Journal of Pharmaceutical and Biomedical Analysis 47 (2008) 541–546

Contents lists available at ScienceDirect

Journal of Pharmaceutical and Biomedical Analysis

journal homepage: www.elsevier.com/locate/jpba

Use of slurry suspension sample introduction technique in fast multielement analysis of multimineral and multivitamin formulations by inductively coupled plasma atomic emission spectrometry

George A. Zachariadis*, Agathi F. Olympiou

Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

ARTICLE INFO

Article history:
Received 30 November 2007
Received in revised form 25 January 2008
Accepted 12 February 2008
Available online 17 February 2008

Keywords:
Metals
Slurry suspensions
Inductively coupled plasma emission spectrometry
Multiminerals
Analysis of variance

ABSTRACT

A slurry suspension sampling technique has been developed and optimized for rapid multielemental analysis of multivitamin/multimineral preparations using inductively coupled plasma atomic emission spectrometry (ICP-AES). The following macro-, micro- and trace-elements: Ca, Mg, Mn, Fe, Cr, Al, Ag, B, Ba, Bi, Cd, Co, Cu, Ga, In, Ni, Pb, Zn, As and Se were determined by the proposed method. The lower detection limits were obtained for Mn, Mg, Cu and Ca whereas the highest for Bi, Pb, As and Se. Consequently the method can be used as a fast screening method. A wet-acid mineralization method was applied as total recovery method for comparative purposes. Samples were prepared as slurries at a concentration of 5% (m/v) in aqueous acidic media (0.8 M HNO_3). Various factors affecting the sensitivity of the method were optimized. The obtained results were subjected to two-way analysis of variance to examine any significant difference between the developed slurry procedure and the wet-acid complete decomposition. Finally, the slurry suspension technique was found to be applicable in routine quality control and contamination monitoring of multimineral preparations. For the analyzed commercial preparations, the found elemental concentrations are compared to those appearing in the label of the products.

1. Introduction

Multivitamin and multimineral supplements are designed specifically to provide a variety of essential nutrients for the body. Multivitamin supplements can help to prevent both vitamin and mineral deficiencies, and are used by many to increase essential nutrients in the body and achieve additional health benefits. Multivitamins usually contain at least 100%, if not more, of the recommended dietary allowance of essential vitamins and minerals [1]. Nutrients that are commonly included in a multivitamin preparation are: vitamins A, B-complex, C, D, E, K, and among minerals, magnesium, zinc, calcium, iodine, selenium, copper, manganese, chromium and molybdenum, etc. Reference daily intakes for 11 significant metallic elements have been established to the following amounts: Ca (1000 mg), Cr (120 μg), Cu (2 mg), Fe (18 mg), K (3500 mg), Mg (400 mg), Mn (2 mg), Mo (75 μg), Na (2400 mg), Se (70 μg) and Zn (15 mg) [2]. The various commercial products differ at the levels of each element and furthermore some of them do not contain several of the necessary metals. Generally, two to four tablets may provide the daily amount of minor nutrients like iron and copper, but for major nutrients like calcium the amount is much lower. However these products do not replace the common food sources but are used only as supplements.

Considering the toxicity of some elements such as chromium, lead, cadmium, etc., inspection of their content in multivitamin preparation is a necessity [3]. However, taking into account the very low content of these analytes in studied preparations, analytical methods of high sensitivity should be used. On the other hand, a suitable sample preparation procedure is usually the key step in the whole method. Conventional wet-acid digestions [3–5] require about 2–3 h but are typically faster than dry ashing procedures. An alternative but less reported technique is the slurry suspension nebulization, including direct aspiration of suspended sample into a suitable atomizer [6]. In this case, it is necessary to optimize the aspiration and atomization conditions to obtain reproducible results.

Various element-specific detectors have been used for the analysis of multivitamin preparations including flame atomic spectrometry or graphite furnace spectrometry [7–9]. Using flame atomic absorption spectrometry, Soriano et al. reported the acid extraction of four nutritional elements in HCl [9] with comparable results to the total digestion procedure. Despite of the fact that these techniques provide good sensitivity, they are in principle single-element detectors, thus they are not convenient for multielement analysis of samples like multiminerals. For this reason recently, inductively coupled plasma-based techniques coupled either with

* Corresponding author. Tel.: +30 2310997707; fax: +30 2310997719.
E-mail address: zacharia@chem.auth.gr (G.A. Zachariadis).

