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Determination of macro and trace element in multivitamins preparations by inductively coupled plasma optical emission spectrometry with slurry sample introduction

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Abstract

A slurry sampling technique has been utilised for elemental analysis of multivitamins preparations using inductively coupled plasma-emission spectrometry (ICP-OES). For results comparison, samples were mineralised. Slurry concentration 0.1–0.2% m/v in 6% v/v HNO_3, was used. The calibration by water standard solutions, slurry standards and standard additions were tested for determination above-mentioned elements in slurries. The method offers good precision for macro elements (RSD ranged from 5% to 10%). For in-home control sample, the measured concentrations are in satisfactory agreement with independent laboratories. For the analysed multivitamin preparations, the found element concentration is compared to amount declared by producer. The concentrations of Ca, Mg, P, K, Fe, Mn, Zn, Cu and Cr, Ni, V were determined in the range 1000–100,000 and 5–50 μg g^{-1}, respectively. The slurry ICP-OES analysis was found to be suitable for quality control monitoring of multivitamin preparations and could be useful as a routine procedure.

Keywords: ICP-OES; Slurry; Elemental analysis; Multivitamin preparation

1. Introduction

Vitamins, mainly multivitamin preparations are the largest supplement category −48% of the supplement market (Nardinelli et al., 1999). Reference daily intakes for 12 significant elements have been established: calcium (1000 mg), chloride (3400 mg), chromium (120 μg), copper (2 mg), iron (18 mg), iodine (150 μg), potassium (3500 mg), magnesium (400 mg), manganese (2 mg), molybdenum (75 μg), sodium (2400 mg), phosphorus (1000 mg), selenium (70 μg) and zinc (15 mg) (Mindel, 2000). The dietary supplement manufacturer is responsible for ensuring that a dietary supplement is safe before it is marketed and that product label information is truthful and not misleading. With respect to multivitamins preparation safety, toxic element contamination in them is an important topic. A multi-element analysis method that is applicable to a large variety of food supplements and easy to use is needed to verify accuracy of element content on multivitamin labels and to screen for toxic elements contamination eventually. Many techniques have been utilised for the elemental analysis of a range of matrices, including less common stripping voltammetry, X-ray fluorescence, neutron activation analysis, capillary zone electrophoresis or wide extended flame atomic absorption spectrometry (F-AAS), graphite furnace spectrometry (GF-AAS), flame emission spectrometry and multi-element inductively coupled plasma-emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) (Tolg, 1987).

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Sample preparation remains the major limiting step in analytical throughput. Dry ashing may take 2–3 days to prepare an analytical solution. Conventional acid digestions are typically faster (3–4 h) than dry ashing but need permanent operator attention. Microwave digestion is usually performed with nitric acid in a closed high-pressure vessel (at temperature above the boiling point of nitric acid) and is generally complete within 1 h (Dolan & Capar, 2002). An alternative and relatively less reported technique is the slurry nebulization, involving the direct aspiration of suspended sample directly into and AAS, FES or ICP-OES (Ebdon, Foulkes, & Sutton, 1997).

Hight et al. determined 36 nutritional and toxic elements in 42 dietary supplements by using square wave anodic stripping voltammetry, ICP-OES, instrumental neutron and prompt γ-ray activation analysis, FAAS and GFAAS. Mineral and vitamin preparations (tabs, capsules) were included in sample scale as well as NIST standard reference materials. Supplements were digested with a boiling mixture of HNO_3 and $HClO_4$ or HNO_3, H_2SO_4 and H_2O_2, digests were analysed after centrifugation by using above-mentioned methods. They reported some products contain Pb, Zn, Mn, Mo, Cu and Fe in excess of generally accepted safe levels (Hight et al., 1993).

Dolan et al. determined arsenic, cadmium, mercury and lead contents of 95 dietary supplements product and NIST standard reference materials using microwave digestion and high-resolution ICP-MS. They found some products include arsenic up to 3770 $\mu g\,kg^{-1}$, cadmium 368 $\mu g\,kg^{-1}$, mercury 16800 $\mu g\,kg^{-1}$ and lead 48600 $\mu g\,kg^{-1}$ (Dolan, Nortrup, Bolger, & Capar, 2003).

