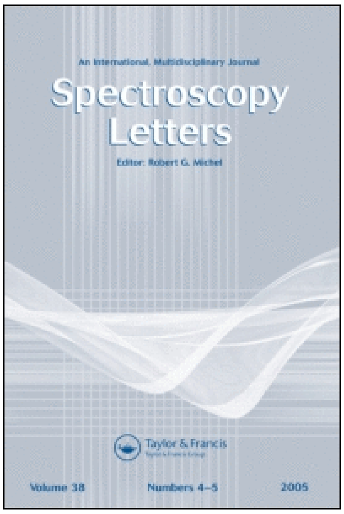

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CHARACTERISTIC MASS AND ATOMIZATION EFFICIENCY OF GRAPHITE FURNACE IN ATOMIC ABSORPTION SPECTROMETRY

Key words: Charateristic mass, atomization efficiency, atomic absorption spectrometry.

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Abstract

Measurements of characteristic masses for 8 elements (Ag, Bi, Cd, Cr, Ga, Ge, In and Tl) have been made using a Hitachi GA-3 graphite furnace with the V-shaped boat over broad temperature intervals. The m_0(exp) values are compared with theoretical data, m_0(cal), to assess the effect of temperature on the correction factor of theorization for value of characteristic mass ($\alpha = m_0(cal)/m_0(exp)$) and the atomization efficiency(β). The atomization efficiency(β) was equal to the correction factor of theorization for characteristic mass value (α) times τ_D/τ_R value. The τ_R was value experimentally measured of atomic residence time and the τ_D value calculated from $\tau_D = l^2/8D$. The β value of element always is smaller than the α value because the τ_D/τ_R value is less than one for elements in the operating conditions. Part of the analyte vapour is readsorbed by the heated tube wall at high temperature and reevaporation of the adsorbed analyte followed by diffusion account for the longer residence time, and it appeared that the τ_R value was larger than the τ_D in graphite furnace.

Introduction

Absolute analysis can be understanded as the ability to correcte the absorbance to the number of analyte atoms deposited into the graphite furnace through a theoretical fundamental equation for the given measurement conditions. When graphite furnace atomic absorption spectrometry was first introduced by L'vov in 1959[1], the possibility was recognized and was pursued up to now with increasingly refined adjusmant and conditions to the experimental data. Unifortunately, it is the difficult that providing an absolute analysis resulted from the use of the peak height absorbance measurement and from the temporal and spatial nonisothermality of commercial atomizer. To overcome these difficulties, it was proposed to measure integrated absorbance and to employ some techniques aimed at removing or reducing the temporal nonisothermality of the furnace. These suggestions together with a number of additional methodological and instrumental developments, have been incorporated in the so-called STPF-concept (stabilized temperature platform furnace)[2]. The term characteristic mass, m_0, the mass of analyte in pg giving a peak area of 0.0044 absorbance · s, has been introduced to describe GFAAS performance, and m_0 (exp) values have been shown to be relatively independent of sample matrix and stable in time when STPF conditions are applied[3-5]. Therefore, the STPF fulfils the requirement for absolute analysis.

Theoretical characteristic masses were calculated, m_0 (cal), and compared with experimental values m_0 (exp) by L'vov et. al.[6, 7]. For 32 elements measured under STPF conditions, the mean value of m_0 (cal) / m_0 (exp) was found to be 0.85 with a SD of 0.10. Baxter and Frech[8] have pointed out that the temperature gradient over length of tube may be the limiting factor for absolute analysis by GFAAS. Afterward they have studied the temperature dependence of m_0 (cal) / m_0 (exp) of some elements in two-step atomizer and pointed out that the value of m_0 (cal) / m_0 (exp) for most elements reaches a plateau, ofter in the higher temperature region[9]. The atomization efficiency of the method above mentioned is actually assumed 100% and the m_0 (exp) values deviate from the m_0 (cal) must include all the factors influencing the atomization process in the furnace.

