

Research Article

**Safety Evaluation of Oil Samples Collected from Different Food Points
of Multan City of Pakistan**

Saeed Akhtar, Mamoon Tanveer, Amir Ismail*, Tariq Ismail, Majid Hussain

Institute of Food Science and Nutrition, Bahauddin Zakariya University, Multan – Pakistan

History

Submitted: Aug 12, 2017

Revision: Nov 14, 2017

Accepted: Dec 2, 2017

Keywords

*Oil, Free Fatty Acids,**Conjugated diene,**Mineral, heavy metal*

*Correspondence

amirismail@bzu.edu.pk

Abstract

Cooking oil has become a part and parcel of modern food system and therefore its safety is of prime significance for health agencies around the globe to ensure good health among the community. Current study was designed to investigate the physicochemical properties including free fatty acids, peroxide value and conjugated dienes; minerals (nickel & cobalt) and heavy metals (lead and cadmium) in oil samples collected from different areas of Multan city of Pakistan. The findings of this study revealed that free fatty acid percentages, conjugated dienes, cobalt and nickel concentrations were in normal ranges while the peroxide values, lead and cadmium concentrations were recorded above the norms. Strict regulatory measures need to be adopted to ensure good quality oil supply and to protect the people from health implications of physicochemical and metallic hazards prevailing in fried oils and fried foods.

1. Introduction

Food is the basic requirement of every individual irrespective of gender, age and race. Diet of an individual must supply every single nutrient required for the normal growth and maintenance of body. The deficiency of even a single nutrient may result in different ailments, on the other hand excess of any of these nutrients is also harmful for human health. Proteins, carbohydrates and lipids (fats and oil) are the major macronutrient while vitamins and minerals are the micronutrients that the human body requires. Food and Agriculture Organization (FAO) estimates that around 0.8 billion people from a total of 7.3 billion are suffering from macronutrient deficiencies (World Hunger Statistics, 2016) but on the other hand World Health Organization (WHO, 2017) estimates more than 1.9 billion adults mostly residing in the developed countries are overweight and around 0.6 billion people are suffering from obesity. Therefore, the proportion of people suffering from overweight and obesity issues is more as compared to macronutrient deficiencies.

The leading factor associated with the growing rate of obesity is elevated rate of fat and oil consumption. World Health Organization recommends that fat/oil of good quality should be consumed in such amounts that not more than 30% of daily energy requirements are met

through them but the reported energy intake through lipids has reached to 40 -50 %. The per capita consumption of lipids was 22kg in 2006 and has reached to 28kg in 2016 (Holdings, 2016). The increasing trend in the consumption of fats and oil is mainly associated with the good taste and appearance of fatty foods as well as the over advertisement of barbequed foods that ultimately has made the consumption of barbequed foods a fashion. The health risks associated with the overconsumption of fats and oil include obesity, cardiovascular diseases, hypertension and diabetes. The health risks due to the consumption of fat and oil rich foods increase to many folds due to the utilization of poor quality fats and oils (Gadiraju et al., 2015).

The quality of an oil is judged on the basis of a number of parameters such as toxic heavy metals (lead, cadmium, mercury), carcinogenic compounds like acrylamides and bis acrylamides, trans fats, free fatty acids and peroxide value. Toxic heavy metals may enter in fats and oil during processing and transportation while nickel is added during the hydrogenation process although it is removed through filtration but residues may remain if not properly treated. Carcinogenic compounds are formed in fats and oil due to excessive heating or their over use for frying of foods. Trans fats are the leading cause of cardiovascular diseases and are formed due to overheating of fat / oil. Free fatty acids

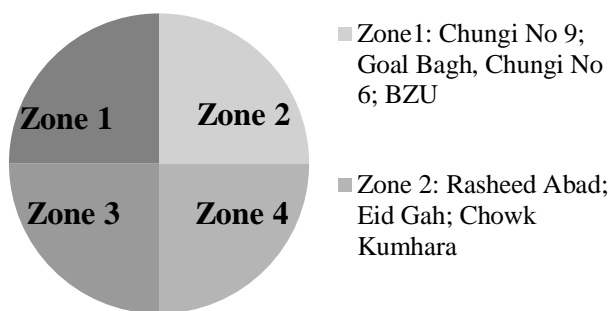


Figure 1: Formation of different zones in Multan city of Pakistan

are naturally found in fats and oil and are removed during processing through neutralization process but may regenerate through enzymatic or hydrolytic oxidation (Hernandez and Kamal-Eldin, 2013).

