Fourier Transformer Infrared Spectroscopy for Quality Assurance of Tomato Products

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Abstract: FT-IR spectroscopic technique was used to evaluate the chemical composition, lycopene, β-carotene and some adulterants (starch, allura red pigment and paprika) of tomato products as a fast technique in comparison with standard methods. The results indicated that, sensory evaluation and color parameters of Hunter measurements (L*, a* & b*) represent color value but the quality of tomato natural pigment (lycopene) not identified. FT-IR spectra of adulterated tomato paste with starch showed spectral peaks at (1137 cm^{-1} and 1040 cm^{-1}) while, in adulterated paste with paprika revealed some peaks at 641 for stretching (CH_2, CH) and at 1520 cm^{-1} for vibrational stretching of (C=C). Ketchup was characterized with stretching (C-O-C) at 1279 cm^{-1}. Adulterated tomato paste with paprika characterized with total phenolic compounds (42.7 ± 2.3) and high antioxidant activity ($78.3.8\%\pm2.9$). The effect of processing on the volatile components present in tomato paste, ketchup and adulterated tomato paste with starch or paprika has been studied by gas chromatography (GC) and gas chromatography-mass spectrometery (GC/MS). The most predominant volatiles were saturated and unsaturated 6-carbon aldehydes and alcohols. Hexanal and (Z)-3-hexen-1-ol, (Z)-3-hexenol, 5-methyl-5-hexen-2-ol and 1-hexanol were present in significant concentrations in all samples. Methyl-(2-hydroxy-3-methyl)-valerate and methyl-(2-OH)-iso-methyl valerate were generated in tomato paste with high concentration (1.0 and 4.25%), respectively.

1. Introduction:

Tomato (*Lycopersicum esculentum*) is one of the most consumed fruits in the world, either as a raw fruit or as a processed product. In fact, in the entire world, tomatoes are second only to potatoes in economic importance and consumption and are used in the foodstuff industry as raw material for the production of several products such as juices, sauces, purees, pastes, and canned tomatoes. In recent decades, the consumption of tomatoes has been associated with the prevention of several diseases (Sharoni & Levi, 2006 and Wilcox et al., 2003) mainly due to the content of antioxidants, including carotenes (lycopene as well as β-carotene), ascorbic acid, tocopherol, and phenolic compounds (Periago et al., 2009). Lycopene is a hydrocarbon carotenoid, $C_{40}H_{56}$, with molecular weight 537.

Lycopene has been shown to have strong antioxidant activity; it exhibits the highest physical quenching rate constant with singlet oxygen; it induces cell-to-cell communication; and it modulates hormones, immune systems, and other metabolic pathways (Rao & Agarwal, 1999). Phenolic compounds exhibit a wide range of physiological properties, such as anti-allergenic, antiatherogenic, anti-inflammatory, anti-microbial, antioxidant, antithrombotic, cardioprotective, and vasodilator effects (Balasundram et al., 2006). Whereas

tocopherol and ascorbic acid are recognized as antioxidant vitamins and heat-labile compounds, lycopene and phenolic compounds are more resistant to thermal processing, being the main antioxidants in processed products. Related to the distribution of both compounds in tomatoes, it is recognized that the peel of tomato is richer in lycopene and phenolic compounds than the pulp (George et al., 2004).

Carotenoids are a group of pigments, varying from yellow to red in color, widely distributed in the vegetable and animal kingdoms. It is estimated that more than 100 million tonnes of these pigments are produced annually in nature, in which they serve as ancillary pigments in photosynthesis, antioxidants, membrane stabilizers, and phytohormone precursors (Fraser et al., 2007).

Monitoring quality of tomatoes is very important at all levels of the industry, including the breading programs, the agricultural productions, and the postharvest managements as well as processing. Several different parameters such as soluble solids, dry matter, acidity, contents of sugars and organic acids are often used to assess the quality of tomatoes. Sugars and organic acids, which are responsible for the sweetness and tartness and influence on tomato flavour, are the major factors affecting consumer acceptability (Baldwin et al., 2008).

Soluble solids and dry matter are very important for the food industry, affecting processing yield of many tomato products such as pulp, paste and concentrate, which are evaporated to a definite percentage of solids (Gould, 1992). In consideration of the role played by sugars and acids contents in the definition of tomato quality, several analytical techniques have been developed to evaluate these parameters. However, traditional methods are not well adapted to on-line and require an expensive and time consuming sample preparation. Thus, the tomato production sector is interested in development of analytical method allowing simultaneous measurement of a large number of samples for routine quality control program.

The volatile compounds present in fresh and processed tomato are included in various chemical classes such as ketones, aldehydes, alcohols, esters, ethers, hydro- carbons, sulfur, nitrogen and oxygen compounds, phenols, oxygen-containing heterocyclic compounds, free acids and lactones (Linforth et al., 1994). Different methods, such as distillation, solvent extraction, head-space analysis and the solid phase micro-extraction (SPME) have been proposed to analyse volatile compounds in foods (Zhang and Pawliszyn, 1993). The SPME is a relatively new method that can be used to evaluate the volatile compounds present in the vapour and/or in the liquid phase of solid and liquid foods (Servili et al., 1998).

During processing the endogenous enzymes catalyze the formation of important compounds of tomato flavour. In fact saturated and unsaturated C6 and C9 alcohols and aldehydes, that are impact compounds of fresh tomato, are originated by lipoxygenase activity, while terpene and carotenoid derivatives can be released from odourless glycosidic compounds by glycosidase activities (Charron et al., 1995). The tomato processing includes thermal treatments applied to inactivate enzymes (blanching) or to stabilize the product (sterilization) that cause changes in sensory and nutritional characteristics of tomato derivatives due to co-oxidation reactions of carotenoids and Maillard reaction (Baldwin, 1996).

Separation and quantification of tomatoes components has been widely studied, and currently relies heavily on analysis by HPLC (Barba et al., 2006). Although reliable and accurate, this method is time consuming, requires extensive sample preparation, and uses and disposes of hazardous organic solvents. New techniques such as matrix-assisted laser desorption ionisation time-of-flight mass spectrometry, and one- and two-dimensional NMR have been successfully evaluated for profiling carotenoids in tomatoes (Fraser et al., 2007).

While relatively rapid and specific, these techniques are complex and rely on costly equipment that limits their application to laboratory environments.