The atomization efficiency is a main factor which decides the sensitivity and the limit of detection of the analytical method in GFAAS. The measurement of atomization efficiency of graphite furnace has been reported in literature[10-14]. Of course, the atomization efficiencies above mentioned were evaluated by the peak height measurement technique with sample vaporized from the tube wall under the condition of continuously increasing temperature. Thus in these cases the measurement conditions were far from conforming to the requirements of STPF. However, Zheng[15] has reported the evaluation of atomization efficency of graphite furnace by peak area measurement technique with sample vaporized from the V-boat and the platform. Thus in this case the measuurement conditions were to fulfil the requirement of STPF. But the experimental values of atomization efficiencies for Ag, Cd, Cr, Ge and In obtained by Zheng were about 2-60%, and it was more less than the m_0 (cal)/m_0 (exp) value in the same meausrement conditoin. Therefore, it would be useful for developing and improving absolute analysis to understand and to investigate the characteristic mass dependence of atomization efficiency in atomic absorption spectrometry.

The present work was undertaken in order to determine the characteristic mass and the atomization efficiency of Hitachi GA-3 graphite furnace for Ag, Bi, Cd, Cr, Ga, Ge, In and Tl. Here the experimental value of atomization efficiency was studied over a wide temperature range for elements above mentioned by comparing characteristic mass obtained from experiment and calculation at each temperature. Experiments were purformed using a V-shaped boat-equipped massmann-type furnace.

Theory

The absolute number of analyte atoms inside the graphite furnace is obtained by measuring the absorbance of a spectral line. At any time, t, the relation between these two quantities can be expressed as[6]

$$A(t) = KN(t)/S_c \qquad (1)$$

Here A(t) is the instantaneous absorbance at time t, Sc is the cross-section of the furnace, K is the atomic absorption coefficient and N(t) is the total number of free analyte atoms in the analysis volume in the furnace at any time t. Equation (1) is valid only if the atoms are homogeneously distributed in planes perpendicular to light beam because otherwise A(t) will not be linearly related to N(t). The constant K can be expressed as[7]

$$K = \frac{0.43\sqrt{4\pi \ln 2}\, e^2 g_l \exp(-E_l/kT)\, \Psi\, \delta\, f H(a,\, \omega)}{m_e C^2 \Delta \nu_D Z(T)} \qquad (2)$$

Here m_e and e are the electon mass and charge, C is the velocity of light, g_l, and E_l are the statistical weight and energy of the lower level for the analytical line, respectively, k is the Boltzmann constant, Z(T) is the partition function at temperature T, f is the oscillator strength, $\Delta \nu_D$ is the Dopple line width of absorption line, H(a, ω) is Voigt integral for the point of the absorption line contour distant from the line centre by $\omega = 0.72a$ (here a is the damping constant of the Voigt profile), Ψ is a coefficient accounting for hyperfine splitting in the analytical line and the Doppler line width in the source, δ is a correction factor for adjacent lines in light source spectrum.

Now its use has been almost substituted by peak area measurement because peak hight absorbance is a value strongly dependent on the experimental conditions of the atomization and on the sample matrix. If the analyte is completely atomized and if all of analyte atoms enter into the analysis volume, the integral value of N(t) can be expressed through the total number of analyte atoms introduced into the furnace (N_0) and residence time of atoms (τ_R)[10]

$$\int_0^{\infty} N(t)\, dt = \tau_R N_0 \qquad (3)$$

However, it must be pointed out that not all of the analytes which were released from the surface of the tube necessarily atomized and enter into the analysis volume, a fraction of them may be lost. The dispersion of analyte atoms must consider the readsorption of atoms in vapour phase on the surface of the tube and the molecular formation of thermal stability except diffusion, explosion and convection. Therefore, a correction factor (β) must be used to account for the atomic loss at each stage of atomization[16]. It is defined atomization efficiency and accounts for the fraction of the total number of analyte atoms that enter into the analysis volume during each stage of atomization. Thus equation (3) takes the following form

$$\int_0^\infty N(t)\,dt = \beta\,\tau_R N_O \qquad (4)$$

The integration of equation (1) and taking account of equation (4) yield

$$A_i = \int_0^\infty A(t)\,dt = K\,\beta N_O\,\tau_R/S_c \qquad (5)$$

Here A_i is the integrated absorbance.
We recall that

$$N_O = m_a N_A/M_a \qquad (6)$$

Here m_a is the analyte mass, N_A is the Avogadro number and M_a is the molar mass of analyte.
Substituting equation (6) into equation (5) yields

