Development of teaching materials using oils and fats

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Abstract

In the curriculum for chemistry students, experiments involving oils and fats include the extraction of oils from plants, the synthesis of soap by saponification, and the observation of micelles. However, these experiments are not easy to implement because they require a lot of preparation and are time consuming. Therefore, the authors attempted to develop teaching materials for experiments on oils and fats that can be performed safely and in a short time.

First, we developed an experimental program for high school students to observe the fluorescence emitted by olive oil and to observe fingerprints on paper using iodine dissolved in oils and fats. We further found that air oxidation was accelerated when highly unsaturated oils and fats were applied to filter paper, and developed the filter paper method, which enables evaluation of the oxidation state of oils and fats using small quantities.

Furthermore, noting that linseed oil is used as a binder for oil painting, we investigated the synthesis of pigments containing copper(II) and iron(III). Although experimental methods have been emphasized in the synthesis of pigments, we were able to explore the background of how the appropriate reagent amounts were determined. Moreover, carbon dioxide foaming was observed in this reaction, which can be exploited to experimentally confirm the acidity of aqueous solutions of transition metal salts.

Keywords: oils and fats, oxidation, iodine value, carbonate, pigments

1. Introduction

Oils and fats are indispensable components of consumer goods used in our daily life. However, when edible oils and fats (salad oil and canola oil) and processed foods (potato chips, cookies, etc.) are left unattended, they develop an unpleasant odor and poor taste. This is especially noticeable in dressings containing linseed oil. This is due to the oxidation of oils and fats, resulting in hardening and the formation of secondary oxidation products. On the other hand, linseed oil is used as a solvent for oil painting, which is a typical example of the exploitation of the oxidation of hardened oil to form a curing membrane.

The loss of unsaturated bonds and the change in the physical properties of oils and fats are taught in high school chemistry classes. The authors have been developing experiments for students using oils and fats, and have been studying them from the following three aspects.

1) Experiments based on the property that oils and fats can dissolve various compounds.
2) Experiments to observe the rapid oxidation of oils and fats.
3) Experiments to synthesize pigments for oil paintings.

In this report, we present an overview of the results of those studies.

2. Experiments based on the dissolution of compounds in oils and fats

2.1 Student experiment to observe fluorescence

In high school chemistry, students learn about the absorption and emission of light. For example, chemiluminescence such as in the reaction of luminol, bioluminescence of fireflies and jellyfish, and the mechanism of photosynthesis are introduced. In addition, terms such as "ground state" and "excited state" are introduced, and the mechanism of emission is explained in detail by considering the flame color reaction of metals.

Oils and fats can dissolve various organic compounds. For example, chlorophyll dissolves in fresh olive oil. Therefore, when a green laser pointer is shone on the solution, the pathway of the light emits red fluorescence, and when a black light is used, the solution shows blue flu-

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orescence [1]. Figure 1 shows a practical example of a high school chemistry experiment.

Fig. 1 Observation of fluorescence using a black light.

In addition, clothes washed with UV-cut detergent, parts of banknotes printed with fluorescent ink, and seashells show fluorescence when irradiated with a black light. Fluorescein, a compound that fluoresces under basic conditions but loses its fluorescence under acidic conditions, was also highly evaluated by the students [2-3].

These experiments are effective teaching materials for arousing the interest of junior high school and high school students because the color change can be observed in a dark room. The effects of COVID-19 have made it difficult to operate in laboratories like before [4]. The experiments using a laser pointer and black light are suitable for live-streamed laboratory activities because they can be safely observed by students at the same time by online demonstration.

2.2 Student experiment to observe fingerprints

Human beings excrete water and fat from inside their bodies to the outside through their skin. When a finger is pressed against a piece of paper, the fatty substance in the contact area adheres to the paper. Moreover, gargles containing iodine are often used in daily life because of their bactericidal effect. When iodine is heated, it sublimates and becomes a gas. Because iodine is readily soluble in fat, the gaseous iodine dissolves in the fat on the paper, causing the paper to turn brown [5]. Therefore, fingerprints can be observed. If the experiment is conducted under conditions where fat is adhered to the fingers, such as after eating potato chips, the fingerprints are clearly visible.

