

Use of Laser Ablation–Inductively Coupled Plasma–Time of Flight–Mass Spectrometry To Identify the Elemental Composition of Vanilla and Determine the Geographic Origin by Discriminant Function Analysis

Ellen M. Hondrogiannis,* Erin Ehrlinger, Alyssa Poplaski, and Meredith Lisle

Masters of Science Forensic Science Program, Department of Chemistry, Towson University, 8000 York Road, Towson, Maryland 21252, United States

ABSTRACT: A total of 11 elements found in 25 vanilla samples from Uganda, Madagascar, Indonesia, and Papua New Guinea were measured by laser ablation–inductively coupled plasma–time-of-flight–mass spectrometry (LA–ICP–TOF–MS) for the purpose of collecting data that could be used to discriminate among the origins. Pellets were prepared of the samples, and elemental concentrations were obtained on the basis of external calibration curves created using five National Institute of Standards and Technology (NIST) standards and one Chinese standard with ^{13}C internal standardization. These curves were validated using NIST 1573a (tomato leaves) as a check standard. Discriminant analysis was used to successfully classify the vanilla samples by their origin. Our method illustrates the feasibility of using LA–ICP–TOF–MS with an external calibration curve for high-throughput screening of spice screening analysis.

KEYWORDS: *Vanilla, geographical origin, discriminant function analysis, LA–ICP–TOF–MS*

■ INTRODUCTION

Historically, an individual's food consumption was determined according to the local natural resources available and their cultural traditions. Because of a number of advancements in food production and transportation technology, most foods are no longer specific to a particular geographic region. Vast consumer demands encourage retailers to supply their products to people all over the world. With consumer demand comes the necessity to abide by costly food and import laws that may lead to retailers misidentifying or misformulating their products in an effort to extend their profits. In 2011, the United States passed the Food Safety Modernization Act in an effort to expand the Food and Drug Administration's authority on food crisis response and food control establishment.¹ It includes strict preventative measures on "high-risk" foods and their suppliers and stipulations that companies set up ingredient testing and traceability, which allows external laboratories to examine a product before it is accepted on the market. Being able to track a food product to its geographical origin is crucial in instances where the origination of a food product or specific ingredient must be identified. In addition, analyzing ingredients can also reveal the adulteration of products containing synthetic compounds when they claim to be authentic.

Vanilla is the bean of a tropical orchid plant and is the world's third most expensive spice after saffron and cardamom.² Because of its value, the possibility exists that a particular vendor may try to substitute a vanilla of a lower quality for one that is of higher quality (and therefore higher price). For example, the average price the U.S. paid in March 2012 for vanilla from India was \$35.00, while the U.S. paid only \$17.00 for vanilla from Indonesia (http://www.vanillabean.com/cvi_imp_exp_update_january_2009.pdf). Recently, our lab reported on the use of wavelength-dispersive X-ray fluorescence

(WDXRF) and discriminant function analysis (DFA) in the discrimination of vanilla by origin and species.³ We were successful at generating a model by which a vanilla sample could be attributed back to Uganda, Madagascar, Indonesia, India, or Papua New Guinea. The only other report in the literature that has been successful at this is that by Sharp and others, who used Fourier transform infrared–attenuated total reflectance (FTIR–ATR) and selected ion flow tube–mass spectrometry (SIFT–MS) with soft independent modeling of class analogy (SIMCA) to cluster the vanilla extracts from the same origins and species but with less separation of three of the five clustered origins.^{3,4} We further noted that our method required less sample preparation and was non-destructive. Nonetheless, it would still be desirable to establish a technique that is capable of acquiring data even faster than WDXRF while maintaining sample integrity. Our focus in this study is therefore on the use of laser ablation–inductively coupled plasma–time-of-flight–mass spectrometry (LA–ICP–TOF–MS) for the differentiation of vanilla samples from the same origins and species.

