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SCREENING OF VARIOUS FRESH AND USED EDIBLE OILS FOR PEROXIDE VALUES USING IODOMETRIC AND ELECTROANALYTICAL METHODS – A COMPARISON

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Abstract

The determination of the peroxide value is the traditional and most used parameter for measuring the primary products of oxidative degradation. Peroxide group that is O-O group is unstable and release oxygen when heated .oxygen reacts with fat molecules to form peroxides in oils. In addition, the analysis of the peroxide content of oil samples is a very analytical task because high peroxide levels in oils have been a threat to human health. The peroxide value is a suitable parameter for measuring the deterioration of quality of edible oils over prolonged heating. A rapid method for the quantitative determination of peroxide value (PV) of fresh and used edible oils by iodometry and colorimetry is described. An attempt was made to show higher peroxide values in used edible oils compared to fresh edible oils by using iodometric titrations,a series of edible oils were taken and analyzed for PV, based on the co-oxidation of Fe(II) to Fe(III) by hydro peroxides from sample (fat) and the formation of the reddish Fe(III)-thiocyanate complex which is read at 500 nm on a colorimeter. Hence the present work suggests the usage of fresh edible oils to prevent rancidity of oils and other side effects.

Key words: peroxide values, iodometric titrations, colorimeter, rancidity

1.INTRODUCTION :

A free radical reaction involving oxygen leads to deterioration of oils which form off- a flavor is an auto oxidation reaction [1]. Peroxide value of oils indicates concentration of peroxides in an oil or fat. It is useful for assessing the extent to which deterioration has advanced. Peroxide value can be used to identify oxidative rancidity in oils. Auto oxidation in oils leads to formation of toxic compounds which are injurious to health , unsaturated oils such as free fatty acids, triglycerides ,phospholipids undergo spontaneous oxidation reaction .They are chain reactions which form lipid hydro peroxides as a primary product .Peroxide value determines primary lipid hydro peroxide .It is usually expressed in mill equivalents (meq). Acceptable limit of PV is ,it should not be above 10–20 meq/kg fat to avoid rancidity flavor [2].Antioxidants in oils minimize auto oxidation reactions[3].Some of the official methods by which PV in oils can be analyzed are AOAC method ,American Oil Chemists Society Method ,Iodometric titrations, Spectrophotometric, colorimetric determination of ferric ions formed by oxidation of ferrous ions by peroxides in presence of xylenol orange also known as ferrous oxidation xylenol orange (FOX) method, International diary federation method (IDF), number of techniques based on chromatography NMR spectroscopy also have been developed for determination of lipid peroxides. The present study is based on IDF method using colorimeter .This method is similar to MFOX method. IDF method uses simple

chemicals, the method was found to be reliable and rapid.IDF method is sensitive requires less sample. It can be used as spot test for peroxide value in oils. A reproducible alternative assay to electro analytical IDF method is conventional iodometric titration.

2. METHODOLOGY

2.1 MATERIALS AND METHODS

Groundnut oil, sesame oil, castor oil, olive oil, sunflower oil, rice bran oil, cow ghee, buffalo ghee, vanaspathi and coconut oil were purchased from local grocery. All the oils were stored at room temperature (25^{o}c) under light and atmospheric conditions. All the chemicals and reagents (analytical grade) used were from Merck (Darmstadt, Germany), or SigmaAldrich Chemical Co. (St. Louis, MO), unless stated otherwise.

2.2 DETERMINATION OF PEROXIDE VALUE – IDF METHOD

IDF modified method for determination of PV. The proposed method was developed as a modification of the IDF standard method that is based on the co-oxidation of Fe (II) to Fe (III) by hydroperoxides and the formation of the reddish Fe (III)-Thiocyanate complex for colorimetric determination of PV.

$$Fe^{2+} + ROOH \rightarrow OH^{-} + Fe^{3+} + RO$$

To quantify the PV, the sample (200mg) was placed in a boiling tube and dissolved in 1 mL of chloroform/acetic acid (3:7), added 50µL Fe (II) solution and added 50µL of saturated ammonium thiocyanate solution to the sample. After 3 min, absorbance at 510nm was measured against a chloroform and acetic acid mixture as blank.

