Atomic Spectroscopy

Article

Numerical Simulation of Heat Conduction in Laser Ablation Based on Optimal Weight Factor

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Received: *July 21, 2023;* ***Revised:*** *September 01, 2023;* ***Accepted:*** *September 06, 2023;* ***Available online:*** *September 06, 2023.*

DOI: 10.46770/AS.2023.151

ABSTRACT: Laser ablation is a crucial process in many types of laser-matter interactions. Therefore, an accurate simulation of the laser ablation is beneficial to understanding the underlying physics in those interaction dynamics. Laser ablation simulation essentially depends on the numerical solution of heat conduction equations, usually based on finite difference strategy. Common finite difference methods include forward-Euler, backward-Euler and Crank-Nicolson schemes, corresponding to three specific finite-difference weight factors, *i.e.* 0, 1, and 0.5. This study proposes a new method based on an optimal weight factor, which is not a fixed value but pertinently searched for each specific problem. Taking the temporal evolution of a one-dimensional temperature field as an example, we have demonstrated that utilizing the achieved optimal weight factor can yield significantly higher accuracy than using the routine weight factors. The results in this study have the potential to better understand the heat conduction dynamics and the laser ablation physics, and hence improve the performance of relevant LMI-based techniques in the future.

INTRODUCTION

Laser-matter interaction (LMI) can bring various physical, biological, and chemical effects. Hence, it is a fascinating field of study with an extensive range of applications. For the straightforward physical effects, the main applications are material processing and material preparation, such as surface heat treatment, cutting and welding,[1,2] deposition of thin films and micro-nano materials.[3,4] As to the biological effects, there are many applications in the biomedical field, mainly in the directions of medical diagnosis[5,6] and surgery.[7,8] From the perspective of chemical effects, the laser-induced plumes and/or plasma can be utilized for analyzing the chemical composition of the ablated material, with many relevant techniques adopted in spectrometry analysis, including matrix assisted laser desorption ionization (MALDI),[9,10] laser microprobe mass spectrometry (LMMS),[11,12] laser absorption spectroscopy,[13,14] laser-induced breakdown spectroscopy (LIBS)[15,16] and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)[17,18], *etc.* A diagram presenting the typical applications of LMI is shown in Fig. 1.

A common feature of the LMI applications mentioned above is that laser ablation plays a crucial role in them. Particularly for those applications utilizing chemical effects, laser ablation is a sampling strategy with apparent advantages. To name a few, it has advantages of fast and micro-invasive sampling, minimal sample pretreatment, and prevention of sample contamination. Taking LIBS and LA-ICP-MS as two examples, we briefly introduce the working principle of them and demonstrate the importance of the laser ablation. In a typical LIBS scheme, a high-intensity pulsed laser is focused onto the target surface to induce ablation: a tiny amount of the material experiences melting during the laser heating, and then evaporation, atomization and ionization take place in succession. The ionization produces countless electrons

Fig. 1 A diagram showing typical applications of LMI. The left panel simply exhibits a few applications utilizing physical and biological effects, while the right panel illustrates some applications utilizing chemical effects in a more detailed way. The abbreviations in the right panel stand for matrix assisted laser desorption ionization (MALDI), laser microprobe mass spectrometry (LMMS), laser absorption spectroscopy (LAS), laser-induced breakdown spectroscopy (LIBS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), respectively. The images are all acquired from Internet public picture library (*e.g.* Google Images), except that the image for LIBS is from our own experiment data.

and ions, forming plasma above the surface. The plasma radiation can then be collected and resolved by a spectrometer.[19] Similarly, in LA-ICP-MS technique, the sample in an ablation cell is heated by a focused laser beam and particulates are generated. Then the particulates (aerosol) are transported by the carrier gas into an ICP module for ionization. After ionization, the ions with different mass-to-charge ratios are filtered by the mass spectrum system and recorded by the detector.[20] From the above two examples we can find that laser ablation plays an important role in such techniques, since it is through laser ablation that the materials for subsequent analysis are generated.

During the sample ablation, the first key process is heating, *i.e.* the incident laser energy is partly converted into the internal energy of the sample and the temperature of the sample increases. Hence it is of considerable interest to command the temporal-spatial evolution of the temperature field, which is critical to the research of the thermal pattern and thermokinetics and the prediction of the subsequent physicochemical conditions of the sample.[21-23]

To acquire the temperature field distribution and evolution, besides direct experimental measurement, one may also choose theoretical simulation. Compared with experimental measurement, theoretical simulation has several major advantages. Firstly, implementing laser-involved experiments can be expensive. Especially for ultrafast optical experiments, merely one femtosecond laser would be a high economic cost, not to speak of the many other supporting facilities. Even for those teams who own complete experimental equipment, adjusting experimental parameters may be laborious and time-consuming, and in addition, the parameter tuning range and tuning fineness are largely limited by real-world technology. By contrast, theoretical simulations need only some computers (computer clusters), and parameter manipulation is much easier and almost unlimited in terms of both tuning range and fineness. Secondly, for laser experiments the researchers usually get a final outcome of a certain physical quantity (*e.g.* the temperature), but the intermediate evolution processes may be too fast to be carefully observed. In theoretical simulations, however, the researchers are able to scrutinize every intermediate process by adopting proper calculation frameworks and parameters, so that they can localize the potential factors which cause unsatisfying experimental results and define the regimes where the experimental problems can be minimized or overcome.[24] Moreover, researchers may flexibly choose different theoretical models so that they can effectively focus on different aspects of a complicated problem. Taking laser-induced plasma phenomenon as an example, when focusing on the heating and ablation process, one may choose a microscopic model which utilizes Boltzmann transport equation to investigate the transport of electrons and the electron-lattice interactions;[25] when focusing on the laser-induced plasma expansion process, one may choose a macroscopic model which regards the plasma plume as fluid based on hydrodynamic models.[26] Thirdly, theoretical simulation can avoid the inherent systematic errors of measuring devices, so that one may achieve theoretically accurate results. Therefore, as a complement to experimental measurement, theoretical simulation is an important means to explore the laws and mechanisms of the multifarious LMI phenomena.

Specifically for temperature field acquisition, theoretical simulation refers to theoretically solve the heat conduction equation (HCE). Since the mathematical form of the HCE is a second-order partial differential equation, there is usually no analytical solution. Hence numerical simulation methods plays an important role in solving the HCE.[24,27]

One of the most popular numerical methods for solving HCE-like partial differential equations is finite difference method, which approximates continuous space and time by finite discrete spatiotemporal grids and replace mathematical differentials with differences.[28] There are three regular finite difference schemes, namely forward-Euler, backward-Euler and Crank-Nicolson.[29] In fact, these three different schemes can be regarded as a uniform weighted implicit scheme, corresponding to three specific weight factors, *i.e.* 0, 1 and 0.5. For a specific heat conduction problem, however, there should exist an optimal weight factor that can lead to the minimum numerical error.[30] Of course, this optimal weight factor is not necessarily the regular values (*e.g.* 0, 1 or 0.5), but depends on the detailed HCE parameters and the selected numerical time-space grid parameters in each specific problem. This study proposes a novel method to solve the HCE in laser ablation, based on the optimal finite-difference weight factor that is pertinently searched for each concrete problem.

