



# Application Note #111

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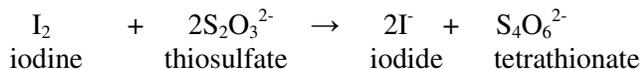
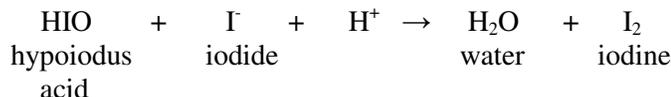
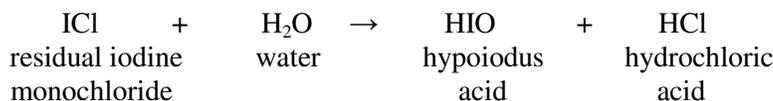
## Iodine Value

### Introduction:

Iodine value refers to the percentage of iodine absorbed by a substance such as a fat or oil<sup>1</sup>. It is an indication of a fat's potential to be oxidized as it measures the reaction of iodine with the double bonds of unsaturated fatty acids<sup>2</sup>. Since fats with a greater number of double bonds provide more sites for oxidation, the iodine value of a fat helps predict fat stability<sup>2</sup>.

Normally, iodine is absorbed quite slowly but this method makes use of Wijs, which is a stable solution consisting of iodine monochloride (ICI) in acetic acid that reduces absorption time to approximately half an hour. The iodine monochloride halogenates the double bonds in the fat, and the residual ICI is reduced to free iodine in the presence of potassium iodide (KI)<sup>3</sup>. The free iodine can then be titrated with sodium thiosulfate.

The reaction is as follows:



This document will show that the PC-Titrate automated titration system is capable of accurately and precisely measuring the % Iodine in various fatty samples. Please contact your local Man-Tech sales representative to find out how this method can work for you.

**Conforms To:** AOAC Official Method 993.2, AOCS Tg 1a-64, ASTM method D1959-97

**Sample:** Fats and Oils

**Concentration Range:** Tested between 0.02 and 15%

### Apparatus:

1. PC-TIS Interface Module (PCM-1002/4)
2. Peristaltic Pump for Reagent Addition (PCM-1000-400)
3. Slow Speed Peristaltic Pump (PCM-1000-408)
4. Non-Aqueous Dosing pump (PCM-1000-650)

5. 2 x Burivar II Buret Modules (PCM-1104-00)
6. Temperature Measuring Probe (PC-1000-120)
7. Stirrer (PC-1000-361)
8. Redox Electrode (PCE-80-OR1002)
9. Electrode Cable (PCE-86-EX1001)
10. Darkened enclosure/fume hood for autosampler or darkened beakers to be used with covering/uncovering system to protect samples from light – **enclosure or beakers to be supplied by customer**
11. Heater Block for 300mL beakers (PC-1000-764)\*
12. Control Box with Visual Alarm Light (PC-1000-761)\*
13. Autosampler with rinse pump and accessories
  - a. STANDARD, 18 sample locations (PCM-3000-223)\*\*
  - b. LARGE, 23 sample locations (or 15, if heater block used) (PCM-3000-271)
  - c. MEGA, 44 sample locations (or 15 if one heater block used, 30 if 2 heater blocks used) (PCM-3000-215)\*\*\*

\*Optional – only needed if solid samples are to be run

\*\*Standard sampler may not be used if a heater block is used

\*\*\*If mega sampler is used with a heater block, a heightening kit is also needed (PC-5000-1077)

