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Observation of a Cobalt as a Chemical Modifier for Lead in Electrothermal Atomic Absorption Spectrometry Using a Tungsten Furnace by Means of a Surface Analysis

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The behavior and effect of cobalt as a chemical modifier for lead were studied by electrothermal atomic absorption spectrometry using a tungsten furnace. The characterization of materials formed on the tungsten surface at the charring stage was performed using of a scanning electron microscope and X-ray photoelectron spectrometer. The experimental results indicate that the effect of a cobalt modifier is related to the formation of granular cobalt crystals during a preheating stage. Under the coexistence of lead, however, the cobalt crystals became irregularly shaped, probably forming an intermetallic compound between cobalt and lead. By an examination using sample materials containing chloride, nitrate, and sulfate salts, it was found that a cobalt modifier is effective for suppressing the interference of chloride and nitrate. All of the sulfate salts gave negative interference; the cobalt crystal, which acted as a chemical modifier, was included inside a large crystal which originated from the sulfate at the charring stage. The thermal stability of lead is difficult to maintain with increasing sulfate salts. The cobalt modifier was applied to the determination of lead in several water samples.

The determination of lead by electrothermal atomic absorption spectrometry is known to be difficult due to interference caused by the presence of coexisting materials. Various chemical species in the system, especially chlorides, are likely to both decrease the sensitivity and to cause a splitting of the absorption signal.[1,2] Slavin et al.[3] have reported on the influence of lead coexisting with chloride by electrothermal atomic absorption spectrometry using a graphite furnace. Imai et al.[4] investigated the influence of lead coexisting with chloride and sulfate, and reported on the effect of chromium(III) nitrate as a chemical modifier. Accordingly, chemical modifiers are used to suppress this interference in the determination of lead; generally effective chemical modifiers include a palladium and a mixture of magnesium nitrite and palladium etc. The behavior and the effect of various chemical modifiers by electrothermal atomic absorption spectrometry have been discussed regarding the interfering action and the atomizing mechanism by obtaining the activation energy from a kinetic analysis,[5—13] etc. These results have been applied to actual samples. However, most of the behavior and effects of the chemical modifiers reported were the results of experiments using a graphite furnace. Fudagawa[14] reported on a measurement method for lead and the atomizing mechanism on electrothermal atomic absorption spectrometry using a tungsten furnace; however, no investigation was performed regarding chemical modifiers.

The author evaluated various chemical modifiers in electrothermal atomic absorption spectrometry using a tungsten furnace, and found that cobalt is an effective chemical modifier for the determination of lead.[15] In addition, we found that the effect of the cobalt modifier depended on the temperature at which it was pre-heated.

This paper describes that the behavior of the cobalt as a chemical modifier was investigated by an observation on the tungsten surface using a scanning-electron microscope and an X-ray photoelectron spectrometer at the charring stage. Furthermore, the interference mechanisms were investigated by experiments concerning the suppression of interference in the presence of inorganic salts.

Experimental

Apparatus and Materials. A lead standard solution was prepared by diluting an AAS-grade lead solution (1000 mg dm^{-3}, 1 M HNO_3, Wako Pure Chemical Industries, Ltd., 1 M = 1 mol dm^{-3}) with water. Cobalt modifier: A solution containing 0.1 (w/v)% as cobalt was prepared by dissolving cobalt(II) chloride hexahydrate (purity: 99.5%) in 100 ml of 1 mol dm^{-3} HCl solution. Ultrapure-grade water purified with a Milli Q-Labo filter (Nippon Millipore, Ltd.) was used thoughtout.

The analysis was conducted using an atomic absorption spectrometer (SAS 7500A) connected to a PS200A electrothermal atomizer, and the furnace was a high capacity U-type metal board (50 μl) made of tungsten; these instruments were made by Seiko Instruments, Inc. An L-233 lead hollow cathode lamp (Hamamatsu Photonics, Inc.) was employed. A deuterium lamp was used for a background correction. A scanning electron microscope (ALPHA 50) was used to observe the tungsten surface; it was made by Topcan Co., Ltd. The surface analysis on tungsten surface was investigated by X-ray photoelectron spectrometer (JPS-90SX, Nihon Denshi Co., Ltd.).

