Measurement of Effective Vapor Temperature in Graphite Furnace of Atomic Absorption Spectrometry

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The availability of several elements as a temperature indicator was studied. Suitable elements were Pd and Ni. Pb could be used only under the condition that Pb did not make an alloy with the matrix element. Sn was not useful because Sn in an alloy did work only in a very narrow dynamic range of temperature measurement. The correction factors of the experimental equations for each element were determined with air-acetylene and N_2O -acetylene flames. The factor obtained with the latter flame was found to be more accurate than that of the former. The effective vapor temperature in a graphite furnace was lower by several hundred degrees than the wall temperature when the factor obtained with the N_2O -acetylene flame was used. On the other hand, the factor obtained with the air-acetylene flame gave a vapor temperature in the furnace which was the same as that of the wall or slightly ($200^\circ C$) lower than it.

Keywords Effective vapor temperature, two-line method, palladium, nickel, lead, tin, graphite furnace, wall temperature

The wall temperature of graphite furnace is conventionally used as one of atomization temperatures of metals. In many cases, however, the temperatures of the sample itself and the atomic vapor being vaporized are different from the wall temperature. In order to make an analysis of the above phenomena, one must measure the temperature of the atomic vapor. In this paper, measurement of the atomic vapor temperature by atomic absorption spectrometry is described.

Several kinds of methods, such as the line reversal, the emission-absorption intensity ratio, and the slope of the Boltzmann plot, have been applied to measurements of the excitation temperature in flames, arc discharges and plasmas.¹⁻⁴ Since these methods were mostly based upon the phenomena of atomic emission, the line profile did not have to be considered, and only the integrated intensity was measured.

The two-line method for the temperature measurement by atomic absorption spectrometry has been investigated by L'vov,⁵ Chakrabarti *et al.*³, Siemer *et al.*⁶, van de Broek *et al.*⁷, Browner *et al.*⁸, Ide *et al.*⁹, and Kitagawa *et al.*¹⁰ These methods include the following conditions. The width of the emission line from the light source was much narrower than the absorption line width. The central wavelengths of the emission and the absorption lines exactly coincide with each other. However, since the ratio of the emission and the absorption line widths is about 1 : 5, both profiles could generally give an influence on the measurement of absorbance. In practice, the absorption line was recognized to shift to a longer wavelength.¹¹ In such a case, it is almost impossible to determine the real absorbance.

It is necessary to observe profiles of both the emission and the absorption lines, and to estimate the line-overlapping area.

The environment surrounding the atoms of interest in light sources such a hollow cathode lamp and an electrodeless discharge lamp is different from that in flames or in graphite furnaces. Accordingly, the difference in the species or concentrations of matrices causes discrepancies in the extent of the pressure effect (the Lorentz effect) on the atomic line. Owing to a big inequality of the pressure effect, the central wavelengths of the emission line from the light source and the absorption line do not coincide with each other, and both of the line profiles also become different. Yet, many studies on the two-line method of absorption have been based on assumptions that both central wavelengths are the same, and that the width of the emission line from the light source is much narrower than that of the absorption line. In the case of Zeeman atomic absorption spectrometry, it is more difficult to know the line profile, since absorption line splits in a complicated pattern depending upon isotopes.

Another way to adequately apply the two-absorption line method is to introduce an experimental correction factor C_f into an equation for the temperature calculation, which is determined by the two-absorption line method with the use of the air-acetylene flame. This method comes down to estimating a temperature of gas phase in the furnace by comparison with that of the air-acetylene flame. The technical difficulties involved in this method are the following. The absorbance observed in the flame is dependent upon the profiles of

contour lines of atomic density and the shapes of the beam from the light source at each cross section of the flame. It is difficult to define an adequate correction factor, because it is almost impossible to know where the light beam crosses over the contour lines of low or high atomic densities.

