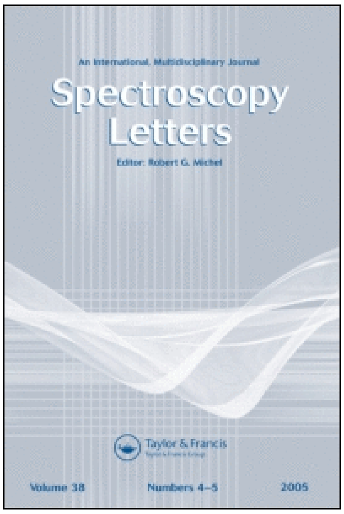

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Atomization Efficiency of Graphite Furnace in Atomic Absorption Spectrometry

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Atomization Efficiency of Graphite Furnace in Atomic Absorption Spectrometry

Key words: Atomization efficiency, graphite furnace, atomic absorption spectrometry.

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Abstract

The atomization efficiency of the Hitachi GA-3 graphite furnace for the production and containment of atomic vapour was determined for Ag, Cd, Cr, Ge and In by a method suggested. The method is based on the measurements of residence time, peak hight and peak area absorbances of analyte atoms. The β and ϵ_a values of above mentioned elements were experimentally determined by a method proposed. The experimental results show that the values of β and ϵ_a for Ag and Cd appeared to be stable in the temperature region studied. However, the β and ϵ_a values of remaining three elements(Cr, Ge, In) reached a stable value in higher temperature region. The β and ϵ_a values of In are increased obviously in the presence of Pd and ammonium salt of EDTA as a matrix modifier.

Atomization efficiency of commercial graphite furnace to produce and contain analyte atoms has been studied by several authors.[1-8] However, the differences in the reported results of different authors indicate that the problem of atomization efficiency still remains unresolved. Probably, part of the problem lies in the definition of atomization efficiency of graphite furnaces. van den Broek and de Galan[1] have reported that the number of analyte atoms at the absorbance maximum, N_m is given by

$$N_m = N_0(\tau_R/\tau_S) \qquad (1)$$

Where N_0 is the total number of analyte atoms initially deposited, τ_R and τ_S are the overall time conatants for the removal and the supply functions, respectively. They calculated the overall atomization efficiencies of two graphite furnaces(CRA-63 and HGA-72) for the atomizations of Ag, Pb, Mn and Cd, and pointed out that the atomization efficiencies averaged less than 10 % for the above elements under commercial operating conditions. Strugeon and Berman[2] have defined the atomization efficiency for an electrothermal atomizer at the time the signal has attained its maximum value, as the ratio of the number of neutral analyte atoms, N_m, plus ionied analyte atoms, N_i, to the total number of analyte atoms introduced as sample, N_0, i.e.,

$$\varepsilon_a = \left(\frac{N_m + N_i}{N_0}\right) \qquad (2)$$

They subsequently calculated the relative values of atomization efficiencies of the HGA-2200 for several elements. Smets[5] in his study of atom formation in and dissipation from open strip atomizer made following estimate of the atomization efficiency: 1 for Au, Ag, Cu, Fe, Mn and Mg, and less than 0.1 % for Al.

Frech and Baxter[7] have defined the calculated atomization efficiecy as the ratio of the calculated and the experimental characteristic masses. They studied atomization temperature dependence of calculated atomization efficiencies of the HGA-600 and the two-step atomizer for several elements and pointed out that the calculated atomization efficiency for most elements reaches a plateau, often in the higher temperature region. Chakrabarti[4] and Cathum[8] have determined the atomization efficiencies of the HGA-400 for several elements under isothermal and non-isothermal conditions. They pointed out that the average values of atomization efficiencies for Al, Co, Cu, Fe, Ag and Ga under isothermal and non-isothermal conditions were found to be about 0.30 and 0.10, respectively.

