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Application of gas chromatography to evaluate the quality of rapeseed oil

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ABSTRACT

Two-dimensional gas chromatography is an analytical technique, which is increasingly being used in food research. Through the analysis of volatile fraction, it is possible to determine the quality of food products. One of the reasons for the deterioration of food is thermal degradation. Products that are often subject to degradation reactions due to temperatures are edible oils. In the thesis, the results of edible oils with different botanical origin are presented. The samples of oil were heated at temperatures of 20 °C, 60 °C, 100 °C, 140 °C and 180 °C. Based on the results of the chromatographic analysis, potential indicators of thermal degradation of edible oils were selected. The last step was to quantify the selected compounds to confirm that the typed chemical compounds are the markers of thermal decomposition of cooking oils. To calibrate, the method of standard additions was chosen

***Keywords*:** edible oils, quality markers, two-dimensional gas chromatography, mass spectrometry, volatile organic compounds, thermal degradation

1. INTRODUCTION

Edible oils are essential components of the daily diet, which provide energy, essential fatty acids, and are the carriers of fat-soluble vitamins. Rapeseed oil is the third most popular oil in the world after palm and soybeans [1]. This is caused by many factors such as price, utility values or taste. Rapeseed oil is furthermore valued for its health-promoting properties associated with saturated fatty acids. Thanks to these features, rapeseed oil can be classified

as functional food. Oils also play a vital role in cooking and food production. Quality of some products made with the use of fats depend on the quality of the oil used. The quality of edible oils depends on a number of factors, including: the conditions for growing the material, the ripening stage, the time and manner of storage, and the technology of production and the way they are processed.

High temperatures have a negative impact on the quality of the oil used because of the polymerization, hydrolysis, cyclization or oxidation processes. Thermal decomposition, or thermal decomposition, is the process by which carbon-carbon chemical bonds break down in edible oil due to heating. The thermal degradation process is conditioned by the effects of heat, light, humidity and the presence of trace amounts of metals in the sample of edible oil [2]. The deep frying process causes oxidative thermal decomposition [3] and change the physical properties of the oil [4]. At the time of exposure of the oil to oxygen, the gas is adsorbed by the fat and reacts with double bonds, since polyunsaturated chemicals are more susceptible to oxygen than saturated [5].

Vegetable oils, including rapeseed oil, contain esters formed by esterification of glycerol and fatty acids. The presence of unsaturated fatty acids in oils makes them more susceptible to thermal degradation. As a result of this process many chemical compounds are formed such as aldehydes, ketones, epoxides, hydroxyl compounds, [6,7]. Many of them are considered to be toxic and carcinogenic [8]. It is important to monitor any changes occurring in used oils. The determination of the volatile compounds allows you to find the quality specifications of edible oils [9]. Chemical quality indicators are chemical compounds whose presence or concentration in the test sample indicates deterioration in product quality. This may be due to a degradation process or thermal degradation due to improper storage, thermal treatment or due to expiry of the shelf-life.

Gas chromatography coupled with mass spectrometry, as well as stationary microextraction, is an analytical technique by which it is possible to characterize the volatile fraction of edible oils and to identify the quality characteristics of these food products.

In many restaurants, the quality of oils and fats in use is becoming more and more important. This is due to legal regulations, and also the desire to keep the highest quality of food served. There are many techniques and methods to evaluate the quality of edible oils, but their use is often labor-intensive, as it requires the sampling and preparation of a sample of the oil to be analyzed or immersed in the test medium. The purpose of the research was to determine the concentration of chemical compounds in the volatile fraction of rapeseed oil samples heated at selected temperatures of 20 °C, 60 °C, 100 °C, 140 °C and 180 °C.

2. EXPERIMENTAL

2. 1. Materials and reagents

The subject of research were rapeseed oils from 3 different producers. Oils for analysis were obtained from local distribution points. The purchased oils belonged to different price ranges. Analytical standards of ethanol,1-heptanol, 2-pentanone, heptane, nonanal, octane (Sigma-Aldrich, St. Louis, MO, USA) were used to identify and determinate indicators of thermal degradation of rapeseed oil.

