



HAL
open science

Tea geographical origin explained by LIBS elemental profile combined to isotopic information

Nadia Baskali-Bouregaa, Marie-Laure Milliand, Sophie Mauffrey, Elodie Chabert, Maureen Forrestier, Nicole Gilon

► To cite this version:

Nadia Baskali-Bouregaa, Marie-Laure Milliand, Sophie Mauffrey, Elodie Chabert, Maureen Forrestier, et al.. Tea geographical origin explained by LIBS elemental profile combined to isotopic information. *Talanta*, 2020, 211, pp.120674. 10.1016/j.talanta.2019.120674 . hal-02456974

HAL Id: hal-02456974

<https://hal.science/hal-02456974>

Submitted on 7 Mar 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Tea geographical origin explained by LIBS elemental profile combined to isotopic information

Nadia Baskali-Bouregaa, Marie-Laure Milliand, Sophie Mauffrey, Elodie Chabert,
Maureen Forrestier, & Nicole Gilon*

Corresponding author : nicole.gilon@univ-lyon1.fr, Institut des Sciences Analytiques, ISA UMR 5280, CNRS, Université Claude Bernard Lyon1

nadia.baskalibouregaa@univ-lyon1.fr: Institut des Sciences Analytiques, ISA UMR 5280, CNRS, Université Claude Bernard Lyon1

marie-laure.milliand@isa-lyon.fr, Institut des Sciences Analytiques, ISA UMR 5280, CNRS, Université Claude Bernard Lyon1

Sophie Mauffrey, Elodie Chabert, Maureen Forrestier former members of Institut des Sciences Analytiques, ISA UMR 5280, CNRS, Université Claude Bernard Lyon1

Abstract

The combined LIBS and ICP HRMS analysis of 13 tea samples are studied in view of identification of tea geographical origin. The elemental signature provided by LIBS spectra is treated by principal component analysis followed by partial least square discriminant analysis and factorial discriminant analysis. Selected element lines are found efficient to discriminate most sample groups. Data analysis model is improved by variable selection and the isotopic ratio $^{11}\text{B}/^{10}\text{B}$ was employed to improve the prediction capacity of the model. The alkaline earth: Ba, Ca, Mg, Sr and alkaline Rb, Na are easily detected by the LIBS system and these elements are important to classify sample according to their geographical origin. Minor elements like P, S, Fe, B ... also bring discriminant information. A five clusters model gave best correct identification in a cross validation test (94.2%). This method also allowed to identify the origin of four unknown teas. In this study the use of FDA or PLS DA after the PCA examination of the LIBS/ICP MS data led to similar conclusions for fast classification of the tea samples and identification of the geographical origin of the four unknown teas.

1. Introduction

Food analysis faces different challenges, one is related to toxic element determination to control human exposure and avoid intoxications. The occurrence of toxic elements may originate from their conditioning the growth procedure as well as from the raw product itself. The determination of toxic elements faces strict regulation and measurement of very low concentrations (below $\mu\text{g}/\text{kg}$) is often required [1].

The second challenge is a commercial one, for an increasing proportion of food products the traceability of food origin is a commercial issue of a great importance, it includes wine, tea, coffee meat, vegetable oils ... [2-8]. The good reputation of a food product is sometime decreased by adulteration or fraud. To prevent the loss of confidence of consumers it is necessary to trace and be able to guarantee the origin of a product. For many products this certification of origin is difficult and requires several methods. The development of proper inspection or monitoring procedures for tracing various food and drink sources is necessary. Increasing interest is towards the use of metals composition and isotopic ratios as primary origin indicators, namely able to trace the direct relationship between soil of origin and food. Tea is one of the main beverages consumed in the world, prepared from water and tea leaves it contains many elements and molecules typically extracted by water from a plant. Element content should reflect the element content of the plant and therefore can be correlated to the local environment (i.e.: rock, soil composition, growing conditions, pollution, use of fertilizers ...) of the plant. According to this process element fingerprint of the tea should also reflect these local conditions [7] and could trace its origin. These observations

have led to the need of developing methods that are simple, sensitive enough and reliable to perform such analyses with also the possibility to be employed online or more reasonably at line.

Methods commonly employed for the investigation of elemental fingerprinting in food and beverages are based on atomic, nuclear and mass spectroscopy techniques, such as Atomic Absorption Spectroscopy (AAS), X-ray Fluorescence Spectrometry (XRF), Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma Optical Emission Spectrometry/Mass Spectrometry (ICP-OES/MS) [9-12]. Although most of these techniques are very sensitive and accurate, they require sample dissolution and consequently time-consuming sample preparation using expensive and toxic reagents.

