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A Study of Atomic Absorption Spectrometry: Determination of Magnesium and Calcium in Slag and Cast Iron*

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Synopsis

Atomic absorption-spectrometric determinations of magnesium and of calcium were carried out and the method was applied to the determination of magnesium and calcium in slag and to the determination of magnesium in cast iron. The absorbance for magnesium was measured at 2852Å by using 30 mA of current of hollow cathode lamp, 1.1 kg/cm² of air pressure and 0.48 kg/cm² of acetylene gas pressure.

That for calcium was measured at 4227Å by using 50 mA of current of hollow cathode lamp, 1.1 kg/cm² of air pressure and 0.5 kg/cm² of acetylene gas pressure. Effects of diverse ions and acid concentrations were also examined.

Aluminium, silicon and several other ions interfered with the atomic absorption of magnesium and calcium in flame, but those interferences were all eliminated by 1.5 mg/ml of strontium in the sample solution. These fundamental results were applied to the determination of magnesium and calcium in slag.

Magnesium in cast iron was also determined by a standard addition method without any preliminary separation. The results were very accurate and highly reproducible.

I. Introduction

Many works have been reported regarding the determination of magnesium and calcium by atomic absorption spectrometry. For example, Allan⁽¹⁾ reported the determination of magnesium, Willis⁽²⁾ the determination of magnesium in blood serum, and David⁽³⁾ also magnesium and calcium in plants.

In recent years, the determinations of magnesium in nickel alloys by Andrew and Nickols⁽⁴⁾, of magnesium in cast iron by Belcher and Bray⁽⁵⁾, of magnesium in uranium by Takahashi and Uruno⁽⁶⁾, and of magnesium in cast iron after extraction of iron with MIBK by Suzuki and Takeuchi⁽⁷⁾ have been reported.

The rapid determinations of magnesium and calcium in slag have been carried out by flame spectrometry⁽⁸⁾, but this method has large interfering effects of

* The 1287th report of the Research Institute for Iron, Steel and Other Metals.

(1) J.E. Allan, *Analyst*, **83** (1958), 466.

(2) J.B. Willis, *Spectrochim. Acta*, **16** (1960), 273.

(3) D.J. David, *Analyst*, **85** (1960), 495.

(4) T.R. Andrew and P.N.R. Nichols, *ibid.*, **87** (1962), 25.

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

(6) M. Takahashi and Y. Uruno, *J. Spectroscopical Soc. Japan*, **10** (1962), 110.

(7) M. Suzuki and T. Takeuchi, *Kogyo Kagaku Zasshi*, **66** (1963), 690

(8) S. Ikeda, *J. Chem. Soc. Japan*, **76** (1955), 1258.

coexisting elements and is not accurate. The detection limit of magnesium was 10 times higher than that of calcium in atomic absorption spectrometry.

So, in the present case, examinations were made of the determination of magnesium and calcium in slag by measuring the same sample solution with only changing the hollow cathode lamp without separation of major elements, because the amount of magnesium in slag was one-tenth as compared with that of calcium.

Working conditions, effects of coexisting elements, elimination of interference, and effects of acids were also examined, and the determination method of magnesium and calcium in slag was established. In addition, the method was applied to the determination of magnesium in cast iron by standard addition method without any preliminary separation.

II. Reagent and apparatus

1. Reagents

Standard magnesium solution: Magnesium metal (99.9%) was dissolved in hydrochloric acid, the solution was evaporated to dryness, and the residue was dissolved in water to make a solution containing 10 mg of Mg/ml. This solution was diluted to the desired concentration at the time of use.

Standard calcium solution: Calcium carbonate (analytical grade), which was dried at 100~110° C for 1 hr, was dissolved in hydrochloric acid and diluted with water to make a solution of 10 mg of Ca/ml. This solution for using was diluted to the desired concentration.

Strontium solution: Strontium chloride (analytical grade) was dissolved in water to make a solution containing 30 mg of St/ml.

Aluminium, iron and titanium solution: The each metal was dissolved in hydrochloric acid to make a solution of 10 mg of each/ml.

Manganese solution: Manganese chloride was dissolved in water and made a solution containing 10 mg of Mn/ml.

