Space-resolved analysis of trace elements in fresh vegetables using ultraviolet nanosecond laser-induced breakdown spectroscopy ☆

Vincent Juvé, Richard Portelli, Myriam Boueri, Matthieu Baudelet, Jin Yu *

Université de Lyon, F-69622, Lyon, France, Université Lyon 1, Villeurbanne CNRS, UMR5579, LASIM

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) has been applied to analyze trace elements contained in fresh vegetables. A quadrupled Nd:YAG laser is used in the experiments for ablation. Analyzed samples come from local markets and represent frequently consumed vegetables. For a typical root vegetable, such as potato, spectral analysis of the plasma emission reveals more than 400 lines emitted by 27 elements and 2 molecules, C_2 and CN. Among these species, one can find trace as well as ultra-trace elements. A space-resolved analysis of several trace elements with strong emissions is then applied to typical root, stem and fruit vegetables. The results from this study demonstrate the potential of an interesting tool for botanical and agricultural studies as well for food quality/safety and environment pollution assessment and control.

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1. Introduction

The intake of trace mineral elements from vegetables is one of the most important pathways for the human body to absorb dietary minerals necessary for its healthy development, along with, unfortunately, harmful elements such as toxic or heavy metals which may lead to intoxication and with prolonged accumulation, a number of neurodegenerative diseases for example [1]. Detection and analysis of trace mineral elements in vegetables, and more generally in food, can provide useful assessment and control for safe and healthy alimentation [2]. Such detection and analysis may also provide assessment and monitoring of the pollutions of the environment (soil, water, air) to which vegetables, or more generally agricultural products, are in direct contact [3,4].

Detection and analysis of trace and ultra-trace elements in these substances need highly sensitive detection technique. According to a study done by the INRA (Institut National de la Recherche Agronomique) on French food [2], for a typical vegetable, such as potatoes produced in France, the mean concentrations of minerals and oligoelements are between 0.001 and 2.80 mg/kg of fresh matter for ultra-traces, and between 156 and 800 mg/kg of fresh matter for others. While for toxic elements, the mean concentrations vary from 0.0021 to 0.59 mg/kg of fresh matter. Table 1, provides the detailed data for potatoes extracted from Ref. [2].

Among available elemental analysis techniques, laser-induced breakdown spectroscopy (LIBS) [5,6] exhibits attractive features, such as capacity of multi-elemental detection, rapid response, easy sample preparation, high spatial resolution, possibility of remote sensing, and high sensitivity. These attractive features provide the potential for LIBS to be a polyvalent monitoring and analysis tool with high performances. Such a tool would be suitable, with proper calibration and validation, to provide laboratory analysis with a high figure of merit, and would be highly appreciated in the field as well as online monitoring and analysis. It is however a challenge to apply the LIBS technique, traditionally and commonly used for inorganic sample analysis, to vegetable or more generally to food analysis [7]. This is because the matrix effect (the dependence of the properties of the plasma on the properties of the sample) is accentuated when dealing with an inhomogeneous medium such as a vegetable tissue. Thus the calibration will be more difficult than for a metallic sample. Several works used LIBS to analyze trace elements in plants [8,9], and in particular in leaves [10,11]. However all these works concentrated on the analysis of a limited number of trace elements.

In this paper, we shall present our results of trace element detection and analysis in fresh vegetables using LIBS. An extensive number of 27 elements are detected in typical vegetable such as potatoes. A space-resolved analysis is especially presented for typical vegetables (root, stem and fruit). We shall first describe our experimental setup and the experimental protocol. Experimental results are then presented by a list of species with spectral emissions identified in LIBS spectra. Detailed spectra emitted by trace or ultra-trace elements are presented in order to show the conditions of their observations. Before concluding the paper, we will present the results of space-resolved analysis showing distributions of detected elements in different parts of a vegetable. Only qualitative analysis and

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* Corresponding author.
  E-mail address: jin.yu@lasim.univ-lyon1.fr (J. Yu).

