



Provenance establishment of coffee using solution ICP-MS and ICP-AES

Jenna L. Valentin^{a,*}, R. John Watling^{a,b,1}^a Centre for Forensic Science, University of Western Australia M420, 35 Stirling Highway, Perth, Crawley, WA 6009, Australia^b TSW Analytical Pty. Ltd., P.O. Box 3143, Broadway Nedlands, Crawley, WA 6009, Australia

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ABSTRACT

Statistical interpretation of the concentrations of 59 elements, determined using solution based inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma emission spectroscopy (ICP-AES), was used to establish the provenance of coffee samples from 15 countries across five continents. Data confirmed that the harvest year, degree of ripeness and whether the coffees were green or roasted had little effect on the elemental composition of the coffees. The application of linear discriminant analysis and principal component analysis of the elemental concentrations permitted up to 96.9% correct classification of the coffee samples according to their continent of origin. When samples from each continent were considered separately, up to 100% correct classification of coffee samples into their countries, and plantations of origin was achieved. This research demonstrates the potential of using elemental composition, in combination with statistical classification methods, for accurate provenance establishment of coffee.

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1. Introduction

Coffee is the common name for the plants of the family *Rubiaceae*, genus *Coffea*, of which there are two main varieties that are significant in commercial trade: *Coffea arabica* and *Coffea canephora*, commonly referred to as *arabica* and *robusta*, respectively. The coffee beans are obtained from the small, red cherry fruit of the coffee plant. The seeds inside this cherry contain the green coffee beans, ready for processing and roasting.

Consumer demands for authentic coffee of high quality are continually increasing. Perhaps due to these demands, there exist significant risks of coffee fraud. As coffee is generally bought and sold and classified according to the specific geographic growing area, its quality and authenticity are consequently inherently linked with its country or region of origin. Attempts to pass off cheaper coffee, or a mix of coffees, as pure expensive types are illustrative of the importance of accurately identifying the origin of coffee (Anderson & Smith, 2002).

In addition to the risk of fraud, the globalisation of food markets, and the ease with which foods are transported around the world, often increase consumer concerns about the origin of the foods they eat (Kelly, Heaton, & Hoogewerff, 2005). The ability to correctly identify the geographical origin of coffee would be of

great benefit to the coffee industry, potentially leading to the identification of fraudulent practices, improvement of quality control and the protection of reputation and consumer confidence throughout the industry. One potential method of determining coffee provenance is the establishment of unique chemical signatures for coffees grown in different geographic regions.

Several studies have been conducted to identify the chemical composition of coffee. However, the vast majority have centered on the identification of volatile organic compounds, involving relatively small sample sets. Bicchi, Binello, Pellegrino, and Vanni (1995) analysed chlorogenic acids in green and roasted coffee in conjunction with principal component analysis to discriminate coffees from different origins. Limited visual separation of coffees according to geographic origin was achieved. Costa Freitas, Parreira, and Vilas-Boas (2001) successfully differentiated between *arabica* and *robusta* varieties based on volatile compound composition. When each variety was considered individually, nine coffee samples were separated to some degree according to geographic origin.

Considerable research has already been carried out to establish the origin of food and plant products with elemental analysis being used to determine the origin of a range of products including beer (Asfaw & Wibetoe, 2005), tea (Pilgrim, Watling, & Grice, 2010), wine (Martin, Watling, & Lee, 2012), olive oil (Watling et al., 2010) and fruit (Perez, Smith, & Anderson, 2006). The ability to determine the geographic origin of foods using these methods is based on the composition of vegetation grown in a particular geographic area, which tends to reflect the elements present in the soil in which it was grown (Kelly et al., 2005; Perez et al., 2006). As a

* Corresponding author. Tel.: +61 8 6488 7044; mobile: +61 423 329 632; fax: +61 8 6488 1800.

E-mail addresses: valenj01@uwa.edu.au (J.L. Valentin), john.watling@uwa.edu.au (R.J. Watling).

¹ Tel.: +61 8 6488 6281, mobile: +61 417 940 254; fax: +61 8 6488 7285.

result, the elemental composition of the vegetation, in this case coffee, may provide a unique marker to enable characterisation of coffee according to geographical origin.

While several studies attempting provenance establishment of coffee based on elemental concentrations have been conducted, these generally have only small sample sets or limited classifications. Krivan, Barth, and Morales (1993) successfully discriminated coffees from eight countries using concentrations of 20 elements determined using a combination of instrumental neutron activation analysis, electrothermal atomic absorption spectrometry, flame atomic absorption spectrometry and combustion elemental analysis. Haswell and Walmsley (1998) used multi-elemental analysis in combination with principal component and cluster analysis to successfully visually separate coffee samples according to brand, which corresponded directly with geographical origin. Anderson and Smith (2002) demonstrated the feasibility of elemental analysis using ICP-AES to differentiate the geographic origin of coffee samples from Central and South America, East Africa and Indonesia. Limited geographical discrimination of coffees grown within these growing regions was achieved.

These and other previous studies have generally been limited in the number of samples analysed, both in total number of samples from different countries, and number of samples from different regions or plantations within each country. Very few of the studies that have used various combinations of statistical classification and visualisation methods have achieved clear and distinct groupings of coffee samples in resultant plots. There is also little research associated with the potential use of ICP-MS in combination with ICP-AES as the analytical platforms for the analysis of coffees.

