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Evaluation of limits of detection in laser-induced breakdown spectroscopy: demonstration for food

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Abstract

Laser-induced breakdown spectroscopy is an emerging technique for fast elemental analyses. It is however known to be less sensitive than the standard techniques, and its capability for trace element analysis is not yet established for most types of materials. To accurately evaluate the sensitivity of LIBS, we propose a procedure that combines a calibration-free LIBS approach with the standard methodology for the evaluation of detection limits. The procedure provides limits of detection not only for the observed elements, but for all elements for which the available spectroscopic data enable the calculation of the element-specific emission spectrum. The method is here applied to food, by determining the limits of detection for 82 elements that may alter the nutritional value of food, or present sanitary risks. Comparing the deduced limits of detection with the typical content of minerals and the upper limits of toxic elements recommended by food safety regulations, we establish a list of elements compatible with food quality monitoring via LIBS. Moreover, we demonstrate that almost all elements can be monitored if the spectra were acquired with a LIBS apparatus of optimized detection efficiency, illustrating thus the capability of LIBS for food quality monitoring.

Keywords: food; elemental analysis; LIBS; calibration-free; limits of detection;

1. Introduction

The growing demand for quality control of food-stuff generated a strongly increasing need to qualify and quantify the food composition in terms of nutritional and salutary income [1, 2]. Beside the evaluation of protein, carbohydrate, lipid, and vitamin fat content, the quantification of minerals and toxic elements is challenging, as it involves measurements of traces at very low concentrations [3]. The standard techniques for these measurements are inductively coupled plasma atomic emission- or mass spectrometry (ICP-AES/MS), atomic absorption spectrometry (AAS), and more recently X-ray fluorescence spectrometry (XRF) [4]. Except XRF spectrometry, these techniques are time- and

cost-expensive as they require extensive sample preparation and the use of hazardous chemicals, incompatible with routine measurements in the innumerable sites of food production and distribution [3, 5].

Laser-induced breakdown spectroscopy is an emerging technique for fast elemental analysis that requires minimal sample preparation [6]. Based on the spectral analysis of emission from a plasma induced by pulsed laser irradiation of the sample, LIBS can be operated in ambient air in a stand-off configuration. It is thus compatible with in situ analysis on industrial production sites [7]. Owing to progress in the technologies of compact and performant laser sources and spectrometers, the sensitivity and velocity of LIBS measurements considerably improved over the last two decades [8]. Thus, even handheld portable LIBS analysers are now available for applications in fields such as waste mate-

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rial recycling, environmental survey, and geology [9].

The relatively late introduction of LIBS in elemental analysis of food is related to its main drawback: due to strong matrix effects, it is challenging to perform accurate quantitative measurements [10]. The difficulties of quantification are particularly severe in the case of heterogenous materials such as food, for which the standard calibration method fails [3, 11]. Huge efforts have thus been addressed to improve the analytical performance via advanced methods of LIBS data analysis. Among these developments, two main directions can be distinguished: (i) multivariate calibration approaches via chemometric methods [12, 13] and, (ii) the so-called *calibration-free* analysis based on modeling of the plasma emission spectrum [14, 15]. Most LIBS analyses of food are performed using one of both types of data analysis.

Compared to the conventional techniques of elemental analysis of food, LIBS has typically lower sensitivity [16]. This is, on one hand, due to the much smaller amount of sample material being analyzed (ng or μg for LIBS instead of mg for AAS or ICP analyses) and, on the other hand, due to the physical mechanisms that govern the LIBS signal generation. In-

deed, the emission of discrete spectral lines exploited for the analytical measurement is in competition with continuum emission generated by the free charges in the laser-produced plasma [17]. Recently, a method for sensitivity-improved calibration-free LIBS measurements was proposed to approach the physical limit of detection imposed by the continuum emission, enabling thus the quantification of trace elements at the ppm-level [15]. The method was validated for seafood [15] and later for optical glass [18].

