

Determination of Some Mineral Elements in Syrian Fresh Olive Fruits and Virgin Olive Oils Extracted From Wild and Cultivated Olive Fruits

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Determination of some mineral elements (K, Mg, Na, Ca, Fe, Cu, Zn, Cr, Ni, Pb and Cd) in four varieties (Sorani, Zeiti, Qaisi and Jlot) of Syrian fresh olive fruits and virgin olive oils extracted from wild and cultivated olive fruits from three regions (Afrin, Raqqa and Horan) in Syria using flame and flameless atomic absorption spectrometry was studied. The limits of quantification were (expressed in mg kg⁻¹ of dry weight) in fresh olive fruits 10460-15903, 264-497, 321-462, 209-329, 13.8-24.8, 5.4-9.9, 4.8-9.8, 1.5-3.0, 1.3-2.1, 0.015-0.042 and 0.012-0.023 for mentioned elements, respectively. The limits of quantification were (expressed in mg kg⁻¹ of oil weight) in virgin olive oils extracted from wild and cultivated olive fruits 15.4-25.9, 3.70-5.42, 7.4-12.4, 22.4-42.8, 5.9-12.2, 0.78-1.38, 1.04-2.38, 0.062-0.152, 0.20-0.73, 0.010-0.029 and 0.001-0.014 for mentioned elements, respectively. In general, the mineral elements in virgin olive oils extracted from wild or cultivated olive fruits have increased in the oil extracted from olive fruits adjacent to the highway, but the Fe, Pb and Cd were more increase up to 2 times for Fe, 80 times for Cd and 140 times for Pb; making the samples of these oils are unfit for food according to CODEX alimentarius, No 33/2009 (FAO/WHO food standards). Finally, the fatty acids in the studied oils were identified. It was found that, the amount of linoleic acid rises when the temperature increases and the content of fruit's oil decreases, contrary to oleic acid.

Key Words: Mineral elements, Olive oil, Wild and cultivated olive fruits, Highway.

INTRODUCTION

Olive oil represents an important component of the Mediterranean diet whose intake is greatly growing in developed and developing countries for its known healing effects¹⁻³. Recently, many studies have been published on the determination of organic oil components by several analytical methods, such as gas chromatography⁴⁻⁷ and determination of some mineral elements⁸⁻¹⁰. The presence of mineral elements in fruits and oils may be due to different factors *i.e.*, from the soil, from irrigation¹¹⁻¹³ and be introduced during the manufacturing of the foodstuff¹⁴. Therefore, it can be assumed that the trace elemental distribution in olive oils varies according to their origin and then it can be supposed that a suitable statistical treatment on trace element data could allow a geographical characterization of different olive oils¹⁴.

Multi-element analysis of organic virgin olive oils from different Italian regions was carried out by inductively coupled plasma mass spectrometry (ICP-MS) aiming at developing a reliable method in the traceability of the origin of oils. An external calibration curve was built for the quantitative analysis. The calibration curves for each element were linear in the range between 0.01 and 100 ng mL⁻¹ and 0.2 to 2000 ng mL⁻¹,

the correlation coefficients were ranging between 0.996 and 0.999. Results from spike and recovery experiments at levels of 30 and 65 ng mL⁻¹ were in the range of 91-119 %, whereas the quantitation limits, based on 10 times standard deviation of the blank, were also in the range of 0.009-10.2 ng g⁻¹, for almost all the elements¹⁴.

Determination of trace elements in edible oils is important because of both the metabolic role of metals and possibilities for adulteration detection and oil characterization. The most commonly used techniques for the determination of metals in oil samples are inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS). For this study, a microwave assisted decomposition of the olive oil in closed vessels using a mixture of nitric acid and hydrogen peroxide was applied as sample preparation. The proposed ICP-AES method permits the determination of Ca, Fe, Mg, Na and Zn in olive oils. Elements present in small amounts (Al, Co, Cu, K, Mn and Ni) were measured by ETA-AAS in the same sample digest. The concentrations of Al, Co, Cu, K, Mn and Ni were in the range from 0.15 to $1.5 \,\mu$ g/g and differ according to the geographical origin of the oils. For the amounts of Fe, Mg, Na and Zn in the samples, no significant differences according to the geographical origin of the oils could be observed, the mean concentrations being 15.31, 3.26, 33.10 and 3.39 μ g/g, respectively. The Ca content varies in the range of 1.3 to 9.0 μ g/g. The dependency of the trace elemental content of olive oils on their geographical origin can be used for their local characterization⁷.

