DETERMINATION OF PEROXIDE VALUE

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INTRODUCTION

Unsaturated fish oils are particularly susceptible to oxidation, developing peroxides under poor cold-storage or frozen storage conditions. Peroxides are the precursors of breakdown products that cause rancid flavours in fat. The concentration of peroxides is indicative of oxidation during the early stages of lipid deterioration. This index becomes less reliable during the later stage of deterioration, because peroxide degradation increases.

The peroxide value (POV) is defined as the reactive oxygen contents expressed in terms of milliequivalents (meq) of free iodine per kilogramme of fat. It is determined by titrating iodine liberated from potassium iodide with sodium thiosulphate solution.

Oils with POV well below 10 meq/kg are considered fresh. A rancid taste begins to be noticeable when the POV is between 20 and 40 meq/kg. In interpreting such figures, however, it is necessary to take into account the particular oil or fat involved.

APPARATUS

1. Evaporating flasks with stoppers (250 ml capacity)
2. Rotary evaporator with vacuum pump
3. Pipettes (1 ml, 5 ml, 10 ml, 20 ml)
4. Measuring cylinders (25 ml, 100 ml)
5. Stop watches
6. Microburette (2 ml)
7. Burette (50 ml)
8. Erlenmeyer flasks (100 ml, 200 ml) with stoppers
9. Balance with at least 0.1 g sensitivity

REAGENTS

1. 0.01N $Na_2S_2O_3$ solution

   Dissolve 25 g of $Na_2S_2O_3.5H_2O$ in freshly boiled distilled water and make up to 1000 ml. Stand for 2-3 days. Add 10 ml of iso-amylalcohol as stabilizer. When required, dilute 10 times with freshly boiled distilled water. Keep in a dark brown bottle.

Standardization of the $Na_2S_2O_3$ Solution

1. Take 20 ml of 0.01N $K_2Cr_2O_7$ solution in a 250 ml flask with stopper.

2. Add 10 ml of 10% KI solution and 5 ml of 25% H_2SO_4.

3. Immediately stopper the flask and stand for 5 min in the dark.

4. Add 100 ml of distilled water and shake.

5. Titrate with 0.01N $Na_2S_2O_3$ solution until yellow colour almost disappears.

6. Add 1 ml of 1.5% starch solution as indicator, and continue the titration until dark blue colour disappears.

7. Carry out blank test by using 20 ml of distilled water instead of $K_2Cr_2O_7$ solution.

8. Calculation:

$$F = \frac{20 \times F'}{V_s - V_b}$$

where F = factor of 0.01N $Na_2S_3O_3$ solution

F' = factor of 0.01N $K_2Cr_2O_7$ solution

V_s = titration volume of sample (ml)

V_b = titration volume of blank (ml)

2. Chloroform-acetic acid mixture (2:3).

Mix $CHCl_3$ and CH_3COOH, 2:3 by volume. Flush with pure, dry nitrogen gas.

3. Saturated KI solution

Dissolve 100 g KI in 70 ml freshly boiled distilled water. Keep the solution with precipitated crystals in a dark brown bottle.

4. 1.5% starch solution

Weigh 1.5 g of soluble starch in a beaker. Add 100 ml of distilled water. Heat and boil for 30 sec.

5. 0.01N $K_2Cr_2O_7$ standard solution

   Weigh 4.9035 g of $K_2Cr_2O_7$ which had been dried at 100 - 110°C for 3 - 4 hr. Dissolve it in distilled water and make up to 1000 ml. When required, dilute 10 times with distilled water.

   $$\text{Factor } F' = \frac{4.9035}{W}$$

   where W is the actual weight of $K_2Cr_2O_7$ used.

6. 10% (w/v) KI solution

   Dissolve 10 g of KI in distilled water and make up to 100 ml.

7. 25% H_2SO_4 solution

   Mix 25 g (13.5 ml) of concentrated H_2SO_4 and 75 ml of distilled water.

PROCEDURE

1. Take about 0.3 g of fat sample or A ml of the extract containing about 0.3 g of fat into a 250 ml flask with stopper.
2. Remove solvent using rotary evaporator under reduced pressure at 40°C (water-bath temperature).
3. Add 10 ml of $CHCl_3$-CH_3COOH mixture and dissolve the fats by shaking.
4. Add 1 ml of saturated KI solution.
5. Immediately stopper and stand in the dark for 5 min.
6. Add 20 ml of distilled water, then shake.
7. Titrate the liberated iodine with 0.01N $Na_2S_2O_3$ solution until light yellow colour. Add 1 ml of 1.5% starch solution as indicator and titrate till colourless.
8. Carry out blank test in the same manner without fats.

CALCULATION

$$\text{POV (meq per 1000 g)} = \frac{(V_s - V_b) \times F \times N \times 1000}{W} \times \frac{(V_s - V_b) \times F \times 1000}{W \times 100}$$

$$= \frac{(V_s - V_b) \times F \times 10}{W}$$

where V_s = titration volume of sample (ml);

V_b = titration volume of blank (ml);

F = factor of 0.01N $Na_2S_2O_3$ solution;

W = weight of fat in volume of extract used (g);

N = normality of $Na_2S_2O_3$ solution (in this case N/100)

$$\text{POV (millimoles per 1000 g)} = \frac{0.5 \times (V_s - V_b) \times N \times 1000}{W}$$

REFERENCES

Japanese Association of Oil Chemists: Standard methods of oil analysis in Japan, (1972) 2(4): 12-71.

Pearson, D. (1976). The chemical analysis of foods (7th Ed.): 494-495.