Silicon solution: Sodium silicate was dissolved in water and the content of silicon was determined by gravimetric method.

Hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid used were all analytical grade.

2. Apparatus

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

III. Determination of magnesium

1. Working condition

The relationship between current of magnesium hollow cathode lamp and absorbance and that between gas pressure and absorbance were examined at the wave length of 2852A and slit width of 0.02mm on the determination of magnesium.

(i) The relationship between current of magnesium hollow cathode lamp and absorbance

The relationship between the current and the absorbance was examined by varying the working current of hollow cathode lamp, with a magnesium chloride solution containing 5 μ g of Mg/ml as sample solution.

The result shown in Fig. 1 shows that the absorbance decreases with the increase of current, but bellow 27.5 mA the intensity of the light from hollow cathode lamp became so weak that the slit width had to be widened.

When the slit width was widened, the fluctuation of spectrometer became great and the precision for determination of magnesium became poor. Therefore, hollow cathode lamp current of 30 mA was adopted.

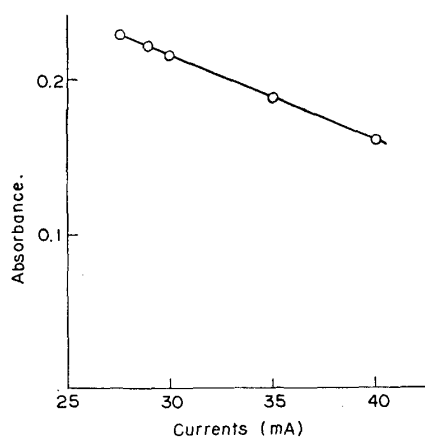


Fig. 1.

Fig. 1. Relationship between current of Mg hollow cathode lamp and absorbance.

Mg 5 μ g/ml, air pressure: 1.1 kg/cm², acetylene pressure: 0.48 kg/cm².

Fig. 2. Relationship between gas pressure and absorbance for Mg.

Mg: 5 μ g/ml, current: 30 mA, air pressure (kg/cm²): (a) 0.8, (b) 0.9, (c) 1.0, (d) 1.1

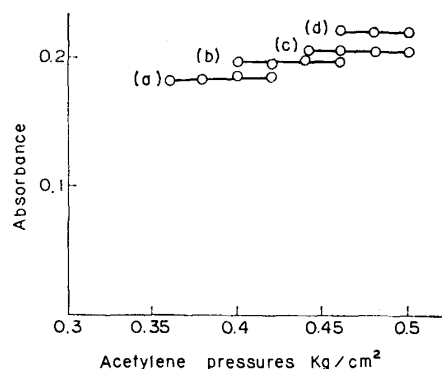


Fig. 2.

(ii) The relationship between gas pressure and absorbance

According to the variation of acetylene gas pressure, the absorbance of aqueous solution of magnesium of 5 μ g/ml was measured at constant air pressure.

As shown in Fig. 2 the absorbance did not change at constant air pressure even if acetylene gas pressure was increased, but the increasing air pressure increased the absorbance.

Therefore, the optimum pressure of air was 1.1 kg/cm² and that of acetylene gas was 0.48 kg/cm². In accordance with the foregoing examinations, working

conditions for the determination of magnesium were chosen as follows:

Wave length: 2852A; current of hollow cathode lamp: 30 mA; slit width: 0.02 mm.

Air pressure: 1.1 kg/cm², acetylene gas pressure: 0.48 kg/cm².

2. Effect of acids on magnesium absorption

The effects of usual acid such as hydrochloric, nitric and sulfuric acid on the absorption of magnesium were examined. The absorption of 5 μg/ml of magnesium in the hydrochloric, nitric and sulfuric acid with the concentration range of 0.05 ~ 3N was measured.

As shown in Fig. 3, a slight decrease in the absorbance was found with the increase of the concentration of hydrochloric and sulfuric acid in the range of 0.05 ~ 0.5 N, and nitric acid was found to give slightly lower effect.

