A ONE-DIMENSIONAL MODEL OF DIFFUSION IN A NON-HOMOGENEOUS DOMAIN

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Abstract. *In electro thermal atomic absorption spectrometry (ET AAS) with graphite tube atomizer the sample is evaporated from the centre of the tube and vapour released from the open ends. The rate of the vaporization process is defined by the thermo-chemical properties of the sample and the temperature of the tube. The atoms present in the cavity of the tube absorb light, thus creating an analytical signal.*

A one-dimensional model describing the diffusion of atoms in the tube atomizer is suggested. The considered tube consists of a number of sections having different cross-sectional areas. The model is based on the solution of the non-homogeneous one-dimensional diffusion equation with diffusion coefficient depending on temperature over the entire (non-homogeneous) domain.

The analytical solution of the problem was found in terms of Green's function. The corresponding orthogonal system of eigenfunctions is a set of continuous functions with discontinuous derivatives.

1   INTRODUCTION

In electrothermal atomic absorption spectrometry (ETAAS) a graphite tube atomizer is used as a sample vaporizer and light absorption cell. The tube, normally about 18-30 mm in length and 4-5 mm in diameter (depending on the manufacturer), is resistance heated according to the pre-set temperature program. Normally, 5-50 μL of the sample solution is injected in the centre of the tube through the dosing hole, which is 1.2-1.5 mm in diameter. The tube is step-wise heated providing sequential drying, pre-treatment and atomisation temperatures. During the atomisation step maximum power is applied to obtain a fast heating ramp and a temperature above 2000 ^{0}C, where it is held for 1-5 s. The element to be determined (analyte) is vaporized during the atomisation ramp and hold time and its vapour is released through the open ends of the tube via diffusion or other mechanisms of mass transfer. The atomic vapour selectively absorbs radiation from the light passing through the tube, thus providing a transient analytical signal. Absorption peak height or integrated absorbance after calibration indicates the amount of analyte in the sample [1].

The analyte vapour can be in atomic and molecular form. The degree of atomisation depends on matrix, volatility of chemical compound and gas-phase temperature during vaporization and vapour transport. Since only atomic vapour is detected, presence of molecular constituents is associated with the analytical errors (interferences). Minimization of the

interferences requires chemical modification of the analyte or increase of gas temperature in the analytical volume.

In practice both methods are used simultaneously. The sample is placed on a special flat or concave substrate (platform) located in the tube and having low thermal contact with the wall (platform furnace). At the atomisation step the platform is heated mainly via radiation, and its temperature lags behind that of the tube. When the sample is vaporized, the degree of atomisation increases due to a higher gas phase temperature. The modification is provided via introduction of excessive amounts of other chemicals together with the sample and long thermal pre-treatment at 500-1000 ^{0}C.

Although broadly used, those methods are prone to substantial limitations. The sample, independent of its origin, must be kept on the platform. This requirement necessitates the platform area to be about 1 cm^2. Nevertheless, even this is not enough to prevent the spilling of some organic liquids beyond the platform. A large platform requires a large tube for accommodation, and that puts additional strain on the power supply and reduces the heating rate. The presence of a large, relatively cool surface in the tube reduces the average gas temperature [2], and slow heating deteriorates the vaporization kinetics, thus affecting the limits of detection. The injection of excessive amounts of other chemicals increases the probability of contamination and long thermal pre-treatment slows down the analysis.

It was earlier suggested [3] to substitute the platform for a compact body (e.g. cylinder) or refractory material loosely located on the bottom of the tube (ballast). In a tube furnace furnished with a ballast, the sample

location is not critical. That is, the solution to be analysed can be injected on the top of the ballast or on the wall next to it. When the temperature of the tube rises rapidly, the temperature of the ballast lags behind. Therefore, if the sample is vaporized from the tube wall, its vapour undergoes condensation on the colder ballast and then re-evaporation into the absorption volume. Compared to the flat or concave platform, a compact ballast of similar mass to the platform should have less impact on gas temperatures because of the smaller surface area. Both sample re-evaporation and higher gas temperature should cause reduction of spectral and chemical interferences.

Possible impact of the idea to practice might be embodied in the reduction of detection limits without the use of chemical modifiers, faster determination and direct analysis of organics. An opportunity to apply ballasts in tube atomizers of various sizes and configurations, present in the instrumental market, can also be attractive.

It is shown that the performance of the ballast furnace should depend on multiple parameters including configuration and dimensions of the tube, physical parameters of the ballast, heating rate, temperature and vapour transport [4,5]. An optimal combination of all those parameters should provide a low limit of detection and independence of measured signals from the matrix.

A simulation of processes in the ballast furnace was performed earlier [4] using the admission about quasi-stationary distribution of vapour in the tube during the sample vaporization. Although it introduces a variety of crucial factors, the approach used in [4] can not provide a guiding line for optimisation since it is inconsistent with rapid heating and vaporization. The approach to general solution is presented in this work.