In the present paper, we evaluate the capability of LIBS for elemental analyses of food by determining the limits of detection (LOD) for a LIBS apparatus that was designed for calibration-free analysis under controlled atmosphere. The system covers the entire spectral range from the ultraviolet to the near infrared and enables therefore LOD evaluation for all elements. It suffers however low sensitivity, and we complete therefore the present investigations by estimating the limits of detection being achievable with a sensitivity-optimized spectroscopic apparatus.

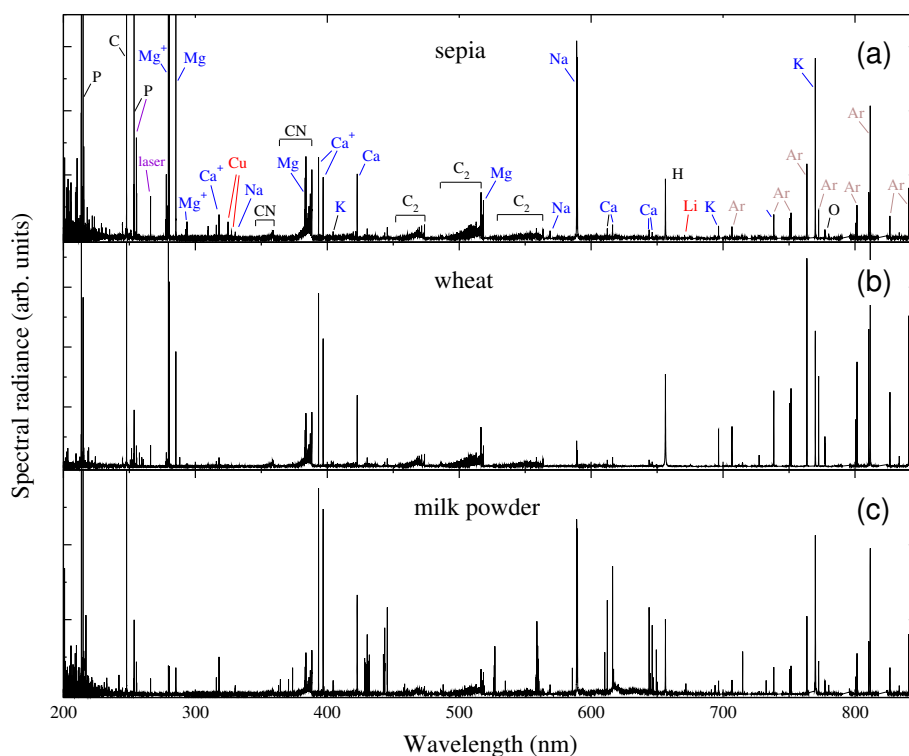


Figure 1: Spectra recorded for different types of dried foodstuff using a delay of $2\ \mu\text{s}$ between the laser pulse and the detector gate and a gate width of $5\ \mu\text{s}$.

2. Experimental Section

The LIBS spectra were recorded in experimental conditions that were previously found to enable accurate compositional analysis via calibration-free LIBS [19]. A detailed description of both the experimental setup and the sensitivity-enhanced calibration-free LIBS approach can be found in a previous paper [15]. We give here a brief summary only.

2.1. LIBS spectra recording

Ultraviolet (266 nm) laser pulses of 4 ns duration and 6 mJ pulse energy were focused onto the dried food samples with a lens of 150 mm focal length. The samples were placed on a motorized sample holder in a vacuum chamber that was filled with argon at 5×10^4 Pa pressure during the experiments.

The LIBS spectra were recorded by imaging the plasma with two lenses of 150 and 35 mm focal lengths onto the entrance of an optical fiber of 600 μm core diameter. The fiber was coupled to an echelle spectrometer of 1×10^4 resolving power equipped with an intensified charge-coupled device matrix detector. The spectroscopic apparatus was calibrated in wavelength and intensity using appropriate lamps (See SI 1 in the Supporting Information). To compensate the low throughput of the optical system, the spectra were recorded by averaging over a large number of ablation events. Thus, 3 laser pulses were applied on 400 different irradiation sites, separated by a distance of 150 μm .