In recent years, LIBS spectroscopy has become a tool adapted for many analysis currently performed by more classical atomic spectroscopic methods or even X-Ray Fluorescence Spectrometry. Many advantages of the LIBS spectroscopy are quite interesting for food analysis: i.e. it represent a micro destructive analysis, reduced sample preparation and fast analysis [11]. If qualitative analysis is strait forward, quantitative measurements with drastic levels of accuracy is still a challenge. As many analytical techniques dealing with solids, the sample homogeneity and calibration protocols are two main critical points. Selection of the calibration protocol and standards is essential. Matrix matching protocols are often selected [13-14]. But a small difference in the matrix composition may drive to drastic changes in the laser induced plasma properties. As an example, mixing one single reference material with a binder in different ratios produces different temperatures and electronic densities of the created plasma [13]. When quantitative analysis is concerned, this phenomenon has dramatic consequences, i.e. errors caused by the non-matrix match between standards and samples. On the contrary, when sample discrimination is expected differences in plasma formation and excitations processes are expected. One should nevertheless pay attention to differences caused by the sample and those arising from the LIBS instrumentation (i.e. focalization, laser stability ...) [15-18]. In this view the use of dedicated normalization procedures and careful control of instrumentation can be helpful [19].

Characterization of sample geographical origin using trace and major element analysis is also often performed or ICP-OES and ICP-MS and the further use of isotopic information obtained from IRMS or ICP MS offers a complementary discriminant information [20-22]. Among the isotopic tracers boron is an interesting element, consisting of two stable isotopes (^{10}B and ^{11}B) with 19.9 % and 80.1% relative abundances, respectively. Boron is a naturally-occurring element in groundwater, provided by the weathering of rocks, seawater intrusion and precipitation. Its isotopic fractionation is caused by different phenomena evaporation and condensation, boron bio-uptake by plants and animals or sorption into mineral clays. Some anthropogenic sources have different boron concentration: ammonium rich fertilizers with a low B concentration, human wastewater and animal manure with high B concentrations [23].

Most of the published data analysis applied to food analysis has merged data from analytical techniques that provide similar information. In the present study, information from two complementary techniques producing distinct information was evaluated. Particularly, ICP-MS, providing isotopic information, complements the spectral contribution from LIBS. The aim of this work is to study the spectroscopic signatures likely to provide discriminant information in view of tracing the origin of a food product. Tea was selected as it is possible to obtain it from very distinct geographic regions of the world. Principal component analysis, Partial least square discriminant analysis and factorial discriminant analysis were selected to provide an overview of the data collected and evaluate the ability to determine successfully the origin of tea on a large scale.

2. Material and Methods

Tea samples were all commercial, either bought from China, Mongolia or in European supermarket depending on the origin (table 1). Samples were selected as these originates, and were labelled as originating from tea major producing areas. Samples were composed of dried leaves containing small pieces of fruit (lemon and red fruits) or flower (jasmin tea). The leaves were carefully separated from

other pieces before analysis. Samples were analyzed as five different replicates using five different pellets of grinded material in LIBS spectroscopy and five different sample digestion in ICP-HRMS.

Teas were grinded (Retsch S1, Retsch, Germany) and pressed as 13 mm diameter pellets using a hydraulic press (Lightpath Optical, Great Britain): 10 tons applied during 2 minutes. Five different pellets were created for each sample. For the flavoured teas, only the leaves were collected to press the pellets.

For $\delta^{11}\text{B}$ determination, all tea samples were digested using HNO_3 (Merk suprapur) and further diluted in 18 megohm ultra pure water (Elgastat UHQ II system, Elga, Buckinghamshire, Great Britain). The final boron concentration of the analysed sample were adjusted by dilution to 10 $\mu\text{g/L}$. The heating system is a laboratory made electric device allowing to heat samples in a closed quartz vessel to avoid any loss of water or volatile analyte. NIST 951a boron standard reference material (NIST standard purchased from Sigma-Aldrich, Saint Quentin Fallavier, France) was employed for standard bracketing method. It was dissolved in acidic (HNO_3 2%) deionised water. The digestion protocol employed was successfully applied to the NIST 951a 10 $\mu\text{g/L}$ solution with a 99.8% recovery with a 0.8% uncertainty (95% confidence interval, $n=6$).