Burgoin et al. (1992) analysed three brands of Ca supplements, a laboratory-reagent grade $CaCO_3$ and a certified reference material for Cd and Pb by different analytical techniques anodic stripping voltammetry, ICP-MS, FAAS and GFAAS. Krone, Wyse, and Ely (2001) analysed for zinc seven zinc-containing dietary supplements by means ICP-MS and Scelfo and Flegal (2000) determined lead in calcium supplements using ICP-MS.

Haji Shabani et al. reported a simple and sensitive flow injection FAAS analysis for the determination of cobalt in vitamin B_{12} and B-complex ampoules and a rapid on-line pre-concentration technique for the determination of copper in multivitamin tablets by flow injection FAAS (Dadfarnia, Salmanzadech, & Haji Shabani, 2002; Haji Shabani, Dadfarnia, & Dehghan, 2003). Van Staden and Hattingh (1998) designed the electrodialyse unit, incorporated it into flow injection FAAS system, and determined copper in multivitamin tablets. Long and Snook applied ICP-OES to the analysis of major constituents of pharmaceutical capsules. They compared pneumatic nebulization of aqueous solutions and vaporization of slurries of the capsule preparation (Long & Snook, 1982).

ICP-OES, respectively, ICP-MS is widespread in multi-element analysis of micro- and macronutrient and toxic elements in food (Barnes & Debrah, 1997; Dolan & Capar, 2002; Flajnik, 1995; Ikem, Nwankwoala, Odueyungbo, Nyavor, & Egiebor, 2002; Zhou & Liu, 1997).

McKinstry et al. reported the determination of nine macro and microelements in milk powders, liquid milk and infant formulas by ICP-OES. Samples were prepared as slurries and analysed against aqueous standards following internal standard compensation for potential matrix effect. Approximately 0.25 g of powdered sample was suspended in warm water, Lu internal standard and Triton X-100 solution was added and made to final volume 25 mL. The slurry/ICP-OES results are compared with dry-ash sample preparation/ICP-OES results and wet digestion sample preparation/ICP-OES and F-AAS results from independent laboratory (McKinstry, Indyk, & Kim, 1999).

Matusiewitz and Golik have utilised a slurry sampling technique coupled with microwave-induced plasma optical emission spectrometry for the determination of macro and trace elements in biological reference materials. Slurry concentrations up to 1% m/v (particles <20 μm), prepared in 10% HNO_3 containing 0.01% Triton X-100, were used with calibration by the standard additions method (Matusiewitz & Golik, 2004).

Ebdon et al. have been thoroughly reviewed several attributes of slurry which have been acknowledged as critical to the stability, homogeneity, transport and nebulization efficiency of the suspended sample. The influence of particle size, slurry concentration, and the use of dispersants have been discussed (Ebdon et al., 1997). As well as in Goodall, Foulkes, and Ebdon (1993) subscription, the fundamental parameters of slurry nebulization ICP-OES have been analysed.

This paper reports the development of a facile and convenient sample preparation for determination of Ca, Mg, P, K, Fe, Mn, Zn, Cu, Cr, Ni, and V in multivitamins preparations following slurry nebulization of suspended samples into ICP-OES, with quantification incorporating standard slurries or standard addition method.

2. Materials and methods

2.1. Equipment

The measurement was carried out with the sequential, radially viewed ICP atomic emission spectrometer INTEGRA XL 2 (GBC, Dandenong Australia), equipped with a ceramic V-groove nebulizer (Glass

expansion, Australia) and a glass cyclonic spray chamber (Glass expansion, Australia). The slurries preparation and sample leaching were carried out by means of an ultrasonic bath Powersonic UCC 1 (Czech Republic). The samples were decomposed in the microwave decomposition apparatus BM 1 S/2 (Plazmatronika, Poznan, Poland). The demineralised water was taken from a Milli-Q Plus water-purification system (Millipore, Bedford, USA). Other equipment used included a magnetic stirrer and calibrated volumetric glassware.

2.2. Reagents

The single component standards of Ca, P and Mg (each one with the content of $10{,}000 \pm 30\ \mu g\ mL^{-1}$, CPI International, USA) and K, Fe, Cu, Cr, Mn, Ni, V and Zn ($1000 \pm 3\ \mu g\ mL^{-1}$, CPI International, USA) were used. For the slurry preparation, decomposition and leaching study, analytical grade concentrated (65% w/v) HNO_3, and (35% w/v) HCl (Lachema, Czech Republic) were used.