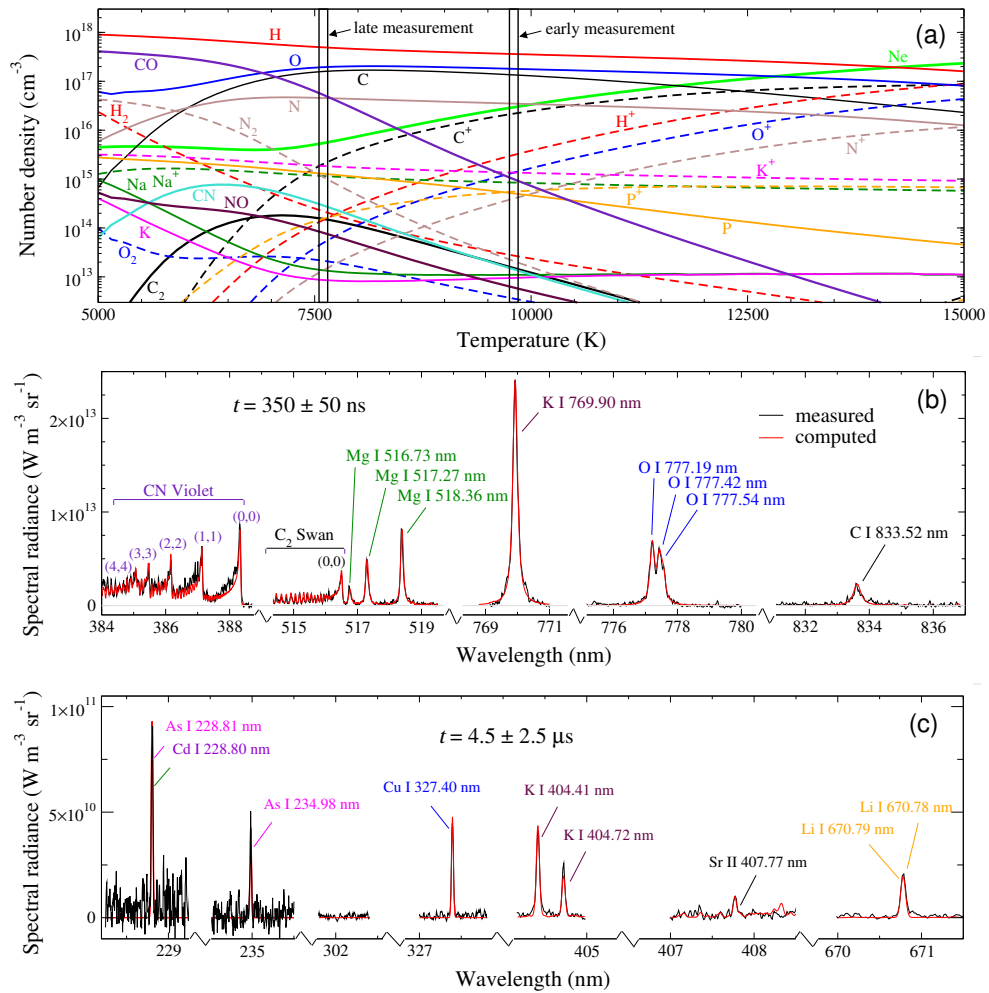


Figure 2: (a) Number densities of plasma species versus temperature computed for a plasma in LTE at atmospheric pressure with the elemental composition of the sepia sample (see Ref. [15]). For simplification, only elements with mass fractions $> 0.1\%$ are displayed. (b) The early spectrum is compared to the spectral radiance of a plasma in full LTE to deduce the fractions of major and most abundant minor elements. (c) The late spectrum is compared to the radiance of a plasma in partial LTE to deduce the fractions of minor and trace elements.

