COMPARISON OF GAS CHROMATOGRAPHY AND NEAR-INFRARED REFLECTANCE SPECTROSCOPY METHODS FOR THE DETERMINATION OF FATTY ACID COMPOSITION OF SUNFLOWER SEED

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ABSTRACT

This study was performed in order to evaluate performance of Near-Infrared Reflectance Spectroscopy (NIRS) which is used to determine oil and fat content, oleic and linoleic acid percentages of sunflower seed by comparing with soxhelet extraction and gas chromatography methods (GC). Oil and fat contents of 34 different sunflower seeds were determined by soxhelet extraction method. Oleic and linoleic acid contents were then evaluated using GC equipped with capillary column and FID detector. Sample spectrums and approximate results were determined by a previously developed calibration method with determinate parameters (RSQ:0.8001, 0.9960, 0.9974 for raw oil content, oleic acid and linoleic acid, respectively) using Foos NIRS System XDS near-infrared Rapid Content Analyzer. Average oleic and linoleic contents of sunflower seeds using GC equipped with capillary column and FID detector were calculated as 53.24 and 33.13%. When the averages of oleic and linoleic acid contents were determined by NIRS, average oleic acid content were found to be 53.40% while 33. 48% was average linoleic acid content. The results of this study showed that NIRS-based method can be reliably used in the determination of oil and fat content, oleic and linoleic acid contents of sunflower seeds. The important contribution of this study is that NIRS-based method can be used as a quick and accurate method in the marketing of sunflower seed and as an environment-friendly method since no chemicals used in this method.

Keywords: Sunflower oil, Oil and fat content, Oleic acid content, Linoleic acid content, NIRS

INTRODUCTION

History dating back to 3000 B.C. and cultivating in a large area in Turkey, sunflower (Helianthus annuus L.) is considered to be one of the most important oil plants in both in Turkey and in the world with the rate of 22-55% oil content. With approximately six million decares planting area, sunflower can be grown in almost all regions in Turkey and contains high amount and good quality oil (TÜİK, 2016). It supplies half of our vegetable oil consumption (BYSD, 2016).

Sunflower oil containing approximately 15% saturated, 85% unsaturated fatty acid and consisting of 14 - 43% oleic and 44 -75% linoleic acid in its unstaurated fatty acids,standard type sunflower oil is one of the most important vegetable oil in terms of oil composition. It is

also among most important oils in human nutrition. In recent years, a range of variety and quality sunflower oil has been produced via the development of mid-oleic type (43.1-71.8%) and high oleic type (75-90.7%) sunflower varieties that has higher oleic acid content than standard sunflower type. There is a growing need for the oils that are less saturated, resistant to oxidation and durable to heat treatment by the change of our consumption habits. In last years, there is also another growing interest in sunflower oil due to its use in other fields apart from food industry. Since the development of high oleic sunflower hybrids, sunflower oil has become more important raw material for the oleochemical industry which includes cosmetics industry.

Food safety and food quality that have close relations with social development and human health are still considered as an important issue in all countries of the world. Day after day, consumers are searching for quality labels on food products and signs that are reliable, they expect high quality products from manufacturers. All of these factors emphasize the importance of reliable techniques for assessing the quality of food.

When the application needs are taken into consideration, the development of fast and effective methods like NIRS technology become apparent. In recent years, there is a growing interest in fast, reliable and enviromentally friendly technologies both in food production and food research. Consequently alternative technologies are being developed to conventional ones. One of the most important of these technologies widely used is the NIR spectroscopy (Cen and He 2007). Used in food analysis after appropriate calibration, fast, reliable and environmentally friendly, NIR Spectroscopy is a technology used for analysis and based on electromagnetic radiation absorbtion in 400-2500 nm wavelength range. (Davies ve Granth, 1987).