Procedure. In case of the determination of lead using the cobalt modifier, a 10 μl aliquot of the cobalt modifier was dropped onto the tungsten board. Drying was carried out for 20 s at 130 °C followed by pre-heating for 10 s at 1200 °C. After cooling the tungsten board, a sample solution containing lead was introduced into the furnace, and the absorbance (the height of the absorption peak) corresponding to atomized lead was measured in accordance with the measurement conditions given in Table 1. Manual pipetting was employed for injecting the solutions.

For observing of the surface of the tungsten board, the cobalt solution was dried on the tungsten board and heated at an arbitrary temperature for 10 s. To study the influence of diverse ions, a diverse ion was added to the tungsten board and heated until the charring stage. The temperature program was stopped just before the furnace reached the atomization stage, and the tungsten board was removed from its atomizer so that its surface could be observed.

Results and Discussion

Crystal Characteristics of Cobalt under Thermal Conditions. The effect of the cobalt modifier appeared by preheating it above 1000 °C prior to the introduction of a lead solution. Furthermore, in case of the pre-heating of cobalt, constant absorbances of lead were obtained at the charring temperatures of lead, between 400—1250 °C.[15)] The obtained results indicate that the effect of cobalt modifier is dependent on pre-heating temperature of cobalt.

A tungsten surface was then combined with a scanning electron microscope (SEM) to observe the behavior of the cobalt as a chemical modifier under thermal conditions. The obtained results are shown in Fig. 1. The microstructure was characterized by the columnar crystals at a heating temperature of 400—600 °C (Fig. 1(a)); it changed when large plate crystals were developed upon extending the heating temperature to 700—900 °C (Fig. 1(b)) on the tungsten surface. Furthermore, the large plate crystals were destroyed at heating temperatures above 1000 °C; these then became ensembles of very small granular crystals at the 0.1—0.2 μm diameter level (Fig. 1(c)).

The changes in the crystal structure corresponded to the behavioral changes of cobalt as a function of the pre-heating temperature;[15)] cobalt acted as an effective chemical modifier when it had been pre-heated over the range of temperatures at which granular crystals of cobalt oxides are produced.

Crystalline Characteristics of Cobalt in the Presence of Lead under the Thermal Conditions. The tungsten surface was observed with the addition of 1 ng of lead ($\mathrm{Co:Pb} = 1:10^{-4}$) after granular crystals of cobalt formed on the tungsten surface and charring was carried out for 10 s at 1000 °C. Similar to the case in which only the cobalt was pre-heated, granular crystals were observed on the tungsten surface; however, in the presence of lead, the granular crystals tended to aggregate in three-dimensions.

Table 1. Instrumental Operating Parameters for Lead

Parameter	Ramp time/s	Hold time/s	Temperature/°C
Dry	10	20	130
Charring	10	15	1000
Atomization	0	2	2400
Clean	0	1	2600

Wavelength 283.3 nm, Spectral bandwidth 1.00 nm, Lamp current 10 mA, Gas flow rate Ar: 8.0 $\mathrm{dm^3\,min^{-1}}$, H_2: 1.0 $\mathrm{dm^3\,min^{-1}}$.

