STUDY OF PHYSIOCHEMICAL PROPERTIES AND HEAVY METALS CONTENT IN EDIBLE OIL CONSUMED IN MUMBAI

Gavali Laxman Vithoba[1], **Kadam** Dhanraj Dashrath[1], **Shivankar** Vitthal Subrao[1]
[1]Department of Chemistry, Karmaveer Bhaurao Patil College Vashi, Navi Mumbai, Maharashtra, India-400703
E-mail: laxmanvg70@gmail.com

Abstract
Vegetable oil belongs to a large group of a substance obtained from plants. Edible vegetable oil product had been consumed by most of the peoples for cooking purpose, cosmetic, pharmaceutical and chemical industries. Quality of edible oil is analysed by evacuating physicochemical properties such as acid value, turbidity temperature, peroxide value, iodine value, saponification values, unsaponiflable matter, refractive index (BR reading), turbidity temperature using standard methods. Metal has become a common contaminant to the food products through environment and processing contaminations Ca, Cd, Cu, Fe, Mn, Ni, Pb and Zn in six varieties of edible oils collected from Mumbai area and analysed by Industrial Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Elements such as Copper, Zinc, Iron, Mn are essential elements since they play an important role in the biological system. In the present study, significant differences observed in the concentration of essential elements among different varieties of edible vegetable oils. Poor health can cause by lack of the required elements. Butyro-refractometer reading and Iodine value for analysed samples like groundnut oil and palm oil is higher than prescribed standards, such samples do not conforms as per food safety and standards regulation 2011. It is also observed that Biller test turbidity temperature is higher in mustard oil and lower in groundnut oil. So people should choose proper edible oil based on an individual health condition. Estimated intake of essential metals from daily consumption of 25g of investigated edible oil should pose no risk to human health.

Keywords: Edible vegetable oils, physicochemical properties, Heavy metals

Received: 26.03.2020 Reviewed: 20.05.2020 Accepted: 29.05.2020

1. INTRODUCTION

The human uses oils and fats in their diets as an energy source. Vegetable oils are a dietary source of lipid that constitutes an essential component of a healthy diet. The commonly used vegetable oil differs significantly for their triacylglycerol (TAGs) profile and fatty acid esterifies with glycerol leading to several positional isomers. Triacylglycerol can be considered as good fingerprint for quality control and many studies have been performed to develop rapid and low cost analytical methods to determine the authenticity, origin and eventually evidence fraud or adulteration Nikolaos et. al. (1999)

Edible vegetable oils are liquid at room temperature and comprised mainly triacylglycerides that are made up of three fatty acids attached to a glycerol molecule through ester bonds. A physical, chemical and nutritional property of vegetable oils very significantly depending on the type of fatty acids contents of vegetable oils is significantly higher than that of animal fats Justyna et.al. (2011). Acid value is expressed as the amount of potassium hydroxide necessary to free fatty acids of contain in 1g of oil. Free fatty acid content is formed by the hydrolysis of oils .crude oils and fats in natural form, not refined contains small amount of free fatty acid which are usually removed during the refining process. Peroxide value is an index used to quality evaluation of hydroperoxides present in fats and oils Erum et. al. (2017)

Vegetable oils have become more attractive recently because of its economical benefits as they are used as components in many manufactured product and the fact that it made from renewable resources. The qualitative and quantitative determination of the major and minor constituents of vegetable oils are done by gas chromatography and primary high performance liquid chromatography which are the two techniques widely applied for analysis of edible oils and fats (Erum et. al.). The metal contents of blood are gaining important because of toxicological as well as their nutritional view point. The seed drying processes using direct firing for product in of hot air can be responsible for major polycyclic aromatic hydrocarbon contamination of some vegetable oils such as coconut and grapeseed oil, fortunately refining can drastically reduce the amount of these contaminates. PAH are classes of well known carcinogenic compounds originating from incomplete combustion of organic compounds and geochemical process. At high temperature organic compounds are partially cracked to smaller unstable fragments, mostly radicals which recombine to give relatively stable polycyclic aromatic hydrocarbon Aluyor et. al. (2009).

Soybean oil, sunflower oil and peanut oil contains substantial amount of phospholipids. These phospholipids contribute to the stability and quality of edible oils, fats and fatty acids through their antioxidative activity or contribution to the texture Apostolos et. al. (2010). The determination of minor components is a great importance in establishing the oil quality and their genuineness. Oils containing long chain saturated fatty acids give a precipitate at a particular temperature which is specific for the oil when their alcoholic soap solution is treated with dilute acetic acid solution and 70% ethyl alcohol is determined by using Bellier test (turbidity temperature) acetic acid method.