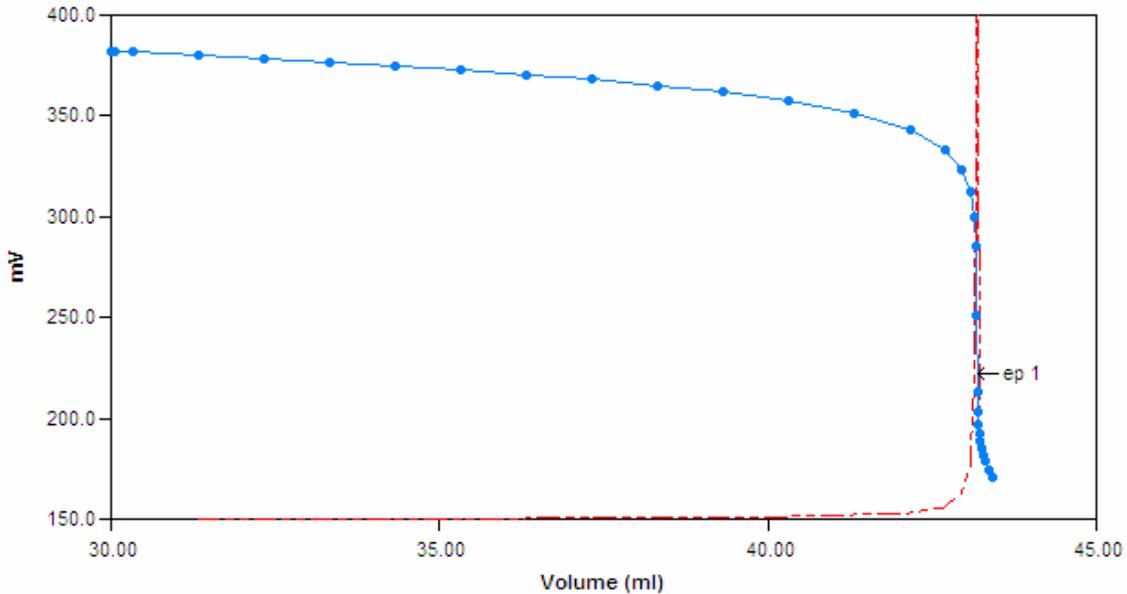
### Reagents:

1. Iodine Monochloride (Wijs Solution) – can be purchased from most chemical supply companies)
2. Chloroform or Cyclohexane
3. 0.1N Sodium Thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ )
4. 10% Potassium Iodide (100g in 1L DI water)
5. Deionized Water

### Procedure:

#### Blanks:

1. Place 3 empty beakers into the first 3 positions on the autosampler, and ensure that the beakers are protected from light.
2. Load a template to run the blanks, and press start.
3. The probes will move to the rinse station where they will be rinsed in DI water prior to moving to the first beaker position.
4. 25mL of chloroform will be added to each beaker, followed by 20mL of iodine monochloride (Wijs solution), which is added by buret.
5. The beakers will be left to react in the dark for 30 minutes.
6. 10mL of 10% potassium iodide, along with 100mL of DI water will be added to each beaker.
7. The first blank will be titrated with 0.1N sodium thiosulfate, and the endpoint will be recorded.
8. The probes will move to the flowing rinse station where they will be rinsed with DI water, and then they will move to the first stationary rinse position where the probes will be submerged in a 50/50 mix of ethanol and chloroform, followed by one last rinse in DI water.
9. Steps 7 and 8 will be repeated for the second and third blanks.
10. The endpoints for each of the blanks will be automatically analyzed for precision. When two of the three blanks are found to fall within 0.25mL of each other, they will be averaged and saved to the equation set to be used when analyzing samples.



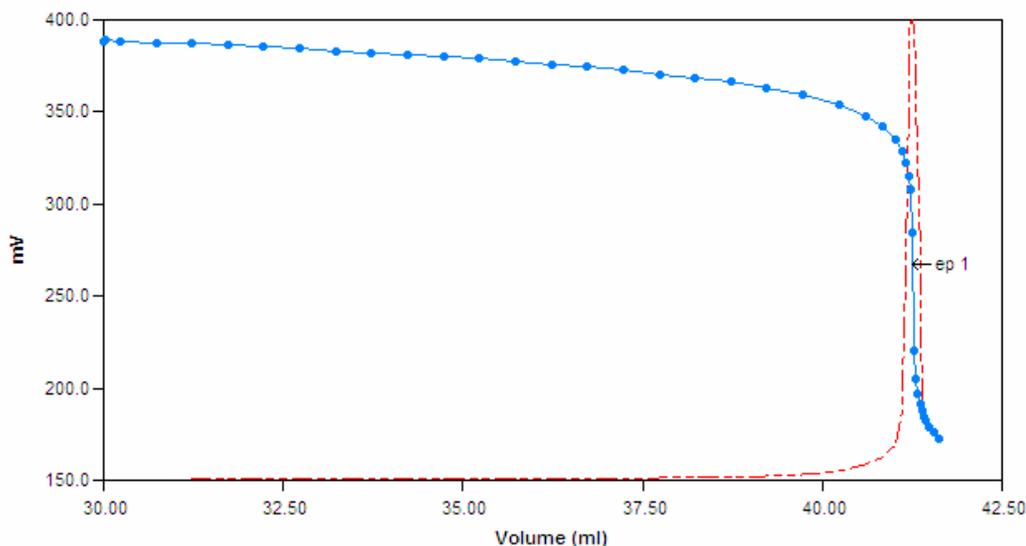
**Figure 1:** Example Titration Curve for a Blank

