# Supplementary material for : Measurement error due to self-absorption in calibration-free laser-induced breakdown spectroscopy

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# 1. Computational details

# 1.1. Atomic number density vs number density of electronic state

The number density of an electronic state  $n_i$  is related to the number density  $n^z$  of the atomic species of charge z via the Boltzmann law

$$n_i = n^z \frac{g_i}{Q^z(T)} e^{-E_i/kT},\tag{1}$$

where  $g_i$  and  $E_i$  are the statistical weight and the energy of the level, respectively,  $Q^z$  is the partition function, T is the temperature, and k is the Boltzmann constant. Neglecting the presence of molecular species, the atomic number density associated to an element is given by

$$n_A = \sum_{z=0}^{z_{max}} n^z, \tag{2}$$

where the sum includes all species of significant abundance up to a maximum charge  $z_{max}$ . The number densities of atomic species of successive charges are related via the Saha equation

$$\frac{n^{z} n_{e}}{n^{z-1}} = \frac{2 Q^{z}}{Q^{z-1}} \frac{(2\pi m_{e} kT)^{\frac{3}{2}}}{h^{3}} e^{-\frac{E_{ion}}{kT}},$$
(3)

where  $n_e$  is the electron density,  $m_e$  is the electron mass, h is the Planck constant, and  $E_{ion}$  is the ionization energy. According to eq S3, the ratios between the number densities of species  $n^z$  are constant for given values of T and  $n_e$ . Thus, according to eq S2, the number density of each species  $n^z$  is proportional to the atomic number density associated to the element  $n_A$ , and finally, following eq S1, the population number density of the electronic state  $n_i$  increases linearly with  $n_A$ .

# 1.2. Intensity and line shape alteration due to self-absorption

The influence of self-absorption on the spectral line shape is illustrated in Figure S1 for different line profiles. In the upper row (a-c), the spectral radiance computed according to eq 1 is displayed. In the center (d-f) and lower (g-i) rows, the convoluted intensity computed according eq 3 is displayed for two different values of apparatus spectral width  $w_{ap}$ .

The spectral radiance (a-c) in the line center is shown to increase with  $\tau_0$  independently of the line profile, reaching a value close to the blackbody spectral radiance for  $\tau_0 \simeq 5$ . According to the weak contribution of the line wings to the gaussian profile, broadening due to self-absorption is limited to a narrow spectral range (a). Contrarily, strong broadening due to self-absorption occurs for the Lorentzian profile (c). Consequently, the line-integrated emission intensity  $I_{line}$  (area of line profile) of the Lorentzian profile is much less affected by self-absorption than the  $I_{line}$ -value of the Gaussian profile. For the Voigt profile with a Lorentz width three times smaller than the Gauss width (b), broadening due to self-absorption is characterized by two different regimes. For moderate  $\tau_0$ -values, broadening is weak, the line shape evolves like the self-absorbed Gaussian profile (a). At large  $\tau_0$ -values, the contribution of the Lorentzian line wings becomes predominant, and the line shape evolves similar to the self-absorbed Lorentzian profile (c).

When the spectral radiance is convoluted with an apparatus spectral profile (assumed to be Gaussian) with a width equal to the line width (d-f), the line-center intensity is reduced and reaches the blackbody spectral radiance at larger  $\tau_0$ -values compared to the non-convoluted spectral radiance (a-c). The line shape is weakly changed compared to the non-convoluted case.

The situation is different when the spectral radiance is convoluted with an apparatus spectral profile of width 5 times larger than the line width (g-i). In that case, the line shape is strongly altered compared to the non-convoluted case. The line-center intensity is now correlated to the line-integrated intensity that depends on the line profile. For a Gausian profile (g), the line-center intensity does not reach the blackbody intensity level, and both  $I_0$  and  $I_{line}$  saturate whereas the line width remains constant. For the Lorentzian (i) and the Voigt (h) profiles, the line-center intensity reaches the blackbody intensity level, but for  $\tau_0$ -values much larger than those that characterize the  $I_0$ -salutation of the non-convoluted case (a-c).



