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Analysis of herbal supplements for selected dietary minerals and trace elements by laser ablation- and solution-based ICPMS

Kaixuan Bu *, James V. Cizdziel, Lorlyn Reidy

Department of Chemistry and Biochemistry, University of Mississippi, University, MS 38677, USA

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ABSTRACT

Concentrations of twelve elements (Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) were determined in six herbal supplements, Korean Panax Ginseng (*Panax ginseng*), Golden Seal (*Hydrastis canadensis*), Ginger Root (*Zingiber officinale*), St. John's Wort (*Hypericum perforatum*), Green Tea (*Camellia sinensis*) and Valerian Root (*Valeriana officinalis*), by both laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) and conventional closed-vessel digestion solution nebulization-ICPMS (SN-ICPMS). For LA-ICPMS, powder from supplement capsules and leaf reference materials were pressed into pellets, the later being used for calibration and quality assurance. Laser ablation was performed using line scans with a scan rate of 30 μm min^{-1}, a frequency of 20 Hz and a spot size of 100 μm; ^{13}C served as the internal standard. For LA it was found that low resolution ($m/\Delta m \approx 400$) yielded good recoveries for the reference materials and results comparable to SN-ICPMS for most elements, except for Ca, which was better determined in medium resolution ($m/\Delta m \approx 4000$). Overall, this study shows that LA-ICPMS can serve as an alternative way for determining the concentration of elements in herbal supplements in a rapid and pragmatic fashion.

1. Introduction

The use of herbal supplements has expanded rapidly during the past decade, and it is now estimated that in excess of 3 billion US dollars is spent on herbal supplements annually [1,2]. The public is attracted to these drug alternatives for a variety of reasons, including their relatively low cost and their perceived safety and effectiveness [3]. In the US, commercially available herbal supplements are regulated under the Dietary Supplement Health and Education Act of 1994 (DSHEA) by the US Food and Drug Administration (FDA) [4]. Unlike chemically synthetic drugs, herbal medicines are classified as nonprescription and are not required to undergo strict approval procedures, which sometimes leave the mechanism of medicinal action, effective dose range, and chemical and elemental composition uncertain [5].

In 2007, the US FDA established Rule 21 CFR 111 to ensure the quality of the dietary supplements available to the public. This rule established regulations requiring current good manufacturing practices (cGMP) during the manufacture, labeling, and storage of herbal and botanical dietary supplements. This rule also requires products to be accurately labeled and to not contain hazardous contaminants [6]. However, most supplement manufacturers do not independently test their raw materials or finished products for trace metal concentration, or, if they do, use outdated analytical techniques (e.g., USP Method #231) [7].

Dietary supplements are considered a significant potential source of metal contamination, and supplements at the greatest risk for toxic metal contamination are botanicals (single herb or herb combinations in extract, powder, capsule, or tablet forms) [7,8]. Thus, consumers, especially those that take high doses of supplements often as alternative medicine, may receive overloads of metals over time [7,9]. Even essential nutrient elements become harmful or toxic when they exceed a certain level [10]. Thus, it is important to have modern analytical techniques that can rapidly measure elements in herbal supplements.

Elemental analysis of supplements can be carried out using a variety of atomic spectrometry techniques including flame atomic absorption spectrometry (FAAS), graphite furnace (GFAAS), cold vapor-AAS (for Hg), and hydride generation-AAS (for As and other elements that readily form volatile hydride species). These techniques, however, are generally operated in single element mode greatly reducing throughput. Inductively coupled plasma atomic emission spectrometry (ICPAES) is a multi-element technique but may not have the limit of detection needed to measure some trace elements. Inductively coupled plasma mass spectrometry (ICPMS) is considered one of the most sensitive techniques for measuring a wide-range of elements and isotopes in a variety of sample matrices. It has been employed in a number of studies examining heavy metals in supplements [11,12]. Generally, supplements are digested with hazardous acids (e.g., HNO_3, HCl and sometimes HF) followed by analysis using solution nebulization(SN)-ICPMS [12]. Such sample preparation is labor intensive and can increase the likelihood of contamination and loss of volatile elements [13].

An approach which avoids or minimizes sample preparation and dissolution is laser ablation (LA)-ICPMS. Laser ablation introduces solid samples, as ablated particles and vapor, to an ICPMS where signal intensities from isotopes of elements can be measured and

* Corresponding author. Tel.: +1 662 380 3303; fax: +1 662 915 7300.
E-mail address: kbu@olemiss.edu (K. Bu).

