

Matrix Modification for Graphite Furnace Atomic Absorption Spectrophotometric Determination of Volatile Elements(III). Trace Bismuth

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Abstract : A matrix modification was studied for the determination of trace bismuth in water samples by graphite furnace atomic absorption spectrophotometry. The type and quantity of modifiers as well as the use of auxiliary modifiers were investigated to realize the efficient modification. Palladium was chosen as a single modifier. By the addition of palladium(5 μ g/mL) to 100 ng/mL bismuth solution, the temperatures could be raised from 500°C to 1,300°C for the charring and from 2,000°C to 2,200°C for the atomization as well as the sensitivity and reproducibility were improved. The absorbance of bismuth was maximum and not changed in the range of Pd 3-25 μ g/mL. And several materials were examined as an auxiliary modifier. The mixed solution of 1 μ g/mL palladium and 200 μ g/mL nickel have raised the temperatures as with 5 μ g/mL palladium only. The maximum absorbance of bismuth was shown in the nickel concentration range of 100-300 μ g/mL in 1 μ g/mL palladium modified system. With such optimum conditions, the trace amount of bismuth in several water samples could be determined by a calibration curve method, and good recoveries were also obtained.

Keywords : Electrothermal atomic absorption spectrophotometry, Bismuth, Matrix modification, Palladium modifier

1. Introduction

The more the society is industrialized, the more human beings will be exposed to the toxic materials such as heavy metals. It is

known that even trace heavy metals in environmental pollutants can greatly affect the metabolism in a human body. Particularly, among them, bismuth has so serious toxicity similar to lead that the convenient and accurate

method should be developed for the determination of the trace bismuth. Recently, the great interest is being focused on its determination in various samples. In addition to bismuth, several elements such as arsenic, selenium, lead and so on have a high volatility so that it is very difficult to get the low detection limit by a graphite furnace atomic absorption spectrophotometry (GF-AAS). Therefore, the preconcentration is needed prior to the AAS measurement. But the technique is sometimes time-consuming or troublesome and contaminates a sample especially for a large volume of sample¹.

To overcome such disadvantages, the matrix modification was introduced by R. D. Ediger in 1974. That is, the volatility of arsenic and selenium was decreased by the addition of nickel, and cadmium was stabilized by an ammonium phosphate². Since that, molybdenum³, lanthanum⁴, phosphoric acid⁵, magnesium nitrate⁶, potassium dichromate⁷ and so on were developed as a matrix modifier for the determination of volatile elements.

Some studies on the matrix modification have also been conducted for the determination of trace bismuth in various kinds of samples. Jin et al.⁸ introduced some palladium as a matrix modifier to the solution for the determination of trace bismuth, that was extracted from a waste water with MIBK, by GF-AAS. But this was an indirect method because a solvent extraction was preceded before its determination. Sato et al.⁹ have applied the coprecipitation with zirconium hydroxide to concentrate a trace bismuth in spring water for AAS determination, in which the zirconium hydroxide was used as a matrix modifier as well as coprecipitant. Sotera et al.¹⁰ have changed the shape of graphite tube and used nickel as a modifier to determine several trace elements. The nickel was not so desirable because it had large

memory effect due to its remaining property inside of the tube. Particularly, its application can not be allowed in case of complicated matrix because the charring temperature was relatively low. Matsusaki et al.¹¹ had described that the chloride interference was due to the coordination of chloride ions to bismuth(III) so that the interference should be removed by the addition of diammonium-EDTA. But the application could be limited to the samples of the complex matrix having low charring temperature. From the above considerations, those can be said to be indirect methods for the determination of trace bismuth by using a matrix modifier.

Up to present, nickel has been most frequently used in the GF-AAS as a modifier, but it needs so high temperature at the clean step of graphite tube to remove memory effects and residual materials that it is nearly not being used at present¹. But Jin et al.⁸ reported that palladium was a universal modifier because it could eliminate such effects and had a good modification efficiency. So it has been widely used for the determination of various volatile elements. However, the palladium is so expensive that much effort has been tried to enhance the modification efficiency with a small amount of palladium.

In this work, the matrix modification by the use of modifier as well as auxiliary modifiers were studied in the determination of trace bismuth in various waters. That is, the type and quantity of the main modifier and the synergistic effects of the auxiliary modifier were investigated to raise the charring temperature prior to the atomization.

2. Experiment

Apparatus and Reagents All reagents used

were of extra pure or guaranteed reagent grade. Water was purified by the filtration of a distilled water with Milli-Q water system.