Current research project was designed to evaluate the safety status of oil being consumed through different fried foods sold in Multan city of Pakistan. The quality parameters tested in the said study included heavy metals (lead, cadmium, nickel and cobalt), free fatty acids (FFAs), peroxide value and conjugated dienes.

1. Material & Methods

1.1. Sample Collection

From different sale points of fried foods in Multan city, samples of the oil ($N = 60$) used for frying of different food items were collected (Figure 1). Samples of oil were immediately transported in UV light protected (amber glass) clean glass bottles to the Food Analysis Laboratory of Institute of Food Science and Nutrition, Bahauddin Zakariya University, Multan. Oil samples were stored at $-80\text{ }^{\circ}\text{C}$ until further analysis.

(Insert figure 1 here)

1.2. Free Fatty Acids

The FFA values of oil samples were calculated by adopting the method of AOAC (2002). Briefly, the oil sample was homogenized first and then seven gram oil sample was added in a 250ml volumetric flask. The neutralized ethyl alcohol (50 ml) was added in the sample flask along with few drops of phenolphthalein indicator and was titrated against 0.1 normal sodium hydroxide solution until the light pink end point was

achieved. Following formula was used to calculate the FFA value of an oil sample;

$$\text{Free Fatty Acid \% (as oleic acid)} = \frac{V \times N \times 28.2}{M}$$

Where, N is the normality of sodium hydroxide (0.1 N), M is sample weight i.e. 7g, and V is the volume of NaOH used in titration (ml).

1.3. Peroxide Value

The peroxide values of oil samples were calculated by using the method of Zahir et al. (2017). Briefly, oil sample (5g), chloroform and acetic acid solution (2:3) and saturated solution of potassium iodide (0.5ml) were added in a volumetric flask of 250ml. The contents of flask were mixed and 30 ml distilled water was added in the flask. The flask contents were titrated against sodium thiosulphate (0.1 N) by using starch as an indicator. The blanks values against titration were also calculated.

Following formula was used to determine the peroxide values of different oils;

$$\text{Per oxide value (meq/kg)} = \frac{(V \times N \times 1000)}{W}$$

V is the volume (ml) of sodium thiosulphate (blank corrected), N is sodium thiosulphate normality and W is sample weight

1.4. Conjugated Dienes

Determination of conjugated dienes was performed by adopting the method proposed by International Union of Pure and Applied Chemistry (IUPAC) (Privett and Blank, 1962). Conjugated dienes were measured spectrophotometrically on UV visible spectrophotometer at 233nm.

1.5. Heavy Metals Analysis

For the analysis of heavy metals in oil samples, the samples were first wet digested according to the method of Anwar et al. (2004). Briefly, 2g sample was placed in flask containing 10ml nitric acid and 5ml perchloric acid. The flask was placed at room temperature in dark for one night. Next day, the sample was heated at $180\text{ }^{\circ}\text{C}$ until the volume decreased to 2-3ml. After that the sample was diluted up to 50ml with the help of deionized water. The diluted samples were run on flame atomic absorption spectrophotometer (Solar,

Thermoscientific 3000 series, Waltham, MA, USA) for the quantification of lead (Pb), cadmium (Cd), nickel (Ni) and cobalt (Co). The instrumental conditions for the analysis of selected metals are described in Table 1.

(Insert table 1 here)

1.6. Statistical Analysis

The calculation of mean and standard deviation values was performed by using Microsoft Excel 2013. The statistical analysis for the calculation of ANOVA and LSD values was performed through Statistics 8.1 software (Softonic, Barcelona, Spain). The level of statistical significance was $P < 0.05$.