The spectra recorded for different types of food are shown to have very close morphology (see Fig. 1). In addition to the samples indicated in Fig. 1, measurements were performed for sardine and octopus. We emphasize that the similarity of the spectra, and thus of the plasma properties, was obtained for dried samples only. The drying process does not only minimize the moisture content but also increases the sample hardness. Both effects are known to increase the brilliance of the laser-induced plasma [20, 21].

2.2. Spectrum calculation

In elemental analysis, the intensity of the analytical signal is related to the elemental fraction via the calibration curve that is equivalent to the so-called *curve of growth* [22]. In LIBS experiments under appropriate experimental conditions [19], the curve of growth can be computed using the calibration-free LIBS methodology [23]. The here applied sensitivity-improved calibration-free method [15] is based on the analysis of two spectra, recorded with different delays between the laser pulse and the detector gate. The early spectrum, recorded for full local thermodynamic equilibrium (LTE) conditions, is used to quantify major and most abundant minor elements. The late spectrum is recorded for partial LTE conditions, when atoms and ions from the organic matrix are out of equilibrium, and only metal species have Boltzmann equilibrium distributions. According to the reduced electron density, the line over continuum emission intensity ratio is enhanced, and trace elements can be quantified.

In plasmas produced by laser ablation of organic materials, chemical reactions play an important role [24]. They are therefore considered in the calculation of the plasma composition (see Fig. 2a). The spectra recorded for short and large delays are displayed with the computed spectra in Fig. 2b and c, respectively. The deduced values of plasma temperature, electron density and elemental fractions were reported for sepia and two other types of seafood previously [15]. The plasma properties were found to be equal within the measurement uncertainties, and differences in the sample composition appeared for minor and trace mineral elements only.

2.3. LOD evaluation procedure

The limit of detection in elemental analysis is the minimum elemental fraction C_{LOD} for which the analytical signal can be distinguished from the background signal within a stated probability. Assuming a normal

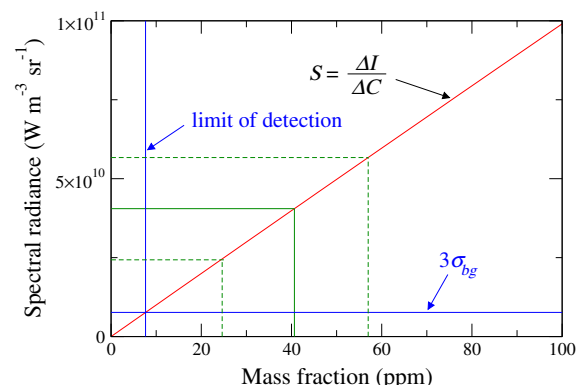


Figure 3: Curve of growth generated for the As I 234.98 nm transition by the calibration-free LIBS model. The quantification of arsenic for sepia (see Fig. 2c) is indicated by green line.

distribution of the background signal fluctuation, the limit of detection within a confidence interval of 99.7% is given by [25]

$$C_{LOD} = 3 \sigma_{bg} / S . \quad (1)$$

Here, σ_{bg} is standard deviation of the background signal and S is the sensitivity given by the slope of the curve of growth (see Fig. 3). The limit of detection defined by eq 1 is thus the elemental fraction for which the offset-subtracted signal intensity equals $3 \sigma_{bg}$ (see Fig. 4).

In LIBS experiments, the analytical signal is the spectral line emission, and the background signal is generally dominated by the continuum emission. The fluctuation of the background signal is characterized via the standard deviation of the data point variation. Therefore, the measured spectrum is smoothen using an ap-

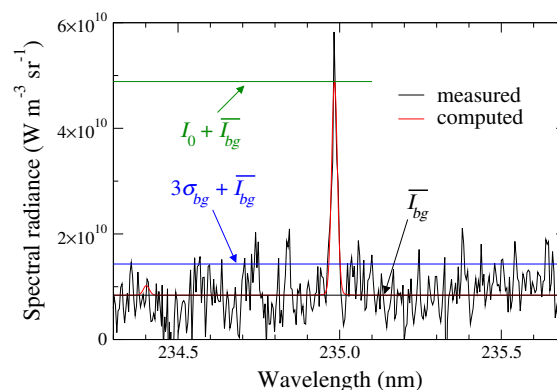


Figure 4: Measured and computed spectra of the As I 234.98 nm transition observed for sepia. The LOD is obtained by adjusting the elemental fraction so that $I_0 = 3 \sigma_{bg}$.

