Temperature Measurement by Maximum Absorbance Comparison Method—A Resonance Line and Doublet Lines of Lead—

Yukio IDE, Masaaki YANAGISAWA,
Kuniyuki KITAGAWA and Tsugio TAKEUCHI

Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464

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井手由紀雄, 柳沢雅明, 北川邦行, 武内次夫

名古屋大学工学部合成化学科, 名古屋市千種区不老町 (〒464)

The measurement of excitation temperature has usually been carried out by comparing intensities of a pair of emission lines. On the other hand, the measurement of lower temperature that can not be achieved by the above method has been required in flameless atomic absorption spectrometry with an electrically heated strip atomizer. To meet this requirement we propose a theory for the measurement of excitation temperatures in atomic absorption spectrometry that uses a pair of lead absorption lines having different lower levels. The theory has been successfully applied to flameless systems using a tantalum and a glassy carbon strip, and also to an air-acetylene flame system. The equation for calculating the excitation temperature T is given by $\exp[0.797A_R \exp(-11240/T)] + 14.21 \exp[-11.32A_R \exp(-11240/T)] - 15.21 \exp(-A) = 0$ in terms of the apparent absorbance for the lead doublet, A , and of that for the resonance line, A_R . It is recommended to use the present method in discussing the degree of dissociation or the effect of chemical interferences in practical atomic absorption spectrometry.

1. Introduction

Temperature determination is the basis of evaluating diverse properties associated with atomic absorption spectrometry, such as the degree of dissociation, atomic population and so on. Winefordner¹⁾ reported a two-line method for atomic absorption of In, Ga or Tl, but no worker has published a paper concerning the measurement of temperature directly above electrically heated atom reservoirs by means of the maximum absorbance

comparison method.

In the present paper, a method is described for the measurement of the excitation temperature, utilizing a resonance line and doublet lines of lead which have different lower energies. Atomic excitation temperature above electrically heated atom reservoirs (tantalum or glassy carbon strip^{2,3)}) is examined in an argon atmosphere. It is also shown that the excitation temperature of analytical flame can be determined quickly with this method.

2. Theory

If the current for a hollow cathode lamp is small enough for one component of the doublet lines not to be absorbed by the other and the spectral band-pass width of a monochromator is wide enough to pass them through, the apparent absorbance for the doublet can be expressed as

$$A = \ln [(I_1^0 + I_2^0)/(I_1 + I_2)], \quad (1)$$

where I_1^0 , I_2^0 and I_1 , I_2 are the intensity of the incident- and the transmitted- light, respectively. Subscripts 1 and 2 stand for the components 1 and 2 of the doublet, respectively.

The intensity of the incident light, I_1^0 and I_2^0 are written as^{4,5)}

$$I_2^0 = [(g_2 f_2 \lambda_1^3)/(g_1 f_1 \lambda_2^3)] I_1^0 \exp[(E_{1h} - E_{2h})/(kT_H)], \quad (2)$$

where g_1 and g_2 , f_1 and f_2 , λ_1 and λ_2 , and E_{1h} and E_{2h} are the statistical weight, the oscillator strength, the wavelength, the upper state energy for the doublet lines, respectively, k is the Boltzmann constant and T_H is the excitation temperature in the hollow cathode lamp.

Since $E_{1h} - E_{2h}$ is small and T_H is high, the factor $\exp[(E_{1h} - E_{2h})/kT_H]$ in Eq. (2) can be replaced by unity; i.e.,

$$I_2^0 = \frac{g_2 f_2 \lambda_1^3}{g_1 f_1 \lambda_2^3} I_1^0. \quad (3)$$

The intensity of the transmitted light, I_1 and I_2 may be expressed as

$$I_1 = I_1^0 \exp(-K_{1, \max} l)$$

$$\text{and} \quad I_2 = I_2^0 \exp(-K_{2, \max} l),$$

where $K_{1, \max}$ and $K_{2, \max}$ are maximum absorbances for the doublet lines and l is the thickness of the absorbing layer. Then, Eq. (1) becomes

$$e^A = \left(1 + \frac{g_2 f_2 \lambda_1^3}{g_1 f_1 \lambda_2^3}\right) \left[\exp(-K_{1, \max} l) + \frac{g_2 f_2 \lambda_1^3}{g_1 f_1 \lambda_2^3} \exp(-K_{2, \max} l) \right]. \quad (4)$$

We have

$$\Delta\nu_D = 2\sqrt{\frac{2R \ln 2}{c}} \nu_0 \sqrt{\frac{T}{M}}, \quad (5)$$

where $\Delta\nu_D$, R , c , T , and M are the Doppler breadth, the gas constant, the light velocity, the absolute temperature of gas and the molecular weight, respectively.