As a Zeeman atomic absorption spectrophotometer was used in this study, the line profiles were very complex and difficult to observe. Accordingly, the temperature calculation method by using the correction factor described above was applied in this study. The experimental equation used is given by Eq. (1), which was proposed by Reif *et al.*¹

$$\ln\left(\frac{g_{m1} \cdot A_{n1 \rightarrow m1} \cdot \nu_1}{B(em_1)}\right) - \ln\left(\frac{g_{m2} \cdot A_{n2 \rightarrow m2} \cdot \nu_2}{B(em_2)}\right) = \frac{E_{m1} - E_{m2}}{kT_{\text{eff}}} \quad (1)$$

Here, g is the degeneracy, T_{eff} is the effective vapor temperature*, and m_1 and m_2 are the ground state or the lower slightly higher level above the ground state. $B(em_1)$ and $B(em_2)$ are the induced transition probabilities from excited states n_1 and n_2 to m_1 and m_2 levels, respectively. $A_{n1 \rightarrow m1}$ and $A_{n2 \rightarrow m2}$ are the spontaneous transition probabilities. ν is frequency. This equation can be simplified into Eq. (2):

$$T_{\text{eff}} = \frac{E_{m2} - E_{m1}}{\ln\left(C_f \cdot \frac{\text{Abs.}(m_1 \rightarrow n_1)}{\text{Abs.}(m_2 \rightarrow n_2)}\right)} \quad (2)$$

Here, $\text{Abs.}(m_1 \rightarrow n_1)$ or $\text{Abs.}(m_2 \rightarrow n_2)$ corresponds to $B(em_1)$ or $B(em_2)$ ¹, and C_f is the correction factor. The intersectional area between the contour map of atomic density and the shape of the light beam is different in each flame and under each burning condition. In order to overcome this problem, two kinds of flames were chosen, and the following experimental procedures were established.

Experimental

Procedure for determination of C_f value

1-1. To select suitable elements, absorbances of the two lines for several elements are measured with the air-acetylene and N_2O -acetylene flames, and the correction factor C_f in Eq. (2) is calculated.

1-2. Comparing the C_f values obtained with the two different flames, and choosing the elements being yielded closer C_f values. This is necessary because errors occurring from the differences in the spatial distribution of atomic density in the flames should be eliminated.

* There are many expressions to this temperature as follows: excitation temp.^{9,10}, gas phase temp.⁴, furnace atmosphere temp.², effective gas phase temp.⁶, gas temp.⁷, effective vapor temp.³ and so forth are used.

2-1. Of several two-line pairs of thus selected *elements*, suitable two-line pairs giving a closer C_f value are nominated.

2-2. For the selected line pairs of the chosen *elements*, each C_f value is checked under fuel-lean and fuel-rich conditions of the flames, and the best line pair is chosen on the basis of the closest C_f value.

3. Choice of element as the reference temperature indicator. Using the best line pair, (a) temperatures on the fuel-lean and fuel-rich conditions are determined on the assumption that the temperature under the stoichiometric condition of the air-acetylene flame is 2600 K.¹² (b) The same measurement is made in the N_2O -acetylene flame. The temperature on the stoichiometric condition is assumed to be 3000 K.^{8,13} The *element* and *line pair* selected are used as the reference temperature indicator.

4. Setting up the experimental equation for each element. C_f value for each element in each burning condition of each flame is determined with use of the reference temperature indicator. The C_f values obtained under the extremely fuel-lean and fuel-rich conditions which are not routinely used in atomic absorption measurements are eliminated. Finally, the experimental equations are derived for each element.

Experimental measurement of C_f values

A Zeeman atomic absorption spectrophotometer with a flame assembly (Hitachi Z-6000) was used. This utilizes the inverse polarized Zeeman effect, in which a magnetic field is applied to the flame.

1. The C_f values for Ni, Pb, Pd and Sn were determined with the air-acetylene and N_2O -acetylene flames under different conditions from fuel-lean (the stoichiometric condition; which is at the left-most side of the measured points in Fig. 1) to fuel-rich conditions. The C_f values of Ni obtained with the air-acetylene and N_2O -acetylene flames are closer than the others. Ni was therefore chosen as the reference element for the temperature indicator.

Fig. 1 Flame temperature.

