Some Studies on Atomic Absorption Spectrometry Using Ultrahigh-Frequency Plasma as Atomizer

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Some preliminary works were performed in the use of ultrahigh-frequency plasma as an atomizer for atomic absorption spectrometry. The plasma flame was set at the position of the burner of a conventional atomic absorption spectrometer. As sodium chloride was added, the absorbance of the atom lines for magnesium and calcium considerably increased and that of the ion lines for them increased rapidly at first and reduced until near nil absorbance. This may be caused by the fact that the thermodynamic equilibrium between atom and ion or between ions changes with the variation of sodium chloride concentration in plasma flame. The detection limit (1% absorption) in the presence of moderate amounts of sodium chloride was 0.04 ppm (2852.1 Å atom line) for magnesium and 0.03 ppm (4226 Å atom line) and 0.003 ppm (3968.5 Å ion line) for calcium. The detection limits for some other elements were also determined.

INTRODUCTION

An important problem in atomic absorption spectrometry is to enhance the conversion degree of the aimed element in the sample solution into atoms. This is sometimes troublesome for some easily oxidized elements even with the hottest reducing flames normally available because of the presence of some atomic oxygen. The use of the nitrous oxide-acetylene flame has overcome some of the problems, and even such elements as rare earths, thorium *etc.* are beyond its reach.

The radio-frequency discharge plasmas are well known as an excitation source to offer considerable promise for the simultaneous multielement determination of trace constituents in solution.[1] However, the studies on the plasma torch as an atomizer for atomic absorption spectrometry are very scant[2,3] although these argon plasmas have some characteristics which suggest that these plasmas may be better than the chemical flames for atomic absorption spectrometry. Namely, the atomic absorption spectrometry using the plasma flame may be available for the vaporizing refractory elements which show extremely low sensitivity in usual chemical flame, because the higher temperature and non-oxidative atmosphere will lead to a greater degree of conversion of these elements into free atoms. It is considered that there exists simpler chemical environment in argon plasma flames than in complex combustion flames.

The purpose of the present study is to examine whether the ultrahigh-frequency plasmas are a versatile and useful atomizer for atomic absorption spectrometry.

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EXPERIMENTAL

Apparatus

Atomic absorption measurements were made with a Japan Jarrell-Ash Model AA-781 spectrometer in connection with the plasma torch, which was an emission device for Hitachi UHF plasma spectra scan, Model 300. The discharge generator consists of a magnetron, a dc power source for the magnetron, a rectangular waveguide and a coaxial waveguide (25 mm i.d. × 10 mm o.d.),[4] and ultrahigh-frequency power of 2469 MHz was supplied to the coaxial waveguide through the rectangular one. The discharge was generated at an open end of the coaxial waveguide where an aluminum electrode was placed on the tip of the inner conductor. The outer cylinder of the waveguide had two rectangular windows (10 mm in width × 30 mm in height) to pass the light from a hollow-cathode lamp. Argon of 99.99 percent purity was used to nebulize the sample solutions with a nebulizer which was the attachment to Hitachi UHF plasma spectra scan. A schematic diagram of the mounting of the nebulizer and the discharge generator was shown in Fig. 1. The discharge generator and the nebulizer were essentially operated at a condition specified in Table I. Conventional hollow cathod lamps were used (Hamamatsu TV) as light sources and operated at the recommended current.

Reagents

Stock solutions were prepared by dissolving pure metals or metal oxides of reagent grade (Nakarai Chemicals, Co. Ltd.) in dilute hydrochloric acid or nitric acid, and
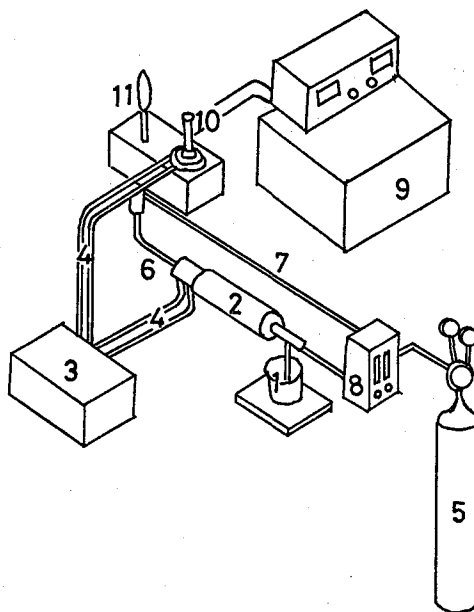

Fig. 1. Schematic diagram of the mounting of the nebulizer and discharge generator. 1: sample solution, 2: heater (2 KW), 3: cooler, 4: cooling water (20°C), 5: argon gas, 6: argon plasma gas, 7: argon sheath gas, 8: argon flow meter, 9: d c power source, 10: magnetron, 11: argon plasma flame.