The use of ICP–MS techniques in the determination of geographic origin of food is well-documented in reviews involving analytical techniques used to determine geographic origin of food and beverages.^{5,6} More recent work includes provenance determination of coffee, wheat, and Chinese cabbages.^{7–10}

Recently, Husáková et al. showed that ICP–TOF–MS with external calibration is capable of quantitating elemental

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concentrations in foods. They used dairy, meat, and cereal samples with certified concentrations and showed that there was no significant difference between the results obtained from ICP–TOF–MS and the certified values.¹¹ There are, however, no reports on LA with ICP–TOF–MS for use in measuring elemental concentrations in food. Laser ablation introduction in combination with ICP–TOF–MS further offers the advantage of the ability to measure transient signals. An overview of additional advantages and disadvantages of LA sample introduction has most recently been presented by Orellana et al.¹² The disadvantages briefly include the necessity for optimization of the laser parameters based on the matrix and correction for signal drift and fractionation if quantitation is desired. Correction for the above, however, is difficult because of the lack of matrix-matched calibration standards, internal standards, and reference materials. Orellana et al. further offer a review of the applications of LA–ICP–MS in chemical analysis of forensic evidence, in which they also present different strategies that have been applied for the quantitative analysis of glass samples, paints, and other forensic evidence.¹² Chen and others offer strategies for quantitative analysis of major and trace elements in carbonate samples, while Narukawa and Willie offer a technique for the evaluation of dried deposits of biological tissues.^{13,14}

Currently, there are no reports in the literature for the use of LA–ICP–TOF–MS for food attribution. The goal of our work was to determine if the accuracy and relative standard deviations (RSDs) obtained using one set of laser ablation parameters for the ablation of both National Institute of Standards and Technology (NIST) standards, to generate an external calibration curve, and for the vanilla samples, with ¹³C internal standard correction, are sufficient to measure elemental data found in vanilla from four different geographic origins (Madagascar, Uganda, Indonesia, and Papua New Guinea) and use them to generate a model with the purpose of classifying unknown vanilla samples from the same origins.

MATERIALS AND METHODS

Vanilla Samples. Ground and previously cured vanilla samples were received as gifts from McCormick and Company, Inc. and had been secured through McCormick's routine commercial route from their representatives for each of the countries. The cured beans are initially ground in a Wiley 4 mill with a knife blade. The coarse material is then frozen in a container immersed in solid carbon dioxide, and 50 g are further ground in a chilled (15 °C) IKA M20 mill using a M21 cutter until it is able to pass a –20 Tyler sieve. The filtrate is immediately placed in a plastic jar with a lid until use. The typical moisture content of the ground beans is 8–25% moisture. The total number of samples from each origin included the *Vanilla planifolia* species: seven from Madagascar (from the years 2003–2008), five from Uganda (from the years 2003–2011), nine from Indonesia (from the years 2003–2011), and four of the *Vanilla tahitensis* species from Papua New Guinea (from the years 2009–2011). The number of vanilla types from each origin were unequal because they were provided on the basis of the availability from the McCormick Technical Innovation Center reserves.

Certified Reference Samples. Certified reference standards from NIST (Gaithersburg, MD) were used to generate external calibration curves to quantify the elements in the vanilla samples. The following standards were used: NIST 1549 (non-fat milk powder), NIST 1575a (pine needles), NIST 1515 (apple leaves), NIST 1547 (peach leaves), NIST 1570a (spinach leaves), and the Chinese standard GSB-30 (green tea). The NIST 1573a (tomato leaves) standard was used in this study as a validation check to confirm that our instrumentation

and calibration curves could obtain reliable results concurrent with reported NIST concentrations.

Sample Preparation. All vanilla samples and NIST standards were pressed into pellets in our lab using a SPEX 3630 X-Press and a 3614 40 mm evacuable die set. The die components were cleaned using 80% ethanol prior to the addition of the sample. Thin-walled aluminum cups (Spec-caps) were added for extra stability and to facilitate the labeling and handling of the samples once pressed. A total of 3.0 ± 0.1 g of each vanilla sample was weighed and poured into the bore of the die. The samples were pressed and held for 3 min at 25 tons of pressure. Each vanilla sample and a duplicate were pressed into pellets, resulting in two pellets of the same exact sample.

Elemental Analysis Using LA–ICP–TOF–MS. Analysis of all NIST standards and vanilla samples was carried out using a GBC OptiMass 9500 ICP–TOF–MS (GBC Scientific, Australia) equipped with a GeoMed cryocell set at –15 °C and a Cetac LSX-213 LA system. The OptiMass 9500 is described in ref 15.

LA–ICP–TOF–MS Method Development. Initial method development was carried out on NIST standard reference material (SRM) 1573a to optimize laser and integration parameters. This involved varying the spot size (up to 200 μm to retain the advantage of “small” sample size), number of spots, laser power, burst counts, and integration parameters until the RSD for the element of interest (Mn) was <10%. The final combination of integration and laser parameters that yielded the lowest RSD was with a 20 Hz laser shot frequency (10 s shutter delay) at 700 bursts over five 200 μm spots and to integrate the second, third, fourth, and fifth spots over four 4 s integrations. The average of this was taken, and the gas blank, which was acquired during a 4 s period prior to ablation, was subtracted. A total of 800 spectra were recorded during the 260 s acquisition time. The total counts resulting from this integration were normalized to ¹³C to correct for signal drifts and mass bias between samples. The rest of the operating parameters are given in Table 1.