2. 2. Sample preparation

5 g of each of rapeseed oils were measured in 20 ml vials. Vials were capped using a silicone-teflon membrane cap. The samples were then heated in a laboratory oven at 60 °C, 100 °C, 140 °C and 180 °C for 24 h and cooled. After chromatographic analysis, quantitative determination of substances selected as potential indicators of thermal degradation was made. For this purpose, 100 µl of standard mixtures of different starting concentrations using a gas-tight syringe were added to each sample so that the concentration of each of the samples added in the sample was respectively 0.050 mg/kg, 0.250 mg/kg, 0.500 mg/kg, 1.000 mg/kg, 5.000 mg/kg and 50.000 mg/kg.

2. 3. Isolation and enrichment of analytes

The analytical technique used for the isolation and enrichment of the analyte was microextraction to the stationary phase. A 50/30 µm divinylbenzene/carboxen/ polydimethylsiloxane (DVB/CAR/PDMS) fiber (Sigma-Aldrich, St. Louis, MO, USA) with 2 cm thick was used. The extraction was carried out at 100 °C for 45 min. Upon completion, the fiber was transferred to an injector, where the thermal desorption of its analytes at 250 °C occurred. This desorption lasted for 4 min. The extraction step was done using the Gerstel Multi-Purpose Sampler (GerPel Multi-Purpose Sampler) Gerstel Multifunction Automatic Sampler.

2. 4. Instrumentation

Two-dimensional gas chromatograph Agilent 7980A (Agilent Technologies, Palo Alto, CA, USA) equipped with liquid nitrogen cooled, two stage cryogenic modulator was used. Pegasus 4D mass spectrometer with fragmentation time fragment analyzer produced by LECO (LECO Corp., St. Joseph, MI, USA) was used to identify the chemicals. A column set comprise a 30 m × 0.25 mm × 0.25 µm with an Equity 1 stationary phase (Supelco, Bellefonte, PA, USA) column in the first dimension followed by a 1.6 m × 0.10 mm × 0.10 µm column with a SolGel-Wax stationary phase (SGE Analytical Science, Austin, TX, USA) as the second dimension.

2. 5. Data analysis

Processing of received data was performed using the ChromaTOF Chromatographic Peak Deconvolution Algorithm (Version 44). Identification of analytes was made by comparing spectral spectra with spectra contained in the NIST 11 and Wiley spectral library.

2. 6. Conditions of chromatographic analysis

Separation of the substance was possible with the following temperature program: the initial temperature of 40 °C was maintained for 3 min followed by a linear temperature increase of 250 °C at 5 °C min^{-1}. The final temperature was held for 5 min. The temperature program used in secondary oven was 5 °C higher. The modulation period was 6 seconds. Liquid nitrogen was used as the cooling medium to cool the nitrogen gas to about -110°C. Hydrogen was used as the carrier gas. Its volume flow rate was 1 ml/min. A single analysis lasted 50 min. The injector worked in splitless mode at 250 °C. The transfer line and sources

of ions work at 250 °C. Fragmentation ions were analyzed in the range of 40 u to 500 u. The data acquisition rate was of 125 spectra/s.

Based on the results obtained by performing analyzes using a two-dimensional gas chromatograph coupled with a time of flight mass spectrometer, it was possible to identify volatile compounds in rapeseed oil samples stored at room temperature or heated in a laboratory oven. As the indicators of thermal degradation of rapeseed oil, the following compounds were chosen: octane, nonanal, heptane, 1-heptanol, 2-pentanone. Linear growth with increasing temperature ($R^2 > 0.95$) of their content was assumed as a criterion of choice.

Table 1. Quality indicators of rapeseed oil selected on the basis of the results of chromatographic analysis

Quality indicator	Producer	Unique mass [u]	Area of chormatographic peak				
			20 °C	60 °C	100 °C	140 °C	180 °C
heptane	1.	43	1411064	2419958	3636914	5071627	6892140
	2.		1310410	2394856	4372471	4211541	4968284
	3.		2127928	2776263	2675878	4464895	5512238
octane	1.	43	1392374	3201948	4677237	7087593	9139216
	2.		1069341	3095862	4817551	8444824	10618150
	3.		1635621	3279081	4413180	7285440	10710366
1-heptanol	1.	56	0	339485	524941	1332694	1330126
	2.		0	302918	423653	435389	1279660
	3.		0	337718	523811,9	1041182	991888,9
nonanal	1.	57	133679	2305958	3519906	7079024	8518222
	2.		109289	2104950	3220856	6319673	8233129
	3.		210082	2030209	3136600	5580917	7871202
2-pentanone	1.	43	953184	934055	1752026	1518709	2034504
	2.		810568	1102938	1141508	1676430	1779785
	3.		678831	1208116	1533250	1632099	2026049

A regression analysis to determine the determinant R^2 was done with the use of the data obtained by performing the chromatographic analysis. The averaged results for oil samples from different vendors were considered. The results of the analysis are presented in the following graphs.