The determination of element in edible oil is important because of both the metabolic roe of metals and possibilities for adulteration detection and oil characterization. Trace levels of metal ion are known to have adverse effect on the flavor, colour and odor Bewig. Et.al.(1994) Vegetable oils are beneficial and popular due to their cholesterol-lowering effect. The level of trace metals like Iron (Fe), Copper (Cu), Calcium (Ca), Magnesium (Mg), Cobalt (Co), Cadmium (Cd) and Manganese (Mn) are known to increase the rate of oil oxidation while other element such as Chromium (Cr), Cadmium (Cd) and Lead (Pb) at certain level are toxic (Fangkun et. al.). The Significance of trace metals and toxicological effects of heavy metal on human health and nutrition have been increasingly studied in recent year Anthemidis et. al. (2005) Oils and fats are most important as valuable commodes in world trade and for human nutrition is well recognized. These oils and fats used for edible purpose are of either plant or animal origin contains higher proportion of unsaturated fatty acid and which are essential fatty acids to human being.

2. MATERIALS AND METHODS

The six vegetable edible oil samples were purchased from Mumbai local market. The collected oil samples were packed in polyethylene bags and kept refrigerated till analyzed. In all cases, analyses were completed before mentioned expiry dates. All reagents were of analytical reagent (AR) grade unless otherwise stated. Double deionized water was used for all dilutions. HNO_3 and H_2O_2 were of suprapure quality (E. Merck, Dermsdat, Germany). All the plastic and glassware were cleaned by soaking in a 10% nitric acid solution and then rinsed with double deionized water. Ca, Cd, Cu, Fe, Mn, Ni, Pb and Zn in six varieties of edible oils collected from Mumbai area and analysed by Industrial Coupled Plasma atomic emission spectroscopy (ICP-AES). Quality of edible oil is analysed by evacuating physicochemical properties such as colour, rancidity suspended or foreign matter, added flavouring or colouring substances or mineral oil and conform by various standards like butyro-refractometer reading at 40^{o}C, acid value, turbidity temperature, peroxide acid, iodine and saponification values, unsaponiflable matter, bellier test (turbidity temperature) acetic acid, polenske value conformed by using standard methods Erol et. al. (2008). Deterioration in the vegetable oils is reflected by the decrease in iodine value. Iodine value is used to measure unsaturation or the average number of double bonds in fats and oils. It is defined as the number of grams of iodine that could be added to 100 g of oil, which is measured with the FSSAI.

3. RESULTS AND DISCUSSION

All samples clear transparent liquids, normal free from extraneous matter and rancidity.

The Iodine Value:

The iodine value is an important characteristic of oils as it indicates the proportion of unsaturated fatty acids present. The iodine value difference arises from the differences in fatty acid composition of these oils. Thus about 95% of the fatty acids in coconut oil are saturated. Sunflower oil, about 70% PUFA, has a high iodine number, and soyabean oil, rich in the monounsaturated oleic acid, has a moderately high iodine number. Oxidation of the oils depend on number of double bond, decrease in the number of double bonds less is the iodine value. These low iodine values may have contributed to its greater oxidative storage stability. The oxidative and chemical changes in oils during storage are characterized by an increase in free fatty acid contents and a decrease in the total unsaturation of oils. The observed iodine values for selected six edible vegetable oil are as shown in table 1. The iodine value in palm oil and groundnut oil is higher than standard so these two oils does not conforms as per FSSAI (2015).

Table 1: Determination of Iodine value in selected edible oils

Type of oil	Iodine value	Recommended standards
Palm oil	60.47	46-56
Sunflower oil	124.15	100-145
Coconut oil	7.63	7.5-10
Soyabean oil	131.31	120-141
Mustard oil	108.22	96-112
Ground nut oil	99.77	85-99

The Acid value:

We have seen that the calculated value (observed value) shows deviation from corresponding standard value. The maximum deviation gives the direct consequences of more oxidation of given oil. That means that the given oil is not in a standard form but they have been oxidized. The observed acid values for selected six edible vegetable oil is as shown in table 2.