Table 1 Ratio of C_f values

	229.0 nm (0→) ^a	323.3 nm (0→) ^a	337.0 nm (0→) ^a	233.7 nm (0→) ^a
232.6 nm (1332→) ^b	0.94	0.94	0.91	0.85
301.2 nm (3410→) ^b	1.42	1.41	1.37	1.28
338.1 nm (3410→) ^b	1.53	1.52	1.47	1.38
356.6 nm (3410→) ^b	1.24	1.24	1.21	1.12
361.9 nm (3410→) ^b	1.44	1.43	1.39	1.30

a. Transition from the ground state.

b. Transition from the non-ground state located at a higher energy level, and the number in the parentheses indicates the energy gap expressed in wavenumber (cm^{-1}).

2. The ratios of C_f values (C_f in N_2O -acetylene/ C_f in air-acetylene) in each pair of Ni lines are listed in Table 1. It seems that the two-line pairs of 229.0/232.6 nm, 323.3/232.6 nm and 337.0/232.6 nm are desirable, because the ratios are closer to unity. Unfortunately, as the atomic line of 232.6 nm has highly intense neighboring lines, these two-line pairs were not available because a wide slit was employed for measurements on a multi-channel atomic absorption spectrophotometer. This caused some spectral interference of the neighboring lines with the line at 232.6 nm. Finally, the 233.7 and 356.6 nm were chosen as the optimum pair, and the experimental equation was derived.

3. The flame condition was altered by change of the flow rate of acetylene from 1.5 to 2.5 l/min in the air-acetylene flame. The flow rate of air was kept at 15.0 l/min throughout this experiment. We assumed that the flame temperature at an acetylene flow rate of 1.5 l/min is 2600 K.

In the case of the N_2O -acetylene flame, the flame temperature was assumed to be 3000 K under the condition of N_2O and acetylene flow rates of 6.0 l/min and 3.8 l/min, respectively. The flame temperatures were measured under different flame conditions from fuel-lean to fuel-rich. The most conventional flame conditions are flow rates of acetylene between 4.8 l/min and 5.5 l/min. The corresponding temperatures range from 2950 K to 2850 K (see Fig. 1). These values are in good agreement with the results obtained by Browner *et al.*⁸ The temperature curve shown in Fig. 1 was used as the reference temperature, based on which the C_f value for each element was estimated.

4. The C_f values of the experimental equations for each element were obtained by changing the flame conditions. The flow rate of acetylene of the air-acetylene flame changed from 1.5 to 2.5 l/min and that of the N_2O -acetylene flame from 3.8 to 5.8 l/min.

The line pair of Ni 233.7/356.6 nm did not have

enough intensity for the multi-channel atomic absorption spectrophotometer. Therefore, this line pair was replaced by another pair: 323.3/356.7 nm. Sample concentrations were adjusted to about 100 g/ml so that the absorbance did not exceed 0.25.

Measurement of effective vapor temperature in a graphite furnace

A multi-channel atomic absorption spectrophotometer (Hitachi Z-9000) was used, because the simultaneous two-line measurement is feasible. This is also the inverse polarized Zeeman atomic absorption configuration in which the magnetic field crosses the graphite furnace. Light beams from two hollow cathode lamps for an element were focused in the central part of the furnace, and atomic absorptions were simultaneously measured at two different wavelengths.

Two kinds of atomization were studied. One was a slow atomization under the condition that the temperature was linearly rising from 1000°C to 3000°C during 20 s, and the other was a rapid atomization controlled by an opto-pyrometric feedback circuit. Two kinds of sample conditions were applied; in the presence and in the absence of Pd matrix modifier. As the modifier for Pd measurement, Ni was used. Measurements of the wall temperature of the graphite furnace were made by an optical pyrometer, which was calibrated by measurement of the melting point of Mo. The gas flow of argon inside of the furnace was stopped when the atomization process started.

Results and Discussion

The flame temperatures estimated on different conditions are shown in Fig. 1; these were used as the reference temperatures. The flame temperature on the conditions used for routine atomic absorption measurements (a flow rate of acetylene of 1.7 l/min) was found to be about 2400 K. This value is close to those obtained by Browner *et al.*⁸ and Ide *et al.*⁹

The C_f values thus obtained for the test elements are listed in Table 2.

The T_{eff} values calculated from Eq. (2) in the presence and absence of the matrix modifier on the slow atomization are plotted in Figs. 2a and 2b, respectively.