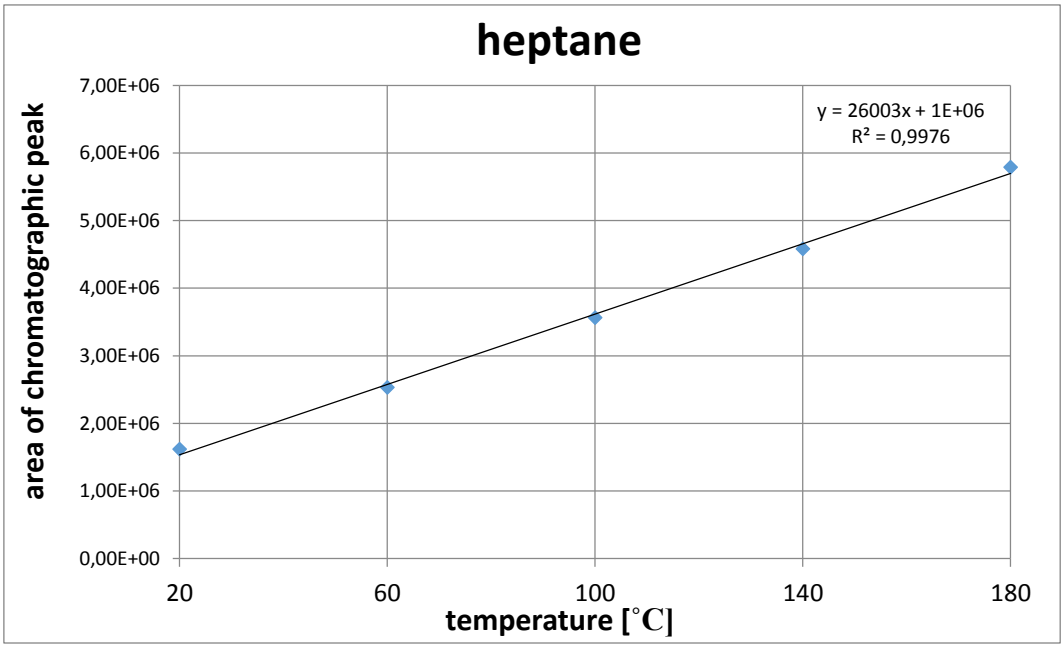

Figure 1. Correlation between the content of heptane in the volatile fraction of rapeseed oil and the temperaturę of heating samples