Table 2: Determination of Acid value in selected edible oils

Type of oil	Acid value (%)	Standards as per FSAS regulations 2011 (%)
Palm oil	1.35	10
Sunflower oil	0.21	6.0 (0.5% for refined oil)
Coconut oil	1.84	6.0
Soyabean oil	0.23	6.0 (0.5% for refined oil)
Mustard oil	0.69	6.0
Ground nut oil	0.34	6.0

The more the deviation in acid value the less the good quality of oil. This contamination of oil may be due to long time storage of the sample in non-evacuated container with less precaution. The result gives bitter taste and pungent smell. If we use such contaminated oil for our daily and domestic, it will cause the illness and take very long time to recover. The acid value is a measure of the amount of fatty acids which have been liberated by hydrolysis from the glycerides due to the action of moisture, temperature and/or lypolytic enzyme lipase.

The Butyro-refractometer readings:

Refractive index of oils increases with the increase in unsaturation and also chain length of fatty acids. The observed BR readings and respective refractive index for edible vegetable oil shown in table 3. It is observed that the butyro-refractometer readings for palm oil, coconut oil and groundnut oil are higher therefore these oil samples does not conforms as per food safety and standard.

Table 3: Determination of **Butyro-refractometer readings and refractive index** of selected edible oils

Type of oil	**Butyro-refractometer**		**Standards as per FSAS regulations 2011**
	reading	Refractive index (nD)	
Palm oil	44.4 at 50^0C	1.4555	35.5 - 44.0
Sunflower oil	60.6 at 40^0C	1.4663	57.1 - 65.0
Coconut oil	35.8 at 40^0C	1.4494	34.0 - 35.5
Soyabean oil	60.8 at 40^0C	1.4494	58.5 - 68.0
Mustard oil	60.5 at 40^0C	1.4492	58.0 - 60.5
Ground nut oil	58.3 at 40^0C	1.4648	54-57.1

The saponification value of edible vegetable oils

Saponification value is an index of average molecular mass of fatty acid in the oil sample. The saponification for the oil samples in following table showed for various edible vegetable oils. The values are below the expected range of standard values as specified by FSSAI regulation 2011 .The lower value of saponification values suggest that the mean molecular weight of fatty acids is lower or that the number of ester bonds is less. The saponification value is an index of mean molecular weight of the fatty acids of glycerides comprising a fat. Lower the saponification value, larger the molecular weight of fatty acids in the glycerides and vice-versa. The observed saponification values for selected six edible vegetable oil is as shown in table 4.

Table 4: Determination of saponification value for selected edible oils

Type of oil	**Saponification value**	**Standards as per regulations 2011**
Palm oil	201.38	195-205
Sunflower oil	192.31	188-194
Coconut oil	254.58	250
Soyabean oil	194.01	189-195
Mustard oil	173.58	168-175
Ground nut oil	190.68	188-196

Unsaponificable value

Many vegetable oils present interest in amounts of carotenoids, phytosterols, tocopherols and phenolic compounds, known as the unsaponifiable matter shown in table 5. Tocopherols have vitamin and antioxidative properties that provide them with food importance. Application of natural antioxidants such as tocopherols has been increasingly growing due to their ability in neutralizing free radicals and carcinogenic effects of synthetic antioxidants. The antioxidant properties and the many health benefits resulting from the use of unsaponifiable matter and its derivatives in foods and health supplements have raised an immense amount of interest in the industry. The unsaponifiable matter is defined as the substances soluble in an oil which after saponification are insoluble in water but soluble in the solvent used for the determination. It includes lipids of natural origin such as sterols, higher aliphatic alcohols, pigments, vitamins and hydrocarbons as well as any foreign organic matter non volatile at 100°C e.g (mineral oil) which may be present. USM content in edible oils were determined 0.56 and 0.62% respectively.