Table 1
Mean concentrations in minerals, oligoelements, and toxic elements in potatoes

Elements	Oligoelements											
	Li	Cr	Mn	Co	Ni	Cu	Zn	Se	Mo	Na	Mg	Ca
Mean concentration (mg/kg fresh matter)	0.002	0.05	1.43	0.001	0.07	0.94	2.80	0.011	0.418	800	208	156
Elements	Toxic elements					
	Al	As	Cd	Pb	Hg	Sb
Mean concentration (mg/kg fresh matter)	0.59	0.017	0.0109	0.005	0.007	0.0021

Data extracted from Ref. [2].

distributions of relative concentrations in a vegetable will be presented in this work as the first step of further works which would lead to quantitative trace or ultra-trace element analysis in fresh vegetables.

2. Experimental setup, sample preparation, and measurement protocol

In our experiments, a quadrupled Nd:YAG laser (266 nm) with 10 Hz repetition rate was used in order to get higher detection sensitivity thanks to the efficient UV laser-induced ablation of organic materials [12]. Pulse energy used was 10 mJ measured by a calorimeter. Laser pulses were focused on the sample surface using a bi-convex quartz lens with a 50 mm focal length. The focused spot size was estimated to 100 μm in diameter, which led to a fluence of 127 J/cm^2. Emission from the plasma was collimated into a coupling fiber (50 μm core diameter) using a bi-convex quartz lens of 100 mm focal length and 50 mm diameter. The used fiber presented good transmission from 200 nm to 850 nm. The fiber was connected to an Echelle spectrometer (spectral resolution $\lambda/\Delta\lambda = 5000$) coupled with an ICCD camera to record the spectra (Mechelle and iStar from Andor Technology). The spectrometer calibration for the wavelength was done with a mercury argon calibration light source (HG-1 from Ocean Optics), and that for the intensity with a deuterium tungsten halogen light source (DH-2000 from Ocean Optics). Used samples came from local markets. They were washed and cut into small pieces as done for cooking preparation.

A delay generator (Stanford Instrumentation) was used to synchronize the laser and the ICCD camera. To avoid the strong continuum emission immediately after the laser impact on the sample, a delay of 100 ns was applied before the opening of the ICCD. A detection window of 5 μs was used to integrate the plasma emission after each laser shot. Each spectrum was accumulated over 1000 laser shots. The sample was moved quickly during the accumulation in order for each laser shot to have a fresh sample surface. For each type of sample, 5 spectra of 1000 laser shots were typically taken to calculate the mean emission intensities and the associated standard deviations for detected spectral lines.

In our experiments, 4 types of vegetables were analyzed, among them two roots, potato and carrot; one stem, celery; and one fruit, aubergine. For the roots, spatially resolved analysis was performed to get the distribution of trace elements from the center to the outer part. For stem, measurements were carried out at different heights of the plant from its lower part to its upper part. For the fruit, trace elements were detected from its beginning (the part close to the stem) to its endpoint.

3. Results and discussions

3.1. Overall analysis

A typical spectrum of a potato is shown in Fig. 1. The plasma was induced on the skin of the potato. The spectrum is corrected for the spectral response of the detection system (fiber+spectrometer+ICCD). And the dark charge of the ICCD is negligible. We can see a spectrum with a large number of lines over a quite acceptable background. A meticulous line-by-line identification of this spectrum using the NIST spectral database [13], yields a list of 422 identified lines, among which 391 lines were emitted by atomic or ionic species, 9 lines by molecules (C_2 and CN), and 22 ghost lines. The ghost lines are due to the overlapping of the most intense spectral lines over several orders of the Echelle spectrometer. The identification procedure first takes into account the wavelengths of the lines. Then their intensities (height of the line minus the background) are compared to the relative intensities (or transition probabilities) indicated by the NIST database. For elements with multiple observed emission lines, correlation between experimental intensities for different lines and the relative line intensities indicated by the NIST database is established in order to find out eventual false line designations. Such correlation is not exact because matrix effect and self-absorption for strong lines. The typical mean abundances of the elements are also taken into account to be compared with the experimental intensities of spectral lines. These supplementary checks allow us to identify different elements that emit in very close wavelengths for the resolution of the spectrometer. It is also important to consider the shape of the spectral lines since a ghost often has a shape different from a spectral line.

