UV Photolysis Digestion Method for the Multielemental (Major to Ultratrace) Analysis of Liquid-based Dietary Supplements by ICP-MS and ICP-OES

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ABSTRACT

A UV photolysis digestion (UVPD) method using a mixture of HNO_3 and H_2O_2 was developed for the determination of major, minor, and trace elements in dietary supplements (ethanolic extracts, liquid phytocaps, and syrups) as a possible alternative to conventional digestion methods. Optimization of the procedure involves the initial reaction with dilute nitric acid, followed by UVPD to yield a clear, colorless solution. Parameters affecting the UVPD method, such as acid concentration, amount of H_2O_2 , digestion time and sample weight, were optimized to obtain the quantitative recovery (>95%) of the analytes. The extent of

mineralization was determined on the basis of total organic carbon (TOC) measurement of the sample digests. Total digestion of the sample (i.e., complete colorless solution) can be achieved within 20–40 minutes of UV exposure time for a 300-mg sample. The clear sample solution obtained after UV photolysis digestion was used for the determination of Na, K, Ca, Mg, Fe, P, Si, Al, Cr, Mn, Cu, and Zn using inductively coupled plasma optical emission spectrometry (ICP-OES), while for the quantification of the elements Co, Ni, Cu, Zn, As, Se, Sr, Tl, Cd, Cs, Mo, Hg, Pb, and Bi, inductively coupled plasma mass spectrometry (ICP-MS) was used.

ous stages of manufacturing processes, such as grinding. Thirdly, raw materials may accumulate some metals from polluted soil or they may absorb metals present in the environment due to various anthropogenic and agricultural practices. It has been reported that some plants can accumulate up to 10% of the metals present in the soil (7).

More recently, Krishna et al. (8) have carried out arsenic speciation studies in ethanolic kelp and bladderwrack extracts by liquid chromatography particle beam electron ionization mass spectrometry (LC/PB-EI-MS). These investigations revealed that the majority (90–95%) of the total arsenic content ($\sim 7 \mu\text{g g}^{-1}$) in the samples is in the form of inorganic arsenic, with minor amounts of dimethyl arsenic acid (DMA).

Hence, the determination of metals in dietary supplements is of importance for nutritional and toxicological reasons. Previous studies of dietary supplements indicate that fairly high concentrations of these elements may occur (2,3).

The number of dietary supplement samples submitted for trace elemental analysis is continuously growing. Hence, the demand for rapid, simple, and efficient analytical methods for the determination of the elemental composition in different types of dietary supplement sample matrices is increasing.

Several analytical techniques have been widely used for determining elemental composition data in various dietary supplement matrices which include atomic absorption spectrometry (AAS)

INTRODUCTION

Herbs and medicinal plants have been used for treating various diseases for a long time because of their beneficial properties for health (1). Since our lifestyles have become increasingly busy and leave less time to prepare well-balanced meals, our diets are at an increased risk of becoming nutrient-deficient. Dietary supplements sold as capsules, liquids, or in syrup form offer a simple and convenient way to supplement our diets and reduce the risk of nutrient deficiency.

Many people believe that products labeled "natural" are safe and good for them. This is not necessarily true because the safety of a botanical depends on many things,

such as its chemical composition, how it functions in the body, how it is prepared, and the dosage. The majority of people taking supplements combine them with conventional drugs, which opens the possibility of herb-drug interactions, such as allergic and toxic reactions (2–5). Some herbs can also be hepatotoxic (6).

Although organic components with medicinal properties often form the bulk of the supplement, dietary supplements also contain significant quantities of metals due to their ubiquitous nature. Several other possibilities exist to explain the presence of metals in dietary supplements. First, heavy metals may be added intentionally for their alleged medicinal properties, as done in the case of Indian Ayurvedic and traditional Chinese medicines. Secondly, the metals may be introduced as contaminants during vari-

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(9,10), inductively coupled plasma optical emission spectrometry (ICP-OES) (11-14), inductively coupled plasma mass spectrometry (ICP-MS) (15-17), and anodic stripping voltammetry (ASV) (18). One of the most powerful analytical techniques for trace and ultratrace elemental analysis is ICP-MS due to its simultaneous multi-elemental detection capabilities, speed of analysis, and low detection limits (19-20).

The determination of the elemental composition in complex matrices such as food (in this case, botanical dietary supplements) often requires extensive sample preparation prior to instrumental analysis. Sample digestion methods for various matrices are largely limited to the conventional techniques of aqueous digestion based on an acid digestion with a heated mixture of mineral acids (21), dry ashing using a muffle furnace at around 500 °C, fusion techniques, hot plate heating at ~75 °C (9,15, 22), and microwave digestion. But most of these conventional digestion procedures are limited by several primary factors: long dissolution times (hours to days), potential loss of volatile elements, contamination of the sample through large quantities of reagents, and generally require a great deal of operator attention, skill, and experience in order to obtain accurate and precise results.

Very few methods have been reported in the literature for the mineralization of liquid-based dietary supplements, including ethanolic tinctures, liquid phyto-caps, and syrups. More recently, Castro et al. (14) published a microwave digestion method suitable for multiple matrices (i.e., ethanolic tinctures, raw material, tablets and/or powders). Analytical chemists continue to search for sample preparation procedures that are faster, easier, and less expensive to perform, yet provide accu-

rate and precise data with reasonable quantitation limits.

It is well-established that ICP-MS is a highly powerful and sensitive technique for pure aqueous solutions. Introduction of organic solvents into plasmas tend to cause complications due to cooling of the plasma and deposition of carbon on the cones which leads to a continuous variation in the signal. When the solvent content increases, it can lead to impedance mismatch thus extinguishing the plasma. These problems may be avoided sometimes by introducing a measured flow rate of oxygen into the argon carrier gas. In the absence of the provision to introduce oxygen, the organic solvent content must be kept to a minimum as possible. Hence, it is necessary to destroy the organic matrix before introducing the sample solution into the plasma.

An alternative to intensive sample preparation (usually requiring long periods of time, high temperatures, large quantities of concentrated acids, and tedious procedures) is oxidative UV photolysis with the use of a photodigester equipped with a high-pressure mercury lamp. UV photolysis digestion is not based on direct interaction between UV radiation and the organic matrix, but rather involves the formation of many intermediate species such as the excited states of hydrogen peroxide, hydroxyl radicals, singlet oxygen, super-oxide ions, and radicals (23). However, the decomposition of organic matter requires the addition of substances such as HNO_3 and H_2O_2 which facilitate the UV oxidation process.