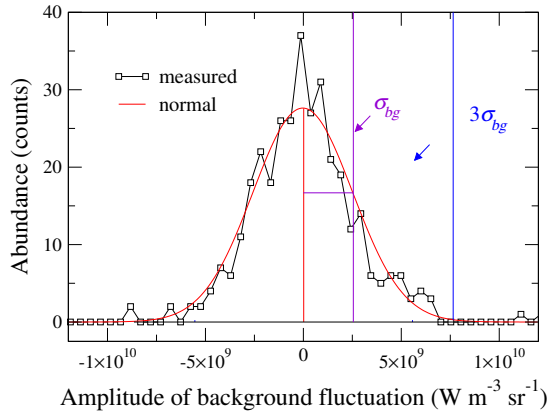


Figure 5: Comparison of the statistical distribution of the background fluctuation with the normal distribution.

appropriate procedure, and the statistical analysis is applied to the noise obtained by subtracting the smoothen spectrum from the original measured spectrum (see Fig. S2 in the Supplementary Material). The width of the considered spectral range of the order of a 1 nm (about 300 data points) was chosen to obtain reliable statistical analysis (see Fig. 5). The distribution of the background fluctuation is shown to feature a slight decay from the normal distribution (see Fig. 5) that is attributed to the presence of low intensity atomic or molecular transitions.

The operation of the LOD evaluation procedure is illustrated in Fig. 6. The procedure starts with the calibration-free LIBS analysis of the measured spectrum. Then, the spectrum of a trace element y is calculated according to the plasma properties. The most intense lines are selected, avoiding interferences with atomic and molecular transitions in the computed

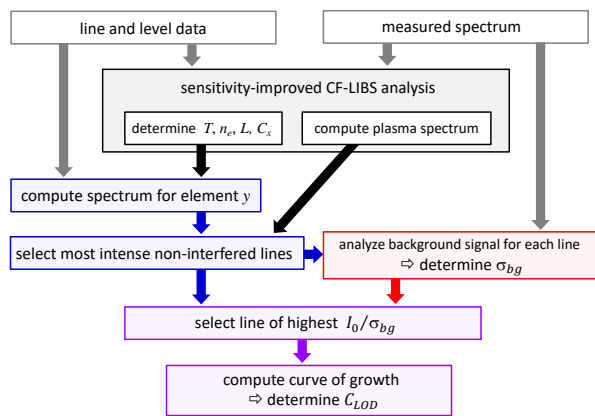


Figure 6: Flow chart of the LOD evaluation procedure.

plasma emission spectrum. For each selected transition, the background signal is analyzed in the measured spectrum to determine its standard deviation σ_{bg} . The lines are then sorted according to the ratio of computed centre-of-line intensity I_0 over σ_{bg} . The curve of growth is generated for the line of highest I_0/σ_{bg} by computing I_0 for various trace element fractions C_y . Finally, the limit of detection is obtained by adjusting the elemental fraction so that the computed line-center intensity I_0 equals $3\sigma_{bg}$ (see Fig. 3).

The method does therefore not require the experimental observation of the analytical transition. It can be applied to each transition for which (i) the spectroscopic data required for the spectrum calculation are available and, (ii) the wavelength of the transition is located in the measured spectral range to enable the background signal recording.

The confidence of the deduced limits of detection is related to the analytical performance of the calibration-free LIBS method that was validated for various materials [26, 27, 18, 28]. Thus, the C_{LOD} -values obtained for previously quantified elements can be considered as validated (See SI 3).