0731-7085/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpba.2008.02.010

an atomic emission or a mass spectrometric detector (ICP-AES and ICP-MS) have been reported as multielement techniques for the analysis of multivitamin preparations [10–12] or other pharmaceuticals [13] however the relevant reports are very few and usually refer to nutritional elements of the products, although some toxic elements should also be monitored [3]. Lewen et al. [14] reported a rapid method for pharmaceuticals based on the introduction of sample dissolved in butoxyethanol–water into an ICP atomizer coupled with a mass detector, as robust screening method, as compared to the visual semi-quantitative test described in the US pharmacopoeia compendium. Yanes and Miller-Ihli [15] have also reported on the multielement analysis after direct slurry introduction of the suspended sample into the plasma atomizers.

Consequently, the aim of this study was to investigate the possibility of the simultaneous measurement of 20 nutritional and toxic elements in multimineral preparations by ICP-AES, applying a direct slurry suspension procedure and avoiding the time consuming mineralization procedure. In a previous work [16] referring to the direct analysis of antibiotic drugs, we reported on the possibility of the direct introduction of heavily loaded organic matrix slurries into the plasma atomizer. In this context, a matrix-matched optimization study is described here, suitable for the mixed nature of multivitamin/multimineral samples. The critical point of this approach is to maintain plasma stability in presence of increased amounts of colloidal organic matter in the injected solution. The analytical performance of the developed method, including limits of detection, precision of the overall procedure and accuracy, was assessed statistically using the standard addition procedure. Furthermore, the results were compared to those obtained after a conventional wet-acid mineralization method, which was applied as a reference. Finally, the proposed method was applied to a number of commercial multivitamin preparations.

2. Experimental

2.1. Instrumentation

A PerkinElmer Optima 3100 XL axial viewing inductively coupled plasma atomic emission spectrometer was used, according to the operating conditions given in our previous work [15]. The analytical wavelengths were also listed in the previous reference. For the optimization of the instrument's performance different radio frequency (RF) incident power levels and sample introduction flow rates were investigated. A Berghof DAB 2 aluminum block equipped with a BTR 941 temperature controller and closed Teflon vessels was employed for the acid digestions.

2.2. Reagents and standards

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). Throughout the work, de-ionized water of 18 MΩ cm^{-1} specific resistance was used. Concentrated nitric acid solution (65%, m/m) was supplied by Riedel de Haen and used for digestions. Dilute nitric acid solutions were also used for slurry suspensions in acidic environment. A stock ICP multielement stock standard solution (CertiPUR IV, traceable to NIST, Merck, Darmstadt, Germany), containing 18 elements at a concentration of 1000 mg l^{-1} and stock solutions of As and Se at concentration of 1000 mg l^{-1} were used for preparation of the final working standards containing 20 analytes.

Aqueous working standards were prepared by appropriate stepwise dilutions of multielement stock standard solution and stock standards of As and Se with 0.8 M nitric acid. The final working standards had concentrations ranging between 50.0 μg l^{-1} and 20.00 mg l^{-1} for each analyte. Finally, a solution containing 0.8 M HNO_3 was used as blank and 0.2 M HNO_3 was introduced for periodical aspiration and rinsing of the nebulization system.

Matrix-matched digestion standards were also prepared by digesting 0.2 g of the sample together with appropriate amount of aqueous standards and after digestion, dilution up to 20 ml with de-ionized water. No other acidification is needed, because the remaining HNO_3 concentration after digestion and dilution is sufficient. It is slightly variable in the range ca. 0.5–1.0 M, but this variation is not important for plasma atomization. The final concentrations of each element in these matrix-matched standards ranged from 50 to 1000 μg l^{-1} and were used to prepare standard addition calibration curves in wet digestion method.