Table 2 provides a list of 27 elements that can be identified in the spectrum of the skin of a potato. For species that emit a large number of lines in the observed spectral range, only the most intense lines are presented. Apart from organic elements (H, C, N, O), we can see a large number of inorganic elements including metals (Li, Be, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Mo, Ba) and nonmetals (F, Si, S, Cl). As indicated in Table 1, a certain number of these elements should have a very low mean concentration in a typical vegetable.
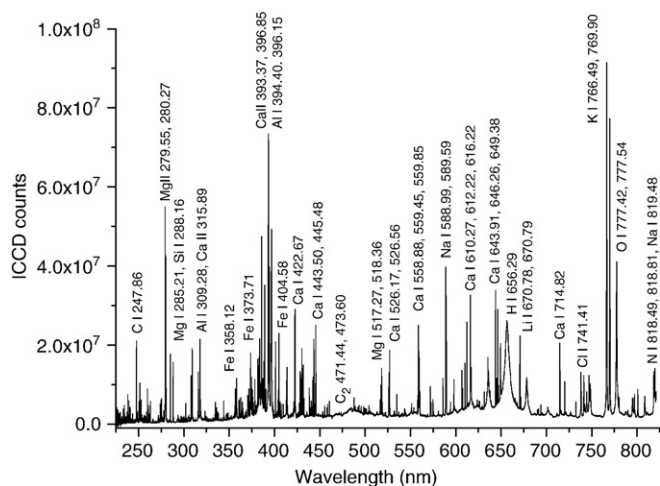

Fig. 1. Typical LIBS spectrum of a fresh potato. The plasma is induced on the skin of the potato. The identifications of some strong lines are indicated in the figure.

Table 2
Identification of spectral lines observed in the LIBS spectrum of a potato

Species	Line position (nm)	Line intensity
H I	656.28	21 528 685
Li I	670.78	18 344 315
Be II	313.04	476 975
C I	247.86	20 811 762
C II	431.73	11 121 647
	431.86	12 455 170
C III	432.56	4 225 518
N I	746.94	8 983 483
	818.48	9 780 670
	818.83	10 840 440
N II	532.08	1 037 862
O I	543.70	1 517 848
	777.32	35 212 163
	777.46	37 534 888
	795.22	4 698 630
F I	690.22	1 041 120
Na I	588.99	37 250 850
	589.59	30 200 025
	819.47	11 707 917
Na II	305.73	1 339 610
	444.74	3 258 285
Mg I	285.21	17 095 010
	383.23	12 121 288
	383.81	16 718 213
	518.37	11 630 600
Mg II	279.56	54 698 980
	280.26	41 928 574
Al I	308.22	11 614 054
	309.28	18 599 680
	394.39	34 690 660
	396.16	33 427 835
Al II	606.87	9 531 770
Si I	251.61	10 409 136
	288.16	15 113 149
Si II	598.02	7 739 093
Si III	433.84	441 392
S I	742.43	2 877 733
	744.32	4 840 810
Cl I	741.40	10 171 165
	808.64	4 489 727
	819.96	5 424 905
K I	404.41	3 503 115
	693.89	2 509 280
	766.47	87 734 738
	769.95	73 719 788
Ca I	422.68	26 277 775
	445.48	22 803 550
	616.21	26 552 255
	643.91	29 489 033
	646.26	23 640 818
Ca II	393.37	64 398 650
	396.85	44 178 785
Ti I	364.26	1 534 623
	468.17	2 107 902
	499.10	1 563 030
	499.96	1 433 507
Ti II	323.44	2 216 021
	334.93	4 451 782
	336.10	3 066 503
V I	572.69	3 269 793
	572.78	1 600 820
Cr I	425.40	310 925
Mn I	279.81	9 906 765
	403.07	1 496 870
	403.29	1 286 720
Mn II	257.60	1 360 467
	260.56	533 155
	293.91	412 141
Fe I	373.46	11 811 718
	373.71	12 653 718
	374.93	8 153 670
	382.04	10 247 898
Fe II	238.20	7 479 192
	239.56	5 581 030
	259.94	8 454 326

Table 2 (continued)

| Species	Line position (nm)	Line intensity
Co I	243.22	510 329
	243.69	212 691
Ni I	300.26	276 224
	300.35	265 705
Ni II	333.19	311 669
Cu I	324.76	954 713
	327.39	356 696
Rb I	794.78	4 768 852
	780.02	4 430 985
Sr I	460.73	3 688 732
Sr II	407.76	3 469 758
	421.55	2 430 395
Mo I	368.00	1 071 505
	379.83	1 600 107
	390.29	1 316 135
	442.17	2 282 325
Ba I	553.56	1 189 355
Ba II	455.39	2 769 838
	493.39	1 418 700

The plasma is induced on the skin of the potato. More than 400 lines are identified belonging to 27 elements and 2 molecules, C_2 and CN. Only lines emitted by elemental species, atoms and ions, are presented in the table. For species that emit a large number of observable lines in the observed spectral range, iron (284 lines), calcium (45 lines), titanium (44 lines), magnesium (14 lines), silicon (13 lines), manganese (10), sodium (8 lines), only the most intense lines are presented. The column "Line position" indicates the wavelengths of the lines in the experimental spectrum; "Line intensity" provides the heights of the lines measured from the background.