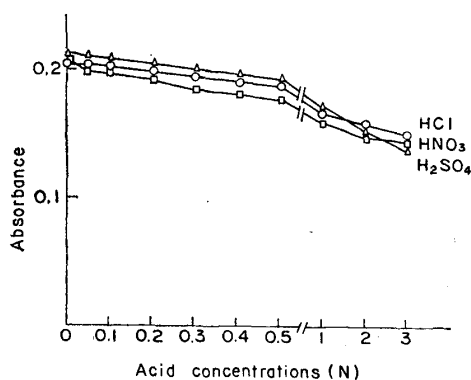


Fig. 3.

Fig. 3. Effect of acids on Mg absorption. Mg: 5 μg/ml

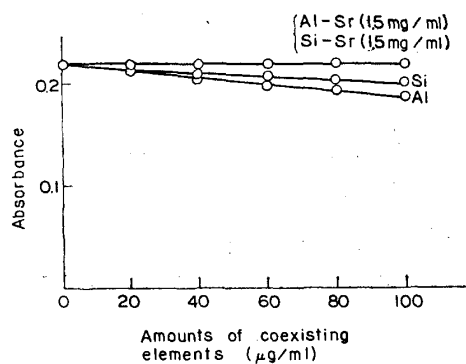


Fig. 4.

Fig. 4. Effect of coexisting elements on Mg absorption and elimination of their interference by addition of Sr. Mg: 5 μg/ml

3. Effect of coexisting elements and elimination of their interferences

Effects of aluminium, silicon, iron, calcium, titanium, manganese and phosphorus, which were found in basic slag of 5 μg/ml of magnesium, were examined. As shown in Fig. 4, the presence of aluminium or silicon more than 20 μg/ml decreased the absorbance of magnesium of 5 μg/ml.

The interference of coexisting elements with magnesium in the flame spectrometry or in the atomic absorption spectrometry can often be eliminated by adding a third element. In the present work, the possibility of the elimination of the interference of aluminium or of silicon with magnesium was examined by adding 1.5 mg/ml of strontium solution. As shown in Fig. 4, these interfering effects on magnesium could be removed. The presences of iron, titanium, manganese and phosphorus in the range of 0 ~ 100 μg/ml had no effect on the absorbance of magnesium.

4. Calibration curve for magnesium

The calibration curve for magnesium from 0 to 10 $\mu\text{g/ml}$ was prepared under the working condition in III-1-ii.

As shown in Fig. 5, a linear relationship was obtained between the concentration of magnesium and the absorbance.

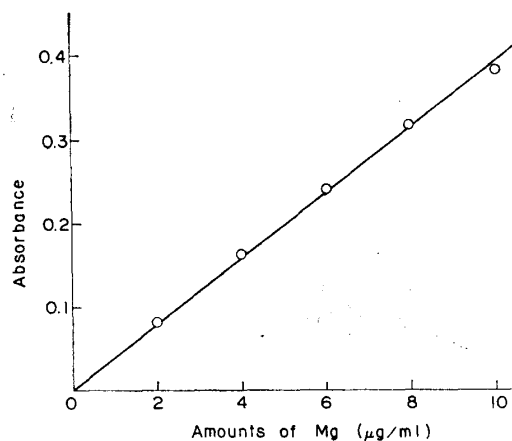


Fig. 5. Calibration curve for Mg.

IV. Determination of calcium

1. Investigation of working condition

The relationship between the current of calcium hollow cathode lamp and the absorbance of calcium, and that between the gas pressure and the absorbance were examined, at the wavelength of 4227Å and slit width of 0.03 mm.

(i) Relationship between current of calcium hollow cathode lamp and absorbance

To see the relationship between the current of hollow cathode lamp of calcium and the absorbance, the absorbance of calcium was measured at various currents of hollow cathode lamp with calcium chloride solution of 30 $\mu\text{g Ca/ml}$. As shown in Fig. 6, the optimum current was 50mA.

(ii) The relationship between gas pressure and absorbance

Using calcium chloride sample solution containing Ca of 30 $\mu\text{g/ml}$, the absorbance of calcium was measured at constant air pressure and at various acetylene pressures. As shown in Fig. 7, the absorbance increases with higher acetylene gas pressure at constant air pressure and also increases with air pressure.

