Determination of Iodine Value Without Chlorinated Solvents

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ABSTRACT: A modified determination of iodine value in fats, fatty acids, and fatty acid derivatives is reported. The described procedures, visual and potentiometric, have wide applicability and generate less solvent waste. These analytical procedures are based on a nonchlorinated solvent system. The performance of the new procedures was evaluated in a multiple-laboratory study.

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KEY WORDS: Iodine value, nonchlorinated solvent, potentiometric, titration, visual.

In the past decade, inevitably due to the Montreal Protocol (1) and reported ozone depletion in the stratosphere (2), the use of chlorinated solvents in industrial plants and commercial products has steadily declined. Although the major reduction has come from reduced industrial usage and reformulations, laboratory use of chlorinated solvents was also targeted to decline. In quality control laboratories, where a large number of samples are routinely analyzed, such a reduction becomes both important and necessary. The problems with the use of these solvents in analytical laboratories are twofold—one is operator exposure, and the other covers their disposal. The latter, especially, is costly, and the chore of segregation from other laboratory wastes is labor-intensive.

Determinations of iodine value (IV) in fatty acids and their derivatives are routinely performed in practically every quality control laboratory dealing with oleochemicals. In general, chlorinated solvents (chloroform, carbon tetrachloride, or methylene chloride) make up about 25% of the solvents used in a typical IV determination.

The Wijs (3) method for IV determination has been the industry standard for many decades. In recent years, various modifications of the method (4) have also been introduced. None of the methods, however, cover the range of IV (0.5–120) or are applicable to the wide range of compounds associated with oleochemicals.

In this paper, a modified Wijs method of analysis is described which is suitable for a broad range of oleochemicals with varied unsaturation. The method eliminates use of chlorinated solvent and catalyst (mercuric acetate), and lowers the total solvent and reagent volume used by about 35%. Table 1 compares the solvents and reagents used in a typical method and the one described in this paper.

TABLE 1
A Comparison of the Volume of Reagents and Solvents Used in a Typical Determination of Iodine Value (IV) and the One Described in This Paper

Solvents/reagents	A typical IV method (mL)	Modified method (mL)
Acetic acid	20	20
Wijs solution[a]	25	25
KI (aqueous)	20 (6%)	6 (33%)
Chloroform	25	none
Water	50	none
Cyclohexane	none	20
IPA	none	25
Total	145	96

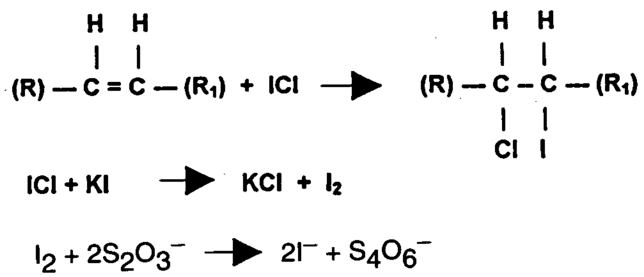
[a]Wijs solution is an acetic solution of iodine monochloride; IPA, isopropyl alcohol.

EXPERIMENTAL PROCEDURES

The modified IV method is presented in two versions or procedures. One utilizes a visual end-point detection, and the other is applicable to a potentiometric titration.

The Wijs classical reaction is shown in Scheme 1. In practice, a sample is first reacted with an excess amount of iodine monochloride (Wijs solution), then the remaining iodine monochloride is reacted with potassium iodide. Finally, liberated iodine is titrated with sodium thiosulfate.

Materials. All solvents and reagents are of analytical grade. The samples analyzed are commercially available Akzo Nobel (Dobbs Ferry, NY) products or their precursors.



$$(R)-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-(R_1) + ICl \longrightarrow (R)-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{I}{|}}{\overset{\overset{H}{|}}{C}}-(R_1)$$

$$ICl + KI \longrightarrow KCl + I_2$$

$$I_2 + 2S_2O_3^- \longrightarrow 2I^- + S_4O_6^-$$

SCHEME 1

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Reagents. The temperature is maintained below 30°C in the preparation of 0.2 N iodine monochloride (Wijs solution) in acetic acid. Potassium iodide solution is prepared by dissolving 100 g KI in 200 mL deionized water. The titrant, 0.1 N potassium thiosulfate solution, is properly standardized with potassium dichromate.

In visual titration, starch indicator solution (10 g/L) is prepared by making a homogeneous paste of 5 g of soluble starch in cold distilled water; 500 mL boiling distilled water is added; the solution is stirred rapidly and then cooled to room temperature. For preservation of the indicator, 0.65 g of salicylic acid is added to the starch solution.

