



# Model calculation of the characteristic mass for convective and diffusive vapor transport in graphite furnace atomic absorption spectrometry



László Bencs<sup>a,\*</sup>, Nikoletta Laczai<sup>a</sup>, Zsolt Ajtony<sup>b</sup>

<sup>a</sup> Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

<sup>b</sup> Institute of Food Science, University of West Hungary, H-9200 Mosonmagyaróvár, Lucsony utca 15–17, Hungary

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## ABSTRACT

A combination of former convective–diffusive vapor-transport models is described to extend the calculation scheme for sensitivity (characteristic mass –  $m_0$ ) in graphite furnace atomic absorption spectrometry (GFAAS). This approach encompasses the influence of forced convection of the internal furnace gas (mini-flow) combined with concentration diffusion of the analyte atoms on the residence time in a spatially isothermal furnace, i.e., the standard design of the transversely heated graphite atomizer (THGA). A couple of relationships for the diffusional and convective residence times were studied and compared, including in factors accounting for the effects of the sample/platform dimension and the dosing hole. These model approaches were subsequently applied for the particular cases of Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, V and Zn analytes. For the verification of the accuracy of the calculations, the experimental  $m_0$  values were determined with the application of a standard THGA furnace, operating either under stopped, or mini-flow ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) of the internal sheath gas during atomization. The theoretical and experimental ratios of  $m_0(\text{mini-flow})$ -to- $m_0(\text{stop-flow})$  were closely similar for each study analyte. Likewise, the calculated  $m_0$  data gave a fairly good agreement with the corresponding experimental  $m_0$  values for stopped and mini-flow conditions, i.e., it ranged between 0.62 and 1.8 with an average of  $1.05 \pm 0.27$ . This indicates the usability of the current model calculations for checking the operation of a given GFAAS instrument and the applied methodology.

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## 1. Introduction

The possibilities of absolute or standardless analytical spectrometric methods were first mentioned in Walsh's landmark paper on atomic absorption spectrometry (AAS) [1]. Development of absolute AAS methods has been gaining a continuously increasing attention [2–8], since L'vov exposed that these methods were in connection with solving some methodological difficulties in graphite furnace atomic absorption spectrometry (GFAAS) [2]. These tasks were formulated in three main points [2]:

1. Elimination of analytical matrix interference effects.
2. Stabilization of calibration over time and ensuring the identity in calibration for all instruments of the same type.
3. Theoretical calculation of the calibration based on fundamental parameters and actual measurement conditions, for example, model calculation of the sensitivity, which is called as characteristic mass ( $m_0$ ) in GFAAS, i.e., the amount of analyte giving 0.0044 s integrated absorbance ( $A_{int}$ ).

In relation to the third topic, several studies have been documented in the GFAAS literature, devoted to describe the vaporization and atomization processes, and also concerned with the time dependent change of analyte atoms in various designs of graphite atomizers [2–11].

In the GFAAS literature, first L'vov [2] developed a model to describe the vaporization/atomization behavior of the analyte atoms in the graphite furnace. This model represents a mass balance between the supply and loss functions, and includes atom generation by zero order kinetics and atom loss by diffusion. Fuller [3] presented a phenomenological kinetic approach to estimate the free atom formation of Cu (transient signal) in GFAAS. Sturgeon et al. [4] proposed a thermodynamic-kinetic model, assuming that analyte surface–gas phase equilibrium exists in the graphite furnace and the production of observable atoms is characterized by a unimolecular rate constant. From this approach, the activation energy of the limiting step in the atomization pathway could be calculated.

Later on, Paveri-Fontana et al. [5] and Torsi and Tessari [6] developed a model to calculate a time-resolved distribution of analyte atoms in a graphite rod atomizer, based on the recovery of the source parameters from the response function, and verified their model by experiments [7]. Sturgeon and Chakrabarti [8] concluded that the major loss of vapor during atomization occurred by thermodiffusion to the cooler parts of the graphite atomizer tubes, while sample injection port

\* Corresponding author. Tel.: +36 1 392 2222/1684; fax: +36 1 392 2223.  
E-mail address: [bencs.laszlo@wigner.mta.hu](mailto:bencs.laszlo@wigner.mta.hu) (L. Bencs).

aperture and loss through the graphite walls contributed each ~20% loss. These results indicate the importance of some of the concerned factors (e.g., sample dosing port) for present commercial designs of graphite tubes, e.g., transversely heated graphite atomizers (THGAs).

Slaveykova and Tsalev [9] further extended and simplified a kinetic model for estimating various analyte loss mechanisms (volatilization, re-condensation, convection and diffusion) during pre-atomization thermal treatment in GFAAS with and without the use of chemical modifiers. Their approach indicated much higher activation energies of the analyte loss in the presence of chemical modifiers. Güell and Holcombe [10] applied Monte Carlo simulations for exploiting various analyte transfer mechanisms (desorption, adsorption and spatial re-distribution), as well as activation energies and peak shapes of Cu in electrothermal graphite atomizers. They concluded that for elements with similar desorption kinetics, the presence of re-adsorption shifted the peak to higher temperatures (later times), but does not alter the appearance temperature. The width of the peak increases with an accompanying decrease in peak height and atomization efficiency. These effects imply an increase in the average residence time of analyte atoms in the atom-reservoir, but during the increased time the analyte is absorbed on the graphite surface.

Gilmutdinov and Fishman [11] gave a systematic theoretical description on various sample transfer processes occurring in graphite tube furnaces of various sizes, including thermal and concentration diffusion, convective gas expansion, and gas phase chemical reactions. This theory possesses the advantage of describing the spatial and temporal variation of atomic vapor in non-isothermal graphite tube atomizers. They pointed out that the sample/platform dimension caused a certain increase in the sample vapor loss in each furnace design.