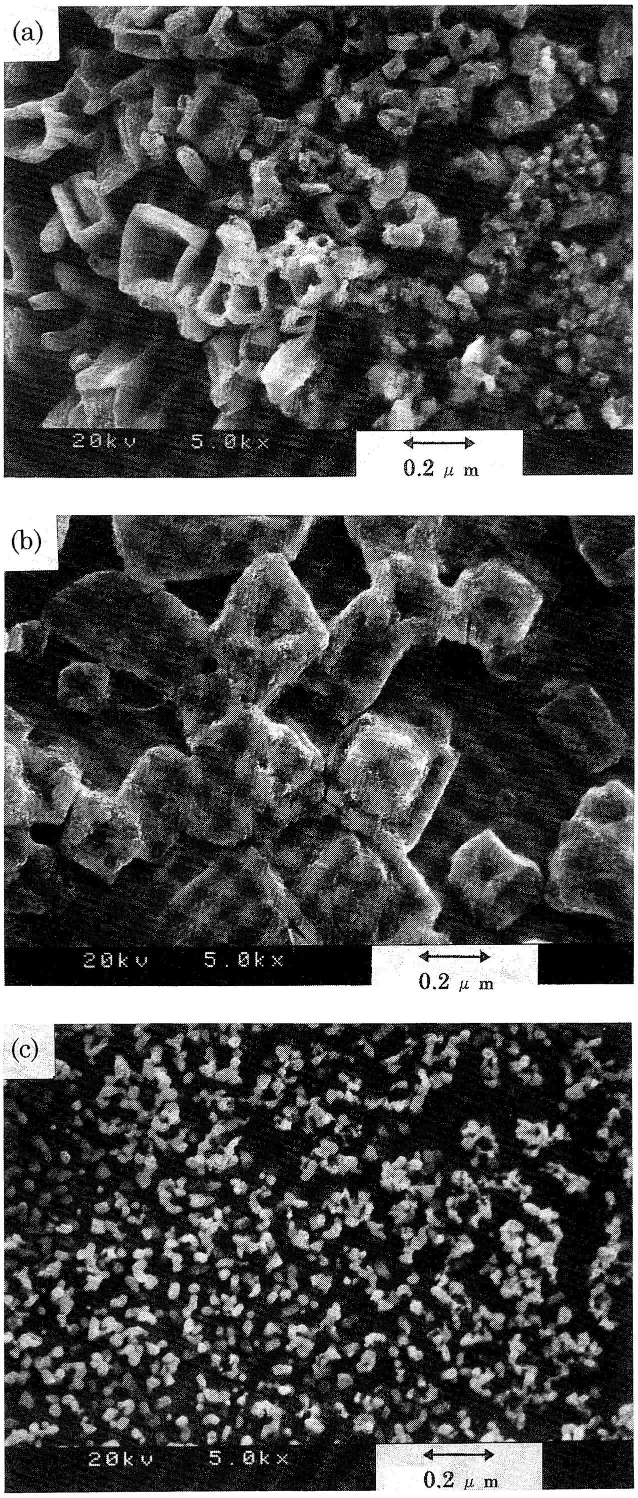

Fig. 1. Crystal of a cobalt compound on the tungsten surface of various temperature.
Cobalt: 10 μg; Heating temperature: (a) 600 °C, (b) 800 °C, (c) 1000 °C.

To clarify the changes in the crystalline characteristics of cobalt as a function of charring, 0.1 μg of lead ($\mathrm{Co:Pb} = 1:10^{-2}$) was added to the furnace after the cobalt was preheated. The obtained result is shown in Fig. 2. The granular cobalt crystals changed into irregular-shaped fine particles in the presence of lead.

Yasuda and co-workers[16—18] investigated the behavior of various chemical modifiers, and reported that the effect of a chemical modifier depended on intermetallic compounds between an analyte metal (As, In, and Sn etc.) and a chemical modifier (Pd) during the charring stage.

In the experiments when the lead was present, the cobalt modifier possibly formed intermetallic compounds, because the granular crystals became irregularly shaped. Regarding the conditions for the generation of intermetallic compounds, the ratio of the modifier to the analyte metal is an important factor in addition to the temperature. Therefore, identical processes do not necessarily take place when the ratio of Co : Pb is $1:10^{-4}$. However, similar processes for the generation of intermetallic compound may occur inside or on the surface of granular cobalt crystals, thereby maintaining the thermal stability of lead.

Surface Analysis Using XPS. A product analysis on a tungsten surface was investigated by X-ray photoelectron spectroscopy (XPS). It was used to measure the binding energy of cobalt at $2p_{3/2}$ and of lead at $4f_{7/2}$. To correct for mechanical errors in the measurements, $C1s_{1/2}$ and $O1s_{1/2}$ were also measured. The obtained results are given in Fig. 3.