When, on the other hand, the doppler broadening alone is present, the maximum absorption coefficient, K_0 , can be calculated by

$$K_0 = \frac{2}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\pi e^2}{mc} N f, \quad (6)$$

where $N = [N_0 g/Q(T)] \exp(-E/kT)$ and $Q(T)$ is the partition function of atom.

When Eq. (5) is substituted into Eq. (6), K_0 becomes

$$K_0 = \frac{\pi e^2}{mc} \sqrt{\frac{M}{2\pi RT}} \frac{N_0 g f \lambda_0}{Q(T)} \exp\left(\frac{-E}{kT}\right). \quad (7)$$

Using Eq. (7), we have

$$\frac{K_{1, \max} l}{K_{R, \max} l} = \frac{g_1 f_1 \lambda_1}{g_R f_R \lambda_R} \exp\left(\frac{E_{LR} - E_{L1}}{kT}\right), \quad (8)$$

$$\frac{K_{2, \max} l}{K_{R, \max} l} = \frac{g_2 f_2 \lambda_2}{g_R f_R \lambda_R} \exp\left(\frac{E_{LR} - E_{L2}}{kT}\right), \quad (9)$$

where the subscripts L and R stand for the lower energy level and resonance line, respectively. Since $E_{LR} = 0$ and $K_{R, \max} l = A_R$, Eqs. (8) and (9) are written as

$$K_{1, \max} l = A_R \frac{g_1 f_1 \lambda_1}{g_R f_R \lambda_R} \exp\left(\frac{-E_{L1}}{kT}\right), \quad (10)$$

$$K_{2, \max} l = A_R \frac{g_2 f_2 \lambda_2}{g_R f_R \lambda_R} \exp\left(\frac{-E_{L2}}{kT}\right). \quad (11)$$

Substituting Eqs. (10) and (11) into Eq. (4), we obtain

$$\begin{aligned} \exp \left[-A_R \frac{g_1 f_1 \lambda_1}{g_R f_R \lambda_R} \exp\left(\frac{-E_{L1}}{kT}\right) \right] \\ + \frac{g_2 f_2 \lambda_2^3}{g_1 f_1 \lambda_2^3} \exp \left[-A_R \frac{g_2 f_2 \lambda_2}{g_R f_R \lambda_R} \exp\left(\frac{-E_{L2}}{kT}\right) \right] \\ - \left(1 + \frac{g_2 f_2 \lambda_2^3}{g_1 f_1 \lambda_2^3}\right) \exp(-A) = 0. \end{aligned} \quad (12)$$

Table I. Physical properties of lead⁽⁹⁾.

Lines		Wavelength (nm)	<i>gf</i> -values	Energy Levels (eV)
Resonance line (<i>A_R</i>)		283.3	0.22	0—4.375
Doublet lines (<i>A</i>)	1	261.37	0.19	0.969—5.711
	2	261.42	2.7	0.969—5.712

As for the Pb 1 lines in Table I, Eq. (12) can be written as

$$\begin{aligned} & \exp[-0.797A_R \exp(-11240/T)] \\ & + 14.21 \exp[-11.32A_R \exp(-11240/T)] \\ & - 15.21 \exp(-A) = 0. \end{aligned} \quad (13)$$

If *A* and *A_R* are provided as data, *T* can be computed with trials-and-errors calculation by a computer.

3. Experimental

Apparatus A Nippon Jarrell-Ash AA-1E atomic absorption and atomic emission spectrometer fitted with an electrically heated atomizer was used. The radiation from a hollow cathode lamp of lead (current of 7 mA) was focused right above the center of the atomizer through a lens and a tantalum slit (0.5 mm dia.) A Hitachi Model QPD-54 recorder was employed. The atomizer system was designed to allow the strip to move over a range of 15 mm.

