UNIVERSITI PUTRA MALAYSIA

ELEMENTAL COMPOSITION OF FRUITS AND VEGETABLES USING INAA, AAS, AND ICP-MS

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By

MOHAMMAD ALI SHAFAEI

May 2012

This thesis dedicates to

My Family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia, in fulfillment of the requirement for the degree of Doctor of Philosophy

ELEMENTAL COMPOSITION OF FRUITS AND VEGETABLES USING INAA, AAS, AND ICP-MS

By

Mohammad Ali Shafaei

May 2012

Chairman : Professor Elias Bin Saion, PhD

Faculty : Science

Industrial growth has provided peerless progress in living standards and comforts for mankind, but it has been the cause of menace of environmental pollution. The issues like chemical toxicology, acid rain, greenhouse effect, ozone depletion, industrial effluents, and marine pollution are universal in nature. Man is being unceasingly divulged to a large number of inorganic elements in a great variety of chemical forms and when they enter the human body they can cause toxicity effects resulting in deterioration of man general health. Knowledge of base line data of elemental compositions in fruits and vegetables is important to manage dietary adequacy of the population. In Malaysia, no systematic study on the dietary adequacy of essential heavy elements through fruits and vegetables has been published. The purpose of the present study is to determine the concentration of essential elements in fruits and

vegetables and to extrapolate the data for the dietary adequacy and regional dietary standards.

Instrumental Neutron Activation Analysis (INAA), Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were employed in this study to determine the major elements (K, Mg, Ca) and heavy metals (Fe, Zn, Cu, Mn, Al, Co, Se, Ni, As, Hg, Pb, Cd, Cs, Th, Cr, La) of 14 types of fruits and 11types of vegetables planted in Malaysian. Neutron irradiation and counting were performed using 500 kW of 1.1 MW TRIGA Mark at the Malaysian Nuclear Agency's research reactor. Sample powder was irradiated with thermal neutrons at flux average of $\phi = 2.03\times10^{12}$ $n.cm^{-2}.s^{-1}$ and the analysis was carried out using a hyper-pure germanium (HPGe) detector, multichannel analyzer module and Gamma Vision software. Biological standard materials (NIST-Tomato Leaves 1537a) and soil standard materials (IAEA-SOIL-7) were used as reference materials in the INNA technique. In ICP-MS, the elements of solution sample were identified by their mass-to-charge ratio (*m/e*) and the intensity of a specific peak in the mass spectrum is proportional to the amount of that element in the sample. In AAS, the solution sample was atomized before allowing light to pass and produced a line absorption spectrum, characteristics of the particular elements in the fruits and vegetables. No biological standard materials are needed in ICP-MS and AAS techniques. Samples were collected from a number of fresh markets at the centre of Kuala Lumpur, the capital of Malaysia and transported to the laboratory within one day to prepare the final samples for INAA, ICP-MS and AAS techniques.

The results of INAA, ICP-MS and AAS analyses, we found that there is a variation in the amount of each element for Malaysian fruits and vegetables. For the major elements (K, Mg, Ca), K concentrations in fruits were from 10,615±500 ppm (Jasopine pineapple) to 33,353±600 ppm (melon) and from 9,749±1000 ppm (egg-plant) to 51,196±900 ppm (red spinach) in vegetables. Mg concentrations in fruits were from 680±30 ppm (Morise pineapple) to 5,543±400 ppm (red banana) and from 690±140 ppm (carrot) to 3,852±500 ppm (cucumber) in vegetables.Ca concentrations were from1,064±127 ppm (baby banana) to 6,888±800 ppm (durian) in fruits and from 1100±130 ppm (chili) to 8,000±900 ppm (green bean) in vegetables.

For the heavy metal elements in fruits Mn concentration ranged from 12.0±0.5 ppm (Morise pineapple) to 69±1 ppm (Max banana), Fe concentration from 23.4±2.8 (papaya) to 126±15 ppm (watermelon), and Zn concentration from 19±2 ppm (max banana) to 168±20 ppm (pisang banana). While for the heavy metal elements in vegetables, Mn concentration ranged from 32.0±0.9 ppm (carrot) to 316±16 ppm (spinach), Fe concentration from 58±3 (pumpkin) to 470±56 ppm (spinach), and Zn concentration from 26±3ppm (pumpkin) to 312±37 ppm (spinach).