3. Results and discussion

3.1. LOD with echelle spectrometer

The limits of detection deduced for 82 elements are given in Fig. 7. The corresponding analytical transitions are listed in Table S1. The C_{LOD} -values deduced for different types of dried food samples were found to be equal within the uncertainties associated to both the statistical fluctuation of the background signal and the computed line intensity [23]. According to the estimated uncertainty of the order of 100%, the limits of detection are rounded to values 1, 2, 5, etc..

More than half of the elements (green colored) are characterized by $C_{LOD} \leq 1$ ppm, and most of the remaining elements (blue colored) have limits of detection up to a few tens of ppm. The lower LIBS measurement sensitivity for most of these elements is due to the low detection efficiency in the ultraviolet spectral range (see Fig. S1). The use of a spectrometer with appropriate blazing wavelength coupled to a UV-sensitive detector may improve the sensitivity by one or two orders of magnitude, and bring the limits of detection to the sub-ppm level for most elements.

The very low sensitivity for nitrogen, sulfur and the halogens (red colored) is due to the particular structure of these atoms. According to the huge energy gaps between their electronic levels, these elements are

Legend																																																			
Light Green	≤ 1 ppm																																																		
Light Blue	2 ... 50 ppm																																																		
Light Yellow	100 ... 1000 ppm																																																		
Light Orange	0.2 ... 20 %																																																		
H	•																			He	-																														
Li	•	Be	○															B	•	C	•	N	•	O	•	F	○	Ne	-																						
0.1		0.1																0.2	-	5%	-	20%	-	-																											
Na	•	Mg	•															Al	•	Si	•	P	•	S	○	Cl	○	Ar	-																						
1		0.02																1	0.5	20	1%	1%	-	-																											
K	•	Ca	•	Sc	○	Ti	○	V	○	Cr	○	Mn	○	Fe	•	Co	○	Ni	○	Cu	•	Zn	•	Ga	○	Ge	○	As	•	Se	○	Br	○	Kr	-																
200		0.02		0.2		0.2		1		1		0.2		1		2		2		0.1		1		1		1		10		50		5000																			
Rb	•	Sr	•	Y	○	Zr	○	Nb	○	Mo	○	Tc	○	Ru	○	Rh	○	Pd	○	Ag	○	Cd	•	In	○	Sn	○	Sb	○	Te	○	I	○	Xe	-																
5		0.02		0.5		0.5		1		1		0.5		1		1		0.5		0.2		0.2		5		2		5		10		5000																			
Cs	○	Ba	○															Hf	○	Ta	○	W	○	Re	○	Os	○	Ir	○	Pt	○	Au	○	Hg	○	Tl	○	Pb	○	Bi	○	Po	○	At	○	Rn	-				
1000		0.2																2		0.5		10		1		1		5		2		1		20		5		2		2		5		20							
Fr	○	Ra	○																			La	○	Ce	○	Pr	○	Nd	○	Pm	○	Sm	○	Eu	○	Gd	○	Tb	○	Dy	○	Ho	○	Er	○	Tm	○	Yb	○	Lu	○
50		1																				1		5		2		1		10		5		0.5		2		1		0.1		1		0.5		0.1		0.1			
																						Ac	○	Th	○	Pa	○	U	○	Np	○	Pu	○	Am	○	Cm	○	Bk	○	Cf	○	Es	○	Fm	○	Md	○	No	○	Lr	○
																						0.5		5		?		0.5		?		?		?		?		?		?		?		?		?		?			