In order to evaluate the sensitivity of detection of trace metallic elements in a typical root as potato by LIBS, we present in Fig. 2 detailed LIBS spectra of the skin of a potato. In these spectra, we see that for a certain number of elements, Co (Fig. 2a), Ni (Fig. 2b) and Cr (Fig. 2f), emissions are detected in the spectra with a poor signal to noise ratio: ~2.9 for Co, ~3.1 for Ni, and ~1.6 for Cr. We can think that for these elements, the concentrations in the skin of the potato are not far from the limit of detection for these elements allowed by our setup. Without calibration of the LIBS setup, we cannot know to what concentrations these limits correspond. From the data published by the INRA [2], we can have an idea of the orders of magnitude of these concentrations. According to Table 1, for typical potato samples the mean concentrations of Co, Ni and Cr are respectively, 0.001, 0.07 and 0.05 mg/kg of fresh matter. These data suggest a sub-ppm limit of detection for these elements in a fresh potato for our LIBS setup and under our conditions of experiment. We precise that this order-of-magnitude estimation has to be validated by either a calibration procedure using standard samples with known element concentrations, or by other calibrated measurement techniques (ICP-MS for example). For other elements, emissions are detected with quite good signal to noise ratios. This is because their higher concentrations, above the corresponding limits of detection in the skin of the potato, for example Na, Mg, Al, K, Ca, Ti, V, Mn, Fe, Cu, Mo. Other alkaline metals or alkaline earth metals (Li, Be, Rb, Sr, Ba) are detected with high signal to noise ratios thanks to their simple electronic configurations, which leads to the concentration of the emission in one or two spectral lines.

The spectra presented in Fig. 2 indicate the spectral regions for highly sensitive detection of trace and ultra-trace elements in vegetables. This information is important for the improvement of the detection sensitivity by using a dedicated narrow bandwidth, high resolution and high throughput spectrometer (Czerny-Turner spectrometer for example) instead of an Echelle spectrometer. Such dedicated detection system can be optimized for one or several elements in order to get higher sensitivity and lower limit of detection for targeted elements.