BCR – 402 White clover standard reference material (standard purchased from Sigma-Aldrich, Saint Quentin Fallavier, France) was employed for LIBS sensitivity check. The clover powder was spiked using solutions containing Ca, B, Ba, Mg, Mn, Ni, Na, P, S, Sr, Rb, Zn (ICP standard solutions, Sigma-Aldrich, Saint Quentin Fallavier, France), freeze-dried and then pelletized. The resulting pellet was employed daily to check LIBS sensitivity. The final concentration of the elements are 100 mg/kg for B, Ba, Mn, Ni, Rb, Sr, Zn and above 500 mg/kg for Al, Ca, Mg, Na, P, S. Iron is already present in the clover powder at 244 mg/kg. This test sample allows verifying the signal measured in tea sample is detectable but does not allow an accurate quantification of element concentrations, which was not the aim of this work.

LIBS

The LIBS system was made of a quantel (Brio, Quantel, France) Nd:YAG laser frequency doubled emitting at 532 nm, the pulse duration was 5ns, and the repetition rate 20 Hz. The laser beam was focalized using first a beam expander followed by mirrors and a focal lens with a 10 cm focal distance. Laser spot is 130 μm , the optimized energy for tea pellets analysis was 25 mJ. The emitted light was collimated to a bundle of fibers (Idil Optics, France) and analysed by 5 ocean optics spectrometer (HR2000+ and Maya from Ocean Optics, Great Britain). Spectra were collected after a 1.5 μs delay and a 10 ms integration time.

Spectra are averaged from 100 shots obtained from rastering the laser beam at the sample surface. The 100 rastered shots are analysed in five replicates using different pellets for each sample. Data analysis was performed using a laboratory made macro from excel. PCA and PLS are calculated from a commercial software (SIMCA Umetric, Sweden) and FDA from XLStat (Addinsoft). All the spectra and line intensity measurements are normalized to total spectrum intensity (measured by integrating the total response from the spectrometer channels [24]). The RSD reduction is significant and drops below 5% for most lines, even when the signal to background ratio was low i.e., close to 1.

To avoid short-term variations all the measurement of the tea pellets were acquired within a few days. The sensitivity check made using the spiked reference material pellet allows comparison of spectra collected from different days. In case of a sensitivity difference the system is re-optimized to keep sensitivity variation acceptable (<5%). This procedure is mandatory to compensate for long time variation of the LIBS system. Even in this case all the samples were re-analysed in order to obtain rigorously comparable spectra.

ICP-HRMS

The boron measurements are performed using a single collector double focusing ICP-HRMS (ELEMENTXR, ThermoFisher, Germany). The optimization of the ICP-HRMS is done according to both the manufacturer instructions and using the procedure developed by Tirez et al. [25] on a similar instrument. The description below summarizes the important points of the procedure.

Samples are analyzed as five different solutions and by bracketing with the NIST SRM 951 standards [25-26]. The average $^{11}\text{B}/^{10}\text{B}$ ratio of NIST SRM 951 measured before and after each sample is used to calculate the delta ^{11}B value of the bracketed sample, which is the recommended routine procedure for isotopic ratio measurement. All measurements are done using counting mode of the detector, and therefore sample containing high boron concentration were diluted. Blank measurements (2% HNO_3 solution) allow verifying the boron level brought by the sample introduction system. ^{11}B reading is kept lower than 8,000 cts. In our study the sample solutions measurements are kept significantly higher than the blank with a minimum ratio of 30, so that the blank was considered negligible.

Boron isotopic ratio measurement may also suffer from mass discrimination due to the large percentage mass difference between ^{11}B and ^{10}B . Correction of this mass discrimination is performed by bracketing samples with SRM NIST 951 boron standard. Furthermore, a similar signal intensity for the SRM NIST 951 boron standard and tea diluted sample was employed. This procedure is commonly employed for $\delta^{11}\text{B}$ calculation. Boron isotope ratios are also calculated from dead time corrected intensities. Due to the four folds difference in natural abundance of B isotopes, a dead time correction in counting mode is necessary to obtain concentration-independent and accurate values of $\delta^{11}\text{B}$. Boron isotopes are measured by an ion counting system requiring a finite time for pulse processing, during this so-called "dead time" the arrival of further ions cannot be registered. The dead time is iteratively deduced from the measurement of the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio in 0.4, 0.6, 0.8 and 1 $\mu\text{g}/\text{L}$ standard solutions according to the manufacturer instructions. The optimized dead time obtained was 10 ns.