2 MODEL OF DIFFUSION, GOVERNING EQUATIONS

Figure 1 shows a schematic cross-sectional view of the atomizer. The ballast is assumed to have no effect on the diffusion of atoms through the open ends of the atomizer. Since the atoms diffuse from the centre of the atomizer, diffusion is assumed to be symmetrical with respect to the centre of the atomizer. That is, it is necessary to consider one half of the atomizer only.

Suppose that $u_1(x,t)$ is the concentration of atoms at some point x (in domain $\mathcal{D}_1$) and time t, and $u_2(x,t)$ is the concentration of atoms at some point x (in domain $\mathcal{D}_2$) and time t. To describe the physical model of diffusion, let the concentrations $u_1(x,t)$ and $u_2(x,t)$ satisfy the diffusion equations:

$$\frac{\partial}{\partial t}u_1(x,t) = D(t)\frac{\partial^2}{\partial x^2}u_1(x,t) + f_1(x,t) \quad 0 \le x \le L_1$$
$$\frac{\partial}{\partial t}u_2(x,t) = D(t)\frac{\partial^2}{\partial x^2}u_2(x,t) \qquad\qquad L_1 \le x \le L_2 \tag{1}$$

in the domains $\mathcal{D}_1$ and $\mathcal{D}_2$.

The function $f_1(x,t)$ is the density of the sources of atoms in the atomizer at some point x and time t, and characterizes the rate of vaporization of the sample. The diffusion coefficient $D(t)$ depends on time through temperature:

$$D(t) = D_0\left(\frac{T_w(t)}{T_0}\right)^{\lambda} \tag{2}$$

where $D(t)$ is the diffusion coefficient at time t, D_0 is the initial value of the diffusion coefficient, $T_w(t)$ is the temperature of the atomizer wall at time t, T_0 is the initial temperature of the atomizer wall, and λ is the gas combination factor. The value of the diffusion coefficient, D_0, can vary between 0.05 and 0.1 $cm^2.s^{-1}$ for various methods. As shown in [6], the value of the gas combination factor, λ, can vary between 1.60 and 2.00.

The temperature of the atomizer wall is given by the heating program of the atomizer, which can be defined by a piecewise continuous function:

$$T_w(t) = \begin{cases} T_0 + \alpha t & 0 \leq t < t_c \\ T_f & t_c \geq t \end{cases} \tag{3}$$

where $T_w(t)$ is the temperature of atomizer wall at time t, T_0 is the initial temperature of atomizer wall, T_f is the final temperature of atomizer wall, $\alpha = (T_f - T_0)/t_c$ is the heating rate of atomizer, and t_c is the time taken to heat the atomizer to temperature T_f. The initial temperature of the atomizer wall can vary between 293 and 1073 K. The final temperature of the atomizer wall can vary between 1500 and 3000K. The heating rate of the atomizer can vary between 2×10^3 and 1×10^4 $K.s^{-1}$.

The rate at which the quantity of analyte atoms on ballast surface is reduced due to vaporization may be described by the Arhenius-type equation [7,8]

$$\frac{d}{dt} N(t) = -k_0 e^{-\frac{\Delta H}{RT_b(t)}} N(t) \tag{4}$$

subject to the initial condition

$$N(0) = N_0 \tag{5}$$

$N(t)$ is the quantity of analyte atoms on the ballast surface at time t, N_0 is the initial quantity of analyte atoms on the ballast surface, ΔH is the

enthalpy of formation of free atoms, R is the universal gas constant, k_0 is the frequency factor, and $T_b(t)$ is the temperature of the ballast at time t. Typically, a few micro litres of sample are introduced into the atomizer, and the initial quantity of analyte atoms on the ballast surface, N_0, thus depends on the physical properties (such as atomic mass) of these atoms. The enthalpy of formation of free atoms, ΔH, can vary between 50 and 300 kJ.mol^{-1}.

The ballast is heated by radiation from the walls of the atomizer, and its temperature, $T_b(t)$, is given by the Stefan-Boltzmann equation [4]:

$$\frac{d}{dt}T_b(t) = \sigma \frac{E_b}{c_b\rho_b} \frac{S_b}{V_b}\left(T_w^4(t) - T_b^4(t)\right) \tag{6}$$

where σ is the Stefan-Boltzmann constant, E_b is the emissivity of the ballast material, c_b is the heat capacity of ballast material, ρ_b is the density of ballast material, S_b is the surface area of ballast, and V_b is the volume of ballast.