3.2. Space-resolved analysis

The results of space-resolved analysis are shown in Figs. 3–5. To represent the relative concentrations of the analyzed elements Mg, Al,
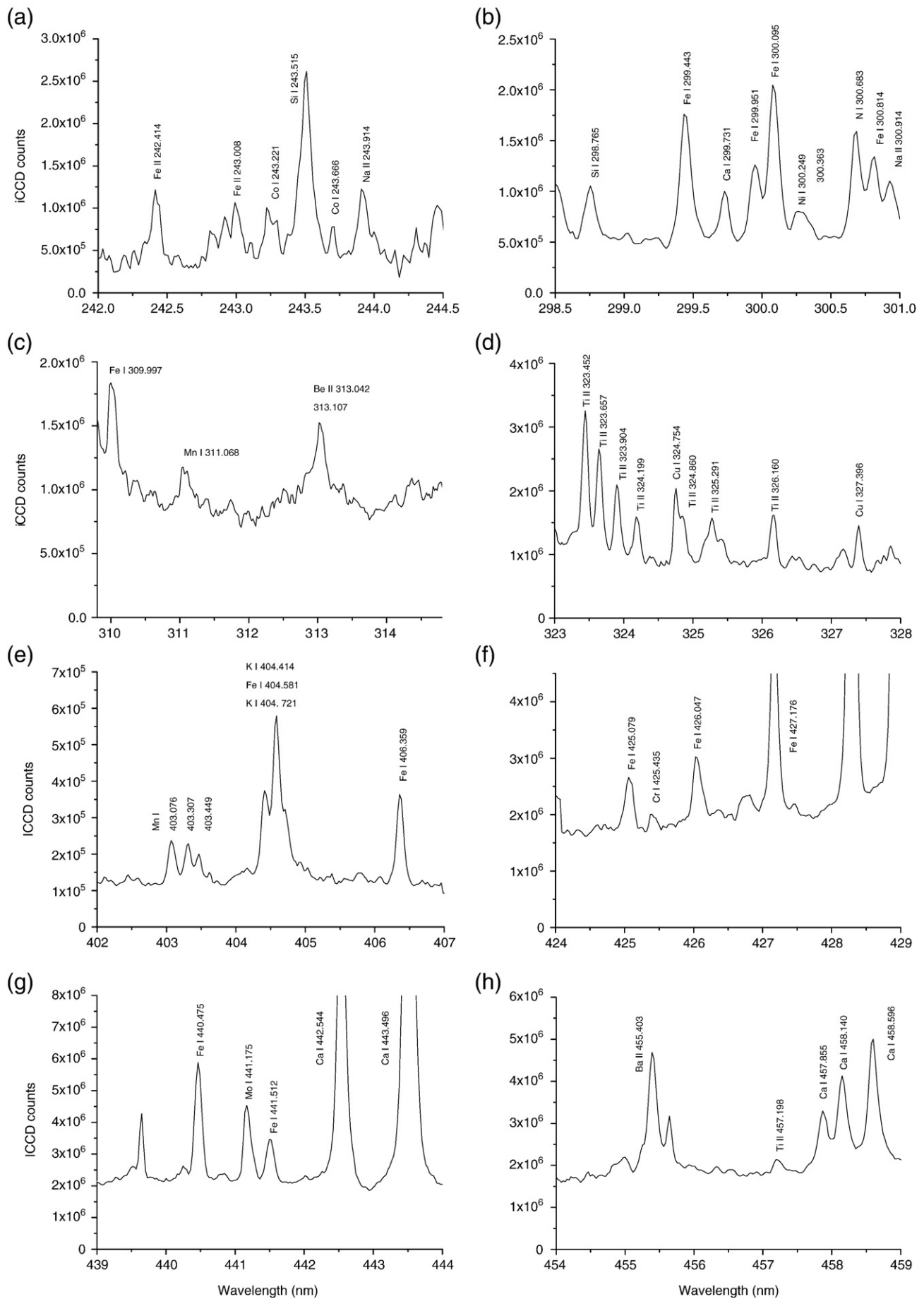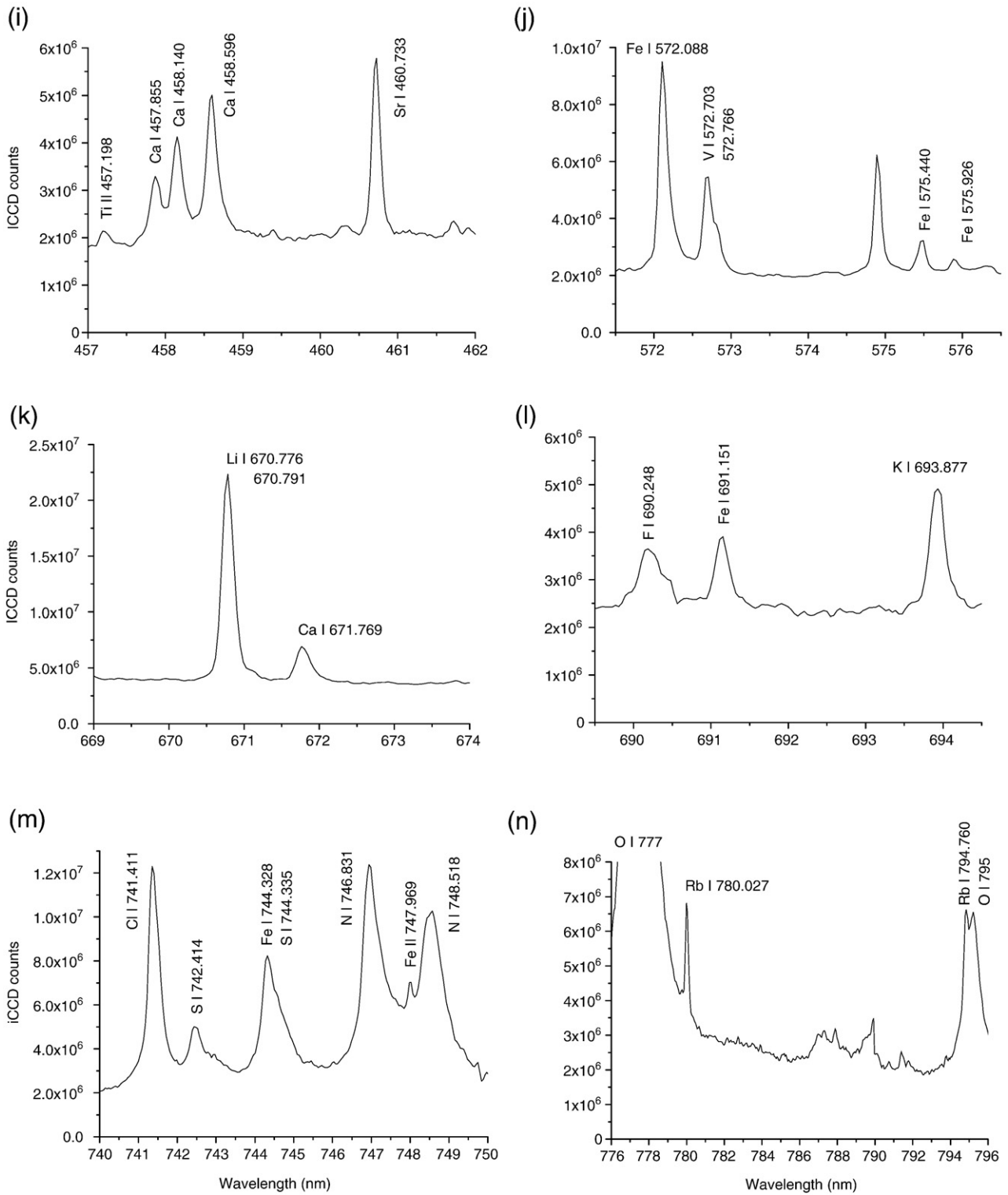
Fig. 2. Detailed LIBS spectra from the skin of a fresh potato.