2. Results and Discussion

2.1. Physicochemical Properties of Oil

The most widely accepted indicator of oil quality is its Free Fatty Acid (FFA) value. The FFA percentage increase during excessive frying because of hydrolytic and oxidative rancidity of oil (Nor et al., 2008). Mean FFA percentage in different zones ranged between $0.51 \pm 0.31 - 0.72 \pm 0.63$, while the overall mean values was 0.62 ± 0.42 % (Table 2). Statistical analysis revealed non significant difference in the FFA values of different zones of Multan city. The initial maximum permissible level of FFA in an oil sample as set by Pakistan Standards Quality Control Authority (PSQCA) is 0.2% (PSQCA, 2003), while USDA recommended maximum tolerable level for FFA above which the oil should be discarded is 2%. Comparing these standards with our results, 100% of our sample were found in satisfactory range of FFA values while the initial FFA value for oil i.e. 0.2% is for oil manufacturing industries only, not for the under use oil in hotels, restaurants or industries and therefore was not the point of concern in this study. In a similar study conducted in Canada, FFA percentage was recorded in the used oil samples of hotels and restaurants and was found in the range of 0.25 – 3.99 %, that is much higher as compared to our values. In another study conducted in Saudi Arabia the reported FFA values ranged between 1.40 – 2.5 % and these values are also less as compared to our results (Al-Harbi and Al-Kahtani, 1993). The low FFA percentages in our samples might be due to the good quality of oil used in restaurants of Multan city or due to the reason that the oil samples collected in our study were relatively fresh.

Table 1. Instrumental conditions for the quantification of metals in oil

Metal	Wavelength	Bandpass (nm)	Fuel flow rate (L/min)
Pb	216.8	0.5	0.8
Cd	229.2	0.5	0.9
Ni	231.7	0.2	0.9
Co	241.1	0.2	0.8

Table 2. Chemical characteristics of analyzed oil samples

Areas of Multan	Peroxide Value (meq/kg of fat)	Free Fatty Acid (% Oleic acid)*	Conjugated Dienes (mmol/L)*
Zone 1	188.18 ± 86.91^a	0.57 ± 0.38	0.47 ± 0.23
Zone 2	162.29 ± 76.06^a	0.51 ± 0.31	0.51 ± 0.26
Zone 3	75.93 ± 86.63^b	0.66 ± 0.36	0.33 ± 0.05
Zone 4	59.89 ± 34.23^b	0.72 ± 0.63	0.15 ± 0.08
Overall Mean	121.57 ± 70.98	0.62 ± 0.42	0.36 ± 0.21

PV=Peroxide Value; FFA=Free Fatty Acid; CD=Conjugated Dienes; *= Non significant

Oxidation of oil is measured in terms of its peroxide value, therefore peroxide value is an important indicator of the quality of oil. The peroxide values of oil samples in different zones were in the range of $18.18 \pm 86.91 - 59.89 \pm 34.23$ meq/kg while the mean peroxide value was 121.57 ± 70.98 meq/kg. The maximum peroxide value of fresh oil proposed by PSQCA is 5 meq/kg while the peroxide value above which the oil is considered unfit for consumption is 10 meq/kg (Gunstone, 2008). Comparing this limit with our results all the samples were found exceeding the maximum limit. In a study conducted in Korea the peroxide values of different types of used oils ranged between 15.48 – 71.04 meq/kg. These results are in range of with our findings but lower as compared to our mean peroxide value (Park and Kim, 2016). In another study conducted in Taiwan (Liao et al., 2005), the peroxide values of oil in use in different restaurants ranged between 6.01 -9.05 meq/kg, these values are much lower as compared to our results indicating the use of good quality oil in Taiwan. The higher peroxide values in our study might be associated with the storage of oil in poor conditions, poor quality of vessels used in frying and low educational status of food handlers.

