), 264.

(3) S. J. Socolar and J. I. Salach, *ibid.*, **31** (1959), 473.

(4) R. S. Volodarskaya and G. N. Derevyanko, Report of Symposium: "Sovrem. Metody Anal. Metall., M. Metallurgizdat," 1955, 190; Ref. Zhur., *Khim.*, 1956 Abstr. No. 29,311.

from those of magnesium, it is not necessary to separate calcium from magnesium prior to the determination of calcium in spite of the presence of a large amount of magnesium. Therefore, a spectrographic method was studied to determine microamount of calcium in magnesium.

As the porous-cup technique has successfully been applied to the determination of magnesium, calcium and aluminium in cast iron,^{(5),(6)} this technique was also adopted in the present study.

II. Apparatus, electrode and reagents

Spectra were excited with the transient discharge source unit,⁽⁶⁾ and photographed with Carl Zeiss Qu 24 quartz spectrograph of a medium type, and the blackness of spectral lines was measured with Carl Zeiss spectral line photometer. The auxiliary electrode used was the Hitachi graphite electrode for spectral analysis, 6 mm in diameter, of regular grade, and it was shaped in the following dimensions: the length 20 mm, the inner diameter of a cavity 3 mm, and the thickness of the bottom 0.6 mm. The top of the counter-electrode was a cone with a flat, 3 mm in diameter. The porous-cup electrodes were used after preburning with itself as positive in a direct current arc, giving 9.5A at 120V, for 10 sec.*

Magnesium solution (50 mg/ml) was prepared by dissolving 5 g of pure magnesium metal in a small amount of hydrochloric acid and diluting to 100 ml. A trace of calcium was found in this magnesium metal by spectral analysis. The amount of the residual calcium will be later referred to. *Calcium solution* (1 mg/ml) was prepared by dissolving special grade calcium carbonate in hydrochloric acid. *Strontium solution* (1 mg/ml) was prepared by dissolving special grade strontium chloride hexahydrate in distilled water, and zinc solution (25 mg/ml) and aluminium solution (20 mg/ml) were prepared by dissolving high purity zinc and aluminium in hydrochloric acid, respectively. These substances were found not to contain calcium and strontium as impurities by spectral analysis.

III. Experiments and results

1. Preparation of sample solution

At first the attempt was made to prepare the sample solution by the following procedure: dissolution of sample with hydrochloric acid—drying-up of this solution—redissolution of the residue with a definite volume of hydrochloric acid containing an internal standard element. Accordingly the concentration of hydrochloric acid which is required to dissolve the residue was examined. The residue obtained by drying up the solution of pure magnesium metal could be dissolved not with 0.6N hydrochloric acid, but with the 1.2 N acid solution. When

(5) Y. Yokoyama, Sci. Rep. RITU, A12 (1960), 525.

(6) Y. Yokoyama, Sci. Rep. RITU, A13 (1961), 8.

* When 0.15 ml of a solution was injected into the porous-cup electrode preburned by this procedure, the amount of the residual solution after excitation was 0.05 ml. It shows that the permeability of the electrode is moderate.

magnesium alloys containing aluminium or zirconium were dissolved in hydrochloric acid and then concentrated until nearly dried up, it could not be brought to clear solution even by 1.2N hydrochloric acid.

By exciting calcium solution by the excitation conditions which will be shown in Table 3 the intense radiation of calcium spectral lines was obtained. So the concentration or drying-up procedures were omitted and the hydrochloric acid solution of sample was diluted with distilled water to a definite volume after the addition of the internal standard element.

2. Concentration of sample solution

The optimal concentration of magnesium in sample solution was studied. The *magnesium solution* was diluted stepwise to prepare magnesium solutions of various concentrations (1.2N in hydrochloric acid), which were excited in porous-cup electrode according to the excitation conditions shown in Table 3. The solution containing 50 mg magnesium per ml was too viscous to continue a stable discharge, and so it permeated the bottom of the porous-cup electrode slowly during discharge period. Consequently the greater part of the solution remained in the cup, which caused the decreasing of the spectral intensity of calcium. The solutions in concentration less than 50 mg/ml showed moderate permeability.

Next the *calcium solution* was diluted stepwise to prepare calcium solutions of various concentrations (1.2N in hydrochloric acid), which were excited under the same conditions as mentioned above, and the spectral intensity of calcium was measured. Exciting the calcium solution in concentration above 0.1 γ /ml, the spectral line Ca II 3933.67 \AA showed the intensity enough for the determination of calcium. The calcium concentration 0.1 γ /ml is as little as that of the solution which is prepared by diluting to 50 ml after dissolution of 0.5 g magnesium containing 0.001 per cent calcium. Consequently the subsequent experiments were carried out by dissolving 0.5 g of sample, diluting to 50 ml and adjusting the acidity to 1.2N.

3. Preparation of magnesium standard sample solution

By quantitative spectrographic analysis a trace of calcium was determined in the pure magnesium metal used for preparing the *magnesium solution*. The calcium content was found to be 0.010 per cent by "addition method."⁽⁷⁾ A series

Table 1. A series of magnesium standard sample solutions.