The mineral element characterization of olive fruits is acquiring interest to evaluate the link between their nutritional status and the olive oil quality. A method for the analysis of mineral elements in fresh olive fruits is proposed. The presence of mineral elements such as potassium, sodium, calcium, magnesium, zinc, copper, iron and manganese in olive fruits was quantified by flame atomic absorption spectrometry. The limits of quantification (expressed in mg kg⁻¹ of dry weight) were 1.266, 1.569, 0.272, 0.172, 0.268, 0.316, 1.017 and 0.513 for K, Na, Ca, Mg, Zn, Cu, Fe and Mn, respectively. For all of the mineral elements the precision of the instrumental method was < 2.03 % and that of the analytical procedure was always ≤ 10 %. The accuracy of the method was evaluated according to the standard additions method, the recoveries being > 98 %for all of the added concentrations, indicating no noticeable interference of the matrix. The results showed the method is a robust, reliable and simple analytical procedure for the mineral element characterization of olive fruit¹⁵.

Determination of some fatty acids in laurel oil extractive from wild fruit and cultivated laurus nobilis using gas chromatographic analysis with capillary columns (OPTIMA-FFAP-0.25 mm, $60 \times 0.32 \text{ mm}$ ID) and FID detector was studied. This study showed that the components of oil is clearly influenced by the environment in which to grow the laurel trees as the following : laurel oil extractive from the fruits of wild laurel trees of the mountains from (Alkanaif, Salhab, Hama, Syria): lauric acid = 33.736 %, palmitic acid = 10.669 %, oleic acid = 21.841 %, linoleic acid = 22.870 % (total of these four fatty acids = 89.116 %), laurel oil extractive from the fruits of wild laurel trees of the plains from (Darat Ezah, Aleppo, Syria): lauric acid = 26.525 %, palmitic acid = 11.166 %, oleic acid = 29.151 %, linoleic acid = 23.094 % (total of these four fatty acids = 89.936 %) and laurel oil extractive from the fruits of cultivated laurel trees from (Nahr al-Bared, Salhab, Hama, Syria): lauric acid = 12.100 %, palmitic acid = 19.329 %, oleic acid = 33.062 %, linoleic acid = 20.355 %, palmitoleic acid = 12.062 % (total of these five fatty acids = 96.908 %). It was found that, the laurel oil extracted from the fruits of wild laurel trees of the mountains was contained of laurel acid 2.79 times more than laurel oil extracted from the fruits of cultivated laurel trees and 1.27 times more than laurel oil extracted from the fruits of wild laurel trees of the plains¹⁶.

In the present study, determination of some mineral elements (K, Mg, Na, Ca, Fe, Cu, Zn, Cr, Ni, Pb and Cd) in four varieties (Sorani, Zeiti, Qaisi and Jlot) Syrian fresh olive fruits and virgin olive oils extracted from wild and cultivated olive fruits from three regions (Afrin, Raqqa and Horan) in Syria using flame and flameless atomic absorption spectrometry were applied.

EXPERIMENTAL

Atomic absorption spectrometer used for analysis was manufactured by Shimadzu type AA-6601G equipped with lamps type HCL particular of analysis studied elements and corrected for background reference BGC-D2 with flame (Air- C_2H_2) and with graphite furnace for determination of K, Mg, Na, Ca, Fe, Cu, Zn, Cr, Ni, Pb and Cd. The analytical used line of K, Mg, Na, Ca, Fe, Cu, Zn, Cr, Ni, Pb and Cd were at 766.5, 285.2, 589.0, 422.7, 248.3, 324.8, 213.9, 357.9, 232.0, 283.3 and 228.8 nm respectively. A furnace (300 ± 1 °C) from Ecocell was used for drying samples. A Shimadzu GC-2010 gas chromatograph with capillary column (OPTIMA-FFAP-0.25 mm, 60 × 0.32 mm ID), auto injecter-AOC-20i and FID detector were used. For microwave digestion of the samples, a high performance microwave digestion apparatus MLS-1200 MEGA with EM-30 unit (Milestone GmbH) was used.

Samples preparation: Samples were taken from four different varieties (Sorani, Zeiti, Qaisi and Jlot) Syrian fresh olive fruits. The samples were dried and mixed and kept in polyethylene packages for next procedures. 1 g of each previous samples was treated with 20 mL solution content 5 M of HNO₃ and H_2O_2 concentrations. The mixture was digested on microwave then filtered and transferred into volumetric flask of 25 mL capacity and the final volume was completed to 25 mL using distilled water.