The problem (4)-(5) can be easily solved to reveal that the quantity of atoms on the ballast surface at any time t, $N(t)$, is given by:

$$N(t) = N_0 e^{-k_0\int_0^t e^{-\frac{\Delta H}{RT_b(\tau)}}d\tau} \tag{7}$$

Hence, the rate at which the analyte atoms are supplied to the furnace is given by

$$q(t) = -\frac{d}{dt}N(t) = -N_0 k_0 e^{-\frac{\Delta H}{RT_b(t)} - k_0\int_0^t e^{-\frac{\Delta H}{RT_b(\tau)}}d\tau} \tag{8}$$

The rate at which the concentration of analyte atoms in the furnace changes as a result of vaporization is:

$$f_1(x,t) = \begin{cases} \dfrac{2q(t)}{A_1 l_b} & 0 \le x \le \dfrac{l_b}{2} \\ 0 & otherwise \end{cases} \tag{9}$$

where $f_1(x,t)$ is the density of the sources of atoms in the tube, $q(t)$ is the rate of atom formation in the tube, A_1 is the cross sectional area of the tube (in domain $\mathcal{D}_1$), and l_b is the length of the ballast. That is, the concentration of analyte atoms in the furnace changes at a rate equal to $f_1(x,t)$ in a small volume $A_1 l_b / 2$. It is assumed that $f_1(x,t)$ is distributed uniformly along the x-axis. Since half of the atomizer is considered in this model, it is necessary to use only half of the length of the ballast in this calculation.

3 BOUNDARY AND INITIAL CONDITIONS

Equations (1) must be solved with the following boundary and initial conditions:

$$x = 0: \qquad \frac{\partial}{\partial x} u_1(0,t) = 0 \tag{10}$$

$$x = L_1: \qquad u_1(L_1,t) = u_2(L_1,t) \tag{11}$$

$$A_1 \frac{\partial}{\partial x} u_1(L_1,t) = A_2 \frac{\partial}{\partial x} u_2(L_1,t) \tag{12}$$

$$x = L_2: \qquad \frac{\partial}{\partial x} u_2(L_2,t) = \varphi(t) \tag{13}$$

$$t = 0: \qquad u_1(x,0) = 0, \qquad u_2(x,0) = 0 \tag{14}$$

Condition (10) follows from symmetry of the problem about $x = 0$. Condition (11) follows from the requirement that the solution be continuous at $x = L_1$. Condition (12) follows from the requirement that, at $x = L_1$, the concentration of atoms per unit time diffusion out of section 1

of the atomizer (domain $\mathcal{D}_1$) must be equal to that diffusion into section 2 (domain $\mathcal{D}_2$). Conditions (11) and (12) are typical for problems of mathematical physics with a non-homogeneous medium [9,10]. Condition (13) prescribes a value to the concentration gradient at the open end of the atomizer ($x = L_2$) at any time t. Condition (14) describes the initial concentration of free atoms in the tube.

At this point it is convenient to introduce a new unknown function $\tilde{u}_2(x,t)$

$$u_2(x,t) = \tilde{u}_2(x,t) + \psi(x,t) \tag{15}$$

representing the deviation of $u_2(x,t)$ from a certain known function $\psi(x,t)$. The auxiliary function $\psi(x,t)$ is chosen as

$$\psi(x,t) = \begin{cases} 0, & 0 \le x < L_1 \\ \dfrac{(x - L_1)^2}{2l_2}\varphi(t), & L_1 \le x \le L_2 \end{cases} \tag{16}$$

Substitution of equation (15) into the diffusion equations (1) and boundary and initial conditions (10)-(14) shows that $u_1(x,t)$ and $\tilde{u}_2(x,t)$ are the solutions of the following diffusion equations:

$$\begin{aligned} \frac{\partial}{\partial t}u_1(x,t) &= D(t)\frac{\partial^2}{\partial x^2}u_1(x,t) + f_1(x,t) \quad 0 \le x \le L_1 \\ \frac{\partial}{\partial t}\tilde{u}_2(x,t) &= D(t)\frac{\partial^2}{\partial x^2}\tilde{u}_2(x,t) + f_2(x,t) \quad L_1 \le x \le L_2 \end{aligned} \tag{17}$$

subject to the homogeneous boundary and initial conditions:

$$x = 0: \qquad \frac{\partial}{\partial x}u_1(0,t) = 0 \tag{18}$$

$$x = L_1: \qquad u_1(L_1,t) = \tilde{u}_2(L_1,t) \tag{19}$$

$$A_1\frac{\partial}{\partial x}u_1(L_1,t) = A_2\frac{\partial}{\partial x}\tilde{u}_2(L_1,t) \tag{20}$$

$$x = L_2: \qquad \frac{\partial}{\partial x}\tilde{u}_2(L_2,t) = 0 \tag{21}$$

$$t = 0: \qquad u_1(x,0) = 0, \qquad \tilde{u}_2(x,0) = g(x) \tag{22}$$

where

$$f_2(x,t) = \frac{2D(t)\varphi(t) - (x - L_2)^2 \, \dot{\varphi}(t)}{2l_2} \tag{23}$$

and

$$g(x) = -\frac{(x - L_2)^2 \varphi(0)}{2l_2} \tag{24}$$

4 EIGENVALUES AND EIGENFUNCTIONS

Let us introduce the following notation for system (17):

$$\frac{\partial}{\partial t}\tilde{u}(x,t) = D(t)\frac{\partial^2}{\partial x^2}\tilde{u}(x,t) + f(x,t)$$

