

X-Ray Diffractometric Study on Modification Mechanism of Matrixes for Electrothermal AAS Determination of Volatile Lead and Bismuth

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The mechanism of a matrix modification for the trace determination of volatile lead and bismuth by an electrothermal atomic absorption spectrophotometry was studied by a X-ray diffractometry (XRD). For the investigation of structures, the ash products of the elements were produced by using a palladium as a matrix modifier with or without aluminum or nickel as an auxiliary modifier. The same charring conditions as in the analysis of samples were applied together with much concentrated solution of analytical elements and modifiers in a graphite furnace to get a large amount of the product for XRD. The XRD patterns showed $PbPd_3$ for lead and $BiPd_3$ for bismuth. These mean that the reaction procedures through the charring and atomization were changed from $Pb^{2+} \rightarrow PbO \rightarrow Pb^0$ to $Pb^{2+} \rightarrow PbO \rightarrow PbPd_3 \rightarrow Pb^0$ for lead and from $Bi^{3+} \rightarrow BiO \rightarrow Bi^0$ to $Bi^{3+} \rightarrow BiO \rightarrow BiPd_3 \rightarrow Bi^0$ for bismuth by the addition of modifiers. The volatile elements were stabilized by the formation of palladium alloys through a charring process. Charring temperatures were raised about 500 °C by the alloying and the atomization was also stabilized for the enhancement of sensitivities.

Introduction

In our previous studies,^{1,2,3} the sensitivity of the atomic absorbance measurement has been increased by raising charring temperatures and stabilizing an atomization. The temperature raise and stabilization could be accomplished by a matrix modification, and the loss of volatile elements⁴ was suppressed because their volatility could be decreased by the matrix modification. The addition of palladium as a matrix modifier together with an auxiliary modifier had improved the modification.^{1,2,3} But the modification mechanism have not directly been manifested in spite of much improvement of a detection limit by the increase of the sensitivity.^{5,6,7} In this work, the mechanism was investigated by manifesting the structure of ash products. At a given charring temperature, the products were obtained from the solution of lead and bismuth in which a significant amount of palladium was added.

In general, the sample solution is proceeded through steps of dryness, charring and atomization for an electrothermal AAS. The analytical element is mainly changed to its oxide by charring at a proper temperature. At this charring step, volatile materials are partly lost by the volatilization so that the sensitivity is decreased. Especially, volatile elements such as arsenic, selenium, cadmium, mercury, lead, bismuth are easily volatilized at the range of 200-500 °C.^{1,2,3} Many researchers have been devoted on studies about the matrix modification by using various modifiers.⁸

In 1974, the matrix modification was firstly introduced by R. D. Ediger.⁹ He had depressed the volatility of arsenic and selenium by the addition of nickel and stabilized cadmium by an ammonium phosphate. Suzuki and Ohta¹⁰ showed that the use of thiourea had improved the atomization profiles and decreased the effects of coexisted species in electrothermal AAS. Since then, molybdenum,¹¹ lanthanum,¹² phos-

phoric acid,¹³ magnesium nitrate,¹⁴ potassium dichromate¹⁵ and so on have been widely used as a matrix modifier for the determination of volatile elements.

Shan and coworkers¹⁶ had proposed palladium as the best modifier. They reported that the atomization of the elements could be stabilized by forming a binary alloy at the charring step. Besides, they¹⁷ have closely examined the formation of the alloy by X-ray photoelectron spectrometry. Recently, Wendle and coworkers¹⁸ had confirmed the formation of inter-metallic alloy of $PbPd_3$ and Pb_2Pd_3 by X-ray diffractometry. They had formed the alloy by charring the solution of lead and palladium in a graphite tube outside AAS. But their method was only an indirect one in another tool with similar conditions to produce the charring product. In order to investigate the mechanism with a correct form of ash product, a direct product should be obtained in an AAS furnace with the same condition.