Titration instrument. In potentiometric titration, an automatic titrator, similar to a Brinkmann Model 716 Titrino (Brinkmann Instruments, Westbury, NY), equipped with a double-junction platinum electrode (Brinkmann model 6.0415.100), is used. In this procedure, a four-ounce, wide-mouth glass jar with a Teflon-lined cap is recommended.

Procedure 1—Visual titration. An appropriate amount of sample (expected IV of 1–5, 5–10, 10–30, 30–50, and 50–100; with corresponding sample weights of 3–8, 1–5, 0.3–1.0, 0.2–0.3, and 0.1–0.2 g, respectively) is weighed to within 0.1 mg into a 250-mL Erlenmeyer flask. The sample is dissolved in 20 mL acetic acid, warming slightly if necessary. The solution is allowed to cool to 25 ± 5°C. Wijs solution (25.00 mL) is pipetted into the flask, which is then stoppered. The flask is stored in a dark place for 30 min at 25 ± 5°C and swirled occasionally. After the 30-min reaction period and while stirring, 6.0 mL of potassium iodide solution, 20 mL cyclohexane, and 20 mL isopropyl alcohol are added. The solution is titrated with 0.1 N sodium thiosulfate solution until a slightly yellow color appears; 1–2 mL starch indicator solution is added, and titration is continued until the blue color has disappeared. The final color change is from yellow to white or, if the sample itself is not colorless, to off-white. After the starch solution is added, additions of thiosulfate should be followed by a 10–30-s waiting period. This is due to a slight "lag" in the color change at this point in the titration. A blank titration is also carried out at the same time in the same manner.

Procedure 2—potentiometric titration. The sample preparation is similar to procedure 1 with the following two exceptions: A four-ounce, wide-mouth glass jar with a Teflon-lined cap is used in place of a 250-mL Erlenmeyer flask, and the jar should be fitted with some type of tight-fitting cover, such as a piece of parafilm with holes to accept the electrode and dispenser tip during titration, fitted over the lip of the jar. After 30 min of reaction time, an additional 6 mL potassium iodide solution is added. Then, while stirring, 20 mL cyclohexane and 25 mL isopropyl alcohol are added. The solution is titrated potentiometrically with sodium thiosulfate solution using a double-junction platinum electrode. Similar to visual titration, a blank titration is also carried out at the same time in the same manner. Figure 1 shows a typical potentiometric titration curve.

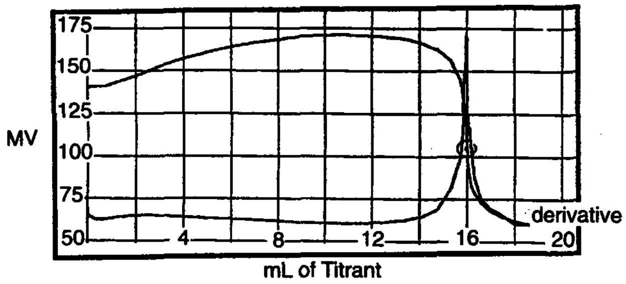

FIG. 1. A typical titration graph and its first derivative for potentiometric iodine value method; MV, millivolts.

Calculations. $IV = [(V_1 - V_2) \times N \times 12.69] \div W$ where IV = IV in centigrams of iodine per gram of sample, V_1 = mL of thiosulfate solution to titrate the blank, V_2 = mL of thiosulfate solution to titrate the sample, N = normality of the sodium thiosulfate solution, W = sample weight in grams, and 12.69 = iodine atomic weight/10.

RESULTS AND DISCUSSION

An internal round-robin test of these methods was conducted. The visual "chlorinated" IV method (5) was used as reference. Laboratories at three sites (two quality control and one research) participated in this study. Ten samples from Akzo Nobel's line of commercial products or their feedstocks were selected for the round-robin test. The samples were dodecyl amine (Armeen® 12), tallow amine (Armeen® T), oleyl amine (Armeen® OL), oleyl diamine (Duomeen® OL), tallow amine acetate salt (Armac® T), dihydrogenated tallow dimethyl quaternary ammonium chloride salt (Arquad® 2HT-75), oleyl amide (Armoslip® CP), fatty acid (Neofat® 9004), coconut oil (triglycerides), and soya triglyceride.

The suggested reaction time in all of these methods was 30 min. To address the time constraints in quality control laboratories without the use of any catalyst, a 10-min reaction time for the potentiometric method was also included.

