Notes

Enhancement Effect of Some Matrix Modifiers on the Tin Sensitivity in Graphite Furnace Atomic Absorption Spectrometry and Direct Evidence for Pd_3Sn_2 Formation during Ashing in the Presence of a Palladium Modifier

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The authors have reported that the addition of palladium and albumin to tin in carbon-furnace atomic absorption spectrometry remarkably enhances the sensitivity to *ca.* 11 times.¹ This enhancement ratio is unusually high, since all other elements in group IIIB – VIB are not enhanced to such a high degree by palladium.¹ Tin is an unusual element in the sense that its sensitivity is enhanced not only by a reducing agent, such as ascorbic acid², but also by an oxidizing agent, such as potassium dichromate³, potassium tungstate^{4,5} and potassium molybdate.⁴ This is particularly unusual if one considers that reducing agents are usually used as matrix modifiers to other elements. It therefore seems worthwhile extending the mechanistic study of matrix modifiers to tin determination.

Several different, and sometimes contradictory, descriptions have been reported concerning the atomization mechanisms of a simple tin solution as well as a tin solution containing a matrix modifier. Iwamoto *et al.*⁶ and Lundberg *et al.*⁷ reported the formation of volatile compounds in the presence of chloride, which causes a tin loss at as low as 100°C. Aggett *et al.*⁸ have suggested that Sn on the graphite surface exists as a mixture of free metal and oxide(s). Wendl *et al.*⁹ concluded that SnCl_2 in an aqueous solution is hydrolyzed to SnO during drying, which is then oxidized to SnO_2 during the ashing process. The SnO_2 is then reduced to metal during atomization by carbon of the furnace. With regard to matrix modifiers for tin, Lundberg *et al.*⁷ used ammonia to remove chloride as NH_4Cl and to suppress the loss of tin. Zhu¹⁰ used a mixture of ascorbic acid and iron to improve the sensitivity and to increase the tolerable ashing temperature.

In the present study the effect of four different matrix modifiers were compared; their sensitivity enhancement mechanisms are discussed based on the X-ray powder

diffraction data of the ashing products. The examined modifiers were: (i) Pd, (ii) Pd + serum, (iii) Pd + ascorbic acid, and (iv) ascorbic acid. The formation of Pd_3Sn_2 in the presence of Pd as the modifier was confirmed by X-ray powder diffraction. Although such alloy formation has been postulated and claimed in many matrix modification systems, convincing direct evidence has always been lacking. The present study provides unambiguous evidence for Pd_3Sn_2 formation during ashing.

Experimental

A Perkin-Elmer Model 5000 atomic absorption spectrometer equipped with a Perkin-Elmer HGA-500 graphite-furnace atomizer was used for the measurements. A 10- μl sample solution was injected into the furnace.

The atomic absorption measurements were carried out with the 224.6-nm Sn atomic line and a spectral band width of 0.7 nm. The peak heights were used for measurements. The drying, ashing and atomizing conditions were as follows: drying, 120°C, ramp 40 s, hold 30 s; ashing, 600 – 1400°C, ramp 30 s, hold 30 s; atomizing 2100°C, hold 3 s. The Ar purge gas flow was interrupted during the atomization stage. The X-ray diffraction pattern was measured on a Hitachi transmitting electron microscope (Model H600) having an additional X-ray diffractometer function.

A tin stock solution (1000 ppm) was prepared by dissolving spectro-grade Sn metal (0.1 g) with aqua-regia (10 ml) upon heating, then cooling and diluting the solution to 100 ml. All working standard solutions were prepared from the 1000 ppm stock solution by a suitable dilution with a 0.2% nitric acid solution. A

palladium stock solution (1000 ppm) was prepared by dissolving 250 mg of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (analytical reagent grade) in 100 ml of 0.2% nitric acid. The solution did not contain any detectable amount of tin. The palladium working solution (100 ppm) was prepared by diluting the 1000 ppm solution with 0.2% nitric acid. Bovine serum was obtained from the biological laboratory, Dalian Institute of Chemical Physics, and was diluted with 0.2% nitric acid. Ascorbic acid of analytical reagent grade was purchased and diluted with 0.2% nitric acid to 10%.

Matrix modifier solutions were added to the tin solution before measuring to the desired concentrations.

Results and Discussion

Effect of modifiers on the ashing temperature and sensitivity of Sn.

The following solutions were measured and the enhancement factors were determined for each modifier: (i) Sn (0.5 ppm) only, (ii) Sn (0.5 ppm) + Pd (100 ppm); (iii) Sn (0.5 ppm) + ascorbic acid (10%); (iv) Sn (0.5 ppm) + serum (0.2%), (v) Sn (0.5 ppm) + Pd (100 ppm) and serum (0.2%), (vi) Sn (0.5 ppm) + Pd (100 ppm) and ascorbic acid (10%). The drying and atomizing temperatures were set as described in the experimental section, and only the ashing temperature was varied, as shown in Fig. 1. The dependence of the tin sensitivity on the ashing temperature is shown for each modifier in Fig. 1. By using most of the modifiers, the ashing temperature could be made higher than that without any modifier, while increasing the sensitivity. However, the addition of only serum decreased the Sn sensitivity; its curve is located too low to be seen in Fig. 1. This effect of serum addition is different from what was previously reported for an albumin modifier, the addition of which to a Sn solution increases the Sn sensitivity by 8.8 times¹, although albumin is a major protein component of