Vibrational spectroscopy, on the other hand, represents a cost effective simple alternative for the rapid profiling of carotenoids that could easily migrate to in-field applications thanks to the development of FT-IR and Raman portable devices. Rapid spectroscopy techniques for the evaluation of carotenoids have been developed, including the application of resonance Raman spectroscopy, mid-infrared (Halim et al., 2006) and near-infrared spectroscopy (Baranska et al., 2006). These novel quantification techniques could be improved with the development of a rapid and simple profiling method that can identify both components in tomatoes and their concentrations.

In the present study, the authors investigate the changes of chemical compositions and volatile components in tomato products by using GC and GC-MS. Spectroscopic techniques as FT-IR and FT-Raman used as fast methods to evaluate the chemical composition of tomato products and investigate the adulterants in tomato products.

2. Materials and Methods

Dichloromethane, sodium sulphate anhydrous, starch, gallic acid, 1,1-diphenyl-2-picrylhydrazyl (DPPH), tert-butyl hydroquinone (TBHQ),acetone, hexane, ethanol, β-carotene, allurared pigment, Folin–Ciocalteau reagent, n-alkanes and methanol,were purchased from (Aldrich and sigma company, Germany), standard lycopene was obtained from (Commercial Quimica Masso, S.A. Barcelona, Spain); Starch and paprika purchased from local market.

Fully matured tomatoes were procured from local market. Natural tomato juice, paste, ketchup and adulterated tomato paste with paprika, synthetic color (allura red) and starch were prepared in food technology Lab., National Research Centre as follows:

Tomato Juice and Paste

Fresh tomatoes were washed, crushed, scalded at 90°C for 5 min, and juice was obtain in the usual way after sieving and then sterilized at 100°C for 30 min, filled in bottle then cooled. The obtained tomato juice transferred to an open kettle which was heated until the concentration of the paste reached to > 25 brix, then filled in bottle and cooled (Apaiah and Barringer, 2007).

Ketchup:

The basic formulation of tomato ketchup was prepared as described by Srivastava (1982). Tomato pulp (4.7% TSS) was mixed with spices (sodium chloride, red chilies), onion and garlic pulp; heated on a low flame with constant stirring till 23%

TSS, then vinegar was added to the mixture and the ketchup was heated until the final TSS was reached. The thickening agents (starch) were pre-blended with the sugar and salt and added to the ketchup during the final stages of cooking, then hot ketchup filled in glass bottles and stored at ambient temperature (30°C) up till use.

Physico-chemical Analysis:

Tomatoes and their products were analyzed for Total Soluble Solids (TSS) using Digital Hand-held "Pocket" Refractometer; and pH was measured by digital pH meter, (Hanna, Italy)**.** Also, Moisture, crude protein content, lipid content, and ash were estimated using AOAC (1990).

Extraction of lycopene

For extracting lycopene, 1 g of homogenized fresh or semi-dried tomato sample was weighed into a screw-top, which was covered with aluminum foil to exclude light and the lycopene from the samples was extracted using the method of Sadler et al (1990). In brief, a 25 ml mixture of hexane–acetone–ethanol (2:1:1, v: v: v) was added to the samples, which were then placed on the rotary mixer for 30 min. Agitation was continued for another 2 min after adding 10 ml of distilled water. The solution was then left to separate into distinct polar and non-polar layers and then the hexane layer was collected in a 50 ml flask.

The residual solids were re-extracted to ensure complete extraction of lycopene. The absorbance of the combined hexane layers was measured at 472 nm on UV–Vis recording spectrophotometer (UV-2100, Shimadzu) using hexane as a blank. The purity of the extracted standard lycopene was checked using its extinction coefficient ($E_{cm}^{1\%}$) of 3450 (Davis, 1976) and a standard curve was prepared. The amount of lycopene in the tomato samples was determined from this standard curve, and the results were expressed as mg/100 g.

Total carotenoid content

Total carotenoids were determined using the modified method described by Koca et al (2007). Extractions were carried out using 25ml of hexane: acetone (7:3) and 0.5 g of freeze dried sample using conditions described for antioxidant extractions. The residue was re-extracted until it became colorless. The filtrates were combined in a separating funnel and washed with 50 ml distilled water. The water phase was discarded and Na2SO4 (10 g) was added as desiccant. The hexane phase was transferred to a 50ml volumetric flask and brought to volume with hexane. The absorbance of this solution was then determined at 450 nm using a UV–Vis spectrophotometer. External calibration with authenticated β-carotene standards solutions (0.5 μg/ml–10 μg/ml) in hexane: acetone (7:3) was used to quantify carotenoids in the solutions. Carotenoid content was expressed as β-carotene equivalents (βCE) in mg/100 g dry weight of sample.

Total phenolics content (TPC)

Total phenolics in tomato paste, ketchup and adulterated tomato paste with paprika or starch were measured by the method adapted from Spanos and Wrolstad (1990). In brief, the extracts were appropriately diluted and then oxidized with 2.5 ml of freshly diluted 0.2 M Folin–Ciocalteau reagent. This reaction was neutralized by adding 2.0 ml of 7.5% w/v sodium carbonate, and the samples were vortexed for 20 sec. The samples were then incubated at 45 °C for 15 min and the absorbance of the resulting blue color was measured at 765 nm on an UV–Vis recording spectrophotometer (UV-2100, Shimadzu). Gallic acid was used as a standard, and results were expressed as gallic acid equivalents (GAE) per 100 g fresh weight (FW). The results were corrected for the contribution of ascorbic acid to the total phenolics as described by Toor (2004).

Antioxidant activity by DPPH method

The hydrogen atom or electron-donation ability of the corresponding extracts/ fractions was measured from the bleaching of a purple-colored methanol solution of DPPH. The antioxidant activity of the extracts/fractions, on the basis of the scavenging activity of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical, was determined by the method described by Gordon et al (2001). A methanolic solution (100 μL) of the extracts/ fractions was placed in a cuvette and 0.5 ml of a methanolic solution of DPPH (50 mg DPPH/100 ml MeOH) was added. After 30 min absorbance at 515 nm was determined using a spectrophotometer (Shimadzu Co. Ltd., Kyoto, Japan), all determinations were performed in triplicate.

Instrumental Color Analysis

Color measurement (L^*, a^*, b^*) were measured using Hunter Lab. This color assessment system is based on the Hunter L^*, a^{*-} and b^* coordinates. L^* was representing lightness and darkness, $+ a^*$ redness, $-a^*$ greenness, $+ b^*$ yellowness and $- b^*$ blueness (Hunter, LabScan XE - Reston VA, USA). The instrument was standardization against a White Tile of Hunter Lab Color Standard (LX No.16379): X= 77.26, Y= 81.94 and Z= 88.14 before each measurement.

