Removal Effect of Carbon Powder on Chloride Interference in the Determination of Metals by Atomic Absorption Spectrometry with Electrothermal Atomization

By Koji MATSUSAKI* and Takashi YOSHINO**

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Abstract

The interference from coexisting chloride in the determination of metals by atomic absorption spectrometry with a graphite furnace could be removed by the carbon powder which was suspended in the sample solution or placed in the furnace. In order to form carbon powder in the graphite furnace at ashing step of operation, the addition of sucrose to the sample solution was also investigated. The effect produced by this method was more than that by suspension of carbon powder, but less than that by addition of EDTA. These results indicate that the formation of carbon powder from sucrose or EDTA in the furnace contributes to the removal efficiency of sucrose or EDTA on the chloride interference, however the interaction between analyte and additive in the solution acts largely on that.

Introduction

Atomic absorption spectrometry with a graphite furnace is widely used for determination of metals because of its high sensitivity and rapidity. However, severe interference is caused by chloride present originally in the specimen and/or added during preparation of the test solution. On the basis of reactions taking place in the solid and/or gaseous state in the furnace, this chloride interference has been interpreted in terms of volatile compound formation1)~3), a vapor-phase process4)~6) and analyte occlusion in the matrix7)~10). In previous work11), the mechanism of chloride interference in the determination of trace metals was investigated with particularly regard to chemical reaction, mainly chloride complexiation, occuring in aqueous solutions. Diammonium-EDTA was found to be most suitable additive for removal of chloride interference, because the metal ions were masked by EDTA against chloro complex formation.

The mixture of carbon powder with the sample has enhanced the atomic absorbance of analyte and decreased the interference of coexisting acids and salts12)~14). These efficiencies have been interpreted in terms of deoxidation effect, accelation of thermal conduction and suppression of vaporization and activation of deconposition of metal salts. However, the removal effect of carbon powder on the chloride interference has not yet been investigated. Furthermore, EDTA may form carbon powder in the graphite furnace at ashing step of operation, and this carbon formed must contribute to the removal efficiency of EDTA on the chloride interference. Sucrose has been used as matrix modifier in the determination of lead in the presence of magnesium chloride15). In this case, the carbon formed from

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*Department of Industrial Chemistry, Technical College, Yamaguchi University
**Department of Industrial Chemistry

sucrose may also contribute to the removal efficiency. In the present work, therefore the removal effect of carbon powder on the chloride interference were investigated and compared with those of sucrose and EDTA.

Experimental

Apparatus and reagents

A Varian-Techtron model 63 carbon-rod atomizer used in conjunction with a Varian-Techtron model 1200 atomic absorption spectrometer run with a time constant of 0.3 sec (DAMP A). Tube and cup types of graphite furnaces were used and the absorption was measured under a nitrogen atmosphere. The signal was recorded with a Hitachi model 056 chart recorder. Hitachi hollow-cathode lamps were used for each metal studied and a Varian-Techtron deuterium lamp was applied for background correction. The applied voltage between the atomizer terminals was measured with a digital voltmeter connected in parallel and the temperature of the center of the graphite furnace was measured with a platinum/platinum-rhodium thermocouple. Samples were 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 1000 μg ml^{-1} stock metal solutions were prepared from their nitrates. All solutions were finally made 0.1 M in nitric acid.

Procedure

A 5 μl sample was deposited in the center of the graphite furnace and dried, ashed and atomized with nitrogen flowing over the furnace. The instrumental settings except for ashing condition for each metal are summarized in Table 1 together with the concentrations used.

Table 1 Experimental conditions for the atomic absorption mesurements

Analyte	Conc. (μg ml^{-1})	Wavelength (nm)	Slit width (nm)	N_2 flow rate (l min^{-1})	Atomization voltage[a] (V)
Pb	0.25 (1.0)[b]	283.3	0.5	4.0	4.2
Cu	0.25 (0.5)[b]	324.3	0.5	4.0	5.4
Al	2.5	309.3	0.5	5.5	7.0
Mn	0.05	403.1	0.2	4.5	5.5

[a] Drying for 30 sec at 110℃ (0.65V); atomization time 3 sec.

[b] In the case of using the cup type furnace.