When only cobalt was added to the furnace, the binding energy of the products pre-heated at 1200 °C following drying was approximately 780 eV, which is the same as the binding energy for products pre-heated at 400 °C. Because the binding energies of all cobalt oxides are around 780 eV (Table 2),[19] identification of the generated oxides was difficult. However, regarding the products, it is speculated that the number of bound oxygen atoms differs depending on the pre-heating temperature. When a small amount of crystalline powder of cobalt oxides, such as cobalt(II) oxide (CoO), cobalt(III) oxide (Co_2O_3) and cobalt(II) dicobalt(III) tetraoxide (Co_3O_4), is used in place of a cobalt solution as the chemical modifier for lead, the behavior and effects are similar to those of the Co_2O_3 and Co_3O_4 powders, whereas, in the case of CoO powder, no effect of the chemical modifier was observed and extremely great interference was detected.

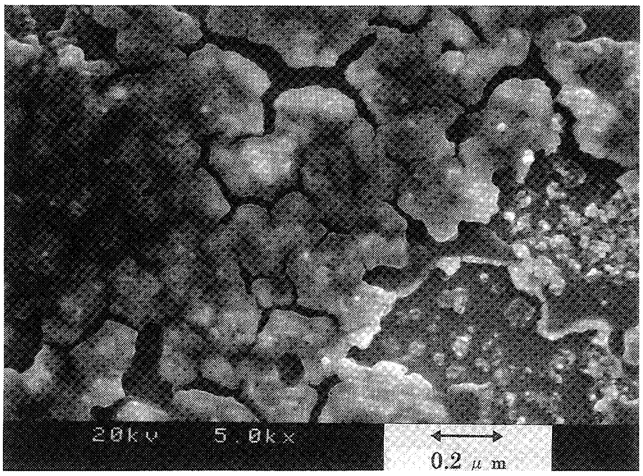

Fig. 2. Crystal of cobalt-lead on tungsten surface.
Cobalt modifier: 10 μg as Co; Lead: 0.1 μg; Pre-heat temperature of Cobalt modifier: 1200 °C; Charring temperature: 1000 °C.

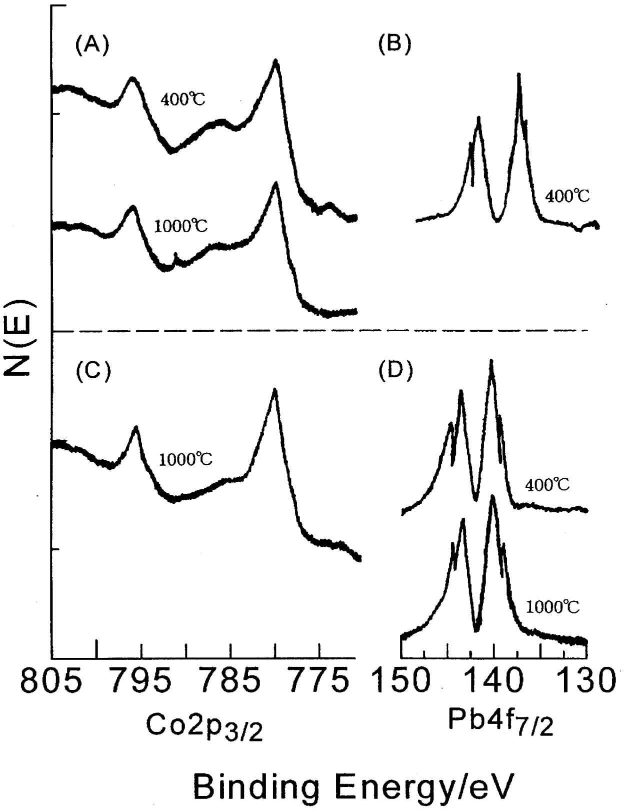

Fig. 3. X-Ray photoelectron spectra of $Co2p_{3/2}$ and $Pb4f_{7/2}$ on tungsten surface.
(A) Cobalt; (B) Lead; (C), (D) Cobalt–lead; Cobalt modifier: 10 μg as Co; Lead: 1.0 ng.