Fig. 2 (a) A diagram demonstrating a target sample heated by a laser pulse (Gaussian envelope). A portion of the laser energy would be lost through reflection. (b) A diagram exhibiting the heat conduction that originates from the absorbed laser energy. The black arrow indicates a 1D space model (only one spatial dimension x). The 2D pseudo-color image is a symbolic illustration of the temperature field evolution, with the horizontal axis standing for time, the vertical axis for space, and the color for temperature.

A brief comparison of the three regular schemes and the novel scheme is provided as follows. For the forward-Euler scheme, the numerical accuracy is not very high, and the result is not unconditionally stable (numerical grid parameters must meet certain requirements); for the backward-Euler scheme, although the result would be unconditionally stable, the numerical accuracy is generally even lower than the forward-Euler scheme; as to the Crank-Nicolson scheme, although it is superior to the former two in terms of accuracy, its weight factor is still a fixed value and hence this scheme lacks pertinence based on specific heat conduction problems and grid parameters. Unlike the three conventional schemes, the weight factor in the novel scheme proposed herein is not a fixed value, but needs to be elaborately searched for each specific problem. As the term suggests, the optimal weight factor scheme can achieve much higher numerical accuracy, with the error being able to infinitely approach zero. Meanwhile, the result achieved by the optimal weight factor scheme would be unconditionally stable. The disadvantage of the optimal weight factor scheme is about the time cost. Compared with simply choosing 0, 1, or 0.5, searching the optimal factor surely takes more time. The extraordinary superiority of the new scheme over the three regular ones regarding numerical accuracy would be illustrated in the relevant part of the following text.

Since the general solving procedure is not beyond the finite difference methodology framework, the core point of this new method is to search the optimal weight factor. In the following text, the basic model of HCE numerical solution and the detailed methodology of our new method is introduced in Experimental Section. In Results and Discussion Section, a specific computation example adopting practical physical parameters is demonstrated, and the results achieved by the three routine methods and the novel method are exhibited and discussed. Finally, a summary is provided in Conclusion Section.

EXPERIMENTAL

Physical Model of Heat Conduction. When a laser pulse is incident onto the surface of a target sample, the sample material will reflect a portion of the laser energy while absorbing the remaining energy. The absorbed laser energy will be converted into heat and then heat conduction occurs throughout the material, as illustrated in Fig. 2.

Although the heat conduction practically occurs in three-dimensional space, in many cases one may pay major attention to the conduction along the normal-to-surface direction. Hence it is intuitive and reasonable to use the one-dimensional (1D) space model to describe the heat conduction, and the 1D modelling can also considerably save the computation time.

Within the 1D space model, the evolution of the temperature field $T(x,t)$ can be described by the HCE as Eq. (1):

$$\frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\frac{\kappa}{C_p\rho}\frac{\partial T(x,t)}{\partial x}\right] + \frac{a}{C_p\rho}I(x,t) \quad (1)$$

where $T(x,t)$ represents the temperature, x denotes the position (*i.e.* the depth from the surface), t is the time; κ represents the thermal conductivity of the material, C_p is the heat capacity, ρ is the mass density, a is the absorption coefficient.

The $I(x,t)$ term on the right stands for the laser irradiance as a function of time and position in the target, and can be expressed by Eq. (2) supposing the laser pulse has a Gaussian-shaped time envelope:

$$I(x,t) = I_0 \cdot \exp\left[-4\ln 2\left(\frac{t-t_c}{\tau}\right)^2\right] \cdot (1-R) \cdot \exp(-ax) \quad (2)$$

where I_0 denotes the peak intensity of the laser pulse, t_c and τ are the central time and width of the Gaussian pulse, respectively; and R is the surface reflectivity of the target.

Now Eq. (1) can be rewritten into a standard HCE form, as shown in Eq. (3)-(5):

$$\frac{\partial T(x,t)}{\partial t} = \beta\frac{\partial^2 T(x,t)}{\partial x^2} + f(x,t) \quad (3)$$

$$\beta = \frac{\kappa}{C_p\rho} \quad (4)$$

$$f(x,t) = \frac{a}{C_p\rho} \cdot I_0 \cdot \exp\left[-4\ln 2\left(\frac{t-t_c}{\tau}\right)^2\right] \cdot (1-R) \cdot \exp(-ax) \quad (5)$$

where β is the so-called second-order term coefficient, $\beta > 0$, and $f(x,t)$ represents the external heat source term, $f(x,t) > 0$. It is worth emphasizing that the heat conduction problem discussed in this study contains external heat source, hence more complicated than those non-source problems.[31]

Numerical Simulation Grid. For the 1D space model, the evolution of the temperature field $T(x,t)$ is numerically simulated in the *x*-*t* grid. The *x*-dimension grid is determined by the minimum x value x_{min} and the maximum x value x_{max}, where $x_{min} = 0$ represents the position on the surface and x_{max} is the deepest position from the surface. The space step is denoted as dx, standing for the spacing between adjacent grid points on the x dimension. The *t*-dimension grid is determined by the minimum t value t_{min} and the maximum t value t_{max}, where $t_{min} = 0$ and t_{max} are the starting and ending time of the evolution respectively. The time step is denoted as dt, standing for the interval between adjacent grid points on the t dimension.

The number of rows and columns in the grid are $Nx + 1$ and $Nt + 1$, respectively, where $Nx = (x_{max} - x_{min})/dx$, and $Nt = (t_{max} - t_{min})/dt$. The temperature field $T(x,t)$ is then represented by the $(Nx + 1) \times (Nt + 1)$ matrix. Denote the matrix element in the j^{th} row and the k^{th} column as (x_j, t_k), where $1 \le j \le Nx + 1$, $1 \le k \le Nt + 1$. An important parameter for solving the HCE is the so-called step ratio parameter r, which is defined by Eq. (6):

$$r = \beta \frac{dt}{(dx)^2} \tag{6}$$

where β has been defined in Eq. (4) and $r > 0$ is constantly valid.

Method of Searching Optimal Weight Factor. As mentioned above, the heat conduction problem investigated herein contains external heat source, *i.e.* the laser source in the practical laser ablation process. Unlike those non-source HCE, such kind of HCE can hardly have analytical solution. Therefore, it is necessary to formulate an alternative HCE which has an exact analytical solution, and the optimal weight factor of the formulated HCE is regarded as approximately identical to that of the original HCE. Based on this "bridge" HCE, one can monitor the real-time error under the weight factor at the current iteration step, and thereby know the direction of the next step to search the weight factor. The procedures of formulating the alternative HCE with exact analytical solution are introduced as follows.

Firstly, extract the time-dependent exponential term in $f(x,t)$ and define it as $f(t)$:

$$f(t) = \exp\left[-4 \ln 2 \left(\frac{t - t_c}{\tau}\right)^2\right] \tag{7}$$

which stands for the Gaussian envelope of the laser pulse. Secondly, select a truncation time t_z, calculate $f(t)$ within the $[0, t_z]$ interval, and fit it by a new exponential function $F(t)$ with the form of

$$F(t) = b_1 \cdot \exp(b_2 t) \tag{8}$$

where the two coefficients b_1 and b_2 should satisfy $b_1 > 0$ and $b_2 > 0$. This approximation procedure is physically reasonable since the leading edge of a short laser pulse plays a significant role in determining the solid heating status.[32, 33] This is easy to understand if we consider an ultrashort intense pulse. Before the intensity peak occurs, the forepart of the pulse may have already changed the solid sample into liquid/gas, and hence only the portion of pulse within the earliest $[0, t_z]$ interval is suitable for the solid sample heat conduction considered herein.

