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Laboratory Experiment

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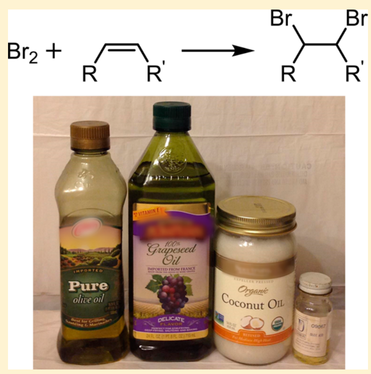
Obtaining the Iodine Value of Various Oils via Bromination with Pyridinium Tribromide

Michael Simurdiak,* Olushola Olukoga, and Kirk Hedberg

Park High School, Cottage Grove, Minnesota 55016, United States

Ⓢ *Supporting Information*

ABSTRACT: A laboratory exercise was devised that allows students to rapidly and fairly accurately determine the iodine value of oleic acid. This method utilizes the addition of elemental bromine to the unsaturated bonds in oleic acid, due to bromine's relatively fast reaction rate compared to that of the traditional Wijs solution method. This method also uses pyridinium tribromide as a bromine source in an effort to eliminate many of the safety hazards of working with elemental bromine. After the addition of a known quantity of bromine to the reaction flask, excess bromine is reduced with potassium iodide forming elemental iodine. The elemental iodine is then titrated with sodium thiosulfate and a starch indicator in a back-titration to determine the amount of excess bromine added to the oleic acid. Students then determine the iodine value of oleic acid by using a 126 g iodine/80 g of bromine ratio. This exercise can yield results fairly close to the accepted iodine value of 90 for oleic acid, as several of the groups who tried out the experiment obtained iodine values close to 90. In addition, this exercise was also able to determine the iodine values of olive, coconut, and grapeseed oils. Finally, this experiment can be used to reinforce organic chemistry concepts as well as biochemistry concepts to IB Chemistry students.



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The International Baccalaureate (IB) chemistry curriculum covers a wide array of topics, including a mandatory unit in organic chemistry as well an optional biochemistry unit.[1] The IB curriculum guide requires that 40 h of investigations are carried out in a standard level chemistry class and that 60 h of investigations are carried out in the higher level class. IB also suggests that the investigations chosen cover the topics put forth in the curriculum guide as much as possible. Most required topics such as stoichiometry, thermochemistry, and acid–base chemistry have several laboratory investigations available for teachers to choose from, due to the common nature of these topics in chemistry curriculums. However, it is more difficult for high school teachers to select laboratories for topics such as organic chemistry and biochemistry, due to the often specialized equipment needed and/or hazardous nature of the reagents required to perform these investigations.[2]

One of the topics discussed in the organic section of the IB chemistry curriculum is the halogenation of alkenes via an addition reaction. Similarly, the IB biochemistry option also covers the topic of determining the iodine value of lipids (which is defined as the grams of iodine that will add to the unsaturated carbon bonds in 100 g of a substance). These topics are usually unfamiliar to any high school chemistry student who encounters them. Both of these topics would be underscored by an investigation that allows students to determine the iodine value of a substance in the laboratory.

Perhaps the most common method for determining the iodine value of an oil is by using Wijs solution (0.1 M ICl in acetic acid).[3−7] Oils to be tested using Wijs solution are often suspended in an organic solvent like carbon tetrachloride. They are then reacted with Wijs solution and placed in a dark place for at least 30 min before they are to be titrated with sodium thiosulfate in a back-titration to determine the amount of excess Wijs solution added to the oil. This method has three drawbacks that make it undesirable for a high school laboratory. First, this method uses Wijs solution which does not have many other uses in the high school classroom other than determining the iodine value. Second, many high school chemistry classes are approximately 50 min long. Therefore, it is not feasible to let a reaction sit in a dark place for 30 min and still be able to finish a single titration in an allotted class period with the usual setup and cleanup time. Third, Wijs solution poses many safety hazards and should be handled in a fume hood.[8] High school classrooms often have only one fume hood that cannot accommodate all students at once, making this method impractical for most high school classrooms.