It would be useful to investigation and to compare the atomization efficiency of graphite furnace operated under various conditions since the various ways atomized are used in routine analysis and also in studying the mechanism of atomization. A low value of atomization efficiency , for instance, indicates formation of a non-absorbing species, which must be taken into account in proposing the mechanism of atomization.

The absolute number of analyte atoms inside the graphite furnace is obtained by measuring the absorbance of a characteristic spectral line. At any moment, t, the relation between those two quantities can be expressed as[9]

$$A(t) = \frac{0.434\sqrt{4\pi \ln 2}\; e^2 g_i \exp(-E_i/kT) f \psi \delta \; H(a,\omega)}{m_e\, c^2 \Delta\nu_D\, Z(T) s_c} N(t) \qquad (3)$$

Here A(t) is the instantaneous absorption signal, N(t) is the total number of analyte atoms present in the furnace at time,t, m_e and e are the mass and the charge of an electron, c is the velocity of light, $\Delta\nu_D$ is the Doppler line width, g_i and E_i are the statistical weight and energy of the lower level of the analytical line, Z(T) is the partition function at temperature T, k is the Boltzmann constant, f and $H(a,\omega)$ are the oscillator strenght and the Voigt integral for a point of the analytical 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 light source, δ is a correction factor for adjacent lines in the light source spectrom, s_c is the cross-section of the tube.

The atoms need not be distributed homogeneously by over the tube length, but they must maintain a homogeneous distribution in the plane perpendicular the light beam, because otherwise the A(t) measured will not be linearly related to N(t).[1,10] The constant

$$K = \frac{0.434\sqrt{4\pi \ln 2}\; e^2\; g_i \exp(-E_i/kT) f \psi \delta \; H(a,\omega)}{m_e\, c^2\, \Delta\nu_D\, Z(T)} \qquad (4)$$

will be called the atomic absorptivity(cm^2) by analogy molecular spectrometry. In the rapidly heated graphite furnace the number of analyte atoms present in the analysis volume at time t is determined by the release, and the transport of atoms into and their loss from the analysis volume.[11] The efficiency of the graphite furnace to produce and contain the analyte atomic vapour is governed by its ability to release neutral analyte atoms from atomizer surface and to transport them into the analysis volume. The idealization condition of this process requires that the amount of analyte atoms released from the atomizer surface at any time of atomization should enter the analysis volume. However, some of the analyte atomic vapour formed may be lost during any stage of atomization by various atom loss processes, for example, loss by diffusion to the cooler ends of the atomizer and through the injection hole, by readsorption, by explosion and by convection. In addition it is also possible that analyte atoms are lost as non-absorbing molecular species, such as, oxides, carbides, chlorides etc. In fact, the time-dependent variation of N(t) can be expressed as a convolution[1]

$$N(t) = \int_0^t S(t')R(t-t')dt' \qquad (5)$$

here $S(t')$ is the supply rate of the atoms and $R(t)$ is the removal function(describing loss from the furnace). The integrated form of equation (5) is

$$\int_0^{\infty} N(t)dt = [\int_0^{\infty} S(t)dt] [\int_0^{\infty} R(t)dt \qquad (6)$$

It should be pointed out that not all of the atoms which are transported to the gas phase necessarily enter the analysis volume; a fraction of them may be lost. Therefore, a correction factor must be used to account for the atom loss at each stage of the atom formation. Smets[5] has suggested that β was used as a correction factor to account for the fraction of the total number of analyte atoms that enter the analysis volume during each stage of atomization. The integrated rate of atomic formation, $\int_0^{\infty} S(t)dt$, has been assumed to be directly proportional to the number of analyte atoms, N_0, initially deposited in the graphite furnace as given by the following expression:

$$\int_0^{\infty} S(t)dt = \beta N_0 \qquad (7)$$

Using equations (6) and (7) we get

$$\int_0^{\infty} N(t)dt = \beta N_0 \tau_R \qquad (8)$$

here τ_R is the mean residence time of atoms in the furnace.