Table I. Operating Condition

Anode voltage	2 KV
Anode current	200 mA
Flow rate of plasma gas	3.2 l/min.
Sheath gas	3.0 l/min.
Feed rate of the solution	3.8 ml/min.

diluted with pure water. High purity grade argon was served as the plasma gas. Redistilled and deionized water was used throughout the experiment.

RESULTS AND DISCUSSION

Sensitivities of Elements

The sensitivities observed for several elements in aqueous solution are given in Table II. The sensitivity is defined here as the concentration required to produce 1 per cent absorption. The absorbance was observed at a position of the plasma flame specified by d=0 mm or 3 mm and h=10 mm, where d and h show the off-axis and the height above the electrode tip, respectively, and the higher values of absorption were shown in Table II. The measurements of sensitivities were performed for neutral and ion lines usually by simple pass and sometimes by using the multipass assembly (3 ways). Sodium was added into the sample solution in the form of sodium chloride to examine

Table II. Sensitivities for Several Elements

atom	line (Å)	Na (ppm)	plasma flame 1 way	plasma flame 3 way	Chemical flame
Mg	2852.1	0	0.08	—	0.008
	//	50	0.04	0.015	
Ca	4226.7	0	0.15	—	0.08
	//	300	0.03	—	
	3968.5*	120	0.003	—	
	3933.7*	120	0.0035	—	
La	3949.1*	100	2	—	40
Cu	3247.5	0	0.35	—	0.07
	//	100	0.3	0.1	
Fe	2483.3	0	1.7	—	0.1
	//	100	0.8	0.5	
Pb	2170.0	0	2.3	—	0.4
	//	150	1.5	0.6	
Mn	2794.8	0	0.22	—	0.06
	//	50	0.16	0.04	
Zn	2138.6	0	0.04	0.01	0.02

* ion line.

the inter-element effects.   No effort was made to seek ideal conditions for each element beyond this by varying yet other parameters except a few elements as described below. Hence, further refinement is possible in some cases.   As shown in Table II, the observed sensitivities for lanthanum were very high in comparison with the best reported flame absorption values.

In order to examine whether the plasma flame can be utilized as the atomizer of atomic absorption spectrometry, the determination of magnesium and calcium with this method was investigated in detail.

Determination of Magnesium

The plasma flame has the general appearance of a bright flame with five regions or zones.[5]   This shows that there exists a gradient in the vertical and radial distribution of the plasma temperature.   Therefore, the distribution of magnesium atoms in the plasma flame in their ground state was studied to search the optimum region for magnesium.   The distribution was shown in Fig. 2.   The figure indicates that the distribution function of the absorption of neutral magnesium has a tendency to have a minimum on the central axis of the flame.   This may be caused by the fact that the concentration of magnesium atoms is lower in the central high-temperature zone of the flame than in the outer low-temperature-zone, since the degree of ionization of Mg^0 to
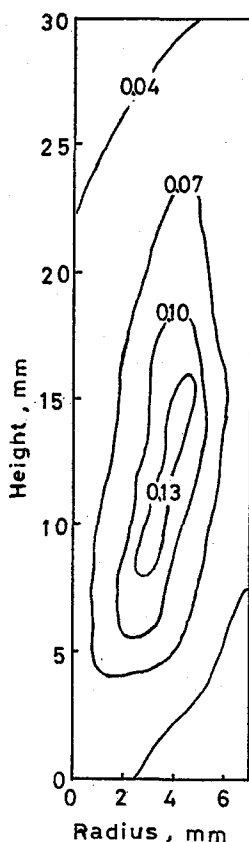

Fig. 2.   Distribution of Magnesium atoms in plasma flame.
Mg; 1 ppm.