2.3. Samples

Five brands of multivitamin supplements were purchased at pharmacies. Characteristic of the samples is shown in Table 1. In order to no suitable matrix reference material is available, one sample (number 1) was used for the in-home control sample (CS) preparation. It was analysed in 10 independent laboratories: a classical dry ashing, conventional acid digestions and microwave digestion followed FAAS, GFAAS, FES, ICP-OES and ICP-MS were employed.

2.4. Standards preparation

2.4.1. Aqueous standards

Three multi-element standards were prepared containing: (i) Ca ($150\ mg\ L^{-1}$), P ($100\ mg\ L^{-1}$), Mg ($100\ mg\ L^{-1}$), K ($50\ mg\ L^{-1}$), Zn ($10\ mg\ L^{-1}$), Fe ($20\ mg\ L^{-1}$), Cu ($2\ mg\ L^{-1}$), Mn ($2\ mg\ L^{-1}$), Cr ($0.1\ mg\ L^{-1}$), Ni ($0.1\ mg\ L^{-1}$), V ($0.1\ mg\ L^{-1}$); (ii) the same elements with half concentrations as in the first one; (iii) the same elements tenfold diluted as the first one. All standards were stabilised with 6 mL 65% w/v HNO_3/100 mL of solution. As well a standard blank containing 6 mL HNO_3/100 mL was prepared.

Table 1
Description of multivitamin preparations analysed

Preparation	1	2	3	4	5
Elements declared	17	15	12	18	17
Tablet weight (g)	1.43	1.46	1.71	1.38	1.33
Main matrix	Vitamins, microcrystalline cellulose, talc, silicon dioxide, sweetener, food colourings and flavourings				

2.4.2. Standard slurries

Approximately (i) 0.1 and (ii) 0.2 g of in-home control sample was accurately weighed into a 100-mL volumetric flask, 6 mL of HNO_3 and 30–50 mL of water was added and treated in ultrasonic bath for 15 min. After cooling to room temperature, the standard slurries were made to volume with water and mixed. The water standard blank containing 6 mL HNO_3/100 mL was used.

2.4.3. Standard additions

Approximately (i) 0.1 and (ii) 0.2 g of in-home control sample was accurately weighed into a 100-mL volumetric flask, and 50, 25 and 10 mL of the most concentrated aqueous standard and appropriate amount of HNO_3 was added (in total 6 mL HNO_3/100 mL of suspense) and treated in ultrasonic bath for 15 min. After cooling to room temperature, the standard slurries were made to volume with water and mixed. The water standard blank containing 6 mL HNO_3/100 mL was used. All solutions and slurries were stored in polyethylene flasks.

2.5. Sample preparation

Prior to analysis, samples were homogenised and digests, acid extracts and slurries were prepared for ICP-OES determination.

2.5.1. Microwave digestion

Approximately 0.3–0.5 g of multivitamins preparation powder were accurately weighed into an acid washed teflon digestion tube. Six milliliter of concentrated nitric acid (65% w/v) was added, and the tube was heated in a microwave oven at the power setting of 80% for 10 min and at 100% for 10 min. The maximum total output of the microwave generator was 700 W (minimum pressure $= 24 \times 10^5$ Pa, maximum pressure $= 25 \times 10^5$ Pa). The digest was transferred into a 100-mL acid washed volumetric flask, filled up with demineralised water and stored in polypropylene flasks. Two water blanks were run with each batch of samples.

2.5.2. The acid extraction

About 0.1–0.2 g of multivitamin sample was accurately weighed into an acid washed beaker and extracted with 6 mL concentrated nitric acid (65% w/v) and 50 mL demineralised water. Suspensions were treated by sonification for 15 min, then filtered into a 100-mL acid washed volumetric flask, filled up with demineralised water and stored in a polyethylene flask. Two water blanks were run with each batch of samples.