The oxidation of organic matter and freeing of organic-bound metals and non-metals in water matrices under the influence of UV radiation was initially described by Armstrong et al. (24) as an efficient sample preparation method. Since its introduction, UV photo-oxidation has

been effectively used for the decomposition of organic phosphates in waters and detergents (25), the determination of total nitrogen and phosphorus by spectrophotometry, trace element determination and speciation by atomic spectrometry, (26), and the determination of trace metals by voltammetry (27). The UV-assisted digestion method has also been utilized for the ion chromatographic and voltammetric determinations of heavy and transition metals in honey and the destruction and mineralization of organic compounds in urine (28). Recently, Manjusha et al. (29) developed a UV oxidation procedure to completely digest biological and food-related samples for the determination of selenium at trace levels. But to our knowledge, no study has yet been reported on the UV-assisted digestion of liquid-based dietary samples of botanical origin – until now.

The objective of this study was to determine the levels of various elements (major to ultratrace) in three diverse and widely used dietary supplements: ethanolic extracts, liquid phyto-caps, and syrups. It is well known that not only is the determination of element concentrations in these supplements very important, but also a reliable analytical procedure for sample preparation is a critical step. In this work, the capability of the UV photolysis digestion method for the quantitative determination of major to ultratrace elements using a mixture of HNO_3 and H_2O_2 was evaluated for the analysis of these types of dietary supplement samples.

EXPERIMENTAL

Instrumentation

The determination of elements in the samples after extraction was carried out using a VG PQ ExCell inductively coupled plasma mass spectrometer (ICP-MS) (VG Elemen-

tal, Winsford, Cheshire, U.K), located in a class 10,000 area. The system is equipped with a Meinhard® concentric nebulizer and an impact bead Peltier-cooled spray chamber. The ion lens voltage settings and other parameters of the instrument were tuned every day, employing a 10-ng mL⁻¹ solution containing Li, Be, Ba, Ce, Co, In, Pb, Bi, and U. ¹⁰³Rh was used as an internal standard for all determinations to correct for instrumental drift and matrix effects, if any.

Determination of the major elements Al, Pb, Na, K, Ca, Mg, Fe, P, and Si was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES) (JY-2000, France), whereas the determination of Zn, Mn, and Cu was carried out by both ICP-MS and ICP-OES. The optimized parameters of both ICP-MS and ICP-OES are given in Tables Ia and Ib, respectively.

Before ICP-MS and ICP-OES analysis, test dietary samples were subjected to UV photolysis in a UV digester (Model No. 705, Metrohm, Herisau, Switzerland), equipped with a high-pressure 500 W mercury lamp. The 705 UV digester is comprised of a sample holder for 12 quartz tubes (15-mL capacity) with fitted Teflon® conical caps. For each set of samples, one quartz tube was reserved for the thermometer that was utilized for monitoring the digestion temperature. The temperature for each digestion under optimal digestion conditions was maintained at 85 ± 5 °C with the help of the water-cooling system connected to the digester.

Total digestion was carried out using a microwave digestion system (CEM Corporation, Mars 5 Express, Mathews, NC, USA). The total organic carbon (TOC) content of the samples before and after UV photolysis was determined with a TOC analyzer (ANATOC II series, SGE, Australia).

Reagents and Materials

Sub-boiled HCl and HNO₃ were prepared by sub-boiling distillation in quartz stills. Ultra-pure water with >18 MΩ resistivity, obtained using a Milli-Q™ high purity water system located in a class 200 area, was used for dilution of the standards, preparing the samples, and final rinsing of the acid-cleaned vessels. Hydrogen peroxide of Suprapur® grade (E. Merck, Darmstadt, Germany) was used during the UV

digestion process. All containers were cleaned in 20% HNO₃ prior to use. Multi-element standard solutions (1000 µg mL⁻¹, CertiPUR® reference material, E. Merck, Darmstadt, Germany) were used in the preparation of the working standards by sequential dilutions for ICP-MS and ICP-OES analysis. Sets of mixed working standard solutions, each consisting of four or five concentration levels (2.5, 5, 10, 50, and 100 ng mL⁻¹) with Rh as the internal standard (25 ng mL⁻¹) were

TABLE I (a)
ICP-MS Instrumental and Operating Parameters

Instrumental Parameters		Scanning Parameters	
Coolant gas	13.4 L min ⁻¹	Scanning mode	Peak jump
Auxiliary gas	0.88 L min ⁻¹	Number of replicates	3
Nebulizer gas	1.06 L min ⁻¹	Dwell time	100 millisec/channel
Sampler cone	1.0 mm Ni	Sample uptake time	50 sec
Skimmer cone	0.7 mm Ni	Washing time	70 sec
Torch type	Fassel	Sample uptake rate	~1.0 mL min ⁻¹
Plasma FW power	1300 W	Isotopes used:	m/z ⁵³ Cr, ⁵⁵ Mn, ⁶⁵ Cu, ⁶⁰ Ni, ⁶⁶ Zn, ⁷⁵ As, ⁷⁸ Se, ⁸⁸ Sr, ⁹⁵ Mo, ¹¹² Cd, ¹³⁷ Ba, ²⁰⁵ Tl, ²⁰² Hg, ²⁰⁸ Pb, and ²⁰⁹ Bi
Reflected power	<0.8 W		

TABLE I (b)
ICP-OES Instrumental and Operating Conditions (Jobin Yvon JY 2000)

Parameters Use		Operating Conditions	
Plasma gas flow rate		12 L min ⁻¹	
Sheath gas flow rate		0.2 L min ⁻¹	
Sample uptake rate		1.0 mL min ⁻¹	
RF Generator		1000 W, Frequency 40.68 MHz	
Monochromator		0.64 M, 2400 lines/mm, Czerny Turner mounting	
Torch		Jobin Yvon demountable quartz with argon sheathing gas	
R. F. Forward power		1.05 KW (<10 W reflected power)	
Element	Wavelength (nm)	Element	Wavelength (nm)
Zn	213.856	Mg	279.553
P	214.914	Cu	324.754
Fe	238.204	Ca	393.367
Si	251.611	Al	396.152
Mn	257.610	Na	589.592
		K	766.490

employed for calibration of the ICP-MS. Similarly, another set of mixed working standard solutions ranging from 100 to 3000 ng mL⁻¹ (Al, Cu, Zn, Mn, Na, Ca, K, Mg, Si, and P) was used for calibrating the ICP-OES.

Dietary supplements of the following three different matrices were used in this study and provided by GAIA Herbs (Brevard, NC, USA): ethanolic tinctures (consisting of 20 to 65% ethanol), liquid phytocaps (40–60% glycerin), and syrups.

UV Photolysis Digestion Procedure (UVPD)

For optimization of the UVPD procedure, an ethanolic extract of green tea, ginger phytocap, and syrup for bronchial wellness were chosen as representatives of the three diverse matrices: ethanolic tinctures, liquid-phytocaps, and syrups, respectively.