The current study investigates the potential of using multi-elemental analysis of coffee samples to establish the provenance of coffee. The effects of differences between green and roasted beans, ripe and unripe green beans and harvest year on elemental concentrations have also been studied. Linear discriminant and principal component analyses have been applied to obtain separation of coffees according to growing origins and to identify the provenance of samples from different coffee growing regions. The validity and robustness of the method for the determination of origin of coffee samples was then tested through the analysis of an addition set of samples originating from four different plantations across a small geographical area in Bali, Indonesia, collected 2 years after the initial samples were analysed.

2. Materials and methods

2.1. Samples

For the initial study, a total of 39 green and roasted single origin coffee samples from 15 countries across five continents were obtained from a coffee retailer (see Table 1). Additional ripe (red cherry) and unripe (green cherry) green coffee samples were collected from four plantations over a small geographic area in Bali, Indonesia, picked directly from the tree as cherries (samples from Delod Tiing, Dajan Umah, Palung An and Batur plantations in Table 1). Details were recorded as to the GPS coordinates of growing location, elevation, tree age, and whether the samples were ripe (red cherry) or unripe (green cherry).

2.2. Solution analysis using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES)

The coffee samples collected from Bali were manually processed to separate the outer flesh of the cherry from the coffee beans. Green beans were dried overnight at 90 °C. All samples were

Table 1

Summary of coffee samples analysed throughout the study.

Continent	Country	Plantation	Sample ID	
			Roasted	Green
Africa	Kenya	–	03KENYR	03KENYG
Africa	Kenya	AA	08KEAAR	08KEAAG
Africa	Kenya	AB	–	10KEABG
Africa	Ethiopia	Harrar	06ETHAR	06ETHAG
Africa	Ethiopia	Harrar Gr4	–	12ETHAG
Africa	Ethiopia	Yirgacheffe	07ETYIR	07ETYIG
Africa	Ethiopia	Yirgacheffe	–	13ETYIG
Africa	Uganda	–	09UGANR	09UGANG
Africa	Uganda	Bugisu AA	–	11UGBUG
Asia	India	Plantation A	04INPAR	04INPAG
Asia	India	Malabar	–	16INMMG
Asia	India	Tiger A	–	17INTAG
Asia	Indonesia	Gajah Mt.	–	15INGMG
Asia	Indonesia	Subuk Abian	–	14BASAG
Asia	Indonesia	Delod Tiing	–	31BADT1
Asia	Indonesia	Delod Tiing	–	31BADT2
Asia	Indonesia	Delod Tiing	–	31BADT3
Asia	Indonesia	Dajan Umah	–	32BADU1
Asia	Indonesia	Dajan Umah	–	32BADU2
Asia	Indonesia	Dajan Umah	–	32BADU3
Asia	Indonesia	Palung An	–	33BAPA1
Asia	Indonesia	Palung An	–	33BAPA2
Asia	Indonesia	Palung An	–	33BAPA3
Asia	Indonesia	Batur	–	34BABA1
Asia	Indonesia	Batur	–	34BABA2
Asia	Indonesia	Batur	–	34BABA3
Oceania	East Timor	–	02EATIR	02EATIG
Oceania	East Timor	FTO	–	19ETFTG
Oceania	Australia	Capricorn	–	18AUSCG
Oceania	PNG	Elimbari	–	20PNGEG
Oceania	PNG	PSC A	–	21PNGAG
Oceania	PNG	Purosa FTO	–	22PNGPG
C America	Cuba	–	–	23CUBAG
C America	Dom. Rep.	FTO	–	24DOMRG
C America	Costa Rica	Terazzu	–	25CORIG
C America	Guatemala	Antigua	–	26GUANG
S America	Colombia	–	01COLUR	01COLUG
S America	Colombia	Supremo	–	28COSUG
S America	Colombia	Supremo Sc	–	29COSSG
S America	Brazil	Bourbon	05YEBOR	05YEBOG
S America	Brazil	Delarisse	–	27BRDEG
S America	Peru	FTO	–	30PERUG

ground separately in a commercial coffee grinder to a homogenous particle size. Samples were then subject to acid digestion. The digestion procedure was based on the generic dissolution method previously reported in Watling et al. (2010). Modifications to the method were developed to simplify and refine the digestion process, resulting in fewer dissolution and evaporation steps, shorter total time for digestion and the use of less harsh reagents, removing the need for the perchloric acid digestion step.

Samples of ground coffee (1 g) were accurately weighed into 50 ml polyethylene screw topped tubes in triplicate. Nitric acid (5 ml) (Ajax Finechem, NSW, Australia, sub-boiling quartz still redistilled) was added to each sample and the mixture left for 4 h to react at room temperature with the tube lids resting loosely on the tubes. The tubes were then transferred to a water bath, and suspended in water at approximately 90 °C for a further 12 h. After this time, the lids were removed before adding hydrogen peroxide (2 ml). The solutions were left to evaporate to residue. The residue was then taken up into solution with approximately 20% nitric acid (25 ml) and the solutions weighed accurately. Solutions were diluted fivefold with a 2 ppb iridium–rhodium internal standard diluent in 2% nitric acid.

Triplicate analyses of two Certified Reference Materials (CRMs), peach leaves and apple leaves (National Institute of Standards and Technology SRM 1547 and 1515, respectively), were also included as samples during the digest. These underwent the same acid dis-

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