$$A_i = K\,\beta m_a N_A\,\tau_R/S_c M_a \qquad (7)$$

If K' is used in place of K, then the equation (7) becomes

$$A_i = K' m_a N_A\,\tau_R/S_c M_a \qquad (8)$$

and

$$\beta = K'/K \qquad (9)$$

The constant K' is the apparent atomic absorption coefficient. The atomic absorption coefficient (K) is the absorption character of atomic species and it is dependent only on the absorption line shape and relates to the source profile. However, the apparent atomic absorption coefficient (K') is dependent on environmental factors, the experimental conditions must be specified when discussing the K' value of an element. The β value of an element which is defined atomization efficiency is equal to the ratio of K'/K in this paper.

In the literature following an IUPAC indication, the quantity used for the evaluation of a method or an atomizer is not K or K', but m_O(exp), and the m_O(exp) value can be calculated from the integrated absorbance using following formula

$$m_O(\mathrm{exp}) = (0.0044\ A\cdot s/A_i)\,m_a \qquad (10)$$

Substituting equation (10) into equation (8) and taking account of equation (9) yield[15]

$$\beta = 2.30\times10^{-14} r^2 M_a / K \tau_R m_O(\mathrm{exp}) \qquad (11)$$

Here r is the tube radius and unit of $m_o(\mathrm{exp})$ is pg.

According to the model of L'vov et. al[6], the analyte is totally atomized and the removal proceeds exclusively via diffusion through the tube ends. Thus the equation (7) is simplified

$$A_i = K m_a N_A \tau_D / S_c M_a \qquad (12)$$

and

$$\tau_D = l^2/8D \qquad (13)$$

Here l is the tube lenght and D is the diffusion coefficient of the analyte atoms considered. Assuming A_i = 0.0044 A · s, we derive from equation (12) a relation to calculate the theoretical value of characteristic mass on the basis of L'vov model[7]

$$m_O(\mathrm{cal}) = 2.30\times10^{-14} r^2 M_a / K \tau_D \qquad (14)$$

We know that the K value can be calculated from the equation (2) on the basis of physical parameters of element determined, and its value is only dependent on the temperature, but independent on the experimental conditions for given analytical line and light source. The $m_O(\mathrm{exp})$ and τ_R values may be measured experimentally in the specific condition. Thus the β value can be obtained readily from equation (11).

From equations (11) and (14) we get

$$\beta = m_O(\mathrm{cal})/m_O(\mathrm{exp}) \cdot \tau_D/\tau_R \qquad (15)$$

and

$$\alpha = m_O(\mathrm{cal})/m_O(\mathrm{exp}) \qquad (16)$$

Here α is a extent of correction factor to account for the difference between the $m_O(\mathrm{exp})$ obtained in spcific measurement conditions and the $m_O(\mathrm{cal})$

calculated on the basis of L'vov model, and the α is called the correction factor of theorization for characteristic mass value[17].

Experimental

Apparaturs

A Hitachi 180-50 atomic absorption spectrometer with a GA-3 graphite furnace was used. Pyrocoated graphite tubes (made in China) and the V-shaped boat (made in our laboratory)[18] were used for this study. The spectral slit width of the spectrometer was 1.3 nm. The size of the graphite tubes used in our experiments was r = 2.35 mm and l = 30 mm. Hollow cathode lamps of Ag, Bi, Cd, Cr, Ga, Ge, In and Tl (made in China) were used as a light source. A deuterium arc background system was used throughout. Nitrogen gas was used as the purge gas at a flow rate of 150 ml/min and the purge gas was stopped during the atomization step. Sample solution was injected into the graphite tube with a 10 or 20 μl Eppendorf micropipette.

Reagente

The stock solutions (1 mg/ml) were prepared from metals or their compounds (analytical reagent grade) in sub-boiling distilled water. The working solutions were prepared by diluting the stock solution with sub-boiling distilled water directly before measurements.