A reaction blank containing all the reagents, except the sample, was also performed, and the resulting absorbance value was subtracted from that of the sample.

Fe(II) stock solution was prepared by gently mixing a solution of 0.4 g of $BaCl_2.2H_2O$ in 50 mL deionized water with a solution of 0.5 g of $FeSO_4 \cdot 7H_2O$ in 50 mL deionized water. Concentrated hydrochloride acid (2 mL) was added to the resulting solution, which was filtered and stored under cover. It is strongly recommended to prepare this solution as fresh as possible and check its stage before use by addition of a few drops of thiocyanate solution. Solution should be discarded ifa pale pink color appears.

2.3 Fe (III) CALIBRATION

A working solution of Fe (III) 25µg/mL was prepared from a standard stock solution [20mgFe (III)/mL with 10NHCl by dilution with chloroform/acetic acid (3:7). For calibration, aset of solutions of increasing Fe (III) concentration in the range (1-25) µg/mL with 50µL of saturated ammonium thiocyanate was prepared by successive dilutions of the working solution.. The calibration curve was obtained by plotting absorbance (Abs nm) vs. Fe (III) concentration. Peroxide value was calculated by using the following equation:

$$PV\ (meq/kg) = \{\frac{(As - Ab) \times m}{55.84 \times mo \times 2}\} \times 0.5$$

WhereA_s is Absorbance of the sample
A_b is Absorbance of the blank
m is the slope, obtained from calibration curve
m_o is the mass in grams of the sample
55.84 is atomic weight of Iron
0.5 is the correction factor
The denominator gives the concentration of Fe^{+2} oxidized to Fe^{+3} in micrograms. The division by factor 2 is necessary to express the peroxide value as mill equivalents of oxygen, as mentioned in the IDF method [4].

2.4 DETERMINATION OF PEROXIDE VALUE – IODOMETRY

Peroxide values various fresh and used edible oils was carried out using the method described by Pearson (1981) and Ranken (1988). Unless otherwise directed.

The peroxide value method is referenced in both the American Oil's Chemist Society (AOCS) and the Association of Analytical Chemists (AOAC) as methods 965.33 (AOAC) or Cd-8b (AOCS).The principle behind the method involves measurement of iodine liberated from potassium iodide by a peroxide present in oil sample, where sodium thiosulfate solution used as the titrant. In the presence of acetic acid. Mechanism in procedure is represented as below.

Step – 1 Peroxide + KI + $H^+ \rightarrow I_2$
Step – 2 I_2 (purple) + $2Na_2S_2O_3 \rightarrow Na_2S_4O_6$ + 2NaI

Peroxide value of both fresh and used oil is calculated using the equation below:

$$\text{Peroxide value} = \frac{2(a-b)}{\text{Weight of oil sample used}}$$

Where a = sample titre value b = blank titre value

2.5 DETERMINATION OF SMOKE POINT IN ^{O}CELSIUS

Smoke point indicates the temperature limit up to which oil can be used. Beyond smoke point oils start liberating harmful free radicals .smoke point of various selected oils was determined in open lab with lots of fresh air flow. About 150ml of oil was taken in a beaker and heated until it starts giving out smoke; it is considered as smoke point. Smoke point was noted using digital thermometer.

3 RESULTS&DISCUSSION

In the present study, colorimetric technique and iodometric methods were used for the qualitative and quantitative evaluations of peroxide values of various edible oils. Lot of nutrients is destroyed when oils reach their smoke point. Oils with low smoke point are not suitable for high temperature cooking. IDF method is based on the oxidation of Fe^{+3} ions in the presence of Ammonium thiocyanate .R-O-O-R of peroxide oxidizes Fe^{2+} ions to Fe^{+3} ions. The Fe^{3+} ions resulting from oxidation are grouped and form a red complex. Its colorimetric intensity, measured at 510 nm, is directly proportional to the concentration of peroxide value in the sample. In iodometry, peroxides of oils liberate iodine in presence of KI, liberated iodine is titrated against hypo solution. The amount of peroxide value of fats indicates the degree of primary oxidation and therefore its likeliness of becoming rancid. A lower number of peroxide values indicate a good quality of oil and a good preservation status [5].

