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Inductively coupled plasma optical emission spectrometric determination of fifteen elements in dietary supplements: Are the concentrations declared in the labels accurate?

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ABSTRACT

A study was carried out to establish a reliable procedure for determining 15 elements (As, Bi, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, V and Zn) in different brands of dietary supplements purchased in Argentina and USA. Supplements were digested with HNO_3 and H_2O_2 using an optimized microwave procedure. Inductively coupled plasma optical emission spectrometry (ICP OES) was selected for total element determination. The overall approach was tested in tablets of: (i) Se supplement, (ii) two multimineral supplements, (iii) cholesterol control tablets, (iv) multivitamins for men, and (v) a multivitamin + multimineral supplement. Arsenic, Cd and Pb concentrations were in all the analyzed samples below the detection limits for these elements (As, 1.2 μg g^{-1}; Cd, 0.09 μg g^{-1} and Pb, 1.5 μg g^{-1}). Elemental concentrations of the other elements investigated showed a great variability depending on the trade mark analyzed. Measured metal concentration ranged from 0.78 ± 0.19 μg g^{-1} (Ni) to 13.5 ± 0.7% (Ca). Most abundant elements, detected as percentage were Ca, Mg and Fe. In general terms, the study evidenced that metal content reported by the manufacturer in labels of dietary supplements agree with found values. On the other hand, significant differences in metal concentration were found among tablets of the same bottle.

1. Introduction

Many metals and metalloids have been known to be a necessary component in the human diet for a long time and its occurrence and function in biological systems has been well-documented [1–3]. In this connection, clinical studies showed that some metals and metalloids, despite their reported toxicity, may play an important role in therapeutic effects of the herbs containing these metals [4]. In general terms, dietary supplements can be considered as a potential source of metals and metalloids contamination, especially when they content toxic or potentially toxic elements constituting a risk for consumers.

In the last years, especially in the developed countries, the consumption of dietary supplements has increased. These compounds are considered by the consumers as drug alternatives for a variety of reasons, including their relatively low cost and their perceived safety and effectiveness [5]. They are defined as a product that intends to supplement the diet, which contains vitamins, minerals, herbs, or other botanicals, amino acids, or any combination of the above ingredients [6–9].

Another important issue to consider is that these products are regulated as food, and producers are not required to register these supplements before sale [6,10]. It is difficult to determine the quality of a dietary supplement product from concentrations declared in the labels. The degree of quality control depends on the manufacturer, the supplier, and others related to the production process. The first question to answer is: are the concentrations declared in the labels accurate? Tablets from the same bottle have the same elemental composition.

Numerous analytical techniques and instrumental approaches have been proposed for dietary supplement analysis. Valiente et al. [11] reported a comparative study on the determination of Se in tablets of vitamins–minerals–aminoacids, nutritional supplements and Se-enriched yeast by electrothermal atomic absorption spectrometry (ETAAS) and hydride generation-atomic absorption spectrometry (HG-AAS). The study evidenced that Se content reported on the labels was often inaccurate. In addition, significant differences were found among bottles of the same trade mark. García-Rico et al. [12] determined five metals namely, Cd, Cu, Hg, Pb, and Zn by AAS in 24 dietary supplements purchased in Mexico. According to their findings, some products presented more than 10% of the tolerable daily intake of

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Pb, indicating that production processes should be improved. Tumir and coworkers [13] reported the AAS determination As, Cd, Cr, Hg, Ni, Pb, and Zn in 30 samples of widely used vitamins and herbal preparations distributed on the Croatian market. The objective was to estimate contamination due to their potential toxicity if present above the maximum allowable levels (MAL). They found that several analyzed formulations had metal levels above the MAL such as: (i) Pb in one honey-based product and one medicinal herb-based product, (ii) Cr in one product containing vitamins, and (iii) Ni in two products containing vitamins and one product of animal origin.

The presence of Pb in dietary supplement samples (calcium carbonate, dolomite and oyster shell samples) and subsequent determination by graphite furnace atomic absorption spectrometry (GFAAS) was also investigated [14]. Lead concentrations in the ten commercial products analyzed varied from 0.21 to 1.34 μg g^{-1}. Recently, two techniques namely, laser ablation (LA)- and solution-based inductively coupled plasma mass spectrometry (ICP-MS) were used and compared to assess concentrations of 12 elements (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, V and Zn) in six herbal supplements [5]. LA-ICP-MS was chosen to minimize sample preparation and to avoid the use of acids for sample digestion. There was generally good agreement (±15%) between concentrations determined by LA and ICP-MS and certified values.

The daily and continuous use of these products by adults became usual and makes necessary to ensure their quality. In this context, to assess the elemental concentration in these products with emphasis in those toxic or potentially toxic elements for human health is of prime importance.