Oil samples: All samples analyzed were commercially available extra virgin olive oils from three different regions in Syria: Horan (southern Syria the hot and low rainfall); Afrin (northern region in Syria the cold and rains a lot); Raqqa (northern Syria the dry, warm and low rainfall). Ten samples were bought at each sampling site from either different producers or other production-batches.

Chemicals and glassware: For the experimental work, nitric acid (65 % p.a.), sulfuric acid (98 % p.a.), hydrogen peroxide (30 % p.a.) (all Merck, Germany) and p.a. multi element standards (Merck, Germany) were used. Standard stock solutions were used for the preparation of aqueous standard solutions after appropriate dilution. All glassware was cleaned with nitric acid (7 M) prior to use.

Calibration: For both flame and flameless-AAS, measurements were accomplished by calibration using aqueous mixed standards prepared in HNO₃ (1 M). All calibration curves were based on five standards, including blank. Standard solutions were prepared by diluting a 1000 mg/L multielement solution. The calibration ranges were selected according to the expected concentrations of the elements of interest and depending on the technique applied (flame and flameless-AAS).

RESULTS AND DISCUSSION

Fatty acid composition: The mean fatty acid methyl esters (FAMEs) composition of virgin olive oils extracted from cultivated olive fruits from three regions in Syria, is shown in Table-1. Mean values of palmitic acid, linoleic acid and oleic acid were 10.92-18.43 %, 13.99-26.23 % and 48.98-70.57 % respectively for varieties (Sorani,Zeiti, Qaisi and Jlot, respectively) in Afrin region (the cold and rains a lot) and 14.27-21.43 %, 17.04-28.16 % and 44.08-64.37 % for varieties (Sorani, Zeiti, Qaisi and Jlot, respectively) in Raqqa and Horan regions (the hot and low rainfall). However, the mean fatty acid methyl esters (FAMEs) composition of virgin olive oils

TABLE-1 MEAN VALUES OF ANALYTICAL PARAMETERS AND FATTY ACIDS COMPOSITION (%) OF VIRGIN OLIVE OILS EXTRACTED FROM CULTIVATED OLIVE FRUITS FROM THREE REGIONS IN SYRIA

Doromotoro		Af	rin			Ra	qqa		Horan				
Parameters	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	
Acidity (%)	0.42	0.40	0.68	0.92	0.84	0.82	0.97	1.3	0.97	0.95	0.96	1.5	
Peroxide (meq O ₂ /kg)	6.4	7.3	8.2	9.3	7.5	7.8	8.2	9.5	8.8	8.9	8.7	9.6	
Caprileic acid C ₈	-	0.005	0.004	0.006	0.004	0.003	0.008	0.008	0.002	0.004	0.009	0.007	
Capric acid C ₁₀	-	0.001	0.002	0.002	0.001	0.001	0.002	0.003	-	0.001	0.002	0.002	
Lauric acid C ₁₂	-	0.002	0.009	0.009	0.002	0.008	0.009	0.009	0.006	0.009	0.008	0.009	
Myristic acid C ₁₄	-	0.016	0.018	0.020	0.019	0.018	0.020	0.021	0.001	0.016	0.018	0.019	
Palmitic acid C ₁₆	12.78	10.92	14.51	18.43	17.10	15.40	18.06	21.43	16.34	14.27	17.04	20.72	
Palmitoleic acid C _{16:1}	0.56	0.70	0.97	3.85	0.59	0.78	1.02	4.01	0.61	0.67	0.98	3.91	
Stearic acid C ₁₈	0.052	0.016	0.021	0.029	0.063	0.070	0.20	0.030	0.058	0.072	0.019	0.028	
Oleic acid C _{18:1}	69.58	70.57	62.85	48.98	62.12	62.36	57.10	44.08	63.90	64.37	59.16	46.75	
Linoleic acid C _{18:2}	13.99	14.06	19.00	26.23	18.65	18.34	21.00	28.16	17.04	17.12	20.25	26.45	
Linolenic acid C _{18:3}	0.54	0.45	0.62	0.30	0.36	0.50	0.54	0.32	0.42	0.50	0.60	0.30	
Arachidic acid C20	0.77	0.57	0.66	1.06	0.30	0.59	0.62	0.98	0.48	0.61	0.59	0.91	
Eicosenoic acid C _{20:1}	0.29	0.22	0.28	0.17	0.28	0.23	0.30	0.18	0.30	0.31	0.28	0.18	
Behenic acid C ₂₂	0.13	0.12	0.19	0.09	0.14	0.14	0.20	0.09	0.13	0.11	0.17	0.08	
Erucaic acid C _{22:1}	0.060	0.16	-	0.23	0.08	0.17	0.01	0.21	0.07	0.08	0.010	0.20	
Lignoceric acid C ₂₄	0.64	1.34	0.83	0.20	0.22	1.42	0.88	0.45	0.47	1.38	0.85	0.41	
SFA	14.37	12.99	16.24	19.85	17.85	17.55	20.00	23.02	17.59	16.47	18.71	22.18	
UFA	85.02	86.16	83.72	79.76	82.08	82.38	79.97	76.96	82.34	83.35	81.28	77.79	
MUFA	70.49	71.65	64.10	53.23	63.07	63.54	58.43	48.48	64.88	65.73	60.43	51.04	
PUFA	14.53	14.51	19.62	26.53	19.01	18.84	21.54	28.48	17.46	17.62	20.85	26.75	
UFA/SFA	5.92	6.63	5.15	4.02	4.60	4.69	4.00	3.34	4.68	5.06	4.34	3.51	
MUFA/PUFA	4.85	4.94	3.27	2.01	3.32	3.37	2.71	1.70	3.72	3.73	2.90	1.91	
SEA · Saturated fatty aci	d. LIEA · LI	nsaturated	fatty acid	· MUFA· N	Monounsat	urated fatt	v acid. PI	FA · Polya	nsaturated	fatty acid	· Average	of five	