A second method for determining the iodine value in common oils uses bromine as a halogenation agent and determines the iodine value via the "bromine value" and a mass ratio calculation.[9] This method adds 5% (m/m) Br_2 in acetic acid directly to the oil to be investigated using a dropper.

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J. Chem. Educ. XXXX, XXX, XXX−XXX

Unlike several methods that utilize Wijs solution, this method does not require the oil to be suspended in any organic solvent prior to adding the halogenation agent. Since bromine reacts faster than iodine, the 5% (m/m) Br_2 in acetic acid is slowly added via a dropper to the oil in a flask. When the Br_2 reacts with the oil, a colorless product is the result. Once the product is saturated, the student stops adding the Br_2 at the first sign of the brown Br_2 color. The bromine value is then determined by calculating the mass of Br_2 reacted with 100 g of oil. A 126/79 ratio is then used to determine the iodine value. While this method does not have the drawback of the 30 min wait time of the Wijs solution method, it was nearly impossible for us to determine when to stop adding 5% (m/m) Br_2 to the oil. Sometimes the solution stayed brown after adding only one drop of the Br_2 solution to the unsaturated oil. Due to the inconsistent drop size and the impossibility of finding the titration's end point (or any point close to it), this was the most inconsistent method that we tested. In addition, this method requires students to work with bromine liquid dissolved in concentrated acetic acid. Similar to Wijs solution, this reagent poses many safety hazards and requires students to work in the fume hood. Therefore, this method is also undesirable for use in the high school classroom.

The method described here within is somewhat of a hybrid of the aforementioned methods. It adds bromine to the unsaturated carbon bonds in the oil, which makes the experiment quick enough to perform in a 50 min laboratory period. It also employs a back-titration (similar to the method that uses Wijs solution) in order to make the experiment quantitative. The key difference between this lab exercise and the methods which use either bromine in acetic acid or Wijs solution, is that it uses pyridinium tribromide as the reagent which supplies the bromine for the addition reaction. Pyridinium tribromide is a powder at room temperature that releases elemental bromine in a solution when it is dissolved. Pyridinium tribromide is safer to use than bromine in acetic acid and Wijs solution used in the previously mentioned methods. Pyridinium tribromide has also been reported to be a safer and greener alternative in brominations.[10] Even though pyridium tribromide is safer to use than elemental bromine, it does pose safety hazards (see Hazards) and must only be handled by the instructor. In addition, safety steps must be taken to ensure that no student or instructor will come into contact with the pyridinium tribromide reagent or the small amount of generated Br_2 in solution.

The following experiment was used for several reasons. First, it serves as a connection between biochemistry and general chemistry by allowing students to determine the degree of saturation in a common fatty acid. Second, it allows students to analyze an organic addition reaction, which is rarely attempted in the high school laboratory due to lack of feasible experiments. Third, it combines the chemistry of an addition reaction with the stoichiometry of a back-titration, which is excellent practice for high school students. Finally, this experiment provides a means where students can determine the iodine value relatively quickly in order to finish titrations within allotted class time.

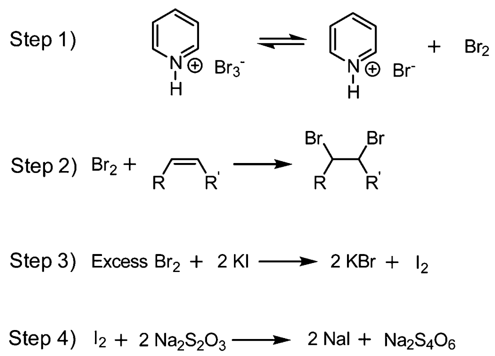
■ MATERIALS

Soluble potato starch, potassium iodide, anhydrous ethanol, and sodium thiosulfate were purchased from Flinn Scientific. Oleic acid was obtained from the Educational Division of Damon Engineering, Inc. Olive, coconut, and grapeseed oils were purchased from a local grocery store. Pyridinium tribromide was purchased from Acros Organics and its purity was obtained from the Acros Organics Web site using the lot number. A 1% starch solution was prepared by dissolving 10 g of starch in 1 L of boiling water. Once cooled, the starch clumps were filtered out of the solution.