Table 1. LA–ICP–TOF–MS Operating Parameters

ICP Source	
power (W)	900
plasma gas flow rate (L/min)	10
auxiliary gas flow rate (L/min)	0.500
nebulizer gas flow rate (L/min)	0.804
Mass Spectrometer (MS) Ion Optics	
skimmer (V)	–1350
extraction (V)	–1375
Z1 (V)	–975
Y mean (V)	–575
Y deflection (V)	0
Z lens mean (V)	–1200
Z lens deflection (V)	15
lens body (V)	–170
Pulse Shaping	
fill (V)	–30
fill bias (V)	–1.00
fill grid (V)	–20.0
pushout plate (V)	670
pushout grid (V)	–490
reflectron (V)	650

Calibration Curves. External calibration curves were generated from the following NIST standards: SRMs 1515 (apple leaves), 1549 (non-fat milk powder), 1547 (peach leaves), 1575a (pine needles), and 1570a (spinach leaves) and from the Chinese standard GSB-30 (green tea) for isotopes ²⁵Mg, ³¹P, ⁴⁴Ca, ⁵⁵Mn, ⁵⁷Fe, ⁶³Cu, ⁶⁴Zn, ⁷⁹Br, ⁸⁵Rb, ⁸⁶Sr, and ¹³⁸Ba. These SRMs were selected in an effort to match the matrix and ablation characteristics of the vanilla samples. Table 2 lists the calibration ranges for the NIST standards. [Our selection of the above isotopes measured in the vanilla was based on the elements

Table 2. Calibration Range for NIST Standards

element	calibration range (ppm)	<i>n</i>	equation	<i>R</i> ²
Mg	1100–9000	6	$y = 0.0006x - 0.2519$	0.9970
P	1100–10600	6	$y = 0.0007x + 0.3791$	0.9994
Ca	12100–15600	4	$y = 0.0001x - 0.1092$	0.9842
Mn	0.26–488	5	$y = 0.0021x + 0.035$	0.9960
Fe	1.78–218	4	$y = 0.00005x - 0.0001$	0.9887
Cu	0.2–12.2	5	$y = 0.0011x - 0.0004$	0.9947
Zn	12.5–82	5	$y = 0.0004x - 0.0006$	0.9982
Rb	10.2–89	6	$y = 0.0025x - 0.0003$	0.9971
Sr	25–56	3	$y = 0.0004x + 0.01$	0.9249
Ba	6–124	4	$y = 0.0024x - 0.0123$	0.9967

that showed a recovery of $> \pm 25\%$ compared to the tomato NIST standard; we were further limited by mass regions that were masked out on the detector to avoid saturation from more abundant gases (m/z 10–12, 14–16, and 37–43)].

Statistical Analysis. The software package Statgraphics Centurion, version 16 (StatPoint Technologies, Inc., Warranton, VA), was used for the generation of all DFA plots and analysis of variance (ANOVA) data. The objective of DFA is to generate mathematical models that consist of the linear combination of the weighted elemental variables (in our case, elemental concentrations) with the goal of maximizing the between group origin clusters while minimizing the within group clustering. We chose a forward fit method of analysis in which the statistical program sets criteria used to decide which variables should be included in the model, which includes maximizing the *F*-to-fit value while maintaining a small Wilkes' λ .

Validation of the LA–TOF–MS Method. The validity of the calibration curve was checked using NIST 1573a (tomato leaves). The accuracy was determined by comparing the measured concentrations of the tomato leaves to the NIST-certified values, while the precision was determined by analyzing the tomato leaves 6 times over a 2 month period. Generally good recovery (83.1–106.3%, with the exception of Zn and Mn, with recoveries of 76.1 and 120.9%, respectively), was achieved for all elements. RSDs ($n = 6$, over 6 months) for NIST 1573a were between 6.2 and 14.3% for all elements. The results are summarized in Table 3.

