Traces of Heavy Metals in Libyan Olive Oil

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ABSTRACT

The determination of Fe, Mn, Cu, Zn, Ni, Cr and Pb in olive oil samples was performed by atomic absorption spectroscopy. Analyses showed that a significant portion of trace metals is removed during refining process but the level of Cu and Fe remained relatively higher to increase oxidation. There is a correlation between peroxide values and contents of trace metals in different commercial olive oil samples.

INTRODUCTION

Traces of heavy metals particularly copper and iron acts as catalyst for the oxidation of unsaturated oils and develop rancidity (3). Experiments have shown that heavy metals are related to the phospholipid content of the oils (4, 5). That is why most of the heavy metals are removed during the process of degumming or alkali refining of oils. Up to 98% Cu is removed in the olive oil refined samples (7). Various crude fats may contain as much as 0.1–0.3 ppm of Cu (2), 0.1–0.7 ppm of Mn and 1–5 ppm Fe (2). There is comparatively little work has been done in this area. Nothing is known about the heavy metal contents of Libyan olive oil in particular. The present work was undertaken to study the total heavy metal contents both in crude and refined Libyan olive oil samples.

MATERIALS AND METHODS

Samples of Libyan olive oil both crude and refined were obtained from an old olive oil refining factory located in Tripoli, S.P.L.A.J. Olive friuts were also collected from the University of Al-Fateh Campus, Tripoli. These were oven dried and crude fat was extracted with petroleum ether (B.P. 40–60°C) using Soxhlet apparatus (5). The free fatty acid and peroxide values were determined according to AOCS official methods (5).

Pre-treatment of oil samples for atomic absorption spectroscopy

One g of each sample (in triplicate) was placed in a previously dried and weighed Vycor Crusible. Crusibles were heated in a 105°C oven for 5 hours. After removing the

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crusibles from oven, were cooled in desiccator and weights were recorded (analytically).

The crusibles were transferred to a muffle furnace at 475° C and allowed to ash for 16 hours. The samples were removed and after cooling 1 ml of concentrated nitric acid was added to each sample. The samples were allowed to stand for 1 hour with frequent stirring. Finally, each sample was transferred to a 15 ml volumetric flask and made up to 25 ml using deoinised water. These samples were analysed by atomic absorption spectrophotometer according to the method of Olejko (6).

RESULTS AND DISCUSSION

The contents of 7 trace metals in different olive oil samples are shown in Table 1. As expected, all heavy metals are reduced during the process of refining in varying proportions. Detrimental effects of many heavy metals on the stability of fats, oils and related products are known. Traces of heavy metals particularly Cu and Fe accelerate oxidation of lipids (3). Libyan crude olive oil samples contain as much as Ca 9–10 ppm of Fe and 0.1–0.11 ppm of Cu. The iron in Spanish olive oil is reported as high as 16 ppm (18). Both Fe and Cu in the samples of Libyan crude olive oil are well within the range as reported in literature (8). During various stages of processing about 60 to 90% trace metals are removed from the edible oils. The Libyan refined olive oil samples contain 0.76 ppm Fe and 0.04 ppm Cu. These values are a bit higher then desired. It appears that during processing Ca, 91% Fe and 64% Cu is washed with gums. Other trace metals are also reduced. There is possibility that small amount of trace metals are formed (as soaps) through the action of free fatty acid on the tanks and other metallic equipment used in processing and storing oils. This may be due to the bad processing conditions, old and absolute equipment which is still in use in the old olive oil factory located in Tripoli. To avoid contamination of metals from equipment during processing there is a growing trend to use stainless steel vessels in modern refineries. The following amounts of metal in ppm lower by half the keeping time of lard at 208° F (2): Cu 0.5, Mn 0.6, Cr 1.2, Ni 2.2 and Zn 19.6. Copper concentration in vegetable oils is maintained below 0.02 ppm. Both Cu and Fe concentration in olive oil samples is high and will have adverse effect on the keeping quality of olive oil. The correlation of concentration of trace metals and peroxide values can be seen from Table 2. Higher the concentration of trace metals are, higher the peroxide values. However, the peroxide values in case of prolonged storage both in case of refined and crude are relatively lower. This may be due to a decline in peroxide value after maximum level had reached. As the peroxide begin to decompose or polymerize more rapidly than are formed (2).