(25)

Using the Fourier method, we search for the solution of (25) in the form

$$\tilde{u}(x,t) = \begin{cases} u_1(x,t) = X_1(x)\phi(t), & 0 \le x \le L_1 \\ \tilde{u}_2(x,t) = X_2(x)\phi(t), & L_1 \le x \le L_2 \end{cases} \tag{26}$$

The functions $X_1(x)$ and $X_2(x)$ must satisfy the boundary conditions (18)-(21). Substituting (26) into the partial differential equations (17), with $f_1(x,t) = f_2(x,t) = 0$, shows that $X_1(x)$ and $X_2(x)$ must satisfy the ordinary differential equations

$$X_1''(x) + \mu^2 X_1(x) = 0 \quad \text{and} \quad X_2''(x) + \mu^2 X_2(x) = 0 \tag{27}$$

where $\mu^2 \le 0$. One example of functions that satisfy these differential equations is

$$X_1(x) = b_1 \cos(\mu x)$$
$$X_2(x) = b_2 \cos[\mu(L_2 - x)] \tag{28}$$

The unknowns, b_1, b_2, and μ can be found by substituting (26) and (28) into the boundary conditions (18)-(21). This results in a system of 2 equations and 3 unknowns:

$$b_1 \cos(\mu l_1) - b_2 \cos(\mu l_2) = 0$$
$$b_1 A_1 \sin(\mu l_1) + b_2 A_2 \sin(\mu l_2) = 0 \tag{29}$$

This system defines the eigenvalues of problem (27)-(28). The system (29) can be solved simultaneously to get a transcendental equation with respect to the eigenvalues μ:

$$A_1 \sin(\mu l_1) \cos(\mu l_2) + A_2 \cos(\mu l_1) \sin(\mu l_2) = 0 \tag{30}$$

This transcendental equation has enumerable solutions $\mu_n \leq 0$. The corresponding eigenfunctions can be written in the form

$$X_n(x) = \begin{cases} X_{1n}(x) = b_{1n} \cos(\mu_n x), & 0 \leq x \leq L_1 \\ X_{2n}(x) = b_{2n} \cos[\mu_n(L_2 - x)], & L_1 \leq x \leq L_2 \end{cases} \tag{31}$$

where $b_{1n} = 1$, and b_{2n} is derived from the equation

$$b_{2n} = \frac{\cos(\mu_n l_1)}{\cos(\mu_n l_2)} \tag{32}$$

for every particular μ_n.

It is possible to prove that the eigenfunctions (31) are orthogonal with respect to a weight function $w(x)$:

$$\int_0^{L_2} w(\xi) X_n(\xi) d\xi = A_1 \int_0^{L_1} X_{1n}(\xi) X_{1m}(\xi) d\xi + A_2 \int_{L_1}^{L_2} X_{2n}(\xi) X_{2m}(\xi) d\xi \tag{33}$$

for $n \neq m$, where

$$w(x) = \begin{cases} A_1, & 0 \leq x \leq L_1 \\ A_2, & L_1 \leq x \leq L_2 \end{cases} \tag{34}$$

When $n = m$, we have the square norm:

$$\left\| X_n(x) \right\|^2 = \int_0^{L_2} w(x) X_n^2(x)dx \tag{35}$$

5 SOLUTION OF THE PROBLEM

Now that the eigenfunctions and eigenvalues of the problem have been found, the solution to equation (25) can be sought in the form of an eigenfunction expansion:

$$\tilde{u}(x,t) = \sum_{n=1}^{\infty} X_n(x) \upsilon_n(t) \tag{36}$$

where the functions $\upsilon_n(t)$ are unknown. The function $f(x,t)$ may also be written as an eigenfunction expansion:

$$f(x,t) = \sum_{n=1}^{\infty} X_n(x) f_n(t) \tag{37}$$

where the Fourier coefficients, $f_n(t)$, can be found using the orthogonality relation (33):

$$f_n(t) = \frac{1}{\left\| X_n(x) \right\|^2} \int_0^{L_2} w(\xi) X_n(\xi) f(\xi,t)d\xi \tag{38}$$

Substituting (36)-(37) into (25) gives:

$$\dot{\upsilon}_n(t) + \mu_n^2 D(t) \upsilon_n(t) - f_n(t) = 0 \tag{39}$$

with initial condition:

$$\upsilon_n(0) = g_n \tag{40}$$

where

$$g_n = \frac{1}{\left\| X_n(x) \right\|^2} \int_0^{L_2} w(\xi) X_n(\xi) g(\xi)d\xi \tag{41}$$