Fig. 1 Effect of the ashing temperature on the tin sensitivity in the presence of various matrix modifiers. ■ Sn (0.5 ppm), △ Sn (0.5 ppm) + Pd (100 ppm), ● Sn (0.5 ppm) + ascorbic acid (10%), ○ Sn (0.5 ppm) + Pd (100 ppm) + serum (0.2%), □ Sn (0.5 ppm) + Pd (100 ppm) + ascorbic acid (10%).

serum. The enhancement ratios of each modifier are given in Table 1. It is obvious that the addition of a mixed modifier of Pd and serum gives the best sensitivity and allows an increased ashing temperature of 1200°C.

X-Ray diffraction patterns of the ashing products and atomization mechanism

(1) Observation of Pd_3Sn_2 in the ashing product of Sn in the presence of Pd and serum. In the presence of these two modifiers, serum would be decomposed to H_2 , CO and some hydrocarbons. Further, a new graphite layer on the carbon tube surface would be formed.¹¹ It is well known that Pd is an excellent catalyst for the reduction of the oxides of some metals, such as Sn, in the presence of H_2 , CO and some hydrocarbons. Palladium accelerates the reduction of SnO_2 to metallic Sn.¹² An X-ray diffraction study of the furnace surface after ashing is shown in Fig. 2(a), which confirmed that Pd_3Sn_2 is formed by the ashing. The observed and reported d values and intensities are listed in Table 2.¹³ Although the existence of other alloys, such as Pd_3Sn_8 , has been postulated to exist during ashing¹⁴, no experimental evidence supporting such an alloy has been reported. The present study clearly demonstrates the formation of Pd_3Sn_2 ; this is the first direct observation of alloy formation in a mechanistic study of matrix modifiers for any element. The formation of Pd_3Sn_2 , which is not as volatile as tin chloride, would reduce the Sn loss during drying and ashing and enhance the sensitivity.

(2) Atomization of Sn in the presence of Pd. In the photograph of Fig. 2(b) the existence of Pd metal was confirmed. SnO_2 was not detected, and it seems that Sn

Table 1 Enhancement ratios and sensitivities for various matrix modifiers

Modifier	Sensitivity (ng/0.0044A)	Enhancement ratio
None	1.47	1.0
Pd	0.23	6.4
Ascorbic acid	0.17	8.6
Pd+serum	0.11	13.4
Pd+ascorbic acid	0.17	8.6
Serum	— ^a	— ^a

a. The sensitivity was so low that neither the sensitivity nor the enhancement ratio could be determined.

Table 2 Observed and reported d spacings and intensities for Pd_3Sn_2

Miller index (h k l)	d spacing/Å		Relative intensity	
	Observed	Reported ¹³	Observed	Reported ¹³
(10 $\bar{1}$ 2)	2.27	2.27	100	100
(21 $\bar{3}$ 2)	1.28	1.28	70	70
(11 $\bar{2}$ 4)	1.20	1.19	70	70
(22 $\bar{4}$ 0)	1.09	1.10	40	40
(41 $\bar{5}$ 0)	0.82	0.83	70	70

Fig. 2 X-Ray diffraction pattern of the tube surface after ashing. (a) Sn+Pd+serum, (b) Sn+Pd, (c) Sn only, (d) Sn+ascorbic acid. The drying and atomizing conditions were the same as described in the experimental section, except that the ashing was stopped at 1000°C.

existed as a metal rather than an alloy. From a comparison of two modifiers (Pd only and Pd + serum), it is obvious that without the serum, no Pd_3Sn_2 nor any other Pd-Sn alloys are formed.

(3) Atomization of Sn without modifier. Figure 2(c) confirms that the ashing product of a simple tin solution is SnO_2 .

(4) Atomization of Sn in the presence of ascorbic acid. Although Qiao *et al.*¹⁵ reported that ascorbic acid is decomposed to CO and H_2 at 192°C, and that no residue is left on the furnace, our experiment showed that many carbon particles and tin metal are formed on the

tube surface after ashing at 1000°C (Fig. 2(d)). Although the addition of serum also forms carbon particles on the tube surface, the serum itself does not enhance the sensitivity. Therefore, the reducing effect of ascorbic acid seems to be the cause of the sensitivity enhancement.

(5) Atomization of Sn in the presence of Pd and ascorbic acid. Table 1 shows that the sensitivity with this mixed modifier is the same as that with the ascorbic acid modifier without Pd. This is because the Pd cation is rapidly reduced to Pd metal by ascorbic acid and is deactivated. The formation of Pd metal can be

observed as black powder in the solution.

The present study shows that a mixture of Pd and serum is the best modifier so far tested in the present experiment as well as those reported in the literature. The existence of Pd_3Sn_2 has been verified as being an intermediate during ashing in the Pd and serum modification. This alloy was not found when only Pd was added as a modifier.

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