Ca, Ti, Mn, Fe the following lines are respectively used 285.21 nm, 394.39 and 396.16 nm, 393.37 and 396.85 nm, 498.17 nm, 279.81 nm, 373.71 nm. These lines are chosen for their high intensities and low fluctuations from a spectrum to another spectrum. Their shapes are checked to be sure that they are not affected by self-absorption. The intensity of a spectral line is calculated using the surface under the line shape. The background is removed by calculating the mean background value around the considered line. In the cases where two lines

are used to represent the relative concentration of an element, the intensities of the two lines are added. To show the distribution (or spatial profile) of the relative concentrations of a trace element in different places of a vegetable, a first normalization is made for a given spectrum by dividing the line intensity of the considered element by that of the carbon line at 247.86 nm. Carbon is chosen as the internal reference because of its relative constant concentrations for different places of the analyzed vegetable sample. This normalization reduces
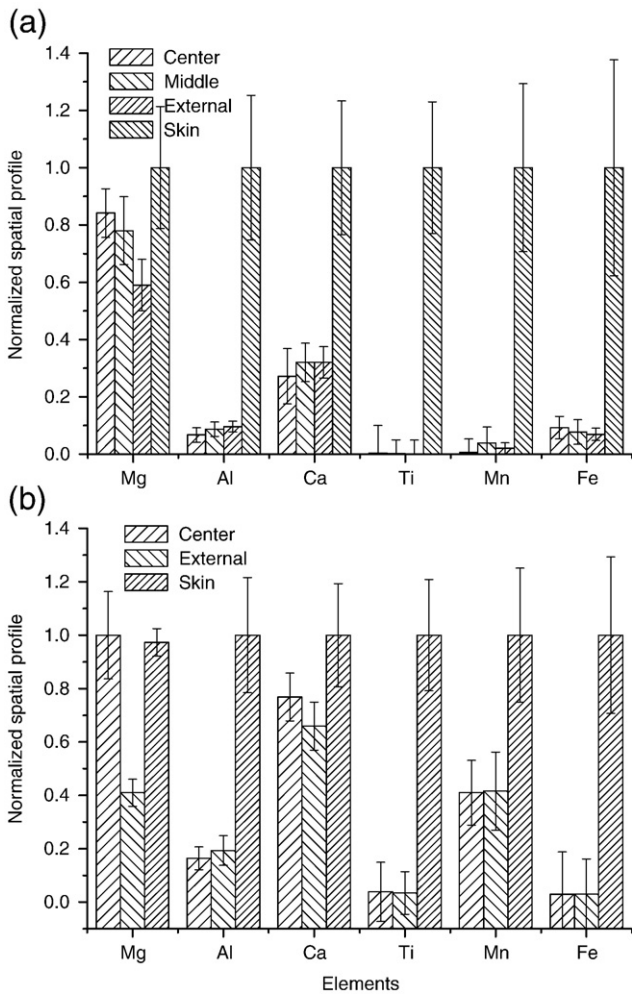
(a)