Quality of oil can be gauged on the basis of its conjugated dienes value, this value is low for fresh oil as it lacks conjugated structures which have the potential to absorb ultraviolet radiations of 233nm, the

conjugated structures are formed as a result of oxidation and the movement of double bonds from their original positions. The mean conjugated dienes value in oil samples from different zones ranged between 0.15 ± 0.08 – 0.51 ± 0.26 mmol/L while the overall mean value was 0.36 ± 0.21 mmol/L. Much higher level of conjugated dienes is reported from Israel (7.87 mmol/L) by Peri and Saguy (2015). The reported level of conjugated dienes from Korea is 0.51 – 0.86 mmol/L that is quite comparable to our results (Liao et al., 2005).

2.2. Minerals & Heavy Metals in Oil

Cadmium (Cd) is a highly toxic heavy metal that may result in a number of health damages but mainly limited to liver and kidney (Ismail et al., 2015). Significant differences were observed in the Cd concentration of oil samples from different zones of Multan city. Mean Cd concentration in used oil samples ranged between 0.004 – 0.157 mg/kg while the overall mean Cd value was 0.065 ± 0.068 mg/kg. The reported concentration of cadmium in edible oil samples from Turkey was 0.09 – 4.57 $\mu\text{g/kg}$ (Mendil et al., 2009) which is much lower as compared to our results. The reported concentration of Cd in different types of oil samples from Saudi Arabia (Ashraf, 2014) and China (Zhu et al., 2011) were 0.002 – 0.006 mg/kg and 0.003 – 0.008 mg/kg, respectively, these values are also lower as compared to our findings. Higher concentrations of cadmium in our samples might be due to contamination during transportation, use of contaminated utensils during frying or due to the contamination of smoke or dust particles during processing.

Lead (Pb) toxicity may result in nervous system damage, retarded growth and cancer of liver and kidney. Statistical analysis revealed significant differences in the Pb concentration of used oil samples from different zones of Multan city. Mean maximum Pb concentration (0.433 ± 0.100 mg/kg) was recorded in zone 2 while mean minimum concentration (0.012 ± 0.003 mg/kg) was recorded in zone 1. Mean total Pb concentration in used oil samples was 0.245 ± 0.17 mg/kg. Mendil et al. (2009) reported 0.01 – 0.03 $\mu\text{g/kg}$ Pb in oil samples and these values are much lower as compared to our findings. The reported concentration of Pb in oil samples from Saudi Arabia was 0.007 – 0.015 mg/kg (Ashraf, 2014). These values are also lower as compared to our findings. The elevated rate of Pb prevalence in current study might be linked with

unhygienic frying utensils or the oil samples might be initially contaminated with Pb during processing.

Nickel (Ni) is a trace mineral element required for the normal growth and maintenance of human body but the excessive doses of Ni may result in carcinogenicity, neurotoxicity, reproductive disorders and may also result in oxidative stress (Ismail et al., 2014; Akhtar et al., 2015). Significant differences were observed in the Ni concentration of oil samples collected from different zones of Multan city. Mean maximum Ni concentration (0.303 ± 0.021 mg/kg) was recorded in oil samples collected from zone 1 and mean minimum was recorded in oil samples collected from zone 3 (0.107 ± 0.025 mg/kg), while the overall mean recorded concentration of Ni was 1.99 ± 0.079 mg/kg. The reported concentrations of Ni in vegetable oil samples from Iran ranged between 0.91 – 2.17 mg/kg (Farzin and Moassesi, 2014) and these values are much higher as compared to our findings. Concentration of Ni in oil samples collected from China (Zhu et al., 2011) and Turkey (Pehlivan et al., 2008) were 0.019 – 0.066 and 0.002 – 0.025 mg/kg, respectively. The concentration of Ni reported from China and Turkey is lower as compared to our findings.