Reagents Standard lead solutions of 1 mg/ml were prepared by dissolving pure metal in a minimum amount of nitric acid and diluted just before using them.

Procedure Aliquots of 4 ng (2 ppm, 2 μ l) and 10 μ g (5000 ppm, 2 μ l) were taken for the measurements of the resonance line and the doublet, respectively, on the depression of the strip using a 5 μ l syringe (S.G.E., PTY., Co., Australia). The atmosphere in the chamber was purged by a regulated stream of argon gas (2.1 l/min.). Evaporation of the solvent was carried out at a low temperature (ca. 100–200°C), and followed by atomization at higher temperature. All atomic absorption signals were recorded as a peak and the absorbance was calculated from the peak height. The temperature on the surface of

the strip was measured with an optical pyrometer which was corrected for spectral emissivities, 0.3 for tantalum and 0.8 for glassy carbon strips.

4. Results and Discussion

4.1 Temperature of the electrically heated atom reservoir

Figure 1 shows the results of temperature measurements for two kinds of atomizers. Temperature measurements were carried out using the beam of about 1 mm diameter in the range of a few millimeters above the atomizer. The absorbance for the doublet lines was observed to be much lower value compared with that for the resonance line, but a linear relationship between the absorbance and the concentration was obtained in the range of 0 to 10 μ g. As is seen in Fig. 2 the observed excitation temperature of lead increases monotonically as the set temperature of the glassy carbon strip increases. However, the increment of the excitation temperature decreases for higher final temperatures, suggesting that atomization of lead must have ended before the final temperature is attained partly because there exists a remarkable leading time for the strip to reach the equilibrium final temperature. Furthermore, oscilloscopic mea-

Fig. 1. Excitation temperature of lead measured at above a tantalum (at 2000°K) and a glassy carbon (at 1800°K) strip atomizer. A: Tantalum strip, B: Glassy carbon strip, Flow rate of argon: 2.1 l/min.

Fig. 2. Excitation temperature of lead vs final temperature of a glassy carbon strip. Flow rate of argon: 2.1 l/min., Height of the beam above the glassy carbon strip: 0.5 mm.

measurements of the transient temperature change also revealed that the atomization of lead was completed at much lower temperature than the finally attained temperature of the strip. For example, the atomization of lead started at 1000°K and finished at 1200°K, showing a maximum at 1100°K when the final temperature was set at 1800°K.

Fig. 3. Excitation temperature of air-acetylene flame measured by the present method as a function of the flow rate of acetylene. Height of the beam above the burner top: 5.5 mm, Diameter of the beam: 3.0 mm.

4.2 Excitation temperature of air-acetylene flame

The present method is also applicable to rapid determination of flame temperatures in analytical flame, simply measuring the absorbance of characteristic lead lines. Figure 3 shows variation of the temperature at 5.5 mm above the burner top as a function of the acetylene flow rate under the constant air flow rate. Figure 4 shows the temperature variations as a function of height above the burner top. The precision of the measurement obtained was about 7%, mainly due to sampling error for the flameless atomization and less than 2% for the flame.

Fig. 4. Excitation temperature of air-acetylene flames measured by the present method as a function of the height above the burner top. Flow rate of acetylene: 2.1 l/min (A), 1.8 l/min (B), Diameter of the beam: 3.0 mm.

5. Conclusion

The present method is promising for estimating relatively low temperature in flameless atomizers, that seems to be difficult to measure by emission method, and is applicable to elements, such as nickel containing a pair of absorption lines having different lower levels. The excitation temperature of flame can easily be measure by this method.

References

- 1) R.F. Browner and J.D. Winefordner: *Anal. Chem.* **44**, 247 (1972).
- 2) T. Takeuch, M. Yanagisawa and M. Suzuki: *Talanta* **12**, 989 (1965).
- 3) M. Yanagisawa and T. Takeuchi: *Japan Analyst* **23**, 364 (1974).
- 4) R.H. Tourin: *Spectroscopic Gas Temperature Measurement* (Elsevier Pub. Co., Amsterdam, 1966).
- 5) J.E. Forretle and E. Lanternman: *Development in Applied Spectroscopy* (Plenum Press, New York, 1964), vol. 3.
- 6) R. Mavrodineanu and H. Boitenx: *Flame Spectroscopy* (John Wiley and Sons, Inc., New York, 1965).