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VIBRATIONAL STUDY FOR CITRUS FRUITS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Abstract

This Fourier transform-infrared (FT-IR) spectroscopy technique allows a rapid analysis and needs little or no sample pre-treatment and has been widely used for the analysis in food science, medicine and pharmaceuticals sectors. In this study, the FT-IR spectroscopy was used as a fast and direct analytical approach in order to analyze three dry citrus fruits species: orange, lemon and tangerine. The results of our trial emphasize the possibility of differentiation of all citrus fruit species took into study, according to their citric acid and sugar content.

Key words*: Citrus Fruits, FT-IR.*

INTRODUCTION

Citrus fruits are grown throughout the world and highly appreciated for their juice and for the numerous benefits for human health. Many therapeutic properties have been attributed to citrus fruits: anticancer, anti-inflammatory, anti-viral activities, cardiovascular diseases (Codoner et al., 2010; Ejaz et al., 2016; Mulvihill and Huff, 2012). They are a rich source of vitamins, minerals, flavonoids and these fruits represent a primary source of vitamin C considered responsible for the numerous health benefits (Marti et al., 2009).

Fourier transform infrared (FT-IR) spectroscopy is one of the most idely used methods to identify chemical compounds and elucidate chemical structure. FT-IR technique is applied to detect compositional differences between samples on the basis of vibrations of various chemical groups at specific wave lengths of the spectrum (400-4000 cm^{-1}).

The above mentioned reasons have been considered when this technique has been gaining popularity for the qualitative and quantitative analysis of citrus fruits, including citric acid and carotenoids. Thus, FT-IR spectroscopy is used as a rapid and accurate method to detect natural compounds in food industry, and is often approached as a simple and fast alternative to other laborious methodologies, with minimum sample preparation.

In the last years, the food products analyzing is one of the actual preoccupations, and for this reason, the development of some quick and accurate ways of determining the additives and toxic substances in foods is needed.

The citric acid ($C_6H_8O_7$) is a tricarboxylic acid naturally occurring in citrus fruits. It is widely involved in the metabolic processes of all the living organisms.

Also known as E330, the synthetically produced citric acid, or lemon salt, is the most widely used acid in the food industry as flavouring and acidifier agent in: food, drinks, food supplements, but also in pharmaceuticals, cosmetics, or for synthesizing various materials involving citrate.

The citric acid solvatomorphs from various solvents have been extensively studied, and they were found solvent dependent as well as crystallization conditions dependent.

The citrus fruits, which are the primary natural resources of citric acid, could present large variation in chemical composition, according to the specific conditions of cultivation. To be able to evaluate the citrus fruits regarding the citric acid content, vibrational spectroscopy techniques may be employed. The citrus fruits are also rich in phytochemicals, a group of non-nutrient bioactive compounds, including carotenoids which is secondary metabolites synthesized by plants, with many beneficial effects for humans' health.

The carotenoids presence in citrus fruits can be usually observed in the 1536-1510, 1179-1151 and 1021-993 cm^{-1} spectral range (Oliveira et al., 2009).

The literature mentions many researches concerning the use of the FT-IR technique for analyzing solid and liquid samples of citrus fruits. The use of the FT-IR technique has also been reported for the analysis of food matrices (Andronie et al., 2016), but literature mentions lots of works that involve the use of this technique and its great potential to be used in a large variety of other research fields (Keseru et al., 2016). Thus, Hirri *et. al* (2015) conducted a study where the vibrational spectral techniques in connection with chemometric methodologies were used as a fast and direct analytical approach to classify citrus cultivars, by quantitative analyze of their juice.

In other study, Gamal *et al*. (2011) used FT-IR spectroscopy for determining sugars, pectin and organic acid contents in same natural and synthetic products (jam).

This technique is also widely utilized for freshness assessments of a series of citrus species (e.g. clementine, mandarins and tangerines). Nekvapil et al. (2018) reported that the intensity of the carotenoid Raman signal is indeed a good indicator for fruit freshness and introduced a Raman coefficient of freshness whose time course is linearly decreasing, with different slope for different citrus groups (Nekvapil et al., 2018).

