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FULL PAPER

Determination of manganese and selenium levels in Iranian herbal drops by graphite furnace atomic absorption spectrometry technique

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In the present work, Se and Mn analysis was carried out among some popular Iranian herbal drops to monitor a possible accumulation of adverse elements. In this study, five different herbal drops present in Iranian market were selected, and 45 samples of each (totally 225 samples) were collected, and analyzed for the presence and determination of selenium and manganese using graphite furnace atomic absorption spectrometry. Samples were prepared by the dry ashing method at 450 °C, and the residue was dissolved in nitric acid. Se and Mn contents were determined using calibration curves at wavelength 196.0 and 279.5 nm respectively. LOD of the methods were determined as 9.1 μgL^{-1} for Se and 0.9 μgL^{-1} for Mn. LOQs were calculated to be 30.0 and 3.0 μgL^{-1} for Se and Mn, respectively. The Se concentrations in the determined samples were between ND-21.0 μgL^{-1} and for Mn were in the range of 7.2-1840.7 μgL^{-1}. Mean Se and Mn concentrations (μgL^{-1}) were 4.7 and 43.7 for Vitagnus, 9.6 and 185.1 for Hypiran, 13.3 and 338.5 for Carminat, 21.0 and 1840.7 for Persica, and ND and 7.2 for Menthol, respectively. The results showed that Mn was present in all of the samples analyzed, but no selenium was detected in some herbal drop samples.

KEYWORDS

Herbal drops; selenium; manganese; graphite furnace atomic absorption; spectroscopy.

Introduction

Medicinal plants have long been used by humans to treat diseases or increase the body's resistance. The use of these plants has been passed down from generation to generation over the centuries. Medicinal plants are still popular in different nations, so that in some countries have a special place in the treatment of diseases [1-4]. Medicinal plants have had a long history of wide applications in public health and treatment of a wide spectrum of diseases globally for thousands of years [5]. Pharmacocompounds extracted from medicinal plants and herbs are beneficial to human health [6]; they have been used in treatment of various ailments around the world because they are easily accessible, affordable with less side effects when compared with synthetic drugs [7]. As documented in the literature, 75% of the world population use medicinal plants for

prevention as well as treatment of disease [5]. In Iran, the use of medicinal plants has a long history, so in ancient Iranian sources, methods of treatment with medicinal plants can be found for various diseases [8].

Unfortunately, with the advancement of technology in the twentieth century and discovery and development of synthetic drugs, the use of traditional therapies was neglected. In recent years, researchers in traditional medicine have resorted to use traditional medicine after years of neglect. In addition to the use of medicinal plants, herbal medicines have been considered due to their benefits such as extraction and aggregation of effective substances, lower occurrence of side effects at prescribed doses, possibility to use for patients with different general conditions, and acceptance of their use by the general public [9,10].

Since the primary source of herbal medicine production is related to medicinal plants, the entry of toxins, pollutants, and mineral compounds such as toxic and non-toxic metals in them is inevitable. Selenium is an essential element for cell function, but it has toxic effects in high amounts. Symptoms of selenium toxicity include nausea, vomiting, nail loss and fragility, hair loss, fatigue, and bad breath. Selenium levels for people 14 years old and older are 55 micrograms per day [11]. In most countries, plant foods are a significant source of selenium. Selenium and their amount varies with the soil composition. Meat and bread are the most important sources of selenium in the United States. Eggs, Brazil nuts, barley, garlic, wholegrain bread, and brown rice are other sources of selenium [12]. In despite of the benefits of selenium, its high levels in the blood can cause gastrointestinal effects, nausea, hair loss, skin damage, irritability, fatigue, and nerve cell damage [13]. The high concentration of selenium in the blood causes toxicity, prostate cancer, cardiovascular disease, diabetes, cell growth, and the destruction of DNA structures [14]. Manganese (Mg) is widely distributed in nature. It exists in five different valences and in several common forms in the environment; the more common are MnO_2 and Mn_3O_4. Trace elements of Mg are essential in the function of the nervous system and normal skeletal growth. Likewise, it has a role as co-factor in many enzymes i.e. superoxide dismutase, arginase, and glutamine synthtase. Similarly, it plays an important role in plant growth in general and aids in chloroplast ultrastructural change, oxidative stress, and proteomic alterations in rice. Lack or excess quantity of Mg in the body can cause serious alteration of biochemical processes [15].