The bar graphs with accompanying statistical summary of each sample are shown in Figures 2–7. Each bar graph is a comparison of four IV methods (1, nonchlorinated visual; 2 and 3, nonchlorinated potentiometric with 10- and 30-min reaction time, respectively; and 4, chlorinated visual IV method). Each IV is an average value calculated from the three sites, except for the 10-min reaction time, which only includes quality control laboratories' values. The statistical summary includes overall maximum and minimum IV, the overall average, average value for chlorinated, and nonchlorinated visual and potentiometric methods, standard deviation (P indicates total population rather than n-1), and percent relative error.

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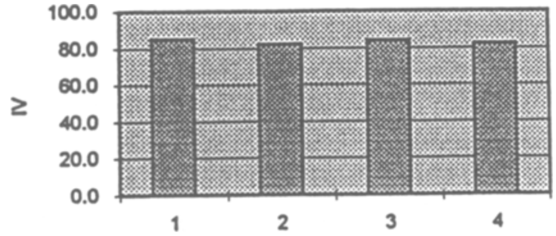


FIG. 2. A comparison of the nonchlorinated and chlorinated (Cl) iodine value (IV) methods for fatty acids. 1 = visual IV average; 2 = potentiometric IV at 10 min; 3 = potentiometric IV at 30 min; and 4 = Cl–IV. Statistical summary: Overall IV: maximum IV, 85.2; minimum IV, 82.1; difference, 3.0; average, 83.4; SD (*P*), 1.2; and % relative error, 1.5%. Individual averages: Cl–IV, 82.3; average nonCl visual, 85.2; average nonCl potentiometric, 83.0; average nonCl IV, 83.7; SD (*P*) nonCl IV, 1.2; and % relative error nonCl IV, 1.5%

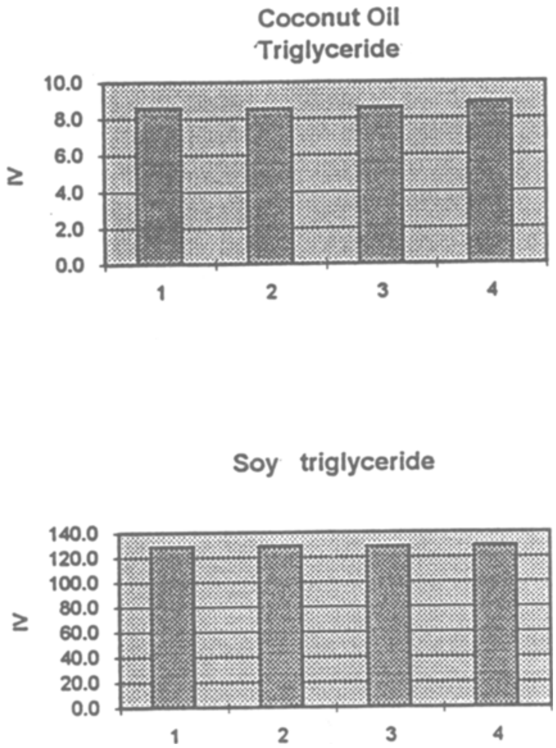


FIG. 3. A comparison of the nonchlorinated and chlorinated (Cl) iodine value (IV) methods for triglycerides; 1 = visual IV average; 2 = potentiometric IV at 10 min; 3 = potentiometric IV at 30 min; and 4 = Cl–IV. Statistical summary for coconut oil: Overall IV: maximum IV, 8.9; minimum IV, 8.5; difference, 0.4; average, 8.7; SD (*P*), 0.1; and % relative error, 1.6%. Individual averages: Cl–IV, 8.90; average nonCl visual, 8.61; average nonCl potentiometric, 8.56; average nonCl IV, 8.58; SD (*P*) nonCl IV, 0.04; and % relative error nonCl IV, 0.45%. Statistical summary for soy triglyceride: Overall IV: maximum IV, 129.2; minimum IV, 128.3; difference, 0.9; average, 128.8; SD (*P*), 0.3; and % relative error, 0.3%. Individual averages: Cl–IV, 129.2; average nonCl visual, 128.7; average nonCl potentiometric, 128.7; average nonCl IV, 128.7; SD (*P*) nonCl IV, 0.3; and % relative error nonCl IV, 0.2%.

