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Application of γ-Radiolysed Natural Silica on the Fractionation of Virgin Olive Oil

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ABSTRACT

The study of γ-radiolysed natural Iraqi silica (Ninivite) as obtained from the main rocks indicated that as we increase the irradiation time, the ratio of amorphous silica to the crystalline one is increased. A significant effect is recognized when irradiation time approximately two hours. The radiation causes cleavage of the polymeric structure of the silica and produce monomeric silica of amorphous type. The application of the irradiated silica to the separation of virgin olive oil indicates a large difference between one fraction and another as shown by the amount of fractions and I.R. measurements. I.R. measurements indicate that olive oil contains fatty acids, fatty acid esters, phenols, alcohol and some other minor components.

تطبيق السليكا الطبيعية المتكونة شعاعيا على تجزئة زيت الزيتون العذري

الملخص

يهدف البحث الى دراسة التفكك الاشعاعي للـسليكا الطبيعيـة كمـا وردت مـن خاماتهـا الام. واوضحت عملية التشعيع ان السليكا البلورية ذات الوزن الجزيئي العالي قد تفككت وازداد تفككها بزيـادة زمن التشعيع حتى اصبحت اعلى ما يمكن عندما كان زمن التشعيع ساعتان. ويعتقد ان السليكا قد تفككت وانتجت وحدات مونومرية متكافئة تقريبا تعاني من خلل بلوري اطلق عليها السليكا غير البلوريـة وكمـا توضح ذلك في عملية الفصل بوساطة هيدروكسيد الصوديوم. ان تطبيق عملية الفصل لزيـت الزيتـون العذري على هذه السليكا المشععة اظهر فروقات كبيرة ما بين الاجزاء المفـصولة واسـتقطابيتها اذا مـا قورنت بتلك التي فصلت من السليكا غير المشععة. وقد اوضح طيف الاشعة تحـت الحمـراء للاجـزاء المفصولة، ان زيت الزيتون العذري خليط من الاحماض الدهنية واستراتها وبعض الفينولات اضافة الـى وجود الكحولات هذا الى جانب وجود بعض المكونات الجزئية .

INTRODUCTION

Silica present in nature either in free or bonded form to some bases to give various silicate minerals. Free silica present either in crystalline form, which is the dominant form in nature or in a non-crystalline form (amorphous); but the non-crystalline is more important and applicable in the purification and industrial production (Taher , 2004).

Natural silica is isolated in its irregular forms from the natural clay minerals which is usually associated with other minerals. It is expected that the silica is obtained by leaching of illite-rich calcareous clay stones by H_2SO_4(Al-Naqib and Al-Dabbagh, 1993).

Natural silica is a white, light density rock, also is very porous with low bulk density. Chemical analysis indicate that quartz is the main mineral constituent; gypsum is the main pollutant of the rock and sometime iron is combined (Taher, 2004; Al-Naqib and Al-Dabbagh , 1993).

Silica gel (silicic acid) is a regenerative adsorbent of silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used in column chromatography for the separation of some fractions of analytes from impurties that have different polarity. Natural silica is activated, by heating to 150-160 ^oC or deactivated by the addition of water . Silica gel occurs in a large quantities in our country. These deposits of silica rich rock named Ninivite (Jassim and Al-Naqib , 1989).

Silica is the most popular base material. It has a high physical strength and a high surface area which is easily chemically modified to give phases suitable for use in a broad range of HPLC modes. However, silicates dissolve in water at pH $\geq$ 6.5, while bonded silicates are unstable at pH$\leq$2.5. Newer bonded silicates may have an extended pH range of 2-10.

Adsorption chromatography using alumina, florisil, and silica gel are useful for separating compounds of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity. These are primarily used for cleanup of a specific chemical group and relatively non-polar compounds i.e., organochlorine pesticides, polynuclear aromatic hydrocarbons (PAHs), nitrosamines, etc. (Taher , 2004 ; Al-Naqib and Al-Dabbagh , 1993 ; Jassim and Al-Naqib , 1989).

Chamblee *et al*. studied the quantitative analysis of the volatile constituents of lemon peel oil using silica gel column chromatography and GC. (Chamblee *et al* .,1991).

The increase in olive oil consumption internationally is related to its recognized unique flavor and nutritional value. The latter is mainly due to its high mono-unsaturation (oleic is the main fatty acid of olive oil) and to the presence of phenols, tocopherols, squalene, and flavor components. (Kiritsakis , 1991 ; Fedeli , 1977 ; Fedeli , 1993).