Infrared and Raman spectroscopy

The spectra or fingerprints of the selected samples were obtained using FT-Raman and/or FT-IR spectroscopy. The samples of FT-IR (FT-IR-6100

Jasco, Japan) were prepared by using potassium bromide disks. FT-Raman spectra were obtained using a Nicolet Raman module 32B (Madison wl, USA) and ND-YAG laser source operated at 1064 nm with a maximum power at 0.7w.

Preparation of volatile concentrate by simultaneous steam distillation-extraction (SDE)

The author used the simultaneous steam distillation-extraction (SDE) described by Shaultz et al. (1977) which used the modified apparatus of Nickerson and Likens, in order to collect the volatile components from tomato products. 200 gm of tomato products was placed in 1 L round flask. The volatiles were extracted by using (DCM) and the extracts were concentrated by using rotary evaporator. The obtained concentrates were analyzed using gas chromatography and gas chromatography-mass spectroscopy.

Analysis of the volatiles
Gas chromatography

The obtained volatiles samples were thermally desorbed, using a modified injector port, directly on the front of a (DB5) (60 m x 0.32 mm i.d) fused silica capillary column, in the oven of a Hewlet-packed HP 5890 gas chromatography, and temperature increase from 45 -240^{0}C by the rate 2^{0}C/min. Kovat's indices were determined by co-injection of the sample with a solution containing homologous series of n-hydrocarbons (C$_6$-C$_{24}$) under the same conditions as described above. The separated components were identified by matching with NIST mass -spectral library data, and by comparison of Kovat's indices with those of authentic components and with published data (Adams, 1995). RI of each compound was calculated from the standard n-alkane retention time and the peak retention time using the following equation.

R. I = [Rt$_x$ -Rt$_n$ /Rt$_{n+1}$-Rt$_n$] x 100.

Where, RI = retention indices.

Rt$_x$ = retention time of sample.

Rt$_n$= retention time of n-alkane before peak.

Rt$_{n+1}$= retention time of n-alkane after peak.

n= carbon number of n-alkane before peak.

3.4.2. Gas chromatography- mass spectrometry (GC-MS)

Analyses were performed on An HP model 6890 GC interfaced to an HP 5791A mass selective detector (GC/ MS) was used for mass spectral identification of the GC components at (MS) ionization voltage of (70 eV. A 30 m x 0.25 mm i.d). (DF = 0.25 lm) DB wax bonded-phase fused-silica capillary column was used for (GC). The linear velocity of the helium carrier gas was 30 cm/s. The injector and the detector temperatures were 250 ºC. The oven temperature was programmed from 40 to 240 ºC at 4 ºC/ min and held for 50 min.

Statistics

All data is reported as mean ± standard error of the mean for three replicates. One-way analysis of variance (ANOVA) was used and the least significant difference (LSD) at $p < 0.05$ was calculated (Genstat, 2000) to determine significant differences between the different fractions of tomatoes. Two-way analysis of variance was also performed to study the interactions between tomato paste and adulterated tomato samples.

3. Results and discussion

Table (1) showed the proximate gross chemical composition of tomato and their products. Fresh tomato and its juice had higher moisture content accompanied with lower other contents. Thermal concentration of tomato products caused a reduction in moisture contents (71.43 and 72.33% in ketchup and tomato paste), while adulterant tomato paste with starch led to a higher decline in moisture content (60.33%) and increment in total carbohydrate (30.5%). These results indicated that gross chemical composition unable to detect adulterant paste with paprika; on contrary adulterant paste with starch showed higher carbohydrate content.

Table (1): Chemical composition of tomato and their products.

Sample	Moisture	Protein	Fat	Ash	Carbohydrate
Tomato	92.57±1.32	1.2±0.09	0.22±0.01	1.28±0.03	4.5±0.2
Juice	93.6±1.05	0.8±0.1	0.23±0.10	1.1±0.1	4.3±0.2
Ketchup	71.43±0.6	3.0±0.25	0.5±0.02	1.4±0.01	22.7±0.3
Paste	72.33±0.55	4.4±0.30	2.4±0.2	2.73±0.25	18.5±0.15
Adulterated Paste					
Paste+paprika	71.3±0.55	4.4±0.30	2.4±0.2	2.73±0.25	18.5±0.15
Paste+starch	60.33±0.5	3.2.4±0.2	2.4±0.2	2.73±0.20	30.5±0.17

Table (2) indicated that, TSS and pH were in accepted range; and tomato ketchup records a high value of TSS (30.3) followed by tomato paste. Also, TSS was unable to detect adulterant tomato paste.

Table (2): Total soluble solids (TSS) and pH of tomato paste, ketchup and adulterated tomato paste with starch and paprika products.

Parameter	Fresh Juice	ketchup	Tomato Paste (Control)	Adulterated Tomato paste	
				(+) Starch	(+) Red pepper
TSS	4.07	30.3	25.79	25.53	23.56
pH	3.56	3.08	3.86	3.89	3.84

Lycopene is the major carotenoid pigment found in ripe tomato fruits and responsible for their characteristic red color. Sensory and instrumental techniques are used to determine the color of food products. Data in Table (3) showed the color variation of tomato and tomato products as affected by heat treatments or by adulteration the color with synthetic, allura red or thickener agent (starch). The highest redness value (a*) was found in tomato paste that treated with synthetic pigments (allura red). This result indicated that, the color parameter of Hunter measurements (L*, a* & b*) represent color value but the quality of tomato natural pigment (lycopene) not identified.

Table (3): Hunter color parameter of tomato fruits, Tomato juice, tomato paste, ketchup and adulterated tomato best with thickener agent (starch) or color agent (red pepper)

Sample	L*	a*	b*
Tomato fruit	30.75[c]±0.116	30.9[d]±2.15	25.57[f]±1.11
Tomato pulp	46.62[a]±0.215	27.48[f]±1.09	30.03[b]±2.48
Tamato juice	43.63[b]±0.419	33.57[c]±0.89	26.28[ef]±0.4
Tomato Paste	27.88[d]±0049	36.11[b]±0.23	26.98[def]±0.129
Ketchup	25.26[e]±0.0552	31.5[d]±0.12	26.98[def]±0.194
Adulterated Tomato Paste:			
Tomato Paste + starch	30.51[c]±0.056	34.64[c]±0.2	27.18[de]±0.1
Tomato Paste + Paprika	25.54[e]±0.045	28.3[ef]±0.024	27.98[cd]±0.067
Tomato Paste + anthocyanine	24.65[f]±0.065	40.71[a]±0.117	38.07[a]±0.33
Tomato Paste + Allura red	25.63[e]±0.344	36.27[b]±0.09	29.31[bc]±0.1
LSD at 0.05	0.586	1.43	1.45

L* = lightness   a* = Redness   b* = Yellowness

Since lycopene is a phytonutrient, so the quality control requires the ability to measure lycopene in tomato product. Hunter color instrument was used to evaluate reflectance spectra of tomato fruits, tomato juice, tomato paste and ketchup; and illustrated in Figure (1). The obtained reflectance spectra of tomato and their products were characterized by a sharp enhancement in 600 and 700 nm till reached 35% reflectance.