The acquisition parameters (table 2) were carefully optimized to obtain an accurate and stable isotopic ratio. Variations obtained between the different solutions prepared from the same tea were in the 0.2-0.5% range. The correction procedures employed allowed avoiding complex chemical separation of the digested tea to obtain accurate $\delta^{11}\text{B}$.

3. Results & discussion

In order to extract the data likely to provide a typical geographical origin fingerprint, principal component analysis is employed for the multivariate statistical modeling of the input data. The search for natural grouping in of both the sample and the variables was one of the major aim of the study so, to allow a better identification of the discriminant information of the different tea samples a PCA was first built from the whole LIBS spectra. This procedure is commonly employed in LIBS or Raman, where the sample's spectrum is not designed to provide elemental or molecular information but to provide a typical signature of the sample. The built PCA brought no sorting (fig.1) possibly due to the very similar spectra combined with variability within the spectra set of a same sample. To obtain 90% of the variance explained by the principal components, 8 components are needed.

An other possibility is to extract the elemental information by selecting data from lines intensities. A second PCA was then built and to improve the capability of the model to classify the samples the molecular information obtained from the LIBS spectra (C2) was also added. This molecular information is one key advantage of LIBS against other classical elemental analysis techniques like, XRF, ICP-OES or ICP-MS. Different lines (2 to 4 according to the occurrence of the lines) for each element were selected and a correlation study allowed to keep only non-interfered lines response for a single element. Figure 2 displays the 3D PCA score plot of the tea samples by using the different normalized line intensities.

The colors have been arbitrarily applied to outline the apparent different clusters. The tea from Mongolia "MON" is clearly distinguished. The green color is a cluster made from two teas from the Jiangsu and Anhui Chinese provinces and the dark green is another Chinese tea from the Hubei region. The light blue is a cluster made from two other Chinese teas from Zhejiang and Fujian provinces. The organically labelled tea (in red) is significantly distinguished from other samples. The grey color group exhibits the strong overlap between samples named: DAR, EARL, FRUIT, JAI and SHAN. These samples exhibits a strong variability within the group. The measurement and especially a lack of surface and depth homogeneity of the tea powder pellet can cause this type of variation;

the grain size may slightly differ from one sample to the other. It can also be related to the data introduced in the PCA model, as the group is made of teas produced in clearly distinct geographical regions: i.e. Sri Lanka, Darjiling province of India and Shandong province of China. In this case, the elemental signature is not discriminant enough.

PCA reveals that 73% of the variance in the dataset can be represented in a 3D space. The cumulated Q2 value for the first three components is 52%. The loadings plot of the PC1, PC2 and PC3 is shown on figure 3. The PC1 includes mainly Al and the alkaline earth elements: Ca, Mg, Sr and Ba.

Loadings of PC1 and 2 are plotted on figure 3, PC1 is represented by major element: Ca, Al, Ba, PC1 is negatively correlated to Rb signal. Alkaline earth (Ca, Sr, Ba ..) and alkaline (Rb, Na) are providing most significant loading values with opposite sign. Minor and trace elements are important in PC2 (i.e. P, S, Mn, Ni) and to a lower extend PC2 is correlated to the C2 intensity. PC3 is negatively correlated to Sr and Mg intensities and positively to C2 and Mn intensity. Alkaline, alkaline-earth and metallic elements are bringing quite distinct information and a minimum of 3 components appears adequate to describe the 25 initial variables.

To improve the model, the boron isotopic ratio was measured. In this view sample were digested according to the procedure described in experimental part. The determination of $^{11}\text{B}/^{10}\text{B}$ was employed using optimized SF ICP MS parameters as reported by Tirez et al [25] on a similar instrument.

Delta ($\delta^{11}\text{B} \text{ ‰}$) values are calculated according to the formula:

$$\delta^{11}\text{B} = 1000 \times \left\{ \frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{ref}}} - 1 \right\} \quad \text{eq 1}$$