2.5.3. The slurry preparation

About 0.1 g of multivitamin sample and 0.2 g for determination of Cr, Ni, V was accurately weighed into an acid washed 100-mL volumetric flask, 6 mL of HNO_3

and 30–50 mL of water was added and treated in ultrasonic bath for 15 min. After cooling to room temperature, the standard slurries were made to volume with water and mixed.

During sample aspiration, the slurries were shaken on a magnetic stirrer. After aspiration of each suspension, a 6% v/v nitric acid was flushed through the nebulizer-torch system to remove any residual sample.

2.6. The ICP-OES method

The measurement conditions were optimised based on signal-to-background ratio of the least concentrated elements (Ni, Cr, V). For aspirated solutions and slurries, the same measurement conditions were used (listed in Table 2). The emission lines are listed in Table 3. Net analyte emission was based on taking the difference of measured emission intensity on top of the peak and background near the peak. In case of digests and extracts, aqueous standards were use. For slurries, aqueous standards, standard slurries and standard addition were used. All detection limits given by ICP-OES software were based on three times standard deviation of the background counts. Including the washing time between slurries, the total time for analysis was approximately 5 min.

3. Results and discussion

3.1. Measurement conditions setting

The in-home control sample was used in this study. Step by step, single operating parameters were changed to obtain a maximum net signal-to-background intensity ratio (SBR) of the least concentrated element (Ni, V, Cr). The nebulizer argon gas flow rate, sample aspiration rate, plasma power and viewing height were optimised. The plasma gas flow and auxiliary gas flow rates were not optimised, but were selected based upon previous experiences to ensure plasma stability. In analysed samples apart from Ni, V and Cr, the other elements were presented in such high concentration that it was possible to use compromise-working conditions.

To investigate the effect of presence of solid particles in plasma, the axial intensity profiles of analysed elements for solutions and slurries were measured. It was found that the maximum intensity for slurries tends to shift to higher observation heights. The highest SBR of Ni was observed with the viewing height 7 mm above coil and the forward power 1000 W for solutions and 8 mm and 1100 W for slurries. Because weight for sample preparation as well as element concentration, was higher in case of solution, only unified conditions (the best for Ni in slurries) were used for both solutions and slurries in further analysis.

The influence of sample aspiration rate on the signal intensity was followed. For the pumping rate greater than some 2 mL min^{-1}, the signal intensity did not increase, slurry nebulization got worse apparently and the mass drained from the chamber increased. Therefore, a slurry and solution sample aspiration rate of 1.5 mL min^{-1} was chosen.

Table 2
The optimum operating conditions for ICP-OES analysis with slurry sample introduction

RF power	1100 W
View height	8 mm
Gas	Argon 99.999%
Plasma gas	0.6 L min^{-1}
Auxiliary gas	10 L min^{-1}
Nebulizer gas	0.65 L min^{-1}
Sample aspiration rate	1.5 mL min^{-1}
Read	On-peak, 3 s
Background correction	Fixed point
Number of replicates	10

3.2. Slurry composition

In order to achieve a good dispersion of multivitamin preparation, various nitric and hydrochloric acid concentration was tested. The effect of both acids was very similar: from their low concentration, they improved wetting and dispersion of multivitamin powder. Finally in this study, HNO_3 was always used in resultant concentration 6% v/v, because it was also employed as the mineralising agent for microwave digestion. Due to its oxidising properties and facilitation of element extraction, nitric acid is suitable for slurry preparation. In multivitamin preparation, a lot of chemical form of element analysed are water-soluble. For the most part or in some cases completely, they are dissolved and are not bound on solid particles. Because presence of nitric acid seemed sufficient for consistence of slurries, an additional surfactant was not added. Tested Triton X-100 (0.01–0.05%) did not

Table 3
Analytical characteristics of proposed method

Parameter	Ca	Mg	K	P	Fe	Zn	Mn	Cu	Cr	Ni	V
λ (nm)	393.366	285.213	769.896	177.495	259.940	213.856	257.610	324.754	267.716	221.647	311.071
LOD (mg g^{-1})	5.13	7.93	2.42	1.85	0.0128	0.0194	0.00866	0.0130	0.00187	0.00247	0.00322
Precision (%, RSD)	5.34	4.64	9.11	8.20	4.81	6.13	6.94	7.41	10.4	19.8	17.1

reduce a gradual solid phase deposition on spray chamber inner surface. A visible sample deposition came into existence after two hours of continuous slurry aspiration approximately. After aspiration of each slurry, 6% v/v HNO_3 was used for flushing through the nebulizer-spray chamber-torch system to remove any residual sample. Thereafter, no visible trace of solid sample on introducing system and no changes of emission signal were detected.