Mg^{+1} increases as the temperature increases as indicated in the Saha formula.

Sodium was added into the sample solution in form of sodium chloride in order to examine the effect of various amounts of sodium on the absorbance of neutral magnesium atoms. The observations in Figs. 3 and 4 were performed at a position specified by h=10 mm. The concentration of magnesium was 1 ppm, and as shown in Fig. 3, the area in which the line Mg^o (2852.1 Å) was absorbed was slightly contracted as the sodium concentration increased until 50 ppm. Figure 4 showed the effect of various amounts of sodium on the absorbance of Mg^o (2852.1 Å) and Mg^{+1} (2795.5 Å) lines at d=2.0 mm. As the concentration of sodium chloride was varied between 0 and 50 ppm, the absorbance of the line Mg^o 2852.1 Å rose rapidly, and was almost constant above the concentration of 50 ppm of sodium. While the absorbance of the line Mg^{+1} 2795.5 Å rose rapidly between 0 and 10 ppm of sodium chloride, decreased considerably steeply above 10 ppm, and became nearly nil at 150 ppm of sodium ion. This suggests that there exists suppression of magnesium ionization by the addition of sodium chloride.

The relative standard deviation calculated from ten measurements at the 1 ppm lebel was 0.6% for the addition of 50 ppm sodium chloride, and 1.3% when sodium was not added.

The relation between the absorbance of the line of neutral magnesium atoms and the concentration of magnesium in the solution was shown in Fig. 5. The measurements were performed at the same position of flame as that in Fig. 4. A fairly linear calibration curves were obtained between 0.5 and 4.0 ppm of magnesium, whether sodium chloride was added or not. The calibration curves showed considerable en-
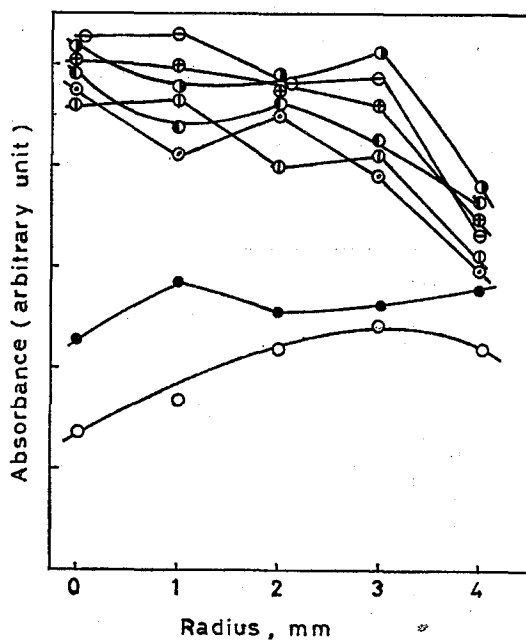

Fig. 3. Distribution of magnesium atoms in the presence of sodium chloride in plasma flame.
Na: ◯; 0 ppm, ●; 10 ppm, ◑; 20 ppm, ⊕; 30 ppm, ⊖; 50 ppm, ◐; 100 ppm, ◐; 200 ppm, ⊙; 300 ppm
height; 10 mm, Mg: 1 ppm.

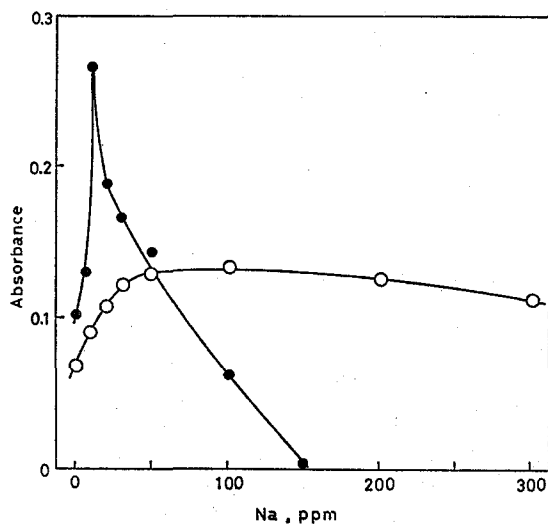M. Matsui, O. Fujino, H. Natsuume, J. Toei, and T. Shigematsu

Fig. 4. Effect of various amounts of sodium on the absorbance Mg° (2852.1 Å)
and Mg⁺¹ (2795.5 Å) lines.
○; Mg° (2852.1 Å), ●; Mg⁺¹ (2795.5 Å) line,
h; 10 mm, d; 2 mm, Mg: 1 ppm.

hancement effect in the presence of sodium chloride.   The detection limit (1% absorption) was 0.08 ppm in the absence of sodium, 0.04 ppm in the presence of 50 ppm sodium.   When a multipass assembly (3 ways) was used, 0.016 ppm of magnesium produced 1% absorption in the presence of 50 ppm sodium.