RESULTS AND DISCUSSION

Analytical Results. The elemental concentrations from a total of 25 vanilla samples were measured using LA–ICP–TOF–MS. The mean elemental concentrations calculated for each origin are listed in Table 4. The relative ordering of the elements present from highest to lowest concentration is Ca, Mg, P, Fe, Zn, Mn, Sr, Br, Rb, Ba, and Cu. An ANOVA test revealed Madagascar has the largest number of elements with

concentrations that are statistically different from the other origins. These elements analyzed are unique to each country of origin and can be viewed as an elemental fingerprint for vanilla from that country. Table 5 shows that the ordering of the concentrations measured with LA–ICP–TOF–MS is similar to the values measured by both WDXRF³ and ICP–MS.³ There are differences in the absolute concentrations, and these are discussed later.

DFA. The vanilla samples were separated into test samples ($n = 42$; 21 in duplicate) and validation samples ($n = 8$; 4 in duplicate, which represents 1 from each origin). The test samples were used to create the model. Of the 11 variables analyzed (Mg, P, Ca, Mn, Fe, Cu, Zn, Br, Rb, Sr, and Ba) only 6 of the variables (Mg, P, Cu, Zn, Rb, and Ba) were retained and needed for the model, which consisted of four discriminant functions (DFs).

The DFs created by the model using the 6 elemental variables can be described as

$$DF_1 = 0.197389Mg - 0.309673P + 2.17782Cu \\ - 0.516024Zn - 1.37343Rb - 0.371644Ba$$

$$DF_2 = -0.725068Mg - 0.943329P + 0.30098Cu \\ - 1.308Zn + 1.4169Rb + 1.3834Ba$$

$$DF_3 = -2.24476Mg + 0.562915P + 0.233132Cu \\ + 0.485008Zn + 1.0276Rb + 0.628218Ba$$

$$DF_4 = 0.597139Mg - 1.04888P + 0.138072Cu \\ + 0.817209Zn - 0.621257Rb + 0.62695Ba$$

DF₁ describes the variability of 68.1% of the data; DF₂ describes an additional 27.69% of the data; DF₃ describes an additional 2.37% of the data; and DF₄ describes the remaining 1.84% of the data. The resulting three-dimensional (3D) plot is shown in Figure 1. The classification model showed 100% classification of the origins, to include the two species, while the eight samples that were left out of the model were further correctly classified.

LA–ICP–TOF–MS with one set of LA parameters, external calibration, and ¹³C normalization was used successfully to acquire elemental data that generated a model by which unknown vanilla samples from Madagascar, Uganda, Indonesia, and Papua New Guinea were clustered, resulting in 100% classification of all origins.

Table 3. Accuracy Measured Using NIST 1573a (Tomato Leaves) in ppm by LA–ICP–TOF–MS

element	determined by LA–ICP–TOF–MS	certified value $\pm U^a$	recovery (%)
Mg	99800 \pm 432	12000	83.1
P	2300 \pm 226	2160 \pm 40	106.2
Ca	53670 \pm 1420	50500 \pm 90	106.3
Mn	297 \pm 21	246 \pm 8	120.9
Fe	356 \pm 22	368 \pm 7	96.8
Cu	4.41 \pm 1.7	4.7 \pm 0.14	93.8
Zn	23.5 \pm 6.0	30.9 \pm 0.7	76.1
Br	1265 \pm 666	1300 ^b	97.3
Rb	13.0 \pm 7.2	14.9 \pm 0.27	87.8
Sr	87.0 \pm 10.4	85 ^b	102.4
Ba	59.5 \pm 7.8	63 ^b	94.5

^aUncertainty. ^bDetermined but not certified by NIST.

Table 4. Mean [\pm Standard Deviation (SD)] Elemental Concentrations by Country (ppm)^a

	Uganda		Madagascar		Indonesia		Papa New Guinea	
	mean	SD	mean	SD	mean	SD	mean	SD
Mg	1200 a	222	2060 b	222	1230 a	444	1170 a	279
P	1490 a	335	1380 a	335	1450 a	267	1120 b	111
Ca	3161 a	627	4900 b	627	3610 a	1890	2860 a	923
Mn	22.5 a	20	54.5 b	19.5	15.2 a	20.5	0 c ^b	3.65
Fe	38.3 a,b	13	58.9 b	13.3	25.3 a	13.1	42.5 a,b	25.8
Cu	1.79 a	0.32	3.64 b	0.32	2.87 a	1.73	3.25 a,b	1.31
Zn	26.3 a	8.24	15.6 b	8.24	12.7 b	7.48	10.4 b	3.83
Br	7.64 a	3.06	1520 b	3.06	462 a	986	227 a	627
Rb	6.74 a	3.14	33.6 b	3.14	12.6 a	7.65	5.51 a	3.14
Sr	22.0 a	6.58	35.0 b	6.58	26.0 a	16.9	14.8 a	4.95
Ba	17.1 a	7.89	32.5 b	7.89	18.9 a	10.9	7.72 c	1.38