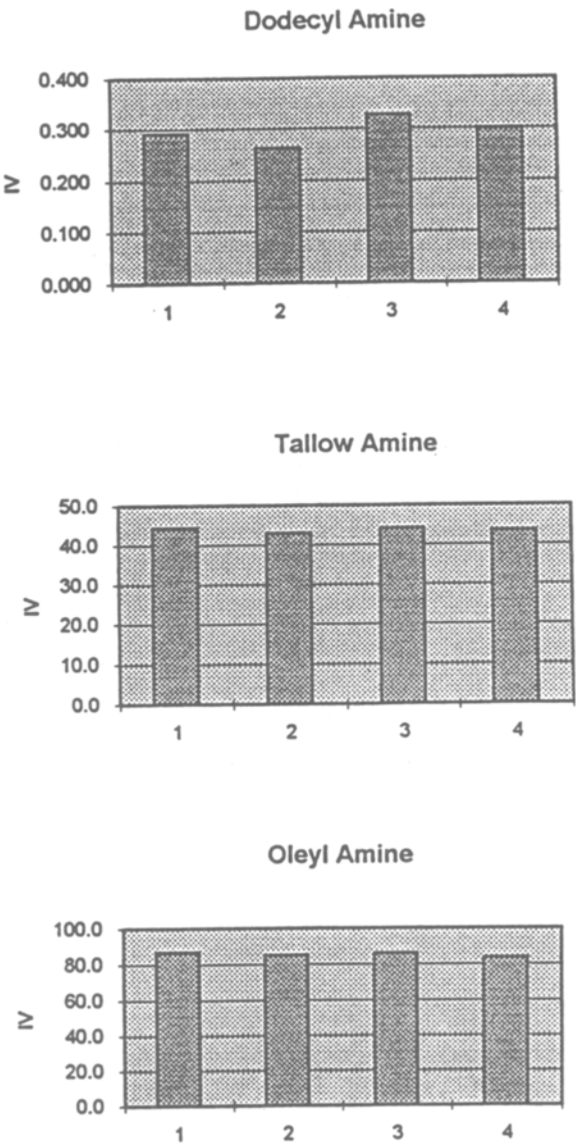
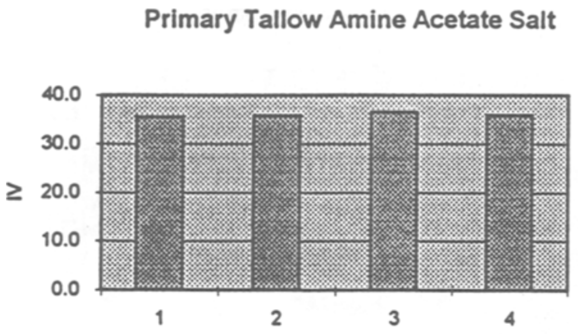


FIG. 4. A comparison of the nonchlorinated and chlorinated (Cl) iodine value (IV) methods for primary amines; 1 = visual IV average; 2 = potentiometric IV at 10 min; 3 = potentiometric IV at 30 min; and 4 = Cl–IV. Statistical summary for dodecyl amine: Overall IV: maximum IV, 0.33; minimum IV, 0.26; difference, 0.07; average, 0.30; SD (*P*), 0.02; and % relative error, 7.85%. Individual averages: Cl–IV, 0.30; average nonCl visual, 0.29; average nonCl potentiometric, 0.30; average nonCl IV, 0.29; SD (*P*) nonCl IV, 0.03; and % relative error nonCl IV, 9.05%. Statistical summary for tallow amine: Overall IV: maximum IV, 44.6; minimum IV, 43.0; difference, 1.6; average, 43.8; SD (*P*), 0.6; and % relative error, 1.4%. Individual averages: Cl–IV, 43.5; average nonCl visual, 44.6; average nonCl potentiometric, 43.6; average nonCl IV, 43.9; SD (*P*) nonCl IV, 0.7; and % relative error nonCl IV, 1.5%. Statistical summary for oleyl amine: Overall IV: maximum IV, 87.0; minimum IV, 83.6; difference, 3.4; average, 85.5; SD (*P*), 1.3; and % relative error, 1.5%. Individual averages: Cl–IV, 83.6; average nonCl visual, 87.0; average nonCl potentiometric, 85.7; average nonCl IV, 86.1; SD (*P*) nonCl IV, 0.8; and % relative error nonCl IV, 0.9%.