Solution No.	Mg (mg)	Sr (mg)	Ca		HCl (N)	Total volume (ml)
			Added (γ)	Total (γ)		
0	500	2	0	50	1.2	50
1	500	2	50	100	1.2	50
2	500	2	150	200	1.2	50
3	500	2	250	300	1.2	50
4	500	2	500	550	1.2	50
5	500	2	1000	1050	1.2	50
6	500	2	1500	1550	1.2	50

(7) L. H. Ahrens, *Spectrochemical Analysis*, Addison-Wesley Press, Inc., (1950), 135.

of magnesium standard sample solutions were prepared by adding to the *magnesium solution* various amounts of the *calcium solution* and a definite volume of the *strontium solution*, which are shown in Table 1. The amount of total calcium is the sum of the residual calcium and the added calcium.

4. Discharge conditions

As the analytical line pair of calcium, Sr II 4215.52Å/Ca II 3933.67Å which was used in the previous study was selected.⁽⁵⁾ In the determination of aluminium in iron and steel,⁽⁶⁾ the transient discharge source unit was used and an arc-like discharge was selected as the best conditions from among various types of discharge. Since Sr II 4215.52Å and Ca II 3933.67Å belong to the group of spark lines, various spark-like discharges were examined. The following five combinations of the discharge voltage E and the capacity C were made, and for each case change of the analytical line pair ratio was examined by "moving plate method."

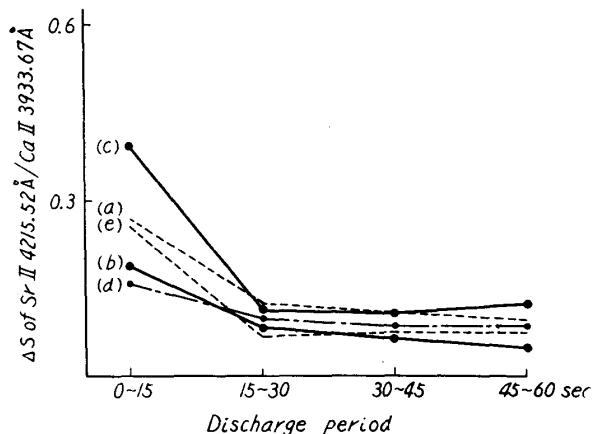


Fig. 1. Change of ΔS of Sr II 4215.52Å/Ca II 3933.67Å.

- (a) $E=200\text{V}$, $C=10\mu\text{F}$
- (b) $E=200\text{V}$, $C=18\mu\text{F}$
- (c) $E=200\text{V}$, $C=26\mu\text{F}$
- (d) $E=175\text{V}$, $C=18\mu\text{F}$
- (e) $E=220\text{V}$, $C=18\mu\text{F}$

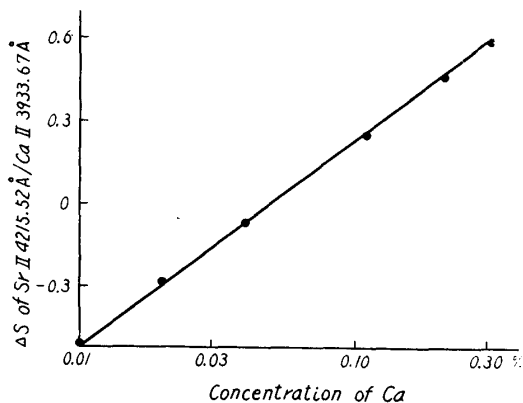


Fig. 2. Working curve of calcium.

- (a) $E=200\text{V}$, $C=10\mu\text{F}$
- (b) $E=200\text{V}$, $C=18\mu\text{F}$
- (c) $E=200\text{V}$, $C=26\mu\text{F}$
- (d) $E=175\text{V}$, $C=18\mu\text{F}$
- (e) $E=220\text{V}$, $C=18\mu\text{F}$

The other discharge conditions were as follows: inductance $L=30\mu\text{H}$, resistance $R=2\Omega$, discharge gap=1.5 mm. The magnesium standard sample solution No. 3 was used, the spectra were photographed at 15-sec intervals for 60 sec, and the difference in blackness ΔS of Sr II 4215.52Å/Ca II 3933.67Å were measured for each 15-sec period. The results obtained are shown in Fig. 1, from which it is obvious that in all cases the first 15-sec period gave large ΔS and thereafter ΔS settled down to almost constant values. And these values for five discharge conditions were close to one another.

Consequently, in the subsequent experiments the conditions (b) situated in the midst of the five conditions were used, and a preliminary discharge was done for the first 15-sec. And thereafter exposure was made within 45 sec. The working curve

obtained under these conditions is shown in Fig. 2.