With considerations on the limit of the gas flow-meter up to 0.5 kg/cm^2 and on the fluctuation of meter due to unstability, 1.1 kg/cm^2 of air pressure and 0.5 kg/cm^2 of acetylene pressure were adopted. In accordance with the foregoing examinations, working conditions for the determination of calcium were proposed as follows:

Wavelength: 4227Å; current of hollow cathode lamp: 50 mA; slit width: 0.03 mm; air pressure: 1.1 kg/cm^2 ; acetylene pressure: 0.5 kg/cm^2 .

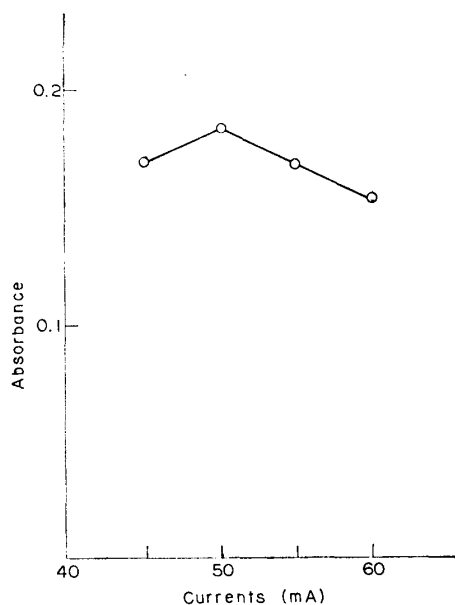


Fig. 6.

Fig. 6. Relationship between current of Ca hollow cathode lamp and absorbance.

Ca: $30 \mu\text{g/ml}$, air pressure: 1.1 kg/cm^2 , acetylene pressure: 0.5 kg/cm^2

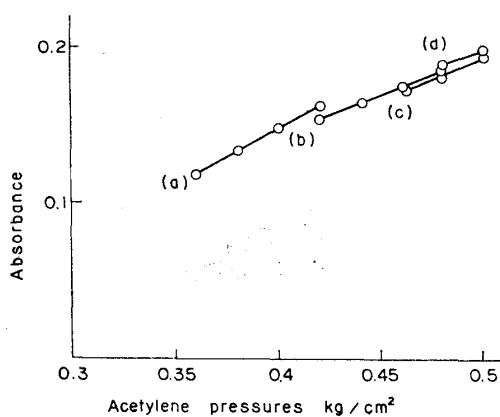


Fig. 7.

Fig. 7. Relationship between gas pressure and absorbance for Ca.

Ca: $30 \mu\text{g/ml}$, current: 50 mA , Air pressure (kg/cm^2): (a) 0.8 , (b) 0.9 , (c) 1.0 , (d) 1.1

2. Effect of acids on calcium absorption

Examinations were made of the effect of acids on calcium absorption in the concentration range of hydrochloric, nitric and sulfuric acid.

As shown in Fig. 8, a slight effect of hydrochloric acid on the absorbance was found with increasing concentration of hydrochloric acid, but nitric and sulfuric acid decrease the absorbance up to 0.05 N , and at the concentration above 0.05 N , the absorbance became constant.

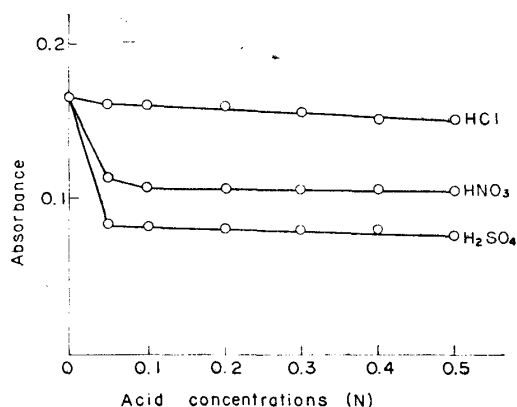


Fig. 8. Effect of acids on Ca absorption. Ca: $30 \mu\text{g/ml}$

3. Effect of coexisting elements was examined by adding aluminium, silicon, iron, magnesium, titanium, manganese and phosphorus in the range of 0 to 50 $\mu\text{g}/\text{ml}$.

As shown in Fig. 9, the interfering effects of aluminium, iron, titanium, silicon and phosphorus on calcium absorption were observable, but manganese and magnesium had not effect. Effects of these interfering elements could be removed also completely by the addition of strontium of 1.5 mg/ml.

