Food Chemistry 158 (2014) 200–206

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Determination of minor and trace elements in aromatic spices by micro-wave assisted digestion and inductively coupled plasma-mass spectrometry

Naeem Khan [a], Ji Yeon Choi [a], Eun Yeong Nho [a], Nargis Jamila [b], Girum Habte [a], Joon Ho Hong [a], In Min Hwang [c], Kyong Su Kim [a,*]

[a] Department of Food and Nutrition, Chosun University, Gwangju 501-759, Republic of Korea
[b] School of Chemical Sciences, Universiti Sains Malaysia, Minden 11800, Penang, Malaysia
[c] World Institute of Kimchi, Gwangju 503-360, Republic of Korea

A R T I C L E I N F O

Article history:
Received 29 October 2013
Received in revised form 18 February 2014
Accepted 22 February 2014
Available online 1 March 2014

Keywords:
Aromatic spices
Minor and trace metals
ICP-MS
Pakistan

A B S T R A C T

This study aimed at analyzing the concentrations of 23 minor and trace elements in aromatic spices by inductively coupled plasma-mass spectrometry (ICP-MS), after wet digestion by microwave system. The analytical method was validated by linearity, detection limits, precision, accuracy and recovery experiments, obtaining satisfactory values in all cases. Results indicated the presence of variable amounts of both minor and trace elements in the selected aromatic spices. Manganese was high in cinnamon (879.8 μg/g) followed by cardamom (758.1 μg/g) and clove (649.9 μg/g), strontium and zinc were high in ajwain (489.9 μg/g and 84.95 μg/g, respectively), while copper was high in mango powder (77.68 μg/g). On the whole some of the minor and essential trace elements were found to have good nutritional contribution in accordance to RDA. The levels of toxic trace elements, including As, Cd, and Pb were very low and did not found to pose any threat to consumers.

1. Introduction

Spices are the storehouse of several elements over a wide range of concentrations with important positive or negative health impacts. More than twenty elements have known physiological activities in humans and other mammals. Some of these elements, such as chromium, manganese, vanadium, cobalt, copper, zinc, and selenium are considered as essential elements belonging to the category of micro-nutrients, which are required by the human body in very small quantities, generally less than 100 mg/day (Karadas & Kara, 2012). In biological systems minor and trace elements are mostly conjugated to proteins forming metalloproteins or other smaller molecules such as phosphates, phytates, polyphenols and other chelating compounds. In the form of metalloproteins, these elements are mostly important parts of enzymatic systems, having specific structural functions or help in transport of the bound proteins to their target sites (Fraga, 2005). Elements like cobalt, copper, chromium and nickel are the essential components of biological structures but can also be toxic at concentrations beyond the limits necessary for their functions. Other elements like arsenic, lead and cadmium have well known toxic roles in various biochemical reactions (Fraga, 2005; Karadas & Kara, 2012).

Several spices are widely used in daily diet in Pakistan and in fact worldwide. Amongst the several benefits of these products, they are well known for their dementia-fighting power (cumin), combating obesity and sugar regulating powers (cinnamon), and anti-cancer properties (turmeric). Much work has been done on organic constituents and bio-activities of the aromatic spices but very little attention has been paid towards their minor and trace element contents. In view of the fact that these spices are being consumed in daily diets or as supplements, to give flavour to dishes and for medicinal effects, it is very important to determine their minor and trace elements composition so that their effect on human health can be clearly understood (Karadas & Kara, 2012).

Around the world different techniques have been employed, from time to time, for carrying out the determination of minor and trace elements, namely: differential pulse anodic stripping voltammetric technique (Tripathi, Raghunath, Sastry, & Krishnamoorthy, 1999), stripping potentiometry (Muñoz & Palmero, 2004), capillary zone electrophoresis (Suárez-Luque, Mato, Huidobro, & Simal-Lozano, 2007), instrumental neutron activation analysis (Singh & Garg, 2006), atomic fluorescence spectrometry (Cava-Montesinos, Ródenas-Torralba, Morales-Rubio, Luisa Cervera, &

* Corresponding author. Tel.: +82 62 230 7724; fax: +82 62 224 8880.
E-mail address: kskim@chosun.ac.kr (K.S. Kim).

http://dx.doi.org/10.1016/j.foodchem.2014.02.103
0308-8146/

De la Guardia, 2004), flow injection spectrometric methods (Nogueira, Mockiuti, Souza, & Primavesi, 1998), inductively coupled plasma emission spectroscopy (Park, 2000), flame atomic absorption spectrometry (Kondyli, Katsiari, & Voutsinas, 2007), inductively coupled plasma optical emission spectrometry (Kira & Maihara, 2007), and inductively coupled plasma mass spectrometry (Chudzinska & Baralkiewicz, 2011; Khan et al., 2013, 2014; Llorent-Martínez, De Córdova, Ruiz-Medina, & Ortega-Barrales, 2012).

ICP-MS technology has been widely used for the analyses of minor and trace elements in foods (Chudzinska & Baralkiewicz, 2011; Giannenas, Nisianakis, Gavriil, Kontopidis, & Kyriazakis, 2009; Khan et al., 2013, 2014; Llorent-Martínez et al., 2012; Nardi et al., 2009; Tüzen, Sesli, & Soylak, 2007) with satisfactory results. The concentrations of some of the elements have already been studied in some herbs and spices from Turkey by Karadas and Kara (2012) using ICP-MS but there was no comprehensive study of all well known minor and trace elements involving large number of spice samples from several varieties widely consumed in Pakistan and around the world. Therefore the objective of this study was to determine the concentrations of 23 minor and trace elements namely As, Pb, Cd, Cr, Cu, Ni, Zn, Tl, U, Rb, Cs, Li, B, Be, Ba, Sr, Bi, Cs, Ga, In, V, Co, and Se, in eleven species of aromatic spices commonly consumed and commercially available to consumers all over Pakistan. The ICP-MS technique was used, because of its well-known advantages of sensitivity, selectivity and multi-element analysis capability. The critical levels specified by WHO and Food and Nutrition Board were used to compare the results for dietary intakes of minor nutritional elements and permissible maximum tolerable intakes of toxic trace elements.