Table 2. X-Ray Photoelectron Spectra Values in the References

	Cobalt $2p_{3/2}$ / eV		Lead $4f_{7/2}$ / eV
Co	778.1	Pb	136.8
Co	778.5	Pb	136.6
CoO	780.2	$Pb(NO_3)_2$	138.5
Co_3O_4	780.0	PbO	137.25
Co_3O_4	780.4	Pb_3O_4	137.4
Co_2O_3	779.9	PbO_2	137.4
$Co(OH)_2$	781.0	$Pb(OH)_2$	137.95
CoOOH	780.3	$PbSO_4$	140.0
		$PbCl_2$	138.9

When only lead was used, the binding energy of the products charring at 400 °C was approximately 137 eV, which is nearly equal to the binding energy of lead oxides. However, when cobalt was pre-heated at 1200 °C and lead was added, the binding energy was approximately 140 eV, showing a slightly higher energy shift. According to a reference,[19] the value is close to the binding energy of lead(II) sulfate (Table 2). Because no sulfate ions are present during this process, the energy shift occurred for the cobalt-lead intermetallic compound.

Effect of Cobalt as a Chemical Modifier. The effects of a cobalt modifier on suppressing interference by diverse ions were investigated. After pre-heating the cobalt modifier, using the absorbance of a lead standard solution as a basis, the relative sensitivities of the absorbance of a lead solution containing diverse ions were measured. The additional diverse ions added to the furnace were prepared by dissolving various chlorides, nitrates and sulfates at a concentration of 100 mg dm^{-3} with respect to the cation (1.0 μg/10 μl). The obtained results are given in Fig. 4; these tests took place under the thermal conditions of Table 1.

For admixed magnesium, nickel and ammonium, the relative sensitivity was almost 100%, indicating no influence of chlorides and nitrates on the absorbances obtained during atomization. For chromium, the addition of nitrates slightly increased the sensitivity. The addition of sodium nitrate and iron, calcium, and copper(II) chlorides showed great negative interference; however, the addition of other chlorides and nitrates exhibited a relative sensitivity of 90±5%, although the amount of admixed diverse ions was 10^3 times higher than the amount of lead present.

The diverse ions showing negative interference have different influence on the absorbance of lead, depending on the temperature of charring and atomization.

In the presence of iron(III) chlorides, the absorbance of lead with a relative sensitivity of 100% appear at a charring temperature of 400 °C; however, at almost the same position as the absorption signal of lead, the background absorption was nearly 3-times higher in intensity than the obtained signals; also, the reproducibility was poor. The absorption signal of lead with coexisting calcium chloride is not influenced by the charring temperature; only the background absorption increased with decreasing the charring temperature over the range 1000—200 °C. In the case of the lead with the coexisting sodium nitrate or copper(II) chloride, no background absorption was observed; however, the absorption signal of lead decreased with increasing the charring temperature range to 400—1200 °C.

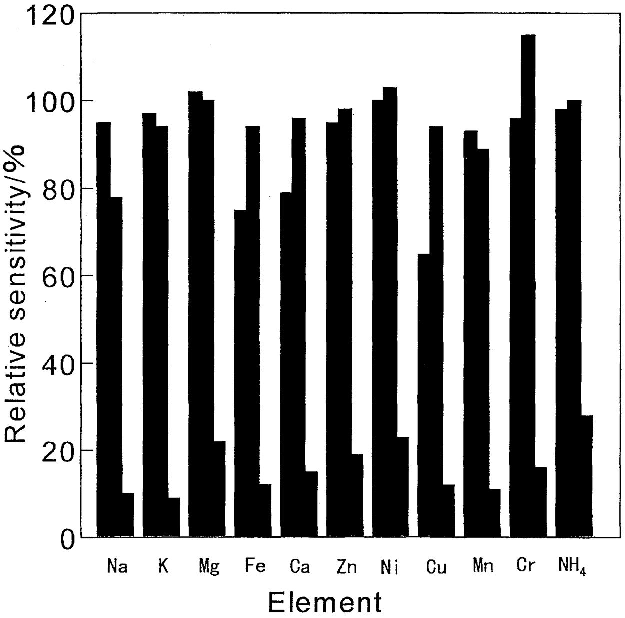

Fig. 4. Influence of diverse ions.
Concentration of lead: 1.0 ng; Diverse ions: 1.0 μg as a cation; Cobalt modifier: 0.1 (w/v)% as Co; Charring temperature: 1000 °C;
Left: Chloride salt; Center: Nitrate salt; Right: Sulfate salt.