Bismuth solution(1,000 µg/mL) was prepared by dissolving bismuth nitrate in dilute nitric acid solution.

Palladium solution(1,000 µg/mL) was prepared by dissolving pure palladium in concentrated nitric acid and diluting it with the deionized water.

Perkin-Elmer Atomic Absorption Spectrophotometer, Model 2380, equipped with a Heated Graphite Atomizer, HGA-400 was used, in which a pyrocoated graphite tube was inserted. Instrumental parameters are shown in Table 1. Test solution 10 µL was manually delivered to the tube with a Gilson micropipette.

Table 1. Instrumental operating parameters

Parameter	
Wavelength	223.1 nm
Slitwidth	0.2 nm
Lamp current	10 mA
Signal mode	Absorbance
Replicate	3
Inert gas	Argon

Test solution Two kinds of solutions were prepared to obtain optimum conditions for the matrix modification of Bi solution as follows: palladium of 5 µg/mL was added to 100 ng/mL Bi³⁺ solution in a 10 mL volumetric flask as single modifier and nickel of 200 µg/mL was also added to 100 ng/mL Bi³⁺ and 1 µg/mL Pd²⁺ solution as an auxiliary modifier. The absorbance of bismuth was measured according to the heating program as Table 2. A sample solution of 10 µL(1.0 ng Bi³⁺) was injected into the graphite tube for it.

Table 2. Heating program

Step	Temp. (°C)	Ramp. time (sec.)	Hold. time (sec.)	Baseline (sec.)	Read time (sec.)	Stopflow (sec.)
1	100	5	5			
2	X	4	6			
3	X	1	2	0	1	2
4	2,700	3	3			

3. Results and Discussion

Type of Matrix Modifier In general, the matrix modification in electrothermal AAS is significantly dependent upon the type of matrix modifier. Unfortunately, any universal modifier that can be commonly used in many kinds of samples have not been reported yet, but only several modifiers were useful in the matrix modification. Even if the same modifier is used, the modification effect is shown differently according to the analyte element, sample condition and method used. Therefore, the increase of charring temperature and improvement of sensitivity for the bismuth were studied in this work using several matrix modifiers developed so far.

Because the detection limit of bismuth was not so low due to high volatility, the relatively high concentration of 100 ng/mL was used to observe the charring and atomization temperature with or without any modifier. The variation of the charring temperature were shown as in Fig. 1. In case of no modifiers, maximum absorbance was appeared at the charring temperature of 500 °C. And if the matrix was more complex and refractory materials were coexisted together with bismuth, the background absorption was highly increased because the sample matrix could not be destructed completely and some fog was

formed. Therefore, the determination of trace elements was difficult because of the relatively high detection limit. And other modifiers except palladium could raise the charring temperature, but the sensitivity was not so improved. Moreover, the detection limit was never improved in the sample solution having some refractory materials. In contrast to these cases, the charring temperature was much raised from 500 to 1,300°C by the addition of palladium as a matrix modifier.

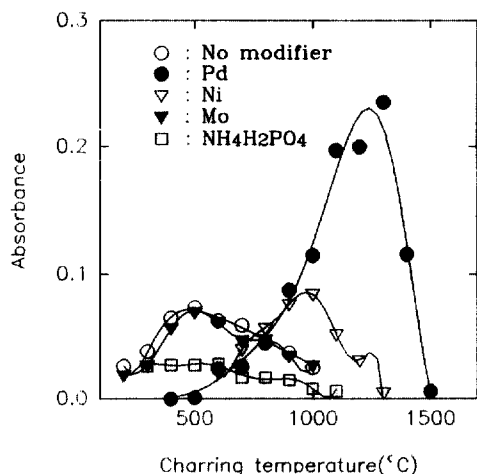


Fig. 1. The effect of matrix modifier on the charring temperature. The absorbances were measured at the atomization temperature of 2,200 °C. Concentration : Bi 100 ng/mL; each modifiers 5 µg/mL(except $\text{NH}_4\text{H}_2\text{PO}_4$ 1.0 %).

And also the atomization temperature could be raised from 2,000°C to 2,200°C(see Fig. 2). Even though the atomization temperature was not so much increased as shown in the figure, the sensitivity and reproducibility could be significantly improved because the atomization efficiency of bismuth was enhanced by the addition of the palladium. From this consideration, it is known that the matrix can be modified with the single modifier of

palladium efficiently.