Table 2 Correction factor C_f

	Line pair (nm)	Air-C ₂ H ₂	N ₂ O-C ₂ H ₂
Ni	323.3/356.7	3.41	4.29
Pb	368.3/280.2	1.44	1.89
Pd	276.3/340.5	9.30	18.1
Sn	224.6/284.0		2.50

Because the burning condition of the air-acetylene flame for the Sn measurement was so different from the others, the datum is not shown.

Fig. 2 Effective vapor temperature in graphite furnace. Solid line indicates wall temperature. $\blacktriangle, \triangle$, Ni (C_f 3.41 and 4.29); $\bullet, \circ$, Pb (C_f 1.44 and 1.89); $\blacksquare, \square$, Pd (C_f 9.30 and 18.1); $*$, Sn (C_f 2.50). a, slow atomization in the absence of the matrix modifier; b, slow atomization in the presence of the matrix modifier; c, rapid atomization in the absence of the matrix modifier; d, rapid atomization in the presence of matrix modifier.

Those obtained on the rapid atomization are presented in Figs. 2c and 2d, respectively. The summarized data are shown in Table 3.

Ni as a temperature indicator

Slow atomization. As seen from comparison between the results in Figs. 2a and 2b, the effective vapor temperature was not influenced by the Pd matrix modifier. T_{eff} estimated with $C_f=3.41$ was lower than the wall temperature by about 300°C. The value of this

temperature difference is similar to that obtained by Chakrabarti *et al.*³

The T_{eff} values obtained with Pb, Pd and Ni are located on the same line. The T_{eff} values with $C_f=4.29$ are lower than the wall temperature by about 600°C.

Rapid atomization. The T_{eff} values estimated with $C_f=3.41$ and 4.29 are lower than the wall temperature by ca. 100°C and 600°C, respectively. This difference becomes larger at higher regions of the effective vapor temperature. T_{eff} becomes higher by 200°C in the pres-

Table 3 Working and dynamic ranges of the effective vapor temperature (K) in graphite furnace

C_f	Slow atomization				Rapid atomization			
	No matrix modifier		Matrix modifier		No matrix modifier		Matrix modifier	
	Working range	Dynamic range	Working range	Dynamic range	Working range	Dynamic range	Working range	Dynamic range
Ni	3.41	1700–2400	700	1700–2400	700	2000–3100	1100	1900–3100
	4.29	1400–2100	700	1400–2100	700	1900–2600	700	1800–2600
Pb	1.44	1000–2200	1200	1300–2000	700	1300–2100	800	2200–3100
	1.89	900–1600	700	1100–1600	500	1200–2300	900	1800–2600
Pd	9.30	1900–2600	700	1900–2600	700	2000–3400	1400	2400–3500
	18.1	1600–2100	500	1600–2100	500	1600–2500	900	1900–2600
Sn	2.50	1200–2000	800	1600–1700	100	1700–2000	300	2000–2300

ence of the Pd matrix modifier than in its absence (see Figs. 2c and 2d). The T_{eff} curve obtained with Ni in the absence of Pd matrix modifier, which is located under the T_{eff} curve with Pd, shifts to a higher temperature region when the Pd matrix modifier exists. As a result, the T_{eff} curve obtained with Ni slightly exceeded that with Pd. The appearance and residence times of the signal peak also become shorter.

Pb as a temperature indicator

Slow atomization. In the absence of the Pd matrix modifier, T_{eff} estimated with $C_f=1.44$ is lower by about 200°C than the wall temperature. This temperature difference is almost the same as that obtained by Chakrabarti *et al.*³ The dynamic range is wider, as seen in Table 3. T_{eff} with $C_f=1.89$ is lower by 500°C to 600°C than the wall temperature. The difference becomes larger as T_{eff} becomes higher. In the presence of the matrix modifier, the temperature-rising becomes faster. The appearance and residence times of the signal peak also become shorter.

Rapid atomization. In the absence of the matrix modifier, the T_{eff} curve obtained with Pb is in line with the T_{eff} curve with Pd, and almost the same as the wall temperature. The T_{eff} curve with $C_f=1.89$ is lower by about 200°C than the wall temperature. In the presence of the matrix modifier, the appearance time of the signal peak is delayed, and T_{eff} is higher by about 200°C than that in the absence.