The integral of equation (1) and taking into account equation (8) yield

$$A_i = \int_0^\infty A(t)dt = K\beta N_0 \tau_R / s_c \qquad (9)$$

here A_i is the integrated absorbance. We recall that

$$N_0 = m \cdot N_A \;/\; M_a \qquad (10)$$

here m is the analyte mass, N_A is the Avogadro number, M_a is the molar mass of the analyte.

Substituting equation (10) into equation (9) yields

$$\beta = \frac{A_i \; s_c \; M_a}{K \; m \; N_A \; \tau_R} \qquad (11)$$

According to the meaning of the atomization efficiency suggested first by de Galan[12], it is defined as the ratio of the number of neutral analyte atoms present in the analysis volume at time when the absorbance reaches its maximum to the total number of analyte atoms deposited in the graphite furnace.

$$\epsilon_a = \frac{N_m}{N_0} \qquad (12)$$

Using equations (1) and (9), equation (12) become

$$\epsilon_a = \frac{A_m \beta \tau_R}{A_i} \qquad (13)$$

here A_m is the peak hight absorbance. We known that the K value can be calculated from the equation (2) on the basis of physical parameters of element determined. The residence time of atoms (τ_R), peak hight and peak area absorbances may be measured experimentally in the specific conditions. Then the final result is that the values of β and ϵ_a can be obtained readily from equations (11) and (13), respectively.

Experimental

Apparatus

A Hitachi 180-50 atomic absorption spectrometer with a GA-3 graphite furnace and a XWT-164 chart recorder(made in China) was used. Pyrocoated graphite tubes(made in China), pyrolytic platform and V-shaped boat(made in our laboratory)[13] were used for this study. The size of the graphite tubes used in our experiments was $r = 2.35$ mm and $l = 30$ mm. Hollow cathode lamps of Ag, Cd, Cr, Ge and In(made in China) were used as a light source. The HCL current was 7.5 mA for Ag, Cd, Cr, In and 10 mA for Ge. A deuterium arc background system was used throughout. N_2 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 graphite tube with a 10 or 20 μl Eppendorf micropipette.

Reagents

The stock solutions(1 mg/ml) were prepared from metals or thier 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.

Procedure

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

For each element and at each temperature, the mean blank signal was subtracted from the average peak hight and peak area absorbances for at least five replicate measurements. The values of β and ϵ_A were then calculated from these blank corrected peak hight and peak area absorbance values.

Results and Discussion

Calculation of K and measurement of τ_R

Calculation of the K value was performed using equation (2). According to Ref.9 the gas temperature is lower by 73 K than set temperature. The temperature dependent parameters of Doppler line width and partition function were evaluated according to expressions given in Refs. 9 and 14. The a-parameter in the Voigt integral was calculated from the values listed in Ref. 9 and 15 using following relation:[16]

$$a \simeq \left(\frac{\Delta\nu_C}{\Delta\nu_D}\right)(\ln 2)^{\frac{1}{2}} \propto T^{-1.2} \qquad (14)$$

from which H(a, ω) was obtained.[7] Correction of the hyperfine structure coefficient ψ was also made using an expression from L'vov[15] to account for the slight temperature dependence of ψ. In all the other cases δ was equal to 1.00 except that $\delta = 0.914$ for Ge.

As state elsewhere,[1,17-19] the atom residence time (τ_R) can be measured experimentally from the A(t) vs. time curves only for times at which the atomic formation is practically zero. This condition is more closely fulfilled as we use the maximum power, in order to reduce the atomization time interval, and use A(t) values distant from the maximum. τ_R is equal to $t_{\underset{\bullet}{\underline{xA}}} - t_{xA}$ ($x = 0\text{-}1.0$) according to definition of mean residence time of atoms. The final choice for the measurement of τ_R was to use intervals from $t_{0.6A}$ to $t_{0.6A/e}$.