NIR spectroscopy , based on the resolution of the analytical and quality factors from food samples with correleation of electromagnetic absorption at aforementioned wavelength, allows to be used routinely in sensory, physical and chemical analysis of food and agricultural products. (Williams ve Norris 1987). For this purpose, studies were conducted to determine crude fat content of the oil plant and fatty acid composition by NIR spectroscopy. (Velasco ve ark. 2004; Koprna ve ark. 2006; Akkaya ve ark. 2015).

It is necessary to determine oil content and fatty acid composition by fast and reliable methods in sunflower seed which holds an important place both in national production and in importation. This study was performed in order to evaluate performance of NIR Spectroscopy which is used to determine oil and fat content, oleic and linoleic acid percentages of sunflower seed by comparing with soxhelet extraction and gas chromatography methods (GC).

MATERIALS AND METHODS

In this study, 34 pieces of different sunflower varieties in which reclamation and adaptation studies are done in East Mediterranean Agronomic Institute testing ground are used as material. Crude oil ratios were determined by Soxhlet extraction method, the ratio of oleic acid and linoleic acid was determined by FID detector gas chromatography capillary column method of sunflower seed oil samples.

FOSS NIRSystem XDS near-infrared Rapid Content Analyser apparatus is used to receive spectrums and determine estimated values of the spectrum of sunflower samples in which classical analysis were completed . Spectra of ground sunflower seed samples were taken to be every 2 nm in between 400-2500 nm wavelength. In determining the estimated

value, the information belongs to NIRS analysis calibration model which is previously developed by using WinISI III v1.61 software package, can be seen in Table 1.

Table 1 The statistics belong to calibration method developed to estimate dry matter, crude oil,oleic acid and linoleic acid rates

Properties	Average±SD	Min (%)	Max (%)	RSQ	SEP	Bias	Slope
Dry Matter Rate (%)	93.79±0.94	90.95	96.62	0.9026	0.286	0.000	1.000
Crude Oil Rate (%)	36.31±5.52	19.75	52.87	0.8001	2.394	-0.076	0.991
Oleic Acid Rate (%)	46.87±16.15	0	95.31	0.9960	0.946	0.043	0.998
Linoleic Acid Rate (%)	40.64±15.04	0	85.75	0.9974	0.793	-0.054	0.998

SD: Standart Deviation, RSQ (Coefficient of determination of Calibration), SEP (Standart Eror of Prediction)

RESULTS

The estimated values of the research in NIRS analysis device and the values determined by conventional analysis methods can be seen in Table 2. In this study, crude oil contents were determined between %32.80 and %48.40 by soxhelet oil extraction method, oleic acid ratio were determined between %34.41 and %80.29 by FID detector capillary column gas chromatography method while the ratio of linoleic acid was determined between %6.45 and %51.93 . Crude oil ratio estimated at NIRS is between 32.45% and 49.61%, oleic acid ratio is between 32.03% and 87.77%, linoleic acid ration is ranged from 3.66% to 51.29% . The average value of the crude oil determined by Soxhlet extraction method was %40.06 while the average values of crude oil estimated by NIRS was found to be %40.44. The average values of oleic acid determined by FID detector gas chromatography capillary column method was %53.24, the average value of linoleic acid was %33.13, while the average value estimated by NIRS was 53.40 for oleic acid and 33.48 for linoleic acid.

In conclusion, this study demonstrates that NIRS can be used reliably to determine crude oil, oleic acid and linoleic acid rates in sunflower seeds. In addition, it shows that NIRS analysis method can be fast and effective analysis method in both vegetable oil industry and sunflower seed trade and marketing and be greener compared to conventional chemical analysis methods due to fact that it has no use of any chemicals.