Tomato Fruit

Tomato juice

Tomato Paste
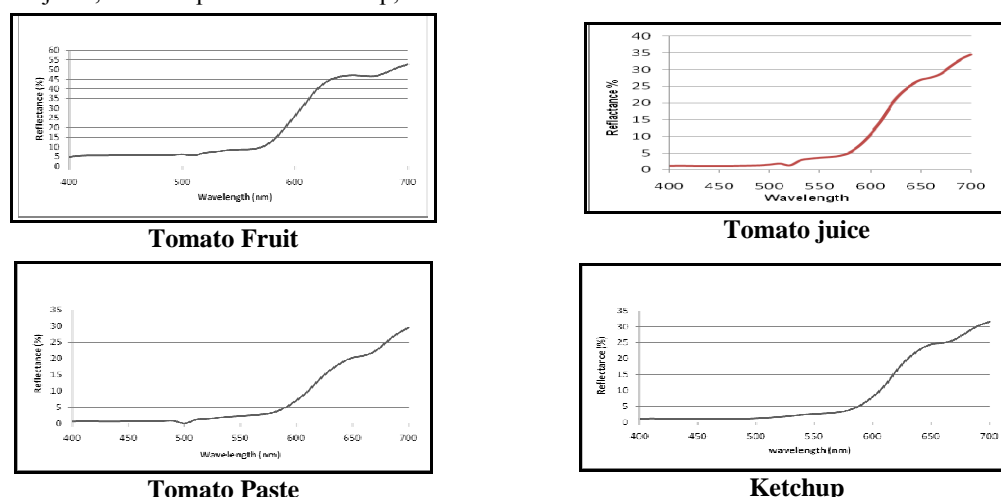
Ketchup

Figure (1): Reflectance of tomato fruit, tomato juice, tomato paste and ketchup.

Fresh tomato Juice

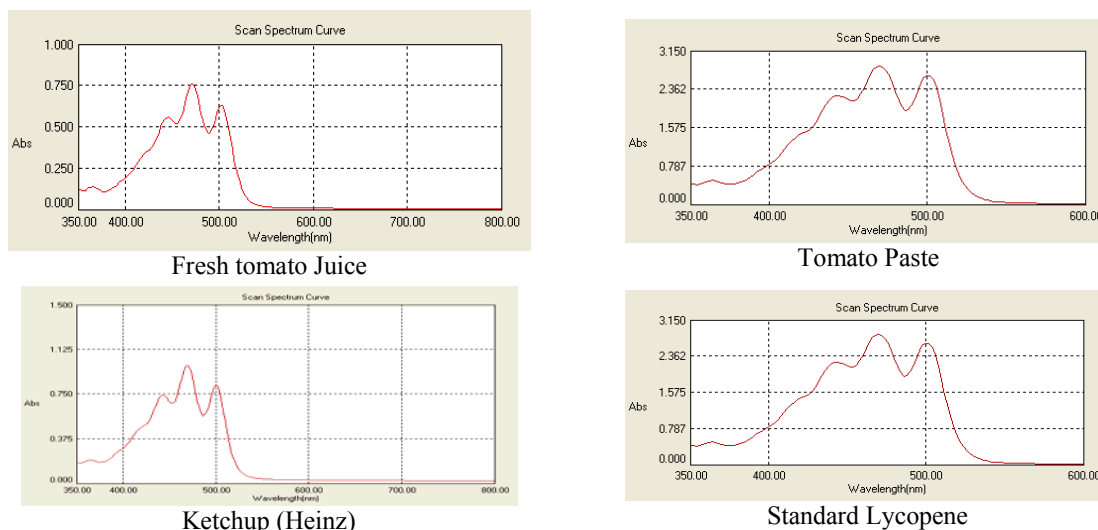
Tomato Paste

Ketchup (Heinz)

Standard Lycopene

Figure (2): UV-visible spectrophotometer scanning of fresh tomato juice, tomato paste and ketchup.

Table (4): Total carotenoids of tomato products.

Tomato products	Total carotenoids (mg/100g)
Tomato Juice	6.74
Tomato Paste	34.31
Ketchup	8.71

The previous results concluded that, traditional methods were not quite enough to identify adulterated products with pigments in tomato products. But, there are chromatographic methods to detect nature and synthetic pigments as Gas Chromatography (GC), Gas Chromatography-Mass spectroscopy (GC-MS) and High performance liquid chromatography (HPLC). These methods are expensive and time consuming due to their extraction technique, purification (clean up) and different types of detector. Mid-infrared spectroscopy have been frequently proposed (Rubio-Diaz et al., 2010) as alternatives to HPLC for the simple, high-throughput and cost effective analysis of tomato carotenoids. This study aimed to evaluate and detect main finger prints of tomato and their products referred to lycopene pigment, so they were measured directly as shown in Table (5) or extracted as shown in Table (3).

FT-IR spectral peaks (Table 5 & Fig 3) of all samples showed stretching OH, stretching C=C of lycopene, aliphatic CH at (3437-3426 cm^{-1}), (1635-1637 cm^{-1}) and (1410 - 1414 cm^{-1}), respectively. While the band at 1150cm^{-1} found in fresh tomato and tomato juice; and also stretching CH$_3$ of polyene system (1033-1037 cm^{-1}) was detected in them. The other bands of carbohydrates were identified in ketchup only.

Moreover, UV-visible spectrophotometer (Choudhary et al., 2009) was used to evaluate natural pigment (lycopene) in tomato and their products. Tomato and their products showed three strong peaks at 450, 470 and 500 nm as shown in Figure (2). Table (4) showed the total carotenoids of some tomato products, where tomato paste was the highest carotenoids value (34.31 mg/100g) among other products. On the other hand, synthetic pigment (anthocyanine and allura red) that used to adulterate tomato products not detected by spectrophotometer method because they found as pigment salts.