^aMeans identified with different letters indicate least significant difference (LSD) at the 95% level. ^bBelow the limit of detection (LOD) of 0.035 ppm

Table 5. Comparison of LA-ICP-TOF-MS Results to Those Obtained Using WDXRF³ and ICP-MS³

element	Indonesia			Uganda			Madagascar		
	WDXRF (n = 2)	ICP-MS (n = 3)	LA-ICP-TOF (n = 2)	WDXRF (n = 2)	ICP-MS (n = 3)	LA-ICP-TOF (n = 2)	WDXRF (n = 2)	ICP-MS (n = 3)	LA-ICP-TOF (n = 2)
Mg	1660 \pm 43.0	2170 \pm 10.3	2070 \pm 160	2410 \pm 45.0	2420 \pm 94.2	1601 \pm 152	1560 \pm 66.5	1990 \pm 5.1	1530 \pm 670
Ba	39 \pm 1.3	39 \pm 0.01	36 \pm 2.5	89 \pm 2.2	74 \pm 0.3	31 \pm 8.5	72 \pm 2.4	53 \pm 0.4	28 \pm 14.3
Cu	6.3 \pm 0.5	6.8 \pm 0.003	5.8 \pm 1.4	3.2 \pm 0	3.9 \pm 0.05	2.1 \pm 0.4	5.1 \pm 1.2	3 \pm 0.02	2.1 \pm 1.3
Rb	49 \pm 0	40 \pm 0.3	26 \pm 7.9	11 \pm 0.5	12 \pm 0.2	3.8 \pm 1.2	94 \pm 7.3	73 \pm 0.3	30 \pm 18
Zn	16 \pm 0.5	21 \pm 0.004	25 \pm 5.8	70 \pm 1.5	52 \pm 0.5	25 \pm 6.7	12 \pm 0.5	14 \pm 0.01	12 \pm 8.0

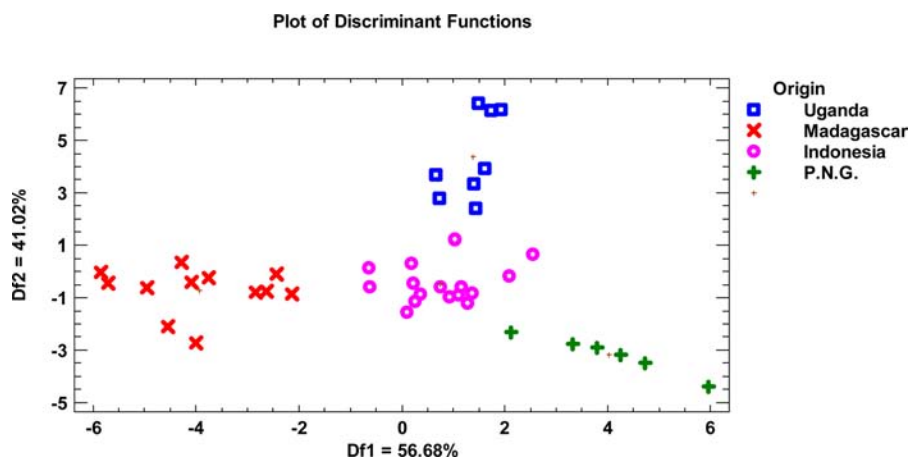


Figure 1. DFA plot.

Analysis of Table 5 however, reveals, disagreement with the concentrations obtained on the vanilla samples when comparing LA-ICP-TOF-MS, WDXRF, and ICP-MS. Calibration standards for LA-ICP-TOF-MS were selected on the basis of availability of standards with certified values for the analytes of interest and of a similar type of sample matrix. The data, acquired by WDXRF in Table 5, was also acquired using an external calibration curve using the NIST standards milk powder, apple leaves, peach leaves, and pine leaves for the same reasons. Both methods demonstrate excellent recoveries when analyzing a NIST SRM check standard, indicating confidence in the methods used (recoveries for the tomato leaves 1573a in our WDXRF work were between 94.8 and 103.2% of the NIST-certified values for all elements, with the exception of Cu and Ba³). The deviation in the measured concentrations for the vanilla samples across analytical methods

may be attributed to a number of issues, including the need for more closely matrix-matched standards for quantification in LA-ICP-TOF-MS over that of WDXRF. In addition, while relatively low RSDs were obtained with the tomato NIST standard, the average RSDs for the elements measured in the vanilla samples and used in the DFA was 36.7%. These RSDs, in addition to the limited concentration ranges for the elements in the standards, likely contribute to the deviation in the measured concentrations for vanilla samples by LA-ICP-TOF-MS compared to WDXRF and ICP-MS.