Figure 1: Spectral radiance computed according eq 1 (a-c) and convoluted intensity computed according eq 3 (d-i) for various values of linecenter optical thickness  $\tau_0$  and different line shapes: (a,d,g) Gaussian profile, (b,e,h) Voigt profile with  $w_G = 3w_L$ , (c,f,i) Lorentzian profile. The convoluted intensity is displayed for an apparatus width equal to the line width (d-f), and an apparatus width 5 times larger than the line width (g-i). The vertical axis is scaled by dividing the spectral radiance by the blackbody spectral radiance.

## 1.3. Atomic number density dependence in the general case

Multiplying the expression of the absorption coefficient (eq 2) by the plasma diameter along the line of sight L, we obtain

$$\tau(\lambda) = \pi r_0 \lambda^2 f_{lu} \left( 1 - e^{-hc/\lambda kT} \right) n_l P(\lambda) L.$$
<sup>(4)</sup>

Using the relation between  $f_{lu}$  and  $A_{ul}$  and integrating over the line profile, eq S4 becomes

$$\tau_0 w_{sd} = C^{st} A_{ul} \left( 1 - e^{-hc/\lambda kT} \right) n_l L, \tag{5}$$

where all constants including the line-shape-dependent corection factor are represented by  $C^{st}$ . According to SM 1.1,  $n_l$  increases linearly with  $n_A$  and we can write

$$n_A = \Theta_2(T, n_e) \frac{\tau_0 \, w_{sd}}{A_{ul} \, L},\tag{6}$$

where  $\Theta_2(T, n_e)$  includes all constants and the dependence on temperature and electron density.

# 1.4. Error of line width due to Doppler and Stark broadening

The spectral line shape due to Stark and Doppler broadening is generally described by a Voigt profile where the Lorentzian and Gaussian contributions correspond to line broadening due to Stark and Doppler effects, respectively.

The corresponding line width  $w_{sd}$  can be either computed by evaluating the contributions of Doppler width  $w_d$  and Stark width  $w_s$ , or deduced from the measured line profile. If  $\Delta w_{sd}^c$  and  $\Delta w_{sd}^m$  are the uncertainties associated to the computed and measured line widths, the line width error  $\Delta w_{sd}$  is set to the smaller value.

# 1.4.1. Error of computed line width

**Case of negligible Doppler width:** In the present case, the spectral lines have a Stark width more than 20 times larger than the Doppler width, and we have  $w_{sd} \simeq w_s$ . For non-hydrogenic lines, the Stark width is proportional to the electron density  $n_e$  and given by

$$w_s = \frac{\omega_s}{n_e^{ref}} n_e,\tag{7}$$

where  $\omega_s$  is the Stark width corresponding to the reference electron density  $n_e^{ref}$ , also called Stark broadening parameter. The error of the computed line width is therefore given by

$$\frac{\Delta w_{sd}^c}{w_{sd}^c} \simeq \frac{\Delta w_s}{w_s} = \sqrt{\left(\frac{\Delta \omega_s}{\omega_s}\right)^2 + \left(\frac{\Delta n_e}{n_e}\right)^2}.$$
(8)

Most of the Stark broadening parameters are tabulated in literature with an uncertainty  $\ge 20\%$ . For a few lines, more precise  $\omega_s$ -values can be found, with an uncertainty of 10%.