5. Influence of coexisting elements

Magnesium alloys contain at the maximum approximately 8 or 9 per cent aluminium, 4 or 5 per cent zinc, 1 or 2 per cent manganese, 0.5 per cent zirconium and 0.6 or 0.7 per cent iron. According to the MIT wave-length table, the spectral lines of zirconium and iron lie in the neighborhood of the spectral lines of calcium and strontium selected for the analytical line pair, that is, Fe I 3933.61Å and Zr II 3934.12Å are situated close to Ca II 3933.67Å and Fe I 4215.43Å and Zr I 4215.31Å are situated close to Sr II 4215.52Å. Therefore, it is possible that these spectral lines of zirconium and iron interfere with the calcium and strontium lines, if the samples contain iron and/or zirconium in the concentration beyond a definite limit. Accordingly the solutions having the same composition as the magnesium standard sample solution No. 1 and besides containing 0.5 per cent zirconium and 0.7 per cent iron, respectively, were prepared, and calcium was determined by the excitation condition shown in Table 3. The analytical results obtained for these samples did not differ from that of the magnesium standard sample solution No. 1, and any influence of coexisting zirconium and iron was not seen.

It is possible that the discharge process is affected by aluminium and zinc, as they are present in magnesium alloys in great quantities. Accordingly the synthetic sample solutions were prepared which contained 2 or 8 per cent aluminium, 2 or 5 per cent zinc and neither aluminium nor zinc, respectively. In all cases the concentration of the other components were 0.5 g magnesium per 50 ml, 800 γ calcium per 50 ml, 2 mg strontium per 50 ml, and 1.2N in hydrochloric acid. And the analytical results for these solutions were compared with one another. As shown in Table 2, there was no influence of aluminium and zinc on the analytical

Table 2. Influence of coexisting aluminium and zinc.

Al (%)	Zn (%)	Ca	
		Present (%)	Found (%)
0	0	0.16	0.16 ₇
2	0	0.16	0.17
8	0	0.16	0.16
0	2	0.16	0.17
0	5	0.16	0.18

results, excepting the case of the presence of 5 per cent zinc.

6. Analytical procedure

From the results of the preliminary experiments, the following analytical procedure was determined. 0.5 g of sample is dissolved in 17 ml of hydrochloric acid (1+1), 2 ml of the *strontium solution* is added to this solution, and then it is diluted with distilled water to 50 ml. The spectra are photographed according to the operating conditions shown in Table 3.

7. Analytical results

According to the above analytical procedure, practical samples were analysed, and the analytical results are shown in Table 4. Since there is no other accurate

Table 3. Operating conditions for the determination of calcium.

Apparatus—	Carl Zeiss Qu 24 medium type spectrograph, and the transient discharge source unit.
Electrode—	The porous-cup electrode is preburned with itself as positive in a direct current arc, giving 9.5A at 120V, for 10 sec. Sample solution is filled up in this electrode.
Excitation—	Discharge voltage 200V, capacitance $C=18\mu F$, resistance $R=2\Omega$, inductance $L=30\mu H$, discharge gap 1.5 mm.
Photographing—	Intermediate screen 3.2 mm, slit width 10μ , preliminary discharge 15sec, exposure within 45sec, photographic plate Fuji spectroscopic process type.
Development—	FD-111, 20°C, for 4 min.
Line pair—	Sr II 4215.52Å/Ca II 3933.67Å.

Table 4. Analytical results.

Sample No.	Observed value (%)		Average (%)
61	0.26,	0.27 ₅	0.27
65	0.27,	0.25 ₅	0.26
92	0.25,	0.29 ₅	0.27
93	0.13 ₇ ,	0.12 ₄	0.13
97	0.15,	0.16	0.16

analytical methods, the accuracy and reproducibility of the present method were studied by analysing the samples containing known amount of calcium repeatedly. As shown in Table 5, satisfactory results were obtained.

Table 5. Accuracy and reproducibility.

Sample No.	1	2
Ca present (%)	0.10	0.16
Ca found (%)	0.09 ₄ 0.09 ₀ 0.10 ₆ 0.10 ₀ 0.09 ₁ 0.09 ₁	0.17 ₅ 0.17 ₀ 0.16 ₅ 0.17 ₂ 0.15 ₀ 0.17 ₀
Average (%)	0.09 ₅	0.16 ₇
Variation coefficient (%)	6.7	5.4

Summary

- (1) Microamount of calcium in magnesium could be determined by exciting sample solution in a porous-cup electrode with the transient discharge source unit.
- (2) The discharge conditions were E (discharge voltage)=200V, $C=18\mu F$, $L=30\mu H$, and $R=2\Omega$.
- (3) Preliminary discharge was done for 15 sec in order to photograph the spectra emitted for a stable discharge period.
- (4) Aluminium, zinc, manganese, iron and zirconium in magnesium alloys had no influence on the analytical results of calcium, excepting the case of the

presence of about 5 per cent zinc.

(5) Samples containing 0.01 to 0.3 per cent of calcium were analysed with Sr II 4215.52Å/Ca II 3933.67Å as the analytical line pair, the reproducibility being 5 to 7 per cent.

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