In addition to the influence of non-matrix-matched standards, internal standards, and reference materials is the dependence of the method upon optimization of laser parameters for the matrix and the isotope measured. We optimized the ablation parameters using only one isotope and employed an external calibration curve. It is expected that our

results would not be as accurate as those obtained with ICP–MS, where the calibration standards and samples are dissolved in the same matrix and the instrument is tuned using more isotopes, while solution introduction into the ICP results in less fractionation than introduction of solid material ablated by the laser. In terms of comparison to WDXRF, while the same external calibration standards were used for both techniques, fractionation is not a problem with WDXRF.

Despite the challenges associated with quantifying LA–ICP–TOF–MS results, the goal of this work was not to optimize the instrumental parameters needed for accurate quantitation of each isotope but instead to develop a set of parameters that would allow for the rapid collection of data that is sufficient to discriminate among the origins. We have illustrated that the LA–ICP–TOF–MS technique is beneficial because of the time advantage in acquiring more data on a smaller sample size. The sample preparation described in the Materials and Methods section is the same as that used for our WDXRF work (with the exception that we used only 3 g of vanilla to make the pellets in this study, whereas we needed 5 g for the WDXRF work). Ablation requires only a very minute amount of sample (in our case, we ablated five spots at depths of 200 μm each), and this is an advantage over WDXRF. Another advantage is that, with LA–ICP–TOF–MS, a complete mass spectrum, including isotopic information, is acquired within a few minutes, whereas instrument collection with WDXRF takes at least 12 min per sample (depending upon the number of elements analyzed). A shorter analysis time could lead to a faster turnaround time in the screening of spice at Customs or at the point of vendor validation. In the WDXRF results, 11 elements were used, while in the case of the TOF–ICP–MS results, we were able to differentiate with only 5 elements. It is possible that our run time/data analysis can be minimized even further by the use of isotope ratios. It is noted, however, that, with the LA–TOF–ICP–MS results, the within-group spread is larger and the between-group clustering of origins is smaller than for the WDXRF results. We discussed possibilities for the within-groups spread previously.³ We further attribute even larger within-group spreads and the smaller between-group separations here to the higher RSDs obtained with LA–ICP–TOF–MS. In comparison to results obtained using FTIR–ATR and SIFT–selected ion monitoring (SIM) with SIMCA, we note that our results show greater between-group separations for Uganda and Madagascar with less separation between the two species Indonesia (*V. planifolia*) and Papua New Guinea (*V. tahitensis*) than that obtained by FTIR–ATR and SIFT–SIM.⁴ Our separation is still sufficient, however, for 100% classification of the two species, and our technique does not require the use of extracts. While Husakova et al.¹¹ showed that ICP–TOF–MS with external calibration is capable of collecting accurate and precise elemental concentrations in foods and beverages with potential for assessing nutritional composition and identifying food contamination and potentially toxic elements, we have illustrated the capability of adding LA to ICP–TOF–MS using one set of ablation parameters, ¹³C normalization, and external calibration to obtain elemental data that can be used for origin provenance. The primary advantage is that of a non-destructive sample introduction, which is critical in the case of sample integrity and, in particular, for potential forensic data analysis. One advantage of WDXRF over TOF–ICP–MS, however, is that portable XRF instruments are available, whereas this is not the case with TOF–ICP–MS.

The feasibility of using LA–ICP–TOF–MS to measure the elemental data of 25 vanilla samples from four different geographical origins (including two species) and origin differentiation using DFA was illustrated. The model showed 100% classification and was successful in correctly classifying the country of origin of four unknowns. These results support the potential for using LA–ICP–TOF–MS and DFA in the determination of the geographic origin of vanilla from Madagascar, Uganda, Indonesia, and Papua New Guinea, with potential to other food spices.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: 410-704-5043. Fax: 410-704-4265. E-mail: ehondrogiannis@towson.edu.

Notes

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