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Nutritional Metals in Foods by AAS

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1. Introduction

It is well known that a balanced diet is essential in maintaining good health. Hence, the nutritional value of foods is an important aspect that should be considered especially with respect to metal intake such as iron, calcium, magnesium, potassium, sodium, selenium, manganese, copper, chromium and zinc. Iron being required for the haemoglobin; calcium for relaxing the central nervous system; magnesium to prevent muscle spasms; potassium and sodium for electrolyte balance; selenium has a number of functions including deactivating heavy metals from external exposure; manganese and copper are linked to superoxide dismutase (SOD): chromium stabilizes blood sugar and zinc is important in the healing of wounds.

An overview of the literature will be given of applications of Fame AA together with some references to Graphite Furnace AA to the analyses of foods such as: meat the main source of iron; dairy products, the source of calcium and fruit and vegetables for a range of metals. Comparisons will be given of metal content in these products particularly in meat and dairy products. Of the metals listed above, not all of these will be considered in every product: only where they are the metal of highest concentration. The aim of this chapter is to give a general comparison of the metal content in these products, which will not be exhaustive, particularly, with respect to fruit and vegetables but the ones most commonly consumed. The emphasis is on nutrition and to give the general reader and health professional a concise view of the metal content of these food products. From scientific aspect the methodology for Flame AA is relative straight forward, as is the work up for instrument presentation but there are often extra procedures that are required depending on the matrix that are essential for obtaining a valid result.

Flame Atomic absorption spectroscopy even though it is a well-established technique that was discovered about fifty years ago is still used extensively today for trace metal analyses in industry, commercial laboratories and universities.

2. History of the discovery of flame atomic absorption spectroscopy

The method for the analyses of metals in a wide range of samples from food, agriculture, mining, environmental, pharmaceutical and biochemical industries was made possible by the discovery of a new technique in the early 1950's by Dr. Alan Walsh. Like many scientists before him, he was not in his laboratory when the idea came to him but in his vegetable garden one Sunday morning in 1952. The idea proved successful and was the basis of the

atomic absorption spectrophotometer, an instrument for quantitative chemical analyses of metals (Hannaford 2002) that did not require slow wet chemical procedures. Techtron Pty. Ltd., Melbourne, Australia, manufactured the first instrument based on his design in the mid 1960's. The company was taken over many years later by Varian Australia Inc. and several months ago by Agilent Technologies Pty. Ltd, Melbourne who still manufactures an instrument based on this early technology. (Hannaford 2002)
The scientific importance of Alan's idea was that he realized in his attempt to measure the concentration of metals in solution by spectroscopic means, he had been trying to measure the incorrect parameter. Rather than measuring emission he should have been measuring absorbance. When he mentioned this to his colleague John Willis (CSIRO, Division of Chemical Physics) he said that they had considered this aspect before and that it would not work because of the emitted light at the same wavelength. The reply Alan gave was that this could be overcome by having a chopper to eliminate this emission and to use an amplifier. Several days later Alan measured the absorbance of sodium but his colleague at this time did not appreciate the significance of this major scientific breakthrough that was the basic principle of the instrument (Hannaford 2002) .

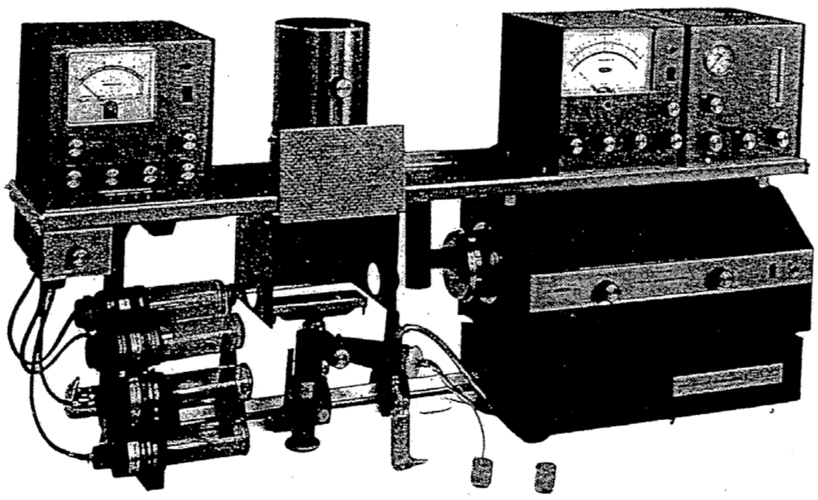

Fig. 1. Photograph of prototype Atomic Absorption Spectrometer build by Dr. Alan Walsh, with permission from Agilent Australia, Mulgrave, Victoria., where the instrument is located.

3. Nutritional significance of minerals in the diet

Minerals are divided into two groups Essential and Trace minerals, which is related to the quantity required and found in the body, the former being present in the largest amounts. These minerals will now be discussed briefly in this order.

3.1 Essential minerals

The essential metals are the macro metals:

- Calcium
- Magnesium
- Potassium
- Sodium

Calcium is responsible for strong bones and teeth and accounts for ninety percent of the calcium in the body whereas the other one percent is circulating in fluids in order to ionise calcium. The metal's function is related to transmitting nerve impulses; contractions of muscles; blood clotting; activation of some enzyme reactions and secretion of hormones Magnesium has many roles including supporting the functioning of the immune system; assists in preventing dental decay by retaining the calcium in tooth enamel; it has an important role in the synthesis of proteins, fat, nucleic acids; glucose metabolism as well as membrane transport system of cells. Magnesium also plays a role in muscle contraction and cell integrity. Potassium and sodium work together in muscle contraction nerve transmission. Sodium is important in muscle contraction and nerve transmission Sodium ions are the main regulators of extra cellular fluid and volume (Whitney and Rofles 2002).

3.2 Trace minerals

These are particularly important for health promotion and prevention of disease. Trace metals being considered in this work are:

- copper,
- chromium,
- iron,
- manganese,
- molybdenum
- selenium
- zinc.

The non-metals also in the group are iodine and fluorine that will not be discussed. Copper has the role of assisting in the formation of haemoglobin, helping to prevent anemia as well as being involved in several enzymes. Chromium function is related to stabilising blood sugar levels with respect to insulin required for release of energy from glucose. Iron is the central metal in the haemoglobin molecule for oxygen transport in the blood and is portion of myoglobin located in muscles. Manganese is one of the co-factors in a number of enzymes as is molybdenum. Selenium has several roles such as regulating the thyroid hormone as well as being part of an enzyme that protects against oxidation (Whitney and Rofles 2002). Selenium has also been reported as assisting in deactivating heavy metals.

3.3 RDI of minerals according to age and gender

The Recommended Daily Intake, RDI of metals is related directly to age, and gender. The requirements for babies,, toddlers,, children , adolescents, and elderly vary with gender and country due to soil type. These requirements are continually being reviewed in the light of more research that is undertaken by food regulating bodies such as Food Standards Australia and New Zealand, FSANZ, United Stated of America, Food and Drug Administration, FDA, and European Authorities to name three such groups. The work done by these bodies includes all food groups in addition to vitamins, minerals: cereals, fat, protein, carbohydrates, sugars and so on, as well as research on different age groups in particular locations in many countries, to assist in maintaining and improving the health of the various groups and the population in general.