Plants incorporate trace quantity of Mg in their tissues. Manganese, also found in trace amounts in the human body, is mainly found in the skeletal system. In the human body, Mg plays a role in the formation of adipose tissue, cholesterol, bone, blood clotting factors, and protein. In addition, it is essential for normal brain function. Moreover, Mg is an antioxidant which protects the body from free radicals [16]. Manganese is essential for normal brain function and the proper functioning of nervous system in the body. As research shows, it is one of the essential minerals for any activity [16,17]. Manganese is one of three toxic minerals in the body that is not recommended for high or low consumption. It is easy to get enough manganese from diet. The best sources of naturally occurring high manganese include green leafy vegetables, brown rice, coconut, almonds, and hazelnuts [18]. However, the excessive consumption of manganese causes severe problems and conditions, some of which are deadly. Excessive consumption of manganese can further cause signs such as Parkinson's disease [19]. For those suffering from liver diseases, large manganese consumption is not recommended, as the liver will face problems at the disposal of additional amounts, which leads to psychosis, psychiatric disorders, vibration, and spasms [17].

Traditional medicine applies to health practices, knowledge and belief that include plant, animal and minerals for prevention, management, and treatment of disease. One of the traditional medicines is herbal drops, which have been used to treat various diseases. There is little information available about the safety of herbal plants and their products with respect to metals in Iran. Because of the significant use of herbal medicine among Iranian population, it is vital to know metal contents of these products. Due to the mentioned materials and preliminary studies on the pharmaceutical products of country, the amount of manganese, and selenium concentration in plant drops was considered. This research has been tried to investigate the amount of two elements, selenium and manganese, in plant drops produced in Iran. The current research was conducted in Iran in 2020.

Experimental

All solutions were prepared in Milli-Q deionized water (Millipore, Milford, MA). All chemicals and reagents used in this study were of analytical and ultra-pure grade. Standard stock solutions of Mn and Se at the concentration of 1000 mg, mg/L (Merck, Darmstadt, Germany) were used to prepare calibration curve. Nitric acid 65% with ultra-pure grade was used to prepare samples and standard solutions of related calibration curves. To prevent contamination, all the glassware was soaked in nitric acid 10% for a night and thoroughly washed with distilled water. Then, the glassware was dried in an oven at 105 ºC and stored in a dust- free environment prior to use.

Apparatus

Atomic absorption spectrometer (240AA FS, Varian, Australia) equipped with a GTA 120 Graphite Tube Atomizer, autosampler (PSD 120) and Se and Mn hollow cathode lamps (Varian, Australia) at the wavelengths 196.0 and 279.5 nm was used for determining Se and Mn in the samples. An electrical balance of 0.0001 g (Sartorius, Germany) was used for weighing the samples before preparation by dry ashing technique with an electrical muffle furnace (Thermolyne 6000, Germany).

Collection of samples

Five different herbal drops were selected from a popular medicinal plant, Purina, in Iran. The Five herbal drops are as follows: Vitagnus (for PMS and Menstrual disorders), Hypiran (Anti-depressant, Anti-migraine, and Sedative), Carminat (Carminative, Gastrointestinal antispasmodic), Persica (mouthwash), and Menthol (for Cold remedy). Forty-five samples from each herbal drop were purchased from Ahvaz (Iran) market (totally 225 samples). Then, five to five samples from each were randomly selected and mixed, and finally nine samples were prepared for each drop. In the end, 45 samples were obtained to determine of Se and Mn.

Sample preparation and analysis

Precisely, 50 mL of sample was transferred to a porcelain crucible and placed on a heater at 120 °C to vaporize. After drying, the sample was flamed. The crucible was placed in a muffle furnace at 450 °C overnight. The white carbon-free ash was obtained. The residue was dissolved in a few milliliters of 0.1 M nitric acid in a 25 mL volumetric flask with 0.1 M nitric acid. Finally, the prepared solution was passed through an ashless filter paper prior to analysis by graphite furnace atomic absorption spectrometry technique (GFAAS). A 240FS AA spectrometer was used to analyze the samples by electro- thermal technique. The operating parameters of instrument are as listed in Table 1. The temperature program of GTA 120 was performed according to the manufacturer's instruction.