Finally, slurry suspension standards were prepared by direct dilution of 0.2, 0.4 or 1.0 g sample mass together with appropriate amount of aqueous standards up to 20 ml with a 0.8 M HNO_3 diluting solution. The concentration of each element ranged from 50 μg l^{-1} to 1000 mg l^{-1} and the solutions were used to prepare standard addition curves.

2.3. Sample preparation

The analyzed brands of commercial multivitamin supplements were purchased from local pharmacies. Composition of each sample as given on the package label is shown in Table 1. Prior to analysis by both methods, all samples were thoroughly pulverized using an agate mortar and sieved through a plastic sieve (<100 μm fraction was collected). The samples are usually in form of tablets of certain weight, thus in all cases 10 tablets were pooled and the resulting sample was ground and homogenized. Next, the samples were subjected to two different procedures, as it is described below. For multimineral formulations available commercially in liquid form, a different analytical method has to be applied.

2.3.1. Wet-acid digestion procedure

0.2 g multivitamin powder was accurately weighted into acid washed polytetrafluoro-ethylene digestion vessel. For spiked samples, an appropriate amount of standard multielement solution was added. A volume of 5 ml concentrated HNO_3 (65%, m/m) was added and after closing the vessel the mixture was heated in an aluminum block at 120 ± 2 °C for 90 min, following a 10 °C/min ramp. This digestion procedure is sufficient to obtain a greenish-yellow clear solution. The residue was diluted in water in a 20-ml flask, and aspirated in the plasma atomizer.

2.3.2. Slurry suspension procedure

An amount of 1 g of the sample was accurately weighed in a 50-ml glass beaker, 5 ml of 0.8 M HNO_3 was added and diluted with about 10 ml de-ionized water. Finally, the mixture was transferred to a 20-ml volumetric flask and diluted to volume with de-ionized

Table 1
Description of commercial multivitamin preparations analyzed

Sample code	CN	SD	MG	SV	VC
Inorganic elements listed on label	Ca, Mg, Fe, Mn, Zn, Se, Cu, Cr, B, Ni,	Ca, Mg, Fe, Mn, Zn, Se, Cr, Cu	Ca, Mg, Fe, Mn, Zn, Se, Cr, Cu,	Ca, Mg, Fe, Mn, Zn, Cu,	Fe, Zn
Tablet mass (g)	5.0 ± 0.1	5.0 ± 0.1	4.0 ± 0.1	3.9 ± 0.1	14.0 ± 0.2

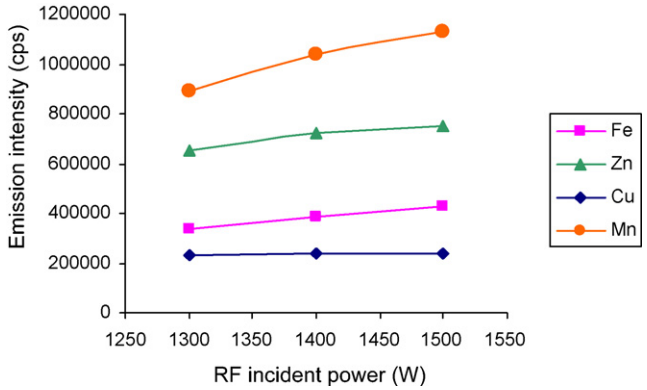

Fig. 1. Effect of RF incident power on emission intensity of Fe, Zn, Cu and Mn in a sample matrix spiked with 2500 μg l^{-1} of these analytes.

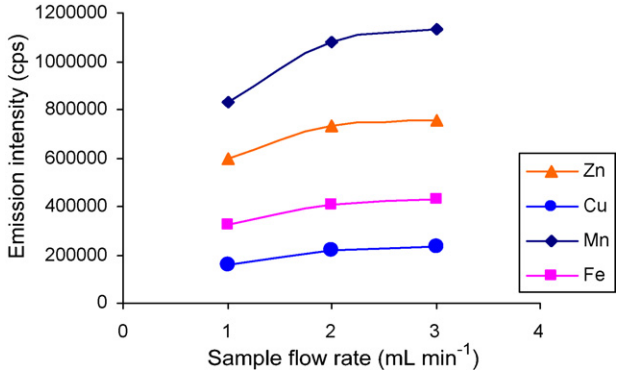

Fig. 2. Effect of sample uptake flow rate on emission intensity of Zn, Cu, Mn and Fe in a sample matrix spiked with 2500 μg l^{-1} of these analytes.

water, to produce 5% (m/v) slurry. During sample aspiration, slurries were continuously stirred by a magnetic stirrer. Clogging of the injector is prevented by frequent flushing with the 0.2 M HNO_3 solution. The use of ultrasonic bath was not beneficial, because although the homogeneity of the slurry is satisfactory, precipitations are formed in the delivery tube.