2. Materials and methods

2.1. Instrumentation

A Multiwave 3000 microwave system (Anton Paar, Graz, Austria) was used for sample preparation. It was programmable for time and power between 600 and 1400 W and equipped with 16 high pressure PTFE (polytetrafluoroethylene) vessels (MF 100), used to digest the samples.

The inductively coupled plasma mass spectrometer (ICP-MS) used was quadrupole Elan DRC II (Perkin–Elmer SCIEX, Norwalk, CT, USA). It was combined with a high-efficiency sample introduction desolvating system equipped with a quartz cyclonic spray chamber and an additional mixing peristaltic pump (APEX-IR, Omaha, NE, USA). The operating conditions of the instrument were: forward power 1.35 kW, argon gas flow rate 16.00 L/min (plasma); 1.2 L/min (auxiliary), 1–1.07 L/min (nebulizer). The argon gas utilized was of spectral purity (99.9998%). The selected isotopes of the elements for analyses were: ^{11}B, ^{52}Cr, ^{55}Mn, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{138}Ba, ^{7}Li, ^{9}Be, ^{51}V, ^{59}Co, ^{69}Ga, ^{82}Se, ^{209}Bi, ^{133}Cs, ^{238}U, ^{75}As, ^{111}Cd, ^{115}In, ^{205}Tl, and ^{208}Pb. Before each experiment, the instrument was tuned for daily performance using Elan 6100 DRC Sensitivity Detection Limit Solution (Perkin–Elmer Pure, USA). It is an aqueous multi-element standard solution of Li, Y, Co, Ce and Tl for consistent sensitivity (^{7}Li, ^{89}Y and ^{205}Tl) and minimum doubly charged and oxide species levels (^{140}Ce).

2.2. Reagents and materials

Analytical reagent grade concentrated HNO_3 (70%) and hydrogen peroxide (30–32%) were obtained from Dong Woo Fine-Chem Co., Ltd Iksan, Korea. HNO_3 was further purified by double sub-boiling distillation in quartz stills. The ultrapure deionised water with resistivity of 18.2 MΩ cm, was obtained from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA). The calibration standard solutions were prepared from 10 mg/L multi-element standard solution (AnApure KRIAT Co, Ltd. Daejeon, Korea). The Standard Reference Material (NIST-1570a), Spinach Leaves, was obtained from National Institute of Standards and Technology, Gaithersburg MD, USA. The plastic/glass containers were soaked in 10% v/v HNO_3 for at least 24 h, and then rinsed extensively with Milli-Q water prior to use. All containers, polypropylene flasks, pipette tips, and reagents that came into contact with samples or standards were checked for contamination.

2.3. Samples preparation and digestion

A total of 165 samples of commercially available spices were collected from local supermarkets all over Pakistan. These were consisted of 15 samples from each of 11 selected spice species as mentioned in Table 1. The samples were purchased in triplicate at different times during February to August, 2013. All the samples were washed thoroughly with deionized distilled water and dried between layers of clean scientific tissue papers (Kimtech Science wipers, Seoul, Korea). For determination of moisture, each spice was dried at 60 °C in oven (HB-502 M, Han Back, Korea) until constant weight was achieved (Pereira et al., 2013). These were homogenized in a blender (MR 350 CA, Braun, Spain), properly labeled and stored in plastic bags at −20 °C in refrigerator (MICOM CFD-0622, Samsung, Korea) until analysis.

For micro-wave digestion, 0.5 g of each sample was accurately weighed directly into PTFE digestion vessel. Then 7 mL concentrated HNO_3 (70%) and 1.0 mL H_2O_2 was added and digested using microwave system. The combustion procedure was as follows: (1) 1000 W at 80 °C for 5 min, (2) 1000 W at 50 °C for 5 min, (3) 1000 W at 190 °C for 20 min, and (4) 0 W for 30 min for cooling. After cooling the contents of the tubes were transferred to 50 mL self standing polypropylene volumetric tubes with plug seal caps (Corning NY, Mexico). The contents were diluted to 25.0 g with ultrapure deionised water, labeled accurately and used for analysis.

Table 1
List of aromatic spices studied.

No	English name	Vernacular name	Botanical name	Family	Part investigated
1.	Green cardamom	Ellaichi	*Elettaria cardamomum*	Zingiberaceae	Fruits
2.	Nigella seed	Kalwanji	*Nigella sativa*	Ranunculaceae	Seeds
3.	Bishop's weed	Ajwain	*Trachyspermum ammi*	Apiaceae	Fruits
4.	Cumin	Zira	*Cuminum cyminum*	Apiaceae	Fruits
5.	Cinnamon	Dalchini	*Cinnamomum verum*	Lauraceae	Bark
6.	Coriander	Dhania	*Coriandrum sativum*	Apiaceae	Fruits
7.	Turmeric	Haldi	*Curcuma longa*	Zingiberaceae	Roots
8.	Mangopowder	Amchoor	*Magnifera indica*	Anacardiaceae	Fruits
9.	Pomegranate	Anardana	*Punica granatum*	Lythraceae	Seeds
10.	Clove	Lowng	*Syzygium aromaticum*	Myrtaceae	Flower buds
11.	Fennel	Saunf	*Foeniculum vulgare*	Apiaceae	Fruits