The ashing condition was varied as required. 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. In the case of using a tube type graphite furnace, the furnace was fired at its maximum temperature for 3 sec after each sample to clear any residue from the surface. The variation of furnace temperature with applied voltage was measured at the drying and ashing steps, in the absence of any salt. The absorbances of metal solution containing various chloride were measured and the ratios of their absorbances to the absorbance in the absence of chloride (i. e., the relative absorbances) were calculated.

When carbon powder was used for the removal of chloride interference, the experimental was carried out as follows. In the case of using a tube type graphite furnace, the carbon powder was added to the sample solution and the suspended solution was used for measurement of atomic absorption. After each sample running, the residual carbon powder was removed from the tube and then the furnace was fired at its maximum temperature for 3 sec. In the case of using a cup type furnace, the carbon powder was placed in the cup, in advance. The cup furnace was fired under the same condition as that of analyte to clear impurities in the carbon powder. After confirmation of no absorption arising from the carbon powder, the sample solution was deposited on the carbon powder in the cup and run.

Results and discussion

Effect of carbon powder on a tube type graphite furnace

Lead, copper, aluminium and manganese were chosen as analyte. The instrumental conditions of drying and atomization steps and of nitrogen flow rate were examined for each standard solution contained only analyte element, and was set as shown in Table 1. The added carbon powder must be as free as possible from impurities which arise background absorption. Several kinds of commercial active carbon powder were therefore tested. A 0.2 g carbon powder was added to 25 ml water. Five μl suspended solution was deposited in the graphite tube and the absorption was measured under the same condition as that of measuring atomic absorption of each analyte. The carbon powder which exhibited smallest absorption at each analyte wavelength was chosen as additive.

The removal efficiency of carbon powder suspension in the sample solution on the chloride interference was at first examined by use of a tube type graphite furnace. The effect of amount of carbon powder suspended was investigated under the recommended condition. The ashing condition was kept for 30 sec at 550℃ (1.6V). The results for lead in the presence of magnesium chloride and in the presence of sodium chloride are shown in Fig. 1. The relative absorbances increase with increasing amount of carbon powder added and the interference from 1×10^{-3}M magnesium chloride is removed completely by above 8 mg ml^{-1} of that. Similar results were observed for the other elements. These indicate that the suspension of carbon powder is effective for removal of the chloride interference. The effect of chloride concentration on the atomic absorption of analyte with the suspension of carbon powder was investigated. Figure 2 shows that the interference from magnesium chloride to the atomic absorption of copper is greatly decreased by carbon powder, and the maximum allowable concentration of coexisting magnesium chloride with 8 mg ml^{-1} carbon

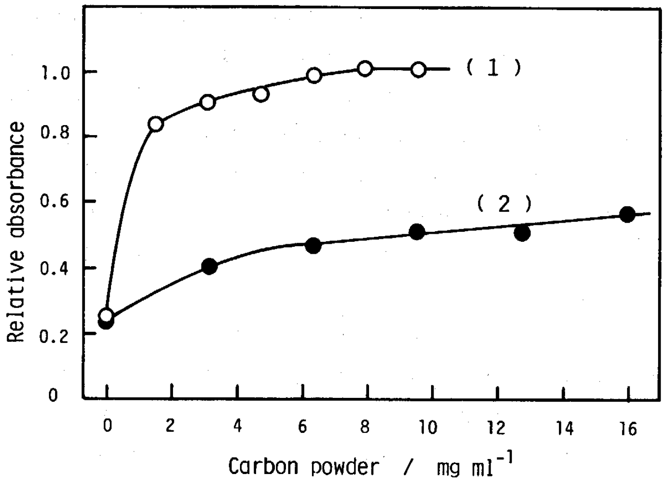

Fig. 1 Effect of amount of suspended carbon powder on the atomic absorption of lead (0.25 μg ml^{-1}) in the presence of (1) 1×10^{-3} M $MgCl_2$ and (2) 4×10^{-2} M NaCl.