3. Results and discussion

3.1. Optimization of the method

3.1.1. Study of the ICP-AES parameters

In order to achieve a maximum signal to background intensity ratio of each analyte, ICP-AES parameters should be optimized. Parameters such as radio frequency (RF) incident power and sample uptake flow rate were optimized whereas other parameters such as nebulizer argon gas flow rate and plasma argon gas flow rate were selected based upon previous experience to maintain plasma stability. The RF incident power affects significantly the plasma temperature and improves atom excitation performance. Accordingly, it was studied in the range 1300–1500 W and it was proved that with increasing RF power, the signal intensity was also increased, and also the overall sensitivity is improved. The effect of the incident power is presented in Fig. 1, for several analytes (i.e. Fe, Cu, Mn and Zn). These elements normally exist in high amounts in the multimineral matrix as nutrient minerals however for uniformity spiked sample matrix was used even for these analytes.

In ICP nebulization, besides the nebulization system employed, the sample flow rate is critical for the amount of analyte introduced into the plasma and affects the overall sensitivity of the method. Consequently, the effect of sample flow rate on the emission intensity was investigated at three levels: 1.0, 2.0 and 3.0 ml min^{-1} while the Ar flow rate in the nebulizer and the RF power were adjusted to 0.8 l min^{-1} and 1500 W, respectively. A multimineral matrix with the common vitamin and other nutrient constituents usually found in commercial formulations was used for the matrix-matched optimization. In Fig. 2 the effect of sample flow rate on the signal intensity of Mn, Cu, Zn and Fe is demonstrated. According to the obtained results the intensity was increased by increasing the sample flow rate for all examined analytes. The above optimization procedures were applied both for the slurry and the total digestion procedure. All obtained results from the optimization procedure were subjected to analysis of variance (at 95% confident level) to examine possible significant variation between slurry and mineralization procedure. Indicative results referring to three analytes after two-way ANOVA are listed in Table 2. The calculated *F* ratios were much lower than the critical ones, giving an evidence of no significant differences between the developed slurry method and the wet-acid digestion procedure.

3.1.2. Effect of slurry concentration

The concentration of the slurry is an important factor to consider during preparation in order to achieve a good dispersion of the multielement preparation. The influence of the slurry concentration on the signal intensity was tested at increasing levels: 1, 5, 10 and 20% (m/v). During the study the RF power and sample flow rate were adjusted to 1500 W and 3 ml min^{-1}, respectively. According to the obtained results, it was found that emission intensities for elements such as Mg, Mn, Zn, Ca and Cu, which are normally present in multimineral preparations, were increased by increasing slurry concentration. On the other hand, for several added elements which did not normally preexist in the samples (e.g. Bi, Pb, Ag) the intensities were decreased by increasing the slurry concentration. Indicative results on the effect of slurry concentration for Cr, Cd, Co and Ag appear in Fig. 3. This effect becomes stronger for higher slurry concentration, thus it is suggested that for high amounts of organic mass the atomization capability of the plasma is deteriorated. Therefore, in the present study a slurry concentration of 5% (m/v) was chosen as a compromised optimal for all analytes and applied for quantification.

3.2. Method evaluation

3.2.1. Regression analysis

Calibration curves were obtained at the most sensitive spectral lines of each analyte, using aqueous standard solutions, slurry suspensions standards and standard addition procedure. The sensitivity of each calibration is expressed by the slope of the linear regression equation. Among the two spectral lines of each analyte

Table 2
Results of two-way ANOVA between the effect of RF power and the type of sample treatment (total digestion or slurry suspension) for selected analytes

Source	Analyte	Degrees of freedom	*F*	$F_{crit.}$
RF power	Mn	1	1.89	18.51
	Zn	1	166	18.51
	Ni	1	725	18.51
Type of treatment	Mn	2	0.99	19.00
	Zn	2	2.50	19.00
	Ni	2	1.57	19.00
Residual error	Mn	2		
	Zn	2		
	Ni	2		

The critical *F* values are given for 95% probability level.

