

### SUMMARY

Onion and garlic are considered major vegetable crops in Egypt. Because of the importance of their essential oils in the international trading, many trials have been carried out for their adulteration with common adulterants such as; aged oil, maize oil, ethyl alcohol and paraffin oil. Accordingly, these studies were carried out to give sufficient information about the authenticity of such oils. Both onion and garlic oils were mixed with abovementioned adulterants in the concentration of 10, 20 and 30%.

A comparative physico-chemical analysis were carried out on the samples of both onion and garlic oils to study the effect of the foregoing adulterants on their physico-chemical properties, which would help to determine the degree of authenticity of such volatile oil.

The obtained results could be summarized as follows:

#### Part 1: Onion volatile oil:

Physical properties for fresh onion volatile oil included; specific gravity, refractive index, acid number were, 1.0965, 1.5614 and 7.27 respectively whereas, the addition of increment amount of various adulterants caused a proportional decrement in specific gravity, refractive index and acid number with the exception of adulterated samples with aged oil caused an increase in specific gravity and acid number.

On the other hand, the solubility in ethanol of adulterated samples with aged onion volatile oil, maize oil and paraffin oil decreased when compared to the solubility of fresh onion volatile oil. On contrary the solubility of the adulterated samples with ethyl alcohol did not changed. Besides, the solubility in organic solvent such as diethyl ether, carbon tetra chloride, n-hexane, benzene and chloroform was the same since, all samples were completely soluble.

UV spectra of onion volatile oil, aged onion volatile and adulterated samples with various abovementioned adulterants showed a maximum absorption at 278 nm, whereas upon using the same concentration the absorption intensities differed proportionally according to the concentration of the used adulterant.

IR spectrum of onion volatile oil showed different functional groups. The dominant active groups were: trans double bond, C-OH stretching, propyl sulphide,  $\text{CH}_3$  (bending), active methylene group, carbonyl group and  $\text{CH}_3\text{-CH}_2\text{-}$  alkane. No new bands were detected in the IR spectra of onion volatile oil adulterated with aged onion volatile oil. Whereas, the adulterated samples with maize oil caused the appearance of new band at  $1740\text{ cm}^{-1}$  (C=O stretching of aliphatic esters). Moreover, the adulteration with maize oil led to broadening in absorption bands at  $910\text{-}980\text{ cm}^{-1}$  (trans double bond) and  $2840\text{-}3000\text{ cm}^{-1}$  (-CH-stretches).

When ethanol was used as adulterant, intensities of absorption bands increased by increasing the amount of ethanol added to onion volatile

oil. Whereas, samples adulterated with paraffin oil caused the appearance of four new bands at 705, 1125, 1270 and  $1730\text{ cm}^{-1}$  which refer to alkenes, C-O in primary alcohols, C-O-C antisymmetrical stretching and C=O stretching in aliphatic esters, respectively. The previous absorption bands were distinguished when commercial paraffin oil was tested alone.

G.L.C. of fresh onion volatile oil showed that the total peaks number were 23. Sixteen volatile compounds were identified while seven compounds were unknown. The main identified components could be stated in a descending order; methyl taurine, methyl propyl trisulphide, undecanal, dipropyl trisulphide and propyl alcohol.

The G.L.C. analysis of aged onion volatile oil was the same when compared with the fresh oil. However, these components slightly decreased except propyl alcohol, propyl disulphide propane and methyl propyl trisulphide were increased.

The G.L.C. of adulterated samples of onion volatile oil with ethanol indicated that all components decreased as a result of the dilution action of ethanol with the appearance of a single peak of ethanol located directly after the solvent peak which disappeared upon washing the adulterated samples with saturated solution of sodium chloride followed by a subsequent drying with anhydrous sodium sulphite.

Glycerol determinations for pure onion volatile oil sample as well as adulterated samples with maize oil indicated that glycerol could not be detected in the pure sample of onion volatile oil whereas, glycerol increased proportionally with the increasing of maize oil used as adulterant.

The qualitative determination of ethanol by iodoform test for the pure onion volatile oil and adulterated samples indicate that no iodoform crystal were formed for the pure onion volatile oil and adulterated samples with aged onion volatile oil, maize oil and paraffin oil. Whereas, flat yellow crystals immediately observed in samples of onion volatile oil adulterated with ethyl alcohol.

On the other hand, the volumetric and colorimetric quantitative determination of ethanol revealed that the volumetric method was less sensitive when compared to colorimetric method. Also, as expected the ethyl alcohol content increased proportionally upon increasing the amount of ethanol used as adulterant. Paraffin oil was determined quantitatively using thin layer chromatography. Results obtained indicate that the paraffin oil content increased proportionally with increasing the percent of paraffin oil in the adulterated onion volatile oil.

#### Part II. Garlic volatile oil:

The physical properties for garlic volatile oil included specific gravity, refractive index, optical rotation and acid number were 1.0770, 1.5665, 0.0 and 0.88, respectively. The addition of

carboxylic acid),  $1740\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching in aliphatic esters) and  $3455\text{ cm}^{-1}$  (bonded OH) which are distinguished for maize oil.

As for the use of ethanol as adulterant the intensities of absorption bands increased by increasing the amount of ethanol added to the garlic volatile oil.

The samples adulterated with paraffin oil caused an appearance of four bands at 700, 1120, 1460 and  $1725\text{ cm}^{-1}$  which referred to alkenes, C-O in primary alcohol, OH bending in carboxylic acids and  $\text{C}=\text{O}$  stretching in aliphatic esters, respectively. The previous absorption bands are distinguished to the use of commercial paraffin oil.

G.L.C. of fresh garlic volatile oil show that the total peaks number were 25. Thirteen volatile compounds were identified while 12 compounds were unknown. The main identified components could be stated in a descending order; diallyl thiophene, dimethyl thiophene, 2-propenyl-2-propane thio-sulphonate, diallyl trisulphide and dipropyl trisulphide.

As for aged garlic volatile oil no new components appeared, whereas, all the components decreased except dimethyl thiophene increased.

Glycerol determination for pure garlic volatile oil as well as adulterated samples with maize oil had the same trend as mentioned before in the results of onion volatile oil.

The qualitative determination of ethanol by iodoform test for the pure garlic volatile oil and adulterated samples indicate that no iodoform crystals were formed for the pure garlic volatile oil and adulterated samples with aged garlic volatile oil, maize oil and paraffin oil, whereas, flate yellow crystals immediately observed in the adulterated samples with ethyl alcohol.

On the other hand, the ethanol determination by volumetric and colourimetric methods had the same pattern as mentioned before in the results of onion volatile oil.

The determination of paraffin oil using TLC technique indicated that paraffin oil content increased proportionally with increasing the amount of paraffin oil in adulterated samples.

Conclusively, it seems that the most important determination which could be used to detect adulteration of both onion as well as garlic volatile oils are; solubility in ethyl alcohol, specific gravity, refractive index, acid number, iodoform test and U.V. spectrum which could be considered as a presumptive test, whereas, quantitative determination of alcohol volumetrically and colourimetrically, glycerol by periodic acid oxidation, paraffin oil by T.L.C., G.L.C. and LR could be considered as affirmative tests for the discovery of adulteration practices.