Figure 7: Limits of detection in ppm mass fraction units for elements in dry food. The values correspond to measurements with the spectral lines of highest analytical performance (see Table S1). The sensitivity available for each element is indicated by the colors. The elements being measured for food and other materials are indicated by the filled and empty red circles, respectively. According to the estimated uncertainty of the order of 50% (See Supp. Mat., Section 3) the C_{LOD} -values are given with a single significant digit. Matrix elements, rare gases, and elements with missing spectroscopic data were excluded from the analysis (white colored).

out of equilibrium during the late measurement. They are therefore quantified using the early measurement, where the electron density is large enough to ensure the Boltzmann equilibrium distributions. As the continuum emission intensity is higher, the signal-to-noise ratio is reduced, and low sensitivity is obtained for these elements.

We stress that, even for calibrated LIBS, the limits of detection are large for these elements. This is due to the fact that the observable transitions occur exclusively between levels of high excitation energy. The upper level population number densities, and consequently the line emission intensities, are therefore low.

The LIBS measurement sensitivity of these elements can be improved by observing the emission of molecules formed by chemical reactions with other elements [29, 30]. However, the improved limits of detection depend on the abundance of the reactants. We thus consider here exclusively the limits of detection obtained straightforwardly with atomic emission.

Comparing the limits of detection to typical amounts of minerals, oligo-elements (Table S2) and toxic elements (Table S3), and to the recommended upper limits of toxic elements (Table S4), we observe that the measurement sensitivity reached with a low optical throughput echelle spectrometer-based LIBS apparatus is compatible with food quality monitoring for most of the dietary minerals. Moreover, several toxic elements have limits of detection below or close to the maximum amount recommended by the safety regulations.

3.2. LOD with high-throughput spectrometer

The present investigations were performed with a broadband echelle spectrometer to enable the observation of spectral lines of all elements presented in Fig. 7. A significant improvement of sensitivity can be reached with a LIBS apparatus of improved detection efficiency. For example, limits of detection similar to the here reported values have been obtained for single-shot micro-LIBS measurements by using a Czerny-Turner spectrometer and an optical detection system of large numerical aperture [31]. The limits of detection are correlated to the standard deviation of the background signal that is expected to decrease as

$$\sigma_{bg} \propto \frac{1}{\sqrt{n_{ph}}}, \quad (2)$$

where n_{ph} is the number of photons from the continuum emission that are detected. The number of photons increases linearly with (i) the solid angle of plasma observation, (ii) with the detection efficiency at the wavelength of interest, and (iii) with the number of ablation events over which the signal is acquired. With respect to the LIBS apparatus used for the present experiment, a system of optimized optical throughput is expected to improve the limits of detection for all elements by more than one order of magnitude (see SI 5 in the Supporting Information). A further increase of sensitivity up to

one order of magnitude can be reached for elements detected via transitions in the ultraviolet range by using an optical detection system with wavelength specific optimized efficiency (see SI 5). Such a sensitivity-improved system would give access to fast monitoring of almost all nutrients and toxic elements that may occur in food (see Fig. S3).

4. Conclusion

We presented a method for the evaluation of the limits of detection in elemental analysis via laser-induced breakdown spectroscopy. Based on the combination of a sensitivity-enhanced calibration-free LIBS approach with the standard methodology of LOD evaluation, this method gives access to the accurate LOD evaluation not only for measured elements but also for non-detected elements, if the data required for the calculation of the element-specific emission spectrum are available.

Applied to dried food samples, the method enabled the evaluation for the LIBS measurement sensitivity of 82 elements that may occur as healthy or toxic input. The investigations were performed with a broadband echelle spectrometer in order to detect lines of all elements of interest. Although this LIBS apparatus has low sensitivity, it enables monitoring of several nutrients and toxic elements. By increasing the sensitivity via the use of a high throughput optical system and a wavelength-specific efficiency-optimized detection system, the here reported limits of detection may be improved by one or two orders of magnitude, giving thus access to quality control of food for almost all minerals, oligo- and toxic elements.

The method of LOD evaluation can be applied to any kind of sample material given that the LIBS spectra are recorded in experimental conditions that satisfy the validity conditions of the calibration-free LIBS model.

5. Appendix A; Supplementary data

Technical details, supporting data, and information about food content and safety regulations are given.

6. Acknowledgements

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