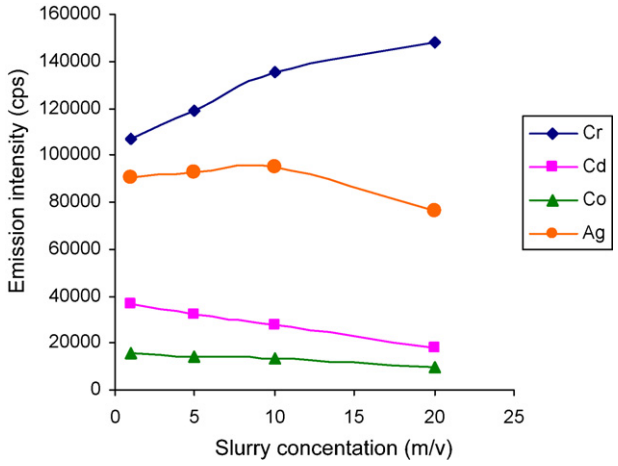

Fig. 3. Effect of slurry concentration on emission intensity of Cr, Cd, Co and Ag in a sample matrix spiked with 2500 $\mu g\,l^{-1}$ of these analytes.

those with the better sensitivity (S), reproducibility (SEs) and linear correlation (r) were given and used for the rest of the study, with the exception of Ca, for which the second line was used, in order to avoid extreme dilutions and separate sample aspirations. The slopes (S) together with their corresponding standard errors (SEs) and the linear correlation coefficient (r), for all elements for the finally selected spectral lines are presented in Table 3. The correlation coefficient for all calibration curves were >0.999 with few exceptions (e.g. Zn, As, Se, Mg) illustrating the good linearity in the studied range. The calculated slopes for the digested matrix are very similar to those obtained by the aqueous standards calibration, with some minor exceptions (e.g. Ag, Ca, Cu and Mg), thus indicating similar sensitivity and also complete organic matrix digestion. Using the slurry suspension method, it was proved that for several analytes the obtained sensitivities are a little different than when using the digestion procedure. This is evidence that the matrix effect on plasma atomization capacity when increased concentration of slurries is injected is observable but not strong enough to alter the total performance of the method. Nevertheless, the use of the standard addition procedure is strongly recommended for these matrices, in order to ensure reproducible and accurate results.

3.2.2. Accuracy and precision

Normally, in order to assess the accuracy of the method, standard reference materials are analyzed, the obtained results are compared to the certified ones and the absolute or the relative error is calculated. However, there are not commercially available CRMs with certified metals concentration and matrix similar to that of multimineral formulations, as already mentioned by Krejcova et al. [2]. Therefore, the accuracy was evaluated by determining the recoveries of the analytes from CT multimineral matrix spiked at a concentration of 250 $\mu g\,l^{-1}$ for each analyte. The recoveries obtained after the total wet-acid digestion procedure and the slurry suspension are given in Fig. 4. As it is shown, the recoveries for most of analytes were ranged between 90 and 110%. The recoveries for Ag, Al, Ba, Ca, Mg, Zn, Se, were very good while those of In, B, Co, and Pb in slurry suspension method were less satisfactory.

The precision of the method was evaluated using relative standard deviation, s_r, of seven repetitive measurements of analytes at concentrations of 250 $\mu g\,l^{-1}$, for mineralization method and for slurry suspension method, respectively. The precision is similar for the two developed methods and s_r ranged between 0.3 and 8.2% for the majority of the analytes as it is listed in Table 4.