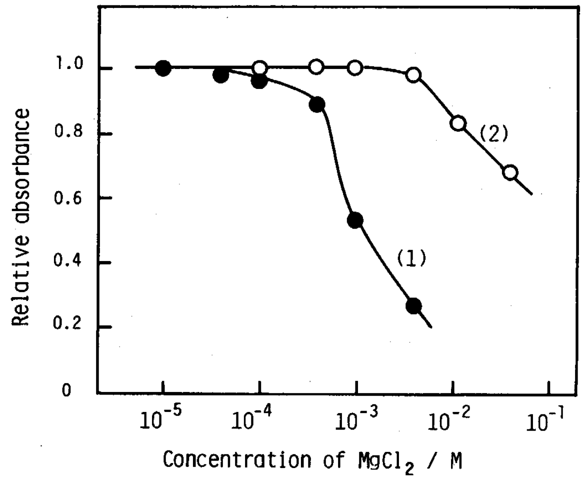

Fig. 2

Removal effect of the suspension of carbon powder on $MgCl_2$ interference to the atomic absorption of copper (0.25 μg ml^{-1}) by use of the tube type furnace; (1) no addition; (2) 8 mg ml^{-1} carbon suspended.

powder is about 40 times larger than that without carbon powder. Similar results were observed for the other chloride and for the other elements. Kanda et al.[12] and Yoshimura et al.[13][14] reported the enhancement of atomic absorbance of analyte by the mixture of carbon, but in this work the enhancement effect was not observed.

Effect of carbon powder on a cup type graphite furnace

When the tube type graphite furnace was used, the chloride interference could be removed by the suspension of carbon powder in the sample solution. In this method, however, impurities in the carbon and the scattering of carbon arised background absorption and the background correction was necessary with a deuterium lamp, in addition the residual carbon powder must be removed from the tube after each sample.

The method which in advance the carbon powder was placed in a cup type graphite furnace and then the sample solution was deposited on the carbon powder in the cup was attempted. In this method, several measurements of atomic absorption are possible for each carbon placing, and the background correction is not necessary because of clearing impurities in the carbon by pre-firing. However, the sensitivity of atomic absorption of analyte by use of the cup type furnace is less than that by use of the tube type furnace. One mg carbon powder was suited for each placing in a cup. When large amount of carbon powder was placed, the scattering powder shaded the light pass at atomization step. Ashing condition was set for 30 sec at 550 ℃ (1.6V). The effect of chloride concentration on the atomic absorption of analyte was investigated. The result for copper is shown in Fig. 3. The interference from magnesium chloride is greatly decreased by carbon. Similar results were observed for the other elements. For the elements having a high atomization temperature, e. g., aluminium, however, this method was not so effective, because the carbon powder was scattered out by steep rise of furnace temperature at atomization step.

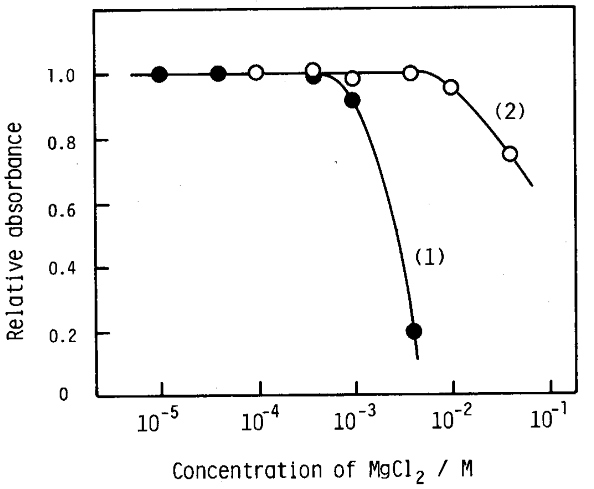

Fig. 3
Removal effect of the carbon on $MgCl_2$ interference to the atomic absorption of copper (0.5 μg ml^{-1}) by use of the cup type furnace; (1) without carbon; (2) with carbon.

Effect of sucrose

The suspension of carbon powder in the sample solution and the deposition of the sample solution on the carbon powder in the furnace were effective for removal of the chloride interference. However, the procedures were rather tedious as described above and the reproducibilities of the atomic absorption signal in these methods were slightly poor. The formation of new carbon powder in the graphite tube at ashing step of operation by the use of organic compound, therefore, was attempted. Watersoluble organic compound having comparatively larger molecular weight is desired, because it is soluble in the sample solution. Sucrose was chosen as additive to the sample solution. The ashing condition was kept for 30 sec at 670 ℃ (1.7V). As the amount of residual carbon powder after firing was very small, in this method, background absorption arised from sucrose was negligible and it was not necessary to remove the residual carbon from the furnace.