Because the citric acid, obtained from natural products, fruits mainly, is very important for human body having important nutritional and curative properties, more experimental studies concerning this compound, are needed. Therefore, the aim of this study is to analyze and compare the molecular structures of lemon, orange and tangerine pulps of fruits, using vibrational spectroscopic techniques (FT-IR).

This study can also be used in order to make a difference between natural and non-natural juices.

MATERIALS AND METHODS

In this research, we analyzed different varieties of citrus fruits according to the analytical information obtained from dried citrus by means of Fourier transform infrared spectroscopy (FT-IR).

Mature fruits of three common varieties of citrus species: lemon, orange and tangerine, respectively, were purchased from the local Romanian market. The fruits were washed with tap water, and then the pulps were dried at 40 ^0C for 24 h. The dried citrus samples were crushed using a commercial blender.

The sample from FT-IR spectrum was obtained from 0.005 g of citrus fruits used without previous purification. The citric acid (E330, commercial form) was used as reference material (fig.1)

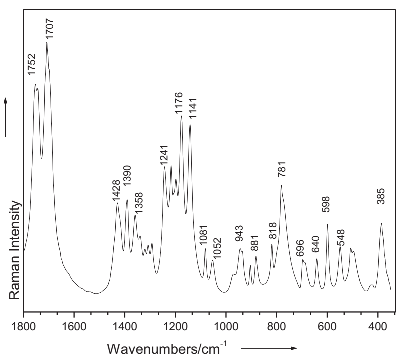


Figure 1. The FT-IR spectrum of citric acid

The specific footprint is a particular combination between molecular vibration and rotational vibration and has a great significance to identify specific molecules. The measurements were carried out on the infrared scale of 650-4000 cm^{-1}, spectral resolution was set at 4 cm^{-1}, and all spectra were acquired over 256 scans. The spectral data were analyzed using Origin 6.0 software (Fig.2). These spectra were analyzed by comparing the obtained vibrational bands with those of similar functional groups mentioned by the literature.

The FT-IR spectra were performed with a Jasco FT-IR-4100 spectrophotometer using KBr pellet technique. The IR frequencies are expressed by a light number that is directed to the sample. When radiant energy is equal to the vibrational frequency of the molecule, it realizes the suction and vibrates. Absorption intensity for each frequency of vibration is monitored by a detector.

RESULTS AND DISCUSSIONS

The absorption peak obtained at the wave length around 3367cm^{-1}, of high intensity, indicates the existence of free and intermolecular bonded hydroxyl groups.

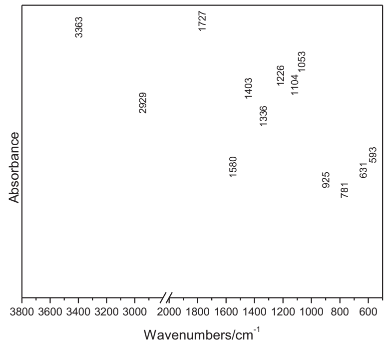
The stretching vibrations of the -OH groups occur within a broad range of frequencies indicating the presence of “free” hydroxyl groups and bonded -OH bands of carboxylic acids. The peaks observed at 2929 cm^{-1} can be assigned to stretching asymmetric vibration of $(CH)_3$ group.

The stretching vibrations of $-COOH$ and $-COOCH_3$ groups are attributed to the very strong peak obtained at the wave length of 1727 cm^{-1}, in lemon spectra and very weak peak obtained in tangerine spectra (Rehman et al., 2013).

