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

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 µl 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 \((T_{\text{eff}})\) of As, the two-line absorption method was employed. It was calculated from the following Eq. (1).

\[
T_{\text{eff}} = \frac{(E_2 - E_1)}{\ln(C \times \text{Abs.}_1/\text{Abs.}_2)}
\]

where \(E_1\) and \(E_2\) are energy levels in the ground state and a slightly higher energy state, respectively, \(\text{Abs.}_1\) and \(\text{Abs.}_2\) are absorbances by a transition from \(E_1\) and \(E_2\), respectively, \(C\) 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 \(C\), 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 \(C\) 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 \(C\) 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 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 NiAs\(_2\), 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
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. 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 Bi$^{13}$, 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. 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.
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. 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 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.

References


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