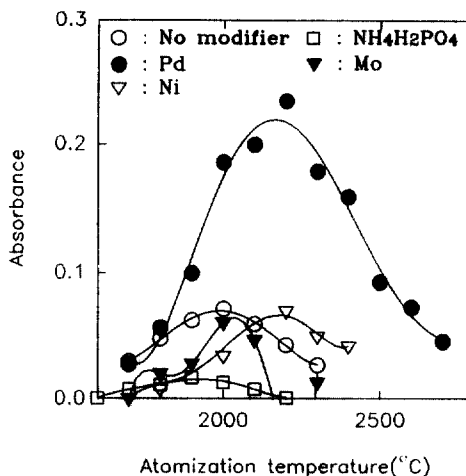


Fig. 2. The effect of matrix modifier on the atomization temperature. The absorbances were measured at the optimum charring temperature according to the type of modifiers. Concentration : Bi 100 ng/mL; each modifiers 5 µg/mL(except $\text{NH}_4\text{H}_2\text{PO}_4$ 1.0 %).

Optimum Concentration of Modifier, Pd In general, an enough modifier is necessary to raise both of the charring and atomization temperatures by the matrix modification, but it can remain the memory effect in a graphite furnace. Therefore, the temperature of clean step should be so high raised to remove the effect that the life of a graphite tube is shortened by the consumption of the graphite¹.

Here, the modification efficiency was investigated according to the concentration of palladium as a modifier. The Fig. 3 and 4 show the variation of the charring, atomization temperature and absorbances depending on its concentration at each other temperature of optimum charring and atomization.

As shown in these figures, the charring and atomization temperatures were increased with the increase of palladium concentration. The

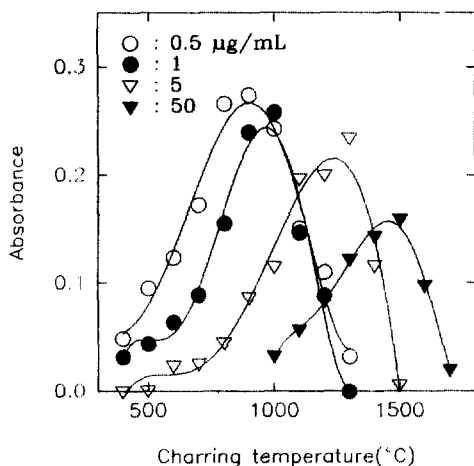


Fig. 3. Concentration effect of Pd modifier on the charring temperature. The absorbances were measured at the atomization temperature of 2,200 °C. Bi concentration : 100 ng/mL.

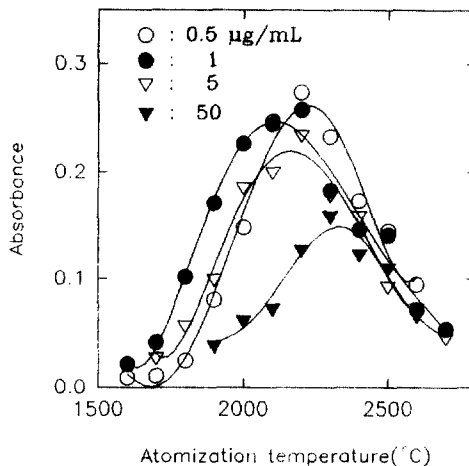


Fig. 4. Concentration effect of Pd modifier on the atomization temperature. The absorbances were measured at the optimum charring temperature according to the concentration of Pd modifier. Bi concentration : 100 ng/mL.

reason was considered to be due to the formation of the thermally stable compound or alloy during the charring and atomization¹². But the decrease of bismuth absorbance was shown on the addition of an excess palladium compared to the recommended value obtained previously.

Usually, the matrixes of real samples are so various and impossible to be adjusted at discretion that a suitable amount of modifier should be used for the efficient atomization. But because most of sample matrixes can be destructed at the temperature of more than 1,000 °C, the concentration of palladium is optimized to give such a charring temperature. From above considerations, it can be known that 1,300°C and 2,200°C are the optimum charring and atomization temperatures obtained by the presence of 5 µg/mL palladium as a modifier.

In fact, the content of bismuth can be so widely variable even in a given sample that the specific concentration of the modifier to cover

such some wide range should be easily selected. In this work, the optimum concentration range of the palladium was investigated to give the charring and atomization temperatures of 1,300 °C and 2,200 °C, respectively. That is, the effect of the palladium concentration on the matrix modification was studied in the range of 0 - 50 µg/mL with the same conditions obtained with 5 µg/mL palladium(see Fig. 5). As shown in the figure, a constant absorbance was appeared from 3 to 25 µg/mL of palladium and the absorbance was gradually decreased at more than 25 µg/mL by the delay effect in the matrix decomposition due to the high content of palladium. On the other hand, at the concentration of less than 3 µg/mL, the deficient palladium could not so enough suppress the volatility of bismuth that the absorbance was drastically decreased.