The presence of sodium chloride also produced favorable results for co-existing of some foreign substances.   Figure 6 showed the effect of increasing amounts of mineral acids on the absorbance of magnesium in the presence and absence of sodium chloride. Hydrochloric and nitric acids scarcely interfered with the absorbance of magnesium at the concentration of 0.1 M.   The effect of varying concentrations of such foreign ions
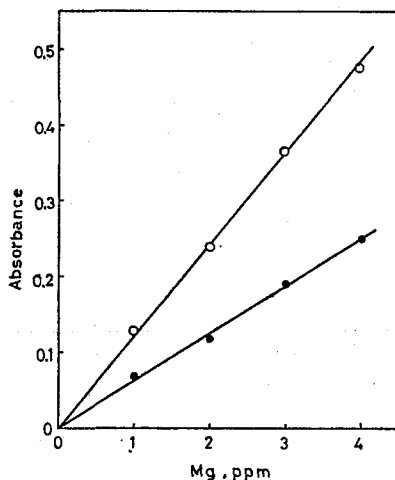
Fig. 5. Calibration curves for magnesium.
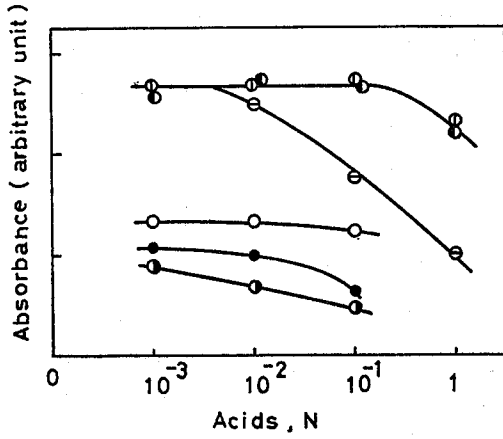●; Mg, ○; Mg+Na 50 ppm.

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Fig. 6. Effect of increasing amounts of mineral acids on the absorbance of magnesium in the presence and absence of sodium chloride.
Mg; 1 ppm, ○; HCl, ⦶; HCl+Na 50 ppm, ●, HNO₃, ◐; HNO₃+Na 50 ppm, ◑; H₂SO₄, ⊖, H₂SO₄+Na 50 ppm.
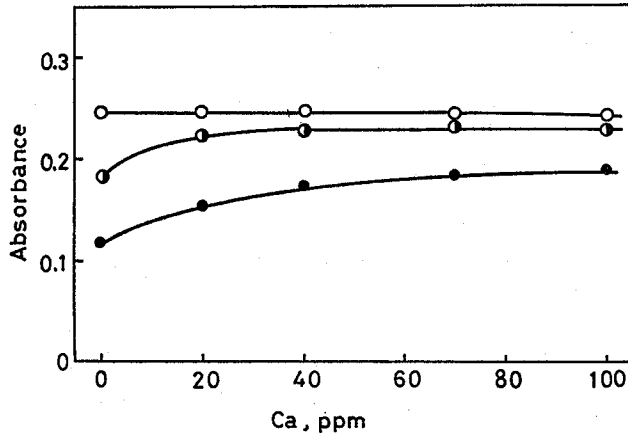

