Lessening Unexpected Increases of Atomic Vapor Temperature of Arsenic in Graphite Furnace Atomic Absorption Spectrometry

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It was found that the atomic vapor temperature of Se increased unusually in the analysis of Se added with Pd as the matrix modifier. To make an advanced study on this phenomena, and to lessen the interference, the (effective) atomic vapor temperature of As was measured by the two-absorption line method, and its relation to matrix modifiers was studied by using a multi-channel atomic absorption spectrometer. The atomic vapor temperature of As was measured by referring to the atomic vapor temperature of Pb in the furnace. The results are discussed along with the phase diagrams of As-alloys. In the presence of Cu or Co, it was presumed that As was atomized before formation of intermetallic compounds. In the presence of Pd or Ni, atomization of As began near the melting point of intermetallic compounds. An unexpectedly higher temperature of As atomic vapor was observed in the case of the rapid atomization. The atomic vapor temperature rose higher than one would have expected. Addition of potassium permanganate effectively reduced the unexpected temperature increase, and allowed a clear absorbance profile of atomization for As analysis of urine to be obtained.

Keywords Matrix modifier, effective atomic vapor temperature, arsenic, alloy

Arsenic has important roles in a human body as a toxic or an essential element¹, thus the methods for determination of As in biological samples are needed. Owing to severe matrix interferences, the determination of As by the graphite furnace atomic absorption spectrometry is said to be difficult, and different kinds of experimental conditions have been studied. The key technology is to use a suitable matrix modifier. Mixtures of Pd and magnesium nitrate², Ni and magnesium nitrate³, Pd and potassium persulfate⁴ were reported. Studies on the mechanism of As atomization process in the presence of Pd modifier were done by Styris *et al.* using atomic absorption spectrometry and mass spectrometry.⁵ However, the mechanisms of As atomization from complex matrices in the presence of mixtures of matrix modifiers are still not clear. Hirano *et al.*⁶ measured the (effective) atomic vapor temperature of Se by using the two-line method and observed unexpected rising of the atomic vapor temperature in analysis of urine. For further studies, the authors took another approach by measuring the (effective) atomic vapor temperature of As in the graphite furnace, and analyzed a urine sample by using a double system of the matrix modifiers of Pd and Mn.

Experimental

A multi-channel Zeeman atomic absorption spectrophotometer Hitachi Z-9000 was used with an installed

auto-sampler. Two kinds of furnaces were used; one was a pyrolytic graphite coated tube, the other was a pyrolytic graphite platform inserted in the tube. Injection volume was 10 μ l each for sample and matrix modifier solution. Each injected sample was dried at 80–140°C for 50 s, and ashed at 400°C for 30 s. When a urine sample was analyzed, ashing temperature was set to 1200°C to reduce the background absorbance. Two kinds of atomization programs were used. One program was temperature rising from 1400°C to 2800°C during 20 s by a current control mode. This operation mode was called a slow atomization by a slow heating. In the other program, the temperature was raised within 1.5 s by using an opto-pyrometric feedback system, and kept at 2800°C for 5 s. This mode was called a rapid atomization by a rapid heating. As a reference, the temperature of graphite tube wall was measured by an optical pyrometer (CHINO Pyroscope Q). The carrier gas flow rate of argon was 200 ml/min; it was stopped during atomization.

Nitric acid, potassium permanganate, potassium persulfate, and hydrogen peroxide were of special reagent grade or for AAS (Wako). Arsenic, Co, Cu, Ni and Pd solutions for AAS (Cica-Merck) were used by diluting with 0.1 mol/l nitric acid. These solutions were used at concentrations of 10–400 mg/l for analyte elements, and 200–400 mg/l for matrix modifiers. A normal human urine sample was used by diluting 4-fold, to which Triton X-100 (Sigma) was added to prepare a final concen-

tration of 10 ml/l. Hydrogen peroxide, potassium permanganate, and potassium persulfate was added to prepare a final concentration of 50, 10, and 10 g/l, respectively.

For measurement of the (effective) atomic vapor temperature (T_{eff})*¹ of As, the two-line absorption method was employed.

