QUANTITATIVE AND CHEMOMETRIC STUDY OF PATTERNS, DISTRIBUTIONS AND HEALTH STATUS OF CHROMIUM, COBALT, NICKEL AND MOLYBDENUM IN SELECTED MALAYSIAN DISHES

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Abstract
Data about dietary mineral elements suggest that foods have potential to play positive roles in a number of mineral deficiency cases. Mineral malnutrition is said to account for 11 per cent of the global burden of disease. These mineral elements consumed in foods have implications on degree of toxicity, health risk and safety of the foods as well as to the individuals eating them. Essential micro-elements such as Co, Cr, Ni and Mo have dual health effects. They play vital health biochemical roles. However, their presences above the upper limit or regulated range in foods are toxic and detrimental. These elements were determined by in selected Malaysian dishes in Skudai area of Johor Bahru using ICP-MS. The all-serving-units-inclusive samples were oven dried until constant weights were obtained. Wet acid digestion was carried out with nitric acid and hydrogen peroxide before instrumental determination. The values of the elements were in the ranges of chromium (1.5-80.8), cobalt (0.5-21.7), molybdenum (1.1-39.4) and nickel (5.6-341.5) µg per average serving dish. Both cluster and the principal component analysis show the existence of some exceptional foods in the list like chapatti kima with optimum element content. Overall results showed the concentrations of the essential micro elements in the dishes are significant and safe within the limit of Dietary Allowance Values.

Keywords: Foods, malnutrition, safety, upper limit, Dietary Allowance, all-serving-units-inclusive

Introduction
Foods are important as nourishments and nutritive chemical substances in the body. However, it is possible to find some foods to be harmful to the body on the account of their contents. Some mineral elements play vital roles in promoting good health when present in foods. These health active elements are called essential major and trace elements. Some trace elements are essential for health. They could also be harmful depending on their degree of presence in foods. Notable among the broad list of essential trace elements are chromium, cobalt, nickel and molybdenum (Namik & Yavuz, 2006). These elements function in the varied body organs as regulators and body health maintainer. Essential elements are also known to function in synergy with other food classes including carbohydrates, fats, proteins and vitamins (Salau & Hasan, 2009). This important role played by these essential elements can be marred in excessive intake or accumulated presence (Tuzen, 2009).

Chromium can be sourced from vegetable or plant products as it constitutes part of plant tissue in low concentration. However, most foods of plant origin like white flour and sugar that are refined have Cr deficiency (Namik & Yavuz, 2006; Tuormaa, 2000). This reason accounts for why most western diets lack these essential elements. During refining process, the element gets discarded in the food (Namik & Yavuz, 2006; Tuormaa, 2000). Chromium is important in stimulating the action of insulin which is the major player hormone in the metabolism of carbohydrate (normalising sugar level against diabetes), lipid (controlling ischemic heart disease) and protein (fertility and fetal growth). Chromium as environmental contaminant can be traced waste from industrial processes such as from electroplating, heat exchange inhibitors of corrosion, urban sewage, tanning processing and effluents. When chromium intake is in excess, notably in its Cr (VI) state, there is risk of lung and possibly gastrointestinal cancers (Cabrera-Vique *et al*., 1997). Chromium can be sourced from Bread, whole grains, meat, cereals, potatoes and fresh vegetables.

Cobalt is an essential element which is known for its even distribution across tissues and organs of the body. Bones, kidney and livers are the organs that contain substantial amount of cobalt (Namik & Yavuz, 2006). Its important role includes participation in the formation of red blood cell. Cobalt also functions as active constituents of vitamin B12 which is relevant in nerve functioning (Mohammed and Lamand, 1986; Henry, 1995). The hazardous effect on health is the dust attack on the respiratory tract organ in the lung parenchyma (Lison, 1996). The major natural source of cobalt is food of animal origin like meat, fish and egg. Cobalt toxicity could arise from its excess or environmental contamination. Industrially, dust of cobalt metal from its powder or alloy production processes.

Nickel is said to be possibly essential. This is in view of the observable metabolic abnormality in liver as a result of nickel deficiencies (Nielsen & Sandstead, 1974; Nielsen, 2011). Studies have also revealed that nickel deficit in humans have caused reproductive function defects (Cheah & Yang, 2011). Nickel is a natural constituent of plants and some micro-organism enzymes. They are carbon monoxide dehydrogenase, hydrogenase, methylcoenzyme M reductase and urease. Intake of Nickel is majorly from bread cereal and beverages. Foods contamination that may lead to excess nickel can be through leaching of nickel containing vessels like stainless steel flour mills. Hardening of oil in catalytic hydrogenation may also introduce nickel to foods (Cempel & Nikel, 2006). The adverse health effect of nickel toxicity include: lung fibrosis, skin allergies and the cancer of the respiratory tract (Cempel & Nikel, 2006; Gawkrodger et al., 1986).