Major minerals	Recommended Daily Intake , RDI
Calcium	1000 mg
Magnesium	**350** mg
Potassium	**3500** mg
Sodium	2400 mg
Trace minerals	
Chromium	120 µg
Copper	2 mg
Iron	15 mg
Manganese	5 mg
Molybdenum	75 µg
Selenium	35 µg
Zinc	15 mg

Table 1. The table above represents RDI values recommended by experts and agencies for a normal adult population. http:// lenntech.com/recommended-daly-intake.htm

3.4 Analyses of foods with respect to safety and toxicity

Fresh foods and others are monitored regularly for safety and to be sure that the level of undesirable metals is below the safe limit or not present at all. Similarly, the dietary surveys test for these as well as the nutritional value of the various food groups.

4. Variation of mineral content according to soil and country

According the age of the rocks that contain the minerals and type of rocks and soil with respect to their geological age, the mineral content will vary considerably, as well as different minerals being found in the respective rocks. There can be similar soil types that occur in countries that are not near each other. For example, gold was found in California and in Australia in the mid 1800's when the gold rush took place and prospectors came from many countries to make their fortunes. Soil can vary considerably within a particular region, state, territory or through out a particular country with respect to minerals found in the soil. Soils are studied by agriculturalists and farmers, so they can add certain minerals when they are in low levels in order to increase the yield and quality of crops. Even within a particular paddock or field the soil can vary so farmers need to add fertilizers and minerals appropriately in order to obtain a uniform yield of the crop (Dundas and Pawluk 1977). Hence mineral levels for the countries will vary accordingly to the soils and the additives required for maximum crop yield and the fortification of crops, cereals or grains to ensure that the products manufactured would still give sufficient portion of the RDI to maintain the health of the population . RDI allowances of minerals will essentially be very similar in most countries for the various age and gender groups but in some cases extra fortification of foods will be required where there is a low level of an essential or trace mineral.

5. Metals in meat

The principal source of iron in the diet is mainly from meat, particularly, red meat. Other metals are also important such as calcium, magnesium, sodium and potassium, but are generally in lower amounts. Trace metals include: copper, manganese, zinc and chromium. Metal analyses in meat including beef, pork, poultry and fish will be discussed with some comments on sample preparation and values of the metals obtained in these samples

5.1 Selected metals in some meat

A comprehensive study of the analyses of iron, calcium, magnesium, potassium, sodium, manganese, copper, zinc and manganese in foods including meat was undertaken by Maurer (Maurer 1977) here he compared three extraction methods using HNO_3 or HCl/HNO_3 or dry ashing at 450°C. The main focus of this research was to thoroughly evaluate each of the three extraction procedures for the metals listed on a wide variety of food, to determine the daily consumption per person over given time intervals. Recoveries were also determined for the different extraction methods. Results obtained indicated that extraction with the combined acids was the most suitable procedure for all metals, particularly for copper and zinc when compared with dry ashing, which was markedly, affected by the matrix. Recoveries were high for all metals: in the high nineties except for zinc that was only 87%. A Perkin-Elmer (model 300) instrument was employed where calcium and magnesium were analysed with nitrous oxide/acetylene while air/acetylene was used for the other elements. Siong (Siong, Khor Swan, and Siti Mizura 1989) compared the analysis of iron in meat and other foods using AA and the phenanthroline colorimetric method. The two methods compared well for the foods tested and also gave satisfactory recoveries. Values iron obtained for some meat products are as follows: beef extract 10.66; canned beef liver rendang 4.20; canned chicken curry 2.82; chicken heart 2.05; corned beef 1.67; duck 0.69; roast4ed duck 0.84; canned mutton curry 3.67 where all values are expressed as mg Fe/100 g.

	Cu	**Mn**	**Se**	**Zn**
PIG				
meat	**0.90** ± 0.61	**0.12** ± 0.052	**0.044** ± 0.017	24 ± 11
liver	**9.0** ± 4.0	**3.0** ± 0.52	0.50 ± 0.062	**74** ± 2
kidney	6.1 ± 2.0	1.5 ± 0.24	**1.9** ± 0.35	**22** ± 3.3
CATTLE				
meat	**0.87** ± 0.12	**0.093** ± 0.044	0.030 ± 0.020	**49** ± 18
liver	**39** ± 27	**3.2** ± 0.67	0.030 ± 0.035	40 ± 8.5
kidney	3.7 ± 0.59	1.1 ± 0.24	**0.86** ± 0.28	16 ± 1.5

Table 2. Portion of data extracted from (Jorhem et al. 1989) showing in a horizontal row the concentrations in mg/kg of the four elements per product.

A study was conducted by (Jorhem et al. 1989), on the levels of the trace metals aluminium, chromium, cobalt, copper, manganese, nickel and selenium in the kidney, liver and meat of Swedish cattle and pigs at the slaughter houses and verified using standard reference materials. Data for aluminium and nickel will not be discussed, only the other beneficial

metals. In general, all the samples were prepared for analysis by dry ashing at 450°C with some extra procedures required for some metals before ashing. Copper, manganese and zinc were analysed by Flame AA employing a Vanian AA-6 instrument equipped with a H_2 lamp for background; correction using an air/acetylene flame. The method of standard addition was used for manganese, hydride/generation AAS for selenium whereas chromium and cobalt were analysed by graphite furnace AA.
In Table 2, it can be seen in at a glance, the metal content in meat, liver and kidney from pigs and cattle. From the results shown, it is clear that liver and kidney are good sources of dietary copper. The manganese levels in this study are low and the authors attribute it the method of standard additions used in the AA analyses. Reported data shows the best source of selenium is pig kidney but the results are generally low in Scandinavian due to the soil. Meat products are an excellent source of zinc, especially liver. Data for chromium is not shown but the results indicated that these products are a poor source of this metal in the diet. Cobalt data also is not shown was found to be four times higher in cattle liver than in pig's liver being 0.043 ± 0.028. The authors compared their results with the published literature for the above metals, as well as others, not stated here, for the three parameter in Table 2 for pigs and cattle and found there was good agreement with other countries that included Austria, Australia, Finland, FRG, Italy, Norway, Sweden and USA, however, not all metals studied had data from all of these countries.
Tinggi'group (Tinggi, Reilly, and Patterson 1997) have reported chromium and manganese levels in some meat products. The samples that were anlysed included the following: chicken (cooked); beef steak; ham; lamb chops and sausages. Results obtained are given below:

Meat	**Cr (ng/kg)**	**Mn (mg/kg)**
Chicken (cooked)	12.2 ± 5.0	0.19 ± 0.01
Beef steak	49.0 ± 1.8	0.52 ± 0.2
Ham	26.4 ± 2.7	2.0 ± 0.2
Lamb chops	30.0	0.36
Sausages	32.0 ± 1.4	1.2 ± 0.3

Table 3. Chromium (ng/kg) and Mn (mg/kg) concentrations in meat products.