The reference value is the isotopic ratio measured from NIST 951a reference material. The confidence intervals are calculated as $\pm 2\sigma$. In the tea samples, the average $\delta^{11}\text{B}$ values varied from -16 to + 15. The variation between two groups is significant (Fig. 4) due to the very low intra sample variability (0.2%) of the isotopic $^{11}\text{B}/^{10}\text{B}$ ratio. Negative deltas are group 1: MON, ZHE, SHAN, DAR and JAI. This includes samples grown in India, China, Sri Lanka and Mongolia. Group 2, with a positive

delta value, contains four Chinese teas POR, FUJ, HUB and BEIJ, and three other teas FRUI, VER, and BIO of unknown geographic origin. It is important to notice that performing multiple analysis of the same tea sample is necessary, a five replicate measurement for one solution is performed and five solutions are prepared independently, as a consequence, the average $\delta^{11}\text{B}$ of a tea sample is calculated from 25 isotopic ratio measurement. The variations in $\delta^{11}\text{B}$ values among the different teas are likely due to different local growing conditions. Boron originates from the soil, the water supply and from an eventual addition of fertilizers. The soils and water supply are typical of a localization. The fertilizers may differ from one country to the other and it has different origins (mineral, organic) and may also not be commonly employed in all the tea growing regions. Distinct values of $\delta^{11}\text{B}$ are reported for fertilizer according to their nature, this can be translated to the boron isotopic composition of the plant.

A new PCA model is then built (Model 2) from the isotopic measurements and the LIBS results. The score scatter plot of the first three components is presented on figure 5. The total explained variance is 70 % using the new three components, with component 1 representing 35% and next PCs 21.5% and 13.5% respectively. As seen from figure 5 the PCA chemometric inspection exhibited 6 different groups according to a minimum of 3 components. The model including isotopic ratio data gave a 0.903 value of R^2 instead of 0.900 when not including $\delta^{11}\text{B}$ for a total of 6 PC, it shows the two models fits well the provided data. The Q^2 value increased with the addition of $\delta^{11}\text{B}$, rising from 0.47 to 0.56, this means a better prediction capacity for the second model. The loadings plot shows the most important variables for sample characterization. According to this second model, the loadings plot was similar to the one obtained previously (Fig.3), the isotopic ratio appeared mainly in the PC2 and PC3 component with a behavior similar to Rb lines.

The PCA score plot (Fig. 5 a-b) exhibited also clusters similar to those proposed by model 1 (Fig. 2). Samples MON and VER were different from all other teas, the ZHE, FUJ, HUB and POR, BEIJ samples appeared as two distinct clusters while the other teas were not distinguished. The three unknown teas (BIO/JAI/FRUI) are clustering with the Darjiling, Ceylon Earl grey and Shandong teas. While

coming from three distinct geographical regions, these last three samples could not be distinguished neither using PC1/PC2 plot nor PC1/PC3 plot.

To further establish the possible determination of geographic origin of the samples based on multispectral fingerprint, model 2 was further selected for PLS discriminant analysis.

Partial Least Square Discriminant Analysis (PLS – DA)

The aim of a supervised pattern recognition is to establish a classification model, a training set with known class memberships is used to create a classifying model. A prediction set, also with known class memberships, that is not employed in the training set is employed to evaluate the model performance. A classification clustering the 13 tea samples into four to seven groups was tested with PLS-DA. Models were built from 3 out of the 5 measurements from each sample as training set and the left 2 values were included in a prediction set. According to the clusters established by PCA N°2, classes were assigned to the tea samples. As seen from figure 5 at least seven groups could be identified.

By changing the 3 samples employed for model and the 2 used unknown the cross validation led to an average of 84.6 % of correct identification. As the overlap between classes is not negligible, 6, 5 and 4 clusters were selected and identified as classes mentioned in table 3. The level of correct identification for the prediction set was improved using a five classes model were only the organic tea and the sample coming from Mongolia were isolated. In this case, a 94.2 % of correct assignment was obtained.

Assuming the samples with unknown origins could originate from one of the identified groups, a similar procedure was applied with the 10 known origin samples, leading, as expected, to a 100 % correct identification (Mod 4b). The tea labelled bio was identified as class 3 (i.e; group including teas from the Anhui and Jiangsu regions of china) while the FRUI and VER samples could belong to group 4 of the model. The group 4 includes teas from Ceylon, Darjiling and Shandong. These three regions are

located quite far one from the others, the classification based on the PCA components could not clearly distinguish these three samples as seen from figure 2 and 5.

Factorial Discriminant Analysis

The Factorial Discriminant Analysis (FDA) does so by maximizing the between-class scatter, while minimizing the within-class scatter at the same time. As the PLS DA procedure, this supervised procedure was applied to known geographical origin teas and the model was also employed to test the unknown samples. FDA plot using only samples with known origin is shown on figure 6 (a,b).