■ EXPERIMENTAL PROCEDURE

The overall method for determining the iodine value in this experiment is outlined in Scheme 1. Approximately 0.2 g of oil

Scheme 1. Four-Step Sequence Used to Determine the Iodine Value[a]



[a]The first step is the equilibrium that is established when pyridinum tribromide is dissolved in the ethanol. The second step is the addition of bromine to the unsaturated carbon bonds. The third step reduces excess bromine and creates elemental iodine. The fourth step reduces the iodine with sodium thiosulfate.

is added to an Erlenmeyer flask, and it is dissolved in ~20 mL of anhydrous ethanol. To carry out the addition reaction, 0.4–0.5 g of pyridinium tribromide is dissolved in the ethanol/oil solution. This releases elemental bromine in the ethanol, and it proceeds to brominate the unsaturated carbon bonds. Approximately 30 s after adding the pyridinium tribromide to the ethanol/oil solution, 20 mL of distilled water is added to the flask. An excess of potassium iodide (~1.5 g) is then dissolved in the flask mixture to convert any unreacted bromine to bromide, generating elemental iodine. Several drops of 1% starch are then added to the flask as an indicator. The flask is then titrated with 0.1 M sodium thiosulfate until the cloudy/clear end point is reached (Figure 1). Students determine the

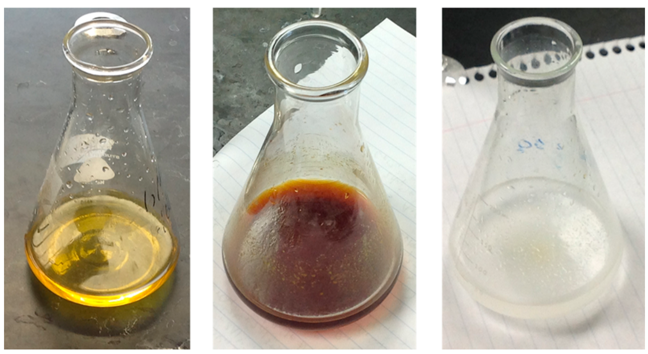


Figure 1. (Left) The reaction after the addition of pyridinium tribromide. (Center) The reaction flask after the excess Br_2 has been reduced with potassium iodide. (Right) The reaction mixture after the starch/iodine has been titrated with sodium thiosulfate.

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J. Chem. Educ. XXXX, XXX, XXX–XXX

amount of excess Br_2 added to the oil using stoichiometric relations, and they subtract this amount from the total amount of Br_2 added to the oil to determine the mass of Br_2 that reacted with the oil. This ratio is then scaled up to determine the mass of bromine that would react with 100 g of oleic acid. The result is the "bromine value", which students can easily convert to the iodine value using the mass ratio 126 g iodine/80 g of bromine. (See Supporting Information for instructor notes, hazards, a sample lab handout, and sample student data and calculations.)

■ HAZARDS

Pyridinium tribromide is a corrosive substance and contacting it with the skin must be avoided. It can cause severe burns if inhaled or ingested; therefore, it should only be handled by the instructor who is using proper personal protective equipment (gloves, labcoat, safety goggles, and a method to protect against accidental inhalation and ingestion). The instructor must add the pyridium tribromide, water, and potassium iodide to the reaction flask before handing the reaction flask back to the students. This will ensure that all of the excess Br_2 will be reduced to bromide ions. Even though a small amount of elemental bromine is generated in this reaction (the equivalent of ~2 drops of elemental bromine) and we did not detect any bromine vapors during this experiment, the instructor part of the lab should be conducted in a fume hood to ensure no accidental inhalation of bromine. This experiment should not be attempted if possible contact by the students and the instructor with the pyridinium tribromide and the generated bromine cannot be eliminated.