It is interesting to note in Table 3 that the highest level of chromium is in beef steak 49.0 ng/kg and since it is related to blood sugar levels would account for the feeling of satiety and sustaining of energy after consuming beef in comparison to chicken with the low level of 12.2 ng of chromium. Manganese in contrast is highest in ham 2.0 mg/kg but lowest in chicken .12 mg/kg.
Siong *et al* (Siong, Khor Swan, and Siti Mizura 1989) analysed the calcium content of eight food groups that included meat and fish. Samples were from local markets and stores, they were homogenized, oven dried in air then the charred and ashed in a muffle furnace at 550°C. A Varian instrument was used employing an air/acetylene flame. Some selected values from the large range of products analysed reported in mg Ca/100g included: de-bonded chicken feet 25.1; chicken heart 6.0; canned beef rendang 31.1; canned mutton

curry 16.1 and beef extract 40.4. They compared the AA analyses with potassium permanganate titration where both methods were satisfactory using the paired t-test ($p< .0.05$). For only two groups legumes and vegetables there was a significant difference in the two methods. Analyses of mechanically de-boned poultry from five Dutch processors was undertaken by (Germs and Stennenberg 1978) employing AA and oxidimetry procedures. The mean AA calcium content was found to be 2.36 g/kg. Of the two oxidimetry methods used, the AOAC procedure gave the best agreement with the AA method where the coefficient of correlation was equal to 0.9996 and the standard error of regression, 0.05. Nakamura (Nakamura 1973) determined the water-extractable calcium content of chicken breast during postmortem aging by AA where he addressed the anionic and cationic interferences. In order to eliminate the anionic interferences, he added a 1% solution of the di-sodium salt of EDTA to the test solutions. In contrast, cationic interferences were overcome by adding a known amount of calcium to the test solutions to being the concentration to 0.1 mM. Results showed that the calcium content increased during the postmortem aging and reached a maximum after twenty-four hours. Atomic absorption spectroscopy and a modified AOAC fibre method were used to determine magnesium and manganese in meat –soy blends. It was found that in regular ground beef the magnesium and manganese levels were 151 mg/kg and 7.4 mg/kg, 4.9% soy flour, respectively (Formo, Honold, and MacLean 1974).

Copper and other metals in meat were analysed by (Ybanez, Montoro, and Bueso 1983) using both dry ashing and wet digestion with HNO_2 and H_2O_2 , essentially there was not any significant difference in the two methods of sample preparation. Samples analysed included both cold and cooked ham; mortadella, Frankfurters and liver paste. Recoveries for added metal for copper was found to be 100%. Copper determined in bovine liver standard was 193 ± 10 µg/g. The limit of detection for copper was determined as 0.17 µg/g. An analysis of copper and zinc in meat and meat analogues was done by Schaefer *et al* (Schaefer et al. 1979). Sample work up was carried out with nitric/perchloric acid digestion followed by flame AA. The mean zinc content found in meat and meat analogues was 3.36 and 1.07 mg/100g respectively while the copper content was 0.09 and 0.32 mg/100 g in the same product order. It can be seen that there is a contrast between the two metals in meat products: zinc being higher is meat whereas copper is higher in the analogues. Work undertaken by (Dalton and Malanoski 1969) determined copper and lead in meat ad meat products but used dry ashing at 500^{o}C for sample preparation unlike Schaefer's group who used wet digestion. Copper was found to be in the 1–5 ppm range.

Zinc and magnesium were analysed in a range of Philippine foods by AAS. Samples were prepared for analyses by hydrochloric acid extraction of the metals. One of the major advantages of the technique was the short sample preparation time for AA compared to other procedures such as gravimetric and colorimetric methods. A variety of foods were analysed that included meat and poultry (Lustre and Lacebal 1976)

Selenium is not an easy metal to analyse and reports in the literature are few. Research by (Hoenig and van Hoeyweghen 1986) determined selenium and arsenic in animal tissues and addressed the spectral interferences that are due to calcium and magnesium phosphates. Their method employed platform furnace atomic absorption spectrometry and deuterium background correction. The interferences just mentioned cannot be corrected using the deuterium arc. To overcome these interferences in animal tissues, they added nickel nitrate to the samples. The quantity added is critical as less than 20 mµg nickel nitrate added to a 10 µl sample does not allow correct development of analyte absorbance signals but more than this causes a loss of sensitivity. It was found that the measurement of peak height was the most suitable approach as integrated absorbance was partly influenced by the matrix. For different animal matrices the slope constants of working curves obtained were very close hence direct calibration was possible. Results were verified by analyses of a number of reference materials.

Investigation of the effect of adding selenium to chicken feed on the amount found in chicken meat and eggs was done by (Turker and Erol 2009). The method used was hydride-generation atomic absorption spectrometry. Optimisation of conditions for the technique such as HCl and $NaBH_4$ concentrations; flow rate of carrier gas; analytical parameters and the effects of digestion procedures on the analyses were all determined. The limits for detection and quantification were 0.78 and 2.35 mg/l respectively. Validation of the method was done by means of certified reference materials. Fortification of the chicken feed increased the levels of selenium in the meat and eggs. Four digestion methods: two dry ashing and two wet ashing procedures for trace metal analysis of Pb, Cd, Cu and Zn were evaluated for pork meat and fish (Zachariadis et al. 1995). Results showed that the wet ashng with HNO_3/HCl mixture gave the best results: For pork meat the copper level was determined to be 0.208 mg/kg and zinc 7.63 mg/kg. The data was collect on a Perkin-Elmer Model 2380 instrument with a HGA-400 graphite furnace that included a Deuterium lamp background corrector.

6. Metals in fish

Most of the analyses of metals in fish are related to heavy metals analysis to monitor pollutants such as zinc, cadmium, mercury and arsenic. Such metals find their way into the marine life in estuaries and rivers due to effluent from heavy industry accidentally leaking into the water ways or by faulty filtering systems and practice that do not comply with the Environmental Protection Agency in that particular country. Most commercial fishing is undertaken in deep-sea waters where these metals would not be a problem, however, fish caught in rivers and estuaries that are many kilometers from heavy industry can sometimes still be affected by metals carried by currents that cause pollution where it is not expected. Reports of beneficial metals analysed by AA in fish are few. Salmon, for example is a good source of calcium since in canned products the bones are not usually removed, except in specialty products. In this discussion emphasis will be given to t nutritional metals and the other metal pollutants will not be mentioned. In their paper, (Carvalho, Santiago, and Nunes 2005) stated that fish are an important source of lipids, proteins, liposoluble vitamins and polyunsaturated fatty acids that are important in assisting to reduce hypertension, cancer risk and coronary heart disease.

6.1 Limited references to some beneficial metals in fish

An analysis of essential and heavy metal levels in edible fish muscle was undertaken by (Carvalho, Santiago, and Nunes 2005) who employed two different techniques: energy-disperive X-ray fluorescence (EDXRF) and flame AAS. Samples of nine fish were analysed, namely, Forkbeard (For), Meagre (Mea), White sea bream (WSB), Axillary sea bream (ASB), Red sea bream (RSB), Common sea bream (CSB), Rockfish (Roc), Common sole (Cso), Anglerfish (Ang) and Octopus (Oct) that came from coastal markets in Portugal. Flame AAS was used to determine the content of Cu, Cr, Ni, Hg, Pb and Cd employing a Varian (Australia) Spectr AA20 spectrometer. Sample preparation was achieved by means of incineration and dissolution in nitric acid. An EDXRF spectrometer was used for the determination of K, Ca, Fe, Rb, Se and Zn. Of the elements studied, it was fond that calcium and potassium were the most abundant elements detected in the fish samples. The highest potassium level detected was found in octopus with an average value of 12,660 µg/g dry weight and the lowest in Axillary sea bream being 6.170 µg/g. Common sea bream had the highest calcium content of 788 µg/g whereas White sea bream had the lowest value of 444 µg/g. The highest iron concentration in these fish was observed for Octapus at 109 µg/g and the lowest for Forkbeard at only 6.4 µg/g. In a Turkish study, nine fish were studied for their trace metal levels. The fish from the Black Sea were: European anchovy; Whiting; Red mullet; Bluefish; Atlantic horse mackerel; Flathead mullet and Atlantic bonito. Two species from the Aegean Sea were Black swordfish and Gilthead sea bream. A Perkin Elmer AAnalyst 700 AAS instrument equipped with a HGA graphite furnace and deuterium background correction was used for the analyses of chromium, copper, lead and nickel. Flame AA with an air/acetylene flame was employed by (Uluozlu *et al*. 2007) to determine the copper, iron, manganese and zinc content of fish samples.. Of the fish studied, Bluefish had the highest copper content of 1.83 ± 0.10 µg/g and the lowest level for European anchovy ± 0.08 µg/g. For chromium, the highest level was again for European Anchovy at 1.98 ± 0.10 µg/g but the lowest value for Atlantic horse mackerel 0.95 ± 0.07 µg/g; red mullet has the highest iron level 163 ± 12 µg/g and Bluefish the lowest 698.6 ± 5.3 µg/g; manganese gave the highest level of .54 ± 0.50 µg/g and the lowest for Bluefish 1.28 ± 0.10 µg/g and lastly zinc had the highest level for Red mullet of 106 ± 9.1 µg/g and the lowest level for Bluefish at 35.4 ± 3.2 µg/g. Hence, it can be seen that Red mullet had the highest zinc and iron levels, which were considerably higher than any of the other metals just mentioned in this analysis.