SFA: Saturated fatty acid; UFA: Unsaturated fatty acid; MUFA: Monounsaturated fatty acid; PUFA: Polyunsaturated fatty acid; Average of five measurements (n = 5)

TABLE-2
MEAN VALUES OF ANALYTICAL PARAMETERS AND FATTY ACIDS COMPOSITION (%) OF VIRGIN
OLIVE OILS EXTRACTED FROM WILD OLIVE FRUITS FROM THREE REGIONS IN SYRIA

	Afri	n			Rad	qqa		Horan				
Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	
0.54	0.43	0.71	0.94	0.87	0.80	1.05	1.4	0.99	0.96	0.97	1.6	
5.3	7.1	5.8	7.9	7.0	7.3	7.6	9.2	8.3	8.7	8.5	9.1	
0.006	0.008	0.007	0.010	0.008	0.009	0.007	0.012	0.007	0.008	0.006	0.010	
0.003	0.002	0.002	0.004	0.005	0.003	0.002	0.005	0.005	0.002	0.002	0.004	
0.014	0.016	0.015	0.018	0.021	0.020	0.021	0.028	0.012	0.018	0.020	0.020	
0.021	0.024	0.022	0.029	0.027	0.019	0.026	0.032	0.024	0.023	0.021	0.029	
13.1	12.13	14.14	16.25	15.47	14.30	15.78	20.13	15.04	13.67	15.72	17.51	
0.64	0.71	0.65	2.14	0.62	0.73	0.97	3.12	0.63	0.70	0.78	2.64	
0.028	0.019	0.025	0.020	0.034	0.040	0.14	0.031	0.030	0.031	0.022	0.025	
70.80	71.29	64.53	55.18	64.48	65.10	59.85	47.00	66.20	66.80	61.99	52.20	
13.62	13.40	18.57	24.10	17.92	17.14	20.68	27.43	16.18	16.01	19.15	25.37	
0.50	0.55	0.54	0.41	0.31	0.52	0.51	0.38	0.46	0.48	0.52	0.40	
0.72	0.58	0.61	0.97	0.48	0.63	0.80	0.80	0.68	0.80	0.74	0.96	
0.24	0.23	0.23	0.19	0.21	0.25	0.27	0.22	0.20	0.26	0.26	0.21	
0.10	0.11	0.33	0.12	0.10	0.16	0.18	0.11	0.12	0.13	0.31	0.10	
0.043	0.10	0.08	0.20	0.06	0.10	0.04	0.23	0.09	0.11	0.062	0.22	
0.18	0.82	0.23	0.23	0.21	1.02	0.71	0.35	0.20	0.97	0.37	0.28	
14.15	13.71	15.38	17.65	16.35	16.20	17.66	21.47	16.14	15.66	17.21	18.94	
85.84	86.28	84.60	82.22	83.60	83.84	82.32	78.38	83.76	84.36	82.76	81.04	
71.72	72.33	65.49	57.71	65.37	66.18	61.13	50.57	67.12	67.87	63.09	55.27	
14.12	13.95	19.11	24.51	18.23	17.66	21.19	27.81	16.64	16.49	19.67	25.77	
6.07	6.29	5.50	4.66	5.11	5.18	4.66	3.65	5.19	5.39	4.81	4.28	
5.08	5.18	3.43	2.35	3.59	3.75	2.88	1.82	4.03	4.11	3.21	2.14	