The concentration of the slurry is an important factor to consider during preparation. The influence of slurry concentration on the signal intensity was followed from 0.05% to 2.5% (w/v). For the solid phase amount in suspension less than 1% (w/v) approximately, the signal intensity was depended on concentration linearly. For the concentration greater than 1.5% (w/v) approximately, the signal intensity did not increase linearly and the mass drained from the chamber increased probably. Regarding elements with the highest amount, routine analysis was conducted with a slurry concentration 0.1–0.2% that is sufficient for determination "minerals" and the most of trace elements in multivitamin preparations.

For slurries aspiration, a very significant parameter is particles size that limited analytical recovery. The improved recoveries are likely to be the results of a more efficient evaporation of a lesser size particles slurry. Multi-vitamin tabs were crushed with a agate mortar. For this way of sample preparation, it was found that a median particle size of 90 μm resulted. The pre-crushed samples were then grinded in the planetary mill Pulverisette 5 (Fritsch GmbH, Germany) for one hour. Particle size distribution of fine-powdered samples was determined by examining a suspension using Mastersizer 2000 (Malvern Instruments Ltd., United Kingdom). For all samples, the volume average of particle was less than 13 μm. After prolonged periods of grinding above 2 h, it was appeared to make for agglomeration of small particles, so grinding was stopped after 1 h.

In order to solid matrices are to be efficiently atomised, ionised and excited, Ebdon et al. (1997) recommended in their review a slurry particle size less than 20 μm. Larger particles do not reach the plasma and are responsible for the loss of signal. Furthermore, a slurry nebulization into plasma requires that both the analyte transport efficiency through the sample introduction system and the atomisation efficiency of particles in the plasma are identical with those of a solution. Although nitric acid used in suspense preparation facilitates of element extraction and some chemical forms are easily solvable, a significant part of analysed elements is bond on solid particles and is not dissolved. So that we did not feel sure of the simple aqueous calibration is suitable for that analysis, both the standard suspension calibration and the standard addition were employed.

Mermet used the Mg II 280.270 nm/Mg I 285.213 nm intensity ratio to express the analytical performance response of the plasma to changes in operating conditions and chemical composition (Mermet, 1991). The Mg II 280.270 nm/Mg I 285.213 nm intensity ratio is used as a practical tool for assessing the energy transfer between the plasma and the injected species and it can also evaluate matrix composition effect. This factor calculated for Mg in the most concentrated aqueous multi-elemental standard was 16.40, for 0.05% w/v suspension of the in-home control sample 16.42, for 0.1% suspension 16.40, for 2% suspension 15.97. Theoretically, the ratio can be affected by presence of easily ionised elements in multivitamins preparation, e.g., K, Ca and Mg. In 0.1% w/v slurry of the in-home control sample used for routine analysis, 130 mg L^{-1} Ca, 70 mg L^{-1} Mg and 30 mg L^{-1} K is presented approximately. This amount does not induce the matrix interference (Krejčová, Černohorský, & Čurdová, 2001). It has been shown by Ebdon et al. (1997) that transport effects are the most important interference effects in slurry nebulizations.

3.3. Analytical characteristics and validation of the process

For the slurry analysis, all limits of detection given by ICP-OES software were calculated as the concentration equivalent to three times standard deviation of the background counts ($3\sigma_{slurry}$, in μg mL^{-1}). For Ca, K, Mg, P, Zn, Fe, Mn and Cu, the least concentrated standard suspension of the in-home control sample (0.1% w/v) was use. In case of Cr, Ni, V, 0.2% w/v standard suspension was employed for this propose. The procedural limits of detection (LOD, in mg g^{-1}) were worked out as $LOD = f_{dilution} * 3\sigma_{slurry}$. The dilution factor $f_{dilution}$ takes into account the dilution of sample during the preparation step. The $3\sigma_{slurry}$ were determined by ten repetitive standard suspension measurements. Mainly in case of Mg and Ca in multivitamin preparations, it was necessary to reduce the photo-multiplier voltage to let down their signal intensities and the real ICP-OES detection ability for Mg and Ca is far better. They are summarised in Table 3.