(b)

Fig. 3. Normalized spatial profiles of relative concentrations of Mg, Al, Ca, Ti, Mn, and Fe for a fresh potato (a) and for a fresh carrot (b). The vegetables are cut into slices in order to take spectra from the center to the skin with several different zones.

the fluctuation of the spectral line intensities due to the fluctuation of the ablation (laser energy fluctuation, sample surface asperity…) for different spectra. A second normalization is then made for a given
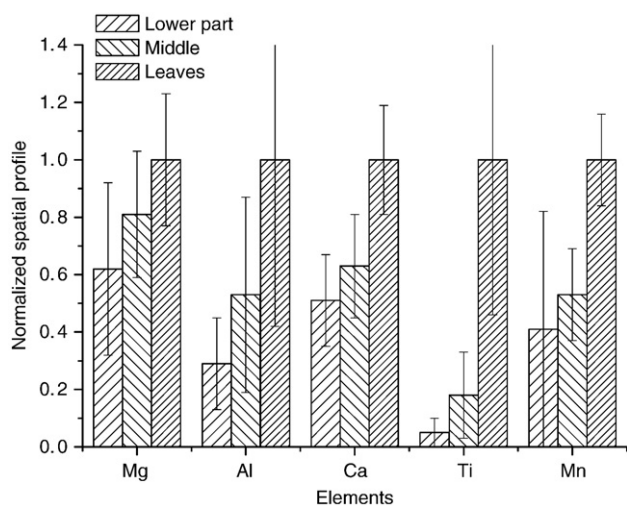

Fig. 4. Normalized spatial profiles of relative concentrations of Mg, Al, Ca, Ti, and Mn for a fresh celery. Spectra have been taken on the outer surface of the plant from its lower part to its upper part in order to obtain a vertical profile of the relative concentrations of the elements.
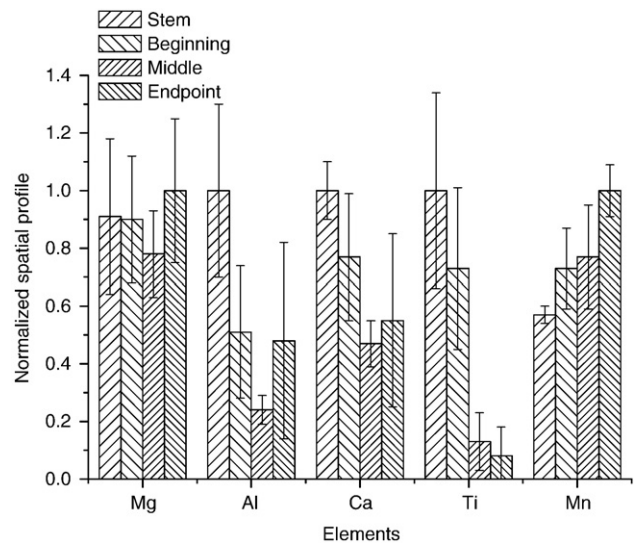

Fig. 5. Normalized spatial profiles of relative concentrations of Mg, Al, Ca, Ti, and Mn for a fresh aubergine. Spectra have been taken on the skin of the aubergine from its stem to its endpoint in order to obtain a profile of the relative concentrations of the elements across the vegetable.

element over its intensities measured in different places of a vegetable in order to fix the highest intensity to the value to the unit. These two normalizations are made because we are only interested in the distributions of relative concentrations in different places of a vegetable for a given element. The error bars in the figures represent the standard deviation calculated over different spectra. The determinations of absolute concentrations (quantitative analysis), even of relative concentrations between different elements, require the detailed knowledge of the properties of the plasma (temperature, electronic density) [6]. Another way to accede to the quantitative analysis is to use reference samples with known concentrations. However in the case of the analysis of vegetables, the large number of elements to be analyzed and the variation of the properties of the samples from a vegetable to another, make the calibration procedure difficult to be implemented.

