Enhancement Effect of Alkaline Earth Metal on the Determination of Aluminium by Atomic Absorption Spectrometry with a Graphite Furnace

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Abstract

In the determination of aluminium by atomic absorption spectrometry with a graphite furnace, coexisting oxyanion salts of alkaline earth metal enhanced the aluminium atomic absorption. The relative absorbance was increased with decreasing of the ramp atomization rate and with decreasing of the sheathing gas flow rate less than 5 l min^{-1}. These results show that the enhancement effect is caused by the reductivity of the carbide of alkaline earth metal which is formed in the furnace at ashing and atomization steps. The relative enhancement followed the sequence : Ca>Sr>Mg. The addition of mixture of calcium nitrate and ammonium salt of EDTA enhanced the atomic absorption of aluminium and also removed the interference of chloride in the atomic absorption of aluminium.

Introduction

A flameless atomic absorption spectrometry with a graphite furnace generally has a poor sensitivity in the determination of elements such as tungsten, lanthanum and tantalum. This has been explained by that these metals react with graphite and yield thermally stable carbides. Applying this effect, treatment of inner surface of the graphite furnace with these elements improves sensitivity of other elements[1)-7)]. Addition of a large excess of calcium nitrate enhances sensitivity for aluminium and other elements. This is also due to calcium carbide formed in the furnace[8)]. The other alkaline earth metal nitrates were found to enhance the atomic absorption of the elements. However, the chlorides of alkaline earth metals suppress the atomic absorption of aluminium[9)]. Hence, addition of oxyanion salts of alkaline earth metal is expected to improve the sensitivity in the analytical application. In this work, the enhancement effect of alkaline earth metal on the atomic absorption of aluminium was investigated by using the oxyanion salts, and application of this method has been discussed.

Experimental

Apparatus and reagents

A Varian-Techtron model 63 carbon-rod atomizer was used with a Varian-Techtron model 1200 atomic absorption spectrometer. A tube-type graphite cell was used and the absorbance in a nitrogen atmosphere was measured. The signal was

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recorded with a Hitachi model 056 chart recorder. A Hitachi aluminium hollow-cathode lamp was used as the radiation source and a Varian-Techtron deuterium lamp was used for background correction. The applied voltage between the atomizer terminals was measured with digital voltmeter connected in parallel ; the temperature of the center of the graphite tube was measured with a platinum/platinum-rhodium thermocouple. The sample was added with a 5-μl Excalibur Autopet fitted with disposable tips.

All solutions were prepared from analytical reagent-grade chemicals and demineralized water, and stored in polyethylene bottles. The stock aluminium solution (1000 μg ml^{-1}) was prepared by dissolving aluminium metal (99.99% pure) in the minimum volume nitric acid ; the stock solution was made 0.1 M in nitric acid.

Procedure

A 5-μl sample was deposited in the center of the graphite tube and dried, ashed and atomized with nitrogen gas flowing over the furnace. The instrumental settings are summarized in Table 1. The absorption signals during the atomization step were recorded and the peak height was taken as the analytical signal. A reagent blank was run under the same conditions and a suitable correction applied. The absorbances of aluminium solution containing various salts were measured and the ratios of their absorbances to the absorbance in the absence of salt (i. e., the relative absorbances) were calculated.

Table 1 Instrumental conditions

Wavelength	309.3 nm (0.5 nm bandwidth)
N_2 flow rate	5.5 l min^{-1}
Drying	110℃ (0.56V) for 30 sec
Ashing	620℃ (1.7V) for 30 sec
Atomization	7.0V (step mode) for 4 sec

Results and discussion

The concentration of aluminium in the test solution, unless otherwise specified, was 2.5 μg ml^{-1}. Aluminium atomic absorption signals in the presence of various oxyanion salts of alkaline earth metal were measured in their concentration range from 10^{-5} to 10^{-1} M in a slightly acidic medium (pH 3-4). The salts were nitrates, sulfates, phosphates and acetates of magnesium, calcium, strontium and barium. All these salts of each metal showed similar behaviors. Therefore, the discussion below will be made by only the nitrates. The results for nitrates are shown in Fig. 1. The effect of coexisting nitrate is dependent on the metal and its concentration. The negative and positive effects are seen on calcium, storontium and barium. The absorbances are depressed at lower concentration, 10^{-4} to 10^{-2} M, but increased above 10^{-2} M. Magnesium shows no depression at lower concentration and enhancement effect is maximum at 10^{-2} M. The negative effects of calcium, strontium and barium may be due to dissociation energy of their metal oxides formed during the ashing step.