The detection limits (c_L) were calculated according to 3s criterion. Using CT multimineral matrix the standard addition procedure was applied for total digestion and slurry suspension methods, respectively. The lower detection limits were obtained for Mn, Mg, Cu and Ca whereas the highest for Bi, Pb, As and Se (Table 4). For all nutritional analytes the detection limits obtained are several orders of magnitude lower than the expected levels in commercial samples, consequently the detectability of slurry method is considered satisfactory for routine analysis and quality control. To further improve the detection limits, one can introduce more concentrated slurries (up to 15–20%, m/v). However it must be taken into account that a decrease in the reproducibility and overall precision is expected.

3.3. Analysis of commercial multivitamin preparation

Five samples of commercial multivitamin/multimineral tabs were ground and analyzed using both the developed mineralization and slurry methods. These results are presented in Table 5, and were compared to the amount declared by the manufacturers, given in the same table. The VC sample consisted only of Zn and

Table 3
Slope ± standard error and correlation coefficient of aqueous calibration and standard addition equations for both spectral lines of each analyte, using the CT multivitamin matrix

Analyte spectral line	Aqueous calibration	Digestion and standard addition	Slurry and standard addition
Ag 328.068	92.6 ± 0.4 (0.9999)	44.2 ± 1.2 (0.9992)	84.4 ± 1.0 (0.9999)
Al 308.215	16.1 ± 0.1 (0.9999)	16.8 ± 0.2 (0.9997)	11.6 ± 0.2 (0.9994)
B 249.772	77.3 ± 0.4 (0.9999)	73.5 ± 2.9 (0.9984)	36.2 ± 0.2 (0.9283)
Ba 233.527	17.0 ± 0.1 (0.9999)	17.6 ± 0.3 (0.9995)	6.75 ± 0.06 (0.9999)
Bi 223.061	2.39 ± 0.02 (0.9993)	2.36 ± 0.02 (0.9999)	1.55 ± 0.05 (0.9988)
Ca 317.933	24.1 ± 0.1 (0.9998)	33.5 ± 1.5 (0.9979)	81 ± 12 (0.9889)
Cd 214.440	24.6 ± 0.1 (0.9999)	28.3 ± 0.4 (0.9996)	14.1 ± 0.4 (0.9995)
Co 228.616	11.7 ± 0.1 (0.9998)	12.7 ± 0.2 (0.9995)	4.67 ± 0.02 (0.9999)
Cr 283.563	56.8 ± 0.2 (0.9999)	59.2 ± 0.6 (0.9998)	24.5 ± 0.8 (0.9984)
Cu 324.752	110 ± 0.5 (0.9999)	189 ± 3 (0.9993)	239 ± 5 (0.9996)
Fe 238.204	38.6 ± 0.2 (0.9999)	46.8 ± 0.1 (0.9999)	75 ± 3 (0.9988)
Ga 294.364	11.5 ± 0.1 (0.9995)	12.1 ± 0.2 (0.9993)	8.53 ± 0.30 (0.9985)
In 325.006	7.86 ± 0.09 (0.9994)	9.30 ± 0.20 (0.9993)	6.43 ± 0.09 (0.9997)
Mg 280.271	579 ± 4 (0.9998)	984 ± 46 (0.9978)	1550 ± 130 (0.9929)
Mn 257.610	226 ± 1 (0.9999)	266 ± 31 (0.9736)	446 ± 11 (0.9994)
Ni 232.003	3.94 ± 0.03 (0.9997)	4.08 ± 0.04 (0.9999)	4.18 ± 0.10 (0.9992)
Pb 220.353	0.67 ± 0.01 (0.9994)	0.59 ± 0.04 (0.9946)	0.39 ± 0.08 (0.9996)
Zn 213.857	26.6 ± 0.3 (0.9965)	27.8 ± 1.1 (0.9992)	38.9 ± 0.1 (0.9999)
As 193.696	0.36 ± 0.3 (0.9966)	0.28 ± 0.03 (0.9982)	0.34 ± 0.01 (0.9993)
Se 196.026	0.44 ± 0.3 (0.9965)	0.30 ± 0.02 (0.9989)	0.44 ± 0.01 (0.9986)