Influences of atomization temperatures on the β values

The β values of Ag, Cd, Cr, Ge and In in various atomization temperatures were calculated from equation (11) on the basis of the values experimentally measured of A_i and τ_R. The results are listed in Table 1. It can be seen from Table 1 that the β values of Ag and Cd do not change significantly in the temperature interval studied whether the samples are evaporated from the wall, or using the platform and the V-shaped boat techniques. Moreover, thier values appeared to be stable and the RSD of average β values were 4-18 %. The β values of remaining three elements (Cr, Ge, In) reached a stable in the higher temperature region. The difference among the β value for Ag, Cd and Cr obtained from the three different ways was not larger than 15 %. But the β values for Cr, Ge and In were slowly increased with the increases of atomization temperatures, and its value reached a stable in the higher temperature region. The β values for In and Ge obtained from the wall were about 1-3 and 10-19 times less than that by the platform and the V-shaped boat techniques, respectively.

It can be seen from equation (11) that the temperature-dependent parameters are A_i, K and τ_R. The temperature can not effect significantly K value calculated. Therefore, it is assumed that the change in the β value with the temperature is determined solely by the altered value of A_i/τ_R . As shown in Figs. 1 and 2, A_i/τ_R values of Ag and Cd do not change significantly in the temperature interval studied. The remaining three elements

Table 1 The values of and for Ag, Cd, Cr, Ge and In in various atomization temperatures*

Element	Temp. (K)	(%)			(%)		
		W	P	V	W	P	V
Ag	1800	26	22	24	15	19	22
	1900	30	25	28	20	23	25
	2000	27	24	26	15	20	23
	2100	27	25	25	14	20	23
	2200	27	28	27	15	21	21
	2300	29	28	28	15	22	21
	2400	29	29	28	15	22	20
	2500	30	32	28	16	22	20
	2600	30	35	29	17	22	21
	2700	31	38	30	17	23	22
Cd	1400	43	47	49	22	38	38
	1500	45	51	53	23	37	40
	1600	47	56	58	25	40	40
	1700	48	52	53	24	37	39
	1800	48	52	54	22	34	37
	1900	47	52	54	19	33	35
	2000	46	51	53	17	31	33
Cr	2400	4.0	3.4	4.1	1.4	2.0	2.6
	2500	4.4	4.5	5.2	2.1	2.2	3.0
	2600	5.7	5.5	6.4	2.6	2.4	3.3
	2700	6.7	6.6	7.6	3.4	2.7	3.7
	2800	7.8	7.6	8.6	3.9	3.0	4.2
	2900	8.7	8.2	9.3	4.3	3.2	4.5
	3000	8.7	8.9	9.7	4.4	3.3	4.2
Ge	2500	0.09	1.4	1.1	0.08	1.0	0.7
	2600	0.2	1.8	1.7	0.1	1.1	1.0
	2700	0.3	2.5	3.3	0.2	1.3	1.3
	2800	0.3	3.0	3.9 (11)	0.2	1.6	1.6 (9.3)
	2900	0.4	3.4	4.8 (13)	0.2	1.9	1.8 (11)
	3000	0.4	4.1	6.7 (11)	0.3	2.2	2.2 (9.2)
	3100	0.4	4.1	7.5	0.2	2.1	2.1
In	1800	2.3 (6.3)	4.3 (15)	7.4 (29)	1.9 (7.7)	4.3 (13)	8.0 (22)
	1900	2.6 (6.8)	4.6 (17)	8.0 (31)	2.0 (8.2)	4.6 (14)	8.2 (22)
	2000	2.8 (7.5)	5.0 (19)	9.1 (34)	2.1 (8.4)	5.4 (14)	9.3 (23)
	2100	3.1 (8.2)	5.4 (22)	9.8 (37)	2.4 (9.1)	5.6 (15)	9.9 (24)
	2200	3.6 (9.4)	5.8 (25)	11 (38)	2.9 (9.4)	5.8 (15)	11 (24)
	2300	3.5 (10)	6.7 (30)	12 (41)	2.7 (9.8)	6.0 (16)	11 (24)
	2400	3.5 (9.9)	6.8 (30)	12 (44)	2.6 (9.5)	5.7 (15)	11 (25)
	2500	3.7 (9.6)	6.9 (32)	11 (45)	2.6 (9.0)	5.6 (16)	9.9 (25)
	2600	3.8 (9.7)	7.0 (32)	11 (46)	2.6 (8.8)	5.5 (15)	9.7 (25)