In this work, concentrated solutions of lead and bismuth were prepared with or without palladium, respectively. After the solution was injected in a graphite furnace, the temperature was increased to a charring temperature by the same method as real conditions. Enough amount of the ash product was gathered. X-ray fluorescence (XRF) spectrometry was applied to confirm elements presented in the products and X-ray diffractometry (XRD) was used to manifest the chemical structure of the ash product.

Experimentals Section

Reagents and Instruments. A deionized water by Milli-Q system and reagents of the first and special grade were used for this experiment without any further treatment.

Pb(II) stock solution, 10,000 µg/mL: a special grade $Pb(NO_3)_2$ (Junsei Co., Japan) was dissolved with a small volume of nitric acid and diluted with deionized water. The

solution was stored in a glass bottle and used as a working solution by a dilution with a deionized water.

Bi(III) stock solution, 10,000 $\mu\text{g}/\text{mL}$: a special grade $\text{Bi}(\text{NO}_3)_3$ (Junsei Co., Japan) was dissolved in a deionized water and stored in a brown bottle.

Palladium solution: a high-purity palladium metal (Fluka Co., Japan) was dissolved with an aqua regia (3 : 1 of HCl and HNO_3) and digested repeatedly by adding HNO_3 to remove HCl . And the solution was diluted with a deionized water to 1,000 $\mu\text{g}/\text{mL}$ for the modification and 30,000 $\mu\text{g}/\text{mL}$ for the investigation of mechanism.

Al(III) stock solution: a special grade $\text{Al}(\text{NO}_3)_3$ (Fluka Co., Japan) was dissolved with a small volume of HNO_3 and diluted to 20,000 $\mu\text{g}/\text{mL}$ with a deionized water.

Ni(II) stock solution: a first-grade $\text{Ni}(\text{NO}_3)_2$ (Junsei Co., Japan) was dissolved and diluted to 2×10^5 $\mu\text{g}/\text{mL}$.

Atomic Absorption Spectrophotometer: Perkin-Elmer model 2380 equipped with Model HGA 4000 was used for the measurement of absorbances. An un-coated graphite tube of Perkin-Elmer Co. was used as a furnace. A 30 μL solution was manually injected into the furnace with micropipette (Gilson Co., Pipetman P100).

X-ray Fluorescence Spectrometer: Rigaku-Denki S/Max-E 3080 was used with Rh-target at the conditions of 50 kV and 40 mA. LiF (200) was used as an analysing crystal in a vacuum spectrometer. And the intensities of $\text{Pb } L_{\alpha 1}(2\theta: 33.93^\circ)$ and $\text{Pd } K_{\alpha 1}(2\theta: 16.76^\circ)$ lines were measured with a scintillation counter using 20 mm Ti-mask.

X-ray Diffractometer: Rigaku-Denki DMAX-2000 was used at 40 kV and 100 mA. Cu target with a Ni filter was used and the diffracted intensity of CuK_{α} line was measured with a scintillation counter.

Experimental Procedure. Three kinds of solutions were prepared for lead as followings: 1) 100 mL of 5,000 $\mu\text{g}/\text{mL}$ $\text{Pb}(\text{II})$ solution, 2) 100 mL of 10,000 $\mu\text{g}/\text{mL}$ $\text{Pd}(\text{II})$ and 300 $\mu\text{g}/\text{mL}$ $\text{Pb}(\text{II})$ solution (mole ratio of 100 to 1), and 3) 100 mL of 10,000 $\mu\text{g}/\text{mL}$ $\text{Pd}(\text{II})$, 300 $\mu\text{g}/\text{mL}$ $\text{Pb}(\text{II})$ and 8,000 $\mu\text{g}/\text{mL}$ $\text{Al}(\text{III})$ solution (mole ratio of 100 : 1 : 200).