Fig. 3 shows normalized spatial profiles of relative elemental concentrations for roots, potato (Fig. 3a) and carrot (Fig. 3b). The roots were washed and cut in slice in order for us to get spectra at different places from the center to the periphery. For the potato in Fig. 3a, we can see two different behaviors: for Al, Ca, Ti, Mn, and Fe, the highest concentration is detected on the skin. The concentration decreases drastically inside the potato. Since the potato is in contact with the soil during its growth, we can consider that trace elements come from the soil and diffuse through the skin into the potato. The fact that, for the above elements, the highest concentration is detected on the skin means that the skin represents a large resistance for the diffusion of these elements. In contrast, a quite different behavior is observed for Mg: the concentration is quite uniform across the potato from its skin to its center. This observation shows an important penetration rate for Mg through the skin of the potato. Even though the uncertainties of the measurements are quite important, the specific role of the skin of the potato to prevent a certain number of elements (Al, Ca, Ti, Mn, and Fe) to penetrate into it and the higher mobility of Mg through the skin are well established. For the carrot, the concentration gradient from the skin to the center observed for potato is somewhat attenuated. Two specific features of carrots compared to potatoes may explain this difference: there is not a specific skin for a carrot; however there is a specific central part in a carrot that is different in structure from the other parts. A quite uniform distribution of Mg is again observed for the carrot. We remark that the large concentrations of trace elements in the skin of a vegetable may also be contributed by the contaminations

during the transportation and the preparation of the samples, for example the washing water. That is, however, the actual state of a vegetable when it is ready for cooking.

Fig. 4 shows normalized spatial profiles of relative elemental concentrations for a stem, celery. Measurements are performed at different heights of the samples while the plasma is generated on the outer skin of the sample. A clear tendency is observed: the concentrations of studied elements increase from its lower part to its upper part. This observation might be explained by the higher photochemical activities in the upper part (leaves), as well as the particulate deposition from the atmosphere, although chemical and biological studies are certainly needed to provide a detailed description of the mechanism of the distribution of trace elements in a vegetable. Mg is always observed to present a more uniform distribution across the vegetable than other elements.

Fig. 5 shows normalized spatial profiles of relative elemental concentrations for an aubergine, a fruit vegetable. Measurements are taken through the aubergine from the stem (the part of the aubergine attached to the plant) to its endpoint. For Al, Ca and Ti, we observe a decrease of the concentration from the stem to the endpoint, showing the direction of the diffusion of these elements. For Mg and Mn, quite uniform distributions are observed, which conforms to the results obtained for roots and stems for Mg. The uncertainties of the measurements are however quite large to provide precise distributions of the elements over the vegetable.

4. Conclusion

We have demonstrated trace and ultra-trace element detection and qualitative analysis in fresh vegetables using LIBS technique. The use of UV nanosecond laser for ablation provides sensitive detection. A large number (27) of trace elements can be identified in the LIBS spectra, including organic elements, metals and nonmetals. The observed metallic elements consist of oligoelements as well as toxic elements (especially Al). Space-resolved analysis has been performed thanks to the high spatial resolution of the technique. The limit of detection can be significantly decreased by using a dedicated spectroscopic detection system optimized for specific elements to be detected. A larger number of spectra can be recorded to reduce statistical dispersions of the measurements, improving therefore the precision of the analysis. However, works are still needed to be accomplished in order to understand in detail the plasma generation in a complex matrix such as a vegetable tissue. Such a detailed understanding would allow a quantitative analysis of trace elements in vegetables. Calibrations with standard samples or comparisons with other calibrated elemental measurement techniques represent also ways to accede to the quantitative measurements. Finally, the results obtained in this work show the potential of the LIBS technique to provide an interesting tool for detection and analysis of trace elements in fresh vegetables and more generally in food. Trace element detection and analysis in vegetables represent important issues for the assessment and the control of food quality and safety, as well as for the detection and the monitoring of the environment pollutions including heavy metal charges in soil, water and air.

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