	Sorani 0.54 5.3 0.006 0.003 0.014 0.021 13.1 0.64 0.028 70.80 13.62 0.50 0.72 0.24 0.10 0.043 0.18 14.15 85.84 71.72 14.12 6.07 5.08	$\begin{tabular}{ c c c c c } \hline Afria \\ \hline Sorani & Zeiti \\ \hline 0.54 & 0.43 \\ 5.3 & 7.1 \\ 0.006 & 0.008 \\ 0.003 & 0.002 \\ 0.014 & 0.016 \\ 0.021 & 0.024 \\ 13.1 & 12.13 \\ 0.64 & 0.71 \\ 0.028 & 0.019 \\ 70.80 & 71.29 \\ 13.62 & 13.40 \\ 0.50 & 0.55 \\ 0.72 & 0.58 \\ 0.24 & 0.23 \\ 0.10 & 0.11 \\ 0.043 & 0.10 \\ 0.18 & 0.82 \\ 14.15 & 13.71 \\ 85.84 & 86.28 \\ 71.72 & 72.33 \\ 14.12 & 13.95 \\ 6.07 & 6.29 \\ 5.08 & 5.18 \\ \hline \end{tabular}$	$\begin{array}{ c c c c } \hline Afrin \\ \hline Sorani & Zeiti & Qaisi \\ \hline 0.54 & 0.43 & 0.71 \\ \hline 5.3 & 7.1 & 5.8 \\ \hline 0.006 & 0.008 & 0.007 \\ \hline 0.003 & 0.002 & 0.002 \\ \hline 0.014 & 0.016 & 0.015 \\ \hline 0.021 & 0.024 & 0.022 \\ \hline 13.1 & 12.13 & 14.14 \\ \hline 0.64 & 0.71 & 0.65 \\ \hline 0.028 & 0.019 & 0.025 \\ \hline 70.80 & 71.29 & 64.53 \\ \hline 13.62 & 13.40 & 18.57 \\ \hline 0.50 & 0.55 & 0.54 \\ \hline 0.72 & 0.58 & 0.61 \\ \hline 0.24 & 0.23 & 0.23 \\ \hline 0.10 & 0.11 & 0.33 \\ \hline 0.043 & 0.10 & 0.08 \\ \hline 0.18 & 0.82 & 0.23 \\ \hline 14.15 & 13.71 & 15.38 \\ \hline 85.84 & 86.28 & 84.60 \\ \hline 71.72 & 72.33 & 65.49 \\ \hline 14.12 & 13.95 & 19.11 \\ \hline 6.07 & 6.29 & 5.50 \\ \hline 5.08 & 5.18 & 3.43 \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	AfrinSoraniZeitiQaisiJlotSorani 0.54 0.43 0.71 0.94 0.87 5.3 7.1 5.8 7.9 7.0 0.006 0.008 0.007 0.010 0.008 0.003 0.002 0.002 0.004 0.005 0.014 0.016 0.015 0.018 0.021 0.021 0.024 0.022 0.029 0.027 13.1 12.13 14.14 16.25 15.47 0.64 0.71 0.65 2.14 0.62 0.028 0.019 0.025 0.020 0.034 70.80 71.29 64.53 55.18 64.48 13.62 13.40 18.57 24.10 17.92 0.50 0.55 0.54 0.41 0.31 0.72 0.58 0.61 0.97 0.48 0.24 0.23 0.23 0.19 0.21 0.10 0.11 0.33 0.12 0.10 0.043 0.10 0.08 0.20 0.06 0.18 0.82 0.23 0.23 0.21 14.15 13.71 15.38 17.65 16.35 85.84 86.28 84.60 82.22 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SFA: Saturated fatty acid; UFA: Unsaturated fatty acid; MUFA: Monounsaturated fatty acid; PUFA: Polyunsaturated fatty acid; Average of five measurements (n=5)

extracted from wild olive fruits from three regions in Syria, is shown in Table-2. Mean values of palmitic acid, linoleic acid and oleic acid were 12.13-16.25 %, 13.40-24.10 % and 55.18-