It was calculated from the following Eq. (1).

$$T_{\text{eff}} = (E_2 - E_1) / \ln(C_f \times \text{Abs.}_1 / \text{Abs.}_2) \quad (1)$$

where E_1 and E_2 are energy levels in the ground state and a slightly higher energy state, respectively, Abs._1 and Abs._2 are absorbances by a transition from E_1 and E_2 , respectively, C_f is a correction factor.⁷ For As, the absorbance for the ground state (at 193.7 or 197.2 nm) was too large, compared with the absorbance from the other levels. Consequently we chose 235.0 and 228.8 nm, both of two-line pair are not transitions from the ground state. For determination of C_f , Terui *et al.* used the flame AAS.⁷ Measurement of As absorbance by the flame AAS, however, was almost impossible because of low sensitivity. Consequently, we determined C_f for As with the graphite furnace by using Pb as a reference temperature indicator. In this experiment, two Pb hollow cathode lamps and two As hollow cathode lamps were installed in the Z-9000 atomic absorption spectrophotometer, because four beams from four hollow cathode lamps are focused in the graphite furnace, and simultaneous measurements are possible. Pb absorbances at 368.3 and 280.2 nm, and As absorbances at 235.0 and 228.8 nm were measured simultaneously by the slow atomization. Pd of 100 mg/l was added because As absorbance was too small in the condition without a matrix modifier. The (effective) atomic vapor temperature of Pb was measured, and the C_f value for As was determined by referring to it. It was 1.54 when the difference of energy levels $E_2 - E_1$ was expressed in wavenumbers as 323. This energy difference was small, so the errors of measured atomic vapor temperature of As may be larger than those of Pb. The absorbance profiles of atomization signals and the (effective) atomic vapor temperatures of Pb and As obtained by the above procedure are shown in Fig. 1. The (effective) atomic vapor temperatures were continuously measured and are plotted in figures in this paper. Although the accuracy of the (effective) atomic vapor temperature of As was poor compared with those for Pb, the measurement of the atomic vapor temperature of As was achieved by this method.

Results and Discussion

Slow atomization

Oishi *et al.* discussed the relationship between the

*1 It is called "effective atomic vapor temperature" in the case that the atomic vapor temperature is obtained by the two-line absorption method. To avoid confusion, we have put parentheses on "effective".

Fig. 1 Absorbance profile of Pb and As simultaneously atomized from graphite tube wall by slow atomization, and the (effective) atomic vapor temperature. a and b: absorbances of Pb at 368.3 and 280.2 nm; c and d: absorbances of As at 235.0 and 228.8 nm, respectively. ○: the (effective) atomic vapor temperature of Pb, ●: the (effective) atomic vapor temperature of As.

metal matrix modifiers and their phase diagrams of alloys.⁸ Atomization of Sn and Pd in the phases of intermetallic compounds in Sn-Pd alloy were observed by electron microscopy.⁹ For discussion on the processes of forming alloys and its atomization, the (effective) atomic vapor temperature of As vaporized from the wall of graphite tube was measured in the slow atomization. Co, Cu, Ni and Pd, which can form intermetallic compounds with As, were used as the matrix modifier. The (effective) atomic vapor temperatures of As in the presence of these metals are shown in Fig. 2. Since the temperatures at the beginning of As atomization were difficult to obtain precisely, these temperatures are indicated in parentheses. Atomization of As in the presence of Co or Cu began at 400–600°C, and the temperature reached 900–1500°C in the end of atomization. On the other hand, As atomization began at 700–900°C in the presence of Ni. Moreover, in the presence of Pd, the atomization of As was delayed and began at 900–1100°C, and reached to about 2000°C.

The phase diagram of Pd-As alloy is shown in Fig. 3;¹⁰ the other phase diagrams of Co-As, Cu-As and Ni-As show similar phase diagrams. In the Co-As and Cu-As alloy, As was atomized at 400–600°C before formation of the intermetallic compounds because the vapor pressure of As is higher than 1 Torr at 400°C.¹¹ In the Ni-As alloy, As was atomized along the intermetallic compound phases such as NiAs and NiAs₂, whose melting points are around 800°C. In the Pd-As alloy, As was atomized at 900–1100°C over the melting points of the intermetallic compound phases.

In the Pd-As alloy, atomization of As was suppressed until the temperature became higher than melting points of Pd-As intermetallic compounds. It is reported that

Fig. 2 (Effective) atomic vapor temperature of As atomized from the tube wall in slow atomization. ○, △, □ and ●: in the presence of Co, Cu, Ni and Pd, respectively. The temperatures at the beginning of atomization were shown in the parentheses. w: wall temperature.

Fig. 4 (Effective) atomic vapor temperature of As atomized from the tube wall in rapid atomization. ○ and ●: in the presence of Ni and Pd, respectively. w: wall temperature.