When the in-home control sample was prepared, all mass of multivitamin preparation was divided into 15 batches. In order to verify its homogeneity, the material was taken from single batches for the slurry, digest and extract preparation and analysis. The precision was also established from analysis of 15 repeatedly prepared slurries of the control sample using the calibration based on standard suspensions. In addition to a plasma fluctuation, the sample preparation process is the main source of uncertainties in analysis. The using of unsuitable calibration standards results in systematic errors and recoveries statistically different from 100%.

Regrettably, any matrix reference materials based on multivitamin preparation are not available commercially. Therefore, the validation of the procedure was based on analysis of the in-home control sample. Compared with ten independent laboratories, results obtained for microwave digests, extracts and slurries analysed using aqueous standards, standards slurries and standard additions are summarised in Table 4, together with corresponding precision.

In order to quantify the solubility of single chemical form of analysed elements, the acid suspension was filtered and only the solution was used for analysis. For copper, which is presented in our in-home control sample as CuO, the poor extraction efficiency approximately 40% was found. For some elements determined, results coming from the analysis of extract were not also favourable. Likewise after microwave decomposition, total amounts in that sample corresponded with results obtained from co-operating laboratories.

For suspense analysis, three calibration models were employed using aqueous standards, standards slurries and standard additions. They provided very similar results. All obtained results were subjected to one-way analysis of variance (ANOVA) to ascertain (at 95% confidence level) the homogeneity across the analytical pro-

Table 4
The analysis of the in-home control sample

	Declared by producer		Other laboratories[a]	Microwave digestion[b]	Acid extract[b]	Slurry/aqueous standards[c]	Slurry/standard suspensions[b]	Slurry/standard addition[c]
	(mg/tab)	(mg g^{-1})	(mg g^{-1})					
Ca	162	113	134 ± 10.4	136 ± 8.43	134 ± 10.1	126 ± 9.62	132 ± 7.05	133 ± 10.2
P	125	87.4	86.5 ± 7.27	68.9 ± 6.19	59.9 ± 4.32	93.5 ± 6.73	87.4 ± 4.06	86.8 ± 6.03
Mg	100	70.0	67.8 ± 2.69	68.4 ± 3.92	70.1 ± 4.77	70.1 ± 4.75	68.6 ± 3.18	66.3 ± 3.46
K	40	28.0	27.7 ± 1.72	29.8 ± 2.12	21.1 ± 1.98	26.8 ± 2.24	26.9 ± 2.09	25.1 ± 1.55
Fe	18	12.6	10.9 ± 0.800	8.80 ± 0.762	9.04 ± 0.632	11.4 ± 0.578	10.3 ± 0.495	10.9 ± 0.472
Zn	15	10.5	9.95 ± 0.653	11.1 ± 0.621	8.62 ± 0.723	9.21 ± 0.532	10.1 ± 0.619	10.1 ± 0.640
Mn	2.5	1.75	1.56 ± 0.131	1.69 ± 0.122	1.44 ± 0.131	1.72 ± 0.147	1.66 ± 0.115	1.71 ± 0.126
Cu	2	1.40	1.33 ± 0.0913	1.37 ± 0.101	0.572 ± 0.0825	1.22 ± 0.0969	1.44 ± 0.107	1.27 ± 0.112
	(μg/tab)	(μg g^{-1})	(μg g^{-1})					
Cr	25	14.8	22.9 ± 4.73	18.9 ± 1.99	20.5 ± 2.35	19.7 ± 2.01	23.8 ± 2.48	16.2 ± 1.70
Ni	5	3.50	8.14 ± 2.03	12.7 ± 0.869	5.09 ± 1.03	6.78 ± 0.723	8.04 ± 0.800	9.99 ± 0.699
V	10	7.00	10.4 ± 1.52	11.6 ± 1.24	7.00 ± 1.52	11.3 ± 1.31	11.1 ± 1.89	9.93 ± 0.898

The results of analysis in control laboratories, analysis after total microwave digestion, partial acid extraction and slurry procedures are compared with content declared by producer.
[a] Mean ± SD of 10 replicates.
[b] Mean ± SD of 15 replicates.
[c] Mean ± SD of 5 replicates.