71.29 % respectively for varieties (Sorani, Zeiti, Qaisi and Jlot, respectively) in Afrin region (the cold and rains a lot), and 13.67-20.13 %, 16.01-27.43 % and 47.00-66.80 % for

Μ	MEAN VALUES OF AMOUNT OF MINERAL ELEMENTS IN CULTIVATED OLIVE FRUITS FROM THREE REGIONS IN SYRIA													
ş					A	mount of	mineral e	elements (mg kg ⁻¹) (ppm) [*]				
umeter		Af	rin		Raqqa					Но		Horan, adjacent to the highway for cars		
Para	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Zeiti	Jlot
Κ	11735	10460	13906	12590	12834	11706	14816	14105	12435	11554	14650	13857	12867	15146
Mg	396	341	392	463	403	362	405	482	406	357	411	480	510	563
Na	321	375	398	401	384	389	410	431	372	370	406	428	418	503
Ca	213	210	215	224	209	217	231	241	216	215	229	234	267	285
Fe	14.1	13.8	15.5	18.9	16.9	14.1	17.2	21.8	16.7	14.0	16.8	21.0	30.4	48.7
Cu	5.5	5.4	5.6	7.2	6.1	6.0	6.2	7.6	6.0	5.9	6.1	7.9	6.8	8.1
Zn	6.1	4.8	6.3	9.0	7.1	5.3	7.2	9.1	6.4	5.1	6.9	9.1	6.8	11.3
Cr	1.6	1.5	1.9	2.4	1.8	1.7	2.1	2.9	1.8	1.6	1.9	2.7	2.4	2.9
Ni	1.5	1.3	1.5	1.6	1.5	1.4	1.7	1.8	1.4	1.4	1.6	1.6	1.7	2.1
Pb	0.021	0.018	0.025	0.036	0.024	0.021	0.028	0.042	0.025	0.023	0.026	0.041	2.5	4.3
Cd	0.015	0.013	0.017	0.021	0.016	0.016	0.018	0.023	0.016	0.015	0.017	0.022	0.73	0.97

TABLE-3

*Average of five measurements (n=5)

varieties (Sorani, Zeiti, Qaisi and Jlot, respectively) in Raqqa and Horan regions (the hot and low rainfall). The content of linoleic acid and palmitic acid were higher in Raqqa and Horan regions (the hot and low rainfall) oils, however, the mean value of oleic acid decreases, *i.e.*, the amount of linoleic acid rises when the temperature increases, contrary to oleic acid. These results are consistent with the determination of the components of the olive oil in Tunisia¹⁷ and does not agree with the so-called Ivanov rule^{18,19}. It was also found that, the amount of linoleic acid rises when the content of fruit's oil (31-32, 28-29, 23-24 and 14-15 % for Zeiti, Sorani, Qaisi and Jlot respectively) decreases, contrary to oleic acid. The ratio of monounsaturated to polyunsaturated fatty acids (MUFA/ PUFA) and unsaturated to saturated fatty acids (UFA/SFA), for varieties (Sorani, Zeiti, Qaisi and Jlot), was higher in oils from the Afrin.

Determination of mineral elements in cultivated olive fruits: The mineral elements (K, Mg, Na, Ca, Fe, Cu, Zn, Cr, Ni, Pb and Cd) in cultivated olive fruits were measured using an atomic absorption spectrometer (to reach a flame temperature of 2600 °C). The hollow-cathode lamps were specific for each element analyzed. To achieve maximum sensitivity and precision, the equipment was equilibrated by alignment of the lamp and lighter and adjustment of the selected wavelength. The analytical conditions for the measurement of mineral elements were established using the respective acidified standard solutions as well as the digested samples evaluated independently. Calibration was carried out with the commercial stock standard of the corresponding nitrate at a concentration of 1,000 mg kg⁻¹, except for the mineral Cu. A daily calibration curve was carried out for the quantification of the different mineral elements. The instrumental precision was evaluated by measuring the absorbance signals 5 times in the same digested sample under the established instrumental conditions. For the evaluation of the precision of the analytical procedure, readings were made of 5 different digested solutions of the same olive fruit sample for each analyze. The results are expressed in mg kg⁻¹ (ppm) for dry fruits (Table-3).