Recent reviews on the chromatographic techniques applied to lipid classes or devoted to the analysis of specific classes of lipids give also information on the applications of solid phase extraction (SPE) in oils and fats (Panagiotopoulou and Tsimidou , 2002). In the present review emphasis was paid to update the information and present in details some of the applications concerning the vegetable fats. Information on other obible fats or fatty foods associated with the above objectives is given in certain cases. The classes of compounds are presented in descending order of frequency of SPE applications found in the literature (Panagiotopoulou and Tsimidou , 2002). Ganiev *et al*. studied the purification of cotton seed oils using highly porous non-crystalline silica gel (Ganiev *et al*.,1976 ; Sacchi et al.,1996).

EXPERIMENTAL

1. Irradiation instrument :

Natural silica was irradiated at room temperature using Gamma Cell - 220 supplied by the Canadian Atomic Energy **.** The irradiation source is Cobalt 60 . The dose of the cobalt source as measured in term of Fricke gave radiation dose of 2.78×10^{16} ev. $ml^{-1}.min^{-1}$. The irradiation of the silica sample was conducted using standard method .

2. Gamma radiolysis of natural silica:

100 g of natural silica dried in an oven at 130 ^{o}C for 3 h. The sample was transferred to a glass container suitable for radiolysis. The radiation process was carried out at 1/2 h, 1 h, 2 h. It was aimed to decompose the crystalline structure of the silica.

3. Chromatographic separation of virgin olive oil:

30 g of natural silica previously irradiated with γ-rays for (0,1/2, 1,2)h .The activated silica gel was packed in chromatographic column of a dimension (50cm×2.2cm). The adsorbant was wetted with small amount of n-hexane. 2-3 g of virgin olive oil was transferred quantitatively to the top of the previously packed silica column. n-Hexane was used for first elution to remove the non-polar fraction. The elution was continued till its original refractive index was retained. The solvent was removed and the recovered fraction weighted and its percentage was calculated.

The second fraction was eluted with toluene and treated in the same manner as in the first fraction. Chloroform was used to remove the third fraction from column. Finally ethanol was used to remove polar fraction, suspected that certain amount of loss would be found due to the increase in the non-crystallinity of the support. Removal of the solvents from all the fractions led to the recovery of fraction 1,2,3 and 4. The isolated fractions were further studied using infrared.

RESULTS AND DISCUSSION

Separation and purification of organic mixture is of a vital importance due to the use of most chemicals in the pharmaceutical industries. Therefore, we aimed in this work to improve and change the ratio of the crystalline silica to amorphous silica throw irradiating the natural silica with γ-rays. The source of gamma is Co-60. The radiation period of time (0,1/2, 1, 2)h .The irradiation of the silica gives a certain information after the determining amorphous and crystalline silica and indicating that it is a change in the ratio of the crystalline to the amorphous silica.

The ratio of amorphous silica is increased by increasing the irradiation time i.e by accumulation of energy. This may be explained by the dissociation of silica in a way or another to give amorphous silica. This was indicating by increasing solubility in NaOH.

Using energy from radioactive element to natural silica (Ninivite) was not been studied before in Iraq .In our research work we aimed to change the structure and the chemical behaviour of the natural silica through the radiation. The result of irradiating natural silica through a different period of time (0 to 2 h) indicates that the silica structure which is explained in the inorganic chemistry as a linear tetrahedral polymer (Taher , 2004) so the use of radiation degradates the polymeric structure into monomeric units,

which could have a certain defect in the structure to lead to unbalanced forces and finally to adsorption and more selective separation. Exposure of natural silica to radiation for half an hour may affect the chemical bonding and structure of the Ninivite silica. Increasing the time of irradiation by the same source to 1 h increases the amount of amorphous silica by almost 81.45% .On the other hand, irradiation for 2 h keeps only 7.8% of the silica in the crystalline form. This point is very advantageous in the industrial production of sodium silicate in the detergent industry. The results of irradiating natural silica are given in Table (1).

Table 1 : Chemical composition of γ-radiated natural silica for various period of time.

% of crystalline silica (wt%)	% of non -crystalline silica (wt%)	Irradiation time (h)
51.41	48.58	0
46.08	53.92	1/2
18.55	81.45	1
7.83	92.17	2

Due to the increase in the non-crystallinity of the natural silica gel by the exposure to the gamma radiation. We attempted to separate virgin olive oil into its generic components by applying a certain gradient elution depending on the polarity of the solvents into four fractions. The non-polar one was eluted from the column by n-hexane and the highly polar one was eluted by ethanol. Also we note that natural silica is a polar in nature .The fractions isolated from virgin olive oil employing the radiated silica are given in Table (2).