The effect of concentration of sucrose added was investigated under the recommended condition. Reproducible values were obtained. The result for aluminium is shown in Fig. 4,

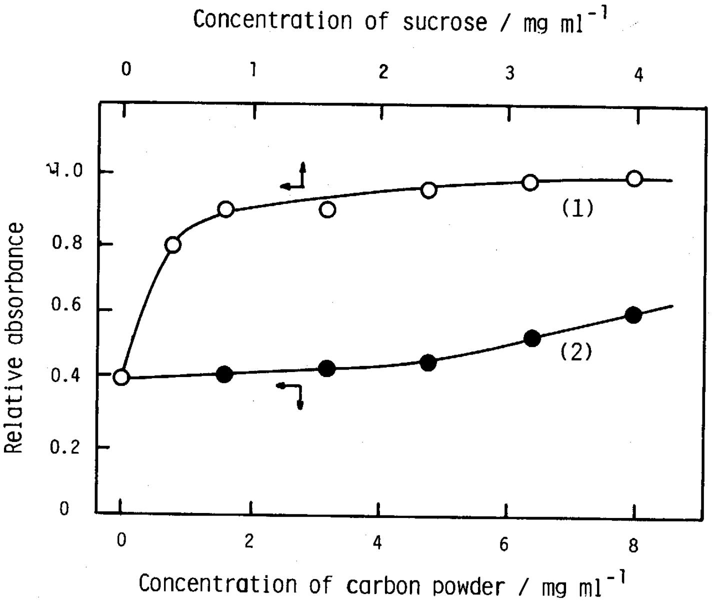

Fig. 4 Effect of amount of additive on the atomic absorption of aluminium (2.5 μg ml^{-1}) in the presence of 4×10^{-3} M $CuCl_2$; (1) sucrose ; (2) carbon powder.

and that from carbon suspension method is also shown to compare these removal efficiencies. The amount of sucrose which needs to remove the interference of copper chloride is less than that of carbon powder. This indicates that the effect of sucrose on removal of the chloride interference is due to not only the formation of carbon in the furnace but also the other factor. It may be the interaction between analyte and sucrose in the solution. This interaction may effect on the condensed phase in the furnace at drying step and the salt form of analyte in this phase may be not chloride. Sucrose may therefore act as matrix modifier in the determination of lead in the presence of magnesium chloride[15].

In the presence of sucrose, the effect of chloride concentration on the atomic absorption of analyte was investigated and that in the presence of diammonium-EDTA was also examined. Figure 5 shows that the interference from copper chloride in the atomic absorption of manganese is greatly decreased by sucrose, however the effect produced by sucrose is slightly less than that by EDTA. Similar results were obtained for the other elements. These indicate that the interaction between EDTA and analyte or coexisting cations in the solution, i. e., coordination of EDTA to cations, is more effective than that between sucrose and cations. But it is also identified by these results that the formation of carbon powder from EDTA in the furnace at ashing step must contribute to the removal effect of EDTA on the chloride interference.

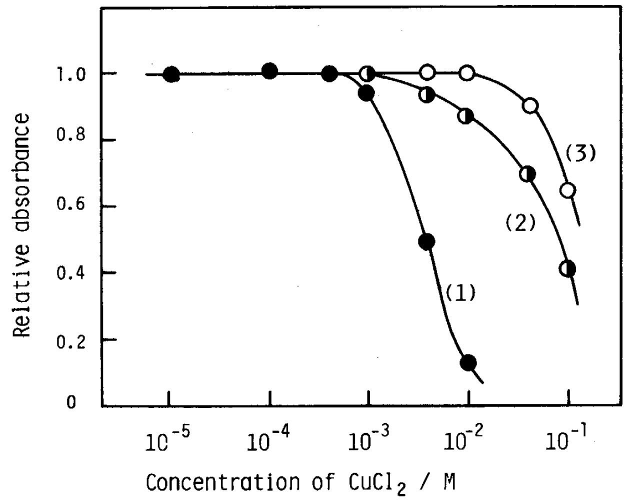

Fig. 5 Removal of $CuCl_2$ interference on manganese (0.05 μg ml^{-1}) by addition of other reagents; (1) no addition; (2) 8 mg ml^{-1} sucrose added; (3) 0.04 M $(NH_4)_2EDTA$ added.

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