Determination of mineral elements in wild olive fruits: The mineral elements (K, Mg, Na, Ca, Fe, Cu, Zn, Cr, Ni, Pb and Cd) in wild olive fruits were measured. A daily calibration curve was carried out for the quantification of the different mineral elements. The instrumental precision was evaluated by measuring the absorbance signals 5 times in the same digested sample under the established instrumental conditions. For the evaluation of the precision of the analytical procedure, readings were made of 5 different digested solutions of the same olive fruit sample for each analyze. The results are expressed in mg kg⁻¹ (ppm) for dry fruits (Table-4). The results show that the amount of most mineral elements for wild olive fruits was higher than in cultivated olive fruits.

Determination of mineral elements in olive oil extracted from wild and cultivated olive fruits: The mineral elements (K, Mg, Na, Ca, Fe, Cu, Zn, Cr, Ni, Pb and Cd) in olive oil extracted from wild and cultivated olive fruits in three areas of known cultivation of olives and far from sources of pollution were measured using a flame and flameless atomic absorption spectrometer. The results in Tables 5 and 6 show that the amounts of mineral elements (K, Mg, Na, Pb, Cd) was lower in olive oil extracted from wild olive fruits, while the amounts of other metal elements were largest.

Determination of mineral elements in olive oil extracted from wild and cultivated olive fruits adjacent to the highway: In order to study the impact of pollution from vehicles on the highways, we have chosen an area adjacent to the road to Damascus-Daraa (not more than ten meters from the road). The results in Tables 5 and 6 show that, the amounts of mineral elements (K, Mg, Na, Pb and Cd) was lower in olive oil extracted from wild olive fruits, while the amounts of other mineral elements were largest. These results show that, in general, the minerals have increased in the oil extracted from olive fruits adjacent to the roads, but the Fe, Pb and Cd were very large increase of up to 2 times for Fe, 80 times for Cd and 140 times for Pb; making the samples of this oil is unfit for food according to CODEX alimentarius, No 33/2009 (FAO/WHO Food Standards)²⁰.

Conclusion

Determination of some mineral elements (K, Mg, Na, Ca, Fe, Cu, Zn, Cr, Ni, Pb and Cd) in four varieties (Sorani, Zeiti, Qaisi and Jlot) Syrian fresh olive fruits and virgin olive oils extracted from wild and cultivated olive fruits from three

TABLE-4
MEAN VALUES OF AMOUNT OF MINERAL ELEMENTS IN WILD OLIVE FRUITS FROM THREE REGIONS IN SYRIA

~	Amount of mineral elements (mg kg ⁻) (ppm)													
meters		Af	rin		Raqqa					Ho		Horan, Adjacent to the highway for cars		
Para	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Zeiti	Jlot
Κ	12804	11542	14386	14086	13705	12486	15874	15903	13057	11958	14987	14702	14176	17015
Mg	410	264	413	485	413	371	408	497	408	384	411	497	564	591
Na	418	398	423	420	412	406	443	462	409	401	435	454	460	548
Ca	224	220	226	251	329	234	248	284	228	230	239	275	292	310
Fe	17.3	15.8	17.1	21.7	18.1	18.3	19.2	24.8	18.2	18.1	19.0	24.0	40.3	57.2
Cu	6.0	6.0	6.1	9.0	7.2	6.7	7.2	9.9	6.7	6.5	7.0	9.8	7.4	9.7
Zn	6.8	5.2	6.7	9.3	7.7	5.9	8.4	9.8	7.5	5.7	7.9	9.6	7.5	11.9
Cr	1.7	1.7	1.9	2.5	2.0	1.9	2.2	3.0	1.9	1.6	2.1	3.0	2.8	3.9
Ni	1.7	1.4	1.8	1.9	1.9	1.8	1.9	2.1	1.7	1.6	1.8	2.0	2.9	3.8
Pb	0.018	0.016	0.020	0.024	0.022	0.020	0.024	0.030	0.019	0.015	0.022	0.029	2.1	4.1
Cd	0.013	0.012	0.014	0.016	0.015	0.015	0.016	0.020	0.015	0.014	0.016	0.019	0.64	0.82

*Average of five measurements (n=5)

TABLE-5 MEAN VALUES OF AMOUNT OF MINERAL ELEMENTS IN OLIVE OIL EXTRACTED FROM CULTIVATED OLIVE FRUITS FROM THREE REGIONS IN SYRIA