Molybdenum is usually found as metalloenzyme of micro-organism of animals and plants. Molybdenum is essential in diets because it potentiates many enzymes functions and promotes cell processes (Mendel, 2005). Molybdenum can be sourced from green vegetable, cereals, milk, bread, kidney, liver, legumes and beans. Environmental toxicity of elevated molybdenum prevalence can be conspicuous from vegetables or crops grown from mineralized granite soil. This environment also affects livestock as well as human consuming them (Namik & Yavuz, 2006). Molybdenum toxicity have been known to lead to considerable damage to adrenals, kidney, liver and spleen (Vyskocil & Viau, 1999).

Chemometrics is a tool employed to interpret, analyze and graphically present complex multivariate data. Its use in food chemistry has assisted in obtaining better information about composition of a food product as well as its physical and sensory properties. The routine in chemometrics is selection of data, construction of suitable models and adaptation of the model to give solution to complex data interpretation (Munck et al., 1998) Unsupervised pattern recognition techniques of chemometrics such as the Principal Component Analysis (PCA) and Cluster Analysis (CA) are much revealing in terms of groupings and close neighbourhood of the food sample respectively. Trace elements analysis with chemometrics has been extensively applied on varying category of foods including tea (Marcosa et al., 1998; Moreda-Pin˜eiro *et al*., 2001) honey (Chudzinska & Baralkiewicz, 2010; Chudzinska & Baralkiewicz, 2011) and infant formulae (Sola-Larra˜naga & Navarro-Blasco, 2006).

This study aims at investigating selected element content in the commonly consumed Malaysian local foods. The foods are analysed in the form of all-serving-units-inclusive as they all include the soups and stews served along with the food dishes. This is the table-ready mode by which the foods are eaten, hence, assessing the foods vulnerability or otherwise to adverse effect on consumer health. This study also examines, quantitatively and qualitatively, the correlations and distribution patterns of Cr, Co, Ni and Mo trace elements across the foods relative to health safety of consumers. The trace element content datasets were subjected to pair-wise correlation, principal component and hierarchical cluster analyses.

Materials and Method

Sample Collection and Treatment

Samples of 21 selected Malaysian food dishes (Table 4 and 5) were chosen for study in Skudai, Johor Bahru Tengah Municipal Council of Malaysia. The all-serving-units-inclusive samples were obtained from three separate well patronised restaurants. The average weight of the serving dishes were recorded. All selected dishes were all-serving-units-inclusive as they are inclusive of the soups and stews served along with the food dishes. The all-serving-units-inclusive dishes were taken to the laboratory in their take-away polymer container and leak proof nylon bags for soups. The fresh food dishes obtained from three locations were mixed and weighed in the laboratory. The mixed foods were then put in large crucible that has been previously cleaned. These crucibles were then transferred to the oven. Temperature of 105 – 1100 C of the oven was maintained for 48 hours to ensure that a constant dry weight of the samples was reached. The dry samples are then homogenised in a plastic chambered and stainless steel cutter bender.

Ashing of Samples and Instrumental Determination

A mixture of nitric acid and hydrogen peroxide were used for digestion of the dried foods. Moderate temperature of 80 – 900 C was steadily maintained to prevent possible loss of analytes of interests (Cr, Co, Ni and Mo). These elements are prone to possible escape at high temperature treatment (Namik & Yavuz, 2006). The pure solutions of H_2O_2 (40%) and concentrated HNO_3 (65 %,) are grade AR preparation of QrëCTM laboratory. The de-ionised water was obtained using Milli-DITM Millipore instrument. Heating was done on hot plate in the fume cupboard. Table 1 presents the adopted digested procedure for all the samples. Although, the sample digests were almost clear and devoid of particles, ADVANTEC 125mm filter paper was used to filter, in order to re-assure particle free sample digest. In addition, the syringe micro-filter (0.2 and 0.45 µm pore sizes), was used to re-filter the sample digest to ensure it is particles free so as to protect the ICP-MS instrument from damage. The PerkinElmer SCIEX ICP-Mass spectrometer, ELAN 610 with WinLab32 computer software was used to determine the Cr, Co, Ni and Mo. Table 3, presents the operating parameters for the ICP-MS.

Table 1: Adopted wet digestion steps I – V

Digestion Steps	I	IIa	IIb	III	IV	V
+De-ionised H_2O cm^3)	Nil	Nil		Nil	30	30
+Conc. HNO_3 (cm^3)	10	5		10	5	10
+Conc. H_2O_2 (cm^3)	Nil	2		4	2	2
Heat Control	Nil	Low	Medium	Medium	Medium	High
Initial Observation	Swollen, yellow residue	Yellow solution	Blackish residue	Dark viscous solution	Brownish solution	Brownish/ Yellow solution
Time (min.) / Termination Point Observation	Overnight	20/ Nil	30/ till Nearly dry	30/ till nearly dry	30/ till nearly dry	20 / till nearly ¼ of initial volume