The analysis of dietary supplement is a challenge because they have a complex matrix and contain many elements in a wide range of concentrations. Plasma-based techniques have gradually assumed prime importance in verifying whether foodstuffs and pharmaceutical products comply with health requirements and/or national or international regulations because they can be applied to all possible matrices and analytes and are characterized by extended dynamic concentration range (several orders of magnitude) and are multielemental in nature and possess high sensitivity and appropriate detection power.

The aim of this study was to investigate the presence of labeled and non-labeled metals and metalloids in different commercial brands of dietary supplements purchased in Argentina and USA. The supplements were selected based on their popularity and frequent usage. The main objective was to establish a reliable methodology for verification of elemental content as well as contribute with useful information to the assessment of product authenticity or adulteration. It is not the scope of this work neither to evaluate possible toxicological effects produced by the intake of these products nor to estimate tolerable daily intakes according to recommendations of health agencies.

2. Experimental

2.1. Instrumentation

A Horiba-Jobin Yvon Model Ultima 2 inductively coupled Ar plasma was used for major, minor and trace elements determination. Instrumental details and operating conditions are summarized in Table 1.

Welding Ar from Indura (Buenos Aires, Argentina) was used for ICP OES determinations. Deionized distilled water (DDW) was produced by a commercial mixed-bed ion-exchange system Barnstead (Dubuque. IA. USA) fed with distilled water.

Plastic bottles, auto-sampler tubes, and glassware were cleaned by rinsing with deionized water, soaking with a 10% (v/v) nitric acid solution for 24 h and then rinsing several times with deionized water. All samples and standards were stored in polyethylene bottles (50 mL) or Falcon® tubes.

Table 1
Instrumental characteristics and settings for ICP OES.

Instrument	Horiba-Jobin Yvon Ultima 2
Frequency of rf generator	40.68 MHz (radial view)
Coolant gas flow rate	12 L min^{-1}
Auxiliary gas flow rate	0.2 L min^{-1}
Sample gas flow rate	0.8 L min^{-1}
Solution delivery	1.0 mL min^{-1}
Automatic sampler	JY AS500
Nebulizer	Concentric gas nebulizer with cyclonic spray chamber
Polychromator	Monochromator use Czerney Turner optical system. wavelength range (nm): 120–450 focal length 1 meter
Detector	Photomultiplier tube
Measurement mode	Continuous nebulization
Wavelengths (nm)	As, 188.93; Ca 317.933; Cd, 228.802; Cr, 205.552; Cu, 327.396; Fe, 238.204; Hg, 253.652; Mg, 285.213; Mn, 257.610; Mo, 203.844; Ni, 221.647; Pb, 220.353; Sb, 206.833; Se, 196.026; V, 209.882; Zn, 206.191

An MLS-1200 (Millestone-FKW, Sorisole, Bergamo, Italy) MW apparatus equipped with ten Teflon-PFA (perfluoroalkoxy) vessels was used to digest the tablets/pills.

2.2. Reagents

Chemicals were of analytical reagent grade unless otherwise stated. Deionized water (Barnstead, Dubuque, IA, USA) was used throughout. All solutions were stored in high-density polypropylene bottles. Commercially available 1000 mg L^{-1} standard solutions (Merck, Darmstadt, Germany) of the elements under study were used. Diluted working solutions were prepared daily by serial dilutions of the stock solutions. Analytical reagent nitric acid (Merck) was used after additional purification by sub-boiling distillation in quartz still.

Nitric acid and H_2O_2 (Merck, Darmstadt, Germany) were used for sample treatment and preparation of the standards.

2.3. Samples and sample handling

Five brands of different dietary supplements for adult's consumption were analyzed for evaluating total content of 15 elements. Dietary supplements were purchased in 2012 in different health food stores in Argentina and USA. Trade marks of dietary supplements were identified according to a code assigned in our lab (A, B, C, D and E). The variety of products and compounds described in the labels are as follows: A: multivitamin/mineral formula; B: vitamins and minerals (ginko + ginsen + guarana); C: selenium; D: cholesterol fighter and E: supplement for men. Content uniformity testing was performed by randomly selecting ten tablets from each bottle. Table 2 shows a detailed description of the composition of the dietary supplements analyzed according to the information reported by the manufacturer in the labels.

Ten tablets of each bottle were ground and mixed thoroughly by mortar and pestle. The grinding was carefully carried out to assure samples are not subjected to conditions that would alter their composition (e.g., heating). Three sub-samples of each mixture were accurately weighed and used for the subsequent microwave assisted digestion.

2.4. Sample treatment

Metals and metalloids determination by ICP OES requires preliminary digestion of the samples into liquid solutions. A ~0.5 g portion of each powdered sample was weighed into a PTFE beaker and 7 mL of nitric acid and 3 mL of H_2O_2 were added. The mixture was left overnight at room temperature. Nitric acid was used due to its