Then formulate a new HCE like Eq. (9):

$$\frac{\partial T(x,t)}{\partial t} = \beta \frac{\partial^2 T(x,t)}{\partial x^2} + f_s \cdot \exp(-ax) \cdot \exp(b_2 t) \tag{9}$$

where $f_s = \frac{a}{C_p \rho} \cdot I_0 \cdot (1 - R) \cdot b_1$ is called the external source coefficient, $f_s > 0$.

The initial condition and boundary condition are shown in Eq. (10) and Eq. (11) respectively:

$$T(x,0) = u_s \cdot \exp(-ax) \tag{10}$$

$$\begin{cases} T(0,t) = u_s \cdot \exp(b_2 t) \\ T(x_{\max}, t) = u_s \cdot \exp(-a x_{\max}) \cdot \exp(b_2 t) \end{cases} \tag{11}$$

It is not difficult to find that the complete HCE defined by Eq. (9)-(11) has an exact analytical solution $T_{ex}(x,t)$, which can be written as:

$$T_{ex}(x,t) = u_s \cdot \exp(-ax) \cdot \exp(b_2 t) \tag{12}$$

where the coefficient u_s is expressed by $u_s = f_s/(b_2 - \beta a^2)$.

In the following, the core scheme is to search the optimal finite-difference weight factor of this newly formulated HCE. The accuracy of a weight factor can be evaluated by the numerical error based on the exact analytical solution.

Firstly, according to the determined Nt value described in Numerical Simulation Grid part, select M time grid point number parameters $Nt_1, Nt_2, \ldots\ldots, Nt_M$, where $M \ge 2$, and $Nt_m < Nt, m = 1,2, \ldots M$. In other words, the Nt value is regarded as the upper limit of the time grid point number parameter, which might be a large number. In order to save total computation time, we can choose to carry out the computation with the series of smaller parameters (namely $Nt_1, Nt_2, \ldots\ldots, Nt_M$), and utilize their results to extrapolate the result of the Nt parameter by nonlinear fitting, as will be expounded later. Of course, directly conducting the computation under the Nt parameter is also feasible, but that would be more time-consuming.

For each selected Nt_m value, it is easy to determine the corresponding time step parameter dt_m and step ratio parameter r_m. Note that it is highly necessary to ensure

$\max\{r_1, r_2, \ldots\ldots, r_M\} \le 1/2$, so that the result would be stable (regardless of weight factor). Then based on the specific dt_m and r_m values, one can numerically solve the newly formulated HCE by means of the standard finite difference procedure, as expressed by Eq. (13):

$$-\left[\theta r_m \cdot T_{j-1}^{k+1} - (1+2\theta r_m)\cdot T_j^{k+1} + \theta r_m \cdot T_{j+1}^{k+1}\right]$$

$$= (1-\theta) r_m \cdot T_{j-1}^{k} + [1-2(1-\theta)r_m]\cdot T_j^k + (1-\theta) r_m \cdot T_{j+1}^k + dt_m \cdot f_j^{k+\theta} \quad (13)$$

where θ is the weight factor, $0 \le \theta \le 1$; T_j^k is the abbreviation of $T(x_j, t_k)$, standing for the temperature value at the (x_j, t_k) grid point. A relatively special term herein is $f_j^{k+\theta}$, representing the value of the external source term $f_s \cdot \exp(-ax) \cdot \exp(b_2 t)$ at the virtual grid point $(x_j, t_{k+\theta})$. This value is a weighted sum of the value of $f_s \cdot \exp(-ax) \cdot \exp(b_2 t)$ at (x_j, t_{k+1}) and (x_j, t_k), *i.e.* $f_j^{k+\theta} = \theta \cdot f_j^{k+1} + (1-\theta)\cdot f_j^k$.

Next, numerically solve the formulated HCE according to the iteration expression shown in Eq. (13), with the two initial weight factors being $\theta = 1$ and $\theta = 0$, and then obtain the temperature value $T_\theta(x,t)$ at the two weight factors, *i.e.* $T_1(x,t)$ and $T_0(x,t)$. For every acquired numerical $T_\theta(x,t)$ result, calculate the relative error values at each grid point $\varepsilon_{jk,\theta}$ by Eq. (14):

$$\varepsilon_{jk,\theta} = \frac{T_\theta(x_j,t_k) - T_{ex}(x_j,t_k)}{T_{ex}(x_j,t_k)} \quad (14)$$

where $T_{ex}(x_j, t_k)$ is the exact temperature value at the (x_j, t_k) grid point. And then calculate the mean relative error $\langle\varepsilon_{jk}\rangle_\theta$ by Eq. (15):

$$\langle\varepsilon_{jk}\rangle_\theta = \frac{\sum_{j=1}^{Nx+1}\sum_{k=1}^{Nt+1}\varepsilon_{jk,\theta}}{(Nx+1)(Nt+1)} \quad (15)$$

and its absolute value $|\langle\varepsilon_{jk}\rangle_\theta|$ is used as the criteria of evaluating the accuracy of the numerical solution $T_\theta(x,t)$.

For $\theta = 1$ and $\theta = 0$, calculate $\langle\varepsilon_{jk}\rangle_1$ and $\langle\varepsilon_{jk}\rangle_0$ respectively. If $\langle\varepsilon_{jk}\rangle_1 \cdot \langle\varepsilon_{jk}\rangle_0 > 0$, then it can be inferred that the optimal weight factor θ_{opt} for the current HCE does not falls in the (0,1) interval. In this case, directly compare the values of $|\langle\varepsilon_{jk}\rangle_1|$ and $|\langle\varepsilon_{jk}\rangle_0|$. If $|\langle\varepsilon_{jk}\rangle_1| < |\langle\varepsilon_{jk}\rangle_0|$, then $\theta_{opt} = 1$; and if $|\langle\varepsilon_{jk}\rangle_1| > |\langle\varepsilon_{jk}\rangle_0|$, then $\theta_{opt} = 0$, and the θ_{opt} searching procedure is complete.

If $\langle\varepsilon_{jk}\rangle_1 \cdot \langle\varepsilon_{jk}\rangle_0 < 0$, then it can be inferred that the optimal weight factor θ_{opt} for the current HCE falls in the (0,1) interval, and the searching should be further carried out. For the case of $\langle\varepsilon_{jk}\rangle_1 \cdot \langle\varepsilon_{jk}\rangle_0 < 0$, there must be a positive term and a negative term. Denote the positive term as $\langle\varepsilon\rangle_+$, and the corresponding θ value as θ_+; denote the negative term as $\langle\varepsilon\rangle_-$, and the corresponding θ value as θ_-.

Afterwards the cyclic iteration would be carried out to search the θ_{opt} value. Before that, the accuracy level requirement of θ_{opt} should be determined, represented by a value called tolerable convergence error *w*. If the difference between the results of two adjacent iterations does not exceed *w*, then the result is regarded as convergent and the searching can be halted. The cyclic iteration module is stated as follows.