Sodium thiosulfate, potassium iodide, oleic acid, and cooking oils can cause irritation if either one is inhaled, ingested, or comes into contact with the skin. Ethanol is a flammable substance and should never be used near an open flame. It is also toxic and should not be ingested. Elemental iodine and a very small amount of pyridine are generated in the reaction flask. They can cause irritation if inhaled or if they come into contact with the skin, and they should not be ingested due to their toxicity. Therefore, caution should be used to avoid contact with the reaction mixture. Once the titration of the reaction mixture is finished, its waste should be placed in the proper organic waste container to prevent brominated oils and pyridine from disposal in the drain.

■ CLASSROOM SETTING

This laboratory experiment was performed during a high school IB chemistry class over the course of 2 days during 50 min class periods. There were 20 students in the class, and the room contained enough lab bench space for up to 32 students. Students worked in seven groups of 2−3 students and each group had access to several 250 mL Erlenmeyer flasks, a 100 mL buret (with 0.2 mL graduations), and several beakers. The oleic acid experiment was performed by the class. After testing the lab experiment, the instructor performed the experiment on oleic acid and other various cooking oils.

■ RESULTS AND DISCUSSION

Each group of students was instructed to conduct four determinations of the iodine value of oleic acid, discarding the value of their first titration. The resulting iodine values obtained by the class are displayed in Table 1.

Table 1. Oleic Acid Iodine Values[a] for Each Group

Group	Average Iodine Value[b]	Iodine Value Range
1	100	95−108
2	102	92−110
3	97	93−98
4	98	93−105
5	90	88−95
6	89	86−92
7	88	81−90
Instructor	92	90−93

[a]Iodine value = grams of iodine reacted per 100 g of sample. [b]The actual iodine value of oleic acid is 90.

As can be seen, the majority of iodine values range from the low 90s to the low 100s, with some groups achieving better results than others. This would be expected in any high school laboratory. The majority of the results for oleic acid tended to be a little higher than the actual iodine value. One possible reason for this could be due to the purity of the oleic acid. If it was contaminated with a small amount of other unsaturated oils, the iodine value could be higher than expected. Another possible reason for experimental values tending slightly higher than the actual value could be caused by the color of the equivalence point of this titration. While the student results do not suggest that it is difficult to achieve a stopping point very close to the equivalence point in this titration, the fact that the end mixture is somewhat cloudy/clear could mask some of the color of the titration mixture. This would then cause students to add a bit less sodium thiosulfate than needed to reduce the excess Br_2, resulting in a slightly higher iodine value. Regardless of the slightly higher values, the results achieved by groups 5−7 as well as by the instructor demonstrate that this method can be used to obtain results adequate for the educational laboratory.

This method was also tested out by the instructor to evaluate how it works with other food oils. The iodine values of olive oil, coconut oil, and grapeseed oil obtained by the instructor are displayed in Table 2. Food oils are a mixture of fats, and therefore, the accepted values are displayed in Table 2 as ranges and not an exact value (as in the case of pure oleic acid).

Table 2. Iodine Values[a] of Various Food Oils

Oil	Average Iodine Value[b]	Accepted Iodine Value Range[11,12]
Olive	94 ± 4	75−94
Coconut[c]	13 ± 2	6−11
Grapeseed	135 ± 7	128−150

[a]Iodine value = grams of iodine reacted per 100 g of sample. [b]Value ± Standard Deviation. [c]Coconut oil was gently warmed in the ethanol to get it to dissolve properly.