Table 2: Optimized ICP-MS operating conditions

Parameters and Operating Conditions

	Operational modes		Instrument mode		Plasma mode
Replicates:	3	Sample update rate:	1.0 $mLmin^{-1}$	Radiofrequency generator	40 MHz
Peak processing mode:	Average	Sample read delay:	30 s	Plasma air flow rate	15 $Lmin^{-1}$
Signal profile processing mode:	Average	Spray chamber:	Cyclonic	Nebulizer air flow rate	0.96 $Lmin^{-1}$
Detector mode:	Dual	Interface:	Pt cones	Auxiliary air flow rate	1.05 $Lmin^{-1}$
Scanning mode:	Peak hopping	Sample cone	Nickel, 1.00mm orifice diameter	Blank solution	De-ionized water (Milli-DI™
Resolution:	High	Blank solution	De-ionized water (Milli-DI™,		
Dead time:	35 ns	Operating environment	25-30 ^{0}C		
Dwell time:	100 ms				
Integration time:	900 ms	Selected analytes' masses (m/v): Cr (52); Co (59); Mo (90); Ni (58)			

Quality Control

Samples tagged QC (quality control) was used as means of re-assuring the efficiency of the machine in determining the analytes of interest. The QC samples were taken after every ten readings. One of the samples previously measured is repeated again to see if there will be significant value difference from what was initially read. If there is a marked difference in the values read, the conditions are refreshed and the standard solutions for recalibrations are reset. The correlation coefficients of $r^2 > 0.995$ are consistently ensured before constructing the calibration plots. Quality assurance practice based on analytical validation procedure as in NMLK (NMLK Procedure No. 4, 1996) was followed. In steps similar to (Salau & Hasan, 2009), accuracy was validated with the use of the certified reference materials SRM 1570a of spinach leaves trace elements purchased from the U. S. National Institute of Standards and Technology (NIST). The recovery obtained was between 73.2- 102.4 %.

Chemometrics and Statistical Analysis

Statistical tools employed include the mean, standard deviation, relative standard deviation, charts and plots and correlation matrix were performed by means of Excel spread sheet statistical data analysis for windows. Chemometrics software package, The Math works Incorporations' MATLAB version 4.0 for windows and the Eigenvectors Research Incorporations' PLS_ Toolbox version 6.2 were used for PCA and CA.

Results and Discussion

Distribution of trace elements in selected foods

The trace element concentrations across foods are shown in Figure 1 and statistically described in Table 3. The positive values of the skewness and kurtosis are indications of elements distribution across foods are not the normal or guassian distribution. Cr and Co elements distribution among foods showed high peaked kurtosis values. This suggests that their presences are much restricted to certain foods. Most other foods have very little value of them. Figure 1 also illustrate the foods' general scanty contents for Cr with high peaks in *Chappati kima, Teh terik and Sambal sotong* respectively in magnitude order. The high positive skewness of Co on Table 3, is illustrated in Figure 1 showing asymmetric Co distribution. The Co distribution across foods tailed prominently towards left. Co has highest concentration (µg/g) in *Roti jalah* with chicken and chicken curry. The Standard deviation values are substantial in value indicating the fact that foods varied significantly and each is unique in content. The same reason of food content diversity can be adduced for the wide range between minimum and maximum values. Concentrations of Cr, Co, Mo and Ni are least in *Serunding, Beef rending with nasi, Serunding and Nasi gorenge kampung* foods. The distribution of Mo and Ni are maximum in *sayur lodeh* and *Nasi biryani*.

Table 3: Descriptive Statistics of the element content of food

	Cr	Co	Mo	Ni
Mean	0.20	0.06	0.10	0.61
Std. Dev.	0.24	0.04	0.08	0.32
Kurtosis	6.45	11.29	1.71	1.45
Skewness	2.61	3.07	1.46	1.42
Minimum	0.06	0.02	0.02	0.29
Maximum	0.98	0.22	0.32	1.38