A 5% (w/v) solution of the ammonium salt of EDTA was prepared by dissolving 5.00 g of EDTA (analytical reagent grade) in sub-boiling distilled water and adding 15 ml of 25% aqua ammonia (analytical reagent grade) and then diluting to 100 ml with sub-boiling distilled water.

A solution of palladium (10 mg/ml) was prepared by dissolving a suitable amount of $PdCl_2$ (analytical reagent grade) in concentration nitric acid, alone with the addition of several drops of concentration hydrochloric acid, and it was boiled to expel nitrogen oxide and diluted with sub-boiling distilled water.

Procedures

The maximum power was used for the heating program of the furnace. The temperature of the furnace was corrected with a MT-2 electro-optical pyrometer (made in China) and chart recorder. To avoid possible analyte loss ashing was carried out at moderate temperature. The graphite furnace operating parameters are the same drying and ashing temperatures, and varying atomization temperature. The signal integration time under stopped flow condition of purge gas was 6 to 10 s.

Instrumental parameters are listed in Table 1. For each element and at each temperature, the blank signal was subracted from the average peak area absorbance for at least five replicate measurements. The experimental value of the characteristic mass was calculated from the average value of the peak area absorbance from aqueous standard solution of the analytical element according to equation (10).

Results and Discussion

Calculations of m_0(cal) and τ_D and measurement of τ_R

So far as the theoretical calculation of characteristic mass is concerned, the vapour phase temperature in a graphite furnace is the major influencing factor for theoretical calculation of characteristic mass as the physical parameters such as $\Delta \nu_D$, D and Z(T) are temperature dependent. However, since the vapour phase temperature varied with the tube wall temperature, an accurate temperature of furnace was required for theoretical calculation. In order to ascentain the vapour phase temperature prevailing in the GA-3 equipped the V-shaped boat measurements were made using the 229.0nm-232.6 nm nickel and 371.9 nm-358.1 nm iron line paires. The temperature was calculated from the expression[19]

$$Tg = \frac{4330}{\lg(9.22\ A_{2371.9}/A_{358.1})} \tag{17}$$

and

$$Tg = \frac{833}{\lg(2.18\ A_{229.0}/A_{232.6})} \tag{18}$$

Here $A_{371.9}$ and $A_{358.1}$ as well as $A_{229.0}$ and $A_{232.6}$ are the measured peak area absorbances at a given time on the iron and nickel signals obtained at correspording wavelengths indicated by the subscript, respectively. The

Table 1. Elements, analytical wavelengths and current used in the present study

Element	Wavelength (nm)	Current (mA)	Modifier
Ag	328.1	7.5	——
Bi	306.8	5.0	——
Cd	228.8	7.5	——
Cr	357.9	7.5	——
Ga	287.4	10.0	——
Ge	265.2	10.0	——
In	303.9	7.5	80 μg/ml Pd + 2% (w/v) $(NH_4)_2EDTA$
Tl	276.5	6.0	80 μg/ml Pd + 2% (w/v) $(NH_4)_2EDTA$

measurement results showed that the average difference between the temperatures of vapour phase and tube wall was 125 K, and it was similar to the result obtained by Yan and Ni[20]. If the difference between the temperatures of vapour phase and tube wall was defined as 123 K, taking bismuth as example, the relative error of m_0(cal) value compared to that with use of 73 K as suggested by L'vov at 2400 K was 2.1%. The error in the calculation of m_0(cal) due to the variction of the vapour phase temperature could be negleted according to experimental results in this study. In order to compare with the data in literature, the vapour phase temperature was defined stilly as 73 K lower than the set temperature in the theoretical calculation of m_0(cal) . According to L'vov model the theoretical calculations of m_0(cal) were performed with the use of equation (14) . The temperature dependent parameters of $\Delta\nu_D$ and Z(T) were evaluated according to the expressions given in Refs. 6 and 21. The Voigt integral, H(a, ω), is a function of the temperature dependent a-parameter, which a can be caluculated as follows[7]

$$a = a_{ref}(T/T_{ref})^{-1.2} \qquad (19)$$

The a_{ref} and T_{ref} values of some elements obtained from Ref. 7. The Voigt integral can be calculated from a polynomical equation given in Ref. 9. Correction of hyperfine structure coefficient Ψ was also made using an expression from L'vov to account for the slight temperature dependence of Ψ. In all the other case δ was equal to 1.00 except that δ = 0.914 for Ge.