The percentage intake of all elements was calculated for the Recommended Dietary Allowance (RDA) values for Malaysian fruits and vegetables per 100 g of eatable section. The highest percentage intakes of elements are for K, Mg, Ca, Mn, Zn, Cu, Ni, Al, and Fe, which can be achieved from eating Malaysian fruits and vegetables. Co in spinach and star fruit were found to be the highest percentage intake of vegetables and fruits. Based on this result, spinach and star fruit can be a good source of Co, respectively each vegetable and fruit with 35% and 5% supply of this element to the recommended value of Co in the form of vitamin B_{12}.

An interesting point is that; the mean range of Pb, Hg, and Cd is lower than the tolerable upper intake level (UL), and some of the other elements such as Cr, Cs, and Se, showed near the range of UL for Malaysian fruits and vegetables, for example, Cr in durian, guava, papaya, cabbage, chili, chili padi, spinach, and red spinach, and Cs and Se, in durian and carrot respectively.

The statistical dependence between concentrations of element presents in fruits and vegetables and between types of fruits and vegetables were determined using the cluster analysis. According to the cluster analysis, the results revealed similarity in two or more than two of different fruits or vegetables, dose not mean the same affection on nutrition health.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KOMPOSISI UNSUR BUAH-BUAHAN DAN SAYUR OLEH INAA, AAS, DAN ICP-MS

Oleh

Mohammad Ali Shafaei

Mei 2012

Pengerusi : Profesor Elias Bin Saion, PhD

Faculti: Sains

Pertumbuhan perindustrian telah memberi kemajuan pesat kepada taraf hidup dan keselesaan umat manusia, tetapi telah menyebabkan ancaman pencemaran alam sekitar. Isu-isu seperti toksikologi kimia, hujan asid, kesan rumah hijau, penipisan ozon, efluen industri dan pencemarah hidupan laut adalah bersifat universal sekarang ini. Manusia sentiasa terdedah kepada sejumlah besar unsur-unsur tak organic dalam pelbagai bentuk kimia dan apabila bahan ini memasuki tubuh manusia boleh menyebabkan kesan toksik dan menjejaskan kesihatan manusia. Pengetahuan tentang data garis asas komposisi unsur dalam buah-buahan dan sayur-sayuran adalah penting untuk mengurus kecukupan diet kepada populasi rakyat Malaysia. Sehingga ini tiada kajian sistematik terhadap kecukupan diet unsur-unsur berat yang penting terdapat dalam buah-buahan dan sayur-sayuran telah diterbitkan. Tujuan kajian ini adalah untuk menentukan kepekatan unsur-unsur penting dalam

buah-buahan dan sayur-sayuran dan membuat penentuan data untuk kecukupan diet dan piawaian pemakanan.

Analisis Pengaktifan Neutron Instrumen (INAA), Spektroskopi Penyerapan Atom (AAS) dan Spektroskopi Jisim Induktif Gandingan Plasma (ICP-MS) telah digunakan dalam kajian ini untuk menentukan unsur-unsur utama (K, Mg, dan Ca) dan logam berat (fe, Zn, Cu, Mn, Al, Co, Se, Ni, As, Hg, Pb, Cd, Th, Cr dan La) dalam 14 jenis buah-buahan dan 11 jenis sayur-sayuran yang ditanam di Malaysia. Penyinaran neutron dan pengiraan dilakukan menggunakan 500 kW daripada reactor penyelidikan 1.1 MW TRIGA Mark di Agensi Nuklear Malaysia. Serbuk sampel didedahkan kepada fluks neutron purata keratin rentas G = 2.03 x 10^{12} n/cm^2. s dan analisis telah dijalankan dalam menggunakan pengesan hiper-tulin germanium (HPGe), penganilisis modul berbilangan saluran dan perisian Gamma Vision. Bahan biologi standard (NIST-Daun Tomato 1537a) dan bahan tanah standard (IAEA-Tanah 7) telah digunakan sebagai bahan rujukan dalam teknik INAA. Dalam kaedah ICP-MS unsur-unsur dikenal pasti dengan cara nisbah (e/m) dan keamatan puncak spectrum jisim adalah berkarar kepada jumlah unsur yang terdapat dalam sampel. Dalam kaedah AAS sampel larutan dijadikan atom terlebih dahulu sebelum membenarkan cahaya menembusi dan menghasilkan spektrum penyerapan garis cirian unsur tertentu dalam buah-buahan dan sayur-sayuran. Tiada bahan biologi piawai diperlukan dalam teknik ICP-MS dan AAS. Semua sampel buah-buahan dan sayur-sayuran dikumpulkan daripada beberapa pasaraya di tengah-tengah Kuala Lumpur, ibukota Malaysia dan dibawa ke makmal dalam tempoh satu hari untuk penyediaan sampel teknik INAA, ICP-MS dan AAS.