Theoretical sensitivity calculations for some analytes in commercial graphite furnaces have been made by van den Broek and de Galan [12], Sturgeon and Berman [13], and Magyar [14]. In some of these papers, the authors evaluated the overall efficiency of the vapor content and atomization in the furnace by the measurement of peak height absorbance and applying wall atomization [12,13]. However, early atomizer designs applied in these works were far of the spatially isothermal ones and also handicapped by the relatively slow heating, which is the main drawback when peak height absorbance is evaluated [15,16].

L'vov et al. [17,18] calculated the theoretical characteristic mass ( $m_{0\text{ cal}}$ ) for several elements considering the diffusion vapor transport (removal function) during atomization from a Massmann-type, end-heated graphite furnace (HGA-design) to be discussed in detail in Section 2.1. This model was found to be an accurate approach for gas-stop conditions during atomization, manifested in the good agreement obtained between the theoretical and experimental  $m_0$  ratios of 32 elements with an average of  $0.85 \pm 0.10$ .

Baxter and Frech [19] and Frech et al. [20] found that temperature gradients within a Massmann-type furnace provided limitations to absolute analysis, in terms of lower sensitivities and analyte losses, as compared to the performance of either the side-heated, spatially isothermal integrated contact cuvette (ICC) [19], or the two-step atomizer [20]. This effect was especially manifested for non-volatile elements [19].

In previous papers from this laboratory, GFAAS methods were developed [21–26] for the determination of a couple of additive/trace elements in bismuth tellurite optical crystals. In these analyses, the application of mini-flow of the internal furnace gas during atomization in an end-heated graphite tube was advantageous compared to stopped flow conditions, due probably to the decreased condensation of analyte and matrix vapors in the cooler parts of the graphite furnace (e.g., the gas phase, a graphite wall and the tube ends). This general characteristic of the mini-flow has been suggested in a few works [27,28], partly in connection with THGAs. This condition was also found to be advantageous for decreasing the degree of halide interference effects [22–25], and also for obtaining more linear calibration curves with standard THGA tubes [24,26].

In the present study, former model approaches were combined to obtain a general formula, which was utilized for the calculation of  $m_{0\text{ cal}}$  for a large set of elements under stopped and mini-flow (forced convection) conditions of the internal furnace gas during sample atomization. As a comparison, the experimental characteristic mass ( $m_{0\text{ exp}}$ ) data were determined under these conditions for the study analytes. It has been concluded by several authors that the contribution of convective flows to the diffusion in the total vapor transport has also some significance under gas-stop conditions, for both longitudinally and transversely heated graphite tube systems [27–29]. Consequently, it might be expected that utilization of the present calculation scheme provides a more accurate approach to real furnace analytical conditions, as well as  $m_{0\text{ cal}}$  values in general.

## 2. Theoretical

### 2.1. General considerations

The present approach is mainly based on a previous GFAAS model of L'vov et al. [17,18], developed for end-heated graphite furnace atomizers. According to their approach, the  $m_{0\text{ cal}}$  values were calculated by the next equation:

$$m_{0\text{ cal}} = 6.36 \times 10^{-14} \frac{A_r \cdot \Delta \tilde{\nu}_D}{H(a, \omega) \cdot \gamma \cdot f \cdot \delta \cdot g_1 \cdot \exp(-E_1/kT) \tau_d} Z(T) \frac{r^2}{\tau_d} \quad (1)$$

where  $A_r$  is the relative atomic mass,  $\Delta \tilde{\nu}_D$  is the Doppler-broadening of the analytical line,  $H(a, \omega)$  is the intensity-distribution (Voigt) integral,  $\gamma$  is the factor accounting for the fine and hyperfine splitting and for the Doppler profile of the hollow cathode lamp,  $Z(T)$  is the atomic partition function or state sum at temperature of  $T$  (K),  $g_1$  and  $E_1$  are the statistical weight and energy of the lower level of the transition of the analytical line, respectively,  $\delta$  is the coefficient accounting for the presence of adjacent lines in the spectrum of the primary light source,  $r$  is the inner radius of the graphite tube;  $f$  is the oscillator strength of the electronic transition,  $k$  is the Boltzmann-coefficient, and  $\tau_d$  is the residence time accounting for the concentration diffusion of analyte atoms.

In this study, a near spatially isothermal furnace (THGA) is applied for the  $m_{0\text{ exp}}$  determinations. Thus, some features of this model differ from the original [17,18], which is described by the properties as follows:

1. The graphite furnace is quasi-isothermal along its longitudinal axis, i.e., there is no considerable temperature fall towards the ends of the graphite tube during the sample atomization.
2. When small internal sheath gas flows (mini-flows) are applied in the graphite furnace during vaporization and atomization, the sample expands to a similar extent as under gas-stop.
3. The sample vapor fills in the total volume of the atomizer, i.e., a small argon flow (mini-flow) causes a negligibly compressed velocity field in the graphite tube.
4. The effective residence time of the analyte atoms in the furnace is determined by the combined effects of concentration diffusional and forced (i.e., mini-flow) convective vapor transports.
5. The sample has certain dimensions, i.e., the vaporization–atomization occurs from a non-point source, which also increases the rate of analyte loss.
6. The distribution of analyte vapor is near uniform over the tube cross-section area.
7. Analyte loss occurs through the dosing hole of the graphite tube.

The next step is to consider the validity of the above model. As the first item, for THGAs, the temperature drop is negligibly low towards the tube ends [30]. In this study, for the sake of simplicity, it is assumed that during sample atomization the graphite furnace temperature is quasi-stationary in time, which condition is fulfilled, when using platform atomization (integrated platforms in case of the THGA).

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