The diffusion coefficients of atoms in nitrogen were calculated with the following formula[22]

$$D_{(M\text{-}N_2)} = \frac{0.002628\sqrt{T^3 (M_M + M_{N_2})/2M_M M_{N_2}}}{P\sigma^2_{MN_2}} \qquad (20)$$

Here P is the pressure in atomsphere, M_M and M_{N_2} are the relative atomic masses of the metal M and of N_2, respectively, and σ (Å) is the collisional diameter of the metal in nitrogen. The σ value of metal was evaluated according to expressions given in Ref. 23.

As stated elsewhere[24-26], the atomic residence time (τ_R) can be measured experimentally from the falling edge of each A(t) vs time curve for time at which the atomic formation is parctically zero. This condition in more closely fulfilled as A(t) values are further from the maximum. The final choice for measurement of τ_R was to use intervals from $t_{0.6A_{max}}$ to $t_{0.2A_{max}}$.

Temperature dependences of the τ_D/τ_R and m_0(exp) values

In the theoretical calculation of m_0(cal), τ_D was calculated from equation (13) assuming diffusion to be the only removal mechanism. However, the use of equation (13) is questionable because with STPF, the values of the tube length (l) and of the temperature T, on which D depends, are not well defined. Moreover, even if l and T were perfactly defined, the presence of the central hole for the sample injection strongly limit the validity of equation (13)[27-29]. In addition, the variation in the analyte atoms of vapour phase comes from the three steps (desorption, readsorption and diffusional loss)[30], reevaporation of the readsorbed analyte followed by diffusion, account for the longer residence time[24]. Even if the diffusion is the main mechanism of atomic removal in the furnace the larger difference between τ_D and τ_R values for some elements is stilly observed in the practical work[31]. The data reported in literature[32-34] showed that it more often occurs that

τ_R value is larger than τ_D in the practical work. Thus it results in artificially high m_0(cal)/m_0(exp) value. Figures 1 and 2 show τ_D/τ_R vs T curves for all eight elements studied. It can be seen that the τ_D/τ_R values for Ag, Cd, Cr, Ga and In do not change significantly in the temperature intervals studied except Bi, Ge and Tl. However, the τ_D/τ_R value decreased and increased for Bi and Ge with the rise of temperature, respectively, and the τ_D/τ_R value of Tl decreased at lower temperature and increased at higher temperature with the rise of temperature. The τ_D/τ_R values of Ag, Cr, Ga and Ge were only about 0. 2-0. 3, and the τ_D/τ_R values of Bi, Cd, In and Tl were also about 0. 5-0. 8. Moreover, as shown in Table 2, the m_0(exp) values for Ag, Bi, Cd, Ga, In and Tl in the temperature range studied and for Cr and Ge in the ranges of 2500-3000 K and of 2700~ 3100 K appeared to be stable, respectively. The RSD of mean m_0(exp) value was better than 5. 1~13. 4%. Ma et. al[32] have pointed out that the τ_D/τ_R value of Cr may vary with the heating rate of the furnace, and the τ_D/τ_R values of Cr obtained at different heating rates in 2900 K of atomization temperature are listed in Fig. 3. It can be seen from Fig. 3 that the τ_D/τ_R value of Cr was increased from 0. 086 to 0. 659 or the τ_R value of Cr was decreased from 1. 302 s to 0. 170 s when the heating rate of the furnace was risen from 1000 K/s to 3670 K/s, but the m_0(cal)/m_0(exp) value of Cr was stable (see Fig. 3). This suggests that the loss of Cr atoms increases more rapidly with increasing heating rate of the furnace than a purely diffusional loss mechanism involving diffusion coefficient with a $T^{1.5}$ dependence would account for. The similar result for Cd and Pb was reported by Chakrabarti et. al[35]. The experimental results above mentioned further explain that it is questionable for calculating the m_0(cal) value to use equation (13).