1 Set the first trial optimal weight factor $\theta_{opt}^0 = 0.5$.

2 Let $\theta = \theta_{opt}^0$, calculate the numerical result $T_\theta(x,t)$, and obtain the corresponding $\langle\varepsilon_{jk}\rangle_\theta$. If $\langle\varepsilon_{jk}\rangle_\theta > 0$, then assign $\langle\varepsilon_{jk}\rangle_\theta$ to $\langle\varepsilon\rangle_+$ and assign θ to θ_+; if $\langle\varepsilon_{jk}\rangle_\theta < 0$, then assign $\langle\varepsilon_{jk}\rangle_\theta$ to $\langle\varepsilon\rangle_-$ and assign θ to θ_-.

3 Perform linear fitting based on the two data points $(\theta_+, \langle\varepsilon\rangle_+)$ and $(\theta_-, \langle\varepsilon\rangle_-)$ by Eq. (16):

$$\langle\varepsilon\rangle = p_1 \cdot \theta + p_2 \quad (16)$$

and acquire the fitting coefficients p_1 and p_2, and then calculate the updated optimal weight factor θ_{opt}^1 by $\theta_{opt}^1 = -p_2/p_1$.

4 Judge whether the condition $|\theta_{opt}^1 - \theta_{opt}^0| \le w$ is valid. If so, then determine that $\theta_{opt} = \theta_{opt}^1$ and the searching is complete. If not, then let $\theta_{opt}^0 = \theta_{opt}^1$.

5 Repeat the above three steps (from Step 2 to Step 4), until $|\theta_{opt}^1 - \theta_{opt}^0| \le w$ is valid.

So far, the cyclic iteration module is finished, and the searching is regarded complete and the θ_{opt} value is acquired. In summary, the above searching scheme is based on linear fitting and iteration, and the logical flowchart is demonstrated in Fig. 3.

According to this searching method, one may obtain a θ_{opt} value for each specific Nt_m value and its corresponding r_m parameter. Denote that value as $\theta_{opt,m}$, and one can acquire *M* groups of $(r_m, \theta_{opt,m})$ data points. Then conduct nonlinear fitting upon these data points by Eq. (17):

$$\theta_{opt} = p_3 + p_4 \cdot \frac{1}{r} \quad (17)$$

and acquire the fitting coefficients p_3 and p_4 (usually $p_3 > 0$ and $p_4 < 0$).

Finally, according to the r value in the formulated HCE determined by Eq. (6), calculate the corresponding θ_{opt} value based on Eq. (17). As stated above, directly implementing the computation under the r parameter also works, and the last nonlinear fitting extrapolation strategy is not indispensable if time saving is not on the list of priorities.

Fig. 3 The logical flowchart showing the procedure of searching the optimal weight factor based on linear fitting and iteration.

After achieving the final optimal weight factor of the specifically formulated "bridge" HCE defined by Eq. (9)-(11), one can easily employ this weight factor to solve the original HCE according to its initial condition and boundary condition in the practical laser heating problem.

RESULTS AND DISCUSSION

Results. In order to make the methodology described in Experimental Section more intuitive and explicit, a practical example is provided here to illustrate the computation procedure.

In this example, international units are adopted for the physical parameters. The laser parameters are as follows: the peak intensity is $I_0 = 1.0 \times 10^{13}\ \mathrm{W/m^2}$, the Gaussian pulse width is $\tau = 4\ \mathrm{ns} = 4 \times 10^{-9}\ \mathrm{s}$ and the central time of the pulse is $t_c = 6\ \mathrm{ns} = 6 \times 10^{-9}\ \mathrm{s}$. The physical property parameters of the target material are described as follows: the thermal conductivity is $\kappa = 14.63\ \mathrm{W/(m \cdot K)}$, the heat capacity is $C_p = 540\ \mathrm{J/(kg \cdot K)}$, the mass density is $\rho = 4510\ \mathrm{kg/m^3}$, the absorption coefficient is $a = 1.0 \times 10^7\ /\mathrm{m}$, and the surface reflectivity is $R = 0.6$. It is worth mentioning that although this study is mainly about mathematical skills for solving partial differential equations, we hope that it can make some contribution to the practical LMI applications in the future, especially spectroscopic techniques. Therefore, rather than randomly fabricated, the above parameters refer to the real physical parameters of titanium, which is an important element in LIBS technique (used for LIBS wavelength[34,35]). For simplicity, the computational expressions generally no longer incorporate physical units in the following.

According to Eq. (1) and Eq. (2), the temperature field $T(x,t)$ should follow the following HCE:

$$\frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\frac{14.63}{540 \times 4510} \cdot \frac{\partial T(x,t)}{\partial x}\right] + \frac{1.0 \times 10^7}{540 \times 4510} \cdot I(x,t)$$

where the laser source term $I(x,t)$ is

$$I(x,t) = 1.0 \times 10^{13} \cdot \exp\left[-4 \ln 2 \left(\frac{t - 6 \times 10^{-9}}{4 \times 10^{-9}}\right)^2\right] \cdot (1 - 0.6) \cdot \exp(-1.0 \times 10^7\, x)$$

Based on easy calculations, one is able to know that this HCE can be expressed in the following standard form:

$$\frac{\partial T(x,t)}{\partial t} = \beta \frac{\partial^2 T(x,t)}{\partial x^2} + f(x,t)$$

where

$$\beta = \frac{\kappa}{C_p \rho} = \frac{14.63}{540 \times 4510} = 6.0 \times 10^{-6}$$

$$f(x,t) = \frac{a}{C_p \rho} \cdot I_0 \cdot \exp\left[-4 \ln 2 \left(\frac{t - t_c}{\tau}\right)^2\right] \cdot (1 - R) \cdot \exp(-ax)$$

$$= \frac{1.0 \times 10^7}{540 \times 4510} \cdot 1.0 \times 10^{13} \cdot \exp\left[-4 \ln 2 \left(\frac{t - 6 \times 10^{-9}}{4 \times 10^{-9}}\right)^2\right] \cdot (1 - 0.6) \cdot \exp(-1.0 \times 10^7\, x)$$

It is easy to know that $\beta > 0$ and $f(x,t) > 0$ are satisfied.

Then set the $x - t$ grid for the numerical simulation. The starting position is on the surface, and the ending position is 10 μm beneath the surface, *i.e.* $x_{\min} = 0$ and $x_{\max} = 10.0 \times 10^{-6}$. The space step is set to be $10.0\ \mathrm{nm}$, *i.e.* $dx = 10.0 \times 10^{-9}$. The starting time is zero moment, and the ending time is $15.0\ \mathrm{ns}$, *i.e.* $t_{\min} = 0$ and $t_{\max} = 15.0 \times 10^{-9}$. The time step is set to be $0.00075\ \mathrm{ns}$, *i.e.* $dt = 7.5 \times 10^{-13}$. Apparently $Nx = 1000$ and $Nt = 20000$, hence the temperature field $T(x,t)$ is represented by a 1001×20001 matrix. The corresponding step ratio parameter r is

$$r = \beta \frac{dt}{(dx)^2} = 6.0 \times 10^{-6} \times \frac{7.5 \times 10^{-13}}{(10.0 \times 10^{-9})^2} = 0.045$$

and $r > 0$ is satisfied.

For the exponential term in the $f(x,t)$, namely $f(t)$

$$f(t) = \exp\left[-4\ln 2\left(\frac{t-6\times10^{-9}}{4\times10^{-9}}\right)^2\right]$$

set the truncation time to be 0.45 ns, $t_z = 4.5\times10^{-10}$. Conduct exponential function fitting upon the $f(t)$ within the $[0, 4.5\times10^{-10}]$ interval based on Eq. (8). The fitting coefficients are $b_1 = 0.002041$ and $b_2 = 1.8876\times10^9$, *i.e.* $F(t) = 0.002041\cdot\exp(1.8876\times10^9\, t)$, and obviously $b_1 > 0$ and $b_2 > 0$ are satisfied.