A wide range of iodine values have been reported for various food oils;[3,8,9] therefore, it is difficult to get an exact range of accepted iodine values. The ranges in Table 2 are based off of suggested standards from Codex Aliementarius. The values for olive, coconut, and grapeseed oil all fall within or very close to these standards suggested by Codex Aliementarius. Also, the three oils present a range of iodine values to test with coconut having low iodine values and grapeseed oil having high iodine values. The results show that this method can be used with different oils that have a wide range of iodine values.

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J. Chem. Educ. XXXX, XXX, XXX−XXX

■ CONCLUSION

Students were able to conduct an investigation that combines the concept of an organic addition reaction with the biochemical concept of degree of saturation of oils. The investigation is a quicker, safer, and fairly accurate hybrid of previous iodine value methods. Determining the iodine value of various oils via this method is simple enough that if students perform the lab carefully, they will obtain decent results. This lab activity adds to the small number of organic reaction activities and biochemistry activities that are available to be performed in the IB Chemistry laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00283.

> Lab handout with details of experimental procedure, a guide showing students how to calculate the iodine value of oleic acid from their experimental data, and sample student data (PDF, DOCX)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: msimurdi@sowashco.k12.mn.us.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) International Baccalaureate Online Curriculum Centre. http://occ.ibo.org (accessed March 2015).

(2) Meszaros, M.; Russo, T. J. Vial Organic – Organic Chemistry Labs for High School and Junior College. *J. Chem. Educ.* **1999**, *76* (1), 69–70.

(3) Pocklington, W. D. Determination of the Iodine Value of Oils and Fats. *Pure Appl. Chem.* **1990**, *60* (12), 2339–2343.

(4) QuadraChem Laboratories Ltd. Iodine Value of Animal and Vegetable Fats and Oils (EN ISO 3961 (1999) & ISO 3961 (1996)). http://www.qclscientific.com/pdfs/Apps%20Notes/Iodine%20Value%20of%20Animal%20and%20Vegetable%20Fats%20and%20Oils.pdf (accessed November 2015).

(5) Corn Refiners Association. Corn Oil Analysis Iodine Number (Wijs Method). http://www.corn.org/wp-content/uploads/2009/12/H-32.pdf (accessed November 2015).

(6) IFFO – The Marine Ingredients Organisation. Recommended Method of Analysis for Determination of Iodine Value of Fish Oils (Wijs Method). http://www.iffo.net/system/files/FOB7.PDF (accessed November 2015).

(7) AOCS Official Method Tg 1–64, Iodine Value, Wijs Method. *Official Methods and Recommended Practices of the American Oil Chemists' Society*; Firestone, D., Ed.; AOCS Press: Champaign, IL, 1998.

(8) Wrolstad, R. E.; Decker, E. A.; Schwartz, S. J.; Sporns, P. *Handbook of Food Analytical Chemistry, Water, Proteins, Enzymes, Lipids, and Carbohydrates*, 1st ed.; John Wiley & Sons: Hoboken, NJ, 2005; p 467.

(9) Heasley, V. L.; Christensen, V. J.; Heasley, G. E. *Chemistry and Life in the Laboratory*, 2nd ed.; Burgess: Minneapolis, MN, 1983; 141 – 145.

(10) McKenzie, L. C.; Huffman, L. M.; Hutchison, J. E. The Evolution of a Green Chemistry Lab Experiment: Greener Brominations of Stilbene. *J. Chem. Educ.* **2005**, *82* (2), 306–310.

(11) Codex Aliementarius. *Codex Standard for Olive Oils and Olive Pomace Oils (Codex STAN 33–1981)*. ftp://ftp.fao.org/codex/Translations/Chinese/STAN_Zh_Translation/CXS_033e.pdf (accessed November 2015).

(12) Codex Aliementarius. *Codex Standard for Named Vegetable Oils (Codex STAN 210–1999)*. ftp://ftp.fao.org/Codex/knovel/updated%202013/CXS_210e.pdf (accessed November 2015).

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J. Chem. Educ. XXXX, XXX, XXX–XXX