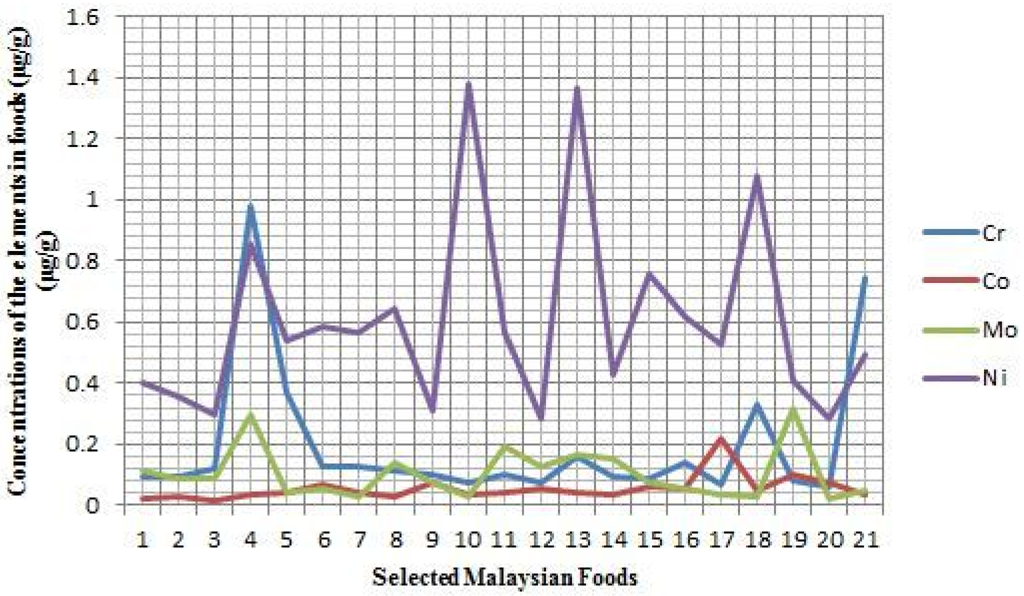

Figure 1: Concentration of elements across selected foods in Malaysia

Trace Elements Content of Foods

The results illustrated in Figure 1, shows that the selected foods contained the trace elements of interest. These quantities compared well with elements studied in previous literatures. The values of Cr (0.09), Co (0.03) and Ni (0.36) in *Ayam percik* (chicken food) in this study, as shown in Figure 1, is close to the study equivalent on chickens in Turkey (Uluozlu *et al.,* 2009). The values are close or within the range (Cr: 0.01-0.72; Co: 0.01 - 0.02; Ni: 0.01-2.08 µg/g) obtained by (Uluozlu *et al.,* 2009). The slightly higher value in Co in this study is probably due to the analysis of the food which is inclusive of the soup and sauces served along with the food. These other food inclusions could have contributed more Co.

Raw fishes separately studied by (Tuzen, 2009; Uluozlu *et al.,* 2007) in Aegean and Black seas in Turkey reported values of Cr (0.63–1.74; 0.95-1.98 µg/g) and Nickel (1.41-3.60; 1.92-5.68 µg/g). The equivalent fish based food: *Fish head curry* has content close to the previous study. The slightly short fall in the value could be attributed partly to cooked nature of the food (Orhevba , 2011; Naseri *et al.,* 2014) partly to the fact that the food is only head part of fish and that other food inclusions may not have contributed the elements.
Teh tarik is a common tea food in Malaysian restaurants. The Cr content (0.74 µg/g) of *Teh tarik* falls within the ranges observed on the previous study of Norwegian and Polish tea infusions (Kronborg, 2013). In a baseline study of trace elements in polished rice from South Korea (Jung *et al.,* 2005), the value of Cr (0.068-0.127 µg/g) with the value range (0.075-0.157 µg/g) of rice based Malaysian foods. The rice based foods include: *Nasi Beriani, Nasi Berlauk, Nasi Goreng Kampung, Nasi Kerabu, Nasi Lemak and Nasi Paprik.* However, the values of the cobalt and nickel in this study are slightly higher probably due to other serving included foods. In another study of cooked rice brands carried out in Iranian market (Naseri *et al.,* 2014), Cr (0.083-0.217µg/g), Co (0.003-0.027µg/g) and Ni (0.069-0.241µg/g) values compares positively with the present studies rice based dishes.

The Content of Food Dishes and Dietary Allowance Compliance

The sampled foods are in the form of served dishes. This is the manner they are served by the local restaurants as well as the form people eat them. Table 5 shows the quantity of each of the trace elements per average dish size. The extent of compliance of the studied foods with the recommended dietary allowance is presented on Table 6. The dietary allowances are computed within the values of various dietary reference data. These data are AMDR (Acceptable Macronutrient Distribution Range), AI (Adequate Intake), RDA (Recommended Dietary Allowance), RNI (Recommended Nutrient Intake) and UL (Upper Limit). Their documented forms were sourced from Dietary Guidelines for Americans (Dietary Guidelines for Americans, 2005) and Malaysians (Malaysian Dietary Guidelines, 2010) as well food research authorities (Acu-Cell, 2014; Hellwig *et al.*, 2006).