Next formulate a "bridge" HCE

$$\frac{\partial T(x,t)}{\partial t} = 6.0\times10^{-6}\cdot\frac{\partial^2 T(x,t)}{\partial x^2} + f_s\cdot\exp(-1.0\times10^7\, x)\cdot\exp(1.8876\times10^9\, t)$$

where

$$f_s = \frac{1.0\times10^7}{540\times4510}\cdot1.0\times10^{13}\cdot(1-0.6)\cdot0.002041 = 3.34724\times10^{10}$$

and $f_s > 0$ is satisfied.

The initial condition is

$$T(x,0) = u_s\cdot\exp(-1.0\times10^7\, x)$$

and the boundary condition is

$$\begin{cases} T(0,t) = u_s\cdot\exp(1.8876\times10^9\, t) \\ T(10.0\times10^{-6},t) = u_s\cdot\exp(-100)\cdot\exp(1.8876\times10^9\, t) \end{cases}$$

where $u_s = 3.34724\times10^{10}/[1.8876\times10^9 - 6.0\times10^{-6}\times(1.0\times10^7)^2] = 25.99596$. For this HCE there is an exact analytical solution $T_{ex}(x,t)$

$$T_{ex}(x,t) = 25.99596\cdot\exp(-1.0\times10^7\, x)\cdot\exp(1.8876\times10^9\, t)$$

It is easy to infer that for arbitrary x and t, $T_{ex}(x,t) > 0$ is satisfied.

According to the determined Nt value (20000), select M time grid point number parameters. Here we let $M = 6$, and set $Nt_1 = 2000$, $Nt_2 = 2500$, $Nt_3 = 3000$, $Nt_4 = 3600$, $Nt_5 = 4000$ and $Nt_6 = 4500$. Note that the selected Nt_m values here are all much smaller than 20000, and hence the computation time for each Nt_m value would be considerably shorter. The corresponding time step parameters would be $dt_1 = 0.7500\times10^{-11}$, $dt_2 = 0.6000\times10^{-11}$, $dt_3 = 0.5000\times10^{-11}$, $dt_4 = 0.4166\times10^{-11}$, $dt_5 = 0.3750\times10^{-11}$, and $dt_6 = 0.3333\times10^{-11}$, and the step ratio parameters are $r_1 = 0.45$, $r_2 = 0.36$, $r_3 = 0.30$, $r_4 = 0.25$, $r_5 = 0.225$, and $r_6 = 0.20$, respectively. It is obvious that $\max\{r_1, r_2, \cdots\cdots r_6\} = r_1$ and $r_1 \le 1/2$ is satisfied.

Taking $Nt_1 = 2000$ as an example, we demonstrate the process of searching the optimal weight factor in the following. Under the series of parameters for $Nt_1 = 2000$, the standard format of the common finite difference method is

$$-\left[0.45\,\theta\cdot T_{j-1}^{k+1} - (1+0.9\,\theta)\cdot T_j^{k+1} + 0.45\,\theta\cdot T_{j+1}^{k+1}\right] = 0.45\,(1-\theta)\cdot T_{j-1}^{k} + [1-0.9\,(1-\theta)]\cdot T_j^k + 0.45\,(1-\theta)\cdot T_{j+1}^k + 0.7500\times10^{-11}\cdot\left[\theta\cdot f_j^{k+1} + (1-\theta)\cdot f_j^k\right]$$

Take $\theta = 1$, and figure out $T_1(x,t)$ according to the finite difference method. According to Eq. (15), one can obtain that $\langle\varepsilon_{jk}\rangle_1 = 0.01009305$. In a similar way, take $\theta = 0$ and find $T_0(x,t)$, and one can know that $\langle\varepsilon_{jk}\rangle_0 = -0.00926238$. Apparently $\langle\varepsilon_{jk}\rangle_1\cdot\langle\varepsilon_{jk}\rangle_0 < 0$, indicating that the θ_{opt} value for the current HCE falls in the (0,1) interval, and the searching should go on.

Denote $\langle\varepsilon_{jk}\rangle_1$ as $\langle\varepsilon\rangle_+$ and $\langle\varepsilon_{jk}\rangle_0$ as $\langle\varepsilon\rangle_-$ and let $\theta_+ = 1$, $\theta_- = 0$. The tolerable convergence error w is set to be 0.00001. Take the first trial optimal weight factor $\theta_{opt}^0 = 0.5$, calculate $T_{0.5}(x,t)$, and one can obtain that $\langle\varepsilon_{jk}\rangle_{0.5} = 0.00038501$. Since $\langle\varepsilon_{jk}\rangle_{0.5} > 0$, it is not difficult to infer that the updating assignment should be $\langle\varepsilon\rangle_+ = \langle\varepsilon_{jk}\rangle_{0.5}$ and $\theta_+ = 0.5$. Next implement linear fitting upon the two data points $(0.5, 0.00038501)$ and $(0, -0.00926238)$ according to Eq. (16). It can be known that the two coefficients are $p_1 = 0.01929479$ and $p_2 = -0.00926238$, and thereby $\theta_{opt}^1 = -p_2/p_1 = 0.48004$ can be acquired. Obviously $|\theta_{opt}^1 - \theta_{opt}^0| = 0.01996 > w$, and hence the iteration needs to be further carried out. Update the θ_{opt}^0 value, *i.e.* $\theta_{opt}^0 = 0.48004$, calculate the corresponding $T_{0.48004}(x,t)$, and obtain that $\langle\varepsilon_{jk}\rangle_{0.48004} = -1.2691516\times10^{-6}$. Since $\langle\varepsilon_{jk}\rangle_{0.48004} < 0$, the updating assignment should be $\langle\varepsilon\rangle_- = \langle\varepsilon_{jk}\rangle_{0.48004}$ and $\theta_- = 0.48004$. Next perform linear fitting upon the two data points $(0.5, 0.00038501)$ and $(0.48004, -1.2691516\times10^{-6})$, acquire the coefficients $p_1 = 0.01935282$ and $p_2 = -0.00929140$, and obtain that $\theta_{opt}^1 = 0.48010$. It is apparent that $|\theta_{opt}^1 - \theta_{opt}^0| = 0.00006 > w$, and hence the iteration needs to go on. Update the θ_{opt}^0 value, *i.e.* $\theta_{opt}^0 = 0.48010$, calculate the corresponding $T_{0.48010}(x,t)$, and obtain that $\langle\varepsilon_{jk}\rangle_{0.48010} = -1.0812718\times10^{-7}$. Similarly assign $\langle\varepsilon\rangle_- = \langle\varepsilon_{jk}\rangle_{0.48010}$ and $\theta_- = 0.48010$, and implement linear fitting upon the two data points $(0.5, 0.00038501)$ and $(0.48010, -1.0812718\times10^{-7})$, and one can get $\theta_{opt}^1 = 0.48010$. This time $|\theta_{opt}^1 - \theta_{opt}^0| = 0.00000$ and the convergence condition $|\theta_{opt}^1 - \theta_{opt}^0| \le w$ is satisfied. Thus the

Fig. 4 The results based on the nonlinear fitting and extrapolation strategy in the specific numerical example.