4. Calibration curve of calcium

The calibration curve of calcium in the range of 0 to 50 $\mu\text{g}/\text{ml}$ was prepared under the working conditions in IV-1-ii.

As shown in Fig. 10, the linear relationship was obtained between the concentration of calcium and its absorption.

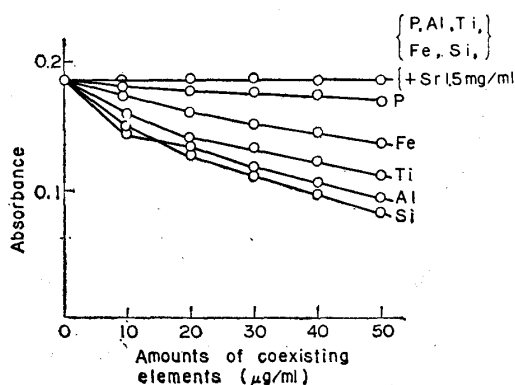


Fig. 9.

Fig. 9. Effect of coexisting elements on Ca absorption and elimination of their interference by addition of Sr. Ca: 30 $\mu\text{g}/\text{ml}$

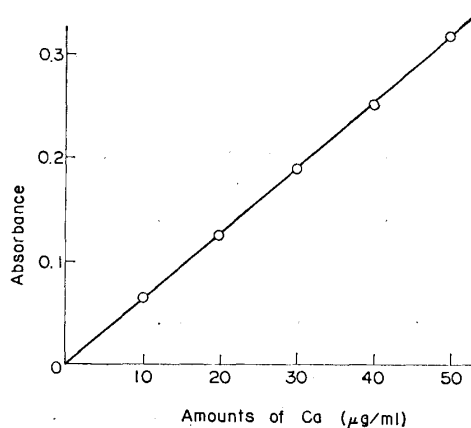


Fig. 10.

Fig. 10. Calibration curve for Ca.

V. Determination of magnesium and calcium in slag

1. Analytical procedure

In order to determine magnesium and calcium at the same time by using the same sample solution and by changing only hollow cathode lamp, the analytical procedure was adopted as follows: About 0.1 g of the sample is weighed accurately and dissolved with 10 ml hydrochloric acid and then evaporated to dryness. The residue is dissolved in 2 to 3 ml of hydrochloric acid and diluted with water.

The solution is filtered to remove silicon and graphite carbon, and the residue is washed with water. The filtrate and the wash solution are transferred to a 100 ml measuring flask and diluted with water to the mark.

A 10 ml aliquate of this solution is transferred to a 100 ml measuring flask by pipette and diluted with water to the mark after the addition of strontium chloride

solution containing 150 mg of strontium. This solution is submitted to the absorption measurement under the conditions listed in III-1-ii on magnesium and in IV-1-ii on calcium. Their amounts were determined from respective calibration curves.

2. Analytical results

The results of determination of magnesium and calcium in basic slag were listed in Tables 3 and 4. These results are in satisfactory agreement with the results obtained by the gravimetric method as pyrophosphate for magnesium and by the volumetric method with titration of permanganate after separation as oxalate for calcium.

Table 1. Analytical results for magnesium in slag.

Sample	Atomic absorption spectrometry		Gravimetric
	Sample taken (g)	MgO found (%)	MgO found (%)
1	0.1406	4.41	4.57
2	0.1022	3.57	3.70
3	0.0996	5.00	5.12
4	0.1009	5.23	5.16

Table 2. Analytical results for calcium in slag.

Sample	Atomic absorption spectrometry		Volumetric
	Sample taken (g)	CaO found (%)	CaO found (%)
1	0.1406	40.82	41.54
2	0.1022	45.20	44.77
3	0.0996	37.95	37.34
4	0.1009	38.15	37.61

VI. Application to the determination of magnesium in cast iron

Belcher reported the determination of magnesium in cast iron. Suzuki and Takeuchi pointed out that by Belcher's method could not take any amounts of samples at will for the necessity of calibration curves in accordance with amounts of iron, and that the operation was complicated due to checking on the calibration curve in the case of the presence of a large amount of iron from the view-point of properties of the atomic absorption spectrometry.