Table 4: Element content of foods

L	Dishes	Chromium			Cobalt			Molybdenum			Nickel		
		M	S	RSD	M		RSD	M	S	RSD	M	S	RSD
1	*Apam Balik*	5.1	0.7	13.4	1.2	0.1	11.5	6.3	0.1	2.1	21.7	0.01	0.02
2	*Ayam Percik*	1.5	0.5	31.7	0.5	0.1	16.6	1.3	0.2	11.9	5.6	0.9	15.3
3	*Beef Rendang with Nasi*	17.6	2.6	14.7	2.4	0.4	15.2	13.3	0.4	2.8	44.1	0.7	1.7
4	*Chapati Kima*	80.8	21.1	26.1	3.1	0.8	26.5	24.8	0.4	1.7	70.4	2.3	3.2
5	*Fish Head Curry*	28.4	8.1	28.5	3.1	0.6	18.6	3.3	0.4	11.6	41.6	2.1	5.1
6	*Kangkung Belacan*	5.9	0.3	5.8	3.2	0.1	3.5	2.4	0.1	4.9	27.0	0.5	1.7
7	*Keropok Lekor*	5.5	0.2	4.0	1.7	0.0	0.3	1.1	0.1	10.0	25.1	0.4	1.8
8	*Ketupat*	5.2	0.1	2.2	1.4	0.1	8.0	6.4	0.2	3.6	29.4	1.0	3.5
9	*Nasi Beriani*	18.9	4.3	23.0	8.3	0.6	7.4	7.4	1.2	16.7	341.1	14.9	4.4
10	*Nasi Berlauk*	21.2	2.6	12.2	9.0	0.5	5.8	39.4	1.5	3.9	116.8	1.0	0.9
11	*Nasi Goreng Kampung*	13.4	1.3	9.9	10.2	0.4	4.3	22.1	0.4	2.0	50.6	1.3	2.6
12	*Nasi Kerabu*	28.5	3.2	11.2	7.4	0.9	12.3	30.3	0.9	3.0	249.2	3.2	1.3
13	*Nasi Lemak*	11.2	0.6	5.5	4.7	0.3	6.6	18.6	0.9	5.0	52.6	0.3	0.6
14	*Nasi Paprik*	16.5	0.5	2.9	11.8	0.5	4.1	14.8	1.0	6.6	146.7	1.5	1.0
15	*Onde-Onde*	3.2	0.4	13.9	8.0	0.2	2.8	2.1	0.2	10.3	17.1	0.3	1.9
16	*Roti Canai*	10.4	2.4	23.2	4.0	0.4	9.3	4.2	0.4	8.9	46.0	5.2	11.3
17	*Roti Jala with Chicken curry*	6.5	1.0	15.2	21.7	0.7	3.4	3.6	0.2	6.8	52.1	0.5	0.9
18	*Sambal sotong*	41.4	1.3	3.0	6.0	0.3	5.2	3.9	0.3	7.9	135.1	4.1	3.0
19	*Sayur Lodeh*	3.9	0.2	6.0	4.8	0.2	4.9	15.0	0.1	0.8	19.2	0.5	2.5
20	*Serundig*	2.7	0.1	4.1	3.4	0.1	3.3	1.1	0.1	10.2	12.8	0.6	4.4
21	*Teh Tarik*	35.0	3.4	9.8	1.7	0.4	21.2	2.4	0.5	19.7	23.4	1.3	5.6

M = mean content (μg per dish) ; S = Standard Deviation; RSD (%) = Relative Standard Deviation, L = label

Table 5: Compliance of Foods Content with Dietary Allowance

L	Dishes	Chromium			Cobalt			Molybdenum			Nickel		
		DA low	DA high	UL	DA low	DA high	UL	DA low	DA high	UL	DA low	DA high	UL
1	*Apam Balik*	20.2	14.4	N/A	11.8	5.9	0.5	25.3	15.8	0.3	7.2	3.1	2.2
2	*Ayam Percik*	5.9	4.2	N/A	4.7	2.3	0.2	5.2	3.3	0.1	1.9	0.8	0.6
3	*Beef Rendang with Nasi*	70.2	50.2	N/A	24.2	12.1	1.0	53.0	33.1	0.7	14.7	6.3	4.4
4	*Chapati Kima*	323.1	230.8	N/A	31.1	15.6	1.2	99.1	62.0	1.2	23.5	10.1	7.0
5	*Fish Head Curry*	113.5	81.1	N/A	31.1	15.5	1.2	13.3	8.3	0.2	13.9	5.9	4.2
6	*Kamgkung Belacan*	23.6	16.8	N/A	32.4	16.2	1.3	9.4	5.9	0.1	9.0	3.9	2.7
7	*Keropok Lekor*	22.0	15.7	N/A	17.5	8.7	0.7	4.4	2.8	0.1	8.4	3.6	2.5
8	*Ketupat*	20.6	14.7	N/A	14.3	7.1	0.6	25.5	16.0	0.3	9.8	4.2	2.9
9	*Nasi Beriani*	75.4	53.9	N/A	83.5	41.7	3.3	29.6	18.5	0.4	113.7	48.7	34.1
10	*Nasi Berlauk*	84.8	60.6	N/A	89.6	44.8	3.6	157.5	98.4	2.0	38.9	16.7	11.7
11	*Nasi Goreng Kampung*	53.5	38.2	N/A	101.9	51.0	4.1	88.2	55.1	1.1	16.9	7.2	5.1
12	*Nasi Kerabu*	114.1	81.5	N/A	74.3	37.1	3.0	121.2	75.8	1.5	83.1	35.6	24.9
13	*Nasi Lemak*	44.7	32.0	N/A	46.8	23.4	1.9	74.3	46.5	0.9	17.5	7.5	5.3
14	*Nasi Paprik*	66.0	47.2	N/A	117.9	58.9	4.7	59.3	37.1	0.7	48.9	21.0	14.7
15	*Onde-Onde*	12.7	9.1	N/A	79.9	39.9	3.2	8.5	5.3	0.1	5.7	2.4	1.7
16	*Roti Canai*	41.8	29.8	N/A	40.1	20.1	1.6	16.8	10.5	0.2	15.3	6.6	4.6
17	*Roti Jala with Chicken curry*	26.0	18.5	N/A	216.7	108.3	8.7	14.6	9.1	0.2	17.4	7.4	5.2
18	*Sambal sotong*	165.6	118.3	N/A	60.2	30.1	2.4	15.8	9.9	0.2	45.0	19.3	13.5
19	*Sayur Lodeh*	15.6	11.2	N/A	48.1	24.1	1.9	60.1	37.6	0.8	6.4	2.7	1.9
20	*Serunding*	10.9	7.8	N/A	33.5	16.8	1.3	4.4	2.7	0.1	4.3	1.8	1.3
21	*Teh Tarik*	140.2	100.1	N/A	16.8	8.4	0.7	9.6	6.0	0.1	7.8	3.3	2.3