Likewise, three kinds of solutions also were prepared for bismuth as followings: 100 mL each solution of 5,000 $\mu\text{g}/\text{mL}$ $\text{Bi}(\text{III})$ only, 10,000 $\mu\text{g}/\text{mL}$ $\text{Pd}(\text{II})$ and 300 $\mu\text{g}/\text{mL}$ $\text{Bi}(\text{III})$ (mole ratio of 60 : 1), and 10,000 $\mu\text{g}/\text{mL}$ $\text{Pd}(\text{II})$, 300 $\mu\text{g}/\text{mL}$ $\text{Bi}(\text{III})$ and 1×10^5 $\mu\text{g}/\text{mL}$ $\text{Ni}(\text{II})$ solution (mole ratio of 60 : 1 : 1,200)

Each of above solutions, 30 μL , was injected into the graphite furnace with a micropipette and it was dried and charred in AAS with heating program as in Table 1. And the

ash product was collected with a small teflon spatula after 20 burnings were performed for each collection. Such collection was done more than 50 times to gather enough product for X-ray study.

Results and Discussion

Preparation of Ash Product. The furnace including the injected solution is heated up to the charring temperature to gather enough ash product, repeatedly. A proper charring temperature is an important step in the ash production. It should be the same as the temperature at which a maximum absorbance can be obtained in the measurement of real samples. And an enough amount of ash is needed for further studies such as X-ray analysis. Because the graphite tube used in AAS is too small, the high concentration of analytical solution should be used under experimental conditions. The concentration of modifier should be determined considering the concentration of analytical element. In this work, the concentration of 10,000 $\mu\text{g}/\text{mL}$ $\text{Pd}(\text{II})$ was fixed as a main modifier.

On the other hand, a high concentration of elements in the large volume of solution is advantageous to produce a sufficient product, but some troubles can be happened in an electrothermal assembly. An excess solution is intruded into the graphite wall of the tube and some solution is sputtered out of the tube by the drastic increase of temperature. Only 30 μL of the solution could be injected into the tube each time.

In general, the ash product is sorbed on inside wall of the tube during charring of sample. A pyro-coated tube adsorb less amount of the product because of thin tantalum film compared to a un-coated tube. Repeated heating and cooling can cause some problems in the pyro-coated tube by the desorption of tantalum. An un-coated one was used in this work. A teflon spatula was used to collect an ash product from the inside surface of graphite tube.

Much graphite also was collected as a mixed state together with the product. A relatively long time was spent to gather a sufficient product. Such product should be so safely stored that the product was put in a teflon bottle with argon gas and kept in a refrigerator for X-ray measurement.

X-ray Fluorescence Analysis. The analysis of ash product was performed using X-ray fluorescence to confirm the presence of the elements in the product. As shown in Figure 1, lead and palladium were confirmed by the indication of their characteristic peaks on XRF spectra. The spectrum for bismuth was not obtained in this work because

Table 1. Heating program for ash products

Analyte	Modification type	Dry		Charring	
Lead	No modification	110 °C	Ramping time: 10 sec Holding time: 10 sec	500 °C	Ramping time: 30 sec Holding time: 1 sec
	With Pd			1,000 °C	
	With Pd + Al			1,150 °C	
Bismuth	No modification			500 °C	
	With Pd			1,300 °C	
	With Pd + Ni			1,300 °C	