**General case:** When Doppler and Stark broadening have to be considered, a rough estimation of the line width is given by

$$w_{sd}^c \approx \frac{w_s}{2} + \sqrt{\frac{w_s^2}{4} + w_d^2},$$
 (9)

where the Doppler width is given by

$$w_d = a \,\lambda_0 \,\sqrt{\frac{T}{m}}.\tag{10}$$

Here, *a* is a numerical constant,  $\lambda_0$  is the line-center wavelength of the transition, and *m* is the atomic mass of the emitting species. From the partial derivative with respect to  $w_s$  and  $w_d$  we obtain from eq S9 the error associated to the computed line width

$$\frac{\Delta w_{sd}^c}{w_{sd}^c} = \frac{1}{\sqrt{\frac{1}{4} + \frac{w_d^2}{w_s^2}}} \sqrt{\frac{1}{4} \left(\frac{\Delta w_s}{w_s}\right)^2 + \left(\frac{w_d^2}{w_{sd} \times w_s}\right)^2 \left(\frac{\Delta w_d}{w_d}\right)^2}.$$
(11)

Here, the error of the Stark width is given by eq S8, the error of the Doppler width is given by

$$\frac{\Delta w_d}{w_d} = \frac{1}{2} \frac{\Delta T}{T}.$$
(12)

In the present case, the temperature was measured with an accuracy of  $\Delta T/T \simeq 2\%$ . The error associated to the Doppler width is thus  $\Delta w_d/w_d \simeq 1\%$ .

#### 1.4.2. Error of line width deduced from measurement

The measured line can often be described by a Voigt profile, where the gaussian and lorentzian contributions represent the apparatus spectral profile and the emission line profile dominated by Stark broadening, respectively. However, this description is only accurate when self-absorption is weak. In the opposite case, the emission line profile is distorted as self-absorption mainly affects the line center where the optical thickness is maximum (see Figure S1). Thus, the accurate value of the measured line width is deduced from the line profile computed according eqs 1 and 3. For error evaluation purposes, the accurate line width value is not required.

A rough estimation of the measured line width is thus given by

$$w_m \simeq \sqrt{w_{ap}^2 + (g_w \, w_{sd})^2},$$
 (13)

where  $w_{ap}$  is the apparatus spectral width and  $g_w$  the factor of line broadening due to self-absorption. For the simplified case of a Lorentzian line shape,  $g_w$  is given by eq S20. The line width due to Doppler and Stark broadening deduced from the measurement is thus

$$w_{sd}^m \simeq \frac{1}{g_w} \sqrt{w_m^2 - w_{ap}^2},$$
 (14)

and the associated uncertainty is

$$\frac{\Delta w_{sd}^m}{w_{sd}^m} = \sqrt{\left(\frac{w_m}{g_w w_{sd}}\right)^4 \left(\frac{\Delta w_m}{w_m}\right)^2 + \left(\frac{w_{ap}}{g_w w_{sd}}\right)^4 \left(\frac{\Delta w_{ap}}{w_{ap}}\right)^2 + \left(\frac{\Delta g_w}{g_w}\right)^2}.$$
(15)

The error associated to the factor of width growth  $\Delta g_w/g_w$  is given by eq S21.

# 1.5. Spectroscopic data

Table 1: Transitions used for electron density  $(n_e)$ , temperature (T), and fraction (C) measurements: transition probability  $A_{ul}$  with relative error  $\Delta A_{ul}/A_{ul}$ , energy E and statistical weight g of lower (index l) and upper (index u) electronic states, Stark broadening width  $\omega_s$  and shift  $d_s$  for  $n_e = 1 \times 10^{17}$  cm<sup>-3</sup>.

meas	transition	$A_{ul}(\mu s^{-1})$	$\frac{\Delta A_{ul}}{A_{ul}}(\%)$	$E_l(eV)$	$g_l$	$E_u(eV)$	$g_u$	$\omega_s(pm)$	$d_s(pm)$
$n_e, T, C$	Si I 390.552	13.3	(15)	1.91	1	5.08	3	31 <sup>a</sup>	16 <sup>a</sup>
$n_e, T, C$	Ge I 326.949	25.0	(25)	0.88	5	4.67	3	20	12
$n_e, T$	Ge II 589.339	92.0	(40)	7.74	2	9.84	4	117	17
Т	Si II 385.602	44.0	(20)	6.86	6	10.07	4	58	0
Т	Ge I 422.656	14.9	(25)	2.03	1	4.96	3	33	19
Т	Ge I 303.906	280	(25)	0.88	5	4.96	3	17	11
С	O I 777.417	36.9	(7)	9.15	5	10.74	5	105	15
С	Al I 308.215	58.7	(10)	0.00	2	4.02	4	35	12
С	Ca II 393.366	147	(25)	0.00	2	3.15	4	10	-4.0