As expected the discriminant analysis is efficient the samples appears as distinct clusters. Tea from Mongolia is well separated, FDA allows also to discriminate tea from the Anhui region (BEIJ). As seen from both fig 6a and 6b, the teas labelled Dar and Ear are still close using the F1 vs F2 and F1 vs F3 projections. Nevertheless using the data provided by LIBS and $\delta^{11}\text{B}$ are not discriminant enough in this case. Looking at the coefficients of the canonical discriminant functions, the signal of Ba, Mg, Rb, S, P and Na obtain highest absolute values in F1, while it is Al, Fe, Mg, Sr and Rb for F2 and Sr, Mn, S, P and Mg for F3. The calculated function based on combination of minor and major element.

Using the previously FDA functions, identification of unknown teas gave good results, samples Jai and Frui were identified as similar to Ear, from Sri Lanka while Ver is identified as coming from the Darjiling region. The Bio tea could be from the Jiangsu Chinese region. These results are in agreement with the PLS DA study previously described, Model 3 (5 clusters) and 4. The FDA allowed a better discrimination between the teas, in this teas from Sri-Lanka (Ear) from Darjeling (Dar).

4. Conclusion

The motivation behind this work was to establish the data necessary to obtain a valuable classification and then to be able to identify an unknown tea, the second motivation was to verify the ability to build classification models especially here, where both strong similarities and high variability within groups are observed.

This study of multispectral analysis combining information from LIBS and ICP HRMS coupled with data analysis by PCA, PLS DA and FDA led to a successful discrimination of the teas samples according to their geographical origin.

The elemental information brought by LIBS brings the most important information together with the molecular C2 measurements. The addition of isotopic information reinforces the classification and the prediction capacity of the PCA model, but it is time consuming and more isotopic ratios could be added.

The spectral LIBS data linked to most important elements provided more significant information than the whole spectra. Furthermore, the PCA analysis allowed to understand what elements were important to distinguish between geographical origins major alkaline earth and alkaline elements are essential for this.

This method allowed identifying the origin of four unknown teas. In this study the use of FDA or PLS DA after the PCA examination of the LIBS/ICP MS data led to similar conclusions for fast classification of the tea samples. On a practical point of view by improving the data obtained by LIBS, improving sensitivity to detect more elements, a complete classification should be obtained using only one instrument. Even if the ICP HRMS is a reliable and accurate tool, it requires a digestion of the tea and further dilution to obtain accurate isotopic ratio, which is far more time consuming than LIBS measurements.

References

- [1] F. S. Evangelista, L. Tormen, T. D. SaintPierre , AJ. Curtius, SS. deSouza, F. Barbosa, The use of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples, *Food Chemistry* 112 (3) (2009) 727-732.
- [2] Y. Tian, C. Yan, T. Zhang, N. Gilon, J. Yu, Classification of wines according to their production regions with the contained trace elements using laser-induced breakdown spectroscopy, *Spectrochimica Acta B* 135 (2017) 91-101.
- [3] L. Lei, W. Bo, Z. Xiaolei, Z. Yue, D. Yu, S. Xiangfei, R. Shuang, W. Yuhua, F. Wanping, Z. Xujun, Geographical origin traceability of tea based on multi-element spatial distribution and the relationship with soil in district scale, *Food Control* 90 (2018) 18-28.
- [4] C. Assis, H. Vinicius Pereira, V. Silva Amador, R. A. L Soares de Oliveira, R. M. Martins Sena, Combining mid infrared spectroscopy and paper spray mass spectrometry in a data fusion model to predict the composition of coffee blends, *Food Chemistry* 281 (2019) 71–77.
- [5] J. O. Caceres, S. Moncayo, J. D. Rosales, F. J. M.de Villena, F. C. Alvira, G. M. Bilmes, Application of Laser-Induced Breakdown Spectroscopy (LIBS) and Neural Networks to Olive Oils Analysis, *Applied Spectroscopy* 67 (9) (2013) 1064-1072.
- [6] C. T. Chang, C.-F. You, S. K. Aggarwal, C. H. Chung, H. C. Chao, H. C. Liu, Boron and strontium isotope ratios and major/trace elements concentrations in tea leaves at four major tea growing gardens in Taiwan, *Environmental Geochemistry and Health* 38(3) (2015) 737–748.
- [7] S. Moncayo, J. D. Rosales, R. Izquierdo-Hornillos, J. Anzano, J. O. Caceres, Classification of red wine based on its protected designation of origin (PDO) using Laser-induced Breakdown Spectroscopy (LIBS), *Talanta* 158 (2016) 185-191.
- [8] M. Necemerc, B. Budicd, S. Lojena, A. M. Opatica, Stable isotope analysis of major bioelements, multi-element profiling, and discriminant analysis for geographical origins of organically grown potato, *Journal of Food Composition and Analysis* 71 (2018) 17–24.