Table (6) and Figure (4) showed FT-IR spectra of standard lycopene and extracted fresh tomato, tomato juice, tomato paste and ketchup. Standard lycopene was characterized with specific spectral functional bands as stretching CH symmetric and asymmetric (2921 and 2854 cm^{-1}), stretching vibration of cis-vinylene (1630 cm^{-1}), deformation CH$_3$, trans-R-HC=CH-R (970 cm^{-1}). Fresh tomato, tomato juice, tomato paste and ketchup extracts showed different spectral function groups in the region (2920-2924 cm^{-1}) to (1381-1390 cm^{-1}) which attributed to stretching CH symmetric and asymmetric, stretching vibration of cis-vinylene, deformation CH$_3$. While, ketchup extract was characterized with multiple trans-double bond at (920 cm^{-1}).
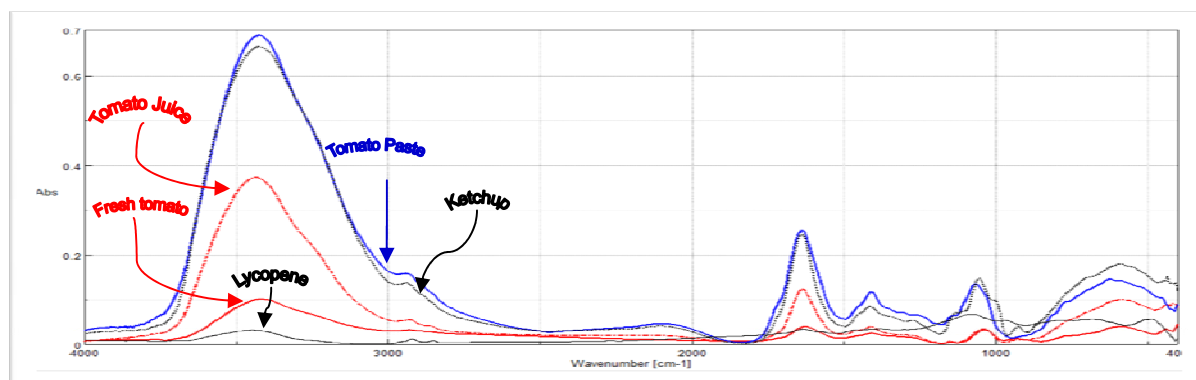
Figure (3): FTIR spectra of standard lycopene pigment, fresh tomato and its products.

Table (5): FT-IR assignments of fresh tomato and their products.

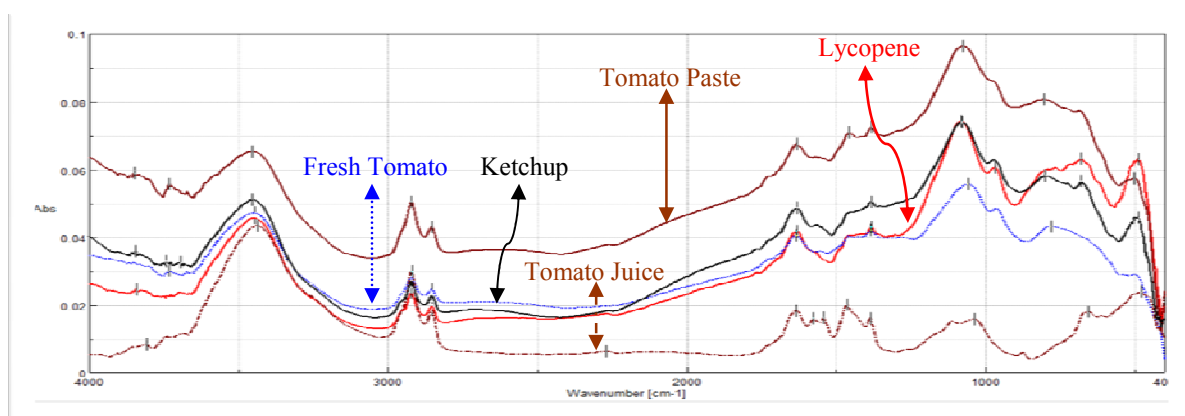| Assignment	Fresh Tomato	Tomato Juice	Tomato Paste	Ketchup
OH stretching	3430	3437	3425	3426
CH_2 asymmetrical	- - - - -	2929	- - - - -	2929
V C=C of olefin	1635	1635	1637	1637
CH stretching of pectin	1410	1410	1410	1410
CH_3 stretching of polyene system	1033	1037	- - - - -	- - - - -
V CO, V CC of glucose	- - - - -	- - - - -	1067	1053
Stretching C-C	1150	1150	- - - - -	- - - - -
Stretching CH+OH of carbohydrates	- - - - -	- - - - -	- - - - -	1271
Stretching CCH, C-OH of carbohydrates	- - - - -	- - - - -	- - - - -	926

Figure (4): FT-IR spectra (fingerprints) of standard lycopene, extracted fresh tomato, tomato juice, tomato paste and ketchup.

Table (6): FT-IR spectra of extracted tomato and tomato products.

Functional groups	Lycopene	Fresh tomato	Tomato juice	Tomato paste	Ketchup
Stretching (CH) symmetric	2921	2923	2920	2922	2924
Stretching (CH) symmetric	2854	2855	2853	2854	2857
Stretching vibration of cis-vinylene	1630	1639	1636	1635	1640
Deformation (CH3)	1381	1390	1385	1387	1385
Stretching (CH-CH)	1082	- - - - -	- - - - -	- - - - -	- - - - -
Trans-R-HC=CH-R	970	957	- - - - -	- - - - -	- - - - -
Multiple trans-double bond	- - - - -	- - - - -	- - - - -	- - - - -	920