<sup>a</sup> Ref. [1]

The spectroscopic data were taken from the NIST[2] and Kurucz[3] databases. As the low  $A_{ul}$ -accuracy of several lines masks the errors due to self-absorption, an error  $\Delta A_{ul}/A_{ul} = 5\%$  was used for all lines to enable a clear presentation of the error evaluation.

#### 1.6. Line broadening due to self-absorption and associated error

The width w of a spectral line, also called full width at half maximum intensity, is defined as

$$\frac{I(\lambda_0)}{2} = I(\lambda_0 + w/2).$$
 (16)

For a self-absorbed line, the intensity is given by eq 1 and we have

$$1 - e^{-\tau(\lambda_0)} = 2\left(1 - e^{-\tau(\lambda_0 + w/2)}\right) \tag{17}$$

For transitions of negligible Doppler broadening ( $w_d \ll w_s$ ), the line width equals the Stark width and the line profile is well described by the Lorentzian function. In that case, the optical thickness is given by

$$\tau(\lambda) = \frac{\tau_0}{1 + \left(\frac{\lambda - \lambda_0}{w_s/2}\right)^2} \tag{18}$$

Substituting  $\tau(\lambda)$  in eq S17 by the optical thickness of Lorentzian line shape (eq S18) we obtain

$$-e^{-\tau_0} = 1 - 2 \exp\left(-\frac{\tau_0}{1 + \left(\frac{w}{w_s}\right)^2}\right),$$
(19)

and finally the factor of width growth due to self-absorption

$$g_w = \frac{w}{w_s} = \sqrt{\frac{\tau_0}{\ln\left(\frac{2}{1+e^{-\tau_0}}\right)} - 1}.$$
 (20)

The error associated to the factor of width growth is derived from the error of the line-center optical thickness by derivating eq S20 with respect to  $\tau_0$ . Introducing  $g'_w = \partial g_w / \partial \tau_0$ , we have

$$\frac{\Delta g_w}{g_w} = \frac{g'_w}{g_w} \Delta \tau_0. \tag{21}$$

# 1.7. Error of elemental fractions

The results of compositional analysis are generally given in atomic fractions or mass fractions of the sample composing elements. Assuming stoichiometric mass transfer from the sample to the laser-induced plasma, the atomic fraction of element A in the sample material  $C_A$  is related to the atomic number density in the plasma  $n_A$  (see eq S2) via

$$C_A = \frac{n_A}{n_{tot}},\tag{22}$$

where  $n_{tot}$  is the total atomic number density of the plasma obtained by summing over the atomic number densities of all elements

$$n_{tot} = \sum_{j} n_{j}.$$
(23)

According to eqs S22 and S23, the elemental fraction  $C_A$  does not only depend on the atomic number density  $n_A$  but also on the atomic number densities  $n_j$  of all other sample composing elements  $(j \neq A)$ . The relative error of the elemental fraction  $\Delta C_A/C_A$  depends therefore on the atomic fractions  $C_j$  and the errors associated to the atomic number densities  $\Delta n_j/n_j$  as

$$\frac{\Delta C_A}{C_A} = \sqrt{(1 - C_A)^2 \left(\frac{\Delta n_A}{n_A}\right)^2 + \sum_{j \neq A}^N C_j^2 \left(\frac{\Delta n_j}{n_j}\right)^2}.$$
(24)

The factor  $(1-C_A)^2$  in first term of the quadratic sum illustrates that elements of large abundance have reduced fraction measurement errors. Contrarily, elements of small abundance are characterized by a measurement error that has significant contributions from the major elements as indicated by the sum of the quadratic errors weighted by the  $C_i^2$ -values.