- [9] B. Sezer, G. Bilge, I. Hakki-Boyaci, Capabilities and limitations of LIBS in food analysis, *Trends in Analytical Chemistry*, 97 (2017) 345 – 353
- [10] S. Waheed, S. Rahman, S. M. Husnain, N. Siddique, Hazardous and other element characterization of new and used domestic plastic food containers using INAA and AAS, *Journal of Radioanalytical and Nuclear Chemistry*, 292(3) (2011) 937–945.
- [11] K. Gopia, D. Mazumderb, J. Sammuta, N. Saintilanc, J. Crawford, P. Gadd, Combined use of stable isotope analysis and elemental profiling to determine provenance of black tiger prawns (*Penaeus monodon*), *Food Control* 95 (2019) 242–248.
- [12] M. Chudzinska, D. Baralkiewicz, Application of ICP-MS method of determination of 15 elements in honey with chemometric approach for the verification of their authenticity, *Food and Chemical Toxicology* 49 (2011). 2741–2749.
- [13] N. Gilon, J. El-Haddad, A. Stankova, W. Lei, Q. Ma, V. Motto-Ros, J. Yu, J. A matrix effect and accuracy evaluation for the determination of elements in milk powder LIBS and laser ablation/ICP-OES spectrometry, *Analytical and Bioanalytical Chemistry* 401 (9) (2011) 2681-2689.
- [14] D. W. Hahn, N. Omenetto, N. Laser-Induced Breakdown Spectroscopy (LIBS), Part II: Review of Instrumental and Methodological Approaches to Material Analysis and Applications to Different Fields, *Spectrochimica Acta B* 66 (4) (2012) 347-419.
- [15] M. El Rakwe, D. N. Rutledge, G. Moutiers, J-B. Sirven, Analysis of time-resolved laser-induced breakdown spectra by mean field-independent components analysis (MFICA) and multivariate curve resolution-alternating least squares (MCR-ALS), *Journal of Chemometrics* 31 (2) (2017) 1-10.
- [16] M. A. Sperança, D. Fernandes, J. P. Andrade, E. Castro, R. Pereira-Filho, Univariate and multivariate calibration strategies in combination with laser-induced breakdown spectroscopy (LIBS) to determine Ti on sunscreen: A different sample preparation procedure, *Optics and Laser Technology*, 109 (2019) 648–653.

- [17]E. Vors, K. Tchepidjian, J-B. Sirven, Evaluation and optimization of the robustness of a multivariate analysis methodology for identification of alloys by laser induced breakdown spectroscopy. *Spectrochimica Acta B* 117 (2016) 16-22.
- [18]D. Diaz, A. Molina, D. Hahn, Effect of laser irradiance and wavelength on the analysis of gold- and silver-bearing minerals with laser-induced breakdown spectroscopy, *Spectrochimica Acta B* 145 (2018) 86-95.
- [19]V. Lazic, A. De Ninno, Calibration approach for extremely variable laser induced plasmas and a strategy to reduce the matrix effect in general, *Spectrochimica Acta B*, 137 (2017) 28-38.
- [20]A. L. Souza, S. Guimaraes Lemos, J. Naozuka, P. R. Miranda Correia, P. V. Oliveira, Exploring the emission intensities of ICP OES aided by chemometrics in the geographical discrimination of mineral waters, *Journal of Analytical Atomic Spectrometry* 26 (2011) 852-860.
- [21]E. P. Pérez-Álvarez, R. Garciab, P. Barrulasd, C. Diasd, M. J. Cabrita, T. Garde-Cerdána, Classification of wines according to several factors by ICP-MS multi-element analysis, *Food Chemistry* 270 (1) (2019) 273-280.
- [22]K. Heaton, S. D. Kelly, J. Hoogewerff, M. Woolfe, Verifying the geographical origin of beef: The application of multi-element isotope and trace element analysis, *Food Chemistry* 107 (2008) 506–515.
- [23]S. Barth, Boron isotope variations in nature: a synthesis, *Geological Rundsch*, 82 (1993) 640-651.
- [24]D. Body, B. L. Chadwick, Optimization of the spectral data processing in a LIBS simultaneous elemental analysis system, *Spectrochimica Acta B* 56 (6) (2001) 725-736.
- [25]K. Tirez, W. Brusten, D. Widory, E. Petelet, A. Bregnot, D. M. Xue, P. Boeckx, J. Bronders, Boron isotope ratio ($\delta B-11$) measurements in Water Framework Directive monitoring programs: comparison between double focusing sector field ICP and thermal ionization mass spectrometry, *Journal of Analytical Atomic Spectrometry* 25 (7) (2010) 964-974.

