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Analytical Methods

Inductively coupled plasma-mass spectrometry (ICP-MS) and -optical emission spectroscopy (ICP–OES) for determination of essential minerals in closed acid digestates of peanuts (*Arachis hypogaea* L.)

Kim-Yen Phan-Thien [a], Graeme C. Wright [b], N. Alice Lee [a,*]

[a] Food Science and Technology, School of Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia
[b] Peanut Company of Australia, Kingaroy, QLD 4610, Australia

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ABSTRACT

Validated methods to measure the essential mineral composition of food matrices are needed to satisfy the analytical requirements of product development, quality control, and food regulatory authorities. We investigated the use of inductively coupled plasma–optical emission spectroscopy (ICP–OES) and -mass spectrometry (ICP-MS), with and without the use of a dynamic reaction cell (DRC), to analyse 15 essential minerals in peanut kernels. We validated methods for Ca, Cu, Fe, K, Mg, Mn, Mo, P, and Zn analyses; however further tests are needed for validation of the B, Co, Cr, Na, Ni, and Se analyses. ICP–OES was applied to a study of genotypic variation among 56 breeding lines grown in the Australian peanut improvement program. We found promising levels of genotypic variation (>10%) in essential mineral traits, especially Ca (18–23%) and Mn (24%). Further investigation of the plant breeding potential for mineral traits may aid in the future development of peanut cultivars with enhanced micronutrients.

1. Introduction

Dietary intake of 'essential minerals' is necessary to support normal growth, reproduction, and health during the life cycle, when all other nutritional requirements are held at optimal levels. The National Health and Medical Research Council (NHMRC), which is the government authority responsible for providing nutritional advice and dietary recommendations in Australia and New Zealand, judges Ca, Cr, Cu, F, Fe, I, K, Mg, Mn, Mo, Na, P, Se, and Zn intake to be essential (NHMRC, 2006). Other elements sometimes considered to be essential, or to have potentially essential functions in the body, include Al, As, B, Cd, Cl, Co, Li, Ni, Pb, Si, Sr, and V (Nabrzyski, 2007; NHMRC, 2006).

Several essential minerals may also be considered as 'functional food' components due to expected preventative or therapeutic effects on chronic diseases. For example, Ca is linked to the prevention of osteoporosis and maintenance of bone health; high K intake may reduce blood pressure and cardiovascular disease mortality, delay the progression of renal disease, and aid in the management of kidney stone disease (He & MacGregor, 2008); high Mg may also aid in treatment of hypertension (Houston & Harper, 2008); and Se has antioxidant properties that may improve immune function and protect against cancer and cardiovascular disease (Reeves & Hoffmann, 2009). Functional foods are a major growth area for food industry, especially in health-conscious markets such as Australia, the EU, and the USA, where ageing demographics and wide acceptance of the link between diet and health have spurred strong interest in self-managed and preventative healthcare.

Whether focusing on the essential or functional food components of food products, there is a need for accurate, reliable, and convenient methods of measuring the essential mineral composition of food matrices, in order to satisfy the analytical requirements of product development, quality control, and food regulatory authorities. Atomic absorption spectrometry has long been a standard technique for measurement of single elements. On the other hand, optical emission spectrometry (OES), also known as atomic emission spectrometry, allows sensitive multi-element analysis because characteristic emission spectra may be generated for a range of elements under the same excitation

* Corresponding author. Tel.: +61 2 93854363; fax: +61 2 93855966.
E-mail address: alice.lee@unsw.edu.au (N.A. Lee).

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conditions. Inductively coupled plasma (ICP), usually argon, has become a popular atomiser because it produces a chemically inert environment, generates very high temperatures that ensure almost complete atomisation, and provides a calibration range of several orders of magnitude. ICP has also become popular as the ion source for mass spectrometry, which permits multi-element analysis of even greater sensitivity, and achieves detection limits typically 2–3 orders of magnitude lower than ICP–OES (Ammann, 2007).

All spectrometric techniques for elemental analysis are subject to spectral interferences. The optimal method for a given sample is often a compromise between minimising the respective interferences affecting analytes and achieving acceptable detection limits in view of the sample matrix and expected elemental composition. In addition, there may be pragmatic concerns to minimise analytical run time and expense. This paper describes the validation of analytical methods for quantitation of several essential minerals in peanut samples. In addition to conventional ICP-MS methodology, we investigated the use of a reaction cell to minimise mass spectral interferences.

Our immediate purpose was to screen a large set of peanut samples from the national peanut improvement program, in order to investigate the extent of genotypic variation and genotype-by-environment (G × E) interaction affecting essential mineral composition, and thereby explore the breeding potential for phenotypes with high kernel concentrations of important elements. Only conventional, non-transgenic techniques are used for peanut breeding in Australia, so traits can only arise from naturally-occurring variation in the breeding population. Appropriate germplasm and adequate genotypic variation are therefore critical to the breeding strategy. An understanding of the G × E interaction is also essential, as this describes the stability of trait expression in different growing environments. The results for the genotypic study are presented in this article, while investigations into the G × E interaction have been published separately (Phan-Thien, Wright, & Lee, 2010).