A calibration curve (Figure 1) for 2-25µg/ml Fe^{+3} were prepared by using 50µl ammonium thiocyanate as indicated in the method and curve was linear.

The amount of peroxides was established in different fresh oils and ranged from 0.689Meq/kg (coconut oil) to 3.25 Meq/kg (Vanaspathi) by IDF method and 1.2 Meq/kg (coconut oil) to 4.3 Meq/kg (Vanaspathi) by iodometry were listed in Table I. It can be observed that highest and lowest peroxide values were measured with vanaspathi and coconut oil respectively. It can be observed that peroxide value is lowest in coconut oil when compared to other oils. Table-1 shows PV of fresh oils are lower than reused edible oils.

Table.1.smoke point (^{O}C) and Peroxide values (Meq/Kg) **of various edible oils**

S.No	Name of oil sample	Peroxide value of fresh oil by IDF Method(Meq/kg)	Peroxide value of used oil by IDF Method(Meq/kg)	Peroxide value of fresh oil by iodometry(Meq/kg)	Peroxide value of used oil by iodometry(Meq/kg)	Smoke point (^{O}C)
1	Ground nut oil	1.7	1.9	1.6	1.8	225
2	Sunflower oil	3.18	3.21	2.0	2.5	232
3	Coconut oil	0.689	0.702	1.2	1.2	205
4	Sesameoil	2.916	3.12	2.2	2.5	202
5	Rice bran oil	2.903	3.05	1.7	2.6	232
6	Castor Oil	2.28	2.32	2.0	2.8	200
7	Olive Oil	1.49	1.63	1.5	1.8	192
8	Vanaspathi/ Hydrogenated vegetable Oil	3.25	3.81	3.5	4.3	212
9	Buffalo Ghee	1.055	1.90	0.5	3.0	198
10	Cow Ghee	3.14	3.54	0.6	1.8	192

Figure-1 Standard $Fe^{(+3)}$ curve for determination of peroxide values by IDF method

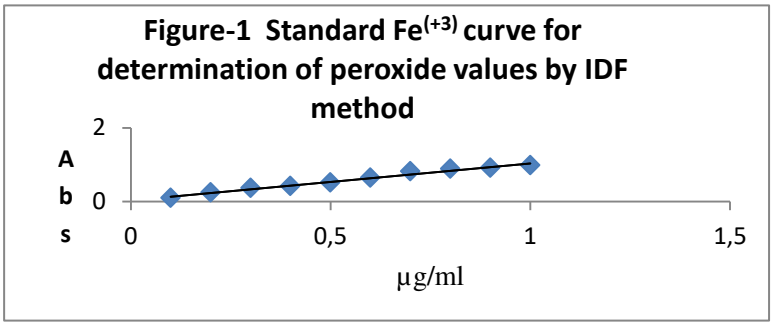


Figure-2 Plot of peroxide value of fresh oils verses peroxide values of reused oils by IDF method