Accurately weighed amounts (0.3–0.5 g) of different aliquots of these representative dietary samples were placed into pre-cleaned 25-mL glass beakers containing 5 mL of 20% HNO₃ solution. The sample mixtures were gently heated on an IR heater (Schott Instruments, Germany) to prevent foaming. This treatment was continued until the reaction was complete (i.e., until no effervescence seen). After this pre-digestion treatment, the sample solutions were transferred into a 12-mL quartz vial, 200 µL of H₂O₂ (30%) was added, and the sample subjected to UV photolysis, while maintaining the sample temperature at 80–85 °C. During the digestion period of 20–40 minutes, at each 10-minute interval, a 100-µL aliquot of H₂O₂ was added. This addition process aims at ensuring that the oxidizing conditions are maintained throughout the UV-assisted digestion process. The samples were exposed to UV light until clear and colorless solutions were obtained. At the end of

the digestion, the samples were made up to the required volume with high-purity water for analysis by ICP-MS and/or ICP-OES.

Corresponding process blanks were also prepared in the same way without any sample material. Three aliquots of each sample were used for each UVPD procedure. With each series of digestions, a blank was also measured. All of the analytical measurements were run in triplicate for the sample solutions. Calculations of the metal content in the samples are based on calibration plots obtained from aqueous standards. Upon the development of the UVPD procedure, the results were compared with those obtained with the recently published microwave digestion procedure without any further modifications.

RESULTS AND DISCUSSION

The different types of dietary samples used in the present work and their main medicinal properties are listed in Table II.

Development of UV Photolysis Digestion (UVPD) Procedure

Initially, UVPD was applied directly to the dietary samples wherein concentrated HNO₃ was added to the quartz vial containing a weighed aliquot of the test sample. But due to the violent reaction of HNO₃ with liquid dietary extracts (in particular, ethanol-based extracts which produce nitrogen dioxide gases), this direct UVPD approach was not successful for dietary samples that contain different percentages of alcohol/ glycerin. To some extent, this procedure was partially successful for the ethanol-based samples. Based on these preliminary studies, this direct UVPD procedure had several disadvantages, including incomplete recovery of the analytes due to splashing, loss of analytes, and the time-consuming (>1hr) nature of the digestion. To overcome

these limitations, a pre-digestion hot plate step was introduced before applying UVPD. The sample volume of 5 mL was kept constant in all of the optimization studies.

Optimization of Pre-digestion Step

A pre-digestion step is generally beneficial especially for samples rich in organic content. In this work, pre-digestion was performed by gently heating the sample and acid on an IR hot plate. One method of avoiding the violent reaction of nitric acid with alcohol-based extracts is to predigest the sample by heating it gently (70–80 °C) on an IR hot plate after the addition of 5 mL of 20% nitric acid. This enables the gases (evolving from the decomposition of easily oxidized organic matter) to escape before commencing the UVPD procedure.

Acid Concentration

Acid treatment of a sample matrix is governed by many complex relationships such as solubility and oxidizing power of the acid to liberate the trace elements. The acid, or a combination of acids, is chosen for its efficiency in decomposing the matrix. It is usually desirable for the acid to form a soluble salt with the metal ion of interest. For these reasons, nitric acid, hydrochloric acid, and perchloric acid are widely used in sample preparations.

Among the acids employed, HNO₃ is reported to have an enhanced performance for oxidation of the organic matter due to its strong oxidizing properties. Hence, nitric acid is a widely used oxidizing agent for liberating trace elements from biological and botanical matrices as highly soluble nitrate salts. However, decomposition of the organic media also requires the addition of H₂O₂ to facilitate the oxidation process.

TABLE II
List of Dietary Supplements Used for the Determination of Elemental Composition

S. No.	Supplement Name	Medium	Medicinal Uses	Suggested Daily Dosage
1	Bladderwrack Fronds (<i>Fucus vesiculosus</i>)	Spring water + 20-30% pure grain alcohol	To treat arteriosclerosis and iodine-deficiency ailments	30-40 drops in water, 3-4 times
2	Echinacea supreme	Water + 50-60% organic grain alcohol	Ultimate support for health human function	40-60 drops in water, 4-6 times
3	Green Tea (<i>Camellia sinensis</i>)	Water + 35-45% organic grain alcohol	Strong source of polyphenols which have strong anti- oxidant, anti-carcinogenic and anti-arthritis properties	30-40 drops in water, 3-4 times
4	Milk thistle seed	Water + 35-45% organic grain alcohol	Ultimate support for healthy liver function	30-40 drops in water, 3-4 times
5	Olive leaf (<i>Olea europaea</i>)	Water + 55-65% organic grain alcohol	Protects the body from viruses, bacteria or retro- viruses, possible Anti HIV activity, etc.	30-40 drops in water, 3-4 times
6	Nicotine Relief	Spring water + 50-60% grain alcohol	Supports healthy response to environmental stresses	15-20 drops in warm water, 3 times
7	Daily Bitters (alcohol-free)	Water and 60% vegetable glycerin	Supports healthy digestion, absorption and elimination	45 drops in water, twice daily
8	Echinacea supreme	Water and 60% vegetable glycerin	Ultimate support for healthy immune function	30-50 drops in water, 4-5 times
9	Ginkgo leaf (<i>Ginkgo biloba</i>)	Spring water and 50-60% glycerin	Promotes memory and circulation	30-40 drops in warm water, 3-4 times
10	Anti-oxidant supreme	Alcohol-free concentrated extract	Whole body support	1 capsule, 2 times
11	Black Elderberry	Alcohol free concentrated extract	Healthy immune function	2 capsules, 2 times
12	Echinacea supreme	Alcohol-free concentrated extract	Healthy immune function	2 capsules with warm water, every 2 hours
13	Green tea	Alcohol-free concentrated extract	Rich in naturally occurring anti-oxidants	2 capsules, 2 times
14	Olive leaf	Alcohol-free concentrated extract	Healthy immune function	1 capsule, 2 times
15	Ginger supreme	Alcohol-free concentrated extract	Supports a healthy inflam- matory response	1 capsule, 1-2 times
16	Ginkgo leaf	Alcohol-free concentrated extract	Promotes healthy circulation and memory	1 capsule, 2 times
17	Kava-kava root	Alcohol-free concentrated extract	Restores calm and relaxation	1 capsule, 3 times
18	Turmeric supreme	Alcohol-free concentrated extract	Supports heart, joint and liver function	1 capsule, 1-2 times
19	Bronchial Wellness	Herbal syrup	Promotes well-being of the respiratory tract by supporting bronchial health	10 mL, twice daily
20	Black Elderberry	Syrup	Flavonoid compounds are directly responsible for many health promoting properties	10 mL, twice daily

S. No 7-18 are phyto-caps; 1 drop = 20-25 mg; 1 capsule weighs ~800-820 mg.

In view of these excellent properties, a mixture of HNO_3 and H_2O_2 was selected for the present studies. As mentioned previously, the reaction of HNO_3 with ethanol is very violent; hence, concentrated HNO_3 could not be used. Therefore, the concentration of HNO_3 required for a reaction to occur was varied from 10 to 50% (v/v). These experiments clearly indicate that pre-digestion time is directly proportional to the amount of HNO_3 that is being used. But the reaction turns violent if the acid concentration is more than 40%. The lower recoveries experienced at >40% can therefore be explained by loss of sample due to an overflowing of the sample during heating. As a tradeoff between pre-digestion time and amount of acid, the concentration of HNO_3 was fixed at 20% for the reaction to complete in less than 5 minutes.