Fig. 5 Comparison of the simulation accuracy achieved by the optimal weight factor and the three routine weight factors.

iterative searching is complete and the outcome is $\theta_{opt,1} = 0.48010$ for $Nt_1 = 2000$. This result is recorded as a data point $(r_1,\ \theta_{opt,1}) = (0.45, 0.48010)$.

In the same way, one can get the optimal weight factors for the other five Nt values, namely $\theta_{opt,2} = 0.47566$, $\theta_{opt,3} = 0.47114$, $\theta_{opt,4} = 0.46566$, $\theta_{opt,5} = 0.46198$, and $\theta_{opt,6} = 0.45737$. Now six $(r_m,\ \theta_{opt,m})$ data points have been achieved, *i.e.* $(0.45, 0.48010)$, $(0.36, 0.47566)$, $(0.30, 0.47114)$, $(0.25, 0.46566)$, $(0.225, 0.46198)$ and $(0.20, 0.45737)$. Based on these six data points, the nonlinear fitting shown in Eq. (17) can be carried out, and the two coefficients can be easily acquired, $p_3 = 0.49838733$ and $p_4 = -0.00819219$. Via the fitting curve, one can infer the θ_{opt} value under the real grid r parameter (*i.e.* $r = 0.045$) by extrapolation. This nonlinear fitting and extrapolation procedure is illustrated in Fig. 4.

The extrapolation result shows that for $r = 0.045$ the corresponding optimal weight factor is $\theta_{opt} = 0.31634$. Since the requirement $\theta_{opt} > 0$ is met, 0.31634 is regarded as the optimal weight factor for the formulated HCE.

In order to demonstrate the effect of the optimal weight factor, the accuracy level of the simulation achieved by the acquired optimal weight factor and the three regular weight factors are compared. The mean relative errors (absolute value) of the forward-Euler, backward-Euler and Crank-Nicolson schemes are 6.05×10^{-4}, 1.33×10^{-3} and 3.62×10^{-4}, respectively; while that of the optimal weight factor scheme is as low as 6.98×10^{-6}. The results are exhibited in Fig. 5, and it should be noted that the y-axis is logarithmic. It is worth recalling that there is no experimental data involved in this work, and the numerical simulation errors are evaluated by comparing the numerical results and the exact analytical results (as expressed in Eq. (12) above).

Afterwards this achieved θ_{opt} value can be employed as the finite-difference weight factor to routinely solve the original HCE of the practical problem, and the further details would not be elaborated herein.

Discussion. In Results part, a numerical example is provided to elucidate how to pertinently search the optimal weight factor for a specific HCE and grid parameters. Some important details that might cause puzzles are further discussed herein.

Firstly, as indicated in Method of Searching Optimal Weight Factor part, an important foundation for the strategy of searching the optimal weight factor is that the factor should be non-negative. If this condition is not true, then $\langle \varepsilon_{jk} \rangle_1 \cdot \langle \varepsilon_{jk} \rangle_0$ would not be negative and the subsequent elaborate searching would not be implemented at all. In fact, such an abnormal situation is beyond the scope of this article. However, since the θ_{opt} value is inferred based on Eq. (17), how can one ensure that the calculated value is non-negative? In fact, $\theta_{opt} < 0$ cases can appear in practical computation. If this situation occurs, it indicates that the step ratio parameter r is too small. One should appropriately modify the relevant grid parameters to obtain a larger r value, until $\theta_{opt} \geq 0$ is satisfied.

Secondly, it has been emphasized that one can choose to directly implementing the θ_{opt} searching scheme under a large Nt value if time expense is not important. In the above numerical computation example, if we directly use $Nt = 20000$ to conduct the searching, then the obtained optimal weight factor is $\hat{\theta}_{opt} = 0.31274$. This "real" optimal weight factor is quite close to the 0.31634 value obtained by the aforementioned nonlinear fitting and extrapolation scheme, indicating that our strategy can yield a rather accurate θ_{opt} value.

Thirdly, if the obtained θ_{opt} value is no smaller than 1/2, then

the result of finite difference simulation would be unconditionally stable when one chooses to adopt $\theta = \theta_{opt}$ in the simulation. However, the obtained θ_{opt} value may also be smaller than 1/2, which means that the result would not be unconditionally stable. As a matter of fact, when $\theta < 1/2$, the result of finite difference simulation would be stable only if the requirement $r \leq {}^{1}/_{2(1-2\theta)}$ is met. Fortunately, since we have intentionally ensured that $\max\{r_1, r_2, \cdots\cdots r_M\} \leq 1/2$ in our scheme (as mentioned in Method of Searching Optimal Weight Factor part), and the final r is surely smaller than each r_m, we can make sure that $r < 1/2$. On the other hand, since $0 < \theta < 1/2$, it is not difficult to know that ${}^{1}/_{2(1-2\theta)}$ must be larger than 1/2. Therefore, the requirement $r \leq {}^{1}/_{2(1-2\theta)}$ can be met, and hence the result of finite difference simulation would be stable even if the achieved optimal weight factor is smaller than 1/2.

Finally, it is worth emphasizing that the heat conduction problem inspected in this work contains external heat source (namely the laser source). Therefore, compared with previous pioneering studies that investigate the weight factor issue for non-source problems, this work is apparently more complicated (for those non-source HCEs, there is an explicit formula to calculate the optimal weight factor[30]). Due to the inclusion of laser source, this work is evidently more valuable for researching practical laser ablation process, and hence has potential to make more significant contribution to the LMI field.

As mentioned in Introduction section, laser ablation is the first key procedure of many spectrometry techniques, such as LIBS and LA-ICP-MS. An accurate knowledge of the temperature field would be helpful to better describing the laser heating process. Note that the temperature information is not only useful in studying the heating process, but also plays an important role in examining the subsequent dynamics (evaporation, ionization, plasma plume expansion, etc.). In the following, we would take LIBS and LA-ICP-MS as two examples to provide some preliminary viewpoints on the potential way to utilize the temperature information for improving the analytical performance.

1) LIBS: When inspecting the evaporation process which follows the heating (melting), the sample surface temperature (also regarded as the vapor temperature at the surface) can be used as an input parameter to calculate the vapor pressure, the vapor density, and the initial flow velocity of the vapor atoms leaving the surface. In addition, the vapor density, the vapor flow velocity, and the vapor temperature at the surface can be employed in simulating the plume expansion, and hence further affect the calculation of the plasma characteristic parameters. Accurate information of the plasma characteristic parameters, such as plasma temperature and electron number density, would be greatly helpful to examining whether the local thermal equilibrium (LTE) condition is satisfied. The validity of LTE is undoubtedly important for the so-called calibration-free LIBS methodology, which can be utilized to circumvent LIBS matrix effects.[36, 37] Another possible way to dealing with the LIBS matrix effect problem is to adopt a sub-model strategy. If a LIBS analyst establishes a quantitative chemometrics model by employing all the samples with various matrices, the analytical accuracy would not be very good, no matter the model is based on classical statistics or sophisticated deep learning.[38] By inspecting the temperature field evolution features of each sample, the analyst may be able to roughly judge the matrices of the samples and make a proper classification. And then several sub-models can be formulated to analyze the samples with different matrices respectively, so that the quantitative accuracy can be improved. Besides the matrix effect, another possible negative effect in LIBS is elemental fractionation, despite this effect is more frequently discussed in another technique, *i.e.* LA-ICP-MS (see below). There are a few experimental studies that investigate the elemental fractionation in LIBS. Lv *et al.* have adopted time-resolved photography to record the dynamics in the nanosecond-laser ablation of a geological standard sample, and pointed out that a main reason for elemental fractionation is the fact that different elements (with distinct melting and boiling point temperatures) in one sample have different plasma generation time.[39] Latty *et al.* have experimentally studied the elemental fractionation in aerosol LIBS by using both nanosecond and femtosecond laser pulses, and figured out that the change of the local plasma temperature plays a key role in causing elemental fractionation.[40] Apparently, an accurate simulation of the temperature evolution would be beneficial to further verifying the proposed mechanisms of the experimental phenomena.