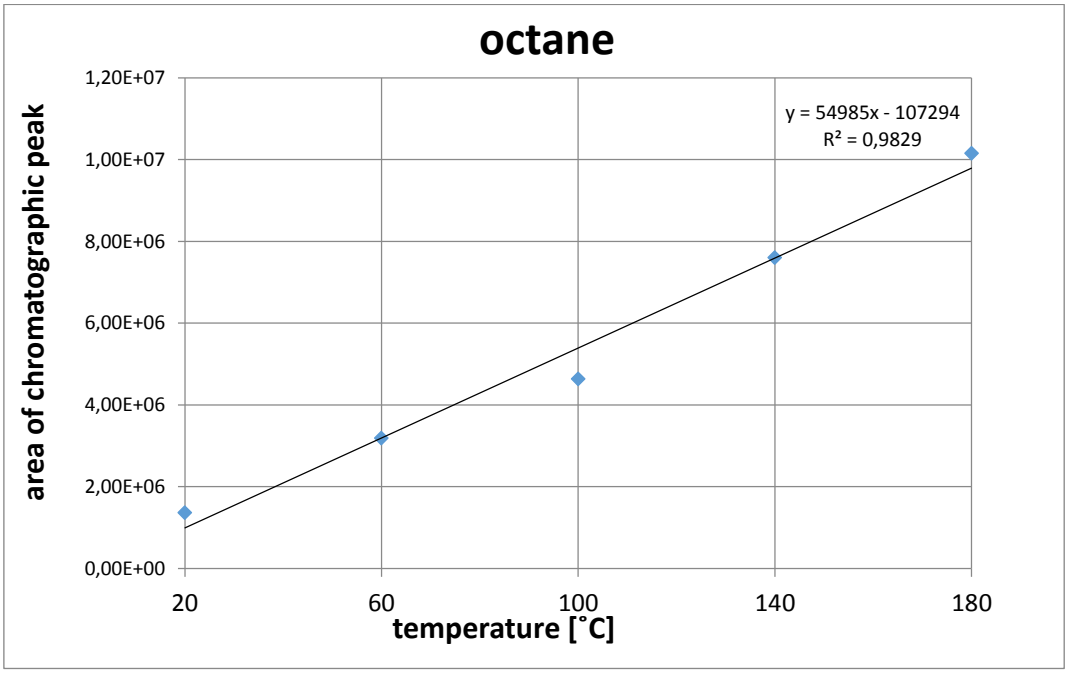

Figure 2. Correlation between the content of octane in the volatile fraction of rapeseed oil and the temperaturę of heating samples

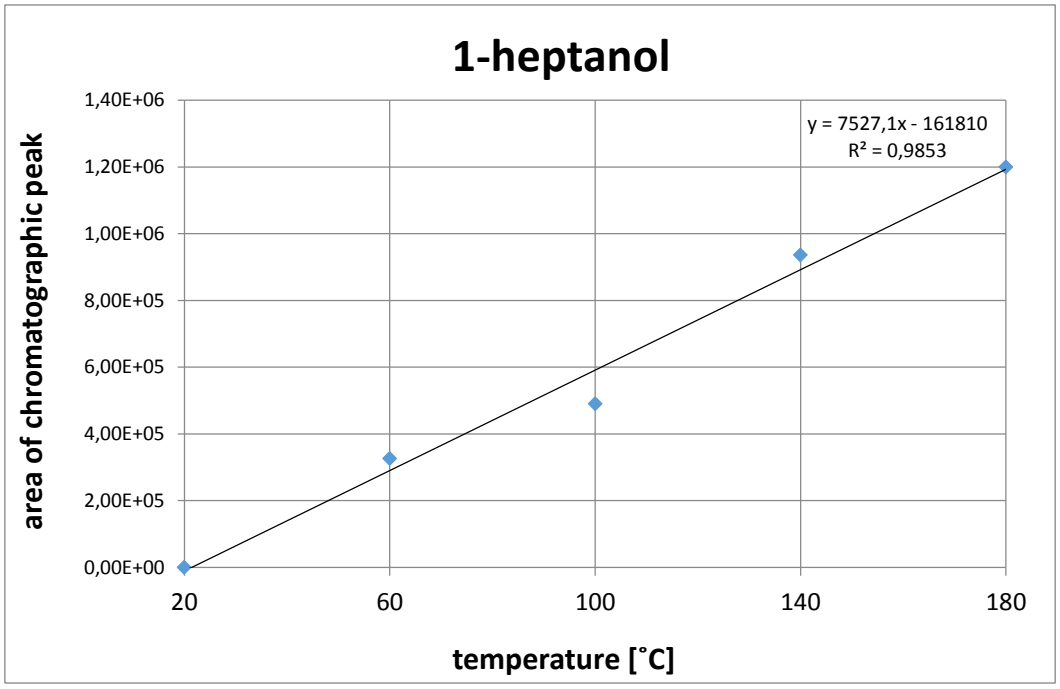

Figure 3. Correlation between the content of 1-heptanol in the volatile fraction of rapeseed oil and the temperaturę of heating samples