*Sample Analysis:*

1. Weigh out between 0.1g and 10g of sample (the appropriate amount of sample is dictated by the expected Iodine Value of the sample – see Table 1 below) into a 300mL beaker and record the weight to 4 decimal places.
2. Place into the autosampler rack (or heater block if running solid samples) and ensure that the samples are protected from light.
3. Run one of the iodine templates according to the number of samples that will be run, and ensure that the correct sample weights are entered into the template.
4. The probes will move to the rinse station where they will be rinsed with DI water prior to moving to the first sample.
5. 25mL of chloroform will be added to each beaker, followed by 20mL of iodine monochloride (Wijs solution).
6. The beakers will be left to react in the dark for 30 minutes.
7. 10mL of 10% potassium iodide, along with 100mL of DI water will be added to each beaker.
8. The first sample will be titrated with 0.1N sodium thiosulfate, and the Iodine Value will be automatically calculated by subtracting the mean blank endpoint value calculated earlier.
9. The probes will move to the flowing rinse station where they will be rinsed with DI water, and then they will move to the first stationary rinse position where the probes will be submerged in a 50/50 mix of ethanol and chloroform, followed by one last rinse in DI water.
10. Steps 8 and 9 will be repeated for each of the remaining samples.

Sample Type	Sample Weight (g)
Cetyl Alcohol	~2
Stearyl Alcohol	~2
Fatty Acid Distillate	~2
Coconut Oil	~2
Methyl Ester	~ 10
Fatty Alcohol	~ 10
Fatty Acid	~ 10

**Table 1:** Appropriate Sample Weights to be used for Each Sample Type for the Iodine Method



**Figure 2:** Example Titration Curve for a Cetyl Alcohol sample

**Calculations:**

**Blank Equations:**

$$\text{Diff1} = \text{ABS}(\text{udv29} - \text{udv30})$$

$$\text{Diff2} = \text{ABS}(\text{udv29} - \text{udv31})$$

$$\text{Diff3} = \text{ABS}(\text{udv30} - \text{udv31})$$

$$\text{Mblk1} = \frac{(\text{udv29} + \text{udv30})}{2}$$

$$\text{Mblk2} = \frac{(\text{udv29} + \text{udv31})}{2}$$

$$\text{Mblk2} = \frac{(\text{udv30} + \text{udv31})}{2}$$

udv29 = Endpoint of the first blank run (mL)

udv30 = Endpoint of the second blank run (mL)

udv31 = Endpoint of the third blank run (mL)

ABS = Absolute Value

Diff1 = Difference between the first and second blank run

Diff2 = Difference between the first and third blank run

Diff3 = Difference between the second and third blank run

Mblk1 = Average endpoint of the first and second blanks run

Mblk2 = Average endpoint of the first and third blanks run

Mblk3 = Average endpoint of the second and third blanks run

**Percent Iodine:**

$$IV = \frac{(MBLNK - ve1) * tcon * 12.69}{swght}$$

$$ERR = ABS(ve1 - MBLNK)$$

MBLNK = Average blank endpoint for two of the blanks run (mL)\*

ve1 = inflection endpoint (i.e. the volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> added during the titration in mL)

tcon = Concentration of sodium thiosulfate (N)

swght = Sample weight (g)

