Metals Determination by Microwave Digestion
ICP-OES of Some Supplements

TUNDE JURCA¹, ELEONORA MARIAN¹, MIHALY BRAUN², LAURA VICAS¹
¹University of Oradea, Faculty of Medicine and Pharmacy, 29 Bicazului Str., 410028, Oradea, Romania
²University of Debrecen, Department of Inorganic and Analytical Chemistry, Debrecen, Hungary

ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) analysis was applied to assess element concentrations in six samples of mineral supplements/multivitamins acquired in pharmacies from Romania. Concentrations of Fe, Ca, Mg, Zn, Li, Ba, Sr, Ni, Cu, Sn, Al, Co, Cr, Mn, Mo, Se, K, Na, Cd, Pb were determined. The digestion method with acid mixture (HNO₃ an H₂O₂) was used to destroy the organic material. Generally, the Ca, Fe, K and Mg contents were normal to higher range compared to the labelled quantity. The Cu, Mn, Se, Ni, Sn and Zn contents were low in most of the formulations when compared to the labelled amounts. Li, Ba, Sr, Na, Al, Cr, Sr, Co were quantified in some formulations where they were not labelled, this may be due to the excipients that may have been used in the formulations. The concentration of the toxic elements Pb and Cd are within the allowed limits. Based on the results obtained in the present study, it is concluded that the present techniques are adequate for the routine determination of heavy metals concentration in mineral supplements.

Keywords: mineral supplements, heavy metals, microwave digestion, ICP-OES

Multivitamins containing mineral supplements are widely consumed mainly by elderly individuals, lactating mothers, pregnant women and athletes. These products are acquired over the counter without medical prescriptions.

The control of element composition in these mineral supplements or multivitamins is of great interest due to their increasingly higher consumption and to the large diversity of minerals offered in the market. Therefore, it has become a necessity to evaluate their mineral composition and to compare it to the values declared on labels, as well as to identify the presence of any toxic element [1].

The accurate analysis of metals in vitamin/mineral preparations and food supplements is very important. These metals can be classified into several groups – major electrolytes (Na, K, Ca, Mg) crucial to normal primary physiological processes such as cellular activity and metabolism; minor minerals (Fe, Mn, Zn, Cu) present in lower levels to act as metabolic agents and enzyme catalysts; and micro (trace) minerals in low levels (Se, Cr, Mn, and K) for less defined reactions [2,3].

In this study, we applied inductively coupled plasma spectroscopy ICP-OES in the analysis of six samples of mineral supplements and multivitamins acquired from Romania.

Materials and methods

All chemicals used in the experiment were of analytical grade (E.Merk/BDH). High quality water, obtained using a Milli-Q system (Millipore, Bedford, MA, USA), was used exclusively.

The ICP-OES measurements were performed with a sequential ICP spectrometer IRIS Intrepid II and samples were digested by acid assisted microwave irradiation using Microwave Milestone MLS-1200.

The samples of mineral supplements and multivitamins were acquired from pharmacies from Oradea City, Romania. All of them were in solid form, in tablets. Eight tablets of each sample were weighted to obtain the mean values of mass per tablet. For the analysis, the tablets were homogenized by grinding in order to obtain a powder form. 0.50 g portion of each sample were placed in PTFE (polytetrafluorethenyl) bombs, and 4.5 mL of HNO₃ (65%, w/w) and 0.5 mL H₂O₂ were added. The PTFE bomb was left to cool for an hour and then carefully opened. The pale yellow coloured solution was transferred into a beaker and diluted to 50 mL with ultrapure water in a plastic volumetric flask.

The blank samples were digested in the same way. Sample solutions were analyzed by ICP-OES.

Results and discussion

Table 1 presents the percentage contents of Ca, Fe, Mg, Mn, and K and table 2 presents the contents of Cu, Sr, Zn, Cr and Na for the analysis of trace metals in these formulations.

Mineral supplement A contains green tea, B wheat germ and yeast, D ginseng and Soya lecithin, and E valerian.