On the other hand, the relative sensitivities for lead were shown to be 10—20% in the case of the addition of a sulfate salt.

As can been seen from the above results, a great negative interference arose for the sulfate salts, and the degree of interference differed depending on the kinds of ions. Therefore, the interference of anions was examined by changing the concentration and their kind.

In the case of both the chloride ion and the nitrate ion in the above experiments, their concentrations were highest in the magnesium solution; they were about 290 mg dm^{-3} and 510 mg dm^{-3}. An improvement in the relative sensitivities of lead containing each ion was achieved as 100% for the cobalt modifier, compared with the absorbance of a lead standard solution using a cobalt modifier. In experiments using a higher concentration of these two anions, they showed no interference up to a concentration of 5000 mg dm^{-3}.

The concentration of the sulfate ion was lowest at about 120 mg dm^{-3} in a potassium solution with a relative sensitivity of 16%. The negative interference was admitted to be unrelated to the cations.

Figure 5 shows the results of an experiment on the relative sensitivities when the concentrations of sulfate ion were varied. Although the behaviors differ depending on the solution, the relative sensitivity approaches 100% only when the concentration of sulfate ion is within a range of 5—50 mg dm^{-3}. The interference is proportional to the melting point of the sulfates present, increasing significantly as the melting points of the sulfate increased. For a comparison, the amount of sulfur(S) equivalent to that contained in the sulfate ions was added to an ammonium sulfide solution to examine the magnitude of interference of sulfur; however, great interference, as observed in the presence of sulfate ion, was not detected.

Crystal Structure with the Addition of Coexisting Diverse Ions. Regarding the sulfates with which a great negative interference was observed, the surface at the charring stage was observed using magnesium sulfate (add to 1.0 μg as Mg) and sodium sulfate (add to 1.0 μg as Na). For a comparison, the surface was also observed in the presence of magnesium chloride (add to 1.0 μg as Mg), which exhibited no interference. In the presence of magnesium sulfate and at a charring temperature of 400 °C, granular cobalt crystal were trapped between layered crystals originating from magnesium sulfate. At a charring temperature of 1000 °C, a small amount of granular cobalt crystals was observed among the products that covered the tungsten surface (Fig. 6(a)).

In the presence of sodium sulfate and at a charring temperature of 400 °C, block crystals covering the tungsten surface were observed (Fig. 6(b)). At a charring temperature of 1000 °C, no change in the crystalline characteristics of the prod-

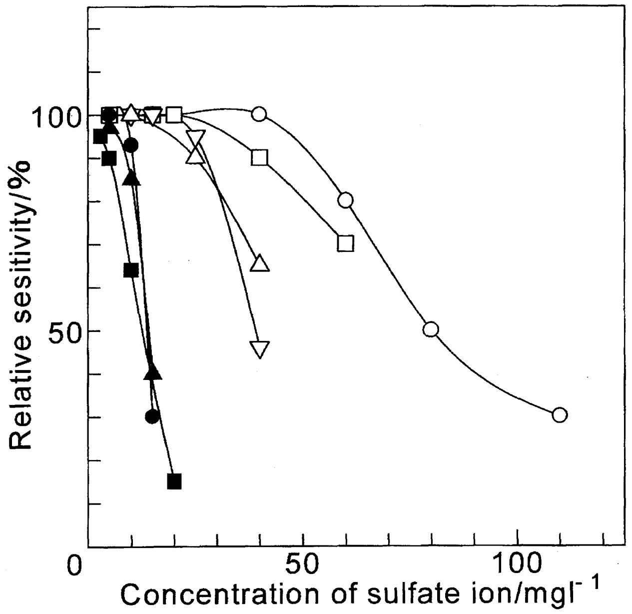

Fig. 5. Effects of sulfate salts and their concentration.
Lead: 1.0 ng; Charring temperature: 1000 °C; Cobalt modifier: 0.1 (w/v)% as Co; ○: $(NH_4)_2SO_4$; □: $FeSO_4\cdot(NH_4)_2SO_4$; △: $ZnSO_4$; ▽: $CuSO_4$; ●: $MgSO_4$; ▲: $MnSO_4$; ■: K_2SO_4.

ucts was admitted; however, the number of crystals observed on the tungsten surface was extremely small compared to that at a charring temperature of 400 °C.