RDA = Required Dietary Allowance; UL = Upper Limit; N/A = Not Available Data, L = label

Table 6: Dietary Allowance Table 9-31]

	Cr	Co	Mo	Ni
DA low (µg)	25	10	25	300
DA high (µg)	55	20	40	700
UL (µg)	N/A	250	2000	1000

DA low = Lower Limit Dietary Allowance; UL = Upper Limit; N/A = Not Available Data, L = label

Source: Dietary Guidelines for Americans (2004), Malaysian Dietary Guidelines (2010). ACU-CELL Nutrition (2014).

Table 5 and 6 and Figures 2a and 2b depict the extent to which the studied food could realize the dietary requirements for the essential elements. For the purpose of this study, all the aforementioned dietary reference data apart from UL, are jointly referred to as DA (Dietary Allowance). The UL (Upper Limit) is the upper intake level that body can tolerate. It is a caution intake value and the amount beyond this can be harmful (Kronborg, 2013). All the studied elements have available data for UL except Cr, whose data is yet to be established (Acu-Cell, 2014; Hellwig *et al.,* 2006).

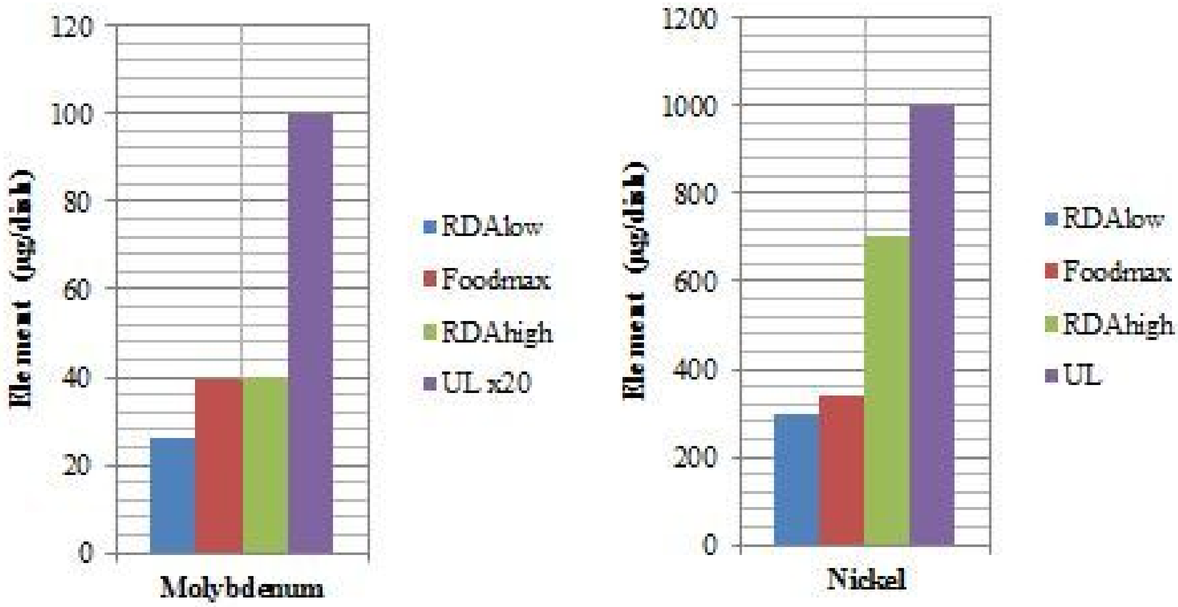

Figure 2b: Mo and Ni in Foods and dietary standards

Generally, it can be observed that there are substantial numbers of foods from which each of the elements can be sourced. Virtually, all the dishes do not accumulate excessive amount above the UL. Chromium elements have good sourcing from *Chapati kima, Sambal sotong* and *Teh tarik*. However, the food Chapati Kima is a food to watch due to the observed 81µg as against the recommended high RDA value of 55µg on Table 6. There is neither an established value that negates the observed value nor a convincing argument that the difference of the two values is significant. More than half of the selected dishes have more than 35% capacity to supply daily Cr needs. The limit of 35% capacity is an assumption by this study for a possibility of three repetitions of same food in a day to make up daily recommended allowance. The food recipe units of *Chapati kima* (flour, eggs and green chillies), *Sambal sotong* (squids, chillies and brown sugars) and *Teh tarik* (milk, brown sugar and drinking water) are good source of chromium (Acu-Cell, 2014)