With the aim of improving pre-digestion conditions for the maximum number of elements, the following acid mixtures were also investigated: HNO_3 (10%) + HCl (10%), HNO_3 (20%) + HCl (10%), and HNO_3 (10%) + HCl (20%) (V/V). No significant improvement in the reaction conditions of the pre-digestion step was observed with any of these acid mixtures. Hence, 20% HNO_3 alone was used for pre-digestion in the subsequent experiments.

About 300 mg of the dietary sample was weighed into a 25-mL glass beaker containing 5 mL of 20% HNO_3 . Then, the sample mixture was heated gently to around 80 °C until the reaction was complete. It was observed that the total pre-digestion time with a 300-mg sample and 5 mL 20% HNO_3 was about 3 minutes. After the pre-digestion step, the sample mixture was transferred quantitatively into a 12-mL quartz vial for carrying out the UVPD procedure. Corresponding blanks were prepared in the same way without any sample material.

UV Photolysis System Optimization

To assess the ability of the UV photolysis system to digest the various dietary supplements in the present work, a study was conducted for the optimization of various parameters, including digestion time (15–45 minutes), temperature (70–95 °C), and the amount of sample (100–500 mg). The optimized concentration of 20% HNO_3 was used for all optimization studies.

Digestion Time

The time necessary to achieve total digestion depends on temperature and amount of sample used for digestion. In the present study, the digestion time was varied between 5 and 45 minutes with 10-minute intervals and maintaining a constant temperature of the UV system (~85 °C), acid concentration (20% HNO_3 , v/v), and sample weight (300 mg). In all cases, the digestion efficiency of the UVPD system increases with increasing UV exposure time. Clear and colorless digests were obtained in almost all cases within a digestion period of 30 minutes. But the digestion time varied from 15 to 45 minutes with different sample viscosities. These studies clearly indicate that the time required for complete digestion of the ethanolic extracts is about 10–15 minutes, while samples of more concentrated botanical material (such as glycerine-based phyto-caps turmeric supreme and kava kava) needed more UV exposure time (up to 45 minutes).

The volume of H_2O_2 was also optimized by adding different amounts (between 100–400 μL) during different intervals of UV exposure. During these optimization studies, it was observed that bumping or overflowing of the sample solution from the quartz vial occurs when the volume of H_2O_2 exceeds 300 μL at each interval. This behavior is possibly due to the generation of high amounts of reac-

tive OH radicals which react with the organic matrix upon UV irradiation, thereby resulting in the release of large amounts of gases such as CO_2 , NO_2 , and NO . Hence, the volume of H_2O_2 added at each interval of UV photolysis was fixed at 200 μL .

Sample Temperature

Experiments were carried out to examine the effect of sample temperature on digestion. Irradiation with a high wattage (500 W power, ~10 MPa pressure) mercury lamp results in high temperatures (up to 600 °C), which must be controlled to avoid loss of analytes due to volatilization and/or overflowing of the sample due to the release of very high quantities of gases. Hence, the sample temperature was always maintained at about 85 °C using a water-cooling system when UV irradiation experiments were performed to prevent the loss of sample.

Sample Weight

It has been reported that digestion time is directly proportional to UV intensity and irradiation time, while it is inversely proportional to the organic content of the sample matrix. In this work, the digestion of liquid-based dietary samples and quantitative recovery were investigated when different sample amounts (0.1, 0.2, 0.3, 0.4, and 0.5 g) were used for UV oxidation. UV exposure time, acid concentration (20% HNO_3), and sample temperature (~85 °C) were kept constant during these studies. It was observed that complete digestion of the sample and quantitative recovery with good precision for most of the elements was achieved when the sample weight was 0.3 g; this mass was used in all further studies of the present work.

Analytical Response Characteristics of the Method

Once optimization of the operating parameters of the UVPD proce-

dures and the complete dissolution of the dietary samples were achieved, the analytical response characteristics were determined for each of the elements of interest using multi-element standard solutions. Five-point external calibrations with standards traceable to the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were used to quantify the elements after UV photolysis digestion. The calibration curves were generated for each element across a concentration range from 0 (i.e., analytical blank) to 100 ng mL⁻¹ for the ICP-MS measurements and 0 to 5 µg mL⁻¹ for ICP-OES. Good linearity and satisfactory correlation coefficients ($R^2 > 0.998$) were obtained for each of the elemental response functions. According to IUPAC definition, the limits of detection (LOD) were calculated from each calibration response as the concentration of an analyte yielding a signal equivalent to three times the standard deviation ($LOD = 3\sigma$) of the blank value. The relative standard deviation (RSD) values were below 2% for the major elements and <8% for all of the trace and ultratrace elements selected in the present study.

Validation of UVPD Method

Validation of the developed UVPD procedure is necessary to ensure the efficacy of the procedure to digest the samples, including the removal of organic matter in such a manner that quantitative recovery and an accurate determination of the elemental composition of the test dietary samples are obtained. Since there is a lack of suitable certified reference materials for liquid-based dietary supplements, the method validation was accomplished by digesting the same set of dietary samples using a recently reported microwave assisted digestion method (14).

In UV-photolysis, oxidizing free radicals are utilized for the oxidation of the organic matrix. But UV radiation can also induce photo-reduction with some of the free radicals (such as H[•] and CO[•]) that promote reduction instead of oxidation, thus giving rise to loss of certain analytes. Hence, it is necessary to carry out recovery studies of the analytes. Prior to carrying out the UVPD procedure for the selected dietary products, it was first carried out for the test elements present in neat aqueous standard solutions. The recovery values obtained for a mixture of the aqueous standards (20 ng mL⁻¹ for ICP-MS and 1 µg mL⁻¹ for ICP-OES) after applying the UVPD procedure (as described in previous sections) followed by ICP-MS and ICP-OES analysis are listed in the first column of Table III. Quantitative recoveries (>95%) for each of the elements obtained with the optimized UVPD procedure demonstrated that there was no significant loss during the UV-photolysis process.