Temperature dependence of α and β values

The β values of Ag, Bi, Cd, Cr, Ga, Ge, In and Tl in different atomization temperatures were calculated from equation (11) on the basis of the values measured of m_0(exp) and τ_R. The results are listed in Table 2. It can be seen that the β values of Ag, Cd and Tl do not change significantly in the temperature interval studied, and their values appeared to be stable and the RSD of average β value was 5. 2~6. 6%. The β values of Bi and In apperared to be stable in two regions of temperature studied, i. e. the RSD of average β value of Bi was 5. 9~6. 5% in the regions of 1600-2000 K and of

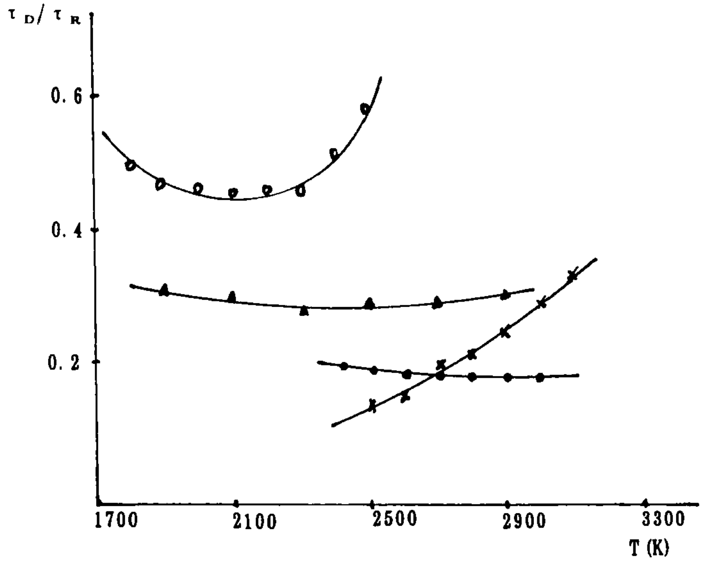

Fig. 1. Atomization temperature dependence of τ_D/τ_R value
(●) Chromium. (▲) Gallium. (×) Germanium. (○) Thallium.

2100-2400 K, and the RSD of average β value of In was 7.3~14.3% in the regions of 2300-2600 K and of 1800-2200 K, respectively. However, the β values of Cr, Ga and Ge reached a stable in the higher temperature region. Temperature dependence of the α values for the elements studied was basically similar to that for β values.

It can be seen from equation (11) that the temperature dependent parameters are m_0(exp), K and τ_R. The temperature can not effect significantly K value calculated. Therefore, it must be considered that the change in the β value with the temperature is determined only by the product of τ_R and m_0(exp). However, it is necessary for calculating the m_0 (cal) value to use equation (13), the τ_D/τ_R value must be considered as a main factor for discussing temperature dependence of β and α values. Since the m_0(exp) value for more elements was stable with varying of temperature, the values of β and α varying with temperature were due to the τ_D/τ_R value varying with temperature except other possible factors. It can be seen