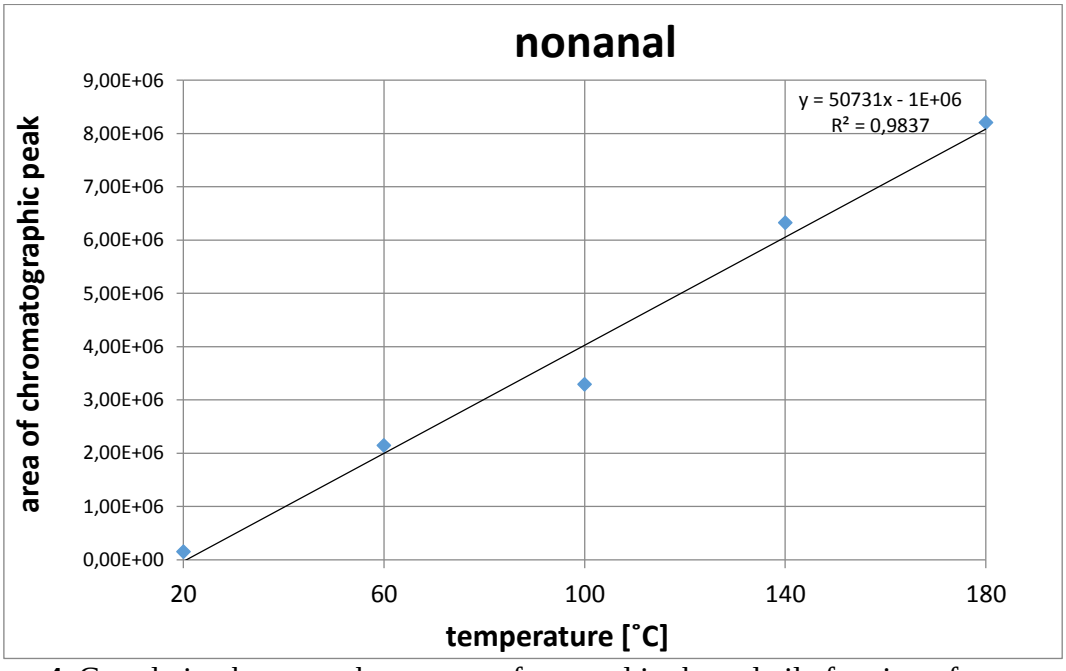

Figure 4. Correlation between the content of nonanal in the volatile fraction of rapeseed oil and the temperaturę of heating samples

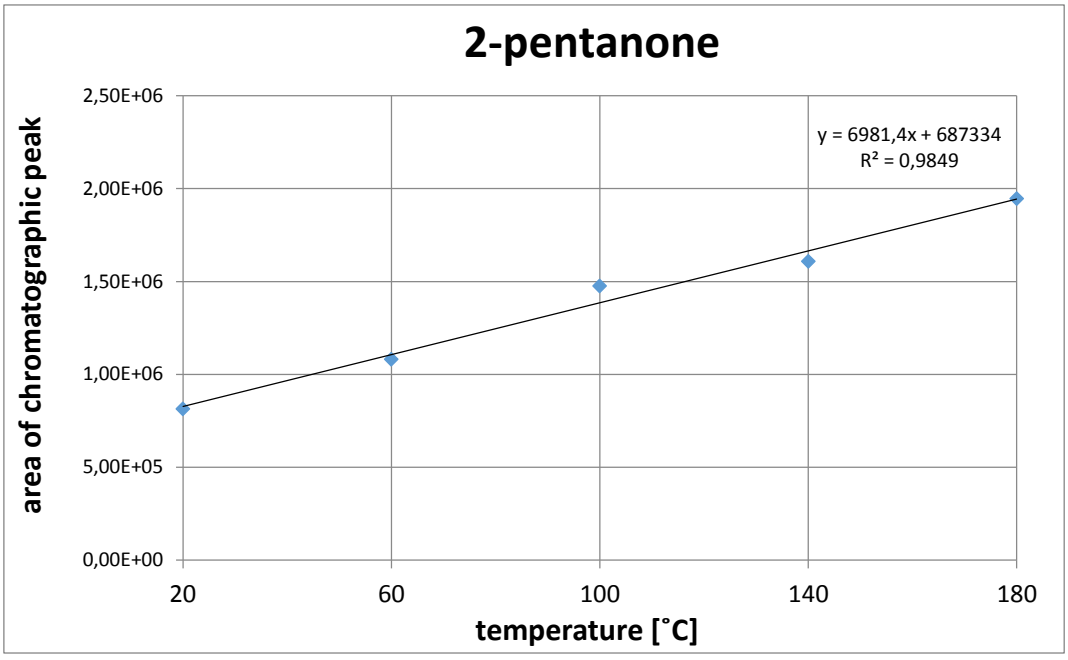

Figure 5. Correlation between the content of 2-pentanone in the volatile fraction of rapeseed oil and the temperature of heating samples