Validation of the UVPD procedure developed for the three different matrices (ethanolics, phytocaps, and syrups) was carried out using both external and standard addition calibrations which are the most common approaches for both ICP-MS and ICP-OES measurements. For this evaluation, three different dietary samples (green tea ethanolic extract, ginger supreme phytocap, and black elderberry syrup taken as representatives for three sample matrix types), were spiked with a mixed standard solution containing each of the test elements prior to the UVPD process. The purpose of this study was to identify the matrix effect of different botanical products on the ICP analyses.

As seen in Table III, recoveries of 95% and higher were obtained for each of the test elements, with the exception of mercury, which gave a 65% recovery for aqueous

standard solutions. The loss of mercury during the UVPD process could mainly be due to the volatility of the element with high power (500 W) UV irradiation, while the recovery of mercury was quantitative (>95%) for the different sample matrices. In this case, UV radiation is mainly utilized for destroying/decomposing organics causing less volatility of the mercury. More studies need to be performed to ascertain the loss of mercury.

Good agreement was also seen between the results obtained with both the external and standard addition procedures. This clearly demonstrates the capabilities of the UVPD method for destroying the organic matrix present in the dietary samples, thus eliminating significant spectral interferences during ICP-OES analysis. Because both the external and standard addition approaches provided good results, analysis of the different dietary extracts was carried out using only the external calibration method in all subsequent studies since a large number of dietary samples were analyzed.

The efficiency of the developed photolysis process of dietary extracts was evaluated by measuring the total organic carbon (TOC) content in three dietary samples (Olive Leaf Extract, Daily Bitters, and Ginkgo Leaf) before and after the complete UV photolysis process. The TOC content was also measured in the samples after applying microwave-assisted digestion for comparison; the results are presented in Table IV. It can be seen that there is a more than 100-fold decrease in the percentage of TOC in all of the samples tested, demonstrating the ability of the UVPD procedure towards the mineralization of various dietary extracts.

TABLE III
Elemental Recoveries (%) for Aqueous Standard Solutions and Three Dietary

Element	Aqueous standards		Green Tea Ethanolic Extract		Ginger Supreme Phytocap		Black Elderberry Syrup	
	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES
Cr	96.0	-	96.0	-	96.0	-	95.0	-
Mn	101.0	99.8	101.0	99.0	99.5.0	98.0	103.0	101.0
Ni	97.2	-	96.5	-	96.0	-	97.0	-
Co	100.0	-	100.0	-	99.5	-	99.0	-
Cu	99.0	101.0	99.0	99.5	98.0	99.0	97.0	100.0
Zn	102.0	103.0	102.0	103.0	102.0	103.0	102.0	103.0
As	96.0	-	95.0	-	95.5	-	96.2	-
Se	95.2	-	95.5	-	95.0	-	96.0	-
Mo	95.5	-	95.0	-	96.7	-	96.0	-
Cd	99.6	-	99.0	-	98.0	-	99.4	-
Cs	98.8	-	100.0	-	99.0	-	100.0	-
Ba	98.0	-	97.0	-	98.5	-	98.0	-
Hg	65.0	-	95.0	-	95.4	-	95.8	-
Tl	96.0	-	97.0	-	96.0	-	99.0	-
Pb	99.0	-	101.0	-	100.0	-	98.0	-
Bi	98.0	-	98.0	-	99.0	-	100.0	-
Al	-	97.0	-	96.0	-	97.0	-	98.0
Fe	-	99.5	-	99.0	-	102.0	-	100.0
Na	-	102.0	-	101.0	-	99.5	-	101.0
K	-	99.5	-	101.0	-	99.0	-	99.4
Ca	-	98.7	-	99.6	-	102.0	-	101.0
Mg	-	99.0	-	98.9	-	99.2	-	99.5
P	-	96.6	-	96.0	-	98.0	-	96.3
Si	-	99.0	-	98.7	-	101.0	-	98.0

TABLE IV
TOC Values Obtained for Some of the Dietary Samples Before and After Applying UVPD and Microwave Digestion

Dietary Sample	Initial TOC	TOC Content After Digestion	
		UVPD	Microwave Digestion
Daily Bitters	34%	0.23%	0.20%
Ginkgo Leaf	33%	0.31%	0.41%
Olive Leaf	30%	0.15%	0.33%

Quantification of Elemental Composition in Dietary Samples

After completing method validation for the UVPD procedure, the three different matrices listed in Table II were taken through the complete sample preparation stages

(pre-digestion and UVPD), followed by ICP-MS and ICP-OES analysis. The major-to-ultratrace elements in the selected dietary supplement samples were determined by ICP-OES (Na, K, Ca, Mg, Al, Fe, Mn, Cu, Zn, P, and Si) and ICP-MS (Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Cs,

Mo, Hg, Tl, Pb, and Bi) after UV photolysis digestion. As described in an earlier section, the analytical figures of merit for the ICP-OES and ICP-MS measurements, as well as the analytical reliabilities of the present method for sample digestion, were evaluated by comparing the results obtained by microwave-assisted digestion.

The concentrations of the 25 elements determined by both ICP-OES and ICP-MS from each of the dietary supplements are collectively listed in Tables V–VIII for comparison and represent the mean of three replicate analyses. As seen from these tables, good agreement was found between the results obtained by UVPD and microwave-

assisted digestion. Average recoveries for many metal concentrations were found to be in the 95 to 103% range. Good accordance was observed between the values for Zn, Mn, and Cu, obtained by both procedures and determined by both ICP-MS and ICP-OES. However, ICP-MS allowed more elements to be measured, such as Cr, Ni, Co, Ni, Se, Sr, Cd, Cs, Hg, Tl, Pb, and Bi, which are not observable by ICP-OES due to sensitivity limitation.

The results given are for total elemental concentrations; no chemical speciation was performed. It is important to emphasize that toxicity is often dependent on individual chemical species of an element. From these results it was also observed that all of the tested dietary samples contain significant amounts of elements (major to ultratrace) with a wide variability. Among them, the highest concentration measured was 12,600 $\mu\text{g g}^{-1}$ for potassium in turmeric supreme phytocaps; the lowest concentration was $<0.1 \mu\text{g g}^{-1}$ for the following elements in all of the samples: Co, Mo, Cs, Se, Tl, Hg, and Bi.

Essential and Other Elements

The elements found in highest concentrations among all of the supplements tested were Na (7–6417 $\mu\text{g g}^{-1}$), Mg (65–623 $\mu\text{g g}^{-1}$), Ca (25–470 $\mu\text{g g}^{-1}$), and K (100–12,600 $\mu\text{g g}^{-1}$) whose ingestion at recommended dosages would range from nanograms to milligrams per day. Castro et al. (14) reported the presence of Na and Ca in various glycerin-based products and ethanolic tinctures of botanical products in the range of 3–6750 $\mu\text{g g}^{-1}$ and 5–1900 $\mu\text{g g}^{-1}$, respectively.