Pd as a temperature indicator

Slow atomization. In the absence of the Ni matrix modifier, T_{eff} estimated with $C_f=9.30$ is lower by about 300°C than the wall temperature. The rising curve of T_{eff} shows almost the same behavior as that of the wall temperature, and shows the same trend as well as that obtained with Ni. T_{eff} with $C_f=18.1$ is lower by about 700°C than the wall temperature, and also 100°C lower than the T_{eff} curve obtained with Ni. Addition of the Ni matrix modifier had little effect on this T_{eff} .

Rapid atomization. In the absence of the matrix modifier, T_{eff} with $C_f=9.30$ is almost the same as the wall temperature. The maximum value of T_{eff} exceeds that

of the wall temperature and is 200°C higher than the T_{eff} curve obtained with Ni. T_{eff} with $C_f=18.1$ was about 200°C lower than the wall temperature in the lower T_{eff} region. This difference becomes larger and reaches 700°C in the higher T_{eff} region. In the presence of the matrix modifier, the appearance time of the signal peak is delayed, and the T_{eff} curve has a steep slope. However, the maximum temperatures of T_{eff} are the same under both conditions.

Sn as a temperature indicator

Slow atomization. In the absence of the matrix modifier, the working range of the effective vapor temperature is from 1200 K through 2000 K, which is a wider dynamic range (800°C) than that of the others. On the other hand, the signal peak exists for a short residence time or within a narrow temperature range of about 100°C in the presence of the matrix modifier.

Rapid atomization. The residence time of the signal peak is limited within a short period, which corresponded to the effective vapor temperature range of about 300°C. In the presence of the matrix modifier, the peak appearance time is delayed, and T_{eff} becomes higher. However, the dynamic range of the effective vapor temperature is too narrow, *i.e.* about 300°C, regardless of the presence or absence of the matrix modifier.

The phenomena described above are summarized as follows.

On slow atomization: the effective vapor temperatures obtained with Pd and Ni were not much influenced by addition of the matrix modifier. Appearance of Pb signal was delayed by addition of the modifier. The Sn signal became very sharp in the presence of the matrix modifier. The T_{eff} 's obtained with Pb, Ni and Pd were lower by about 200°C than the wall temperature, and they are located on the same curve on the time scale when the C_f values were corrected by the results obtained with the air-acetylene flame.

On rapid atomization: every effective vapor temperature was influenced by the presence of the matrix modifier. The appearance of the Pd, Pb and Sn signals were delayed by addition of the modifier. In the

presence of the matrix modifier, the effective vapor temperatures obtained with Pb and Sn became higher than those in their absence.

The width and length of fire tail of the air-acetylene flame were narrower and shorter than those of the N_2O -acetylene flame, respectively. Consequently, the contour lines in the atomic density map densely existed. Therefore, it was not certain that the light beam from the hollow cathode lamp passed only through the high density area of atomic vapor in the air-acetylene flame. This problem was also suggested by the evidence that the T_{eff} values obtained with the N_2O -acetylene flame were lower than those with the air-acetylene flame. T_{eff} obtained with Sn by making use of the N_2O -acetylene flame in the presence of the Pd modifier was 1664 K which was close to the melting temperatures of Pd_3Sn (1599 K) and Pd_2Sn alloy (1560 K).¹⁴ Therefore, these results suggest that the N_2O -acetylene flame is preferable for the determination of the C_f value.

Another problem is as follows. The wall temperature was measured in the middle part of the furnace, while the effective vapor temperature obtained by the two-line method includes that in the central part, but also includes that in the low temperature regions at both ends of the furnace. In other words, the area where the wall temperature was measured was not identical with the area where the effective vapor temperature was measured. It is necessary to correct the effective vapor temperature in conjunction with the longitudinal distribution. The effective temperature in the middle part of the furnace might be slightly higher than that observed in this experiment.

Pd and Ni were found to be widely used as temperature indicators. It should be noted that, even under severe conditions, or rapid atomization, the effective vapor temperature obtained with Pd was less influenced by the presence of a matrix modifier than that with Ni. Sn is not preferred, because its dynamic range was too narrow.

This is probably due to the formation of its alloy with the matrix element.

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