For these reasons, they carried out the determination of magnesium in cast iron after separation of iron with MIBK extraction. Then rapid and simple determinations of magnesium in cast iron were carried out by a standard addition method without calibration curve, in which the operation of extraction was saved and in which any amounts of samples were taken at will.

1. Analytical procedure

Two of the same amount from sample are weighed accurately and dissolved in

20 ml of hydrochloric acid (1+1) and evaporated to dryness. The residues are dissolved in a definite volume of dilute hydrochloric acid by heating.

The solutions are filtered to remove silicon and graphite carbon and washed with water. This filtrate and wash solution is transferred to a 100 ml measuring flask, to which strontium chloride solution containing 150 mg as strontium is added.

When the amounts of graphite carbon and silicon are very large, they adsorb some magnesium, and interfere with the determination of magnesium. Therefore, the residue is transferred together with filter paper to a platinum crucible and ignited.

After the treatment with fluoric acid, the residues are dissolved in hydrochloric acid and the solutions are added to the main solutions respectively. 2 ml of magnesium solution containing 1 mg of magnesium is added to the one sample solution but not to the other solution. Both of them are diluted with distilled water to the mark.

The absorbances of these solutions are measured under the conditions listed in III-1-ii. The difference of absorbance between the two sample solutions is equivalent to the absorbance of 2 $\mu\text{g}/\text{ml}$ of magnesium. The amount of magnesium in cast iron is calculated from this difference of absorbance.

VII. Analytical results

Results of the determination of magnesium in cast iron by the standard addition method are listed in Table 3. These results are in satisfactory agreement with those obtained by the spectrophotometric determination of magnesium with titan-yellow.

Table 3. Analytical results for magnesium in cast iron.

Sample	Atomic absorption spectrometry				Spectrophotometric
	Sample taken (g)	Mg added (μg)	Absorbance	Mg found (%)	Mg found (%)
1	0.9973 0.9973	200	0.060 0.125	0.018	0.016
2	1.0080 1.0080	200	0.065 0.131	0.020	0.018
3	1.0067 1.0067	200	0.009 0.073	0.003	0.002
4	1.0210 1.0210	200	0.042 0.108	0.012	0.011

VIII. Discussion

In general, working conditions of gas pressure have to be varied in accordance with the diameter of bore of nozzle on burner used, and the more the absorbance became, the higher the acetylene gas pressure at a constant air pressure in the case

of calcium but not in the case of Figs. 2 and 7. Considering this reason, by the increase of acetylene gas pressure the temperature of flame rises, and it seems likely that the ratio of calcium as chloride is reduced through the so-called fuel rich effect, and that the sensitivity of calcium increases due to the increase of atomic density of calcium, for the dissociation of calcium chloride occurs rather at higher temperatures than that of magnesium chloride.

Interfering effects of coexisting elements on calcium and magnesium are caused by the formation of "clots", the dissociation of which in flame is difficult as reported by Menzies⁽⁹⁾.

It is possible to infer that aluminium, silicon, titanium form themselves respectively as aluminate, silicate and titanate, all being difficult to dissociate in flame. From this reason, interfering effects of coexisting elements on magnesium are weaker than on calcium, because the chemical affinity of magnesium for aluminate, silicate and titanate is weaker than that of calcium. When calcium or strontium is present together with magnesium, the dissociation of magnesium occurs without the influence of coexisting elements such as aluminium, because calcium or strontium has rather greater chemical affinity for the interfering element than magnesium in processes of formation of clots in flame.

According to the present investigation, aluminium and silicon had interfering effect on the determination of magnesium, but it was possible to eliminate the effect by the addition of calcium or strontium.

Phosphate, sulfate, silicon, aluminium and titanium had interfering effect on calcium, but it was possible to eliminate this effect by the addition of strontium. For example, the formation constants of strontium with sulfate or phosphate are greater than those of calcium.

Coefficients of variation for 5 $\mu\text{g/ml}$ of magnesium and 30 $\mu\text{g/ml}$ calcium were 0.75% and 1.39%, respectively.

From these results, the atomic absorption spectrometry is the excellent method as a rapid determination of micro amount of magnesium. In the case of determination of calcium, this method is superior to the flame spectrometry, except the sensitivity.

(9) A.C. Menzies, *Anal. Chem.*, **32** (1960), 898.