The Fe content in the supplements ranged from 0.2 to 70 $\mu\text{g g}^{-1}$. The highest concentration ($\sim 10 \mu\text{g g}^{-1}$) was found in the turmeric supreme phytocap supplement and the low-

est (0.2 $\mu\text{g g}^{-1}$) determined was in the ginkgo leaf (alcohol-free) sample. Iron concentration levels ranging from 1.2 to 54 $\mu\text{g g}^{-1}$ were reported by Castro et al. (14) in various glycerin-based and ethanolic tinctures of botanical products. The Al concentration (a toxic element) in the herbs varied between 0.5 $\mu\text{g g}^{-1}$ (alcohol-free ginkgo leaf) and 13 $\mu\text{g g}^{-1}$ (green tea ethanolic extract).

The Mn concentrations varied over a wide range from 0.4 to 33 $\mu\text{g g}^{-1}$. The ginkgo phytocap supplement contained the lowest concentration of Mn ($<0.4 \mu\text{g g}^{-1}$), whereas the highest concentration was found in the ethanolic extract of the green tea sample.

The Cu and Zn concentrations in the dietary samples indicated similar maximum and minimum levels. However, the Cu levels in all of the herbs (0.5 $\mu\text{g g}^{-1}$) were higher than the Zn levels (2 – 13 $\mu\text{g g}^{-1}$). The highest Cu and Mn levels were measured in the green tea extract, whereas the lowest concentrations were determined in the ginkgo leaf and daily bitters, respectively.

The minimum Cr and Ni concentrations in the supplements were both 0.12 $\mu\text{g g}^{-1}$, while the maximum Cr concentration was 0.68 $\mu\text{g g}^{-1}$ and the maximum Ni concentration was 2.4 $\mu\text{g g}^{-1}$.

The values obtained for Co, Cs, Mo, Tl, and Bi were at sub-ppb levels ($<0.1 \mu\text{g g}^{-1}$). Of the 20 supplements tested, the six that contained low concentrations of both major and trace metals (nicotine relief, bronchial wellness, olive leaf extract, ginkgo phytocap, daily bitters) were mostly single-ingredient supplements. Interestingly, some of the dietary supplements, including green tea extract, Kava Kava root phytocap, and turmeric supreme phytocap, had higher concentrations of many of these metals.

Heavy Metals

Heavy metals, including As, Cd, Hg, and Pb, are of primary concern due to their toxicity and potential to be present due to indiscriminate use of herbicides, pesticides, and mycotoxins, or because they may be occasionally used as ingredients in dietary supplements (15). Earlier studies on the determination of these elements in dietary supplements indicated that relatively high levels may be found. From Tables V–XI, it can be seen that for most of the analyzed supplements, the concentration levels of As, Cd, and Hg were found to be significantly low ($<50 \text{ ng g}^{-1}$, $<10 \text{ ng g}^{-1}$, and $<50 \text{ ng g}^{-1}$, respectively), except for the bladder wrack sample in which the As concentration was about 8 $\mu\text{g g}^{-1}$. Two of the supplements (ginger extract, turmeric supreme extract) showed as much as 300 ng g^{-1} of Pb. Therefore, the expected intake levels may not lead to any health risk. This assessment is predicted based on the assumption that all of these elements exist in their inorganic form. The degree of potential concern is dependent on the chemical form in which they are present in the sample.

In the studies carried out by Castro et al. (14), the toxic metals As, Cd, Hg, and Pb were not detected in any of the glycerin-based samples or in the ethanolic tinctures, possibly due to the sensitivity limitation of ICP-OES. Dolan et al. (16) determined As, Cd, Hg, and Pb concentrations in 95 dietary supplements and NIST reference materials using microwave digestion and high resolution ICP-MS. The concentration ranges reported were as follows: As $<5\text{--}3770 \text{ ng g}^{-1}$; Cd $<10\text{--}368 \text{ ng g}^{-1}$; Hg $<80\text{--}16800 \text{ ng g}^{-1}$, and Pb $<20\text{--}48600 \text{ ng g}^{-1}$.

TABLE V
Elemental Composition of Ethanolic Extracts of Dietary Supplements ($\mu\text{g g}^{-1}$)

Element	Bladder Wrack Fronds				Green Tea			
	UV Digestion		MW Digestion		UV Digestion		MW Digestion	
	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES
Cr	0.31	-	0.36	-	0.34	-	0.31	-
Mn	5.00	5.40	5.30	5.20	31.60	31.50	31.20	33.20
Ni	0.69	-	0.66	-	2.80	2.90	2.40	2.60
Co	0.05	-	0.06	-	0.12	-	0.11	-
Cu	0.73	0.76	0.73	0.74	4.60	4.70	4.80	4.50
Zn	5.60	5.39	5.80	5.50	12.70	12.30	12.20	12.60
As	8.40	8.59	8.40	9.03	0.05	-	0.05	-
Se	0.35	-	0.40	-	0.06	-	0.07	-
Mo	0.01	-	0.01	-	0.01	-	0.02	-
Cd	0.18	-	0.06	-	0.08	-	0.06	-
Cs	0.01	-	0.01	-	0.02	-	0.02	-
Ba	0.41	-	0.39	-	0.28	-	0.25	-
Hg	0.02	-	0.03	-	0.01	-	0.05	-
Tl	0.02	-	0.02	-	0.02	-	0.02	-
Pb	0.03	-	0.03	-	0.13	-	0.11	-
Bi	0.01	-	0.01	-	0.01	-	0.01	-
Al	-	1.40	-	1.40	-	12.80	-	12.20
Fe	-	1.70	-	1.70	-	2.80	-	2.90
Na	-	6417	-	6408	-	10	-	12
K	-	5603	-	5604	-	5350	-	5330
Ca	-	188	-	185	-	25	-	24
Mg	-	471	-	457	-	218	-	221
P	-	228	-	212	-	432	-	443
Si	-	12.90	-	13.30	-	14.10	-	13.80

Heavy elements are listed in bold font.