7. Metals in some dairy products

Traditionally, dairy foods are the main source of calcium in the diet where milk, yogurt and cheese are the foods commonly consumed. Calcium and also magnesium are the most important metals for building strong bones and teeth and to prevent rickets and osteoporosis in older citizens particularly women. Vitamins A and D as well am magnesium are usually added to over the counter dietary supplements to ensure adequate absorption of the calcium. In addition, magnesium is also present in milk and dairy products but ii is in larger quantities in leafy green vegetables in the form of chlorophyll being the central metal. Although magnesium is present in dairy products it is in considerably lower concentrations so the following discussion with be focusing mainly on calcium.

7.1 Calcium and some other metals in milk and yogurt

A method for the analysis of calcium and magnesium in dairy products has been reported by (Brandao, Matos, and Ferreira) employing a high resolution continuum source flame atomic absorption spectrometer (HF-CS-FAAS) using secondary lines. The advantage of using these secondary lines is that samples with high concentration of these elements did not need substantial dilution. Samples of milk powder, cow milk and yogurt were obtained from local supermarkets in Salvador City Brazil. In order to prepare the samples for analysis two methods were used: slurry sampling and digestion. Data obtained indicated that there was not any significant difference in the results for the two procedures. The instrument used was an Analytik jenna Model ContrAA 300 High Resolution-Continuum Source Flame Atomic Absorption Spectrometer (GI.E. Berlin, Germany) equipped with a xenon short-arc lamp XBO 301 with a nominal power of 300 watt. A nitrous oxide/acetylene flame was used for the for the analysis of calcium and magnesium. For yogurt samples the calcium and magnesium levels were found to be 1.40 and 0.13 mg/g respectively. Values of calcium and magnesium in whole milk were 1.23 and 0.12 mg/mL respectively while for skim milk the concentrations were almost the same. In milk powder, however, the values were higher, namely, 8.92 and 0.83 mg/g for calcium and magnesium in this order. In contrast for skim milk the calcium and magnesium concentrations were 1.21 and 0.118 mg/g. A detailed study by (Miquel et al. 2005) for calcium, iron and zinc in toddler milk-based formula were 861 ±, 27; 12 ± 5; 7 ± 5 mg/L and for soluble fraction in the same product the values obtained were 704 ± 24; 7 ± 1 and 5 ± 1 mg/L, respectively. The chromium content of *acidaphilus* milk culture was reported by (Larsen and Rasmussen 1991) as 0.76 ng/mL: for cream 0.67 ng/mL; low fat cream, 13% fat, 0.77 ng/mL and yogurt 2.2 ng/mL.. A value of 14.3 ± 4.0 mg/kg for chromium and 0.27 ± 0.05 mg/kg for manganese in yogurt was reported by (Tinggi, Reilly, and Patterson 1997).

7.2 Manganese and chromium levels in milk powders

A procedure for the determination of manganese in dried milk employing a Zeeman furnace AAS was reported by (Koops and Westerbeek 1993). Samples were prepared for analysis by boiling them in nitric acid for 15 minutes then adding magnesium and palladium as matrix modifiers. Manganese levels were determined in 36 dried whole milk powder samples. It was found that the average manganese concentration of the samples was 0.21 mg/g of total solids present. Hence, these results showed that it was possible to calculate the manganese content for reconstituted milk as approximately 25 µg/kg. An analysis of the chromium and manganese levels in skim milk was determined by (Tinggi, Reilly, and Patterson 1997) who found they were 6.7 ± 1.5 ng/kg and 0.40 ± 0.20 ng/kg respectively.

7.3 Molybdenum in milk products

Although molybdenum is a essential trace metal, there are few references in the literature of atomic absorption analyses of molybdenum in foods, this may be because it is not a straight forward metal to analyse, as matrix modifiers are required. Determination of the concentration of molybdenum in skimmed milk based drinks and infant food samples was done by (Regina de Amorim et al.) using a graphite furnace AAS. A considerable amount to time was spent in evaluating matrix modifiers and temperature programming to optimize the procedure. Samples were obtained from a local store in Brazil: they were dissolved in ultra pure water, sonicated then used without further pre-digestion. The analyses were performed on a Perkin Elmer AAnalyst 300 atomic absorption spectrometer (Norwalk, CT,USA) fitted with an HGA 800 graphite furnace and AS-72 autosampler using argon purge gas. Values obtained for the molybdenum levels in the milk products are given below:

Milk products	Mo level (g/g)
• Skimmed milk	0.034 ± 0.01
• Whole milk:	
• Sample (A)	0.37 ± 0.05
• Sample (B)	**0.22** ± 0.03
• Sample (C)	0.27 ± 0.02
• Sample (D)	0.30 ± 0.04
• Sample (E)	**0.40** ± 0.02
Infant formula	
• Sample (A)	**0.43** ± 0.03
• Sample (B)	**0.36** ± 0.01
• Sample (C)	0.37 ± 0.06
• Milk based drinks	
• Sample (A)	**1.57** ± 0.28
• Sample (B)	**0.040** ± 0.006
• Sample (c)	0.32 ± 0.01

Table 4. Mo concentrations in µg/g for milk products determined by
(Regina de Amorim et al.).

From Table 4, it can be seen that the range of Mo in whole milk samples was in the range 0.22 to 0.40 µg/g while the level in skimmed milk was considerable lower, 0.034 µg/g; infant formula 0.36 to 0.43 µg/g and milk based drinks 0.040 to 1.57 µg/g.

7.4 Analyses of some metals in butter

A Perkin-Elmer–303 Atomic Absorption Spectrophotometer was used to analyse copper, iron, manganese, magnesium, potassium, sodium and calcium in butter samples. Samples were prepared by two methods, either by direct dry ashing or by dry-ashing of the HNO_3 extract. Dry ashing was not suitable for copper, iron and manganese due sample loss and a wide range of results as well as being a very time consuming procedure. In contrast, for the other metals both methods gave satisfactory results. Three factories were included in the study, namely, 58 butter samples were obtained from Latvian dairy factories (LD); 33 from the Vladimir region factories (VR) and 58 from Krasnodar district factories.(KD). Results from these three factories in mg/kg can be seen in the Table 5 below.