The solution of problem (39)-(40) is

$$\upsilon_n(t) = g_n e^{-\mu_n^2 \int\limits_0^t D(z)dz} + \int\limits_0^t f_n(\tau)e^{-\mu_n^2 \left(\int\limits_0^t D(z)dz - \int\limits_0^\tau D(z)dz\right)} d\tau \qquad (42)$$

Substituting (42) into (36) gives:

$$\tilde{u}(x,t) = \int\limits_0^{L_2} G\big(x,\xi,\kappa(t)\big)g(\xi)d\xi +$$

$$+ \int\limits_0^t \int\limits_0^{L_2} G\big(x,\xi,\kappa(t)-\kappa(\tau)\big)f(\xi,\tau)d\xi d\tau \qquad (43)$$

The function $G\big(x,\xi,\kappa(t)\big)$ is the Green's function [9-11] of the problem (17)-(22), and is defined as

$$G\big(x,\xi,\kappa(t)\big) = \sum_{n=1}^{\infty} \frac{1}{\|X_n(x)\|^2} w(\xi) X_n(\xi) X_n(x) e^{-\mu_n^2 \kappa(t)} \qquad (44)$$

where

$$\kappa(t) = \int\limits_0^t D(z)dz \qquad (45)$$

The solution of problem (1), (10)-(14) is therefore given by

$$u(x,t) = \int\limits_0^{L_2} G\big(x,\xi,\kappa(t)\big)g(\xi)d\xi +$$

$$+ \int\limits_0^t \int\limits_0^{L_2} G\big(x,\xi,\kappa(t)-\kappa(\tau)\big)f(\xi,\tau)d\xi d\tau + \psi(x,t) \qquad (46)$$

It is now possible to find the quantity of atoms in the furnace at any time t by integrating $u(x,t)$ over x and multiplying by the cross-sectional area of the furnace:

$$U(t) = \int\limits_0^{L_2} w(x)u(x,t)dx = A_1 \int\limits_0^{L_1} u_1(x,t)dx + A_2 \int\limits_{L_1}^{L_2} u_2(x,t)dx \qquad (47)$$

6 RESULTS

The results are exposed here in the form of an example, where the derived model is applied to a hypothetical problem.

Consider a tube with dimensions given in table 1.

Table 1. Dimensions of graphite tube atomizer

Parameter	Symbol	Value	Scale
Length of section 1 of atomizer	l_1	1.0×10^{-2}	m
Cross-sectional area of section 1 of atomizer	A_1	1.96×10^{-5}	m^2
Length of section 2 of atomizer	l_2	3.25×10^{-3}	m
Cross sectional area of section 2 of atomizer	A_2	7.07×10^{-5}	m^2

The ballast onto which the sample is introduced is a length Tantalum (Ta) wire with a diameter of 0.2mm. The dimensions of the ballast and physical properties of Ta are given in table 2. Note that the condition of symmetry does not apply to the calculation of the temperature of the ballast. Since the entire surface area and volume must be taken into account, the entire ballast must be considered when making these calculations.

Table 2. Dimensions and physical properties of ballast

Parameter	Symbol	Value	Scale
Stefan-Boltzmann constant	σ	5.671×10^{-8}	$J.s^{-1}.m^{-2}.K^{-4}$
Length of ballast	l_b	1.0×10^{-2}	m
Surface area of ballast	S_b	6.35×10^{-6}	m^2
Volume of ballast	V_b	3.14×10^{-10}	m^3
Density of Ta [12]	ρ_b	1.66×10^4	$kg.m^{-3}$
Emissivity of Ta at 1500 K [12]	E_b	0.2	-
Specific heat capacity of Ta [12]	c_b	160	$J.kg^{-1}.K^{-1}$

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The parameters of the heating program applied to the tube are given in table 3. The temperature of the furnace wall, $T_w(t)$, and the temperature of the ballast, $T_b(t)$, are plotted in figure 2.

Table 3. Heating program of atomizer

Parameter	Symbol	Value	Scale
Initial temperature of atomizer wall	T_0	300	K
Final temperature of atomizer wall	T_f	2500	K
Heating rate of atomizer wall	α	2000	K.s^{-1}
Duration of temperature ramp	t_c	1.1	s

Suppose that a sample containing a known quantity of lead (Pb) atoms is introduced to the atomizer. The dependence of the diffusion coefficient of the Pb atoms on time (through temperature) is shown in figure 3. The rate of atomization will depend on the physical properties of the analyte atoms (Pb), given in table 4. The quantity of atoms on the ballast surface, $N(t)$, and the rate of atom formation in the atomizer, $q(t)$, are plotted in figure 4.