TABLE VI
Elemental Composition of Liquid-based Phytocap Dietary Supplements ($\mu\text{g g}^{-1}$)

Element	Kava Kava Root - Phytocap				Tumeric Supreme - Phytocap			
	UV Digestion		MW Digestion		UV Digestion		MW Digestion	
	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES
Cr	0.25	-	0.29	-	0.35	-	0.37	-
Mn	2.30	2.10	2.10	2.20	9.80	9.6	10.20	9.50
Ni	0.36	-	0.35	-	0.41	-	0.35	-
Co	0.06	-	0.06	-	0.06	-	0.05	-
Cu	3.90	3.60	3.90	3.70	1.60	1.4	1.50	1.60
Zn	8.20	7.90	7.60	8.10	4.00	3.8	4.10	4.00
As	0.03	-	0.04	-	0.04	-	0.04	-
Se	0.08	-	0.09	-	0.03	-	0.04	-
Mo	0.04	-	0.03	-	0.02	-	0.02	-
Cd	0.02	-	0.01	-	0.02	-	0.01	-
Cs	0.03	-	0.03	-	0.03	-	0.03	-
Ba	0.51	-	0.51	-	0.12	-	0.14	-
Hg	0.01	-	0.01	-	0.01	-	0.01	-
Tl	0.02	-	0.02	-	0.02	-	0.02	-
Pb	0.21	0.24	0.23	0.21	0.26	0.25	0.24	0.27
Bi	0.01	-	0.01	-	0.02	-	0.02	-
Al	-	9.60	-	9.70	-	11.60	-	11.30
Fe	-	9.10	-	9.00	-	24	-	23
Na	-	212	-	209	-	96	-	95
K	-	8933	-	8802	-	12608	-	12616
Ca	-	290	-	291	-	270	-	265
Mg	-	390	-	387	-	445	-	440
P	-	2822	-	2890	-	3438	-	3509
Si	-	68	-	65	-	73	-	75

Heavy elements are listed in bold font.

TABLE VII
Elemental Composition of Dietary Supplements ($\mu\text{g g}^{-1}$)

Element	Nicotine Relief (60-60% pure grain alcohol)				Bronchial Wellness (Syrup)			
	UV Digestion		MW Digestion		UV Digestion		MW Digestion	
	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES
Cr	0.23	-	0.21	-	0.12	-	0.13	-
Mn	1.60	1.70	1.70	1.6	1.70	1.40	1.50	1.60
Ni	0.35	-	0.37	-	0.32	-	0.29	-
Co	0.04	-	0.04	-	0.03	-	0.03	-
Cu	0.72	0.68	0.66	0.70	0.97	0.92	0.99	0.95
Zn	5.20	5.10	5.00	5.10	1.90	1.60	1.70	1.80
As	0.03	-	0.02	-	0.04	-	0.04	-
Se	0.04	-	0.05	-	0.09	-	0.11	-
Mo	0.02	-	0.01	-	0.04	-	0.04	-
Cd	0.01	-	0.01	-	0.01	-	0.01	-
Cs	0.01	-	0.02	-	0.02	-	0.02	-
Ba	0.08	-	0.07	-	0.05	-	0.05	-
Hg	0.07	-	0.07	-	0.05	-	0.05	-
Tl	0.02	-	0.02	-	0.03	-	0.04	-
Pb	0.01	-	0.01	-	0.03	-	0.03	-
Bi	0.01	-	0.02	-	0.01	-	0.01	-
Al	-	0.91	-	0.87	-	0.75	-	0.81
Fe	-	1.90	-	2.10	-	1.2	-	1.10
Na	-	92	-	91	-	61	-	59
K	-	2390	-	2362	-	1706	-	1697
Ca	-	135	-	141	-	151	-	145
Mg	-	430	-	425	-	81	-	78
P	-	84	-	89	-	97	-	94
Si	-	13	-	11.80	-	9.40	-	9.10

Heavy elements are listed in bold font.

TABLE VIII
Elemental Composition of Alcohol-free Based Dietary Supplements ($\mu\text{g g}^{-1}$)

Element	Daily Bitters (alcohol-free)				Ginkgo Leaf (alcohol-free)			
	UV Digestion		MW Digestion		UV Digestion		MW Digestion	
	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES
Cr	0.16	0.18	0.20	0.19	0.20	-	0.19	-
Mn	2.50	2.30	2.70	2.40	1.70	-	0.22	0.19
Ni	0.42	-	0.38	-	0.34	-	0.38	-
Co	0.02	-	0.02	-	0.04	-	0.04	-
Cu	1.90	1.60	1.70	1.80	0.55	-	0.49	-
Zn	2.40	2.30	2.10	2.30	4.20	4.10	4.10	4.20
As	0.03	-	0.02	-	0.03	-	0.04	-
Se	0.14	-	0.12	-	0.05	-	0.05	-
Mo	0.01	-	0.02	-	0.02	-	0.0	-
Cd	0.01	-	0.01	-	0.01	-	0.01	-
Cs	0.01	-	0.01	-	0.02	-	0.02	-
Ba	0.51	-	0.52	-	0.29	-	0.30	-
Hg	0.04	-	0.03	-	0.01	-	0.02	-
Tl	0.02	-	0.02	-	0.03	-	0.03	-
Pb	0.03	-	0.03	-	0.04	-	0.03	-
Bi	0.01	-	0.01	-	0.03	-	0.03	-
Al	-	1.10	-	1.20	-	0.50	-	0.46
Fe	-	1.20	-	1.20	-	0.19	-	0.20
Na	-	95	-	92	-	6.90	-	6.70
K	-	1987	-	1980	-	1938	-	1952
Ca	-	87	-	87	-	77	-	76
Mg	-	102	-	105	-	340	-	335
P	-	146	-	140	-	330	-	325
Si	-	14	-	15	-	22	-	23

Heavy elements are listed in bold font.

TABLE IX
Elemental Composition of Dietary Supplements After UVPD ($\mu\text{g g}^{-1}$)

Element	Echinacea Supreme		Milk Thistle Extract		Olive Leaf Extract		Black Elderberry-Phytocap	
	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES
Cr	0.24	-	0.28	-	0.31	-	0.04	-
Mn	0.59	0.57	0.96	0.86	1.70	2.10	8.80	8.70
Ni	0.51	-	1.23	1.25	0.12	-	0.37	-
Co	0.05	-	0.07	-	0.08	-	0.02	-
Cu	1.40	1.30	7.90	7.80	2.90	2.20	2.80	2.60
Zn	6.90	6.60	7.30	7.50	3.20	2.50	12.90	12.70
As	0.05	-	0.06	-	0.06	-	0.05	-
Se	0.24	-	0.02	-	0.02	-	0.23	-
Mo	0.02	-	0.02	-	0.02	-	0.02	-
Cd	0.09	-	0.33	-	0.33	-	0.01	-
Cs	0.05	-	0.04	-	0.02	-	0.02	-
Ba	0.03	-	0.01	-	0.19	-	0.33	-
Hg	0.02	-	0.03	-	0.02	-	0.05	-
Tl	0.02	-	0.12	-	0.08	-	0.05	-
Pb	0.11	-	0.02	-	0.02	-	0.15	-
Bi	0.02	-	0.02	-	0.02	-	-	-
Al	-	0.38	-	1.80	-	1.90	-	4.30
Fe	-	1.05	-	8.10	-	3.30	-	8.90
Na	-	70	-	23	-	244	-	132
K	-	6589	-	2684	-	2013	-	1695
Ca	-	176	-	42	-	220	-	348
Mg	-	312	-	66	-	476	-	720
P	-	197	-	255	-	324	-	1890
Si	-	29.50	-	14.50	-	21	-	52

Heavy elements are listed in bold font.