Cobalt (Co) is a coenzyme and is also a part of vitamin B₁₂. Mean Co concentration in oil samples was 0.069 ± 0.037 mg/kg while the range of Co concentration was 0.020 ± 0.000 – 0.110 ± 0.020 mg/kg. In a study conducted in Turkey by (Pehlivan et al., 2008) the reported concentration of Co in different types of oil samples ranged between 0.000 – 0.004 mg/kg, these values are much lower as compared to our results. Mendil et al. (2009) reported 0.50 – 1.30 mg/kg Co in

Table 3: Concentration (mg/kg) of minerals (Co & Ni) and heavy metals (Cd & Pb) in oil samples

Area	Cd	Pb	Co	Ni
Zone 1	0.004 ± 0.000^c	0.012 ± 0.003^c	0.067 ± 0.025^b	0.303 ± 0.021^a
	0.015 ± 0.002^c	0.433 ± 0.100^a	0.079 ± 0.006^{ab}	0.223 ± 0.031^b
Zone 2	0.157 ± 0.042^a	0.223 ± 0.035^b	0.020 ± 0.000^c	0.107 ± 0.025^d
	0.087 ± 0.035^b	0.313 ± 0.025^b	0.110 ± 0.020^a	0.163 ± 0.015^c
Zone 3	0.065 ± 0.068	0.245 ± 0.167	0.069 ± 0.037	0.199 ± 0.079
Mean	.068	.167	.037	.079
Total				

six different types of vegetable oil samples, these results are comparatively higher than our findings. Based on the review of literature it can be stated that Co values in the tested samples were in normal ranges and can impart beneficial impacts on human health.

3. Conclusion

Physicochemical and metal analysis were performed for the in use oil samples collected from different food points of Multan. The results of the study professed that the oil samples were fulfilling some of the safety parameters but were pathetic in some aspects including toxic heavy metals (lead and cadmium) and peroxide value. The findings of this study indicate that food handlers must be educated regarding the safe processing conditions and the ways that can minimize the prevalence of toxic compounds in oil. Furthermore, the oil industries must ensure that the oil supplied to the market must be of good quality.

