Notes

Mass Effect on the Mechanism of Lead Atomization in Graphite Furnace Atomic Absorption Spectrometry

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Keywords Graphite furnace atomic absorption spectrometry, lead, activation energy, lead atomization mechanism

Although an identity of the sensitivity in both pyrolytic graphite coated (PG) and nonpyrolytic graphite (NPG) tubes was observable¹, Pb is one of the elements that has complex atomization mechanisms in an electrothermal graphite furnace. Its atomization reactions have been proposed: thermal destruction of $\text{PbO}_{(\text{g})}$ ², thermal destruction of $\text{Pb}_{2(\text{g})}$ ³ and bulk vaporization of $\text{Pb}_{(\text{l})}$ ^{4,5}. Recently, Lynch *et al.*⁵ have reported that an apparent first-order rate of release occurs from PG, NPG and glassy carbon tubes and from both deposition sites of the analyte as a solution and as an aerosol vapor, suggesting that Pb desorbes from the surface as individual atoms. In our previous work⁶, the Arrhenius activation energy (E_a) and the reaction-order in a PG tube for the deposition of 1 ng of Pb as an aqueous solution corresponded to their results, indicating that a similar atomization mechanism operates in the PG tube. The identity of E_a for 1 ng of Pb between PG and NPG tubes, however, was not observed, indicating that a different atomization mechanism operates on different atomizer surfaces. In the present work, it was found in an NPG tube that the deposition of PbO as a solid sample and a large quantity of Pb as an aqueous solution (40 and 400 ng) gave E_a values which agreed with that in a PG tube for the deposition of 1 ng of Pb as an aqueous solution.

Experimental

A Hitachi Model Z-8000 flame and a graphite furnace atomic absorption spectrometer with an optical temperature controller system (OTC) (Hitachi Model 180-0341) and an automatic sampler of 20 μl was used. The analytical wavelength and slit width were 283.3 and 1.3 nm, respectively. The atomic absorption spectrometer was modified in our laboratory so as to allow

Table 1 Standard atomizer conditions

Stage	Temp./ °C	Ramp time/s	Hold time/s	Inner Ar/ ml min ⁻¹
Drying	120	30	0	200
Charring	800	20	5	200
Atomizing	2500 ^a	0	2	30
Cleaning	3000	0	3	200

a. OTC was used.

Each measurement was done 5 times.

signals and temperature profiles to be registered with a time constant of 20 ms by using an Oki if-800 Model 50 personal computer. The standard atomizer conditions are shown in Table 1. An aliquot of a commercially available stock solution of Pb (Wako Pure Chemical Industry Ltd.) was diluted with water to a suitable concentration before use as a standard solution. Distilled and deionized water was purified by a Milli-QII system. Other information has already been reported.⁶

Results and Discussion

Atomic absorption signals for Pb were measured in an NPG tube: 0.8, 1.0, 1.2, 1.6 and 2.0 ng of Pb using the standard atomizer conditions and 10, 40 and 400 ng of Pb using the standard atomizer conditions, except for the atomization step which is 3000 °C OTC off mode (typical atomic absorption signals are shown in Fig. 1). Arrhenius plots were made by using Chung's equation⁷ for an analyte mass in the determinable range, and by Sturgeon's equation⁴ for an analyte mass over this range. Table 2 summarizes dependency of the analyte mass of Pb on the T_{app} and E_a values, together with those values in

Fig. 1 Atomic absorption signals for 1 ng of lead in PG and NPG tubes and 400 ng of lead in an NPG tube.

Table 2 Appearance temperature of lead atoms (T_{app}) and Arrhenius activation energy (E_a) for lead

Mass/ng	Tube	T_{app}/K	$E_a/kJ\ mol^{-1}$
0.8	NPG	1160 ± 20	110 ± 3
1.0	NPG	1150 ± 10	113 ± 5
	PG	1050 ± 10	190 ± 7
1.2	NPG	1150 ± 20	103 ± 3
1.6	NPG	1140 ± 10	126 ± 2
2.0	NPG	1120 ± 20	124 ± 9
10	NPG	1070 ± 10	—
40	NPG	1000 ± 20	186 ± 10^a
			116 ± 10^b
400	NPG	1000 ± 20	193 ± 5

a. Obtained in 1000–1090 K.

Obtained in 1090–1190 K.

PG tube. Although the T_{app} values were reduced by increasing the Pb mass, the E_a values were increased. Since this variation of the Pb concentration does not affect the physical characteristics of aqueous solutions (such as viscosity), there are not very dissimilar processes of surface spreading and penetration of aqueous solutions. Thus, the effect of surface spreading and penetration on the variation of the E_a value is negligible in the present case. The E_a value may therefore be affected by the interaction energy between the graphite tube surface and the analyte atoms, or between the analyte atoms.

Arrhenius plots for the signal of an analyte mass of less than 2 ng of Pb gave an average E_a value of $115 \pm 9\ kJ\ mol^{-1}$. This value is in agreement with that reported ($125 \pm 7\ kJ\ mol^{-1}$ corresponding to dissociation energy of $Pb_{2(g)}$) under isothermal conditions.³ The obtained value is not in agreement with Lynch's value⁵ ($218 \pm 20\ kJ\ mol^{-1}$) in an NPG tube, suggesting bulk vaporization. If a gaseous intermediate species exists, it would be swapped, together with the resultant Pb atoms; thus, the reduction of the integrated absorbance with

Table 3 Relative sensitivity and integrated absorbance for 1 ng of lead

Inner Ar/ ml m^{-1}	PG tube		NPG tube	
	R. sens.	Int. abs.	R. sens.	Int. abs.
0	1	0.1369	1	0.1386
30	0.779	0.1067	0.773	0.1072
50	0.575	0.0787	0.602	0.0835
90	0.360	0.0493	0.382	0.053

