MINERAL CONTENT ESTIMATION OF BLACK CUMIN SEEDS

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ABSTRACT

Mineral composition of Nigella S. seed variety having Moroccan origin, was determined. The methodology consisted in Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) determination after microwave assisted digestion. The accuracy of the procedure was assured by recovery studies of Nigella seeds samples spiked at different concentration levels.

The results revealed that potassium was a predominate element, followed by calcium and magnesium. According to the microelements Moroccan black cumin seeds were good source of iron, zinc and aluminum. A comparative study has indicated variations in mineral content among black cumin seeds with different geographical origin.

Keywords: black cumin, minerals, medical plants.

INTRODUCTION

Nigella sativa L. is a member of the Ranunculaceae family and is grown in many parts of the world such as South Asia, Middle East, Mediterranean region, South Europe, Northern India, Pakistan, Syria, Turkey, Iran, and Saudi Arabia [1]. The seeds of *Nigella sativa* are also known as black cumin. Initially, the seeds were used as culinary spices, due to its characteristic aromatic flavor and peppery taste [2].

Furthermore, another application of the seeds was in the field of medicine for treatment of diverse health problems, such as respiratory, allergic, dyspepsia, diabetes, inflammatory. Multiple researches confirm the beneficial health effects of black cumin in dyslipidemia, hypertension, and cancer. *Nigella sativa* L. seeds also possess immune stimulatory, gastroprotective, hepatoprotective, nephroprotective, and neuroprotective activities [1]. Moreover, *N. sativa* has antimicrobial properties against diverse bacteria, fungi, and viruses which is due to its active compounds [3]. Esharkawy et al. revealed that two of the active compounds (dithymoqinone and thymohydroquinone) exhibited a promising *in vitro* activity against COVID-19 [5].

Many studies have shown that the seeds have high nutritional value, containing proteins, fats, carbohydrates, crude fibres [4]. *Nigella sativa* seeds contain also many active pharmaceutical ingredients, the most important being thymoquinone, thymohydroquinone, dithymoquinone (nigellone) [5]. The plant seeds contain two classes of alkaloids: isoquinoline alkaloids such as nigellimine-*N*-oxide, and pyrazole alkaloids such as nigellidine and nigellicine [3]. *N. sativa* seeds are also rich in unsaturated fatty acid such as linoleic, oleic, eicosadienoic, and dihomolinoleic acid, and saturated fatty acids, such as palmitic and stearic acids [1, 3]. In the literature, numerous studies reported the total phenolic content, the level of bioactive constituents and the related antioxidant properties of black cumin (*Nigella sativa*) seed and seedcake [6 - 9].

However, little attention has been paid to the mineral content, which in addition contributes to the nutritional value and health effect of *N. Sativa* seeds.

The aim of present study was to determine mineral composition of *N. Sativa* seeds cultivated in Morocco. As the chemical content of the plants vary with the geographical origin, we compared the Moroccan seeds with previously analyzed *N. Sativa* seeds cultivated in different regions of the world.

EXPERIMENTAL

Samples

Mature black cumin (*Nigella sativa* L.) seeds were purchased from a herbal market from the North-East part of Morocco. The seeds were soaked in water, washed and air-dried. The mineral composition was obtained by sample decomposition with microwave digestion system.

Reagents

All reagents used for the analysis were of analytical-reagent grade. 65 % ultra-pure Nitric acid (LabExpert), 30 % hydrogen peroxide (Fluka) were used for black cumin digestion. A multi-element stock standard solution, (Periodic table mix 1 for ICP), 10 mg L^{-1}, containing 33 elements were purchased from Sigma Aldrich®. The working standard solutions were prepared daily through appropriate dilutions with ultra-pure de-ionized water (MilliQ) ready for ICP-OES use.

Sample preparation

Microwave digestion was used for digestion of the samples. The black cumin seeds were accurately weighed (approximately 0.25 g) into PTFE vessels and 8 mL concentrated HNO_3 and 2 mL H_2O_2 were added. The vessels were closed and placed in the microwave digestion system. The microwave digestion was performed with the following temperature program: 30 min ramp to 210°C and 20 min hold at 210°C (both 1800 W).

After finishing the procedure and the subsequent cooling, the samples were transferred into volumetric flasks and filled up to 50 mL with MilliQ water. The digestion procedure was performed in duplicate for each black cumin sample. Blank samples were passed through the same procedure.