2) LA-ICP-MS: Like the LIBS technique, LA-ICP-MS also has matrix effect and elemental fractionation effect. Zhang *et al.* have analyzed the variations in element signal intensities of standard samples with different laser fluence in a nanosecond LA-ICP-MS experiment, and the influence of ablation behavior on the matrix effect has been inspected based on the morphology and depth of the ablation crater, as well as the dynamics of plasma plume evolution.[41] The physical mechanism of matrix effect has been investigated based on the ablation craters and laser ablation plume in a more recent experimental work conducted by the same group.[42] As mentioned above, elemental fractionation is a more widely investigated effect in LA-ICP-MS. Early in the 1980s, Hager has presented a theoretical model of laser solid sampling to explain the elemental fractionation (called "elemental selectivity" therein) in some LA-ICP-MS experiments.[43] In that work, the elemental selectivity effect was attributed to the different relative elemental response factors of different elements. The calculation of these element-dependent response factors is dependent on a key parameter, *i.e.* ablation temperature, which should be undoubtedly based on the solution of heat conduction equation. In a later work

where the influence of ablation process on the elemental fractionation has been inspected, the whole theoretical model is largely dependent on the solution of a heat conduction equation, since the temperature distribution can determine the liquid-vapor interface movement velocity and hence affect the extent of elemental fractionation.[44] A more recent research has proposed an insight that the elemental fractionation effect is induced by the discrepancies of physical properties (*e.g.* velocity, pressure, temperature and density) between each layer inside the ablation plume.[45] At present experimental techniques can hardly acquire the accurate physical property information of every layer. Nevertheless, theoretical simulation may achieve this goal, hence guiding the experimenter to choose the laser parameters which can narrow the discrepancies and thereby mitigate the elemental fractionation. Again, these studies demonstrate the importance of heat conduction simulation in disclosing the relevant mechanisms and improving the analytical performance.

CONCLUSION

This work investigates the numerical solution of HCE in laser ablation, which is a crucial process in variety of LMI-based technologies. As a popular numerical approach for solving HCE, finite difference method has three regular schemes, corresponding to three specific weight factors, *i.e.* 0, 1, and 0.5. According to relevant mathematical theory, there may exist an optimal weight factor for each specific HCE, which depends on the HCE parameters and the numerical grid parameters. To the best of our knowledge, this is the first work that utilizes the mathematical theory to solve practical HCE problems in which external heat source is included.

In this study, a method for searching the optimal finite-difference weight factor in solving 1D space HCE has been proposed. Moreover, a nonlinear fitting and extrapolation strategy is presented to make the searching more time-saving while keeping the achieved weight factor highly close to the result of exact searching. Through a concrete numerical example using real-world physical parameters and typical simulation grid parameters, we have demonstrated the procedure to find out the optimal weight factor, and further show its superiority over the three regular weight factors in terms of simulation accuracy. Moreover, taking LIBS and LA-ICP-MS as typical examples, we have elucidated the significance of heat conduction simulation in understanding the mechanisms of relevant effects in laser ablation (*e.g.* matrix effect and elemental fractionation effect), and discussed the potential strategies to mitigate the negative impact of those effects and thereby ameliorate the analytical performance of the techniques. Besides LIBS and LA-ICP-MS, it is expected that this study would shed light on more other LMI application domains involving laser ablation.

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Notes

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ACKNOWLEDGMENTS

The authors are grateful to the funding from Shanghai Rising-Star Program (23QA1411000), Natural Science Foundation of Shanghai (22ZR1472400), National Key R&D Program of China (2022YFF0504100), and Key Laboratory of Space Active Opto-electronics Technology, CAS (CXJJ-22S019).

REFERENCES

1. L. Ma, L. Wang, C. Li, J. Guo, P. Shrotriya, C. Deng, and J. Zhao, *Metals-Basel*, 2019, **9**, 668. https://doi.org/10.3390/met9060668
2. C. Scolaro, A. Viscoa, and L. Torrisib, *J. Instrum.*, 2020, **15**, C02037. https://doi.org/10.1088/1748-0221/15/02/C02037
3. A. M. Mostafa and A. A. Menazea, *Radiat. Phys. Chem.*, 2020, **176**, 109020. https://doi.org/10.1016/j.radphyschem.2020.109020
4. T. Chen, W. Wang, T. Tao, A. Pan, and X. Mei, *Appl. Surf. Sci.*, 2020, **509**, 145182. https://doi.org/10.1016/j.apsusc.2019.145182
5. H. Liao, M. Noguchi, T. Maruyama, Y. Muragaki, E. Kobayashi, H. Iseki, and I. Sakuma, *Med. Image Anal.*, 2012, **16**, 754–766. https://doi.org/10.1016/j.media.2010.11.004
6. P. M-M, R. Weiskirchen, N. Gassler, A. K. Bosserhoff, and J. S. Becker, *PLoS One*, 2013, **8**, e58702. https://doi.org/10.1371/journal.pone.0058702
7. M. Tong, S. Li, Y. Li, Y. Li, Y. Feng, and Y. Che, *Int. J. Hyperthermia*, 2019, **36**, 1277–1285. https://doi.org/10.1080/02656736.2019.1700559
8. Y. Fan, Q. Ma, M. Li, D. Luan, and H. Kang, *Lasers Surg. Med.*, 2022, **54**, 459–473. https://doi.org/10.1002/lsm.23491