In the presence of magnesium chloride and at a charring temperature of 1000 °C, needle crystals related to magnesium chloride, the granular cobalt crystals and irregularly shaped crystals formed by lead and cobalt were observed (Fig. 6(c)). In this case, the crystals made from lead and cobalt were separated due to the diverse ions; however, because they maintained their crystalline characteristics, they were also though to maintain their thermal stability.

In the presence of sulfate, granular cobalt crystals, which act as a chemical modifier at the charring stage, are trapped within crystals originating from sulfate, and Co–Pb compounds are trapped. Therefore, the stability against thermal changes contributes to the chemical characteristics of the sulfates produced at the charring stage, and Co–Pb compounds are volatilized with sulfate products at a lower charring temperature (Fig. 7(a)). In addition, because the melting point of lead sulfate is approximately 1100 °C,[20] chemical interference occurs at the charring stage under the thermal conditions of the proposed method; for example, part of the lead sulfate volatilizes as $PbSO_4$ (Fig. 7(b)). The binding energy of the Co–Pb compound determined by XPS is identical to the binding energy of $PbSO_4$. Because of these factors, cobalt is considered to exhibit extreme negative interference upon ionization at the atomization stage. Accordingly, in the presence of a large amount of sulfate, the suppression of interference was difficult due to chemical and ionization interferences at the charring and atomization stages.

Application to the Determination of Lead in Water Samples. In these experiments, highly concentrated di-