Table 2 : The percentage of fractions isolated from virgin olive oil over silica gel

Solvents	Recovery	Irradiation time (h)			
		0	1/2	1	2
Hexane		52.69	44.50	50.33	57.0
Toluene		24.61	27.0	22.33	20.66
Chloroform		8.81	7.0	12.66	10.33
Ethanol		0.70	8.5	3.33	4.66
	Total	86.81	87	88.65	92.65
	Loss	13.19	13	11.35	7.35

Looking at IR spectra with separated fractions indicate that give the following:

Irradiation of silica and separation of olive oil indicate that the first fraction is light and non-polar contains a lot of ester separated or conjugated in n-hexane.In the second fraction, shows some high frequency absorption peaks referring to carbonyl; 1715 cm^{-1}, 1735 cm^{-1} and 1760 cm^{-1} which are either aldehydes, ketones or lactones, respectively. The third fraction as a chloroform extract shows mainly the same absorption as the

second fraction but may be the compounds have as higher molecular weight; while the fourth fraction as an ethanol extract shows a great distribution of carboxylate group 2854 cm^{-1}. Infrared absorption of the fraction indicates the presence of olifenic hydrocarbons or some unsaturated linkage in the carboxylic acid. A broad absorption for the hydroxyl group at 3467 cm^{-1} which could be for the phenols present in the oil as derivative or belong to some hydroxy acid. Irradiation of silica for 1 h and separation of olive oil using different solvents give fractions of n-hexane elute which is almost similar to that of 1/2 h with the exception of some low absorption peaks especially those belonging to the bending area of the C-O group while the second fraction showed the same absorption peaks as the second fraction in the 1 h and the absorption of phenols at 3450 cm^{-1} with a broad peak, also the appearance of the absorption responsible for C=C in the α,β-unsaturated acid in the molecule. The absorption of ketones or aliphatic esters at 1740 cm^{-1} is highly recognized. Chloroform and ethanol showed slight difference in their quantity and almost similar IR absorption.

Looking at the 2 h; absorption spectra showed the first fraction with a high concentration with light materials of aliphatic nature of esters while the second fraction showed some highly substituted acids and sometimes esters while the third fraction showed a great influence of the radiation in the separation process and give recognizable peaks for aromatic compounds; which may be those belonging to phenols, which if it is compared with the first and the second fractions is considered as highly phenolic compounds.

The overall conclusion that irradiation of silica in its mixed form will lead to degradation of the highly polymeric silica to low polymeric non-crystalline which showed some differences in the separation of virgin olive oil as indicated by IR spectra , as given in figure (1 , 2 and 3).

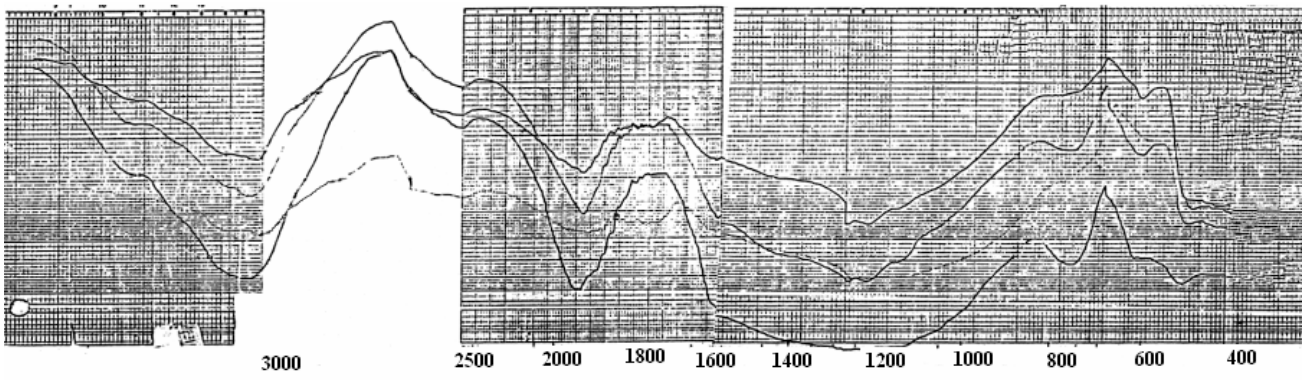

Fig.1: Infrared spectra of virgin olive oil fractions isolated from natural silica gel before irradiation.