# 2. Experimental details

2.1. Sample preparation and LIBS measurement locations



Figure 2: (a) Schematic view of thin film synthesis through combinatorial pulsed laser deposition. (b) LIBS setup with indication of the measurement locations on the deposited thin film.

The Si/Ge binary alloy thin film of compositional gradient was deposited on an alumina substrate of  $25 \times 60 \text{ mm}^2$  area via so-called "*combinatorial*" pulsed laser deposition [4]. Therefore, an ultraviolet (248 nm) beam of a KrF excimer laser is splitted into two beams that are focused onto the surfaces of two different targets as illustrated in Figure S2(a). In the present case, one target is composed of silicon, the other target is composed of germanium. The targets are separated by a distance of 25 mm and placed at a distance of about 50 mm from the substrate. The deposition is operated under vacuum at  $5 \times 10^{-5}$  Pa background pressure with a laser fluence of about 1 J cm<sup>-2</sup>, applying 20 000 laser pulses at a repetition rate of 10 Hz. According to the deposition geometry, a compositional gradient along the longitudinal direction of the substrate (*x*-direction in Figure S2) is achieved.

The LIBS setup is presented schematically in Figure S2(b). The measurements were performed in distinct locations along the longitudinal direction of the sample (*x*-direction), separated by 5 mm. Each measurement was performed via signal aquisition over 200 ablation events, applying single pulses on adjacent irradiation sites, separated by 150  $\mu$ m. The sites were aligned along the orthogonal direction (*y*-direction), over which the thin film composition was almost constant.

# 2.2. Plasma diagnostics

The accuracy of the temperature measurement is illustrated by the Saha-Boltzmann plot displayed in Figure S3. It is stressed that self-absorption is taken into account as the emission coefficient  $\varepsilon$  is deduced by adjusting the spectral radiance computed according to eq 1 to the measured intensity. For details we refer to previous work [5]. The high accuracy of the temperature measurement of 2% is attributed to experimental conditions that favor the formation of a uniform plasma in LTE [6].

For electron density measurements using the Si I 390.55 nm transition, we refer to previous work [7]. The spectra recorded for sample locations for which silicon and germanium have similar atomic fractions were used to deduce the Stark broadening parameters of germanium transitions (see SM 2.3). These were used to measure the electron density for sample locations of poor silicon content.



Figure 3: Saha-Boltzmann plot of silicium (red circles) and germanium (blue squares) transitions for t = 500 ns. In the logarithmic function,  $\varepsilon_{ul}$ ,  $\lambda$ ,  $A_{ul}$  and  $g_u$  are the emission coefficient, the wavelength, the transition probability and the upper level statistical weight of the lines, respectively. Self-absorption is here taken into account as  $\varepsilon_{ul}$  is deduced from the calculations. For details, we refer to Ref. [5]. The deduced temperature is  $T = 13\,100$  K with an error of 2%.

# 2.3. Measurement of Stark broadening parameters

The Stark broadening parameters were deduced from spatially-integrated spectral recordings by taking advantage of the spatially uniform plasma produced by laser ablation in argon [8, 6]. Thus, echelle spectra were recorded for different gate delays with respect to the laser pulse, and the electron density was measured for each time via Stark broadening, using lines of known Stark broadening parameters [9, 10]. In the present case, accurate Stark broadening parameters were found for the Si I 390.55 nm line (see Table S1). Thus, we firstly deduced the Stark broadening parameters of the Ge II 589.34 nm transition from the spectra recorded for the Si/Ge binary alloy thin film. This ionic transition has a large Stark width and is weakly self-absorbed. The Stark broadening parameters of the other Ge transitions were deduced from recording on a bulk germanium sample, using the Ge II 589.34 nm transition for  $n_e$ -measurements. Line profiles of the Ge II 589.34 nm and Ge I 326.95 nm transitions are displayed in Figure S4 for different measurement delays. The Stark width and shift of the Ge I 326.95 nm transition are plotted in Figure S5 as functions of the electron density, deduced from Stark broadening of the Ge II 589.34 nm line.