Metal in mg/kg	**Latvian Distract**	**Valadimir Region**	**Krasnodar District**
Calcium	**144**	**168**	**172**
Copper	0.82	1.45	1.26
Iron	1.57	1.84	2.15
Potassium	**173**	**197**	**144**
Magnesium	14.4	19	21.2
Manganese	**0.05**	**0.1**	**0.004**
Sodium	74	151	146

Table 5. Results from (Lovachev et al. 1972) comparing the seven metal concentrations from the three regions.

It can be seen from Table 5 that the highest metal concentration was potassium in the Valadimir Regiion, 197 mg/kg followed by 173 mg/kg in the Latvian District. Calcium was the metal with the highest concentration of 172 mg/kg in the Krasnodar District. In the Valadimir Region the calcium level was 168 mg/kg but in the Latvian District it was 144 mg/kg. The metal with the lowest concentration in these three regions was for manganese: 0.05 mg/kg; 0.1 mg/kg and 0.004 mg/kg for Lativan, Valadimir and Krasnodar areas, respectively.

7.5 Chromium levels in cheese

Results are given below for analyses obtained by (Larsen and Rasmussen 1991) using a Zeeman graphite furnace atomic absorption spectrometry to determine chromium, cadmium and lead in some Danish dairy products including cheese. Only data for chromium in cheese samples will be presented here. A Perkin Elmer model 5000 Zeenam atomic absorption instrument with a HA 500 graphite furnace and autosampler AS40 were employed for the analyses. Cheese samples were cut into small cubes then ashed in a bomb with nitric acid for four hours then ashed overnight. Chromium concentrations for six cheese samples that the authors state are only indicative, due to the small sample set, will now be given: Brie 45, 20 ng/mL; Camembert 30, 13 ng/mL; Danbo 45, 8.6 ng/mL; Danbo 45, 19 ng/mL; Havarti 60, 4.6 ng/mL and Maribo 45, 20 ng/mL. The authors state that the results obtained in this work compare well with other countries. Chromium and manganese levels in cheese were also reported by (Tinggi, Reilly, and Patterson 1997) as 95.0 ± 29.2 ng/kg and 1.1 ± 0.2 mg/kg, respectively.

8. Selected metals in fruit

Some of the metal analyses on fruit products are, in fact, related to metal analyses in fruit juices and purees that are often related to authenticity and country or region of origin. This is to detect adulteration with an inferior juice since metal analyses are indicative of the soil type and hence the location. Authenticity studies including metal analyses are usually in conjunction with other techniques such as GC/MS as well as AAS. Some examples will be given on juice and fruit with a limited number of metals. Other studies are related to contaminants such as tin from canned fruit and juices. Even though this article is directed to nutritional metals a few examples will be given of tin concentrations in canned fruit products for interest.

8.1 Examples of metal analyses in fruit juices and purees

Selenium levels in wild fruit juice from the mountainous area in north China, Lantingguo, was reported by (Yongming et al. 1996) using a graphite furnace AAS. Electrothermal atomic absorption spectrometry using a Perkin-Elmer 5000 atomic absorption spectrometer linked to a Model HGA 500 graphite furnace with a selenium HCL was the instrument set up employed for this work. This analysis was complicated by the fact that there were other interfering ions present in the juice, hence matrix modifiers were necessary. It was found that the modifier consisting of 10 µg of platinum and 200 µg of nickel gave the most satisfactory results. As already mentioned the metal content in the juice are related to the different fruit growing regions. Other metals found in these locations that interferes with the Se analyses include: potassium greater that 1000 mg/L followed by calcium, magnesium,

manganese, iron, phosphorous and zinc in lower amounts 100 – 1000 mg/l. There were also trace amounts of cadmium, copper, lead, nickel, silicon, strontium and selenium. The average values found for eight determinations of three juices from fruit grown in different locations in the above region were: 0.20, 0.23 and 0.10 mg/L selenium.
Tin is not a desirable metal but a contaminant and was analysed in a number of juices, purees and fruit by the Comite Europeen de Normalisation (Foodstuffs. Determination of trace elements. Determination of tin by flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS) after pressure digestion 2009) in a collaborative study.. Some of the products analysed included: carrot puree, tomato puree, pineapple, mixed fruits, powdered peach and tomato. Samples were prepared by pressure-assisted digestion then analysed by flame AAS or graphite furnace AAS. Data obtained for the products analysed were in the range of 43 – 260 mg/kg for AAS and or 2.5 – 269 mg/kg for graphite furnace AAS.

8.2 Beneficial metal concentrations in some fruits

Slurried fruit samples were tested by (Cabrera, Lorenzo, and Lopez 1995) for the levels of cadmium, copper, iron, lead and selenium by Electrothermal AAS. Only results for copper, iron and selenium will be mentioned, as these are the nutritional metals as distinct from the others that are contaminants. In addition, to the sample preparation of slurries, the samples were also mineralized in a microwave acid-digested bomb and the data compared for accuracy and precision. A total of 40 samples comprising 8 types of fruit that are regularly consumed were tested. These samples were: banana; custard apple; kiwifruit; mango, medlar, papaya; pineapple and strawberries. For these fruit samples the mean range of the metals copper, iron and selenium were 2.00 – 5.50 µg/g; 0.050 - .0.396 µg/g and 0.010 – 0.020 µg/g, respectively. Chromium and manganese were analysed (Tinggi, Reilly, and Patterson 1997) in fruit by AAS, after wet digestion but found that these two metals were relatively low in fruit when compared to other foods. Fruit samples tested were: apple; banana; grapes; orange; pear; pineapple (canned) and rock melon.

Fruit	**Cr (ng/kg)**	**Mn (mg/kg)**
Apple	19.3 ± 3.3	0.5 ± 0.1
Banana	5.2 ± 1.3	**3.3** ± 0.9
Grapes	**4.3** ± 1.2	0.6 ± 0.1
Orange	6.3 ± 1.2	**0.4** ± 0.1
Pear	12.6 ± 1.8	0.8 ± 0.1
Pineapple (canned)	**21.3**	1.5
Rock melon	9.8 ± 1.5	**0.4** ± 0.1

Table 6. Concentrations of chromium (ng/kg) and manganese (mg/kg) in selected fruit samples.

It can be seen in the Table 6 that the chromium levels in these fruit samples ranged from 4.3 ng /kg in grapes to 21.3 ng/kg in pineapple. In contrast the manganese concentrations were higher than those for chromium in these same samples where the range was from 0.4 mg/kg for both orange and rock melon up to 3.3 mg/kg for banana.

Fifteen elements were analysed by flame AAS after microwave-assisted digestion of the cultivar citrus reticulate Blanco CV. Ougan fruits. The analyses gave high concentrations of these metals at both of the ripeness stages (Mojsiewicz-Pienkowska and Lukasiak 2003)

8.3 Analyses of tin a contaminant in canned fruit and fruit juices

A report by (Dogan and Haerdi 1980) on the analysis of the tin content in peaches, pears, pineapple, mandarin, peeled tomato and fruit cocktail by a number ot techniques including AAS will now be presented. Sample preparation was achived by using Lumatom, which is a trade organic chemical that contains quaternary ammonium hydroxide suspended in isopropanol. After this sample preparation procedure the.fruit and juice samples were introduced directly into the graphite AAS instrument. The tin concentrations levels were: quartered mandarin 68 ppm; peeled tomato 57 ppm and fruit cocktail 57 ppm. Rigin (Rigin 1979) used flameless AAS to determine the tin levels in canned tomato, apple and orange juice. The results for 5 replicates of each sample after three months storage for canned tomato, apple an orange juice were 12.1, 2.75 and 30.5 μg/ml respectively. After twelve months, however, the values had increased to 76.3, 4.26 and 45.4 μg/ml for the samples in the same order as for three months storage. Wehrer *et al* (Wehrer, Thiersault, and Laugel 1976) used AAS with wet and dry ashing to determine tin content of canned samples including stewed apples. The concentration of tin in the stewed apples for ten replicates was 52.4 mg/kg after 2N HCl digestion and 57.5 mg/kg after dry ashing that involvd calcinations using magnesium nitrate. Vijan and Chan (Vijan and Chan 1976) determined the tin content of a number of different types of samples including apple, apple/cherry, apple/pineapple and tomato juices. For the first three products the tin level was less than 0.1 μg/ml but for tomato juice it was considerably higher at 90 μg/ml.