4. Conflict of Interest

The authors declare no conflict of interest

5. References

- Akhtar, S., Ismail, T., Riaz, M., Shahbaz, M., Ismail, A., & Amin, K. (2015). Minerals and heavy metals in raw and ultra heat treated commercial milks in Pakistan. *International Journal of Food and Allied Sciences*, 1: 18–24.
- Al-Harbi, M. M., & Al-Kahtani, H. A. (1993). Chemical and biological evaluation of discarded frying palm oil from commercial restaurants. *Food Chemistry*, 48: 395–401. doi:10.1016/0308-8146(93)90324-9.
- Anwar, F., Kazi, T. G., Saleem, R., & Bhanger, M. I. (2004). Rapid determination of some trace metals in several oils and fats. *Grasas y Aceites*, 55: 160–168. doi:10.3989/gya.2004.v55.i2.162.
- AOAC. (2002). *Official Methods of Analysis of The Association of Official Analytical Chemists*. 17th Edition.
- Ashraf, M. W. (2014). Levels of selected heavy metals in varieties of vegetable oils consumed in kingdom of Saudi Arabia and health risk assessment of local population. *Journal of Chemical Society Pakistan*, 36: 691–698. [accessed 2017 Aug 12]. <https://inis.iaea.org/search/searchsinglerecord.aspx?recordsFor=SingleRecord&RN=46065344>.
- Farzin, L., & Moassesi, M. E. (2014). Determination of Metal Contents in Edible Vegetable Oils Produced in Iran Using Microwave-assisted Acid Digestion. *Journal of Applied Chemistry Research*, 8: 35–43.
- Gadiraju, T. V., Patel, Y., Gaziano, J. M., & Djoussé, L. (2015). Fried food consumption and cardiovascular health: A review of current evidence. *Nutrients*, 7: 8424–8430. doi:10.3390/nu7105404.
- Gunstone, F. D. (2008). *Oils and fats in the food industry*. Wiley-Blackwell Pub.
- Hernandez, E., & Kamal-Eldin, A. (2013). *Processing and nutrition of fats and oils*. John Wiley & Sons, Ltd.
- Holdings. (2016). *World consumption of Oils & Fats*. [accessed 2017 Aug 11]. <http://www.rea.co.uk/markets/oils-fats/world-consumption-oils-fats>.
- Ismail, A., Riaz, M., Akhtar, S., Ismail, T., Ahmad, Z., & Hashmi, M. S. (2015). Estimated daily intake and health risk of heavy metals by consumption of milk. *Food Additives & Contaminants Part B, Surveill*, 8: 260–5. doi:10.1080/19393210.2015.1081989.
- Ismail, A., Riaz, M., Akhtar, S., Ismail, T., Amir, M., & Zafar-ul-Hye, M. (2014). Heavy metals in vegetables and respective soils irrigated by canal, municipal waste and tube well waters. *Food Additive and Contaminants Part B, Surveill*, 7: 213–219. doi:10.1080/19393210.2014.888783.
- Liao, L., Huang, S., & Lu, Y. (2005). A survey study on frying oil of restaurants in the Taipei area. *Foodservice Research International*, 16: 60–68. doi:10.1016/j.jhazmat.2008.10.046.
- Mendil, D., Uluözlü, Ö. D., Tüzen, M., & Soylak, M. (2009). Investigation of the levels of some element in edible oil samples produced in Turkey by atomic absorption spectrometry. *Journal of Hazardous Material*, 165: 724–728. doi:10.1016/j.jhazmat.2008.10.046.
- Nor, F. M., Mohamed, S., Idris, N. A., & Ismail, R. (2008). Antioxidative properties of Pandanus amaryllifolius leaf extracts in accelerated oxidation and deep frying studies. *Food Chemistry*, 110: 319–327. doi:10.1016/j.foodchem.2008.02.004. [accessed 2017 Aug 12]. <http://linkinghub.elsevier.com/retrieve/pii/S0308814608001672>.
- Park, J., & Kim, J. (2016). Monitoring of Used Frying Oils and Frying Times for Frying Chicken Nuggets Using Peroxide Value and Acid Value. *Korean Journal for Food Science of Animal Resources*, 36: 612–616.
- Pehlivan, E., Arslan, G., Gode, F., Altun, T., Musa, & Özcan, M. (2008). Determination of some inorganic metals in edible vegetable oils by inductively coupled plasma atomic emission spectroscopy (ICP-AES). *Grasas y Aceites*, 59: 239–244. doi:10.3989/gya.2008.v59.i3.514.
- Peri, I., & Saguy, I. S. (2015). Continuous injection of water and antioxidants possible roles on oil quality during frying. *LWT - Food Science and Technology*, 64: 919–925. doi:10.1016/j.lwt.2015.06.036.
- Privett, O. S., & Blank, M. L. (1962). The initial stages of autoxidation. *Journal of American Oil Chemical Society*, 39: 465–469. doi:10.1007/BF02637226. [accessed 2017 Aug 12]. <http://link.springer.com/10.1007/BF02637226>.
- PSQCA. (2003). *Pakistan Standard SPECIFICATION FOR BANASPATI (3RD REV.)*.
- Statistics, W. H. (2016). *World Hunger, Poverty Facts, Statistics 2016 - World Hunger News*. [accessed 2017 Aug 11].

<http://www.worldhunger.org/2015-world-hunger-and-poverty-facts-and-statistics/>.

WHO. (2017). WHO | Obesity and overweight. [accessed 2017 Aug 11].

<http://www.who.int/mediacentre/factsheets/fs311/en/>.

Zahir, E., Saeed, R., Hameed, M. A., & Yousuf, A. (2017). Study of physicochemical properties of edible oil and evaluation of frying oil quality by Fourier Transform-Infrared (FT-IR) Spectroscopy. *Arabian Journal of Chemistry*, 10: 3870–3876. doi:10.1016/j.arabjc.2014.05.025.

Zhu, F., Fan, W., Wang, X., Qu, L., & Yao, S. (2011). Health risk assessment of eight heavy metals in nine varieties of edible vegetable oils consumed in China. *Food and Chemical Toxicology*, 49: 3081–3085. doi:10.1016/j.fct.2011.09.019.