Instruments

Sample digestion was conducted in a high-pressure microwave oven (Milestone Ethos UP, Italy). The quantification of studied elements in acid digested samples was performed using an Agilent 5100 simultaneous vertical dual view (SVDV) inductively coupled plasma optical emission spectrometer (ICP-OES) under optimal instrumental parameters ensuring the highest signal to background ratio. Instrumental parameters for ICP-OES measurements of studied elements were as follow: RF incident power (1.2 kW); plasma argon flow rate (12 L min^{-1}); auxiliary argon flow rate (1 L min^{-1}); nebulizer argon flow rate (0.7 L min^{-1}); nebulizer (concentric), spray chamber (cyclonic double pass); axial viewing, three replicates.

Limit of detection (LOD) was calculated for each element based on three times the noise of the reagent blank signal (3σ criterium). The limits of detection and wavelengths are presented in Table 1. For elements such as Li and Rb characterized with low sensitivity in ICP-

Table 1. The wavelengths and limits of detection of analyzed mineral elements.

Metals	Emission wavelengths (nm)	Detection limits (μg L^{-1})
Al	396.152	1.0
As	188.980	10.0
Ba	455.403	0.3
Ca	396.847	1.0
Cd	214.439	0.3
Co	238.892	3.0
Cr	267.716	1.0
Cu	327.395	1.0
Fe	238.204	1.0
K	766.491	1.0
Li	670.783	0.3
Mg	279.553	1.0
Mn	257.610	0.3
Na	589.592	1.0
Ni	231.604	3.0
Pb	220.353	3.0
Rb	780.026	3.0
Sr	407.771	0.1
Ti	336.122	1.0
Zn	213.857	1.0

OES determination the most intensive lines free from Ar lines and OH bands interferences were selected [10].

The analytical precision was estimated by triplicate measurements of each solution and expressed as relative standard deviation (RSD). RSD was below 10 % for all elements. The accuracy of the method was established by recovery test. All samples were spiked before digestion with 100 μg L^{-1} K, Ca, Mg, Fe, Na; 50 μg L^{-1} Zn, Al, Sr, Mn, Cu; and 10 μg L^{-1} Ba, Rb, Ti, Li in solution, corresponding, respectively, to 20 mg kg^{-1}, 10 mg kg^{-1} and 2 mg kg^{-1} of the elements in black cumin seeds. The spiked samples were digested and analyzed in a similar condition as non-spiked. The recoveries in the spiked samples were in the range 91 % - 102 %. Results from the recovery test are presented in Table 2.

Table 2. Recovery study of spikes for minerals determination in black cumin seeds by ICP-OES measurements. Three parallel determinations.

Element	Added, mg kg^{-1}	Recovery, %	RSD, %
K	20	96	2
Ca	20	93	1
Mg	20	102	3
Fe	20	98	2
Na	20	101	2
Zn	10	102	6
Al	10	95	4
Sr	10	102	5
Mn	10	97	6
Cu	10	102	3
Ba	2	101	6
Rb	2	93	4
Ti	2	94	5
Li	2	91	9

RESULTS AND DISCUSSION

Chemical analysis of black cumin seeds

The research conducted showed that *Nigella* seeds contained significant amount of important micro and macro elements. Table 3 presents the mineral content of Moroccan black cumin seeds along with the data values obtained in previous studies.

The results of the chemical analysis of the black cumin from Morocco indicated that potassium is dominant element (8600 ppm) followed by calcium (6300 ppm), and magnesium (2700 ppm). Moreover, *Nigella* seeds provide relatively high amounts of the minerals iron, sodium, zinc, aluminum and strontium. The seeds contained also manganese, copper, barium, rubidium, titanium and lithium in trace quantities. Heavy and toxic metals and metalloids, such as arsenic, lead, cadmium, cobalt, nickel, and chromium were below the detection limits.

Compared to the previous analysis it is noticeable that the order of concentration of different minerals in this study (K > Ca > Mg > Fe > Na > Zn > Al > Sr > Mn > Cu) is quite in agreement with the reports on Moroccan and Pakistan black cumin seeds [11, 12]. The literature survey demonstrates that in the most of the analyzed black cumin samples from different regions potassium is the predominate element [11 - 15]. However, in some regions, such as Turkey [16] and Yemen [17], the seeds contained mostly calcium, whereas in Indian and Ethiopian [18] seeds predominated magnesium as the main element.

Amongst the microelements iron stands out with relatively high content. In the current study we found that Fe content with an average value of 130 ppm is in good agreement with the data reported for Turkish *Sativa* seeds (130 ppm) [15]. Additionally, higher Fe content was determined by Nergiz et al. (575 ppm) and by Özcan (181 ppm) in two Turkish black cumin seeds [14, 16]. In general, Fe concentration in the most of the studied *Sativa* seeds ranged between 68 - 107 ppm.