Table 4. Physical properties of analyte atoms (Pb)

Parameter	Symbol	Value	Scale
Initial number of atoms in sample	N_0	1×10^{15}	atoms
Universal gas constant	R	8.314	J.mol^{-1}.K^{-1}
Enthalpy of formation of free atoms [7]	ΔH	195×10^{-3}	J.mol^{-1}
Frequency factor [7]	k_0	1×10^7	s^{-1}
Diffusion coefficient [6]	D_0	6.0×10^{-6}	m^2.s^{-1}
Gas combination factor [6]	λ	1.75	-

The concentration of atoms at some point x and time t in the furnace, $u(x,t)$, is plotted in figure 5. Notice the "jump" in derivative at $x = L_1$. This is a property of the eigenfunctions (31).

The quantity of atoms in the furnace at any time t, $U(t)$, can now be found by integrating the concentration distribution $u(x,t)$ over x (47). Figure 6 shows the normalised quantity of atoms in the atomizer versus time, $U(t)/N_0$.

7 CONCLUSION

A one-dimensional model for diffusion of atoms from a graphite furnace atomiser used in ETAAS was proposed.

A time-dependant model of diffusion is most frequently used in graphite furnace design [7-8]. The configuration of the atomizer is introduced into the model by means of a geometric factor. The model proposed in this paper automatically incorporates the geometry of the atomizer into the solution. In addition to evaluating the number of atoms in the atomizer, the proposed model could also be used to evaluate the distribution of atoms in the atomizer at any time t. This is not possible using the time-dependant model.

An analytical solution for the proposed model was found in terms of a Green's function containing piecewise continuous trigonometric eigenfunctions.

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List of Notations

Symbol	Description	Scale
α	Heating rate of atomizer	$K.s^{-1}$
$\phi(t)$	A function resulting from separation of variables of $\tilde{u}(x,t)$	$atoms.m^{-3}$
$\varphi(t)$	Value of concentration gradient at open end of atomizer	$atoms.m^{-4}$
$\kappa(t)$	Integral of diffusion coefficient	m^2
λ	Gas combination factor	-
μ_n	n^{th} eigenvalue	m^{-1}
ρ_b	Density of ballast material	$kg.m^{-3}$
σ	Stefan-Boltzmann constant	$J.s^{-1}.m^{-2}.K^{-4}$
$\upsilon_n(t)$	n^{th} Fourier coefficient of $\tilde{u}(x,t)$	$atoms.m^{-3}$
$\psi(x,t)$	Auxiliary function introduced to homogenize boundary conditions	$atoms.m^{-3}$
A_1	Cross-sectional area of section 1 of atomizer	m^2
A_2	Cross-sectional area of section 2 of atomizer	m^2
b_{1n}	Coefficient of nth eigenfunction in section 1 of atomizer	-
b_{2n}	Coefficient of nth eigenfunction in section 2 of atomizer	-
c_b	Heat capacity of ballast material	$J.kg^{-1}.K^{-1}$
$D(t)$	Diffusion coefficient of atomized particles	$m^2.s^{-1}$
D_0	Initial value of diffusion coefficient of atomized particles	$m^2.s^{-1}$
E_b	Emissivity of ballast material	-
$f_1(x,t)$	Density of sources of atoms in section 1 of atomizer	$atoms.m^{-3}.s^{-1}$
$f_2(x,t)$	Density of sources of atoms in section 2 of atomizer	$atoms.m^{-3}.s^{-1}$
$f(x,t)$	Density of sources of atoms in atomizer	$atoms.m^{-3}.s^{-1}$
$f_n(t)$	n^{th} Fourier coefficient of $f(x,t)$	$atoms.m^{-3}.s^{-1}$

$G(x,\xi,\kappa(t))$	Green's function	m^{-1}
$g(x)$	Initial concentration distribution of atoms in atomizer	$atoms.m^{-3}$
g_n	n^{th} Fourier coefficient of $g(x)$	$atoms.m^{-3}$

Symbol	Description	Scale
ΔH	Enthalpy of formation of free atoms	$J.mol^{-1}$
k_0	Frequency factor	s^{-1}
l_b	Length of ballast	m
l_1	Length of section 1 of atomizer	m
l_2	Length of section 2 of atomizer	m
L_1	x-coordinate of end of section 1 of atomizer	m
L_2	x-coordinate of end of section 2 of atomizer	m
$N(t)$	Quantity of atoms on ballast surface	atoms
N_0	Initial quantity of atoms on ballast surface	atoms
$q(t)$	Rate of atom formation in atomizer	$atoms.s^{-1}$
R	Universal gas constant	$J.mol^{-1}.K^{-1}$
S_b	Surface area of ballast	m^2
T_0	Initial temperature of atomizer wall/ballast surface	K
T_f	Final temperature of atomizer wall	K
$T_b(t)$	Temperature of ballast material	K
$T_w(t)$	Temperature of atomizer wall	K
t_c	Duration for which atomizer is heated at a rate of α	s
$U(t)$	Quantity of atoms in atomizer	atoms
$u_1(x,t)$	Concentration of atoms in section 1 of atomizer	$atoms.m^{-3}$
$u_2(x,t)$	Concentration of atoms in section 2 of atomizer	$atoms.m^{-3}$
$\tilde{u}_2(x,t)$	Concentration of atoms in section 2 of atomizer resulting from homogenization of boundary conditions	$atoms.m^{-3}$
$u(x,t)$	Concentration of atoms in atomizer	$atoms.m^{-3}$
V_b	Volume of ballast	m^3