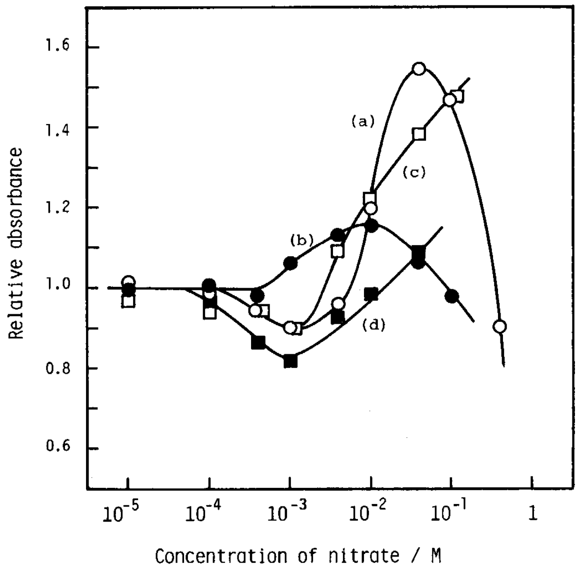

Fig. 1 Effect of alkaline earth metal nitrates on the atomic absorbance of aluminium (2.5 μg ml^{-1}) relative to absorbance without nitrate added : (a) $Mg(NO_3)_2$; (b) $Ca(NO_3)_2$; (c) $Sr(NO_3)_2$; (d) $Ba(NO_3)_2$.

Thompson et al.[8] explained that the enhancement effect observed by addition of calcium was due to preferential formation of carbide by the calcium and also possibly to a reduction with the volatilized calcium atom. If the enhancement of aluminium absorption by the oxyanion salts of alkaline earth metal investigated is caused by formation of their carbide, the higher heating is expected to increase the more enhancement effect. Effects of heating temperature and time on the atomic absorption of aluminium were measured by changing the ramp atomization rate without ashing step in the presence of nitrates of magnesium, calcium and strontium. The lower ramp rate shows the more enhancement as seen in Fig. 2. The lower ramp rate spends the longer heating time to reach a given temperature. This may indicate the more carbide formation under the lower lamp rate. The relative enhancement follows the sequence : calcium >storontium>magnesium. This order may be the formability of their carbide

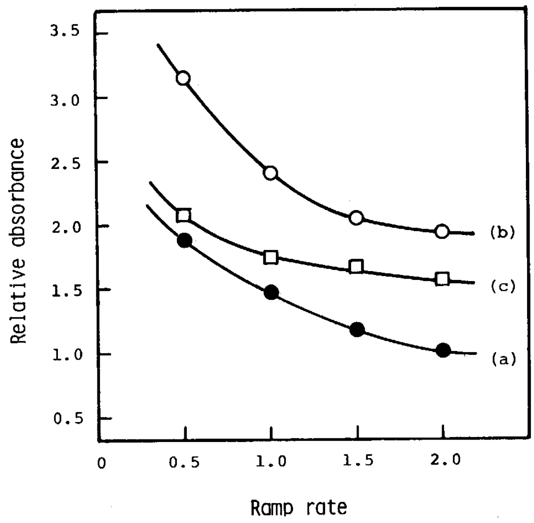

Fig. 2 Effect of ramp atomization rate on the atomic absorbance of aluminium (2.5 μg ml^{-1}) in the presence of alkaline earth metal nitrates relative to absorbance without nitrate added : (b) $Ca(NO_3)_2$; (c) $Sr(NO_3)_2$. Cutoff voltage : 7.0 V.

under the same temperature and heating time.

If the enhancement by the alkaline earth metal salts investigated here is occured by reductivity of the carbide around the analyte, its effectivity would be varied with the amount of oxygen contaminated from the external atmosphere under the condition of same amount of the carbide formed. The furnace chamber used here is open type, and then the oxygen from the external atmosphere may be mixed into nitrogen gas around the furnace under the low rate of the nitrogen gas flowing. Further, the nitrogen gas containing oxygen may reduce the absorption of analyte. In order to investigate the carbide reductivity, therefore, the effect of the oxygen contaminated from the external atmosphere on the atomic absorption of aluminium was measured by changing the nitrogen gas flow rate against the presence of two different kinds of salts, one of which was easy to form carbide and the other was difficult to do under the ordinary temperature condition. The former salts were nitrates of magnesium and calcium and the latter was that of copper(II).

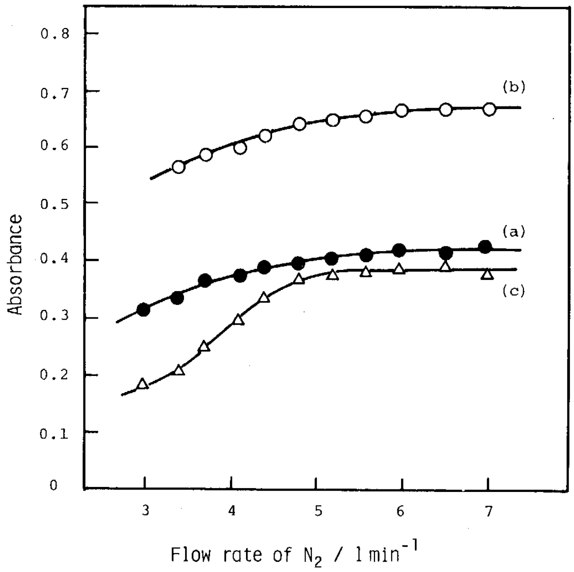

Fig. 3 Effect of nitrogen flow rate on the atomic absorbance of aluminium (2.5 $\mu g\ ml^{-1}$) in the presence of nitrate : (a) $Mg(NO_3)_2$; (b) $Ca(NO_3)_2$; (c) $Cu(NO_3)_2$.