Efficiency of Auxiliary Modifier It was reported that the use of an auxiliary modifier

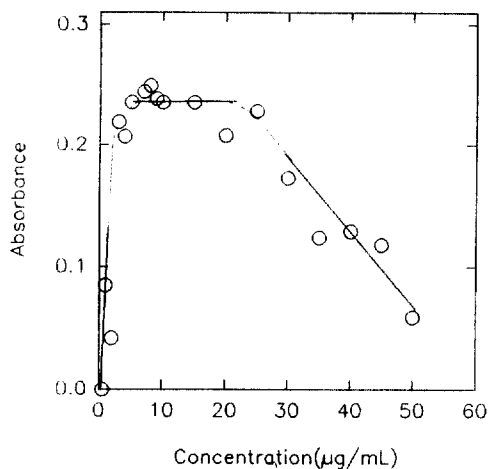


Fig. 5. Concentration effect of Pd modifier on the Bi absorbances were measured at the charring temperature of 1,300°C and atomization temperature of 2,200°C. Bi concentration : 100 ng/mL.

together with palladium could enhance the modification effect.

In the determination of trace lead by GF-AAS, the mixing of palladium with small amount of aluminum have increased the charring temperature. Such a modification was caused by changing injected compounds to more refractory form in the charring and atomization steps¹². Especially, if an auxiliary modifier could enhance the modification, then there was a major advantage that the substitution of it with some cheaper one decreased the amount of expensive palladium used.

So, several materials were tried to be tested as an auxiliary modifier in this work. At the palladium concentration of 1.0 µg/mL, the effects of five kinds of auxiliary modifiers were investigated at their concentrations of 200 µg/mL (see Fig. 6 and 7). From the figures, the nickel was known to be the best one among them. That is, the mixed solution of 1 µg/mL palladium and 200 µg/mL nickel have raised the temperatures for the charring and atomization as much as only 5 µg/mL palladium.

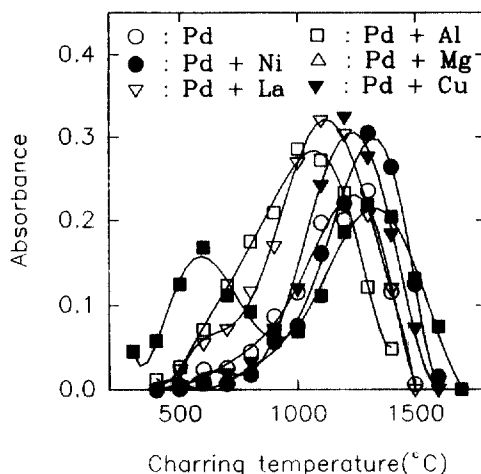


Fig. 6. The effect of matrix modifier on the charring temperature. The absorbances were measured at the atomization temperature of 2,200°C. Concentration : Bi 100 ng/mL; Pd 1 µg/mL; each auxiliary modifiers 100 µg/mL.

But if this modifier is too much used, the memory effect is appeared and a high temperature at the clean step is required to remove the residual materials¹.

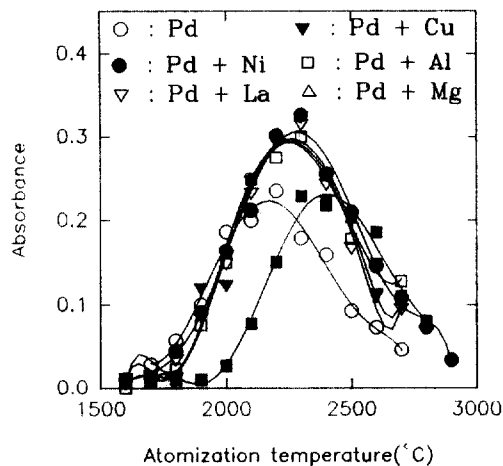


Fig. 7. The effect of matrix modifier on the atomization temperature. The absorbances were measured at the optimum charring temperature according to the type of auxiliary modifiers. Concentration : Bi 100 ng/mL; each auxiliary modifiers 100 µg/mL.