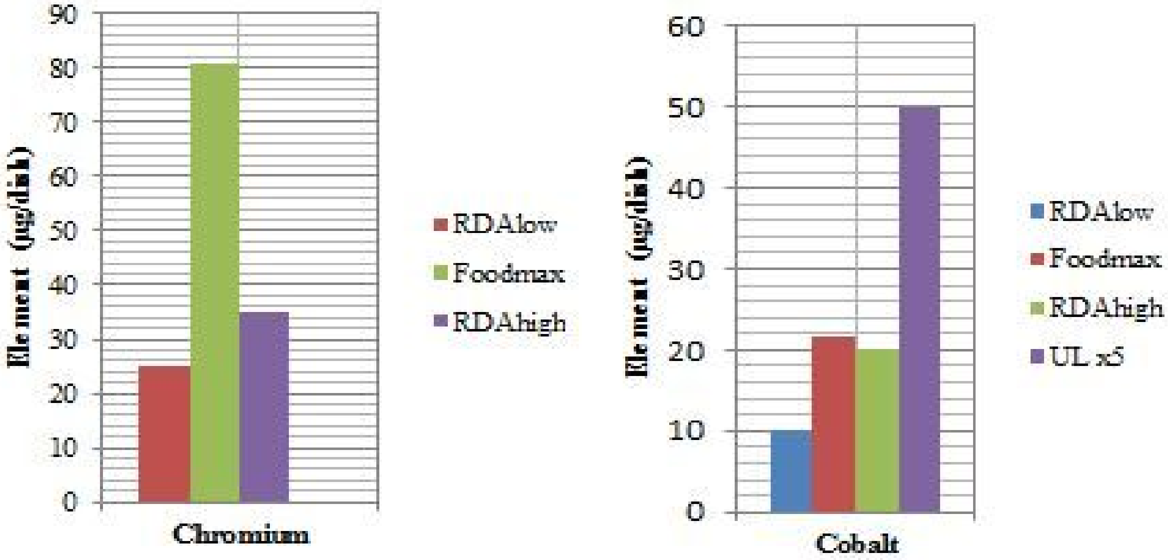

Figure 2a: Cr and Co in Foods and dietary standards

The foods: *Roti jala with chicken and curry*, *Nasi paprika* and *Nasi gorenge kampung* have significant content of cobalt. The meat and vegetable content common to these foods are likely responsible for this (Namik and Yavuz, 2006; Mohammed and Lamand, 1986). Eleven of the studied dishes proved relevant to meet minimal daily dietary needs. Molybdenum has good presence in Nasi berlauk, while, nickel is most prominent in Nasi beriani. Both Mo and Ni are known to have grains as common source (Acu-Cell, 2014; Yahaya Ahmed, 2011). There is a wide gap between the Cr, Co, Mo and Ni contents of the food dishes and the upper limits (UL) set. This suggests the safe and healthy states of the studied food generally.

Unsupervised pattern recognition

Principal Component Analysis (PCA): The studied food data has computational matrix of dimension (21 X 4). It was auto-scaled before applying other PCA procedure. The Ward's method followed (Meloun *et al.,* 1992). Two principal components resulted from the preprocessed data. These two principal components retained the maximum variability of the food samples.

The score plot in Figure 3 and hotelling plot in Figure 4, showed the existence of two major groupings and six exceptional foods (labeled 4, 9, 11, 12, 13 and 17) with *Chapati kimia* labeled as 4, being the most outstanding. The foods are exceptional in the sense that the trace elements contents tend to extreme low or high values. Nasi Beriani labelled as 9 has high Ni but low Mo, Nasi gorenge labelled 11 has very low Ni. The chapatti kima labelled as 4 contains extreme low Co and Ni.

The PCA biplot in figure 5 is a simultaneous loading and score plots. The biplot reveals the correlation of the race elements with food samples. Two major groups: A and B are characterized based the presence of the trace elements. Foods with prominent presence of Cr, Co, Mo and Ni though within permissible limits. The foods in this group are rice (*Nasis*) and flour (*Rotis*) based Malaysian foods. Group B contains foods with very low trace elements contents.