$w(x)$	Weight function	m^2
$X_n(x)$	Eigenfunction corresponding to n^{th} eigenvalue	-

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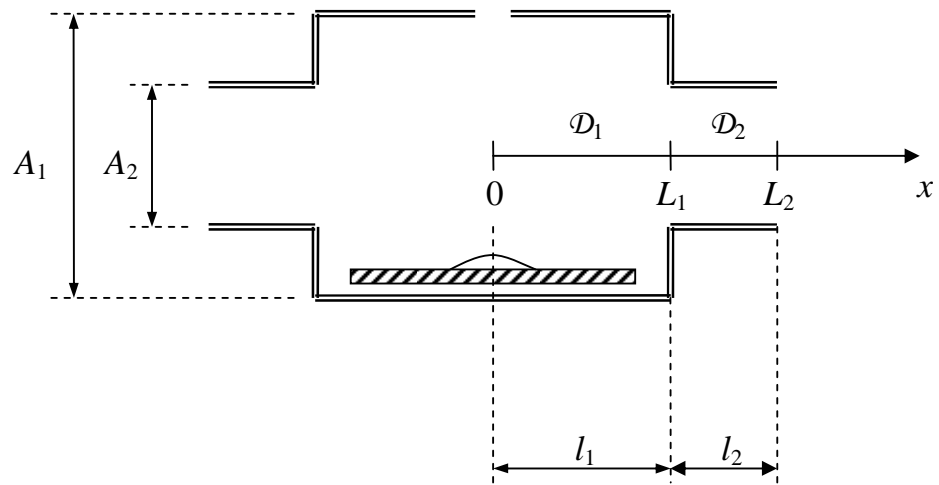
Figure 1. Schematic diagram of domain showing dimensions of atomiser
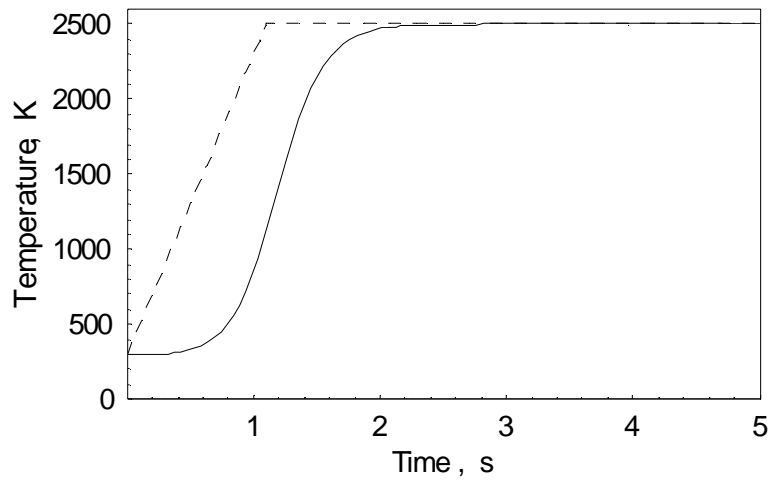
Figure 2. The temperature of the furnace wall (dashed line) and the temperature of the ballast (solid line) versus time.
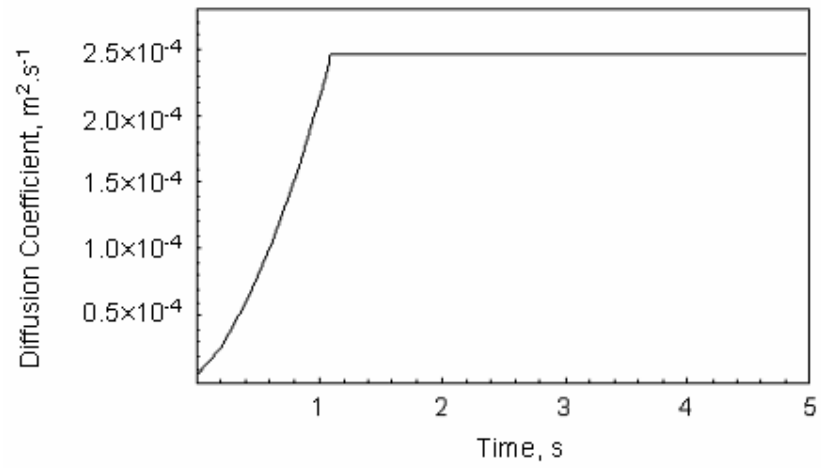
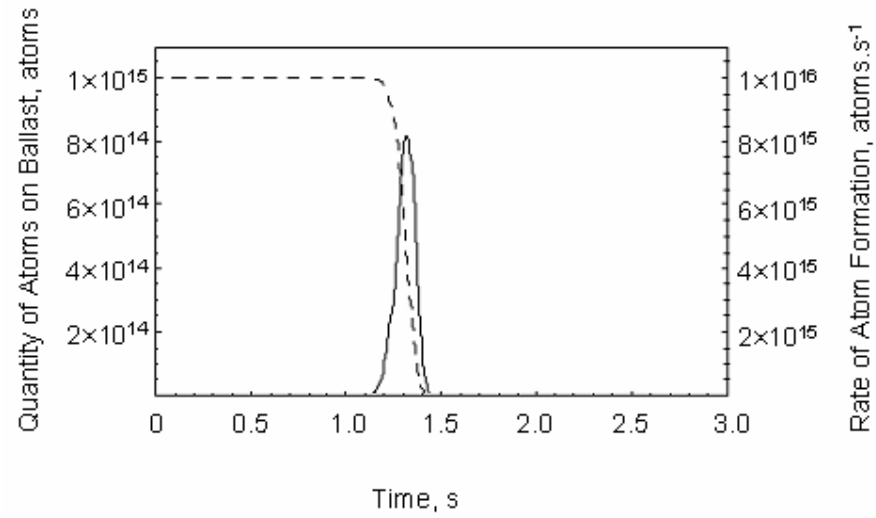*Figure 3. Dependence of the diffusion coefficient of the atomized Pb on time.*