Table 1. Trace metal contents in olive oil samples (ppm)*

Type of oil	Fe	Cu	Zn	Mn	Ni	Cr	Pb
Crude fresh (Factory)	10.3	0.11	1.01	0.21	0.06	2.51	0.55
Virgin (Laboratory)	9.1	0.10	1.00	0.18	0.05	2.24	0.50
Refined (Factory)	0.76	0.04	0.50	0.19	0.50	0.41	0.21
Crude (stored in tin can for 10 years)	10.61	0.11	2.02	0.21	0.06	2.51	0.55
Refined (stored in tin can for 10 years)	1.42	0.06	0.50	0.19	0.50	0.41	0.21

Table 2. Effects of trace metals on Peroxide values of olive oil samples.

Type of oil	Peroxide value* (m/eg/1000 g fat)	
	At the beginning	after 34 days
Crude fresh (Factory)	18.90	83.60
Virgin (Laboratory)	1.28	72.20
Refined (Factory)	7.46	30.00
Crude (stored in glass bottle for one year)	2.20	15.00
Refined + 50% crude in tin (Factory)	1.20	4.30
Refined + crude in glass bottle (Factory)	1.20	26.00
Crude stored in tin can for 10 years)	1.30	5.25
Refined (stored in tin can for 10 years)	0.50	2.50

*Each value is the mean of 3 replicates.

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LITERATURE CITED

1. Bally's Industrial Oils and Fat Products. 1979. Dariel Swern Ed. Vol. 1A. Wiley Interscience Publication, New York. p. 81–83.
2. Lundberg, W. O. and Jarvi, P. 1968. Progress in the Chemistry of Fats and other Lipids. Vol. IX part 3. Ed. R. T. Helman. Pergamon Press, New York, NY. pp. 377–406.
3. Lunde, G. 1971. Activation Analysis of Trace Elements in Lipids with Emphasis in Marine Oils. JAOCS. 45, pp. 517–522.
4. Lunde, G., Landmark, L. H., and Gether, J. 1976. Exchange of Metal Ions in Edible Oils. JAOCS, 53. pp. 204–210.
5. Official and Tentative Methods of the American Oil Chemists' Soc. 3rd rd. 1976. AOCS, Champaign, I1.
6. Olejko, J. T. 1976. Fe, Ni and Mn in Fats and Oils by Flameless AA JAOCS 53. pp. 480–484.
7. Vioque, A. M. del Pilar Villagran. 1957. Separation and Determination of Iron by Means of Ion-exchange Resin. Grassas Y aceitis 8. pp. 152–154.
8. Vioque, A. 1954. A. Trace elements and the Development of Rancidity in Edible Oils. GRASAS Y Aceites. pp. 62–65.

تقدير لمحتويات زيت الزيتون الليبي من العناصر الثقيلة

ملخـص

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بطريقة التحليل الاسيكتروسكوبي أمكن تقدير محتويات الزيتون من الحديد والنحاس والزنك والنيكل والكروميوم والرصاص ، وهذه تراوحت بين ٧٦و٠ و٦١ و١٠ جزء حديد في المليون ، ٠٤ و٠ و١١ و٠ جزء نحاس ، ٥٠ و٠ و٠١ و١ جزء زنك ، ١٨ و٠ و١٢ و٠ جزء منجنيز ، ٠٥ و٠ و٠٥٠ و٠ جزء نيكل ، ٤١ و٠ و٥١ و٢ جزء كروميوم ، ٢١ و٠ و٥٥ و٠ جزء رصاص . وهذا يعني أن الجزء الأكبر من العناصر النادرة لا يزال في مرحلة التكرير ، وبرغم ذلك القدر المتبقي من الحديد والنحاس يعتبر كبيراً إلى الحد الذي يساعد على ازدياد فرصة الأكسدة . وقد لوحظت علاقة بين قيمة البيروكسيد ونسبة العناصر النادرة في عينات زيت الزيتون التجاري .