IAFMM FISH OIL BULLETIN

international association of fish meal manufacturers

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RECOMMENDED METHOD OF ANALYSIS FOR DETERMINATION OF IODINE VALUE OF FISH OILS (WIJS METHOD)

1. General

The iodine value is a measure of the unsaturation of fats and oils and hence of their potential to become oxidized. Iodine values are expressed in terms of the number of grams of iodine absorbed per 100g of sample (% iodine absorbed).

2. Principle

The oil is treated with an excess of iodine monochloride in solution in acetic acid. The amount of iodine absorbed is determined by back-titration with standard sodium thiosulphate solution.

3. Reagents

All reagents shall be of analytical reagent quality unless stated otherwise.

Distilled water, or water of equivalent purity at least, shall be used.

Glacial acetic acid.

Potassium iodide solution (prepared by dissolving 150g in water and diluting to 1 litre).

Carbon tetrachloride.

Starch indicator solution (prepared by making a homogeneous paste of 10g of soluble starch in cold distilled water and adding it to 1 litre of boiling water with stirring; Salicylic acid, 1.25g, is added as a preservative and the solution kept in a refrigerator at 4° to 10°C).

Standard thiosulphate solution, approximately 0.1N (prepared by dissolving 24.8g of $Na_2S_2O_3$, $5H_2O$ in water and diluting to 1 litre; the solution is standardized by titrating against acidified standard dichromate solution, Note A).

Wijs solution (this can be purchased or prepared according to Note B).

4. Apparatus

Glass stoppered, wide mouth bottles or Erlenmeyer flasks (500ml). All glassware used must be clean and dry.

Mechanical or magnetic stirrers.

5. Method

The sample is melted, if it is not already liquid, and filtered to remove any impurities and the last traces of moisture. The temperature should not exceed 150°C above the melting point.

A portion of the sample is weighed accurately (to 0.2mg) in a small glass container which is then placed in the 500ml flask or bottle to which 20ml of CCl_4 has been added. The weight of sample must be such that there will be an adequate excess of iodine in the amount of Wijs solution used and can be calculated as

$$\frac{26}{\text{Expected Iodine Value}} \text{ g}$$

For most fish oils, 0.1g is a suitable weight of sample to take. Wijs solution, 25ml, is added with swirling to the flask which is then stored in the dark for 30 min at 20° to 30°C. After incubation, 20ml KI solution followed by 100ml of recently boiled and cooled water is added. The solution is titrated, with 0.1N thiosulphate solution, gradually and with constant stirring. The titration is continued until the yellow colour has almost disappeared; 1 to 2ml starch indicator solution is then added and the titration continued until the blue colour has just disappeared.

6. Blank test

At least two blank determinations are carried out simultaneously with each group of samples. The same procedure and the same reagents are used, only the oil is omitted.

7. Calculation

Calculate the iodine value, expressed as grams of iodine absorbed per 100g sample by means of the formula

$$\frac{(B-S) \times N \times 12.69}{\text{Weight of sample(g)}}$$

in which

B = titration of blank (ml) and

S = titration of sample (ml)

N = normality of thiosulphate solution.

Express the result to the nearest whole unit.

8. Repeatability

The difference between the results of two determinations carried out simultaneously or in rapid succession by the same analyst should not differ by more than 14g iodine/100g sample.

NOTES

A. Standardization of thiosulphate solution:

Finely ground and dried (110°C) potassium dichromate (4.9035g) is dissolved in water and the volume adjusted to 1000ml at 25°C to make a 0.1N solution. A 25ml portion is pipetted into an Erlenmeyer flask, 5ml of concentrated hydrochloric acid and 10ml of 15% potassium iodide solution are added with mixing. The mixture is allowed to stand for 5 min, 100ml of water is then added and the mixture titrated with the thiosulphate solution, stirring continuously, until the yellow colour has almost disappeared. Starch indicator solution, 1 to 2ml, is added and the titration continued until the blue colour has just disappeared. The strength of the thiosulphate solution is expressed in terms of its normality.

$$\text{Normality of thiosulphate solution} = \frac{2.5}{\text{Volume (ml) of thiosulphate solution required}}$$

B. Preparation of Wijs solution:

Dissolve 26g of sublimated iodine in 200ml of glacial acetic acid, heat gently and then cool. In a 300ml Erlenmeyer flask put 20ml of potassium iodide solution and 100ml of distilled water and then add 20ml of the iodine solution, measured to the nearest 0.1ml, by means of a burette. Iodine is titrated with the 0.1N sodium thiosulphate solution, using a starch solution as an indicator. Separate approximately 60ml of the iodine solution; pass a dry chlorine current through the remaining quantity until the solution begins to clarify. 20ml of this solution are titrated to measure total halogen content. Sufficient chlorine must be added in order to have an I/Cl ration of 1:1 but not less; this is verified by evaluating 20ml portions of the solution after each addition of chlorine.
Finally, add the separated 60ml and then mix carefully.

The procedure for determining this halogen ratio is as follows:

Iodine content: Wijs solution (5ml) is pipetted into a 500ml Erlenmeyer flask containing 150ml of saturated chlorine water and some glass beads. The solution is shaken, boiled briskly for 10 min and cooled. Dilute sulphuric acid (30ml, 2%) and potassium iodide solution (15ml, 15%) are added and the mixture titrated with standard thiosulphate solution to a starch end-point.

Total halogen content: Wijs solution (20ml) is pipetted into a 500ml Erlenmeyer flask containing 150ml recently boiled and cooled water. Potassium iodide solution (15ml, 15%) is added and the mixture titrated immediately with standard thiosulphate solution as above.

$$\text{I/Cl ratio} = \frac{2I}{3H-2I}$$

where I = ml thiosulphate solution required for iodine content and

H = ml thiosulphate solution require for total halogen content.

An alternative method for preparing Wijs solution is as follows:

8g Iodine trichloride ICl_3 (British Drug House or equivalent)

9g Iodine I_2

300ml Carbon tetrachloride CCl_4

Glacial acetic acid

Dissolve the ICl_3 in glacial acetic acid, dissolve the iodine in carbon tetrachloride, mix the solutions and make up to 1000ml with glacial acetic acid.

All Wijs solutions are sensitive to temperature, moisture, and light. Store them in a cool and dark place and never allow them to come to a temperature much above 30°C.