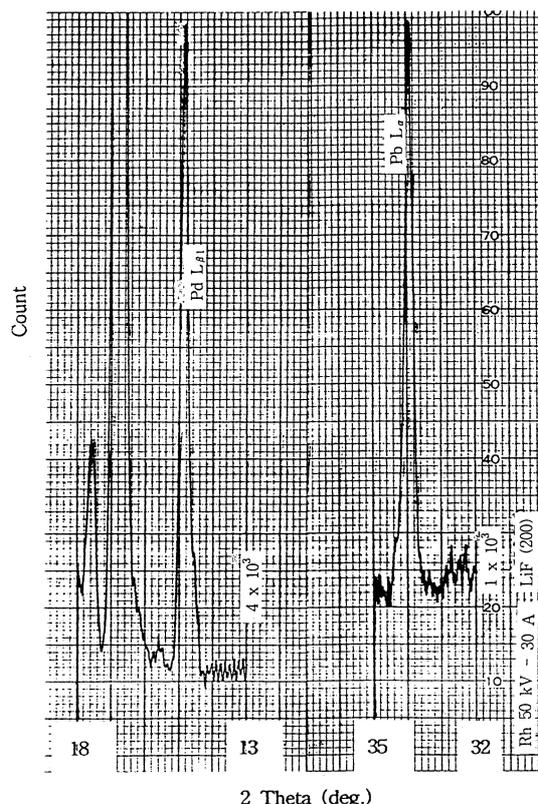


Figure 1. The XRF spectrum of ash product for the mixture of lead and palladium.

bismuth could be confirmed from XRD experiment, later.

X-ray Diffractometry. XRD patterns of three kinds of ash products for lead were obtained with the condition given in experimental section. In Figure 2, (a) is the pattern of ash product for only Pb(II) solution, (b) for Pb(II) + Pd(II) solution, and (c) for Pb(II) + Pd(II) + Al(III) solution. Several characteristic peaks of lead oxide or other lead compounds could be expected in the pattern (a). But it was difficult to identify them because the compounds did not have definitive crystal structure or their peaks could be overlapped with graphite peaks. Other sides, a thin and white section was shown on inside surface of the tube when the graphite tube was cut. Probably, this white one meant a lead compound.

In the pattern (b), several new peaks were indicated. The presence of PbPd_3 could be identified with characteristic d -values of 2.3340, 2.0188 and 1.6434 Å,¹⁹ but other peaks were not possible to be read because of small intensities. Besides, the inner surface of this tube was indicated smoother than that of the tube (a), which meant the formation of PbPd_3 alloy. In the pattern (c), a distinct pattern of PbPd_3 was shown with peaks of following d -values of 4.0478, 2.3340, 2.0188, 1.8024, 1.6434, 1.4278, 1.2177, and 1.1648 Å. There were also small unidentified peaks which meant less crystalline ash products and other compounds. In addition, the inner surface of graphite tube was very smooth like the surface of a mirror.

Because ash product was obtained after the charring product was cooled to room temperature, it can be somewhat dif-

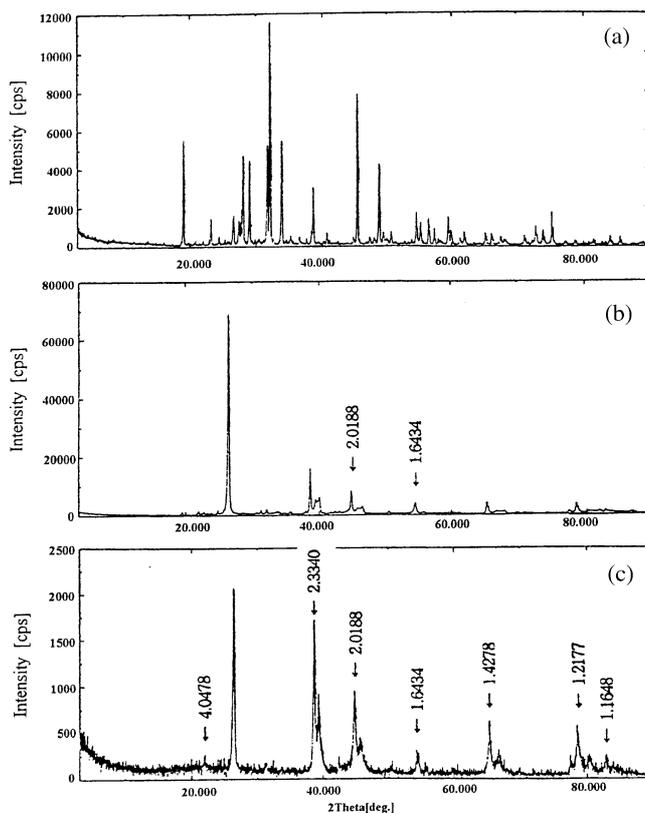


Figure 2. The XRD pattern of ash products for lead (a), mixture of lead and palladium (b), and mixture of lead, palladium and aluminum (c).