FT-IR spectroscopy was applied to identify lycopene content in adulterated tomato paste with paprika. Table (7) and Figure (5) represents the FT-IR spectra of tomato products. The strong absorption of lycopene pigment was matched with fresh tomato juice and their products as tomato paste with paprika and ketchup. Fresh tomato juice, ketchup and paste contain the following functional groups as OH stretching (3442-3446 cm^{-1}), -CH$_2$ vibrational symmetric, vibrational stretching C=C (1634-1640 cm^{-1}). However, amide II, CH$_2$ of trans-lycopene, CH$_3$ attached with polyene system appeared at (1541-1550 cm^{-1}), (1458-1465 cm^{-1}), (1385-1390cm^{-1}),

respectively. The CH stretching of adulterated paste with paprika showed CH$_2$, C-C-H and C-OH stretching of carbohydrates (Inbaraj and Chen, 2008). The lycopene pigment was assigned with specific spectral bands with the region (3450-960 cm^{-1}). The 960, 1082, 1156 and 1444 cm^{-1} were belonged to R-CH=CH-R, CH$_3$ attached with polyene system, stretching C-C, vibrational CH$_3$ of lycopene molecule and vibrational symmetric of lycopene. Vibrational C=C, CH$_2$ stretching symmetrical and asymmetric were found at specific wave number at 1643, 2856, 2924 cm^{-1}, respectively (Irudayaraj and Tewari, 2003).
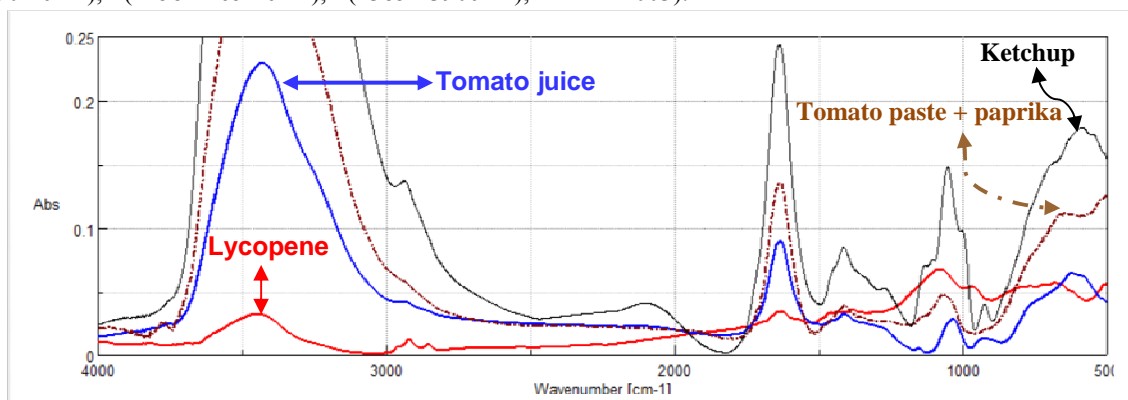

Figure (5): FT-IR spectral (cm^{-1}) assignment of lycopene, fresh tomato juice, paste + paprika and ketchup.

Table (7): FT-IR spectral (cm^{-1}) assignment of standard lycopene, and extracted fresh tomato juice, paste with paprika and ketchup

Assignment	Lycopene	Tomato Juice	Paste+Paprika	Ketchup
Stretching OH	3450	3442	3430	3446
CH$_2$ asymmetrical	2924	2923	---	2924
CH$_2$ asymmetrical	2856	2855	---	2857
V C=C of olefin	1643	1639	1634	1640
Amide II	- - -	1550	- - -	1540
V C=C	1510	1515	1520	----
V symmetrical of CH$_2$ of lycopene	1444	1465	- - -	1458
CH stretching	- - -	- - -	1410	- - -
CH$_3$ stretching of polyene system	- - -	1036	- - -	1022
R-CH=CH-R of lycopene	960	- - -	- - -	- - -
Stretching CCH, C-OH	- - -	920	- - -	- - -

Confirmation of the authenticity of a food or food ingredient is an increasing challenger for food processors and regulatory authorities. Table (8) shows the IR spectra of allura red, and adulterated tomato paste with allura red pigment. The obtained FT-IR spectra attributed to spectra of specific function groups as well as vibrational C=C stretching 1631, 1633 cm^{-1} and vibration C-C stretching at 1048, 1063 cm^{-1} in pigment and adulterated tomato

paste with allura red pigment, respectively (Bureau et al., 2009).

Confirmation of the authenticity of a food or food ingredient is an increasing challenger for food processors and regulatory authorities. So, FT-IR spectroscopy was used to detect starch or paprika that could be added to tomato paste. Tomatoes and various product derived from processed tomatoes are the major source of lycopene, a polyenic

chromophore with trans RH-C=CHR groups, other micronutrients and carotenoids such as β-carotene are present in tomato fruit. In addition, Table (9) and Figure (6) show some difference in FT-IR spectra of tomato paste that mixed with starch or paprika.

Starch carbohydrate peaks at 1137 cm^{-1} and 1040 cm^{-1} detected in paste that mixed with starch only. While, mixed tomato paste with paprika showed specific spectral peaks located at 641 for stretching (CH$_2$, CH) and 1520 cm^{-1} for vibrational stretching of (C=C).

Table (8): FT-IR assignments of adulterated tomato paste with allura red.

Assignment	Allura red	Tomato Paste with allura red
NH stretching in allura red	3444	- - - - -
Stretching C=C aromatic	1631	1633
Vibrational C=C aromatic system	1490	- - - - -
=CH stretching	- - - - -	1410
CH$_2$ bending	1225	- - - - -
C-N=N-C	1192	- - - - -
Vibrational C-C	1048	1063
V CCC of carbohydrate	- - - - -	903

Table (9): FT-IR assignment (cm^{-1}) of tomatoes paste mixed with paprika and starch.

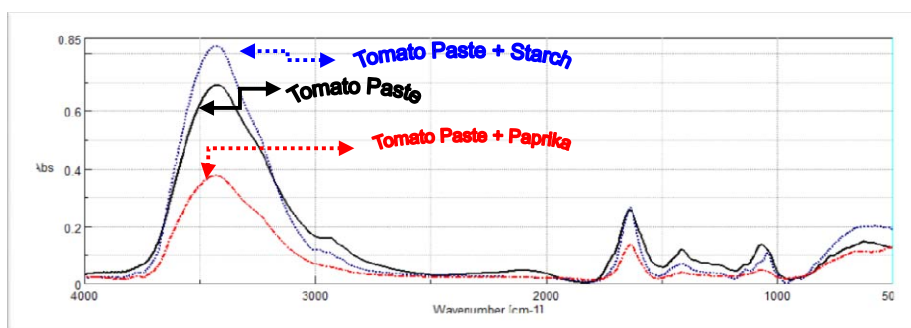| Functional groups	Tomatoes Paste with	
	Red paper	Starch
Str. (OH) of water	3430	3428
Str. (CH)$_{sym.}$	- - - - - -	2982
(OH) $_{bend.}$ of water	1636	1636
(C=C)	1520	- - - - - -
(OCH3, COH) $_{deform.}$ of carbohydrate	1410	1411
(C-C), (C-C) $_{bend.}$ and v (C-O)	- - - - - -	1137
Str. (C-C)	- - - - - -	1040
(CO + CCH), $_{asym.}$ of pyranose ring	- - - - - -	920
CH$_2$+CH of carbohydrate	641	- - - - - -

Figure (6): FT-IR spectra (cm^{-1}) of tomato paste and tomato paste that mixed with starch or paprika

Total phenolic content

Polyphenolic compounds, carotenoids and lycopene are very important tomato and its products constituents, by virtue of their antioxidant activity by chelating redox-active metal ions, inactivating lipid free radical chains and preventing hydroperoxide conversion into reactive oxyradicals. Table (10) summarizes the contents of total phenolics, expressed as gallic acid equivalents (GAE), either as mg GAE g^{-1} or mg GAE/ 100 g $^{-1}$, found in the extracts. These values were obtained from the absorbance of the extracts treated with Folin-Ciocalteau reagent.