12.69 = Milliequivalence of iodine x 100 to adjust for percentage

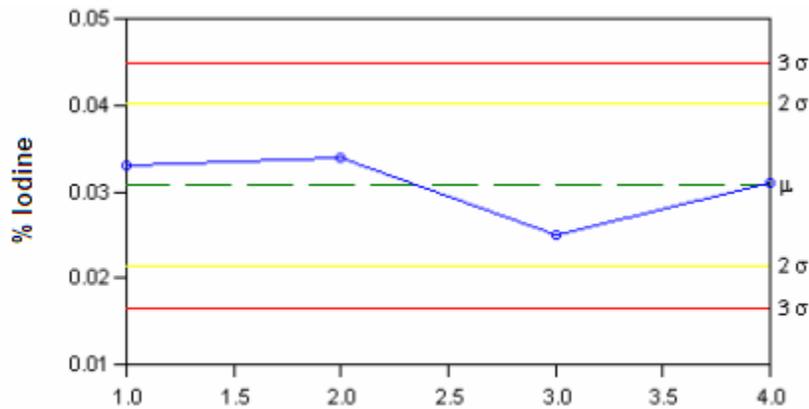
ERR = Error accounting for variation in blank endpoint volume. If this value is less than 0.25, the iodine value of the sample is reported as zero.

\*The average blank value used in the calculation is selected based on the precision of the blanks. All three endpoints are analyzed in turn and when two are found to be less than 0.25mL apart from each other, that value is taken.

**Quality Control**

Various samples were analyzed, with statistical data displayed below.

*Fatty Acid Sample #1:*



**Figure 3: Control Limits Chart for Fatty Acid #1**

Control Limits

μ = 0.031  
σ = 0.004  
CV = 13.11%

95% Confidence Limits

μ-2σ = 0.021  
μ+2σ = 0.040

99.7% Confidence Limits

μ-3σ = 0.017  
μ+3σ = 0.045

Fatty Acid Sample #2:

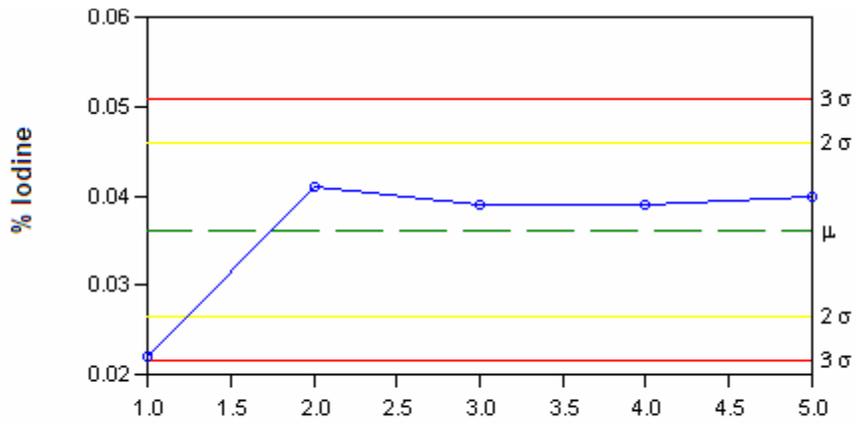


Figure 4: Control Limits Chart for Fatty Acid #2

Control Limits  
 $\mu = 0.036$   
 $\sigma = 0.01$   
 CV = 22.05%

95% Confidence Limits  
 $\mu - 2\sigma = 0.026$   
 $\mu + 2\sigma = 0.046$

99.7% Confidence Limits  
 $\mu - 3\sigma = 0.022$   
 $\mu + 3\sigma = 0.051$

Fatty Acid Sample #3:

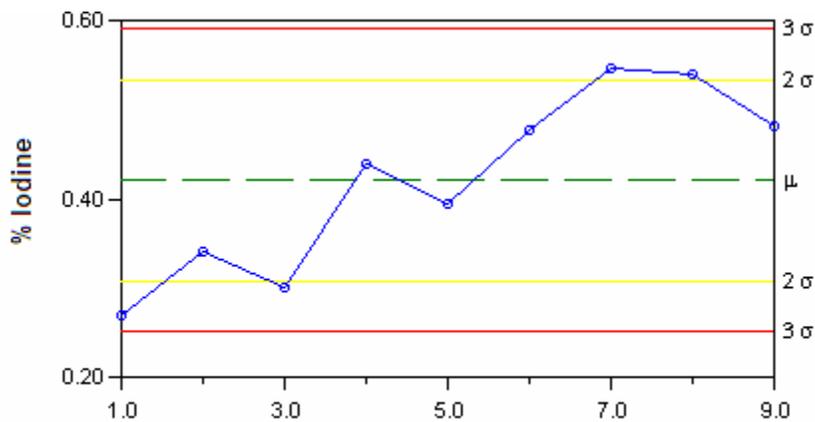


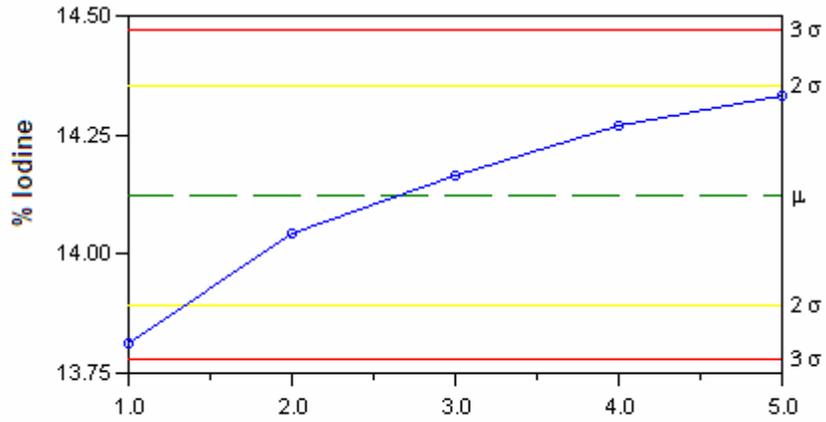
Figure 5: Control Limits Chart for Fatty Acid #3

Control Limits  
 $\mu = 0.421$   
 $\sigma = 0.101$   
 CV = 23.91%

95% Confidence Limits  
 $\mu - 2\sigma = 0.308$   
 $\mu + 2\sigma = 0.534$

99.7% Confidence Limits  
 $\mu - 3\sigma = 0.252$   
 $\mu + 3\sigma = 0.590$

*Fatty Acid Distillate Sample:*



**Figure 6: Control Limits Chart for Fatty Acid Distillate**

Control Limits

$\mu = 14.124$   
 $\sigma = 0.21$   
 CV = 1.46%

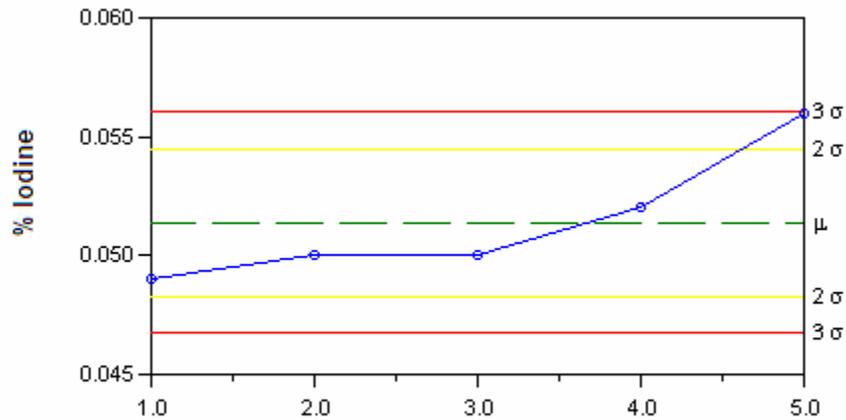
95% Confidence Limits

$\mu - 2\sigma = 13.894$   
 $\mu + 2\sigma = 14.354$

99.7% Confidence Limits

$\mu - 3\sigma = 13.779$   
 $\mu + 3\sigma = 14.469$

*Methyl Ester Sample #1:*



**Figure 7: Control Limits Chart for Methyl Ester #1**

Control Limits

$\mu = 0.051$   
 $\sigma = 0.003$   
 CV = 5.43%

95% Confidence Limits

$\mu - 2\sigma = 0.048$   
 $\mu + 2\sigma = 0.055$

99.7% Confidence Limits

$\mu - 3\sigma = 0.047$   
 $\mu + 3\sigma = 0.056$

Methyl Ester Sample #2:

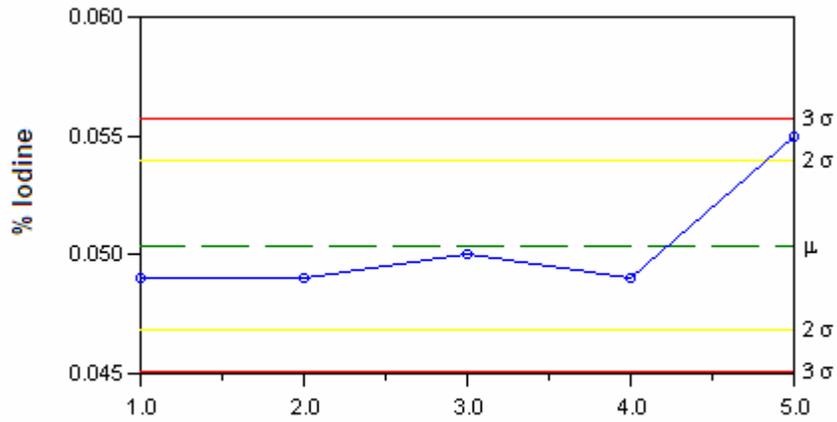


Figure 8: Control Limits Chart for Methyl Ester #2

Control Limits  
 $\mu = 0.050$   
 $\sigma = 0.003$   
 $CV = 5.17\%$

95% Confidence Limits  
 $\mu - 2\sigma = 0.047$   
 $\mu + 2\sigma = 0.054$

99.7% Confidence Limits  
 $\mu - 3\sigma = 0.045$   
 $\mu + 3\sigma = 0.056$

Coconut Oil Sample:

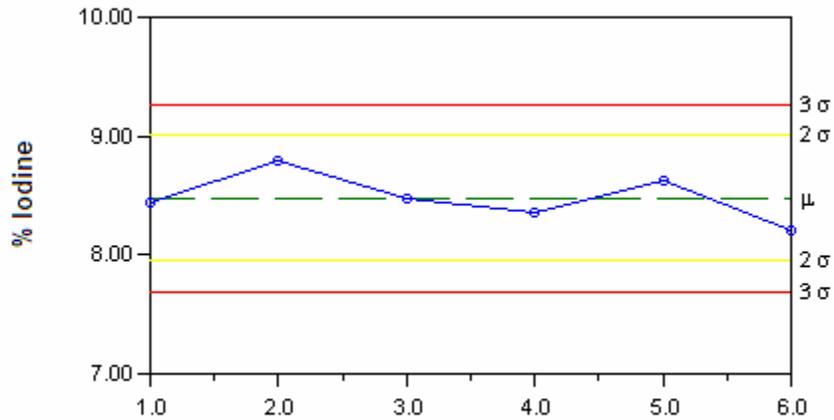


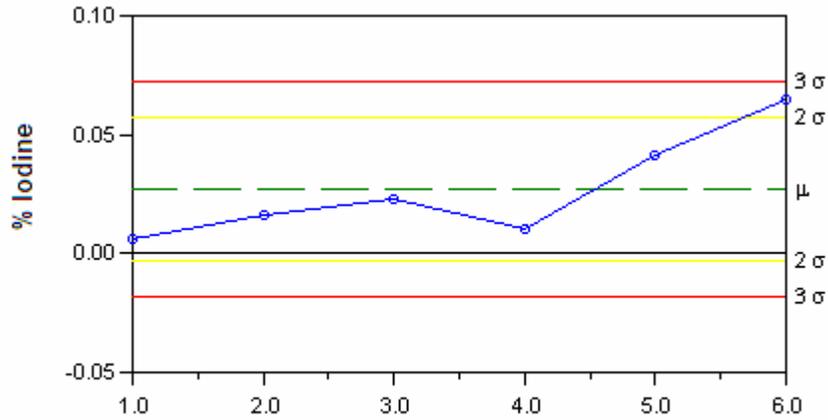
Figure 9: Control Limits Chart for Crude Coconut Oil