Fig. 7. Effect of varying concentrations of calcium chloride on absorbance of magnesium in the presence and absence of sodium.
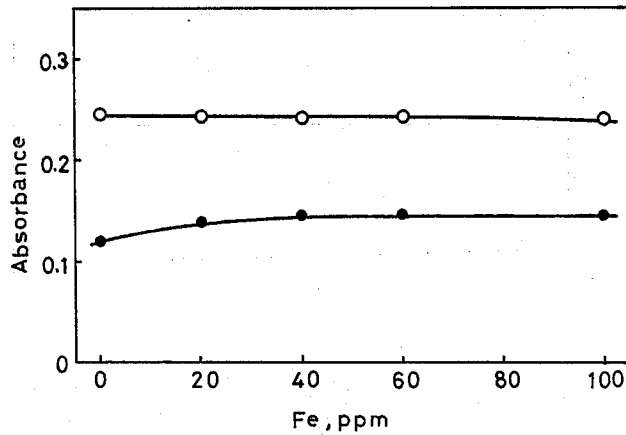●: Mg 2 ppm, ◑: Mg 2 ppm+Na 5 ppm, ○: Mg 2 ppm+Na 50 ppm.

Fig. 8. Effect of varying concentrations of ferric chloride on absorbance of magnesium in the presence and absence of sodium.
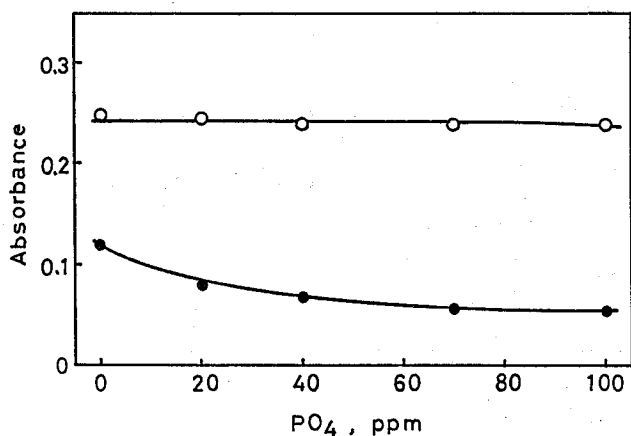●: Mg 2 ppm, ○: Mg 2 ppm+Na 50 ppm.

Fig. 9. Effect of varying concentrations of diammonium hydrogenphosphate
on absorbance of magnesium in the presence and absence of sodium.
●: Mg 2 ppm, ○: Mg 2 ppm+Na 50 ppm.

as calcium, ferric, phosphate and zinc on the absorbance of 2 ppm magnesium in the
presence and absence of sodium was shown in Figs. 7~10. These results also shown
than the presence of sodium chloride considerably suppresses the interference of foreign
elements.

Determination of Calcium

According to the calculation of the partition functions of atoms and ions,[6] calcium
exists mainly in a form of Ca^{2+} at temperature above 7000°C, Ca^+ around 5500°C, and
Ca^o below 4000°C. Therefore, it is possible for the determination of calcium with
atomic absorption spectrometry at plasma flame temperature to be made not only by
employing the atom line 4226.7 Å, but also by using the ion lines 3933.7 and 3968.5 Å.

Radial absorbance distributions of the atom line Ca^o 4226.7 Å were shown in Fig.
11, where the concentration of calcium was 4 ppm and the absorbances were measured
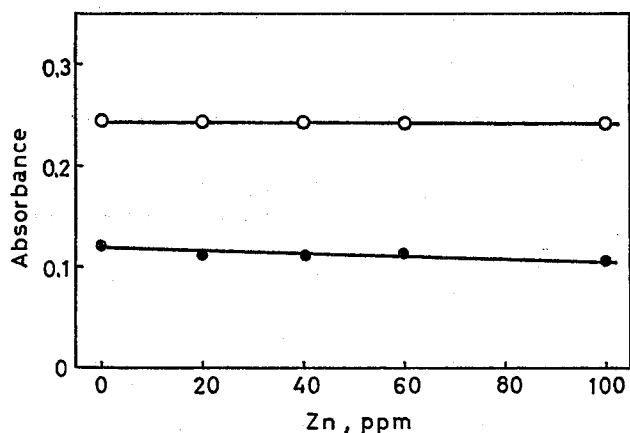