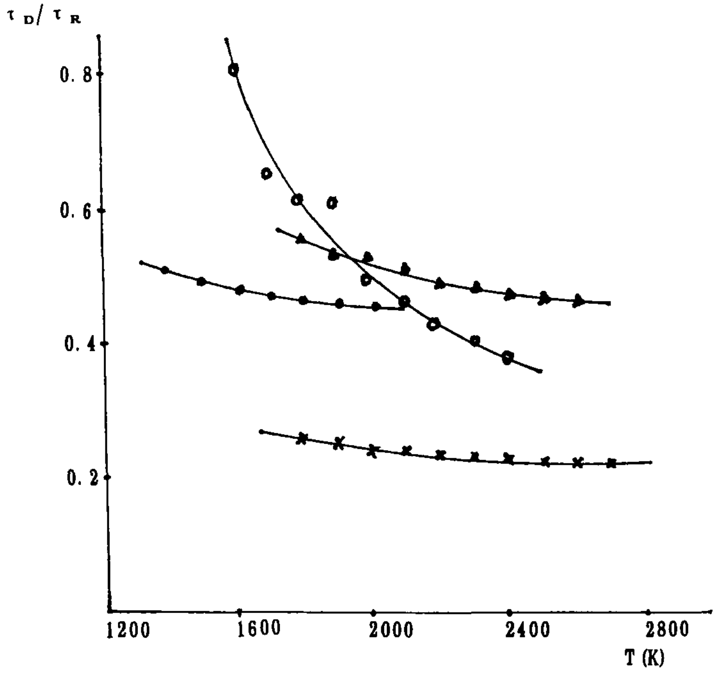

Fig. 2. Atomization temperature dependence of τ_D/τ_R value
(×) Silver. (O) Bismuth. (●) Cadmium. (▲) Indium.

from Fig. 3 that the β value for Cr increased with the rising of heating rate of furnace, and this result was similar to the relation between the τ_D/τ_R value and heating rate of furnace. But the α value of Cr was stable because the m_0(exp) value of Cr was stable at different heating rate, in addition, the m_0(cal) value of Cr was only calculated at 2900 K and it bore no relation to heating rate of furnace.

Analyses of α and β values

It can be seen from Table 2 that the correction factor of theorization for characteristic mass value (α) for all elements studied was larger than the corresponding atomization efficiency value (β). It can be seen from equation (16) that the β value of element is equal to the α value times

Table 2. The values of m_0(exp), α and β for Ag, Bi, Cd, Cr, Ga, Ge, In and Tl in different atomization temperatures

Element	Temp. (K)	m_0(exp) (pg)	α (%)	β (%)	Element	Temp. (K)	m_0(exp) (pg)	α (%)	β (%)
Ag	1800	0.62	89	24	Bi	1600	18.8	47	46
	1900	0.57	105	27		1700	16.2	58	43
	2000	0.63	102	25		1800	15.6	63	44
	2100	0.66	103	25		1900	15.7	68	48
	2200	0.65	110	26		2000	14.0	79	41
	2300	0.66	118	28		2100	14.3	82	36
	2400	0.68	122	28		2200	14.8	84	37
	2500	0.72	122	28		2300	14.8	89	34
	2600	0.73	127	29		2400	15.2	91	32
	2700	0.76	130	29					
Cd	1400	0.16	94	49	Ge	2500	69.8	7.7	1.1
	1500	0.16	100	50		2600	51.2	11	1.7
	1600	0.15	120	58		2700	38.6	15	3.1
	1700	0.17	112	53		2800	34.6	18	3.9
	1800	0.18	111	53		2900	33.6	19	4.7
	1900	0.19	115	54		3000	30.3	22	6.6
	2000	0.21	110	51		3100	31.9	22	7.4
Cr	2400	3.20	21	4.2	In	1800	9.0	38	21
	2500	2.70	27	5.1		1900	8.6	42	23
	2600	2.30	34	6.3		2000	8.2	48	26
	2700	2.10	40	7.4		2100	7.6	55	29
	2800	2.00	45	8.4		2200	7.4	61	30
	2900	1.90	50	9.3		2300	7.0	69	34
	3000	2.00	50	9.5		2400	6.5	79	38
						2500	6.6	83	39
						2600	6.7	87	40
Ga	1900	11.80	26	8.1	Tl	1800	8.4	63	32
	2100	10.90	32	9.3		1900	8.4	64	31
	2300	10.30	38	10.6		2000	8.6	64	30
	2500	10.70	41	12.2		2100	8.7	66	31
	2700	11.80	42	12.6		2200	8.9	67	31
	2900	11.70	48	14.8		2300	9.2	68	31
						2400	9.6	67	35
						2500	9.4	72	42