Figure 4: Measured and computed spectral radiance of the Ge II 589.34 nm and Ge I 326.95 nm transitions for different measurement times.



Figure 5: Stark width and shift of the Ge I 326.95 nm transition vs electron density deduced from Stark broadening of the Ge II 589.33 nm line.

# 2.4. Error evaluation details

Details on the evaluation of the errors associated to the computed and measured line widths due to Stark and Doppler broadening are presented in Tables S2 and S3, respectively. According to the short delay of spectra recording, the electron density is large, and Stark broadening dominates the line width. The error associated to the measured width is therefore small compared to that of the computed width  $(w_{sd}^m \ll w_{sd}^c)$ .

Table 2: Error evaluation of the computed line width due to Doppler and Stark broadening  $w_{sd}^c$ . Doppler width  $w_d$  with error  $\Delta w_d$ , Stark width  $w_s$  with error  $\Delta w_s$ , and resulting error  $\Delta w_{sd}^c$  obtained by eq S11. The widths and associated errors are given in units of pm and %, respectively. As T and  $n_e$  were found to be independent of the measurement location, the errors of the computed line widths are constant.

transition	$w_d$	$\frac{\Delta w_d}{w_d}$	w <sub>s</sub>	$\frac{\Delta w_s}{w_s}$	w <sub>sd</sub>	$\frac{\Delta w_{sd}^c}{w_{sd}^c}$
Ge I 303.91	2.9	1	55	28	55	28
Ge I 326.95	3.1	1	65	28	65	28

Table 3: Error evaluation of the measured width due to Doppler and Stark broadening  $w_{sd}^m$ : apparatus width  $w_{ap}$  with error  $\Delta w_{ap}$ , measured line width  $w_m$  with error  $\Delta w_m$ , factor of width growth due to self-absorption  $g_w$ . The error of the optical thickness  $\Delta \tau_0$  (eq 11), the error of the factor of width growth  $\Delta g_w$  (eq S21), and the error  $\Delta w_{sd}^m$  obtained with eq S15 are given for both line-center- and line-integrated intensity measurements. The widths and associated errors are given in units of pm and %, respectively.

							$I_0$ measurement			<i>I</i> <sub>line</sub> measurement		
transition	meas	$w_{ap}$	$\frac{\Delta w_{ap}}{w_{ap}}$	w <sub>m</sub>	$\frac{\Delta w_m}{w_m}$	$g_w$	$\frac{\Delta \tau_0}{\tau_0}$	$\frac{\Delta g_w}{g_w}$	$\frac{\Delta w_{sd}^m}{w_{sd}^m}$	$\frac{\Delta \tau_0}{\tau_0}$	$\frac{\Delta g_w}{g_w}$	$\frac{\Delta w_{sd}^m}{w_{sd}^m}$
Ge I 303.91	11	24	5	75	5	1.06	6	0.4	8	5	0.3	8
	6			81		1.31	9	2	7	6	2	7
	2			97		1.79	24	11	12	8	4	6
Ge I 326.95	11	25	5	70	5	1.01	6	0.04	6	6	0.4	6
	6			76		1.03	5	0.15	7	5	0.15	7
	2			80		1.07	6	0.4	7	5	0.4	7

Table 4: Line-center spectral radiance  $I_0$ , line-integrated radiance  $I_{line}$ , lower level population number density  $n_l$ , atomic number density  $n_A$ , and atomic fraction C for two germanium lines and different measurement locations.