These data indicate the TPCs of the tested tomato extracts, which could strongly account for the antioxidant activities of the samples. phenolic compounds react with Folin-Ciocalteau reagent only under basic conditions (pH ~10) due to a much higher reactivity of the phenolate anion with the molybdenum-based compounds present in the reagent (Huang and Prior, 2005). TPCs of tomato paste with paprika showed highly TPCs followed with tomato paste, tomato paste, tomato paste and ketchup, respectively with (42.7±2.3, 33.1±2.7, 32.3±1.8 and 29.1±1.8 GAE/100 g). George et al. (2004) reported that the phenolic content in the tomato genotypes

ranged from 9–27 mg catechin equivalents/100 g; and in pulp and tomato products the phenolic content ranged from 12-32 mg catechin equivalents/100 g.

the high TPCs in tomato paste with paprika may due to lycopene, carotenoids and capsenoids contents.

Table (10):Total phenolic contents in tomato products

Samples	mg GAE/100 g [-1]
ketchup	29.1±1.8
Tomato paste	33.1±2.7
Tomato +paprika	42.7±2.3
Tomato paste +starch	32.3±1.8

Antioxidant activity by DPPH method

Table (11) shows the antioxidant activity of tomato products (tomato paste, ketchup and adulterated samples with starch or paprika pepper) as measured by the DPPH assay. The addition of tomato extracts and TBHQ at various concentrations (50, 100, 200, 400 µg/ ml) respectively, prevented the decolourization of DPPH reagent to different degrees. The antioxidant activity was found to increase with the increase in concentration of tomato extracts. For the all tomato extracts, the increase of antioxidant activities were significant between 50µg/ ml and

100µg/ ml (P< 0.05), and 200 µg/ml and 400 µg/ ml (P< 0.01). The free radical-scavenging of tomato paste with paprika pepper was superior to all other extracts in dose dependent manner (78.3.8%±2.9, 70.8±2.3, 69.4%±2.3 and 67%±2.4) at 400µg/ml compared to TBHQ (99.5± 0.64 % at 400µg/ ml), a synthetic antioxidant widely used in food chemistry George et al. (2004). The highly antioxidant activity of tomato paste with paprika is due to the presence of lycopene, carotenoids and capsenoids and other phenolic compounds respectively.

Table (11): Antioxidant activity of tomato paste, adulterated tomato paste with paprika or starch and ketchup by DPPH scavenging assay

Samples	50 µg/ml	100 µg/ml	150 µg/ml	200 µg/ml
Tomato paste	18.9%±2.4	27.5%±2.7	42%±2.6	70.8±2.3
Tomato +paprika	22%±3.1	39%±3.0	57.5%±2.8	78.3.8%±2.9
Tomato paste +starch	19.7%±2.2	31.2%±2.5	52%±2.3	69.4%±2.3
Ketchup	15%±1.8	28%±2.8	40%±3.1	67%±2.4
TBHQ	85%±1.9	95.2%±2.3	99.5%±2.4	99.5%±1.8

Volatile components of tomato paste, ketchup and adulterated tomato paste with starch and paprika

Table (12) shows the relative amounts of most major volatile components obtained by SDE of tomato paste and other products. Tomato volatile compounds have been widely studied and until now, more than 400 volatile components were identified (Beltran et al., 2006). Their formation is the result of different biosynthetic pathways. For instant, saturated and unsaturated C_6-C_9 aldehydes and alcohols are a secondry metabolities originating from the lipoxygenase (LOX) pathways (Russo et al., 2010), while carotenoids and terpene derivatives are originated by glycosides activities (Servilli et al., 2000). These volatiles were identified by matching their recorded mass spectra with those present in the NIST library and comparison of their retention indices (RI) relative to (C_6-C_{24}) n-alkanes with those in the literature at the same chromatographic conditions.

The most predominant volatiles were saturated and unsaturated 6-carbon aldehydes and alcohols. hexanal and (Z)-3-hexen-l-ol, (Z)-3-hexenol, 5-methyl-5-hexen-2-ol and 1-hexanol were

present in significant concentrations in all samples, and contribute a green, leafy herbaceous aroma. These compounds have been previously associated with the characteristic green, tomato fruit-like aroma released by tomato leaves and present in processed tomato products (Buttery et al., 1993).

The reduction products, (Z)-3-hexen-l-ol and (Z)-3-hexenol, were observed at lower concentrations in adulterated tomato paste with paprika and starch and absent in tomato paste and ketchup; (Z)-3-hexen-l-ol was previously reported by Buttery and Ling (1993) to form in tomato via a reductase conversion pathway. Hexanal, one of the major aldehydes in tomato flavor and identified in tomato paste with high concentration rather than other tomato products with (4.1%), also is considered to be important for fresh tomato flavor (Buttery et al., 1989).

Hexanal is a contributor to the green, fatty component of tomato aroma. Similar to the unsaturated aldehydes, it is derived from a linoleic acid breakdown pathway. 1-Hexanol provides a winey, cider-like character and is produced via bio-reduction of hexanal. Other significant aldehydes include 8- to 10-carbon enals including 2-octenal, (E)-2-nonenal, and (E, E)-2, 4-decadienal, which

contribute fatty green aromatics. After the aldehydes, the largest volatile classes of compounds identified in tomato paste, ketchup and adulterated samples with paprika and starch were esters.