9. Metal levels in vegetables

Detailed analyses of chromium and manganese on a wide range of food groups has been undertaken by (Tinggi, Reilly, and Patterson 1997) at this point in time the discussion will be limited to vegetables. The results show that the chromium levels are lower (ng/kg) in the vegetables analysed than in manganese (mg/kg) where the sample sizes ranged from 3 to 5 per vegetable. Vegetables studied included: beans (boiled); broccoli (boiled); carrot (boiled); cauliflower (boiled); lettuce; peas (frozen); potato (roasted); pumpkin (boiled);); tomatoes and zucchini. Portion of the data for these two elements have been extracted from the study under consideration in this section and will be presented below in Table 7.

It can be seen from Table 7 that the highest level of chromium is in tomatoes, 30 ng/kg, and the lowest level in boiled bean 5.3 ng/kg. Whereas for manganese the highest level was for frozen peas, 6.0 mg/kg, while the lowest value was for potato and pumpkin that were equal at 0.9 mg/kg. Hence tomato is a good source of chromium, which stabilizes the blood sugar levels and peas are a good source of manganese.

A study on the mineral levels in some Slovenian foods that are regularly consumed was undertaken by (Zuliani et al. 2005) After sample workup employing microwave-assisted digestion the samples were analysed by flame and electrothermal atomic absorption spectrophotometer. The minerals content investigated in this study were, Zn, Cu, Cd, Pb and Ni. It was found that the samples tested did not contain any Cd, Pb or Ni contamination. Zinc levels reported for cabbage and tomatoes were less than 50 mg/kg. Copper content, in contrast, was between 2 and 3 mg/kg in the majority of the samples while the chromium content was below 0.05 mg/kg. An analysis of Fe, Zn and Cu in some foods consumed in Mexico including vegetables, legumes, fruits, cereals and animal foods was reported by Lopez and co-workers (Lopez et al. 1999). Considering these products, it was found that the zinc level had a range of 0.018 mg/100g to 9.193mg/100 g for strawberry and beef. The iron concentrations were from 0.113 mg/100g to 19.82 mg/10g for yogurt and commercial cereal but the latter was fortified with minerals. Copper was not detected in all foods but was found to be the highest in beef liver, namely 3.371 mg/100g. Selenium levels in some Egyptian foods were determined by electro-thermal (ETAAS) and hydride generation (HGAAS) atomic absorption spectrometry by (Hussein and Bruggeman 1999). They found the metal was only in trace amounts: in the range of 1-33 µg/kg. Other products were tested but are not reported here.

Vegetable	**Chromium (ng/kg)**	**Manganese (mg/kg)**
Bean (boiled)	5.3 ± 1.6	3.4 ± 0.4
Broccoli (boiled)	8.0 ± 2.0	1.2 ± 0.1`
Carrot (boiled)	13.0 ± 2.3	1.5 ± 0.1
Cauliflower (boiled)	6.3 ± 1.6	1.1 ± 0.2
Lettuce	9.2 ± 1.3	1.3 ± 0.1
Peas (frozen)	28.3 ± 3.5	**6.0 ± 1.2**
Potato (roasted)	19.0 ± 2.2	**0.9 ± 0.06**
Pumpkin (boiled)	16.0 ± 2.2	**0.9 ± 0.2**
Tomatoes	**30.0 ± 2.1**	2.0 ± 0.1
Zucchini	6.3 ± 1.2	1.3 ± 0.3

Table 7. Chromium and manganese concentrations in some vegetables in ng/kg and mg/kg respectively (mean ± SD)

Vegetable	**mg Ca/100 g**
Asparagus (fresh)	13.9
Asparagus (canned)	14.7
Leek	16.2
Mushrooms (fresh) - grey oyster	**1.0**
Peak (fresh) – garden	62.5
Radish (pickled) - Chinese	94.9
Rhubarb (petioles) - ;pie ;plant	268.9
Seaweed (agar)	**510.2**
Spinach - Ceylon	116.2
Spinach -*Bayam pasi*	319.4
Tomato – tree	11.2
Yam bean	12.4

Table 8. Results of AAS Ca analyses, selected examples in vegetable, edible portion, from part of a table by Siong.

Calcium levels in many foods have been reported by (Siong, Khor Swan, and Siti Mizura 1989): some results will now be given for a selection of the vegetables tested. Two methods were compared AAS and potassium permanganate titration. A Varian Atomic Absorption spectrophotometer, Model 175 using an air/acetylene flame was used for the analyses. Samples were prepared for introduction into the instrument by ashing. Data for the two methods were in good agreement, however, only AAS results will be given for some vegetables reported by Siong's group.

For the vegetables listed in Table 8, seaweed contains the highest concentration of calcium being 510.2 mg/100 g. Spinach followed next with a value of 319.4 mg/10g.whereas fresh mushrooms contain only 1 mg/100 g of calcium, the lowest concentration reported in this group. Atomic absorption spectroscopy was used to determine the mineral content of hummyad (*Rumex vesicarius*) leaves that are grown in both the northern and central areas of Saudi Arabia.. Elements analysed included calcium, copper, iron, magnesium, potassium, sodium and zinc. The range of values (Alfawaz 2006) obtained for these metals are as follows: calcium 1790 – 2680 mg/100 g; copper 24.1 – 43.5 mg/100 g; iron 1320 – 2270 mg/100 g; potassium 2710 – 3230 mg100 g; sodium 846 – 1100 mg/ 100 g and zinc 3.7 – 8.8 mg/100 g. Hence, it is clear that this plant is very rich in calcium, iron and potassium, the highest mineral content being for potassium followed by calcium and iron indicating that these leaves are a nutritious source of these essential metals The germanium content in different foods including vegetables was determined by (McMahon, Regan, and Hughes 2006) using a Graphite furnace atomic absorption instrument. Sample workup was via drying and ashing. Values for several vegetables are as follows: carrot 0.60 µg/g; potato 1.85 µg/g; garlic 2.79 µg/g. and soy mince 9.39 µg/g. The latter sample having the highest germanium content of the vegetables tested. Food, crops and soils in Taiwan were analysed by (Huang, Wen, and Chern 1987) for the selenium content. Metals found in soils are directly related to the uptake of minerals in plants. Considering soil in the Taiwan region, the selenium level was determined to be in the range 0.03 – 0.23 ppm. Selenium content in crops, fruit and vegetables, in contrast, was reported to be approximately 0.1 ppm, however, for mushrooms the level was higher, namely, 0.55 ppm.