transition	meas	$I_0(W m^{-3} sr^{-1})$	$I_{line}$ (W m <sup>-2</sup> sr <sup>-1</sup> )	$n_l({\rm cm}^{-3})$	$n_A(\mathrm{cm}^{-3})$	<i>C</i> (%)
Ge I 303.91	11	$2.38 \times 10^{14}$	$2.47 \times 10^{4}$	$4.0 \times 10^{14}$	$2.4 \times 10^{16}$	10.0
	6	$7.80  imes 10^{14}$	$9.09 \times 10^{4}$	$1.7 \times 10^{15}$	$1.1 \times 10^{17}$	36.5
	2	$1.14 \times 10^{15}$	$1.65 \times 10^{5}$	$4.1 \times 10^{15}$	$2.5 \times 10^{17}$	80.2
Ge I 326.95	11	$2.93 \times 10^{13}$	$3.13 \times 10^{3}$	$4.0 \times 10^{14}$	$2.4 \times 10^{16}$	10.0
	6	$1.11 \times 10^{14}$	$1.24 \times 10^{4}$	$1.7 \times 10^{15}$	$1.1 \times 10^{17}$	36.5
	2	$2.42 \times 10^{14}$	$2.76 \times 10^{4}$	$4.1 \times 10^{15}$	$2.5 \times 10^{17}$	80.2

# 2.5. Validation of compositional analysis

The compositional analysis of the thin film via calibration-free LIBS were validated by comparing the elemental fractions of the thin film to reference values obtained by Rutherford backscattering spectrometry (RBS). The probe depth of LIBS measurements being larger than the thickness of the thin film, the probe volume contained elements from both the Si/Ge binary thin film and the alumina substrate (see Table S5). The thin film composition deduced from the calibration-free LIBS was found in good agreement with the reference values (see Figure S6). Moreover, we emphasize that the here applied calibration-free method was previously validated for compositional measurements of glasses [7, 11], alloys [5, 12] and thin films [9, 13].

Table 5: Atomic fractions of elements in % for different measurement positions on the sample surface. The fractions of the probe volume correspond to the values measured in the plasma. The fractions in the thin film were obtained from eq S22 considering Ge and Si only.

<b>I</b>		pro	obe vol	thin film			
measurement	Ge	Si	0	Al	Ca	Ge	Si
11	5.0	39.9	33.0	22.0	0.032	$11.2 \pm 2.6$	88.8 ± 2.6
10	6.5	47.6	27.5	18.4	0.020	$12.0 \pm 2.8$	$88.0\pm2.8$
9	7.5	47.7	26.9	17.9	0.017	$13.6 \pm 3.1$	$86.4 \pm 3.1$
8	12.4	49.0	23.1	15.4	0.019	$20.2 \pm 4.3$	$79.8 \pm 4.3$
7	14.9	48.8	21.8	14.5	0.025	$23.4 \pm 4.7$	$76.6 \pm 4.7$
6	23.7	41.3	21.0	14.0	0.025	$36.5 \pm 6.2$	$63.5\pm6.2$
5	32.7	36.0	18.8	12.5	0.018	$47.6 \pm 6.7$	$52.4 \pm 6.7$
4	46.8	28.1	15.0	10.0	0.015	$62.5 \pm 6.5$	$37.5 \pm 6.5$
3	57.9	19.7	13.5	9.0	0.019	$74.6 \pm 5.3$	$25.4\pm5.3$
2	58.8	14.6	16.0	10.6	0.030	$80.2 \pm 4.4$	$19.8 \pm 4.4$



Figure 6: Atomic fraction of germanium within the thin film vs longitutinal position on the sample surface. The values measured via calibation-free LIBS (blue squares) are compared to reference values obtained by RBS (red circles).



Figure 7: Measured spectrum and computed spectral radiance for the ranges of lines selected for the calibration-free analysis (see Table S1). The measurement corresponds to the longitudinal position of 32.5 mm (see Figure S6) labeled 'measurement 6' in the tables.



Figure 8: Measured spectrum and computed spectral radiance of the line selected for the quantification of calcium (see Table S1). The measurement corresponds to the longitudinal position of 32.5 mm (see Figure S6) labeled 'measurement 6' in the tables.

## References

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