The average value for sodium content that we found (105 ppm) is quite close to that reported by Oubannin et al. (110 ppm) in Moroccan seeds from central part of the country [11]. However it is significantly lower in comparison with Ethiopian (1168.6 ppm), Indian (936 ppm) and Turkish (853 ppm) black cumin seeds [18, 14]. Many regions are characterized with Na level between 440 ppm and 550 ppm.

The Zn level measured in this work (69.4 ppm) is in agreement with that obtained for Pakistan (62.3 ppm) and Moroccan (60.3 ppm) seeds [11, 12].

Our data (Table 3) show a relatively high level of aluminum (51.2 ppm) in the *Sativa* seeds from Nord-East Morocco. However, Al concentration of 398 ppm in Turkish *N. Sativa* from Konya suggest possible

Table 3. Concentration of mineral elements (mg kg^{-1}) in black cumin seeds samples (three parallel analyses of each sample) from Morocco. The results in this work are listed along with previously published elemental content (mg kg^{-1}) of *Nigella Sativa* seeds with different geographical origin.

	This work	Thilakarathna et al., 2018	Thilakarathna et al., 2018	Sultan et al., 2009	Oubannin et al., 2022	Nergiz et al., 1993	Özcan, 2004	Al-Naqeep et al., 2009	Takruri et al., 1998	Takruri et al., 1998	Takruri et al., 1998	Takruri et al., 1998	Kooti et al., 2016
	Morocco	India	Ethiopia	Pakistan	Morocco	Turkey (Izmir)	Turkey (Konya)	Yemen	India	Jordania	Syria	Turkey	Iran
K	8600	752.7	579.5	8080	8496.4	11800	6932	4470	5517	4423	5606	5380	-
Ca	6300	1117	1261.1	5700	5230.1	1880	9062	5440	1932	1867	2005	1544	1860
Mg	2700	1983.6	2060.5	2650	2589.0	-	3788	2190	62	59	59	56	-
Fe	130	79.1	68.5	97	93.1	575	181	86	102	107	93	130	105
Na	105	936.0	1168.6	176	110.4	853	-	440	550	419	535	440	-
Zn	69.4	0.2	0.2	62.3	60.3	-	49.7	18.4	-	-	-	-	60
Al	51.2	91.5	47.1	-	-	-	398	-	-	-	-	-	-
Sr	38.1	-[a]	-	-	-	-	28.3	-	-	-		-	-
Mn	19.0	16.7	16.7	85.3	-	-	33.5	-	-	-	-	-	-
Cu	11.7	7.7	9.0	26	13.4	-	11.3	16	24	18	17	18	18
Ba	8.25	-	-	-	-	-	150	-	-	-	-	-	-
Rb	7.11	-	-	-	-	-	-	-	-	-	-	-	-
Ti	1.87	-	-	-	-	-	-	-	-	-	-	-	-
Li	0.44	-	-	-	-	-	0.47	-	-	-	-	-	-

a Not determined

anthropogenic source [16]. The overdose of aluminum can affect various organs and to cause seriously human health problems [19].

The average Mn value (19 ppm) obtained in our investigation is slightly higher than Mn content in Indian and Ethiopian black cumin seeds (16.7 ppm) [17] but significantly lower than in Pakistanian seeds (85.3 ppm) [12].

Our finding for copper content (11.7 ppm) is consistent with that of Turkish (11.3 ppm) [16] and Moroccan seeds (13.4 ppm) [11]. The Sativa seeds studied from other regions showed Cu level between 7.7 ppm and 26 ppm with the highest concentration in Pakistanian seeds [12].

Lithium in the studied *N. Sativa* seeds is present as trace element with value of 0.44 ppm which is in agreement with the Turkish seeds (0.47 ppm) [16].

The observed differences in mineral composition in the studied black cumin seeds from around the world could be due to difference in growth conditions, anthropogenic activity, geographical variations, and climatic differences of areas where the seeds had been grown.

CONCLUSIONS

Nigella sativa L. is an annual herbaceous edible plant, cultivated for its seeds. The mineral composition of Moroccan *N. sativa* L. seeds was investigated using ICP-OES. The results revealed that metals as potassium, calcium and magnesium are the predominant elements in the seeds, whereas amongst the microelements the iron is the most pronounced element.

The obtained data were in good agreement with the values corresponding to black cumin seeds from central part of Morocco previously analyzed, however variations in chemical composition with respect to samples from different part of the world were noticed.

Further investigation is needed to elucidate the relationship between the geographical origin and mineral composition of black cumin seeds.

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