Among these were butyl, iso-butylacetate, butyl acetate, methyl-(2-OH)-valerate, methylhexanoate, methyl-(*2-OH*)-3-methyl iso-valerate, methylbenzoate, ethyldecanoate, linallyl valerate, ethyl-(*E*)-cinnmate and iso-propyl benzoate. Aromatic esters include methyl and propyl benzoate, and ethyl-(*E*)-cinnmate. Two unique hydroxy esters were identified by matches with the mass spectral library: methyl-(2-hydroxy-3-methyl)-valerate, and methyl-(*2-OH*)-3-methyl valerate the latter which was only found in cooked tomato paste.

Carotenoid-derived terpene compounds comprise a third class of volatiles identified in tomatillo flavor. The oxidative decomposition of carotenoids, particularly lycopene and p-carotene, has previously been shown to lead to the formation of terpene and terpene-like compounds in tomato flavor (Buttery et al., 1989).

Unique terpenes identified in tomatillo include aterpinolene, terpinen-4-ol, iso-eugenol and linalool oxide (in adulterated tomato paste with paprika), syringol geraniol (in adulterated tomato samples), linalool (in ketchup and adulterated tomato with starch), cadinene, β-isoabolol, β-terpinene. Identifications of other terpene-derived tomato volatiles previously reported in processed tomato products include 6-methyl-5-hepten-2-one, while eudesmol was found in adulterated starch samples with (8.76%).The amino acid-derived volatiles including 2-phenylethanol, pyridine. These compounds play a considerable role in cooked tomato flavor and are also present in the mature green stage of tomato development (Gabriella et al., 2011).

Table (12): Volatile components of tomato paste, ketchup and adulterated samples with paprika or starch

Peak No.	Compounds	RI	tomato ketchup	Tomato paste	Adulterated Paste	
					Paprika	Starch
1	2-Ethylfuran	715	0.79	nd	nd	0.04
2	Dimethyl disulphide	732	nd	1.17	0.77	0.81
3	Pyridine	745	0.20	0.10	1.3	0.15
4	Acetic acid	758	1.00	6.25	4.81	1.16
5	Iso-butyl acetate	772	1.00	8.08	6.01	1.69
6	Butyric acid	781	0.50	3.96	2.73	0.80
7	Hexanal	789	1.48	4.10	2.57	0.83
8	Butyl acetate	810	24.68	0.80	0.16	0.05
9	3-Furaldehyde	822	nd	1.04	1.06	2.34
10	(E)-2-hexanal	831	nd	nd	0.18	0.39
11	(Z)-3-hexen-1-ol	854	0.96	6.27	6.53	1.97
12	(Z)-3-hexanol	858	nd	nd	0.84	0.32
13	5-Methyl-5-hexen-2-ol	865	0.60	0.84	1.07	0.34
14	(Z)-3-Hexen-1-ol	875	nd	nd	0.41	0.22
15	1-Hexanol	882	2.19	18.81	14.24	4.57
16	Methyl-(2-OH)-iso-valerate	886	3.30	4.25	4.17	1.33
17	2,4-Hexadienal	918	0.20	1.36	0.55	0.09
18	Methylhexanoate	931	3.84	0.56	0.55	0.16
19	benzaldehyde	940	nd	0.93	1.3	0.43
20	(E)-2-heptanal	955	nd	nd	0.34	0.09
21	Dimethyltrisulphide	962	nd	nd	0.33	0.12
22	6-Methyl-5-hepten-2-one	987	nd	nd	0.23	0.31
23	Methyl-(2-OH)-3-methyl)-valerate	994	0.61	1.00	0.34	0.3
24	(Z)-3-hexen-1-yl acetate	1006	nd	nd	0.29	0.16
25	2-Octenal	1062	nd	0.80	0.64	0.33

Peak No.	Compounds	RI	tomato ketchup	Tomato paste	Adulterated Paste	
					Paprika	Starch
26	Methyl benzoate	1089	1.20	nd	nd	0.16
27	2-phenyl ethanol	1115	0.15	0.10	0.42	0.22
28	(E)-2-nonenal	1154	7.80	nd	0.19	0.15
29	Terpienen-4-ol	1168	1.18	nd	nd	nd
30	Ethyl octanoate	1190	36.01	nd	nd	0.11
31	Decenal	1195	nd	nd	nd	1.08
32	Linalool oxide	1210	nd	nd	0.40	1.90
33	(E)-2-decenal	1247	nd	nd	0.25	0.21
34	Geraniol	1282	nd	nd	0.10	1.12
35	(E, E)-2,4-decadienal	1310	0.42	0.30	5.76	1.36
36	Syringol	1364	nd	nd	1.15	0.10
37	Iso-eugenol	1370	nd	nd	4.49	nd
38	Dodecanal	1404	nd	0.68	0.68	nd
39	(E)-octenal	1424	0.30	4.16	0.61	2.70
40	Tridecane	1446	nd	0.54	nd	nd
41	γ-Muurolene	1472	nd	0.99	0.32	0.19
42	(E,E)-2,4-heptadienal	1482	0.42	nd	0.41	0.22
43	Valecene	1491	5.24	nd	0.14	0.16
44	Ethyl laurate	1495	3.83	nd	0.14	0.11
45	Methoxy safrole	1512	0.11	nd	0.23	0.18
46	Linallyl valerate	1522	1.14	2.86	9.86	4.94
47	Linalool	1445	0.36	nd	nd	22.56
48	Iso-propyl benzoate	1573	0.14	1.45	0.62	0.03
49	(E)-ISO-elemicin	1590	nd	0.57	0.49	0.28
50	Cadinene	1614	0.66	2.55	5.12	0.50
51	Iso-eugenol	1628	0.33	1.14	0.80	24.64
52	β-Isoabolol	1676	0.14	15.66	11.40	5.46
53	β-Terpineol	1682	0.25	0.66	0.29	0.24
54	Heptadecane	1722	0.23	1.23	0.54	0.09
56	(E)-Farnesol	1737	0.25	1.67	0.62	0.17
57	Ethyl-(E)-cinnamate	1740	nd	0.96	0.46	0.25
58	(-)-Nootkatone	812	nd	1.34	0.53	0.45
59	Eudesmol	1884	nd	nd	nd	8.76

nd: not detected, RI: retention index

4. Conclusion:

The study suggested using FT-IR spectroscopy as a simple and fast technique for quality assurance of tomato products. The author used FT-IR technique to investigate the presence of adulterants in tomato paste such as synthetic colorants (allura red) and thickening agent (starch). Also, tomatoes paste, ketchup and tomato paste with paprika characterized with high phenolic and antioxidant compounds. Volatile components of tomato paste, ketchup and adulterated tomato paste with paprika and starch were affected by thermal processing.

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