Fig. 2 Arrhenius plots for 40 ng of lead in an NPG tube using Sturgeon's equation.

increasing inner Ar gas flow should be larger than that in the PG tube. It is thus suggested that in a PG tube the Pb is desorbed from the surface as individual atoms, such as vaporization of bulk Pb metal.⁵ However, no noticeable difference in the dependency of the inner Ar gas flow regarding the relative sensitivity between PG and NPG tubes was observed (Table 3). The carbon reduction of intermediate $PbO_{(s)}$ in an NPG tube should be thermochemically favorable at the temperature before Pb atomization occurs (T_{app} : $1150 \pm 10\ K$), since the $PbO_{(s)}$ changes to the Pb metal at a temperature below a T_{app} of $1050 \pm 10\ K$ in a PG tube. The obtained E_a value may correspond to the energy of desorption of Pb atoms from a graphite surface.

Arrhenius plots for the 40 ng signal of Pb were made on the rising edge of the signal, as shown in Fig. 2. It may be decomposed into two straight-line segments which intersect at a temperature of approximately 1090 K, since a shoulder can be observed. In the low-temperature region, 1000–1090 K, the slope corresponds to an E_a value of $186 \pm 10\ kJ\ mol^{-1}$, which agrees with that ($190 \pm 7\ kJ\ mol^{-1}$) obtained for 1 ng of Pb in a PG tube. The identity of the E_a values may be due to the fact that the Pb atoms exhibiting a significant interaction

energy between the Pb atoms and the graphite wall exist, as well as in the case of PG tube. In the higher temperature region, 1090–1190 K, a value of 116 ± 10 kJ mol⁻¹ is obtained, which agrees with that obtained at an analyte mass of less than 2 ng of Pb. This plot shows a change in the mechanism of Pb atomization. Similar Arrhenius plots decomposed into two straight-line segments (which intersect at a temperature of approximately 1160 K) have been reported by Sturgeon for 2 ng of Pb.⁴ A shoulder on the leading edge of the signal can be observed for the 10 ng signal of Pb, as well as in the case of the 40 ng signal of Pb. Although the presence of a shoulder suggests the presence of two atomization mechanisms, reliable E_a values were not available. The smooth rising edge can be observed for 400 ng of Pb without a shoulder, as shown in Fig. 1. Arrhenius plots for it gave an E_a value of 193 ± 5 kJ mol⁻¹, which agrees with E_a in the same temperature region for the rising edge of the signal for 40 ng of Pb in an NPG tube. It was impossible to observe the absorption for the second segment because its mass was much greater.

Arrhenius plots for a common intermediate, PbO, in both PG and NPG tubes gave an E_a of 196 ± 10 for massicot and 190 ± 11 kJ mol⁻¹ for litharge, where a small amount of PbO in its determinable range was introduced into the tube by using a Pt wire at the center of the NPG tube. The obtained E_a values agree with that in the PG tube for the deposition of 1 ng of Pb as an aqueous solution. The following is expected in an NPG tube regarding deposition of a solid sample of PbO. The deposition of analyte as a solid sample results in a significant high density of Pb atoms in the condensed-phase, due to much less spreading and penetration. Since the Pb atoms in the high-density condensed-phase exhibit a significant interaction energy between the Pb atoms and the graphite wall, as well as in the case of a PG tube, its E_a value should agree with that in a PG tube for the deposition of 1 ng of Pb as an aqueous solution. The obtained E_a values are consistent with this expectation.

It was investigated whether the shift of T_{app} is responsible for the change in the atomization mechanism. When 20 µl of an aqueous solution contained 0.05 mg l⁻¹ of Pb was deposited, *i.e.* 1 ng of Pb, the T_{app} value was 1150 K in the NPG tube and 1050 K in the PG tube. The Pb atoms come from a species which had interacted with the graphite tube surface in the NPG tube and from bulk Pb metal in the PG tube. It can be assumed that this reduction in the T_{app} value results from a change in atomization mechanism, due to a change in the density of the analyte in the condensed phase. As the concentration in the deposited aqueous solution was raised to 20 mg l⁻¹ in the NPG tube, *i.e.* 400 ng of Pb, the observed E_a value corresponded to vaporization of bulk Pb metal, and its T_{app} value was observed to be 1000 K. Since solid PbO in the determinable range is deposited in the NPG tube, the observed E_a value also corresponded to a vaporization of bulk Pb metal, and its T_{app} value was observed to be 1080 K. The obtained T_{app} values are consistent with the above assumption.

References

1. C. H. Chung, E. Iwamoto and Y. Yamamoto, *Talanta*, **34**, 927 (1987).
2. J. P. Byrne, C. L. Chakrabarti, S. B. Chang, C. K. Tan and A. H. Delgado, *Fresenius' Z. Anal. Chem.*, **324**, 448 (1986).
3. C. L. Chakrabarti, C. C. Wan, R. J. Tesky, S. B. Chang, H. A. Hamed and P. C. Bertels, *Spectrochim. Acta*, **36B**, 427 (1981).
4. R. E. Sturgeon, C. L. Chakrabarti and C. H. Langford, *Anal. Chem.*, **48**, 1792 (1976).
5. S. Lynch, R. E. Sturgeon, V. T. Loung and D. Littlejohn, *J. Anal. At. Spectrom.*, **5**, 311 (1990).
6. S. Imai and Y. Hayashi, *Anal. Chem.*, **63**, 772 (1991).
7. C. H. Chung, *Anal. Chem.*, **56**, 2714 (1984).

(Received August 28, 1991)

(Accepted October 21, 1991)