The results are shown in Fig. 3. The trend under the presence of copper(II) nitrate is quite similar to that under the no presence. The aluminium absorbance is decreased with decreasing of nitrogen flow rate less than 5.0 1 min^{-1}. This effect may be due to the oxygen contaminated from the external atmosphere. However, in the presence of magnesium nitrate, the decrease of aluminium absorption is reduced and then the relative absorbance is increased with the decreasing of nitrogen flow rate. In the presence of calcium nitrate, the trend is similar to that in the presence of magnesium nitrate, but the enhancement of absorbance of aluminium was more effective. From these facts, the carbides of calcium and magnesium prevent the suppression by the contamination of the oxygen. The same behavior was observed for the other alkaline earth metal salts. Accordingly, the enhancement effect of the carbide of alkaline earth metal on the atomic absorption of aluminium is more effective under the lower sheathing gas flow rate. But the disadvantage of applying this method is that the life of graphite tube is shortened.

As the graphite tube used here is treated with pyrolytic graphite, the reaction of the oxide of alkaline earth metal with carbon to yield carbide in the tube may be difficult. The acceleration of the carbide formation is expected by addition of watersoluble organic compound, e. g., sucrose or EDTA, in the sample solution, because these compounds yield carbon powder in the graphite tube at ashing step[10]. Furthermore, the ammonium salt of EDTA was very suitable as an additive to remove the interference in the atomic absorption of aluminium by coexisting chloride[9]. Therefore, in order to enhance the sensitivity of atomic absorption of aluminium and also to remove the interference of coexisting chloride, the addition of the mixture of calcium nitrate and diammonium-EDTA to the sample solution was attempted. The EDTA was added in large excess to the calcium. When the mixture of calcium and EDTA was added, the pH of solution was kept about 10 with ammonia, because the calcium-EDTA complex is not so stable[11],[12], and calcium is titrated with EDTA at pH 10[13]. Copper(II) chloride was chosen as the coexisting chloride.

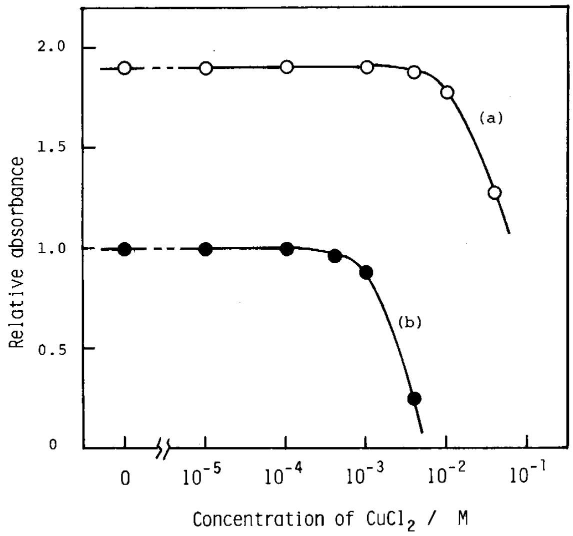

Fig. 4 Removal of $CuCl_2$ interference on aluminium (2.5 μg ml^{-1}) by addition of the mixture of $(NH_4)_2EDTA$ and $Ca(NO_3)_2$ at pH 10 with ammonia : (a) 0.06 M $(NH_4)_2$ EDTA and 0.02 M $Ca(NO_3)_2$ added ; (b) no addition at pH 3.

The results in the presence of 0.02 M calcium nitrate and 0.06 M diammonium EDTA are shown in Fig. 4. Compared with the results in the absence of the mixture of calcium and EDTA, the sensitivity of aluminium absorption is increased about 1.9 times and the maximum allowable concentration of coexisting copper(II) chloride is about 40 times larger. However, the removal effect of EDTA on the chloride interference is not better than that without calcium[9]. As the calcium-EDTA complex is not so stable[11],[12] and also the calcium chloride shows severe interference on the atomic absorption of aluminium[9], the calcium may react with chloride ion which is supplied from copper(II) chloride added, and the interference of the calcium chloride may be appeared. When this method is applied to practical sample, the best conditions, e. g., kinds of alkaline earth metal and organic compound, these concentrations and pH of solution, must be determined for each case.

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