TABLE 1 Operating conditions of AAS for selenium and manganese

	Se	Mn
Wavelength (nm)	196.0	279.5
Lamp Current (mA)	10	5
Slit Width (nm)	1.0	0.2
Modifier	$Ni(NO_3)_2$	$Pd(NO_3)_2$+ $Mg(NO_3)_2$
D_2 lamp	On	On

To determine the limit of detection (LOD) and limit of quantitation (LOQ) in accordance with the IUPAC definition, calculation based on three times the standard deviation of 11 runs of the blank solution was applied and HNO_3 0.1 M was as a blank. Absorption of acidic solution was used to determine LOD and LOQ. The LODs were 9.1 and 0.9 μgL^{-1} for Se and Mn, respectively. Moreover, the LOQs were calculated to be 30.0 and 3.0 μgL^{-1} for Se and Mn, respectively. The calibration graphs for Se and Mn were constructed with different concentrations of standard solutions. It was found that calibration curves were linear for Se concentrations in the range of 30-170 μgL^{-1} ($y=0.00418x+0.00010$, $r^2=0.9989$), and for Mn concentrations in the range of 3-15 μgL^{-1} ($y=0.02697x+0.05569$, $r^2=0.9998$).

Results and discussion

In the present work, Se and Mn analysis was carried out among some popular Iranian herbal drops to monitor a possible accumulation of adverse elements. Tables 2 and 3 list the Se and Mn content of selected herbal drops. The results showed that Mn was present in all of the samples analyzed, but no selenium was detected in some herbal drop samples.

TABLE 2 Selenium; content (μgL^{-1}) of some selected herbal drops found in the Iranian market

Product name	Vitagnus	Hypiran	Carminat	Persica	Menthol
1	ND	17.3	ND	18.4	ND
2	22.6	ND	ND	18.2	ND
3	ND	ND	21.3	17.2	ND
4	ND	37.5	ND	16.1	ND
5	ND	15.6	ND	29.6	ND
6	ND	16.4	30.1	21.9	ND
7	ND	ND	15.8	15.8	ND
8	ND	ND	29.7	27.2	ND
9	19.8	ND	23.2	25.2	ND
Average	4.7	9.6	13.3	21.0	-
Median	0	0	15.8	18.4	-

TABLE 3 Manganese; content (μgL^{-1}) of some selected herbal drops found in the Iranian market

Product name	Vitagnus	Hypiran	Carminat	Persica	Menthol
1	220.3	156.3	6.4	366.6	3.8
2	149.8	16.7	352.6	698.3	10.5
3	4.8	7.4	10.5	991.2	7.2
4	2.2	16.7	1.8	1109.1	4.6
5	2.9	5.0	10.0	11102.5	11.3
6	3.4	560.0	392.2	496.6	7.7
7	3.2	316.2	490.6	335.1	9.2
8	1.2	16.5	1100.9	1100.9	6.4
9	6.1	571.8	682.3	366.6	4.7
Average	43.7	185.1	338.5	1840.7	7.2
Median	3.4	16.7	352.6	698.3	7.2

SPSS statistical package version 20 was used for data analysis. The usual distribution assumption was checked by K-S (Kolmogorov-Smirnov) method. The results indicated no normal distribution for data (P<0.001). Therefore, non-parametric analyses were used to interpret obtained data.

Kruskal-Wallis test was used to investigate the comparison of the mean concentration of Se and Mn in samples. The results indicated a statistically significant difference between the mean concentration of selenium (P-value 0.001) and Manganese (P-value 0.0001) among herbal drops.

Dunn's multiple comparisons test showed a statistically significant difference between the mean concentrations of Se in the Persica vs. Vitagnus herbal products (P-value 0.0311). In addition, Dunn's multiple comparisons tests demonstrated a statistically significant difference between the mean concentrations of Se in the drops of Menthol vs. Persica herbal products (P-value 0.0010). Furthermore, Dunn's multiple comparisons tests indicated a statistically significant difference between the mean concentrations of Mn in the drops of Menthol vs. Persica herbal products (p- value 0.0013).

Conclusion

Due to the growing popularity of medicinal plants and their increasing use worldwide, contamination of medicinal plants with elements can pose serious human health. This requires the study and evaluation of substances in these plants and a thorough study of the safety of their products [20]. In this study, the results indicated that the amount of selenium and manganese in the analyzed herbal drops did not take a risk to consumer's health.

Given that these herbal drops usually have a maximum daily consumption of 5 mL, they cannot be dangerous for the consumer in terms of selenium and manganese, it should be more careful in consuming higher amounts.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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