Fig. 3 Phase diagram of Pd-As alloy.¹⁰

the activity coefficient of analyte element showed a smaller value than 1.0 when some intermetallic compounds were formed; then atomization was suppressed until it reached a higher temperature.¹² In the case of Pd-As, the activity coefficient is thought to be smaller than 1.0, because the beginning of atomization is shifted to a higher temperature, and the shift means smaller activity coefficient than the value of 1.0. When As forms intermetallic compounds with Pd or Ni, the atomization shifts to higher temperature, then the appearance time of As absorption signal is delayed.

Rapid atomization

In an actual determination procedure, the rapid atomization mode is used. The (effective) atomic vapor temperature of As atomized from tube wall in that condition is shown in Fig. 4. The setting temperature is

also shown as a reference. The (effective) atomic vapor temperature of As in the presence of Pd or Ni was higher than those in the slow atomization, as well as, higher than the temperature of the wall of the graphite tube. It means that the density of As atoms in the higher energy level in the two energy levels of E_1 and E_2 was increased. It might be another interference. Similar phenomena were reported in the cases of Ni and Bi¹³, and Se.⁶

Analysis of urine

In the analysis of urine, potassium persulfate was used in addition of Pd in order to oxidize organic compounds.⁴ In this experiment, hydrogen peroxide, potassium persulfate, and potassium permanganate were used as oxidizing agents. The (effective) atomic vapor temperature of As in urine sample atomized from the tube wall in the presence of Ni and these oxidizing agents is shown in Fig. 5. In all cases, an unexpected temperature rise of atomic vapor was observed. The same trend was obtained in case of Pd and the oxidizing agents.

These phenomena were altered when we applied the atomization from the platform. The (effective) atomic vapor temperature of As in the urine sample atomized from the platform in the presence of Ni and the above oxidizing agents is shown in Fig. 6. In the presence of Ni and potassium permanganate, it can be found that the (effective) atomic vapor temperature became lower, and the unexpected temperature rising was consequently reduced to some extent. The absorbance profile of atomization signal of As is also shown in Fig. 6. The profile was obtained clearly in the presence of potassium permanganate.

In the case of Pd, hydrogen peroxide and potassium persulfate were able to lower the (effective) atomic vapor temperature of As as shown in Fig. 7. It can be recognized that some organic compounds cause the unexpected temperature rising in the atomization of As.

Fig. 5 (Effective) atomic vapor temperature of As in urine atomized from tube wall in rapid atomization. $\circ$, Δ , $\blacksquare$ and $\bullet$: in the presence of Ni, Ni+H₂O₂, Ni+K₂S₂O₈, and Ni+KMnO₄, respectively. w: wall temperature.

Fig. 6 (Effective) atomic vapor temperature of As in urine atomized from the platform in rapid atomization. $\circ$, Δ , $\square$ and $\bullet$: in the presence of Ni, Ni+H₂O₂, Ni+K₂S₂O₈, and Ni+KMnO₄, respectively. w: wall temperature. Absorbance profiles of atomization signal at 235.0 nm in the presence of Ni+K₂S₂O₈ (a) and Ni+KMnO₄ (b) are shown.

Decomposition of these compounds by addition of oxidizing agents seems to be effective to reduce the temperature rising. When potassium permanganate was added with Pd, the (effective) atomic vapor temperature of As is lower than that in the case of Ni, and the absorbance signal of As was obtained clearly.

The (effective) atomic vapor temperature of an analyte can be raised by adding metal modifiers in the rapid atomization.¹⁴ On the other hand, the unexpected temperature rising of (effective) atomic vapor can be due to some factors in the furnace. In As atomization, we can say that the unexpected interference occurred in a complex matrix as the urine sample. In this case, addition of a transition metal may be useful to reduce this kind of interference. It is thought that Mn and other

Fig. 7 (Effective) atomic vapor temperature of As in urine atomized from the platform in rapid atomization. $\circ$, Δ , $\square$ and $\bullet$: in the presence of Pd, Pd+H₂O₂, Pd+K₂S₂O₈ and Pd+KMnO₄, respectively. w: wall temperature. Absorbance profiles of atomization signal at 235.0 nm in the presence of Pd+K₂S₂O₈ (a) and Pd+KMnO₄ (b) are shown.

metals take energy from As or As-Pd alloy in the atomization process, and reduces the density of As atom in the higher energy level. In our experiment, a combination of Pd and potassium permanganate is an effective matrix modifier.

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