ferent with the material during the period between charring and atomization. Even though PbPd_3 was formed at high temperature, it can be known from Figure 3 for the phase diagram²⁰ of lead-palladium system that the vertically non-radiative transition of the alloy to room temperature is possible without any phase transition. From above description, lead-palladium alloy (PbPd_3) was formed in the charring step at 1,000 and 1,150 °C by the addition of palladium and aluminum. Because the graphite furnace used was un-coated tube, the temperature on the tube wall might be really different from the temperature programme in Table 1. The temperature can be thought to be maintained at more than 1,250 °C which is higher than the programmed 1,000-1,150 °C. After the heating at charring step was ended, the cooling of charring product was continued according to the cooling curve of phase diagram as in Figure 3. The chemical formula seems to be the same as the real state of charring product. Such phenomena were also described by Oishi and co-workers²¹ as following: the possible structures of the alloy were Pd_3Pb_2 - Pd_3Pb and Pd_3Sn_2 - Pd_2Sn - Pd_3Sn at the volatilization temperature of atomization from their phase diagrams.

On the other hand, ash products of bismuth were obtained with the same procedures as in case of lead. Nickel was used as an auxiliary modifier instead of aluminum. The X-ray diffraction patterns were shown as in Figure 4. Diffraction peaks for bismuth oxide of Bi_2O_3 form were expected to be observed in pattern (a) as in lead, but any peaks could be not

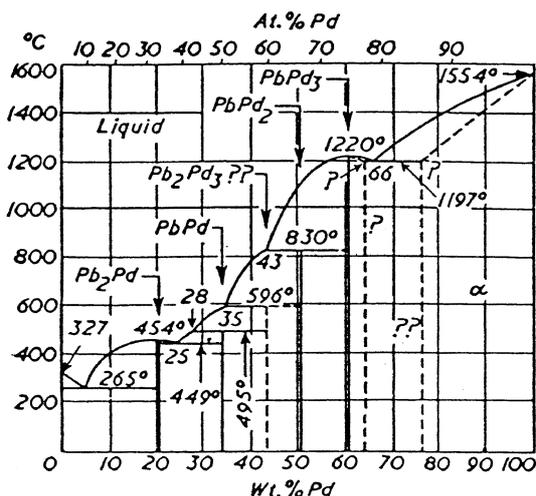


Figure 3. The phase diagram for lead-palladium.²⁰

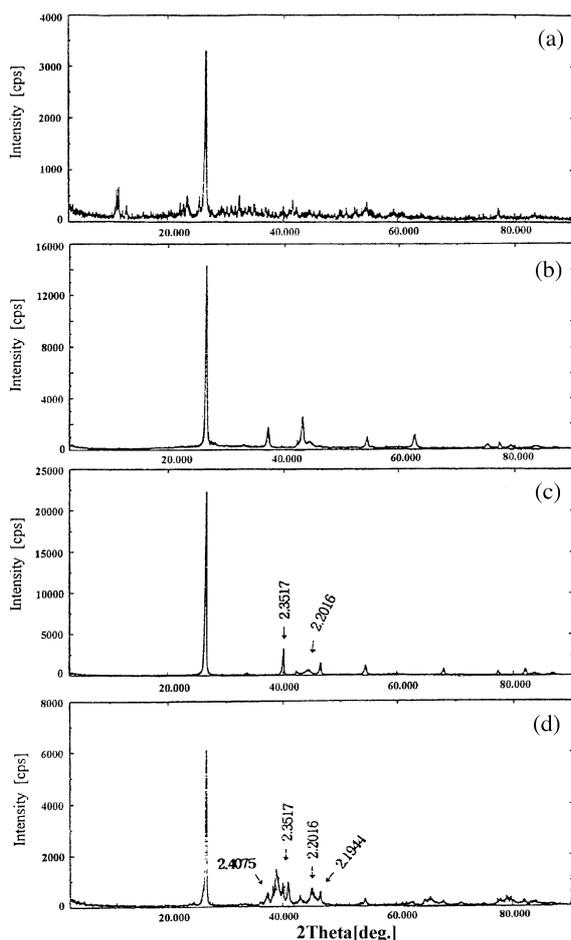


Figure 4. The XRD pattern of ash products for bismuth (a), mixture of bismuth and nickel (b), mixture of bismuth, palladium (c), and mixture of bismuth, palladium and nickel (d).

found because of high noises. The indication of yellow cross-section on the inner surface of tube could be recognized as a bismuth oxide.