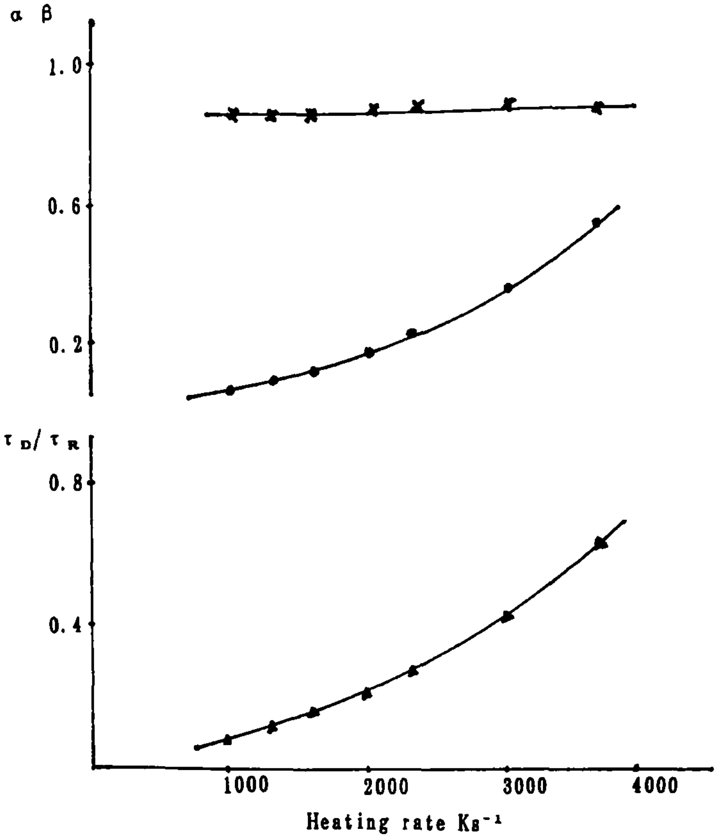

Fig. 3. Atomization effciency (β) (●), m_0(cal)/m_0(exp) (α) (×) and τ_D/τ_R (▲) for chromium obtained at different heating rate. Data from Ref. 32.

the τ_D/τ_R. When the atomic loss through sample introduction hole is neglected the τ_D/τ_R value is approximately equal to one if the dispersion process of analyte atoms from analysis volume does not deviate from L'vov model. But in fact the data reported in literature[32, 34, 35] showed the τ_R value of elements was larger than the τ_D, i. e. the τ_D/τ_R value of elements appeared always to be smaller than one. It is possible reason that part of the analyte vapour is readsorbed by the heated tube wall at high temperature and that reevaporation of the adsorbed analyte followed by diffusion account for the longer residence time. It results in the higher α value. The m_0(exp) value is relatively independent of the sample matrix and stable in time when the STPF and the measurement of integrated absorbance[3-5]. But it can not ensure the τ_D/τ_R value to be equal to one. Therefore, it gives consideration to influence of analyte vapour readsorbed on the surface of heated tube on the delay of atomic residence time, and it resulted in the dispersion process of analyte vapour deviating from the assumption of L'vov model. It can be stated that there are no any interferences of chemical action in the furnace and the atomic loss through sample injection hole is neglected, and thus the absolute analysis can achieve by use of the equations (13) and (14). However, it was possible that the analysis on the basis of m_0(exp) or K' value applied to the determination of element in real sample because their values were relatively independent of sample matrix and stable in time with STPF and the measurement of integrated absorbance. The determinations of some elements in real samples by the analysis method on the basis of m_0(exp) or K' have been reported in literature[20, 36-40]. At present analysis without calibration curve on the basis of m_0(exp) or K' value must be developed and studied since it is more single and rapid than the general calibration curve. The meaning of α value indicates that the deviant level between the atomization behavious of analyte in graphite furnace and the assumption of L'vov model is observed. However, the meaning of β value shows the fraction of the total number of analyte atoms that enter into the analysis volume at a given instant of atom formation, and it represents a fraction of the total number of analyte gaseous species which are released from the graphite tube surface to the gas phase. Therefore, the β value will be of prime importance for research workers because it represents the atomization efficiency of the graphite furnace to produce and contain the analyte atomic vapour in analysis volume under given conditions of measurements. A β value of less than one means that the graphite furnace is not 100% efficient suggesting that more research works can be done in order to increase the efficiency of the furnace to its maximum.

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