9. J. S. Becker, S. Mounicou, M. V. Zoriy, J. S. Becker, and R. Lobinski, *Talanta*, 2008, **76**, 1183–1188. https://doi.org/10.1016/j.talanta.2008.05.023
10. I. Pereira, B. Banstola, K. Wang, F. Donnarumma, B. G. Vaz, and K. K. Murray, *Anal. Chem.*, 2019, **91**, 6051–6056. https://doi.org/10.1021/acs.analchem.9b00566
11. F. HILLENKAMP, E. UNSöLD, and R. KAUFMANN, *Nature*, 1975, **256**, 119–120. https://doi.org/10.1038/256119a0
12. N. Chaoui, E. Millon, and J. F. Muller, *Chem. Mater.*, 1998, **10**, 3888–3894. https://doi.org/10.1021/cm980717
13. S. S. Harilal, C. M. Murzyn, M. C. Phillips, and J. B. Martin, *Spectrochim. Acta B*, 2020, **169**, 105828. https://doi.org/10.1016/j.sab.2020.105828
14. J. Merten, *Spectrochim. Acta B*, 2022, **189**, 106358. https://doi.org/10.1016/j.sab.2022.106358
15. V. N. Lednev, M. Y. Grishin, P. A. Sdvizhenskii, R. D. Asyutin, R. S. Tretyakov, A. Y. Stavertiy, and S. M. Pershin, *J. Anal. At. Spectrom.*, 2019, **34**, 607–615. https://doi.org/10.1039/c8ja00348c
16. P. C. Han, K. Yang, L. Z. Jiao, and H. C. Li, *Front. Chem.*, 2022, **10**, 967158. https://doi.org/10.3389/fchem.2022.967158
17. S. E. Jackson, N. J. Pearson, W. L. Griffin, and E. A. Belousova, *Chem. Geol.*, 2004, **211**, 47–69. https://doi.org/10.1016/j.chemgeo.2004.06.017
18. D. Günther and B. Hattendorf, *TrAC Trends Anal. Chem.*, 2005, **24**, 255–265. https://doi.org/10.1016/j.trac.2004.11.017
19. L. N. Li, X. F. Liu, F. Yang, W. M. Xu, J. Y. Wang, and R. Shu, *Spectrochim. Acta B*, 2021, **180**, 106183. https://doi.org/10.1016/j.sab.2021.106183
20. Y. Liu, Z. Hu, M. Li, and S. Gao, *Chin. Sci. Bull.*, 2013, **58**, 3863–3878. https://doi.org/10.1007/s11434-013-5901-4
21. S. Tatra, R. G. Vázquez, C. Stiglbrunner, and A. Otto, *Phys. Procedia*, 2016, **83**, 1339–1346. https://doi.org/10.1016/j.phpro.2016.08.141
22. S. Sihn, J. Pitz, R. H. Gerzeski, A. K. Roy, and J. P. Vernon, *Compos. Struct.*, 2019, **207**, 966–973. https://doi.org/10.1016/j.compstruct.2018.09.041
23. M. V. Pantawane, Y. H. Ho, S. S. Joshi, and N. B. Dahotre, *Sci. Rep.*, 2020, **10**, 7579. https://doi.org/10.1038/s41598-020-63281-4
24. A. Bogaerts, Z. Chen, R. Gijbels, and A. Vertes, *Spectrochim. Acta B*, 2003, **58**, 1867–1893. https://doi.org/10.1016/j.sab.2003.08.004
25. T. Q. Qiu and C. L. Tien, *J. Heat Mass Transfer*, 1993, **115**, 835–841. https://doi.org/10.1115/1.2911377
26. J. Wang, Y. Zhao, G. Wang, L. Zhang, S. Wang, W. Zhang, X. Ma, Z. Liu, X. Luo, W. Ma, Z. Ye, Z. Zhu, W. Yin, and S. Jia, *J. Anal. At. Spectrom.*, 2022, **37**, 1722–1729. https://doi.org/10.1039/d2ja00105e
27. J. Martín-Vaquero and J. Vigo-Aguiar, *Appl. Numer. Math.*, 2009, **59**, 2507–2514. https://doi.org/10.1016/j.apnum.2009.05.007
28. M. N. Özişik, H. R. B. Orlande, M. J. Colaço, and R. M. Cotta, *Finite Difference Methods in Heat Transfer*, CRC Press, 2017. https://doi.org/10.1201/9781315121475
29. G. Ekolin, *BIT.*, 1991, **31**, 245–261. https://doi.org/10.1007/BF01931285
30. L. Lapidus and G. F. Pinder, *International Journal for Numerical Methods in Engineering*, Wiley, 1982. https://doi.org/10.1002/nme.1620191017
31. X. L. Feng, H. H. Wang, and Abdirishit, *Journal of Xinjiang University*, 2000, **17**, 13–18. https://kns.cnki.net/kns8/Detail?sfield=fn&QueryID=20&CurRec=12&recid=&FileName=XJDZ200003002&DbName=CJFD2000&DbCode=CJFD&yx=&pr=&URLID=
32. A. W. Miziolek, V. Palleschi, and I. Schechter, *Cambridge University Press*, 2006. https://www.cambridge.org/9780521852746
33. J. Wu, W. Wei, X. Li, S. Jia, and A. Qiu, *Appl. Phys. Lett.*, 2013, **102**, 164104. https://doi.org/10.1063/1.4803044
34. W. M. Xu, X. F. Liu, Z. X. Yan, L. N. Li, Z. Q. Zhang, Y. W. Kuang, H. Jiang, H. X. Yu, F. Yang, C. F. Liu, T. T. Wang, C. K. Li, Y. F. Jin, J. Y. Shen, B. T. Wang, W. Z. Wan, J. Chen, S. H. Ni, Y. P. Ruan, R. Xu, C. X. Zhang, Z. Y. Yuan, X. Wan, Y. C. Yang, Z. H. Li, Y. T. Shen, D. Z. Liu, B. Y. Wang, R. J. Yuan, T. Bao, and R. Shu, *Space Sci. Rev.*, 2021, **217**, 64. https://doi.org/10.1007/s11214-021-00836-5
35. X. Wan, C. H. Li, H. P. Wang, W. M Xu, J. J. Jia, Y. J. Xin, H. Z. Ma, P. P. Fang, and Z. C. Ling, *At. Spectrosc.*, 2021, **42**, 294–298. https://doi.org/10.46770/as.2021.608
36. A. Ciucci, M. Corsi, V. Palleschi, S. Rastelli, A. Salvetti, and E. Tognoni, *Appl. Spectrosc.*, 1999, **53**, 960–964. https://doi.org/10.1366/0003702991947612
37. G. Cristoforetti, A. De Giacomo, M. Dell'Aglio, S. Legnaioli, E. Tognoni, V. Palleschi, and N. Omenetto, *Spectrochim. Acta B*, 2010, **65**, 86–95. https://doi.org/10.1016/j.sab.2009.11.005
38. L. N. Li, X. F. Liu, W. M. Xu, J. Y. Wang, and R. Shu, *Spectrochim. Acta B*, 2020, **169**, 105850. https://doi.org/10.1016/j.sab.2020.105850
39. T. Lü, Y. Hu, Z. H. Li, J. L. Meng, C. J. Zhang, Z. C. Hu, and Y. S. Liu, *Spectrochim. Acta B*, 2018, **143**, 55-62. https://doi.org/10.1016/j.sab.2018.02.019
40. K. S. Latty and K. C. Hartig, *Spectrochim. Acta B*, 2023, **202**, 106648. https://doi.org/10.1016/j.sab.2023.106648
41. X. C. Zhang, J. L. Meng, and T. Lü, *Appl. Opt.*, 2020, **59**, 9836–9843. https://doi.org/10.1364/AO.404156
42. J. L. Meng, T. Lü, B. Fang, Y. Ni, and B. W. Fan, *Opt. Laser Technol.*, 2022, **152**, 108092. https://doi.org/10.1016/j.optlastec.2022.108092
43. J. W. Hager, *Anal. Chem.*, 1989, **61**, 1243–1248. https://doi.org/10.1021/ac00186a014
44. R. Hergenröder, *J. Anal. At. Spectrom.*, 2006, **21**, 505–516. https://doi.org/10.1039/b600698a
45. J. L. Meng, *Dissertation of China University of Geosciences*, 2022. https://kns.cnki.net/kns8/Detail?sfield=fn&QueryID=10&CurRec=1&DbCode=CDFD&dbname=CDFDLAST2023&filename=1022750346.nh