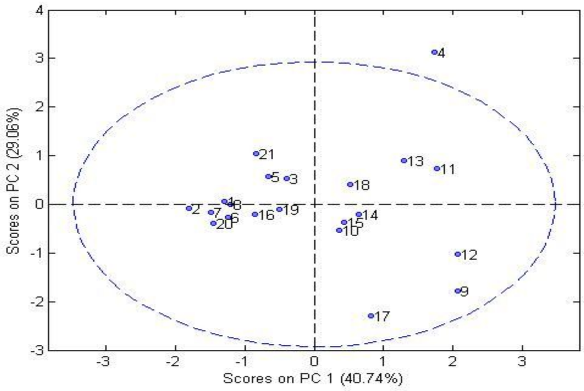

Figure 3: Score plot for dish samples

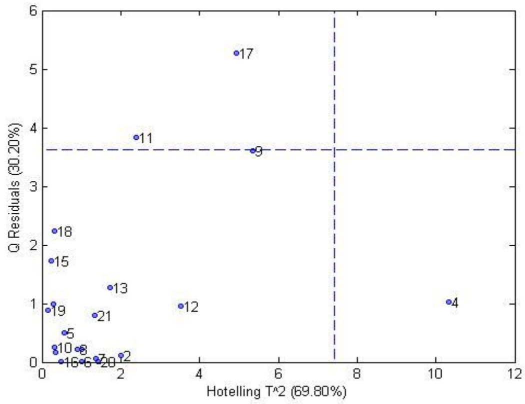

Figure 4: PCA Hotelling T^2 Plot for dish samples

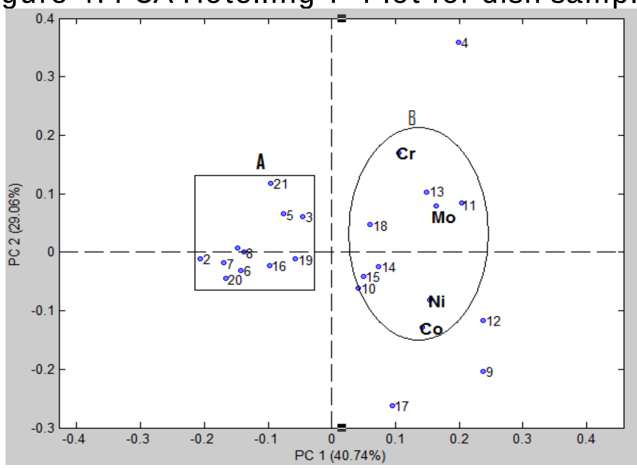

Figure 5: PCA Biplot for dish samples

Cluster Analysis: The similarity and closeness of the foods are illustrated by cluster analysis (Brereton, 2009). Hierarchical Cluster Analysis was performed on the data sets. The output is illustrated in form of dendrogram which is presented in Figure 6. The similarities or closeness of the foods are measured by the variances of the weighted distance between the centres of clusters. The Ward's method was adopted (Meloun *et al.,* 1992). Two major groupings A and B of 11 and 7 membership sizes respectively, can be observed based on the similarity of foods in each grouping. Cluster analysis on the samples reveals information about closely related foods which can be predicted as substitute. The pair of *Apam Balik* (labeled 1) and *Ketupat* (labeled 2) is in closest neighborhood based on variance weighted distance. This suggests substitutability of the foods for each other as they contain similar proportion of the elements.

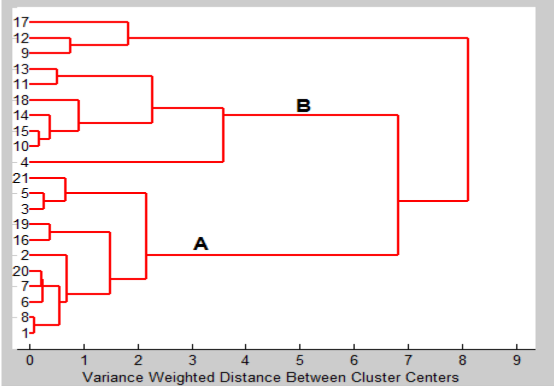

Figure 6: HCA Dendrogram for dish samples

Conclusion

The food dishes studied contain reasonable amount of the essential trace elements (Cr, Co, Mo and Ni). Some of the foods were observed to have significant content of the trace elements to meet the recommended dietary allowance. This level of presence portrayed some of the foods to be relevance in combating mineral malnutrition.

The trace elements in the studied food dishes were found to be far below the standard upper limit (UL) set by health and nutritional authorities. It can therefore be deduced that the foods are generally spared of both excessiveness and the toxicity that usually accompany it. The foods are therefore safe for human consumption.

The chemometrics studies qualitatively revealed that Malaysian foods can be broadly classified into two broad groups: Those with relative presence of trace elements and the hardly present ones. The '*Nasis'* (rice) and '*Rotis*' (Flour) based foods constitute a large number in the group with relative presence of trace elements.

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