* Atomization mode: W Wall; P Platform; V V-shaped boat. Data in brackets are using 80 μg/ml Pd and 2 %(v/v) ammonium salt of EDTA as matrix modifier for In and use of the 0.15 mol/L solution of NaOH for Ge.

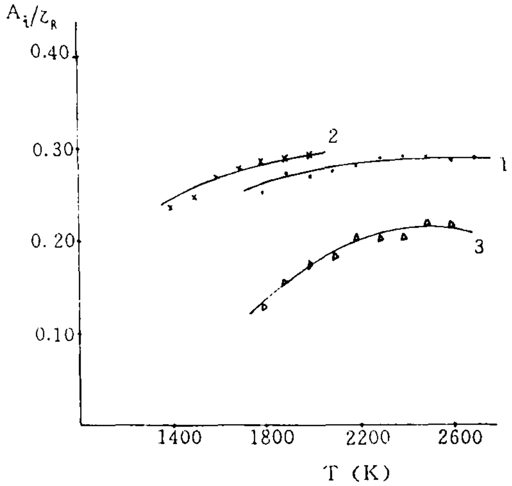

Figure 1. Atomization temperature dependence of A_i/τ_R value.
1 Ag. 2 Cd. 3 In. Units: absorbance for A_i/τ_R .

reached a stable value in higher temperature region. It can explain the reason for influencing of atomization temperature on the β values of elements studied.

Influences of atomization temperatures on the ε_a values

As shown in Table 1, the ε_a values of Ag and Cd do not change significantly in the temperature interval studied whether the samples are evaporated from the wall, or using the platform and the V-shaped boat techniques. Moreover, thier values appeared to be stable and the RSD of average ε_a value was 7-13 %. The ε_a values of remaining three elements(Cr, Ge, In) reached a stable in the higher temperature region. However, the ε_a values of Ge and In obtained from the wall of tube were about 10 and 2-4 times less than that by the platform and the V-shaped boat techniques. The ε_a values of Ag and Cd obtained from the wall were smaller than that by the platform and the V-shaped boat techniques. The ε_a values of Cr obtained from the three ways were the similarty.

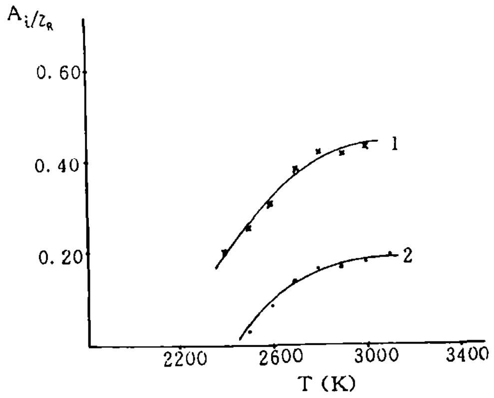

Figure 2. Atomization temperature dependence of A_i/τ_R value. 1 Cr. 2 Ge. Units: absorbance for A_i/τ_R .

It can be seen from equation (13) that all parameters were relevant to temperature. Because influence of temperature on the β value is throught the role of A_i/τ_R , the change in the ε_a value with the temperature is determined solely by the altered value of A_m. Equation (13) shows that ε_a is proportional to the residence time of analyte atoms. Note that as τ_R is decreased, for instance by forced convection, a low peak hight absorbance will result because of appreciable decrease in the residence time, which will also mean that ε_a will decrease. In order to increase ε_a , the experiment should be conducted in the gas-stopped mode and using longer graphite tubes since these two factors will increase the residence time of analyte atoms which will result in a higher value of ε_a .