Primary Tallow Amine Acetate Salt

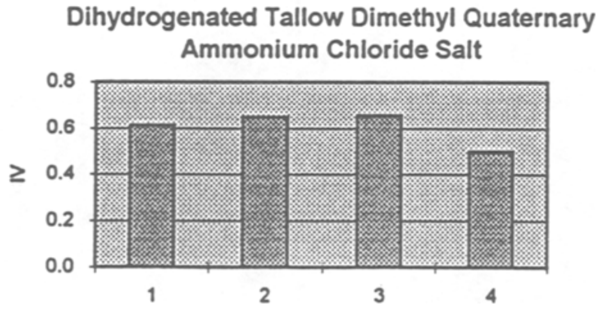

Dihydrogenated Tallow Dimethyl Quaternary Ammonium Chloride Salt

FIG. 5. A comparison of the nonchlorinated and chlorinated (Cl) iodine value (IV) methods for amines salts; 1 = visual IV average; 2 = potentiometric IV at 10 min; 3 = potentiometric IV at 30 min; and 4 = Cl–IV. Statistical summary for primary tallow amine acetate salt: Overall IV: maximum IV, 36.6; minimum IV, 35.5; difference, 1.1; average, 36.0; SD (*P*), 0.4; and % relative error, 1.1%. Individual averages: Cl–IV, 35.9; average nonCl visual, 35.5; average nonCl potentiometric, 36.2; average nonCl IV, 36.0; SD (*P*) nonCl IV, 0.5; and % relative error nonCl IV, 1.3%. Statistical summary for dihydrogenated tallow dimethyl quaternary ammonium chloride salt: Overall IV: maximum IV, 0.66; minimum IV, 0.51; difference, 0.16; average, 0.60; SD (*P*), 0.06; and % relative error, 10.3%. Individual averages: Cl–IV, 0.50; average nonCl visual, 0.61; average nonCl potentiometric, 0.65; average nonCl IV, 0.64; SD (*P*) nonCl IV, 0.02; and % relative error nonCl IV, 3.06%

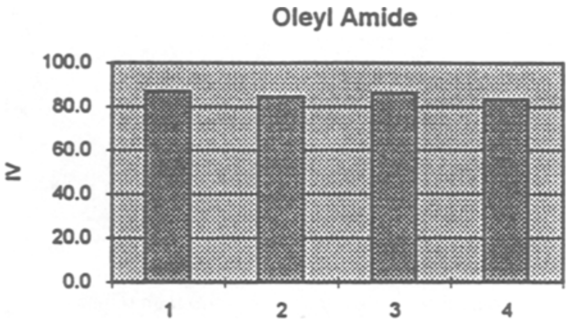

Oleyl Amide

FIG. 6. A comparison of the nonchlorinated and chlorinated (Cl) iodine value (IV) methods for amide; 1 = visual IV average; 2 = potentiometric IV at 10 min; 3 = potentiometric IV at 30 min; and 4 = Cl–IV. Statistical summary: Overall IV: maximum IV, 87.0; minimum IV, 83.5; difference, 3.4; average, 85.3; SD (*P*), 1.4; and % relative error, 1.6%. Individual averages: Cl–IV, 83.5; average nonCl visual, 87.0; average nonCl potentiometric, 85.4; average nonCl IV, 85.9; SD (*P*) nonCl IV, 1.0; and % relative error nonCl IV, 1.2%.

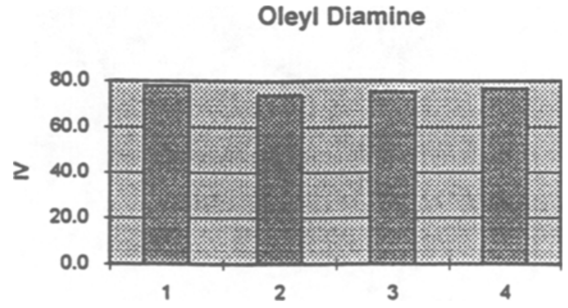

Oleyl Diamine

FIG. 7. A comparison of the nonchlorinated and chlorinated (Cl) iodine value (IV) methods for diamine; 1 = visual IV average; 2 = potentiometric IV at 10 min; 3 = potentiometric IV at 30 min; and 4 = Cl–IV. Statistical summary: Overall IV: maximum IV, 78.2; minimum IV, 74.0; difference, 4.2; average, 76.1; SD (*P*), 1.6; and % relative error, 2.1%. Individual averages: Cl–IV, 76.8; average nonCl visual, 78.2; average nonCl potentiometric, 74.6; average nonCl IV, 75.8; SD (*P*) nonCl IV, 1.8; and % relative error nonCl IV, 2.3%.

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