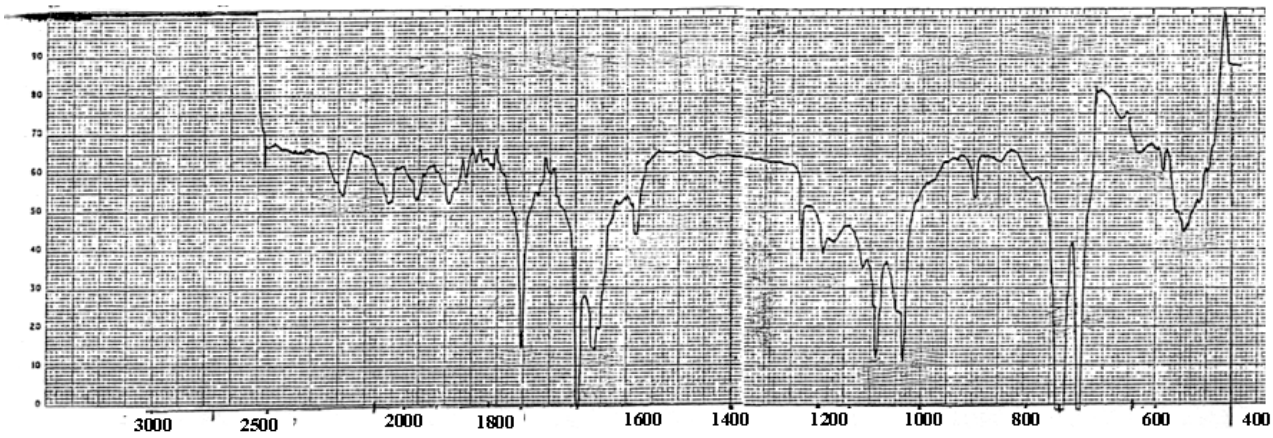

Fig. 2 : infrared spectra for compounds separated from virgin Iraqi olive oil by irradiated natural silica using toluene as solvent (irradiation time 1/2 h).

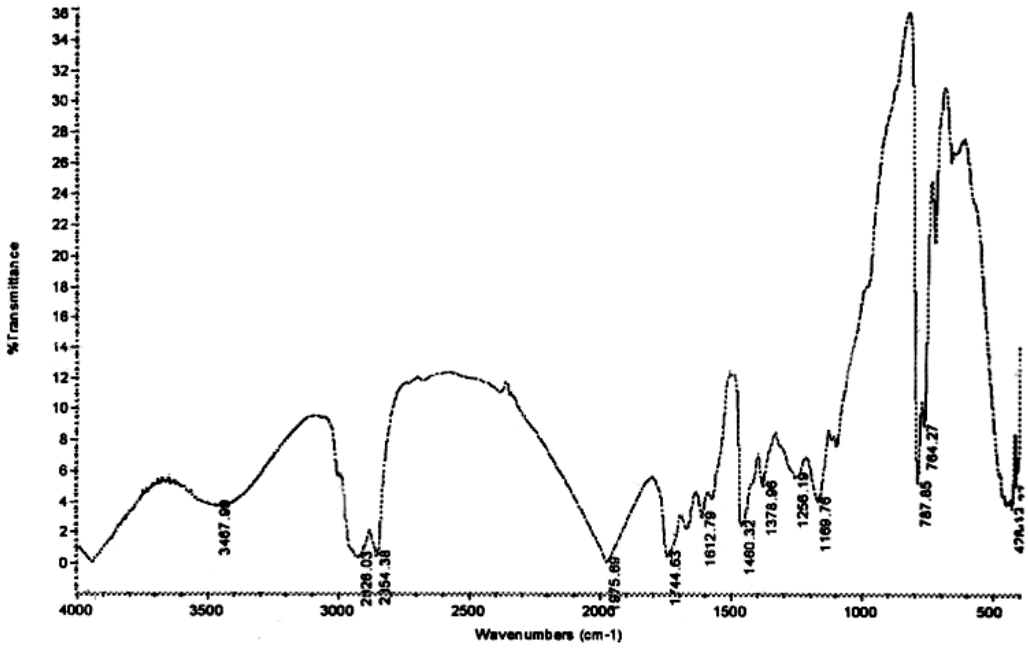

Fig.3 : infrared spectra for compounds separated from virgin Iraqi olive oil by irradiated natural silica using ethanol as solvent (irradiation time 1/2 h).

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