TABLE X
Elemental Composition of Dietary Supplements After UVPD ($\mu\text{g g}^{-1}$)

Element	Echinacea Supreme Phytocap		Ginkgo Phytocap		Green Tea Phytocap		Ginger Supreme Phytocap	
	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES
Cr	0.26	-	0.18	-	0.31	-	0.12	-
Mn	1.50	1.50	0.39	0.35	8.30	8.20	9.30	8.90
Ni	0.34	-	0.21	-	2.10	-	0.35	-
Co	0.01	-	0.01	-	0.01	-	0.06	-
Cu	4.40	4.30	0.80	0.90	3.30	3.30	4.10	3.90
Zn	5.10	5.10	1.70	1.30	7.40	7.20	4.80	4.90
As	0.02	-	0.05	-	0.02	-	0.05	-
Se	0.13	-	0.15	-	0.02	-	0.09	-
Mo	0.02	-	0.01	-	0.03	-	0.02	-
Cd	0.01	--	0.01	-	0.01	-	0.01	-
Cs	0.03	-	0.05	-	0.19	-	0.01	-
Ba	0.18	-	0.26	-	0.21	-	0.11	-
Hg	0.01	-	0.04	-	0.03	-	0.03	-
Tl	0.01	-	0.02	-	0.02	-	0.01	-
Pb	0.02	-	0.07	-	0.05	-	0.02	-
Bi	0.01	-	0.01	-	0.02	-	0.64	-
Al	-	2.60	-	0.35	-	8.70	-	9.05
Fe	-	3.90	-	0.43	-	5.60	-	7.20
Na	-	168	-	130	-	190	-	133
K	-	8650	-	3560	-	2475	-	9307
Ca	-	470	-	87	-	115	-	98
Mg	-	620	-	723	-	93	-	221
P	-	435	-	320	-	245	-	1102
Si	-	36.50	-	29	-	15.50	-	37

Heavy elements are listed in bold font.

TABLE XI
Elemental Composition of Dietary Supplements After UVPD ($\mu\text{g g}^{-1}$)

Element	Antioxidant Phytocap		Olive Leaf Phytocap		Hawthorn Solid Extract		Black Elderberry Syrup	
	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES	ICP-MS	ICP-OES
Cr	0.19	-	0.23	-	0.23	-	0.12	-
Mn	3.90	4.02	2.40	2.90	0.87	0.84	9.80	9.60
Ni	2.20	2.10	1.20	1.40	0.67	-	0.32	-
Co	0.06	-	0.03	-	0.05	-	0.03	-
Cu	3.90	3.60	2.30	2.10	2.90	3.10	5.90	6.00
Zn	3.70	3.60	3.90	3.30	2.07	2.05	6.80	6.80
As	0.08	-	0.03	-	0.03	-	0.03	-
Se	0.22	-	0.06	-	0.06	-	0.09	-
Mo	0.01	-	0.02	-	0.03	-	0.01	-
Cd	0.02	-	0.02	-	0.02	-	0.01	-
Cs	0.01	-	0.02	-	0.23	-	0.01	-
Ba	0.01	-	0.01	-	0.19	-	0.05	-
Hg	0.02	-	0.02	-	0.01	-	0.01	-
Tl	0.01	-	0.02	-	0.02	-	0.02	-
Pb	0.16	-	0.15	-	0.04	-	0.04	-
Bi	0.02	-	0.01	-	0.01	-	0.01	-
Al	-	-	-	1.80	-	0.87	-	0.75
Fe	-	4.70	-	3.20	-	0.51	-	70
Na	-	96	-	450	-	16	-	132
K	-	1850	-	4810	-	4550	-	1695
Ca	-	160	-	460	-	175	-	350
Mg	-	155	-	640	-	355	-	718
P	-	175	-	116	-	650	-	589
Si	-	24	-	13.50	-	17	-	33

Heavy elements are listed in bold font.

Sample Throughput and Reagent Consumption

In the case of the UVPD procedure, the longest time requirement for digestion was about 40 minutes (<5 minutes for pre-digestion), making it possible to prepare as many as 100 to 120 samples per an 8-hour working day. Microwave-assisted extraction requires 60 minutes for digestion, but the time required for the reactor to cool before opening is about 90 to 120 minutes (at room temperature) which limits the number of samples that can be prepared in a day.

The consumption of reagents is reduced with UVPD versus microwave sample preparation. The UVPD procedure requires 5 mL of 20% HNO_3 , which is sufficient to obtain clear solutions and recover most of the analytes from dietary samples. But in the case of microwave-assisted extraction, up to 10 mL of concentrated HNO_3 is required for digestion. The whole process of UVPD is faster and simpler since the reduced number of analytical steps involved minimizes contamination risks.

CONCLUSION

The UV photolysis digestion (UVPD) procedure developed in the present study offers an effective method of sample preparation for the multi-elemental determination (Na, K, Ca, Mg, Fe, P, Si, Al, Cr, Mn, Cu, Zn, As, Se, Sr, Tl, Cd, Mo, Hg, Pb, and Bi) in a variety of liquid-based dietary supplements using ICP-MS and ICP-OES. This is reflected by the excellent recoveries obtained for all of the elements tested in the present study after the UVPD process by keeping acid concentration (20% HNO_3) and sample weight (300 mg) constant. Recovery of the tested elements was obtained by the addition of aqueous standard solutions to the samples prior to the pre-digestion step and it was carried through every step of

UVPD. In addition, method validation was carried out by comparing the results from UVPD to a recently reported microwave-assisted digestion method. UVPD preparations were complete within 40 minutes with a 300-mg sample, a factor of at least 2 to 3 times faster than for the microwave-assisted digestion method. Further work is planned to examine the possibility of identifying the different chemical species (i.e., speciation) of arsenic present in bladder wrack samples for accurate toxicological assessment.

An overall precision of better than 8% was achieved for many elements in multiple digestions. A published closed microwave digestion method was used for validation purposes. These studies demonstrate that the proposed UVPD method is a simple, rapid (20-40 minutes, including pre-digestion time), and viable approach for the determination of various elements at major to ultratrace levels in a variety of dietary supplements for assessing their potential implications for health.

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