Table 5: Determination of unsaponiflable value for selected edible oils

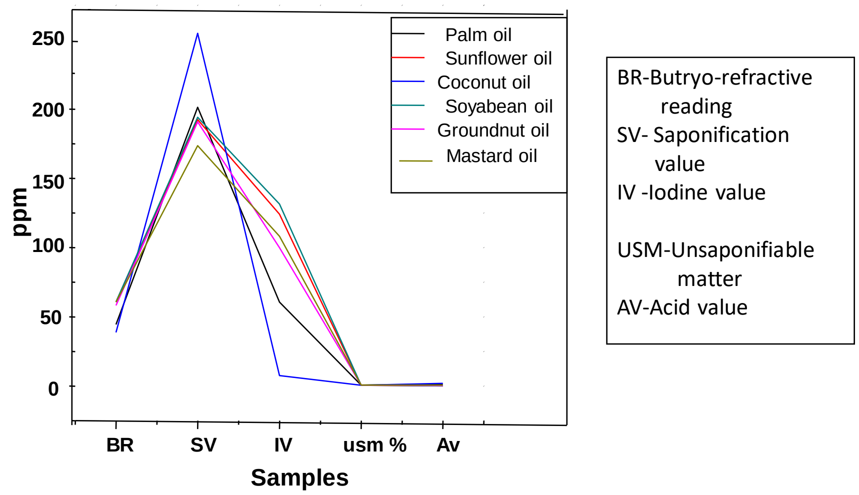
Type of oil	**Unsaponiflable matter (%)**	**Standards as per FSAS regulations 2011 (%)**
Palm oil	0.62	1-2
Sunflower oil	0.59	1.5
Coconut oil	0.56	1.0
Soyabean oil	0.56	2.5
Mustard oil	0.61	1.2
Ground nut oil	0.61	1.0

Bellier Test (Turbidity Temperature – acetic acid method): It is observed that turbidity temperature is higher in mustard oil and lower in groundnut oil were as palm oil result match with literature value. The peroxide value was also found to increase with the storage time, temperature and contact with air of the oil samples The peroxide value determines the extent to which the oil has undergone rancidity. It is observed that Halphen test for groundnut is positive as per standard it should be negative otherwise it is harmful to human health.

Comparative chart and graphically represents physicochemical properties of selected vegetable edible oil is as follows.

Samples	Palm oil	Sunflower oil	Coconut oil	Soyabean oil	Ground nut oil	Mustard oil
BR	44.4	60.6	38.8	60.8	58.3	60.5
SV	201.38	192.31	254.58	194.01	190.68	173.58
IV	60.47	124.15	7.63	131.31	99.77	108.22
usm %	0.62	0.59	0.56	0.56	0.61	0.61
Av	1.35	0.21	1.84	0.23	0.31	0.69

Plot of physicochemical parameters of edible oils



Determination of heavy metals content in six edible oil:

The concentration of heavy metals in vegetable oils is an important criterion for the assessment of oil qualities with regard to freshness, keeping properties, storage and their influence on human nutrition and health. Trace heavy metals in vegetable oil are known to have effect on the rate of oxidation. Among all determined heavy metals, iron was found to be the dominant elemental ion followed by zinc and copper. The FAO/WHO has set a limit for heavy metals intakes based on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intake (PTDI) for copper, zinc, iron and lead are 3 mg, 60 mg, 48 mg and 214 lg g_1,respectively (FAO/WHO 1999).

The minimum and maximum iron levels observed were 0.01 ppm 11.13 ppm mustard oil and coconut oil. The cadmium nickel, lead and manganese levels observed in our oil samples was lower than 0.01 ppm. The percentage of the recommended daily allowance (RDA) for calcium is based on a 1000 mg RDA level for a mature adult.

Health risk assessment of heavy metals in oils and fats.

Copper: Copper is essential for good health but very high intake can cause adverse health problems such as liver and kidney damage. Copper deficiency leads to hypochromic anemia, leucopenia and osteoporosis in children. Minimum and maximum values of copper in our samples were 0.01 and 0.365 ppm in Sunflower oil and mustard oil.

Zinc: Zinc is known to the involved in most metabolic pathways in humans and zinc deficiency can lead to lose of appetite, growth retardation, skin changes and immunological abnormalities. The zinc content of the samples range from 0.01 and 0.973 ppm. Groundnut oil and sunflower oil has lower and palm oil and soyabean oil has higher as compare to others.

Manganese: The Manganese content was lower than 0.01ppm in all oil samples. The deficiency of manganese can produce severe skeletal and reproductive abnormalities in mammals. High doses of manganese produce adverse effect primarily on the lungs and on the brain. The WHO recommended 2-9 mg per day for an adult (World Health Organization, 1994).

Nickel: Trace amounts of nickel may be beneficial as an activator of some enzyme systems, but its toxicity is higher levels is more prominent. The nickel content in all selected oil samples is lower than 0.01ppm.

Cadmium: The cadmium content in all selected oil samples is lower than 0.01ppm. Cadmium is highly toxic metal with a natural occurrence in soil, but it is also spread in the sample during transporting and storage. Excessive cadmium exposure may harmful to human health.