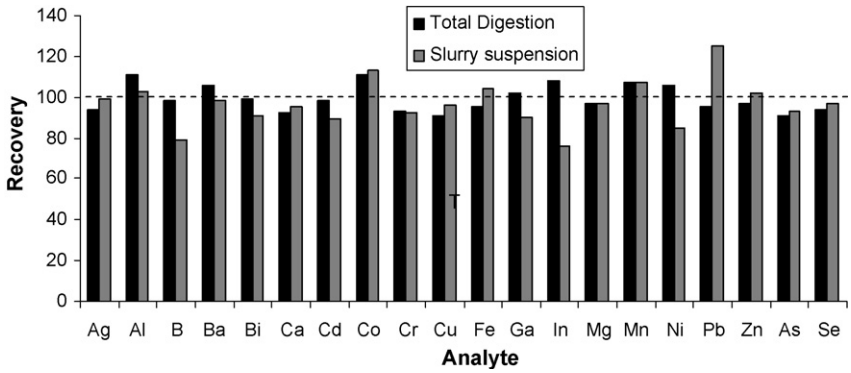

Fig. 4. Recovery of analytes from digested and slurry suspension (5%, m/v) of multimineral formulation spiked with a concentration of 250 μg l^{-1} of each analyte.

Table 4
Precision (relative standard deviation, s_r, %, $n = 7$) and detection limits (μg g^{-1}) of wet-acid digestion and slurry suspension methods using the CT sample matrix

Analyte	Precision (s_r, %)			Detection limits (μg g^{-1})	
	Aqueous	Digested sample	Slurry suspension	Digested sample	Slurry suspension
Ag	0.9	8.2	0.9	0.1	0.1
Al	0.3	0.4	0.4	7.2	11
B	6.3	1.4	0.8	0.02	0.04
Ba	0.7	1.7	0.6	0.3	0.7
Bi	1.4	7.0	0.9	25	43
Ca	2.7	3.2	1.2	2.5	0.3
Cd	1.6	2.4	0.5	0.2	0.3
Co	0.5	2.3	0.9	0.4	0.7
Cr	0.4	0.6	0.8	0.5	1.4
Cu	0.9	0.6	0.8	0.1	0.03
Fe	1.2	0.5	0.6	0.2	0.1
Ga	2.1	18	0.5	2.0	1.3
In	1.4	1.4	1.4	3.6	5.1
Mg	1.5	1.4	1.0	0.01	0.01
Mn	0.7	0.5	0.7	0.4	0.05
Ni	1.3	2.8	0.6	9.7	9.5
Pb	5.2	8.2	0.5	70	114
Zn	1.2	0.6	1.5	0.6	0.4
As	4.0	3.3	1.0	9.1	66
Se	4.6	4.4	2.9	8.6	151

Slurry suspensions contained 5% (m/v) sample mass.

Table 5
Mean concentrations ($n = 7$) of macro-, minor- and trace-elements in five commercial multivitamin/multimineral preparations (mg/tab)

Analyte	CN			SD			MG			SV			VC	
	PL	WD	SS	PL	WD	SS	PL	WD	SS	PL	WD	SS	PL	SS
B	0.070	0.117	0.070	–	Nd	Nd	–	Nd	Nd	–	Nd	Nd	–	Nd
Ca	162	204	162	120	114	145	139	141	120	5.5	4.8	7.6	–	Nd
Cr	0.025	0.012	0.025	0.025	0.028	0.179	0.025	0.005	0.054	–	Nd	Nd	–	Nd
Cu	0.5	0.50	0.52	0.90	0.88	0.73	0.4	0.37	0.50	0.4	0.3	0.5	–	Nd
Fe	4.5	4.2	4.5	8	5	10	10	12	15	2.4	2.7	2.2	0.7	0.3
Mg	100	151	106	–	57	36	–	37	51	–	28	35	–	Nd
Mn	2.5	2.1	2.5	–	1.9	1.7	–	2.6	1.7	–	1.1	0.7	–	Nd
Ni	0.005	0.072	0.005	–	Nd	Nd	–	Nd	Nd	–	Nd	Nd	–	Nd
Zn	15	13	15	8	7.1	2.0	8	6.0	7.7	2.4	2.0	3.9	1.1	0.1
Se	0.025	0.016	0.025	0.055	Nd	0.053	0.015	Nd	Nd	–	Nd	Nd	–	Nd

PL: product label value of analyte in the multivitamin preparation; (–): no information on the label; Nd: not detected; WD: wet digestion; SS: slurry suspension.