Fig. 10. Effect of varying concentrations of zinc chloride on absorbance of
magnesium in the presence and absence of sodium.
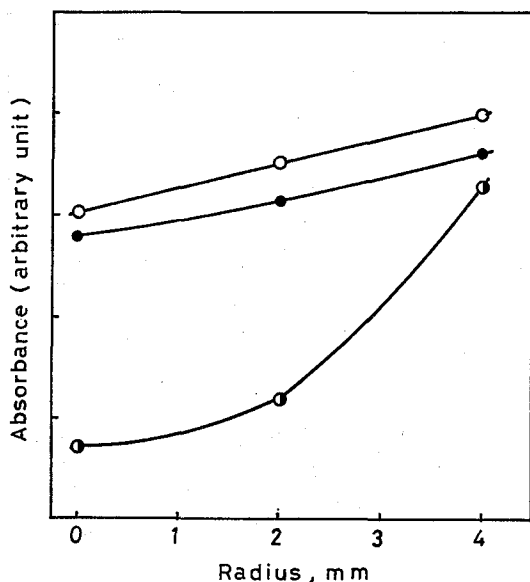●: Mg 2 ppm, ○: Mg 2 ppm+Na 50 ppm.

Fig. 11. Radial absorbance distribution of calcium atoms in plasma flame.
Ca: 4 ppm, height: ●; 15 mm, ○; 20 mm, ◑; 25 mm, atom line:
4226.7 Å.

at a height, h=15, 20 and 25 mm, respectively. The radial absorbance distributions of Ca⁰ as well as those of Mg⁰ have the minimum at d=0 mm.

Figure 12 showed the variation of absorbance of the atom line Ca⁰ (4226.7 Å) and the ion lines Ca⁺¹ (3933.7 and 3968.5 Å) as a function of the concentration of so-
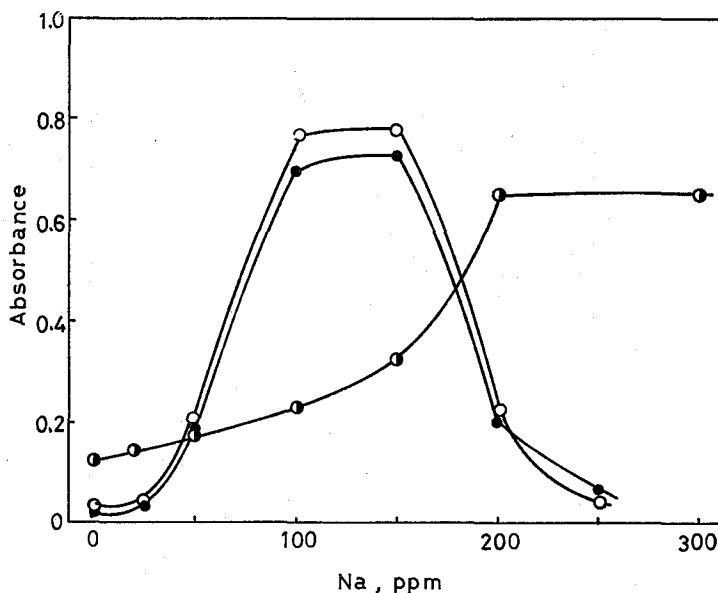

Fig. 12. Variation of absorbance of the atom line Ca⁰ and the ion lines Ca⁺ as a function of the concentration of sodium.
◑: Ca 4 ppm; atom line (4227.6 Å), ●: Ca 0.5 ppm; ion line (3933.7 Å),
○: Ca 0.5 ppm, ion line (3968.5 Å).

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dium chloride in the solution. The measurements of absorbance were made at the position of d=3 mm and h=20 mm. The absorbance of the atom line Ca⁰ increased gradually, and was almost constant above the concentration of 200 ppm sodium chloride as the concentration of sodium increased. The curve indicates that the sodium chloride shows the remarkable enhancement effect on the absorbance of neutral calcium atom line. On the other hand, the matrix effect of sodium chloride on the absorbances of ion lines (3933.7 and 3968.5 Å) aroused our interest. As the increase of sodium chloride in the calcium solution (0.5 ppm), the absorbance of Ca⁺ rose rapidly at first, showed a narrow plateau between 100 and 150 ppm of sodium chloride, and fell to near nil above the concentration. The diminishing region of the absorbance of ion lines Ca⁺ was identical with the increasing region of that of atom line Ca⁰. This suggests that the equilibrium between calcium atoms and ions, $Ca^0 \rightleftharpoons Ca^+ + e$, changes with the variation of sodium chloride concentration. Therefore, in the increment region of the absorbance of ion line Ca^{+1} between 0 and 100 ppm of sodium, there may exist ionization equilibrium between mono- and divalent ions calcium. In the absorbance of ion lines, sodium chloride also shows the distinguished enhancing effect between 100 and 150 ppm of sodium.