Daripada keputusan analisis, kami mendapati bahawa terdapat perubahan dalam jumlah kepekatan setiap unsur untuk semua buah-buahan dan sayur-sayuran. Bagi kepekatan unsur-unsur utama (K, Mg dan Ca), kepekatan K dalam buah-buahan adalah 10,615±500 ppm (nanas Jasopine) kepada 33,353±600 ppm (tembikai) dan dalam sayur-sayuran adalah daripada 9,749±1,000 (terung) kepada 51,196±900 ppm (bayam merah). Kepekatan Mg dalam buah-buahan adalah daripada 680±30 ppm (nanas Morise) kepada 5,543±400 ppm dan daripada 690±140 ppm (lobak merah) kepada 3,852±500 ppm (timun) dalam sayuran-sayuran. Kepekatan Ca daripada 1,064±127 ppm (pisang) kepada 6,888±800 ppm (durian) dalam buah-buahan dan daripada 1100±130 ppm (cili) kepada 8,000±900 ppm (kacang hijau) dalam sayur-sayuran.

Sebaliknya kepekatan unsur-unsur logam berat dalam buah-buahan adalah antara 12.0±0.5 ppm (nanas Morise) dan 69±1 ppm (pisang) untuk Mn, antara 23.4±2.8 ppm (kepaya) dan 126±15 (tembikai) untuk Fe dan antara 19±2 ppm (pisang) dan 168±20 ppm (pisang) untuk Zn. Kepekatan unsur-unsur logam berat dalam sayur-sayuran adalah antara 32.0±0.9 ppm (lobak merah) dan 316±16 ppm (bayam) untuk Mn, antara 58±3 ppm (labu) dan 470±56 ppm (bayam) untuk Fe dan antara 26±1 ppm (labu) dan 312±37 ppm (bayam) untuk Zn.

Pengambilan peratusan semua unsur telah dikira bagi elaun permakanan yang disyorkan untuk buah-buahan dan sayor-sayoran Malaysia bagi setiap 100 g bahagian yang dapat dimakan. Pengambilan puratus tertinggi adalah untuk elemen K, Mg, Ca, Mn, Zn, Cu, Ni, Al, dan Fe yang boleh dicapai dengan memakan buah-buahan dan sayur-sayuran Malaysia. Kepekatan Co dalam bayam dan belimbing merupakan peratusan tertinggi pengambilan buah-buahan dan sayur-sayuran Malaysia. Berdasarkan keputusan ini bayam dan belimbing boleh menjadi satu sumber Co yang baik dengan masing-masing membekalkan 35% dan 5% nilai Co yang disyorkan dalam bentuk vitamin B_{12}.

Suatu yang menarik adalah julat min bagi Pb, Hg, dan Cd adalah lebih rendah daripada pengambilan tahap atas (UL) dan beberapa unsur lain seperti Cr, Cs, dan Se memunjukkan menghampiri julat UL buah-buahan dan sayur-ayuran, contohnya durian, kepaya, kobis, lada, cili padi, bayam dan bayam merah, dan Cs dan Se masing-masing dalam durian dan lobak merah.

Pergantungan statistik antara kepekatan unsur yang hadir dalam buah-buahan dan sayur-sayuran dan antara jenis buah-buahan dan sayur-sayuran telah ditentukan dengan menggunakan kaedah klompok. Menurut analisis kluster, keputusan menunjukkan bahawa kesamaan antara dua atau lebih buah-buahan atau sayur-sayuran tidak menunjukkan kecenderungan yang sama terhadap nutrasi pemakanan kesihatan.

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APPROVAL SHEETS

This thesis was submitted to the Senate of University Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of philosophy. The members of the Supervisory Committee were as follows:

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I certify that a Thesis Examination Committee has met on 7th May 2012 to conduct the final examination of MOHAMMAD ALI SHAFAEI on his thesis entitled "**Elemental composition of fruits and vegetables using INAA, ICP-MS, and AAS**" in accordance with the Universities and University colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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DECLARATION

I declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently submitted for any other degree at UPM or other institutions.

Mohammad Ali Shafaei

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