An analysis of two cultivars of onions grown in Venezuela: Yellow Granex PRR 502 and 438 Granex were tested for the concentrations of calcium, copper, iron, manganese, potassium and zinc, by total reflection X-ray fluorescence (TXRF), then the results compared with those from FAAS. A more efficient sample preparation was employed where the samples were acid extracted from the crude products using an ultrasonic bath, avoiding time consuming digestion. Sample work up was also compared with wet and dry ashing. The mineral content of the onions is important so the soils can have more elements added if, required, to improve their nutritional value. It was found that the ultrasound work up and dry ashing gave similar results. Levels of calcium copper and iron were found to be significantly greater in the Yellow Granex cultivar while potassium, manganese and zinc were significantly higher in 438 Granex. Levels of calcium and potassium were very much greater than the concentrations of the other elements: potassium being slightly higher than calcium, irrespective of the work up procedure: ultrasonic extraction or wet or dry ashing methods (Alvarez et al. 2003). A thorough analyses of a wide range of metals in Jamaican foods has been reported to (Howe et al. 2005) for legumes, leafy and root vegetables, fruit and other root crops. Only some metals levels will be mentioned here for the first three products listed above. Data will be given for calcium, chromium, copper, iron, magnesium, manganese, sodium and zinc. Comparison data was also undertaken with other countries but will not be given here.

Element	Legumes	Leafy vegetables	Root vegetables
Calcium	514	**2580**	**390**
Chromium	**0.07**	**0.08**	**0.09**
Copper	2.28	0.6	0.7
Iron	30.02	15.5	12.9
Potassium	0.67	0.39	0.41
Magnesium	**790.00**	359.0	157
Manganese	10.6	8.3	4.3
Sodium	4.16	90.1	727
Zinc	16.30	4.2	3.4

Table 9. Mean concentrations of metals, mg/kg in legumes, leafy and root vegetable grown in Jamaica

In addition to the analyses on calcium in foods, (Siong, Khor Swan, and Siti Mizura 1989) also undertook a similar study for iron levels, again employing a Varian Atomic Absorption Spectrophotometer model 175 using an air/acetylene flame. Analyses of iron in foods are important as it is a mineral that is often lacking in diets low in red meat, which is necessary to prevent anaemia Readily available information assists consumers and health care professionals to advise on foods that contain this element where the total RDA for that metal is kept in mind. The edible portions of the samples were homogenized, oven dried, charred then ashed in a muffle furnace. The AAS method was compared with a colorimetric phenanthroline procedure where the results indicated that both methods were found to be satisfactory for iron analyses although AAS would be a less time consuming. Only some data for vegetables by AAS will b e given below.

Vegetable	mg Fe/100 g
Asparagus (canned)	**7.06**
Asparagus (fresh)	0.55
Broccoli	0.47
Cucumber (hairy)	**0.15**
Leek	0.33
Mushrooms (fresh) grey oyster	0.84
Mustard leaves (Chinese)	1.35
Mustard leaves (Indian)	1.46
Peas (fresh) garden	0.75
Seaweed (agar)	5.33
Seaweed (dried)	**22.94**
Spinach (Ceylon)	0.88
Spinach (red)	2.64
Spinach (*Bayam duri*)	1..69
Yam bean	**0.26**

Table 10. Concentration of iron in mg/100 g of edible portion of vegetables

It is interesting to note from Table 10 that the highest level of iron is in dried seaweed at 22.94 mg Fe/100 g, followed by canned Asparagus, 7.06 mg Fe/100 g and then seaweed (agar), 5.33 mg Fe/100 g. In contrast the lowest iron content was found in hairy cucumber being 0.15 mg Fe/100 g. Sodium and potassium content of a large number of foods and composite foods consumed in Canada was carried out with respect to a Total Diet Survey. Generally only some unprocessed vegetable data obtained by (Tanase et al.) will be given in this Section. Potassium samples were analysed by AAS, Perkin Elmer AAnalyst 400, but sodium analyses were performed employing atomic emission spectroscopy. The mean potassium and sodium levels in mg/kg of the various unprocessed vegetables will now be quoted in this order. Samples were mechanically homogenized, filtered with Whatman 541 filter paper then diluted with dilute nitric acid that contained $CsCl_2$ (1000ug/ml) , a matrix modifier.

Vegetable	**Potassium mg/kg**	**Sodium mg/kg**
Asparagus (fresh)	2081	40
Baked beans (canned)	2542	**2892**
Beans string (fresh: canned)	1550	**1704**
Broccoli	1647	153
Brussels sprouts (fresh)	2946	64
Cabbage	1694	95
Carrots	2182	163
Cauliflower	1266	148
Celery	1627	626
Lettuce iceberg; romaine 3:1	1520	127
Mushrooms (button)	1844	38
Onions	825	33
Peas (frozen: canned)	**822**	1083
Peppers, green	1698	**4**
Potatoes (peeled; boiled)	2032	20
Potatoes (baked: skin)	**4921**	41
Spinach	**4007**	619
Tomatoes (fresh)	2599	26

Table 11. Selected vegetables (mean values, mg/kg) generally fresh but with some canned or cooked.

It can be seen in Table 11 that all of the vegetables listed have high potassium content with baked jacket potatoes having the highest potassium level of 4921 mg/kg followed by Spinach at 4007 mg/kg. The lowest potassium content is this group is for onions at 822 mg/kg. In contrast, the highest sodium concentration was found to be in canned baked beans at 2892 mg/kg followed by string beans either fresh or canned at 1704 mg/kg. The lowest sodium level was found be in green peppers at 4 mg/kg. Mineral concentrations in a range of vegetables have been reported by (Howe et al. 2005). Calcium, copper, chromium, iron, magnesium, manganese, potassium, sodium and zinc values will be given for some vegetables for the highest observed values expressed on a fresh weight basis. See Table 12 on the next page.

Metal	Vegetable	Level mg/kg
Calcium	Cabbage	20160
Magnesium	Cow peas	1621
Potassium	Corn	3.8%
Sodium	Carrot	1920
Copper	Cow peas	5.0
Chromium	Sweet potato	1.1
Iron	Red kidney beans	76.5
Manganese	Cow peas	27
Zinc	Daheen	76

Table 12. Minerals in selected vegetables in mg/kg

In Table 12, interesting to note that cabbage has such a high level of calcium at 20160 mg/kg and carrots contain 1920 mg/kg of sodium. Red kidney beans are good source of iron having 76.5 mg/kg that is an excellent source of this metal for vegetarians. Cow peas, in addition to containing a very high level of magnesium, 1620 mg/kg also have a concentration of manganese, 27 mg/kg. Dasheen is rich in zinc, 76 mg/kg.

9.1 Mineral and trace mineral content in tomatoes

Essential and trace mineral content in a number of tomato fruit cultivars was determined by (Ruiz et al. 1995) Their work is reported here under the section on vegetables as in Australia and some other countries, tomatoes are regarded as a vegetable. Essential minerals studied were calcium, magnesium, potassium and sodium while the trace metals were copper, iron, manganese and zinc. Data on samples reported here are new cultivars that were being developed in order to increase their health benefits. The four cultivars under consideration are: S. *lycopersicum*; S. *pimpinellofilium*; S. *cheesmaniae* and S. *harbrochaites*. Samples were grown in a greenhouse during the spring-summer time in Valencia, Spain. Preparation of the sample was firstly by freeze-drying,, ashing at 450°C and finally making up in acids: 50% HCl and HNO_3. A Perkin-Elmer 2280 spectrophotometer was employed using an air/acetylene flame for the analyses. Results from the study will now presented in the table below and cam be compared with other data for tomatoes reported by other researchers in this section on vegetables.