Ś	Amount of mineral elements, (mg kg ⁻¹) (ppm)													
meter		Afi	rin		Raqqa					Hor	an	Horan, Adjacent to the highway for cars		
Para	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Zeiti	Jlot
Κ	19.8	17.2	20.1	22.7	23.1	19.6	23.5	25.9	22.8	19.3	23.1	25.1	19.4	25.3
Mg	4.22	3.75	4.21	5.10	4.73	3.94	4.87	5.42	4.70	3.86	4.71	5.34	4.05	5.52
Na	9.6	8.2	9.8	10.5	10.6	9.5	10.7	11.9	10.2	9.1	10.2	11.6	9.2	11.8
Ca	24.6	22.4	24.8	26.9	26.4	24.8	26.7	31.9	26.1	24.7	26.4	32.0	25.2	32.4
Fe	6.0	5.9	6.1	8.4	9.0	6.8	8.5	9.3	8.1	6.7	8.2	9.2	13.3	20.2
Cu	0.90	0.78	0.92	1.21	1.01	0.84	1.03	1.34	0.97	0.82	1.01	1.30	0.87	1.43
Zn	1.36	1.28	1.40	1.97	1.81	1.52	1.85	2.38	1.76	1.50	1.81	2.30	1.57	2.41
Cr	0.082	0.073	0.091	0.100	0.099	0.097	0.120	0.152	0.095	0.084	0.098	0.141	0.273	0.247
Ni	0.55	0.41	0.57	0.62	0.68	0.60	0.71	0.73	0.67	0.58	0.69	0.70	0.86	1.20
Pb	0.015	0.013	0.020	0.021	0.020	0.016	0.021	0.029	0.017	0.015	0.020	0.027	2.1	3.8
Cd	0.007	0.005	0.007	0.009	0.009	0.008	0.010	0.014	0.008	0.006	0.010	0.012	0.49	0.94

*Average of five measurements (n=5)

TABLE-6 MEAN VALUES OF AMOUNT OF MINERAL ELEMENTS IN OLIVE OIL EXTRACTED FROM WILD OLIVE FRUITS FROM THREE REGIONS IN SYRIA

so.	The amount of mineral elements (mg kg ⁻¹) (ppm) [*]													
meter		Afi	rin		Raqqa					Но	Horan, adjacent to the highway for cars			
Para	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Sorani	Zeiti	Qaisi	Jlot	Zeiti	Jlot
Κ	17.2	15.4	18.1	19.7	18.3	15.8	18.9	20.6	18.2	15.5	18.6	20.3	15.7	20.4
Mg	3.80	3.70	3.82	4.67	4.36	4.28	4.58	5.10	4.20	4.03	4.21	4.98	4.12	5.09
Na	8.0	7.4	8.1	10.2	10.9	9.7	10.6	12.4	10.1	9.5	10.4	11.8	9.7	12.2
Ca	28.0	26.4	28.5	39.8	29.2	28.0	30.9	42.8	29.0	26.8	29.6	41.1	28.7	43.7
Fe	7.1	6.6	7.4	9.3	9.0	7.3	9.0	12.2	8.9	7.1	8.9	12.0	14.6	24.7
Cu	0.96	0.80	0.98	1.25	1.03	0.89	1.08	1.38	1.01	0.85	1.03	1.32	0.89	1.37
Zn	1.23	1.04	1.30	1.62	1.43	1.25	1.51	2.04	1.41	1.22	1.46	1.90	1.25	1.97
Cr	0.073	0.062	0.084	0.091	0.099	0.083	0.102	0.124	0.095	0.080	0.100	0.116	0.294	0.342
Ni	0.28	0.20	0.31	0.43	0.46	0.32	0.49	0.48	0.38	0.30	0.42	0.46	0.94	1.53
Pb	0.012	0.010	0.012	0.018	0.020	0.014	0.022	0.026	0.016	0.013	0.021	0.024	1.82	3.4
Cd	0.003	0.001	0.003	0.005	0.008	0.004	0.009	0.012	0.006	0.003	0.009	0.010	0.25	0.81
	0.0			()										

*Average of five measurements (n=5)

regions (Afrin, Raqqa and Horan) in Syria using flame and flameless atomic absorption spectrometry was studied. The accuracy of the method was evaluated according to the standard additions method. In general, the mineral elements in virgin olive oils extracted from wild or cultivated olive fruits have increased in the oil extracted from olive fruits adjacent to the highway, but the Fe, Pb and Cd were more increase up to 2 times for Fe, 80 times for Cd and 140 times for Pb; making the samples of these oils are unfit for food according to CO-DEX alimentarius, No 33/2009 (FAO/WHO Food Standards). Finally, the fatty acids in the studied oils were identified. It was found that, the amount of linoleic acid rises when the temperature increases and the content of fruit's oil decreases, contrary to oleic acid.

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