In the range 0.1–4 ppm of calcium in solutions, calibration curves were constructed for the absorbance of atom line (4226.7 Å) and for that of ion lines (3933.7 and 3968.5 Å). The results were shown in Fig. 13. Linear calibration curves were obtained for both ion and atom lines of calcium when a moderate amount of sodium chloride was added. The detection limit (1% absorption) was 0.03 ppm for the atom line in the solution containing 300 ppm sodium chloride and 0.0035 and 0.003 ppm for ion lines
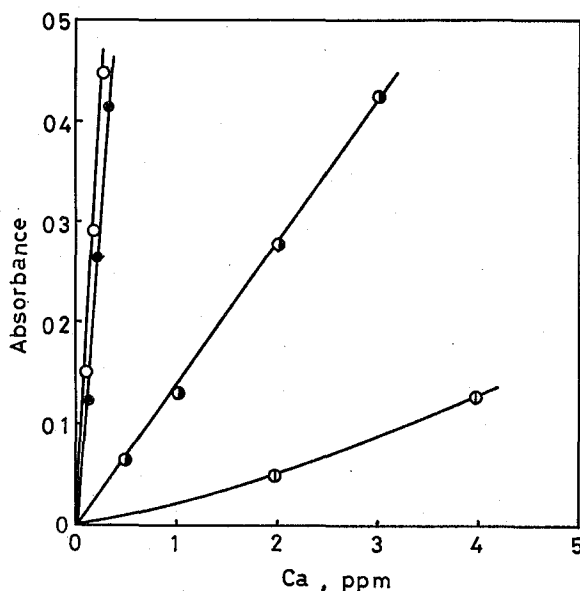

Fig. 13. Calibration curves for calcium.
Height: 15 mm, radius: 2 mm,
①: atom line (4226.7 Å); Ca, ◑: atom line (4226.7 Å); Ca+Na 300 ppm, ●: ion line (3933.7 Å); Ca+Na 120 ppm, ○: ion line (3968.5 Å); Ca+Na 120 ppm.
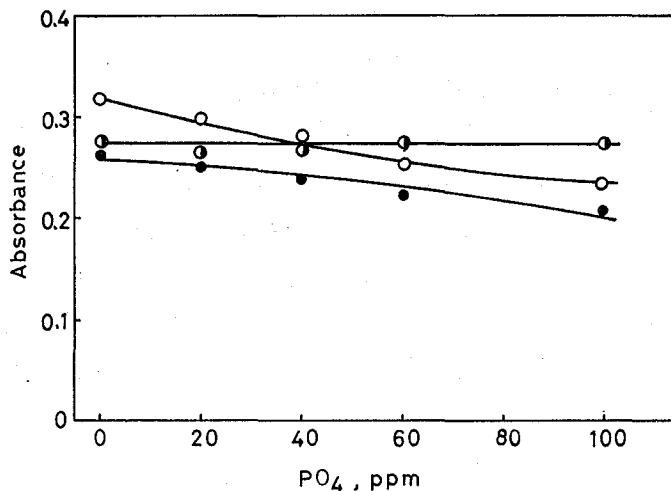
Fig. 14. Effect of varying amounts of phosphate on the absorbance of calcium.
◑: Ca (4226.7 Å); Ca 2 ppm+Na 300 ppm, ○: Ca⁺ (3968.5 Å); Ca
0.2 ppm+Na 120 ppm, ●: Ca⁺ (3933.7 Å); Ca 0.2 ppm+Na 120 ppm.

3933.7 and 3968.5 Å, respectively, when 120 ppm of sodium chloride was added. The effect of increasing amounts of mineral acids on the absorbance of neutral calcium was examined. The interference of 0.1 N hydrochloric and nitric acids was scarcely observed. The effect of varying amounts of phosphate on the absorbance of calcium was shown in Fig. 14. As seen in the figure, the absorbance of ion line was more affected by phosphate ions than that of atom line was.

ACKNOWLEDGMENT

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