Table 5
Macro and trace elements in multi-elements preparations

Sample	1			2			3			4			5		
	P	ICP-OES		P	ICP-OES		P	ICP-OES		P	ICP-OES		P	ICP-OES	
		MW	Slurry		MW	Slurry		MW	Slurry		MW	Slurry		MW	Slurry
Amount (mg/tab)															
Ca	113	136	132	86.3	101	109	29.2	31.9	31.3	27.0	40.4	41.8	122	86.5	84.2
P	87.4	69.1	87.4	67.8	75.3	78.1	17.5	21.8	20.9	21.2	20.7	20.1	94.0	63.6	60.0
Mg	69.9	68.5	69.0	54.8	65.5	66.3	11.7	11.2	10.5	72.5	74.6	76.8	75.2	76.7	75.0
K	28.0	27.8	27.0	13.7	16.9	16.1				29.3	34.5	35.2	30.1	21.3	23.0
Fe	12.6	10.9	10.3	10.3	10.1	10.3	8.77	7.95	8.13	13.0	9.28	9.42	13.5	12.4	13.7
Zn	10.5	10.0	10.1				5.84	6.02	5.85	10.9	9.71	9.49	11.3	10.5	11.0
Mn	1.75	1.56	1.66	1.37	1.77	1.74	0.292	0.329	0.342	1.81	2.18	2.12	1.88	1.77	1.75
Cu	1.40	1.34	1.44	0.342	0.326	0.338	0.292	0.292	0.319	1.45	1.07	1.10	1.50	[a]	[a]
Amount (μg/tab)															
Cr	17.5	22.9	23.8	17.1	13.8	12.8				1.81	6.61	5.51	18.9	9.47	4.59
Ni	3.50	8.18	11.1							3.62	11.2	10.1	3.76	[a]	[a]
V	6.99	10.4	15.9							7.25	18.1	16.7	7.52	12.9	8.80

The result of analysis of elements in multi-element preparations using ICP-OES after microwave digestion and ICP-OES slurry technique are compared with amount declared by producer. P-amount declared by producer of multivitamin preparation.
[a] It was not detected.

cedures. The ANOVA results proved that there was not significant variation between single analytical procedures employed.

In case of elements presented in multivitamin preparation in very low concentrations (Cr, Ni, V), relatively poor precision was mentioned. For these three elements, it is necessary to increase weight of solid sample in suspense in order to get away from near closeness of detection limits. As well as microwave decomposition is suitable, in order to higher weight of sample for decomposition step is applicable in case of multivitamin preparation.

3.4. Analysis of multivitamin preparations

For mutual comparison of the actual elements levels in multivitamin preparations, the element levels in selected five powdered multivitamin tabs were carried out using the ICP-OES slurry analysis with the calibration based on suspension standards. Compared with the amount declared by producer and total amount in mineralised sample, these results are presented in Table 5. The sample No. 1 is the in-home control sample, which is categorised as drug. The other samples are food supplements. In drugs, the content of declared active components must correspond with their actual amount as opposed to dietary supplements. In general, the determined average levels of the elements in the analysed sample correspond with manufacturer labels with few exceptions (e.g., Cu in sample 5). Results for Cr, Ni and V show impropriety of the procedure used in terms of insufficient limits of detection of method as discussed previously.

4. Conclusion

A slurry sampling technique has been utilised for multi-element analysis of Ca, Mg, P, K, Fe, Mn, Zn, Cu, Cr, Ni and V in multivitamins preparations using ICP-OES. In general, the determined average levels of the elements in the analysed sample correspond with manufacturer labels with few exceptions.

Results obtained for the routine slurry ICP-OES analysis of multivitamin preparation show possible work simplification in preparation step especially. Method based on digestion using acids can result in incomplete dissolution of the sample, evaporative losses of the more volatile elements and contamination problems. Dissolution is also time consuming and the sample preparation time often exceeds the analysis time. The proposed analytical method offers an interesting perspective for other similar materials for their direct determination based on slurry sample preparation. It is also an attractive alternative for laboratories not equipped with any digestion technique.

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