The β and ε_a values in the presence of matrix modifier

Previous discussion of atomization efficiency has typically been made without matrix modifier. Authors[20] pointed out that a suitable matrix modifier can increase obviously the calculated atomization efficiencies of some elements in graphite furnace. Therefore, the influences of the Pd and the ammonium salt of EDTA as a matrix modifier on the β and ε_a values of In in the temperature interval studied were observed when the samples were evaporated from the wall, using the platform and the V-shaped boat techniques. It can be seen from Table 1 that the β values of In in the presence of the Pd and the ammonium salt of EDTA were increased by a factor of 2.6 when the samples were evaporated from the wall of tube, but by a factor of 3.5-4.6 from the platform and the V-shaped boat. However, the ε_a values of In in the presence of the Pd and the ammonium salt of EDTA were increased by a factor of 3.5-4.1 when the samples were evaporated from the wall of tube, but by a factor of 2.6-3.0 from the platform and the V-shaped boat techniques. Zheng et al[21] pointed out that the atomization of Ge is relevant to Ge species formed in the solution and the absorbance of Ge is increased obviously in the NaOH solution. As shown in Table 1, when the samples were evaporated from the V-shaped boat the β and ε_a values of Ge were increased by a factor of 1.4-5.5 in the region of 2800-3000 K in the NaOH solution. Therefore, it indicates that it is a important condition to use a suitable matrix modifier for the increase of atomization efficiency.

Analysis of the atomization efficiency values

Table 1 summarizes the values of β and ε_a for Ag, Cd, Cr, Ge and In determined by using equations (11) and (13). The precision, calculated for five replicate determinations, is about 5 % relative standard deviation, which reflect the combined reproducibility of the furnace thermal program and that of atom formation and loss except for uncertainty of calculated K value. Our results for β and ε_a are different from atomization efficiency values in the literature.[1,2,4,8] Probably, the main reason for this different is attributed to experimental conditions and atomizers used determination of atomization efficiency. Certainly, different modes of atomization in various atomizers will result in different atom release processes which will appreciably influence the value of the atomization efficiency. The β and ε_a values determined **which** are applicable only under the specified atomization conditions in a GA-3 furnace used here. Sturgeon and Chakrabarti[22] pointed out that varying the atomization parameters will change the efficiency of the furnace in direct proportion to the change in sensitivity of the system. Therefore, it must be emphasized that the atomization efficiency value is relevant to the mode of atomizer and the experimental parameters. There is only practical meaning for the atomization efficiency value in the given specific conditions measured. I believe that the term of apparent atomization efficiency used by Koirtyohann et al[23] was reasonabler.

Moreover, an important aspect of reseaching atomization efficiency is conducted mainly to improve the sensitivity and limit of detection of the analysis method. Most of the atomization efficiency reported in the literature[1,2,4,8] are of the same order of magnitude as those of this work. As shown in Table 1, the values of ϵ_a in the three ways of samples vaporized show that only a small fraction roughly about 10-40 % of the total number of the deposited atoms are actually atomized, the rest are lost as non-absorbing species. This indicates there is still some more reseach to be done on the graphite furnace to increase its efficiency. As mentioned earlier, ϵ_a can be increased by increasing τ_R, for example, by operating the atomizer in the gas-stopped mode at low atomization temperatures. The effect of forced convection on the absorbance signal of most elements is obvious when the graphite furnace is operated in the gas-flow mode. The ϵ_a value of a particular element should hold constant for a set of experimental conditions, such as, the inner gas flow rate and atomization temperature. The combination of these two factors and other play an important role in determining the residence time of the atomic vapour in the analysis volume, and ultimately the ϵ_a value. Thus in order to make the ϵ_a value as a useful indicator for different atomizers all of experimental and instrumental parameters must be maintained unchanged. Comparison of the atomization efficiency in different graphite furnaces has the significance only if all of above mentioned conditions maintain constant and similarity.

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