The literature describing validation of ICP methods for multi-element analysis of dietary samples, especially nuts and oilseeds, is relatively scant. Some examples include ICP–OES analyses of essential and non-essential minerals in nuts and seeds with reference to peach leaf CRM (Naozuka, Vieira, Nascimento, & Oliveira, 2011), and in nuts and legumes, including peanut, with reference to cabbage and spinach leaf CRM (Momen, Zachariadis, Anthemidis, & Stratis, 2006, 2007). ICP-MS has been applied to analyses of essential and potentially toxic elements in a range of dietary samples and CRM (Cubadda, Raggi, Testoni, & Fabio, 2002; Melnyk, Morgan, Fernando, Pellizzari, & Akinbo, 2003; Nardi et al., 2009). ICP–DRC-MS has rarely been used in the context of routine multi-element analysis, as applications have primarily focused on honing the trace analysis of specific contaminants such as Cd in feed (Guo et al., 2011), or for speciation of potential contaminants such as Cr (Ambushe, McCrindle, & McCrindle, 2009) and Se (Cubadda et al., 2010). In view of this, we hope that the publication of our method validation will be a useful addition to the literature.

2. Materials and methods

2.1. Instruments

Samples were digested in polytetrafluoroethylene (PTFE) vessels using Ethos Plus Labstation (10-vessel capacity) or Ethos 1 Advanced Microwave (24-vessel capacity) systems (Milestone Inc., USA). Elemental analyses were performed on Optima 7300 DV ICP–OES and Elan DRC II ICP-MS instruments (Perkin–Elmer SCIEX, USA), which used WinLab32 for ICP software version 4.0.0.0305 and Elan software version 3.4, respectively. Operating conditions are detailed in Tables 1 and 2.

2.2. Reagents

All reagents were analytical grade. Nitric acid was purified by sub-boiling distillation in a duoPUR acid purification system (Milestone Inc., USA) prior to use. Water was ultrapure grade (18.2 mΩ cm^{-1}, Millipore Corp., USA). Analytical calibration standards diluted in 2% (v/v) nitric acid were prepared daily from stock standard solutions (Choice Analytical Pty Ltd.). Rhodium and yttrium were used as internal standards for ICP-MS and ICP–OES.

2.3. Samples and certified reference materials

Wheat flour (1567a) and peanut butter (2387) certified reference materials (CRM) were obtained from the National Institute of Standards and Technology (NIST, USA) for use in method validation and quality control. Wheat flour contained most of our elements of interest, while peanut butter was the most similar matrix to peanut kernels. The digestion and analytical procedures were also applied to peanut samples obtained from the plant breeding program collaboratively run by the Peanut Company of Australia (PCA), Grains Research and Development Corporation (GRDC), and Queensland Department of Employment, Economic Development and Innovation (DEEDI). The peanuts were grown under non-limiting (nutrient- and water-replete) conditions in 2007/08, harvested and pre-processed (dried, de-hulled, and graded) according to commercial practice, and then transported to the University of New South Wales for analysis. The samples comprised a set of 56 diverse genotypes grown at Kairi Research Station in the Atherton Tablelands of north Queensland, and a set of nine genotypes grown in five distinct environments located in the central Burnett, south Burnett, and Atherton Tablelands production areas.

2.4. Sample preparation

Peanut samples were pulverised using a mortar and pestle after manual removal of the testa and addition of liquid nitrogen to encourage shattering. A portion of each sample was set aside for gravimetric determination of moisture content. Mortars and pestles were cleaned by abrasion with acid-washed sand, rinsed with ultrapure water, and oven-dried between samples. The samples were stored in plastic containers at room temperature until the time of digestion.

The reaction mixture comprised 0.40 g ground sample or CRM, 5.0 mL nitric acid, 2.0 mL hydrogen peroxide, and 3.0 mL water in a PTFE vessel. Digestion bombs were allowed to pre-digest for at least 15 min before loading into the microwave carousel according to the manufacturer's instructions. A stepped microwave program of 100 °C and 190 °C for 10 min each was initially used. This was later adjusted to 200 °C for 20 min, with adjustments in ramp times and hold temperatures according to microwave capabilities, to improve the consistency of digestion. Digestates were unloaded after internal temperatures had declined to less than 50 °C, diluted to 30 mL with water, and stored at room temperature until the time of analysis.

2.5. Quality controls

Each digestion batch contained a reagent blank to allow background correction. CRM were measured regularly throughout the duration of the experiment. Calibration blank (2% v/v nitric acid) and quality check (QC) standard (i.e., a mid-concentration calibration standard) solutions were measured every 20 and 15 samples