Fe and was analyzed only with slurry method. The determined levels of nutrient elements in the analyzed samples were generally in agreement with those declared by the producers on the label, with minor deviations. This is partially due to the fact that the excipients in various commercial preparations are very diverse thus the whole matrix is different and consequently the obtained slurries may have different behavior during atomization process. However, it is very important that in the five examined commercial brand elements like Cd, Pb, As, Ag, Al, Ba, Bi, Co, Ga, In were not detected and not included in Table 5.

4. Conclusions

Methods based on digestions using acids are time consuming and associated with contamination and retention problems. For this reason, the proposed slurry sampling technique can be

used as a good alternative for multielement analysis of multimineral/multivitamin preparations using ICP-AES. Despite of the fact that the optimum conditions and the performance of a multielement method must be compromised in order to include large number of analytes in one run, the proposed slurry suspension method was proved efficient and reliable for the direct determination of almost 20 elements in routine analysis of multimineral formulations. As it was shown, changing from the traditional acid digestion method to the direct slurry suspension introduction did not have strong effect on the performance of each analyte determination. A slurry concentration of 5% (m/v) is a compromise for sufficient sensitivity without nebulizer obstructions. However in this concentration level some analytes like B, Co, In and Pb showed less satisfactory recovery. The proposed method is a rapid method with negligible sample preparation and offers good detection limits and acceptable precision for routine analysis of commercial samples. The detection limits can be further improved using higher sample concentration in the slurries, but with a reasonable sacrifice of the precision.

References

[1] C.P. Champe, A.R. Harvey, Lippincott's Illustrated Reviews, in: Biochemistry, 2nd ed., Lippincott Williams & Wilkins, Philadelphia, 1994, pp. 303–330.
[2] A. Krejcova, D. Kahoun, T. Cernohorsky, M. Pouzar, Food Chem. 98 (2006) 171–178.
[3] K. Soltyk, A. Lozak, P. Ostapczuk, Z. Fijalek, J. Pharm. Biomed. Anal. 32 (2003) 425–432.
[4] A.S. Szabo, D.W. Golightly, J. Food Comp. Anal. 8 (1995) 220–231.
[5] C. Krone, A.J. Wyse, J.T.A. Ely, Int. J. Food Sci. Nutr. 52 (2001) 379–382.
[6] L. Ebdon, M. Foulkes, K. Sutton, J. Anal. Atom. Spectrom. 12 (1997) 213–229.
[7] B.P. Burgoin, D. Boomer, M.J. Powell, S. Willie, D. Edgar, D. Evans, Analyst 117 (1992) 19–22.
[8] A. Abarca, E. Canfranc, I. Sierra, M.L. Marina, J. Pharm. Biomed. Anal. 25 (2001) 941–945.
[9] S. Soriano, A.D. Pereira Netto, R.J. Cassella, J. Pharm. Biomed. Anal. 43 (2007) 304–310.
[10] S.C. Hight, D.L. Anderson, W.G. Cunmighton, S.G. Capar, W.H. Lamont, S.A. Sinex, J. Food Comp. Anal. 6 (1993) 121–139.
[11] S.C. Dolan, D.A. Nortrup, P.M. Bolger, S.G. Capar, J. Food Comp. Anal. 51 (2003) 1307–1312.
[12] I. Chantal, P. Chantal, A. Johnston, R. Jairam, D. Lenny, H.J. Lam, J. Pharm. Biomed. Anal. 31 (2003) 413–420.
[13] A. Lásztity, A. Kelkó-Lévai, I. Varga, K. Zih-Perényi, E. Bertalan, Microchem. J. 73 (2002) 59–63.
[14] N. Lewen, S. Mathew, M. Schenkenberger, T. Raglione, J. Pharm. Biomed. Anal. 35 (2004) 739–752.
[15] E.G. Yanes, N.J. Miller-Ihli, Spectrochim. Acta B 60 (2005) 555–561.
[16] G.A. Zachariadis, C.E. Michos, J. Pharm. Biomed. Anal. 43 (2007) 951–958.