Figure 4. The number of atoms on the ballast surface (dashed line) and the rate of atom formation in the atomizer (dotted line) versus time.
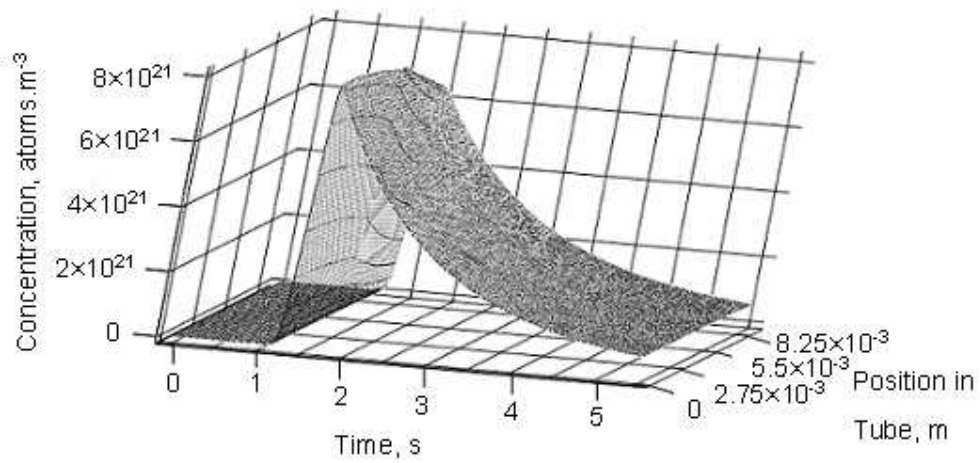
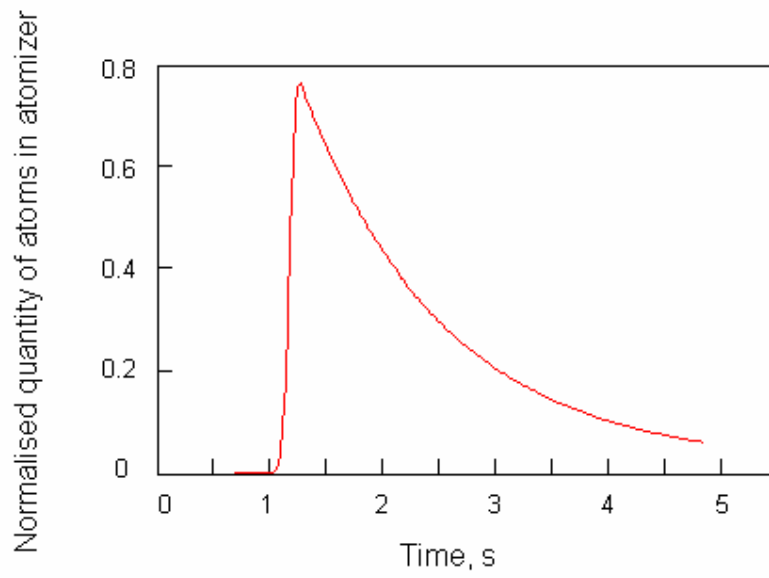*Figure 5. The x - t concentration distribution of atoms in the furnace.*

Figure 6. Normalized quantity of atoms in the atomizer versus time.