Ash product was obtained from Bi(III) + Ni(II) solution with the same charring temperature as with Bi(III) solution and XRD pattern was graphed {pattern (b)}. As expected,

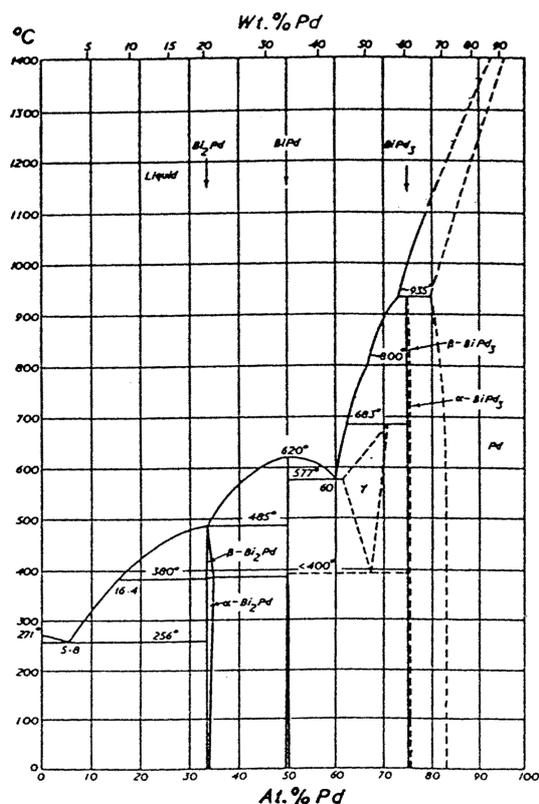


Figure 5. The phase diagram for bismuth-palladium.²⁰

any characteristic peaks could not be observed on the pattern to recognize the formation of bismuth-nickel alloy. In the pattern (c) for Bi(III) + Pd(II), two peaks of d-values (2.3517 and 2.2016 Å) were clearly indicated, which were main characteristic peaks for BiPd₃. And a smooth surface of inside tube could be made due to bismuth alloying. Finally, pattern (d) was for Bi(III) + Pd(II) + Ni(II) solution. Any new peaks for other compounds could not be observed in pattern (d), but many characteristic peaks of BiPd₃ were found at the d-values of 2.4075, 2.3517, 2.2016 and 2.1944 Å.

As in case of lead, ash product for Bi(III) + Pd(II) was also studied with the phase diagram of bismuth-palladium alloy (Figure 5). It could be concluded that the structure of cooled ash product was same as the product in AAS because the vertically non-radiative transition was also observed in the diagram.

Conclusion

The charring temperatures for volatile lead and bismuth could be raised more than 500 °C by the modification of matrix. Even not completely, the matrixes for Pb(II) and Bi(III) could be modified with a single modifier of palladium by the formation of PbPd₃ and BiPd₃ alloys. If an auxiliary modifier such as aluminum or nickel was used together with the main modifier, the better crystalline ash product could be formed than with a single modifier. It could be concluded that the changing process of Pb²⁺ → PbO → Pb⁰ at the step of charring was changed to Pb²⁺ → PbO → PbPd₃

→ Pb⁰ for lead and Bi³⁺ → BiO → Bi⁰ to Bi³⁺ → BiO → BiPd₃ → Bi⁰ for bismuth by the use of modifiers. Such modification could much raise the charring temperatures for the stable atomization and increased absorbances.

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