Table 2. Calibration curves coefficients at selected temperatures

Quality indicator	20 °C		100 °C		180 °C	
	Equation of the calibration curve	R^2	Equation of the calibration curve	R^2	Equation of the calibration curve	R^2
Octane	$y = 521585x + 561236$	$R^2 = 0.985$	$y = 561415x + 3 \cdot 10^6$	$R^2 = 0.977$	$y = 1 \cdot 10^6 x + 8 \cdot 10^6$	$R^2 = 0.994$
Heptane	$y = 1 \cdot 10^6 x + 3 \cdot 10^6$	$R^2 = 0.962$	$y = 2 \cdot 10^6 x + 9 \cdot 10^6$	$R^2 = 0.951$	$y = 6 \cdot 10^6 x + 4 \cdot 10^7$	$R^2 = 0.936$

Nonanol	y = 176326x +22962	$R^2 = 0.999$	y = 281613x +708451	$R^2 = 0.989$	y = 376456x $+2 \cdot 10^6$	$R^2 = 0.954$
1-heptanol	y = 32306x +5134,2	$R^2 = 1.000$	y = 125967x +470562	$R^2 = 0.977$	y = 141676x +885270	$R^2 = 0.96$
2-pentanone	$y = 1 \cdot 10^6 x$ +846773	$R^2 = 0.994$	$y = 2 \cdot 10^6 x$ $+1 \cdot 10^7$	$R^2 = 0.986$	$y = 2 \cdot 10^6 x$ $+2 \cdot 10^7$	$R^2 = 0.964$

After quality indicators had been selected, quantification analysis of them was carried out. The method of standard addition was used. For this purpose, the previously used preparation procedure was used, after which 100 µl of mixture of standard solutions were added to oil samples using gas-tight syringe so that the concentration of each of the added standards in the sample is respectively 0.050 mg/kg, 0.250 0.050 mg/kg, 0.500 mg/kg 0.050 mg/kg. The pattern add-in method has been selected to include the effect of the matrix. The results of measuring the concentration of potential quality factors. Based on the received data, calibration curves were made. The following table summarizes the results of the quantitative determination of potential rapeseed oil quality indicators.

Table 3. Content of rapeseed oil quality indicators at selected temperatures

Quality Indicator	**Conjugated fatty acid**	**Concentration [mg/kg]**		
		20 °C	**100 °C**	**180 °C**
octane	oleic acid	1.17	3.00	5.22
nonanal	oleic acid	0.15	2.51	5.23
heptane	oleic acid	2.60	4.77	6.63

1-hetpanol	oleic acid	0.16	3.63	5.97
2-pentanone	oleic acid	0.63	4.32	7.76

3. CONCLUSIONS

In rapeseed oil samples after the heating process, a linear relationship between the content of each of the selected thermal degradation indicators and the increase of temperature was found. Five quality indicators: 2 aliphatic hydrocarbons - octane and heptane - and 1-heptanol, 2-pentanone as well as all nonanal were selected in the rapeseed oil. All these compounds come from the process of oxidation of oleic acid [10]. Rapeseed oil contains the biggest amount of oleic acid of all fatty acids, about 60%. In samples of non-heating oil, the highest content of heptane was found. The content of 2-pentanone - was 0.63 mg/kg. In rapeseed oil samples, also 1-heptanol was measured in an amount of 0.16 mg/kg. The octane and nonanal concentrations were 1.17 mg/kg and 0.15 mg/kg, respectively, at 20 °C.

After the heating process at 100 °C, all the contents except for nonanal, with a concentration above 3 mg/kg, increased. At this temperature, the main indicators of thermal degradation were heptane and 2-pentanone. At the temperature of 180 °C, all concentrations of thermal degradation indicators selected for rapeseed oil were higher than 5 mg/kg. The chemical compound that was found to have the highest content was2-pentanone - 7.76 mg/kg. The octane content increased by 4 mg/kg during the heating process to 180 °C. In the case of nonanal, a 5-fold increase in the heated sample was observed comparing to the unheated sample. The heptane concentration increased from 2.60 mg/kg to 6.63 mg/kg during 24 hours of 180 heating. The content of 1-heptanol increased to 5.97 mg/kg. In contrast, the concentration of 2-pentanone at the highest temperature was 7.76 mg/kg. Although marked chemicals do not have carcinogenic or mutagenic properties, their presence in the oil is undesirable, due to the reduced health and utility values of the oil.

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