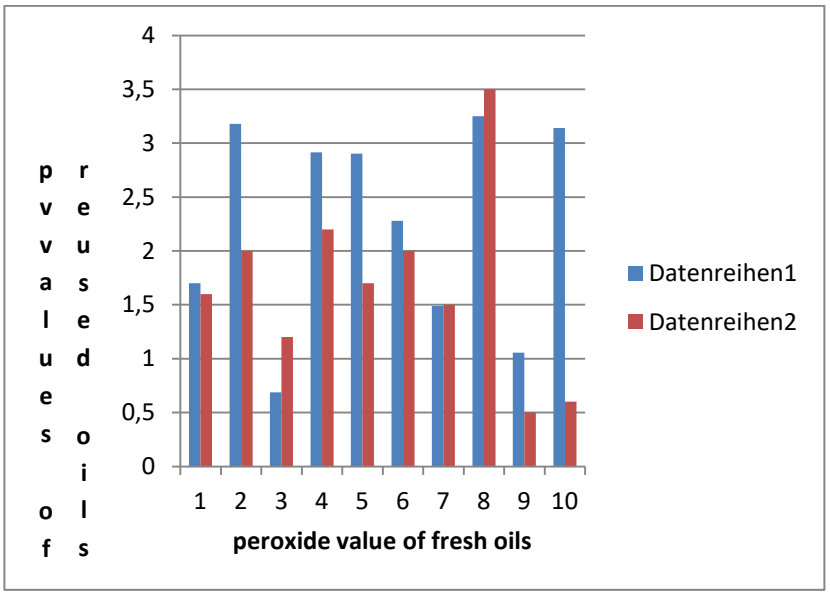
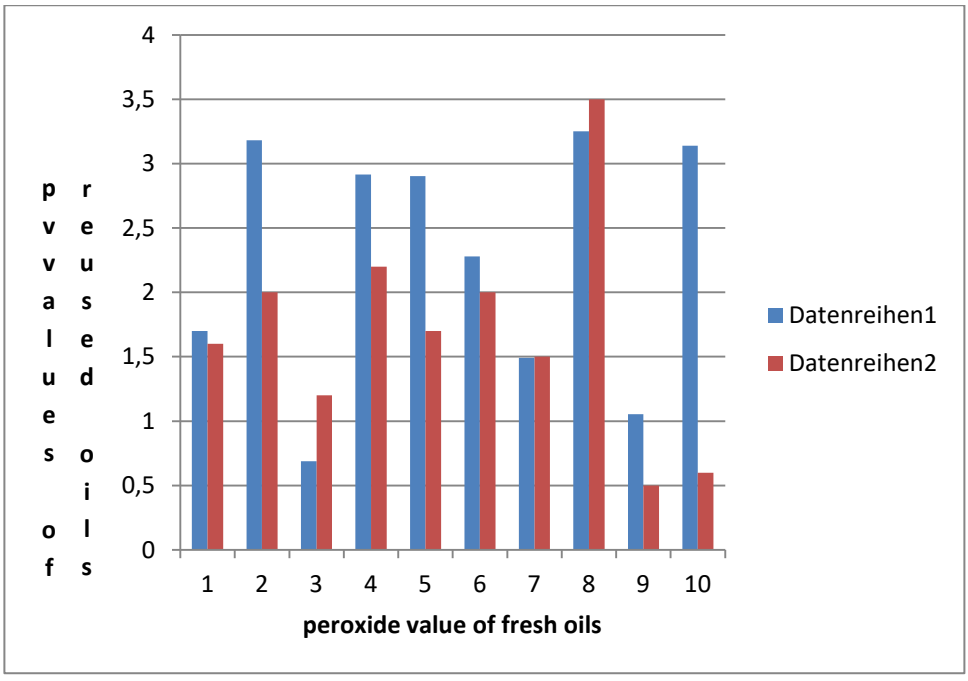


Figure-3 Plot of peroxide value of fresh oils verses peroxide values of reused oils by Iodometry method



4 CONCLUSION

Oils behave differently when they are heated. The important indicator for performance and shelf life of oils is their oxidation [6]. It is complex and depends on the light intensity and temperature. Initially oxidation in oils involves formation of hydro peroxides, peroxides, and then polymers of peroxides [7]. The reproducible alternative method for iodometry is IDF method using colorimeter. Iodometric titration is the traditional method of establishing the PV .It is one of the most developed method providing absolute quantification of LOOH .oil forms potentially harmful compounds when it reaches its smoking point. the present study highlights smoke points of oils considered. PV is applicable for monitoring the formation of peroxides in the early stages of oxidation. Peroxide values of fresh edible oils are in the order coconut oil<rice bran oil < sesame oil<cow ghee<sunflower oil<castor oil <groundnut oil<buffalo ghee<olive oil < vanaspati. This order indicates rancidity or deterioration in oils .Oils containing monounsaturated fats minimize artery blockage, supports the health of brain, heart and other organs and minimizes risk of diet-related ailments. Sunflower oil,groundnut oil , ricebran oils have good combination of monounsaturated and polyunsaturated fats. These oils have high smoke point which means they hold onto their nutritional content at high temperatures so,they can be widely used in deep frying.olive oil is used in breakfast ,pastas,and salads.Coconut oils are rich in monounsaturated fat [8] which helps to reduce cholesterol and triglyceride levels. The “Ceylon Medical Journal” notes that coconut fats do not contain artery-clogging Transfats, making coconut oil a healthy choice for those with heart problems

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