Table 2. Average values were determined by conventional analysis and average values were estimated by NIRS in sunflower seed samples

Sample No	Conventional Analysis Crude Oil Rate (%)	NIRS Crude Oil Rate (%)	Conventional Analysis Oleic Acid Rate (%)	NIRS Oleic Acid Rate (%)	Conventional Analysis Linoleic Acid Rate (%)	NIRS Linoleic Acid Rate (%)
1	44,93	45,80	60,64	64,30	25,88	22,84
2	40,96	38,86	43,12	40,40	44,24	45,06
3	41,43	41,19	44,56	42,83	40,14	44,09
4	43,68	42,18	46,61	49,13	40,79	39,78
5	33,01	32,45	75,03	70,02	12,24	14,56
6	32,80	33,62	80,09	75,89	7,11	10,20
7	40,73	41,08	34,41	32,03	51,93	51,29
8	41,00	42,63	78,53	78,66	7,72	7,00
9	46,96	47,23	45,01	43,17	42,35	42,49
10	39,11	39,13	55,3	53,97	31,65	30,70
11	44,47	43,76	80,29	87,77	6,45	3,66
12	34,22	34,93	46,47	43,25	36,31	40,78
13	34,52	33,71	49,78	49,84	36,11	34,73
14	47,53	48,23	45,06	45,92	41,01	40,39
15	40,11	41,16	47,04	46,41	40,43	42,48
16	42,67	41,10	58,14	61,41	23,74	25,15
17	43,15	40,57	49,85	54,37	36,91	34,52
18	42,20	43,97	48,24	44,76	37,81	39,34
19	37,16	39,25	52,55	58,27	33,14	31,38
20	48,40	49,61	43,67	44,43	44,56	44,31
21	38,32	38,25	43,36	48,00	42,79	42,43
22	41,65	42,80	51,79	51,62	34,78	33,94
23	43,67	44,72	46,2	45,63	42,51	43,39
24	23,57	33,48	44,32	44,86	40,2	39,41
25	40,83	41,60	48,04	45,94	39,6	42,77
26	47,26	47,61	50,88	54,99	35,69	34,86
27	39,05	36,80	52,27	49,88	32,86	36,08
28	33,81	34,99	43,19	41,40	43,72	42,68
29	43,25	44,14	44,08	40,15	40,46	45,19
30	39,81	38,86	56,28	59,38	28,39	28,52
31	39,17	39,64	50,58	54,86	36,18	33,62
32	33,86	33,64	61,86	59,02	26,42	27,53
33	43,79	44,64	55,06	59,40	32,96	28,98
34	35,07	33,27	77,87	73,57	9,36	14,29
Max Value	48,4	49,61	80,29	87,77	51,93	51,29
Min Value	32,8	32,45	34,41	32,03	6,45	3,66
Average	40,06	40,44	53,24	53,40	33,13	33,48

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AROMA DETERMINATION OF A REFINED SUNFLOWER SEED OIL BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY USING DIFFERENT EXTRACTION METHODS

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ABSTRACT

The sunflower (*Helianthus annuus* L.) seeds are eaten raw, roasted, cooked, dried, and ground, and used as a source of oil. Edible vegetable oils are important to our daily life by providing energies, nutritional compounds, and desirable flavors. Sunflower seeds are usually processed in large oil mills using solvent to extract oil and refining it. Three typologies of sunflower oil, characterized by diverse percentage of oleic acid are present on the market: a low, mid and high oleic sunflower oil. Refined sunflower oil, especially high-oleic, is very versatile and due to its neutral flavour and heat stability it can be consumed in many ways in the kitchen, such as frying and cooking. Edible oils play a significant role in the food industry due to both their functional and nutritional features and their impact on taste, aroma and health. Aroma is a main quality factor for edible vegetable oils as a characteristic parameter. Many extraction techniques have been carried out to extract the aroma compounds of oil. Therefore, in this study, aroma compounds of a refined sunflower oil obtained from a local market in Adana was extracted by different isolation methods including solid phase extraction (SPE), simultaneous distillation extraction (SDE) and purge and trap extraction (PTE). Afterwards, aroma compounds of the extracts were identified and quantified by gas chromatography (GC) coupled with a mass spectrometry (MS) and flame ionization detector (FID). Among the extraction methods, the PTE was quantitatively and qualitatively detected as the most suitable method for the extraction of aroma compounds in the studied sample.

Keywords: Refined sunflower oil, aroma profile, extraction techniques, GC-MS