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Fig. 1. Photograph of six powdered herbal supplement samples. From left to right are: Korean Ginseng, Ginger Root, Valerian Root, Green Tea, St. John's Wort and Golden Seal.

quantified [14]. Most applications using LA-ICPMS use quadrupole-based instruments because it offers fast scanning capability which can be advantageous for non-homogeneous samples [15]. However, the quadrupole-based instruments are frequently suffered from low sensitivity and detection limits. Sector field ('high resolution') ICPMS, on the other hand, offers a much higher sensitivity and mass resolution, and allows many common polyatomic and isobaric interferences (e.g. ^{56}Fe from $^{40}Ar^{16}O$; ^{75}As from $^{40}Ar^{15}Cl$) to be resolved (physically separated in the ion beam). Moreover, scanning speeds of modern sector field instruments are no longer considered a limiting factor for quantitative analysis of multi-element analysis on transient signals [16].

In this study, a new and direct approach to rapidly quantify elements in herbal supplements was developed, optimized and evaluated. To our knowledge this is the first report focusing on analysis of pelletized herbal supplement powder by LA-sector field-ICPMS using a leaf reference material as standard. A range of dietary nutrient elements were selected for analysis (Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, and Zn). In addition, Cd, V and Al were determined; Cd is a heavy metal and toxic element, V is regarded by some as a micronutrient, and Al has no proven physiological function [17]. The results are comparable to that obtained from a conventional method using closed vessel acid-digestion followed by SN-ICPMS.

Table 1
LA-ICPMS instrument settings.

UP-213 system	
Laser type	Nd-YAG
Wavelength	213 nm
Power	29.9 J/cm
Frequency	20 Hz
Beam size	100 μm
Carrier gas	He
Scan type	Line scan
Scan rate	30 μm s^{-1}
Duration per scan	~5 min
Plasma	
Cool gas flow	16 L min^{-1}
Aux. gas flow	0.96 L min^{-1}
Sample gas flow	1 L min^{-1}
RF power	1350 W
Data acquisition	
Isotopes monitored	^{25} Mg, ^{27}Al, ^{42}Ca, ^{51} V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{62}Ni, ^{65}Cu, ^{66}Zn, ^{111}Cd
Mass window	1% for LR 3% for MR
Integration time	10 ms
Sample per peak	1 for LR 10 for MR
Runs/passes	250/1
Scan type	E-scan

LR: low resolution; MR: medium resolution.

2. Material and methods

2.1. Sample collection, preparation and calibration strategy

Herbal supplements, St. John's Wort (*Hypericum perforatum*), Ginger Root (*Zingiber officinale*), Korean Panax Ginseng (*Panax ginseng*), Golden Seal (*Hydrastis Canadensis*), Valerian Root (*Valeriana officinalis*), and Green Tea (*Camellia sinensis*) were purchased from a local store (Fig. 1). Powder from several supplement capsules was combined for analysis. It should be noted that the amount of herbal extract per capsule varied between products and ranged from 100 mg to 550 mg. Other common ingredients in the capsules included maltodextrin, gelatin, cellulose, silica and magnesium stearate.

For laser ablation analysis, about 0.5 g of each sample and reference standard material was weighed and pressed into pellets using a hydraulic press operated at 4 MPa. No binder was needed and the resulting pellets were about 2–4 mm in thickness. Standard reference material (SRM) NIST 1573a (tomato leaf) was used as one-point calibration standard. The accuracy of the calibration was verified by analyzing pelletized NIST 1547 (peach leaf), NIST 1570 (spinach leaf) and NIST 1573 (tomato leaf). Carbon has been widely used as internal standard when analyzing organic samples by LA-ICPMS due

Table 2
SN-ICPMS instrument settings.

Plasma	
Cool gas flow	16 L min^{-1}
Auxiliary gas flow	0.9 L min^{-1}
Sample gas flow	1.19 L min^{-1}
RF power	1300 W
Data acquisition	
Isotopes monitored	^{24} Mg, ^{27}Al, ^{44}Ca, ^{51} V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{62}Ni, ^{65}Cu, ^{66}Zn, ^{111}Cd
Mass window	20% for LR 150% for MR
Runs/passes	3/2
Scan type	E-scan

LR: low resolution; MR: medium resolution.