Lead: Lead creates health disorders such as sleeplessness, tiredness, hear and weight loss. WHO has established a provisional tolerable weekly intake for lead of 0.025 $mg.kg^{-1}$ of body weight (World Health Organisation, 1993). The lead content in all selected oil samples is lower than 0.01ppm. Lead is similar to cadmium that has no beneficial role in human metabolism, producing progressive toxicity. Lead creates health disorders such as sleeplessness, tiredness, hear and weight loss.

Iron: The minimum and maximum iron levels observed were 0.01 ppm in sunflower oil and 11.13 ppm in coconut oil. It is known that adequate iron in a diet is very important for decreasing the incidence of anemia. Fe deficiency is frequently associated with anemia and, thus, reduces working capacity and impaired intellectual. High concentrations of iron may lead to tissue damage, as a result of the formation of free radicals.

Intake of elements for food consumption is dependent on the elements concentrations in food and amount of food consumed. In this study, we attempted to evaluate the possible health threats from the consumption of edible vegetable oils from in India.

4. CONCLUSION

The results suggested that significant differences existed in some important test and in some element concentration among different varieties of edible vegetable oil. Groundnut oil, palm oil, coconut shows BR readings and Iodine value higher than standard so this sample is not conform as per food safety and standard. Eight heavy metals (Cu, Zn, Fe, Mn, Cd, Ni, Pb and Ca) in six varieties of edible vegetable oils collected from Mumbai area and determined by Industrial Coupled Plasma atomic emission spectroscopy (ICP-AES) at IIT Bombay. Elements such as Copper, Zinc, Iron, Mn are essential elements since they play an important role in the biological system. The present research may be forwarded in many aspects not only to enhance the quality of oil but also give public awareness not to expose edible oils to high temperatures for long periods many times. So people should choose proper edible oil based on an individual health condition. However, the estimated intakes of Ca,Cu, Zn, Fe, Mn and Ni, from daily consumption of 25 g or weekly consumption of 175 g of the investigated edible vegetable oils should pose no risk to human health.

Acknowledgement: The authors would like to thank the IIT Bombay for providing ICP- AAS for heavy metal and State Public Health Laboratory, Pume for poviding physicochemical parameters. Author also thanks to Principal of KBP College for providing laboratory facilities.

5. REFERENCES

[1]. Nikolaos S. Thomaidis, Constantnos A.Georgiou, (1999) *Edible oil analysis by flow injection,* Laboratory automation and Information Management, 34: 101-114.

[2]. Justyna Gromadzka, Waldemar Wardencki, (2011) *Trends in edible vegetable oils analysis, Part B. Application of different analytical Techniques,* Polish Journal of Food and Nutrition Sciences, 61(2): 89-99.

[3]. Erum Zahir, Rehama Saeed, Mehwish Abdul Hameed, Ajun Yousuf,(2017) *Study of physicochemical properties of edible oil and evalution of frying oil quality by Fourier*

Transform Infrared (FT-IR) spectroscopy, Arabian Journal of Chemistry, 10(2): 53870-53876.

[4]. Aluyor E.O., Ozigaus C.E., Oboh O.I. and Aluyor P., (2009) *Review: chromatographic analysis of vegetable oils*, Scientific Research and Essay, 4(4) 191-193.

[5]. Apostolos Kiritsakis and William W Christie, (2000)*Analysis of edible oils*, Handbook of olive oils 129-158.

[6]. Bewig, K. M., Clarke, A. D., Roberts, C., & Unklwsbay, N. (1994)*Discriminant analysis of vegetable oils by near-infrared reflectance spectroscopy*. Journal of the American Oil Chemists Society, 71.

[7]. Fangkun Zhu,, Wenxiu Fan, Xuejing Wang, Li Qu, Shuwen Yao, (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.

[8]. Anthemidis A.N, Arvanitidis V., Stratis J.A, (2005) *On-line emulsion formation and multi-element analysis of edible oils by inductively coupled plasma atomic emission spectrometry*, Analytica Chimica Acta, 537:271–278.

[9]. Erol Pehlivana, Gulsin Arslan, Fethiye Gode, Turkan Altun and M. Musa Ozcan, Determination of some inorganic metals in edible vegetable oils by inductively coupled plasma atomic emission spectroscopy (ICP-AES), *Grasas Y Aceites*, 59, 3 (2008) 239-244, 2008

[10]. Food safety and standards authority of India, Ministry of health and family welfare Governmentof India, New Delhi, 2015, Table for conversion of B.R. readings to Refractive Index.