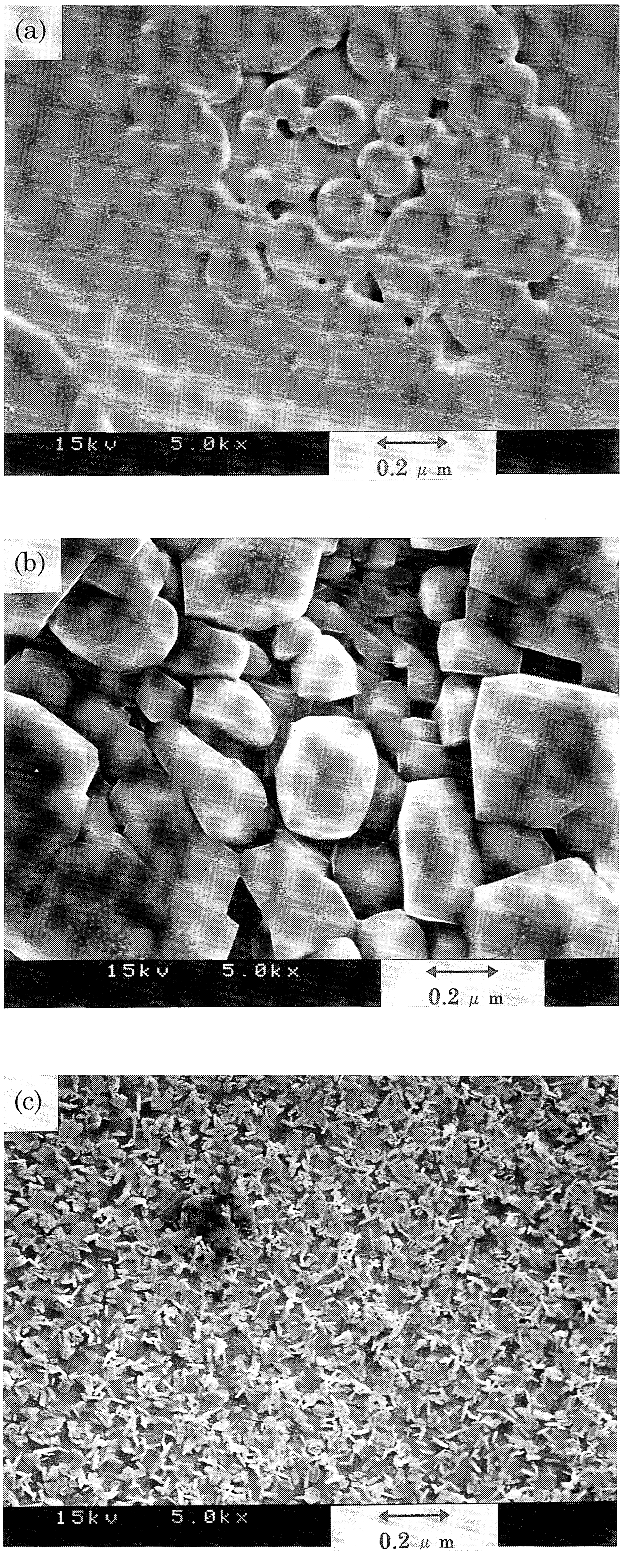

Fig. 6. Crystals of cobalt compounds formed under presence of various ions.
Ions: (a) Magnesium sulfate (10 μg as Mg), (b) Sodium sulfate (10 μg as Na), (c) Magnesium chloride (10 μg as Mg); Charring temperature: (a), (c) 1000 °C, (b) 400 °C; Cobalt modifier: 10 μg as Co; Lead: 1.0 ng; Pre-heat temperature of Cobalt modifier: 1200 °C.

Table 3. Analytical Results of Lead in Water Samples

Sample	Injection volume	Added	Found	Recovery	RSD[d]	Another method[e]
	μl	ng	$\mu g\,dm^{-3}$	%	%	
Rain water[a]	10	—	10.3	—	4.2	10.1
	20	—	20.1	—	3.8	—
	10	0.2	30.6	103	3.2	—
Spring water[b]	10	—	22.3	—	3.7	22.0
	20	—	45.1	—	4.6	—
	10	0.2	42.0	99	3.6	—
Tap water[c]	10	—	7.5	—	4.8	7.5
	25	—	18.8	—	4.1	—
	10	0.4	47.5	100	3.5	—

a) Narashino, Chiba, '97/7/8—'97/7/10; b) Numazu, Shizuoka; c) Narashino, Chiba; d) $n=6$; e) ICP-AES.

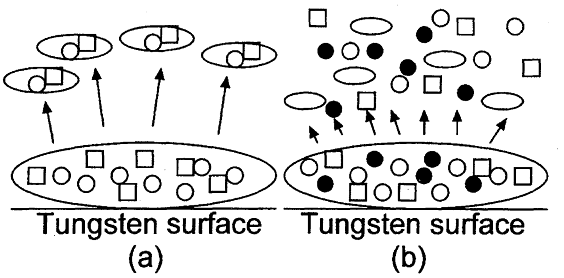

Fig. 7. Interference mechanism.

(a): Volatilization of the Co–Pb compound with sulfate salts; (b): Volatilization of lead(II) sulfate.

○: Co–Pb compound; □: Cobalt modifier; ●: Lead(II) sulfate; ⬭ : Sulfate salt.

verse ions were added to the furnace to assess their influence on the behavior of cobalt as a chemical modifier. The results showed that when the concentration of each added ion was within the range of 5—100 $mg\,dm^{-3}$, the cobalt modifier suppressed interferences well. The absorbance obtained at the atomization of lead using the cobalt modifier increased by 1.5 times compared with the cases in which only the lead standard solution was used.[15] Therefore, a cobalt modifier was applied to rain-water, spring-water, and tap-water samples, which contained fairly trace amounts of sulfate ion.

Table 3 shows the results of determinations performed using a calibration prepared from the lead standard solution using cobalt as a chemical modifier. The results of experiments in which the volume of the samples introduced into the furnace was varied as well as the results of the experiment using the method of standard addition, in which a pre-determined amount of standard solution was added, confirmed the determination with good reproducibility.

The detection limit is 0.07 ng and the relative standard deviation for the measurement of water samples is about 4% ($n=6$).

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