Sample	Ca	Mg	K	Na	Cu	Fe	Mn	Zn
A	23.57 ± 0.86	6.40 ± 0.52	78.47 ± 2.54	36.89 ± 1.48	0.43 ± 0.02	0.55 ± 0.3	0.1 ± 0.00	0.26 ± 0.01
B	37.69 ± 2.25	12.93 ± 0.44	212.83± 5.88	54.94 ± 2.65	0.74 ± 0.02	0.96 ± 0.05	0.17 ± 0.01	0.33 ± 0.01
C	45.78 ± 0.46	14.37 ± 0.25	**222.51±** 2.34	**84.4** ± 1.49	0.72 ± 0.01	**1.17** ± 0.11	**0.19** ± 0.01	**0.70** ± 0.01
D	**46.88** ± 2.73	**20.49** ± 0.16	**194.27±** 8.51	82.61 ± 2.89	0.62 ± 0.03	1.02 ± 0.06	0.15 ± 0.01	0.17 ± 0.01

Table 13. The concentrations of the essential and trace metals for the four cultivars A, B, C and D are given in mg/100 g Where A, B, C and D represent: S. *lycopersicum*; S. *pimpinellofilium*; S. *cheesmaniae* and S. *harbrochaites respectively*.

In Table13, it can be seen that cultivar C has the highest K level at 222.51 mg/100g; as well as highest Na, Fe, Mn and Zn levels: 84.4 mg/ 100g; 1.17 mg/100g , 0.19 mg.100g and 0.70 mg.100g, respectively. Cultivars B and D following closely behind C with Ca levels of 212.83 mg/100g and D 194.27 mg/100 g.. Cultivar D has the highest Ca and Mg concentrations at 46.88 mg/100g and 20.49 mg/100 g respectively.

10. Mineral content in some herbs and spices

Much of the literature on herbs and spices is related to contamination of heavy metals and analyses are undertaken to ensure that they are safe to consume and have not been grown in polluted areas, such as near motorways where there is the pollution from lead in old style cars. Possibly, they have been grown in soil near mining sites where there is pollution from heavy metals. Crops can be grown near polluted waterways where they are down stream from heavy industry factories so heavy metals seep into the soil and/or contaminate the ground water. In this section metals that are of health benefits will be emphasised with only a brief mention of those that are considered to be pollutants. Metals such as iron and calcium and others import in maintaining good health. Studies have also been reported on the metal content of Chinese herbs that have specific health benefits for certain disease states.

10.1 Minerals related to kidney function

Selected metals in Chinese medicinal herbs that are used in order to improve kidney function has been reported by (Kolasani, Xu, and Millikan 2011) Dried, unprocessed herbal samples were purchased from local importers of Chinese herbs in Melbourne. These are herbs that the Chinese medical practitioners would prescribe to their patients. Samples came from different parts of the plant: such as leaves, whole plant, stem, twig, bark or roots. Seven metals were tested by atomic absorption spectroscopy that included: calcium, iron, magnesium, manganese, sodium, potassium and zinc. A Varian spectra-400 Atomic Absorption Spectrophotometer (Varian Inc. Mulgrave, Australia) an air/acetylene flame was employed for the metal analyses. Samples were ground then digested in concentrated nitric. The range of metals found in these samples were as follows: Ca (130 – 560940 µg/g); Fe (20 – 8020 µg/g); Mg (90-5520 µg/g); Mn (20-140 µg/g); K (270-90260 µg/g); Na (30-4500 µg/g) and Zn (10–1010 µg/g); Na (30-4500 µg/g). Results indicated that calcium and potassium levels were the highest elements detected in all sample compared to the other metals. It was also found that the calcium concentration was greatest in fossils, then in plants whereas iron, potassium, manganese and zinc levels were highest in plants. Roots contained the highest magnesium concentration while flowers contained the highest sodium values.

10.2 Iron levels in some commonly consumed culinary herbs and spices

Herbs and spices are added to foods to enhance the flavour and add variety to an otherwise bland dish. In many cases, it is not a single herb but a combination that gives the dish that subtle taste and aroma. Different nationalities characteristically have their own traditional dishes that vary considerably in the choice and number of spices added to different dishes whether they be savoury main courses on spicy deserts. Siong and co-workers who analysed eight food groups, some of which have already been mentioned above, has reported the iron concentrations of a number of spices and herbs (Siong, Khor Swan, and Siti Mizura 1989). Some examples will now be presented in the Table 13 below.

Spice or herb	mg Fe/100 g
Chilli, small	0.68
Nutmeg, fresh	**0.22**
Persimmon, dried	0.99
Chives, Chinese	0.62
Coriander, leaves	3.86
Garlic, bulbs	0.48
Garlic, plants	0.31
Parsley	**9.90**

Table 13. Iron concentration in mg Fe/100 g of a selection of spices and herbs

It can be seen in Table 13 that parsley is an excellent source of iron, 9.90 mg Fe/100 g, that is particularly important for those who eat little red meat or are vegetarians. Iron deficiency is a common problem particularly for women. Coriander leave being the next highest level of iron at 3.86 mg Fe/100 g. It is interesting to note that the iron in garlic bulbs is 0.48 mg Fe/100 g that is greater than in the plants at 0.31 mg Fe/100 g. Of this group nutmeg has the lowest iron level at 0.22 mg Fe/100 g.

10.3 Calcium levels in herbs and spices

In a related study that complements the above work on iron, (Siong, Khor Swan, and Siti Mizura 1989) analysed similar samples for the calcium concentrations. Again, some of these food groups have already been discussed in this review.

Spice	mg Ca/100gm
Anise seed, dried	950.6
Cardamon	**1769.7**
Cinnamon	600.9
Cumin seeds, black	816.8
Cumin seeds, white	1165.1
Curry powder	576.2
Fenugreek seeds	179.8
Pepper, powder, white	**120.4**

Table 14. Calcium content of selected spices in mgCa/100 g

It can be seen in Table 14 that cardamom has the greatest level of calcium at 1769.7 mg Ca/100 g followed by dried anise seed with a value of 950.6 mg Ca/100 g. While pepper, in contrast, has the lowest calcium content, namely, 120.4 mg Ca/100 g.

11. Conclusion

The chapter has taken examples of the literature on the mineral content, both Essential and Trace metals in meat, dairy products, fruit, vegetables and herbs and spices. The review is not exhaustive but a selection of examples of metals extracted from many authors with the data arranged in such a way as to highlight at a glance the concentrations of the metals in the above foods that are generally not processed. It is a collection of information in the one chapter assembled from published work, which allows a convenient comparison of the concentration of certain metals in the products discussed. Such information is of value to health care professionals, researchers and food manufacturers in preparing nutritious products. Levels of metals in some product may also be unexpected and hence informative and may lead on to further analyses and research.

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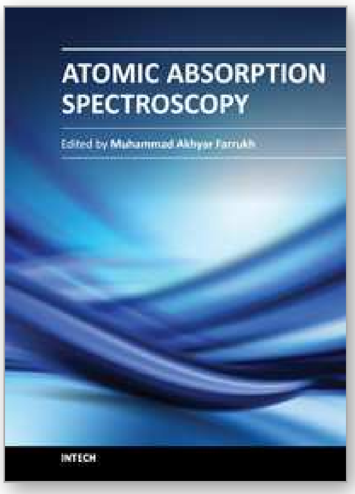

Atomic Absorption Spectroscopy

Edited by Dr. Muhammad Akhyar Farrukh

ISBN 978-953-307-817-5
Hard cover, 258 pages
Publisher InTech
Published online 20, January, 2012
Published in print edition January, 2012