[26]M. Rosner, W. Pritzkow, J. Vogl, S. Voerkelius, Development and Validation of a Method to Determine the Boron Isotopic Composition of Crop Plants, *Analytical Chemistry* 83(7) (2011) 2562–2566.

Table 1

Description of tea samples with the label employed in text and their geographical origin.

Tea		Provenance
MON	Black tea	Mongolia
ZHE	Green tea	Zhejiang/China
POR	Jasmin flavored green tea	Jiangsu/China
SHAN	Black tea	Shandong/China
HUB	Green tea	Hubei/China
FUJ	Green tea	Fujian/China
BEIJ	Green Jasmin flavored tea	Anhui/China
EARL	Earl Grey Black tea	Ceylon/Sri Lanka
DAR	Black tea	Darjiling/India
VER	Lemon flavored green tea	<i>unknown origin</i>
JAI	Black tea	<i>unknown origin</i>
BIO	Green tea	<i>unknown origin</i>
FRUI	Berries flavored black tea	<i>unknown origin</i>

Table 2

Plasma and analyzer settings optimized for ICP HRMS measurements.

Plasma Parameters	
Power (W)	1200
Nebulizer gas flow rate (L/min)	1.2
Solution flow rate (μ L/min)	200
Nebulizer/ spray chamber	Micromist/helix twinabar
Oxide level % UO/U	6
Analyzer settings	
Resolving power ($R=m/\Delta m$)	300
Acquisition mode	E-scan
Number of passes	500
Number of runs	5
Sample time (s)	20 ms for ^{10}B and ^{11}B

Table 3

Elements and wavelengths employed for LIBS spectra analysis.

Element/Molecular band	Selected wavelength
Al	I 308.215 nm ; I 309.271 nm
Ca	I 422.673 nm; II 315.887 nm; II 317.933
B	I 208,957 nm; I 249.700 nm
Ba	II 455.403; II 493.408
C2	<i>molecular</i> 516.672 nm
Fe	I 259.900 nm
Mg	I 518.360 nm; II 279.553 nm
Mn	I 403.075 nm; I 257.611 nm
Ni	I 231.500 nm
Na	I 588.995 nm
P	I 253.561; I 255.326
S	I 921.286 nm
Sr	I 407.672 nm; I 421.552 nm
Rb	I 607.075; I 780.026 nm
Zn	I 334.502 nm; I 481.053 nm

Table 4

PLS DA correct class prediction using 4 to 7 cluster models.

	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6	Class 7	Correct Class prediction (%)
Model 1: 7 clusters	Mon	Ver	Hub	Bio	Fuj, Zhe	Por, Beij	Dar, Ear, Frui, Shan, Jai	84.6
Model 2: 6 clusters	Mon	Hub	Bio	Fuj, Zhe	Por, Beij	Dar, Ear, Frui, Ver, Shan, Jai		92.3
Model 3a: 5 clusters	Mon	Hub	Fuj, Zhe	Bio, Por, Beij	Dar, Ear, Frui, Ver, Shan, Jai			86.5
Model 3b: 5 clusters	Mon	Bio	Fuj, Zhe, Hub	Por, Beij	Dar, Ear, Frui, Ver, Shan, Jai			94.2
Model 4a: 4 clusters	Mon	Fuj, Zhe, Hub	Bio, Por, Beij	Dar, Ear, Frui, Ver, Shan, Jai				90.5
Model 4b: 4 clusters	Mon	Fuj, Zhe, Hub	Por, Beij	Dar, Ear, Shan, Jai				100 %

Caption of figures

Figure 1. 3D PCA score scatter plot of the 13 tea samples using whole spectra.

Figure 2. 3D PCA score scatter plot of the 13 tea samples using selected lines intensities (table 3). Colors are selected according to apparent clusters.

Figure 3. PCA Loading plot for component PC1 and PC2.

Figure 4. Delta 11B values measured for the 13 sample. Each point represents the average of five measurements.

Figure 5. 2D Score scatter plots of the PCA combining Delta 11B and LIBS line intensity measurements. (a) PC1 and PC2. (b) PC1 and PC3.

Figure 6. Factorial discriminant analysis of the 10 tea samples with known geographical origin.

