Control Limits  
 $\mu = 8.48$   
 $\sigma = 0.205$   
 $CV = 2.41\%$

95% Confidence Limits  
 $\mu - 2\sigma = 7.955$   
 $\mu + 2\sigma = 9.006$

99.7% Confidence Limits  
 $\mu - 3\sigma = 7.692$   
 $\mu + 3\sigma = 9.269$

Fatty Alcohol Sample #1:



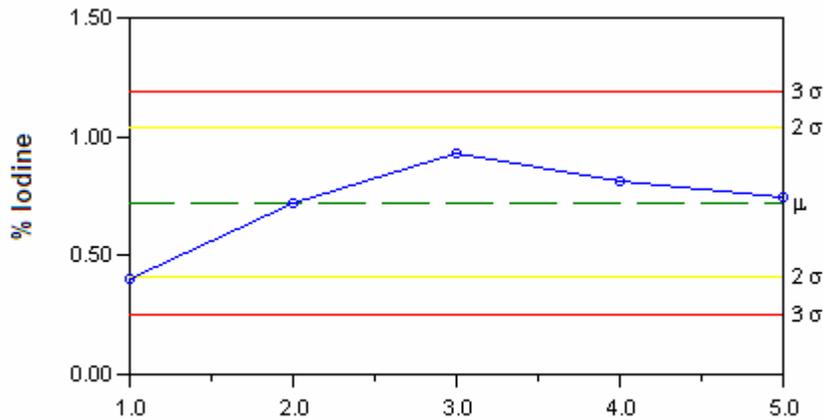
**Figure 10: Control Limits Chart for Fatty Alcohol #1**

Control Limits  
 $\mu = 0.027$   
 $\sigma = 0.022$   
 CV = 82.10%

95% Confidence Limits  
 $\mu - 2\sigma = -0.003$   
 $\mu + 2\sigma = 0.057$

99.7% Confidence Limits  
 $\mu - 3\sigma = -0.018$   
 $\mu + 3\sigma = 0.072$

Fatty Alcohol Sample #2:



**Figure 11: Control Limits Chart for Fatty Alcohol #2**

Control Limits  
 $\mu = 0.722$   
 $\sigma = 0.195$   
 CV = 27.04%

95% Confidence Limits  
 $\mu - 2\sigma = 0.409$   
 $\mu + 2\sigma = 1.035$

99.7% Confidence Limits  
 $\mu - 3\sigma = 0.253$   
 $\mu + 3\sigma = 1.192$

## Hints/Suggestions:

1. Two blanks are required to be run with each batch of samples in order to verify close precision. It is recommended however that three blanks are run as this allows for the possibility of one blank being discarded should it deviate too far from the other two. This eliminates the need to rerun the blanks should they not agree since the average of the other two blanks can be used.
2. This method needs to be run in the dark for accurate results. The entire system can be placed in an enclosure (such as a fume hood) or darkened beakers can be used along with the covering/uncovering system that can add or remove lids from beakers automatically.
3. High-speed stirring is necessary during reagent addition and titration to ensure adequate mixing of the aqueous and non-aqueous phases. A propeller-type stirrer is recommended.
4. The burets (especially the wijs buret) should be purged with fresh solution daily, and every few days should be purged with solvent. This will prevent clogging/sticking of the valve.
5. The samples used for this method are oily and sometimes viscous; therefore an extra solvent rinse (usually a 50/50 mixture of ethanol and chloroform) should be used between samples to ensure adequate cleaning.
6. Stricter stability times are necessary for this method to ensure proper accuracy and precision. To counteract the increased time this may add to the titrations, a large preinjection may be performed. Separate methods may be required if the iodine ranges of the samples are large.

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<sup>1</sup> [http://en.wikipedia.org/wiki/Iodine\\_number](http://en.wikipedia.org/wiki/Iodine_number)

<sup>2</sup> What is the best way to measure the quality and stability of fats and oils?

<http://www.ralstonanalytical.com/%5CFileUploads%5CInformation%5CQuality%20of%20Fats%20and%20Oils%2002.pdf>

<sup>3</sup> Iodine Value of Fats and Oils. AOCS Official Method 993.20. Chapter 41, p.7-9.