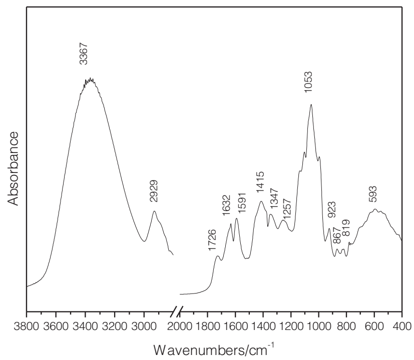
The medium strong band obtained at 1632 cm^{-1} wave length was assigned to the deformation of the –OH groups. The peak reported at the wave length of 1591 cm^{-1} identified in orange and tangerine spectra is specific to stretching vibrations of phenyl group. In the same spectra, a peak that has specific vibrational attribution of CH_3 rocking and CH_3 bending, was found at the wave length of 1347 cm^{-1}. The C-O of aliphatic acid groups are attributed to the peak identified at the wave length of 1257 cm^{-1}. The stretching vibrations of the CC, CO and CCO groups from sugar, were reported for tangerine and lemon, with a peak at 1053 cm^{-1}, of very strong intensity (Gamal et.al., 2011).

Because the band characteristic of tangerine is more intense compared with the band characteristic of lemon, we can affirm that tangerine contain more sugar than lemon. The deformation of -OCH, -COH, -CCH groups, attributed to fructose exhibit a medium band at the wave lengths of 1415 cm^{-1} (tangerine) and of 1403 cm^{-1} (lemon).

The orange fruits were also evaluated by FT-IR spectral data (Fig. 2). In both spectra, the rocking $-CH_3$ group of pectin are attributed to the very weak peak obtained at the wave length of 930 cm^{-1}.



a)



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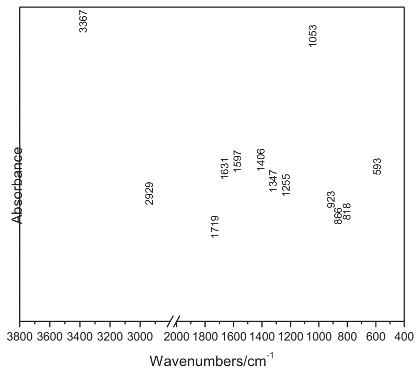

c)

Figure 2. The FT-IR spectrum of lemon a), tangerine b) and orange c).

The peak obtained at the wave length of 867 cm^{-1} is specific to the deformation modes of carboxyl groups, and this attribution is available just for mandarin spectrum. The additional peak reported at the wave length of 625 cm^{-1} can be assigned to bending mode of aromatic compounds (Torab, 2013). The peak present in all spectra of orange at the wave length of 593 cm^{-1} is characteristic to the deformation of the $-CH_2$ group.The FT-IR spectrum of tangerine and lemon pulp clearly indicates carboxyl group is present in abundance.

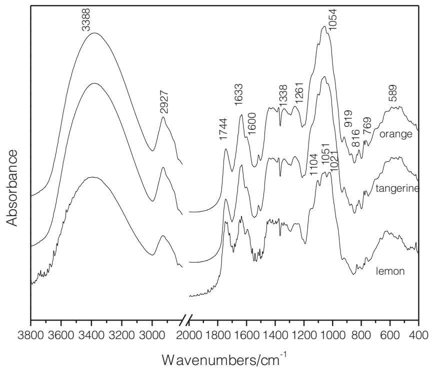

Figure 3. The FT-IR spectrum of a) orange, b) tangerine and c) lemon barks.

Analyzing the spectrum of orange barks (Fig. 3), one can notice the presence of citric acid emphasized by the specific band obtained at the wavelength of 1261 cm^{-1}.

The peak identified at the wavelength of 1054 cm^{-1} in spectrum obtained for orange and tangerine barks, correspond to specific stretching -CO groups of sucrose and it is more intense compared to that obtained for lemon sample. In this case results that the lemon bark contains a smaller amount of sugar.

CONCLUSIONS

According to the results of this study, we may the FT-IR spectroscopy as a potential analytical rapid tool to analyze the natural citrus fruits used as powder in different products of food industries.

The vibrational analysis allowed differentiation of citrus species according to the citric acid and sugar content.

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