The labelled calcium contents ranged from 103.5 mg to 120 mg/tablet in various studied formulations. Formulations B, C and E were not marked to contain calcium, but the analysis showed that these formulations contain 7.34, 2.76 and 7.99 mg of calcium/tablet.

Most of the formulations contain calcium as pantothenate or as dibasic phosphate salts. The concentration of calcium in most of the formulations did not correspond to the labelled quantities.

The addition of unclaimed calcium carbonate or other calcium compounds as inert or inactive ingredients represents, probably, the cause of low analytical values for calcium [4].

The labelled contents of iron ranged between 10.00 mg and 18.00 mg elemental iron under the form of various salts. The iron contents corresponded to the labelled quantities with exception of formulation F where the
The rationale for the availability of such widely varying doses of iron to the consumer, at exorbitant prices, has never been questioned by practitioners of modern medicines and also appears to have escaped the notice of the drug regulatory authorities of this country [5].

The magnesium contents were found exceptionally in good agreement in all formulations. Formulations B and C were not marked to contain magnesium, but the analysis showed that they contain a very low quantity of magnesium because various excipients such as magnesium stearate are commonly used as inactive or inert ingredients in formulating tablets.

Potassium was labelled only in 3 formulations, but the analysis shows that it is present in all preparations under study. The labelled quantity of potassium in these formulations ranged between 0.84 and 40.0 mg/tablet. Formulations B, C and E were not marked to contain potassium, but the analysis showed that they contain 1.31, 0.11 and 1.05 mg of potassium/tablet. The presence of potassium is probably due to potassium salts used as excipients or due to impurities from active and inactive natural ingredients such as talc, gum acacia, gelatin, starch etc. which are employed in formulating the products.

The manganese contents of the six analyzed pharmaceutical multimineral formulations significantly differed from the labelled amounts. The labelled content of manganese for most of the products was however 1-2 mg. In formulations A and B, manganese was not detected. It is possible that these differences in manganese contents are related to manufacturing faults such as improper mixing [6].

The copper contents of the studied pharmaceutical multi-mineral formulations were in a wide range, i.e. 1.00 to 2.00 mg/tablet (labelled contents). The content of copper in formulations A, B, D and E was about 79%, while in the other formulations it was less than 60%. This could be attributed to manufacturing faults, such as inconstant mixing of the small proportion of copper salts in the huge batches of multi-mineral products.

The contents of zinc listed on labels of the different multiminer al pharmaceutical formulations vary from 10 mg to 20 mg/tablet. Compared to the claimed contents, the values of zinc obtained on the quantitative analysis of these products were to a great extent on the lower side. Improper mixing of the relatively minor quantities of zinc salts during the manufacturing process may be the likely cause of this variation. Products B and C contained 0.01-0.02 mg/tablet of zinc, although Zn was not mentioned on the label.

This could be due to some possible contamination during the manufacturing process [7].

All formulations were not marked to contain strontium, but the analysis showed that they contained 0.03-0.04 mg of strontium/tablet. Chromium contents were found exceptionally in good agreement in all formulations. Formulations B, C, D and E were not marked to contain chromium, but the analysis showed that they contained 0.007-0.01 mg of chromium/tablet.

Traces of Cr and Sr appear in herbal supplements maybe due to the presence of these metals in the composition of the plants.

The concentration of toxic elements, Pb and Cd, are within allowed limits.

**Conclusion**

This study indicates that trace metals in these multiminer al formulations were found to be significantly different compared to the labelled amount. This may be
due to the use of various excipients in dispensing or due to contamination during processing. Manganese and zinc contents were usually low, that may be due to improper mixing or addition of inadequate amount of these metals. It can be concluded that it is required more care in the preparation of these formulations, in the use of proper excipients, in the process of cleaning the containers and equipment in order to avoid contamination. The manufacturing process and methods of analysis should be validated before the commercial production.

References
3. GEOLOGY, H.V.W., Social Science & Medicine, 1989, 29, p. 1923

Manuscript received: 5.01.2011