Therefore, the minimum concentration of nickel as an auxiliary modifier was also searched to obtain the same effect as obtained with 5 $\mu\text{g/mL}$ palladium. The modification efficiency was investigated with the concentration range of nickel up to 1,000 $\mu\text{g/mL}$ (see Fig. 8).

As shown in Fig. 8, the maximum absorbance of bismuth was not changed in the nickel concentration range of 100 - 300 $\mu\text{g/mL}$ in the modified system with 1 $\mu\text{g/mL}$ palladium. Here, the absorbance of the bismuth was measured at the charring temperature of 1,300 $^{\circ}\text{C}$ and atomization temperature of 2,200 $^{\circ}\text{C}$. But the absorbance of bismuth was rapidly decreased at less than 40 $\mu\text{g/mL}$ because the matrix could not so sufficiently decomposed by the mixed modifier. In contrast, over 300 $\mu\text{g/mL}$, the absorbance was also depressed gradually due to the excessive delay of the matrix volatilization. **Analysis of Real Samples** With above optimum conditions, the trace amount of bismuth in three kinds of water samples(tap

water and treated waste water of Korea University at Jochiwon, and river water near Jochiwon) were determined by a calibration curve method. For this, two series of standard solutions were prepared: one is with only 5 $\mu\text{g/mL}$ palladium and the another with the mixed modifier of 1 $\mu\text{g/mL}$ palladium and 200 $\mu\text{g/mL}$ nickel. The calibration curves were linear, but the use of a mixed modifier have improved the sensitivity and reproducibility more effectively than the single modifier(see Fig. 9).

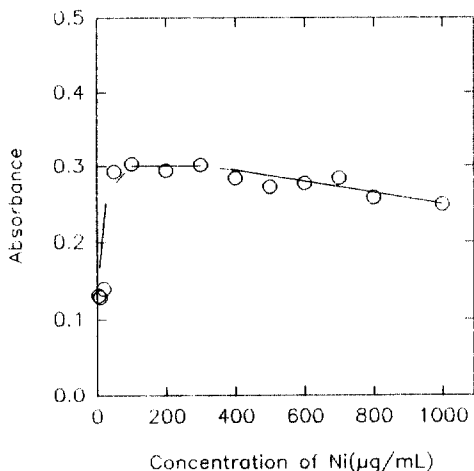


Fig. 8. Concentration effect of Ni on the Bi modified with Pd. The absorbances were measured at the charring temperature of 1,300 $^{\circ}\text{C}$ and atomization temperature of 2,200 $^{\circ}\text{C}$. Concentration : Bi 100 ng/mL; Pd 1 $\mu\text{g/mL}$.

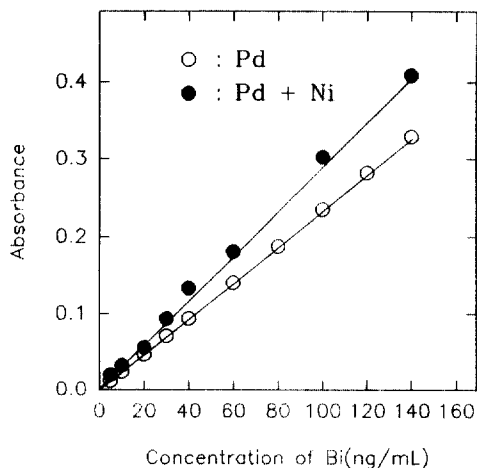


Fig. 9. Calibration curves.

The bismuth contents, which were obtained with the mixed modifier of the 1 $\mu\text{g/mL}$ palladium and 200 $\mu\text{g/mL}$ nickel, were 2.78, 6.53, 8.83 ng/mL in tap water, waste water and river water, respectively. The recovery of more than 97 % was obtained in each sample in which 50 ng/mL of bismuth was spiked. And the detection limit was 1.63 ng/mL corresponding to the absorbance of three times of the standard deviation for the background(see Table 3).

From these results, this method can be concluded to be apply for the quantitation of trace bismuth in water samples.

Table 3. Analytical results of Bi in water samples
Unit : ng/mL

Sample	Spiked	Measured	RSD (%)	Recovered	Recovery (%)
Tap Water	0.00	2.78	1.69		
Waste Water	50.0	57.44	1.00	54.06	109.0
Water	0.00	6.53	1.10		
Water	50.0	57.11	5.51	50.58	101.1
Mi-ho River	0.00	8.83	3.29		
Water	50.0	57.44	1.00	48.61	97.22

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