This experiment is easy. First, press your finger strongly on one end of a thin piece of paper, and fix it with a splitter. Place an empty can with the lid cut out (using a can opener) on a hot plate and heat it at about 200 °C. When the can is heated, add 1 to 2 mL of gargle. Expose the paper to iodine vapor for about 1 min, and remove it from the can (Figure 2). The fingerprints turn purple and appear clearly [6]. Because iodine is volatile, the fingerprints will disappear in a few days.

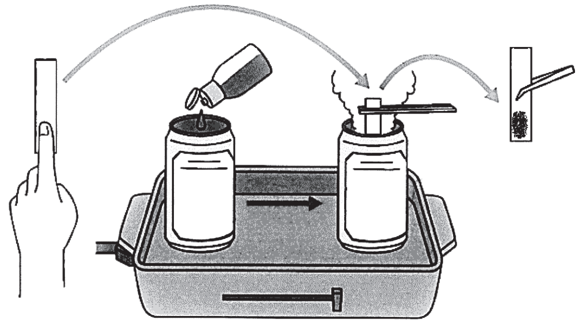


Fig. 2 Fingerprint detection using iodine.

3 Measurement of iodine value of oils and fats by the filter paper method

3.1 Introduction

The degree of unsaturation and oxidation of oils and fats is evaluated based on the "Standard Methods for the Analysis of Fats, Oils, and Related Materials [7-8]", but the air oxidation of oils and fats is slow and it generally takes several weeks to detect the change. Therefore, it is difficult to conduct this experiment as a student experiment.

The authors found that coating oils and fats on filter paper not only accelerated air oxidation due to the increased surface area, but also made it easy to measure changes in the oxidation state over time by using a small amount of oil or fat. In this chapter, the iodine value is used as the main index of the degree of unsaturation and oxidation of oils and fats, and a comparison is made between the paper method (the filter paper method) and the official method.

3.2 Principle of the experiment

The iodine value (the number of grams of iodine that can be added to 100 g of oil or fat) is used as a standard for comparing the degree of unsaturation of oils and fats, and Wijs' Method is known as a representative method for determining the degree of unsaturation of oils and fats. The ICl contained in Wijs' solution (acetic acid solution containing ICl (iodine monochloride) at a concentration of 0.10 mol/L) is added to the double bond of oils and fats, and the excess ICl is converted to iodine by reaction with potassium iodide. This is titrated with sodium thiosulfate solution, and the iodine value is obtained from the titration value (Figure 3).

Step 1 Addition of ICl to the double bond of oils and fats

-C=C- + ICl → -IC-CCl-

Step 2 KI is added to the excess ICl and replaced with iodine

$ICl + KI \rightarrow I_2 + KCl$

Step 3 Titration of iodine with sodium thiosulfate

$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

Fig. 3 Reactions involved in Wijs' Method.

3.3 Experimental method

Other than fish oil (Nature Made Super Fish Oil, Otsuka Pharmaceutical), the oils and fats used in the experiments were those of Nisshin OilliO, which are readily available in Japan. Edible oil (2.00 g) was placed into a 50 mL volumetric flask, and cyclohexane was added up to the marked line. The mixture was transferred to a brown glass screw tube with an inner volume of 50 mL.

Fig. 4 Edible oil used in the experiment.

Filter paper (Circular Qualitative Filter Paper No. 2; 110 mm in diameter, manufactured by ADVANTEC) was quartered and fixed with painting clips. A cyclohexane solution of the oil or fat (0.50 mL) was withdrawn with a measuring pipette and applied to the filter paper, and the solvent was evaporated by lightly fanning the paper (Figure 5).

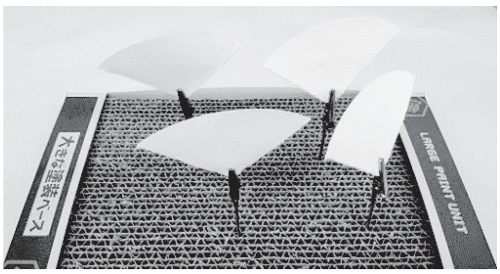


Fig. 5 Oxidation of oil and fat applied to filter paper.

3.4 Determination of iodine value by Wijs' method

A filter paper was cut into about 2 cm strips and placed into a 100 mL conical flask (see Section 3.3). Thereafter, 2.00 mL of Wijs' solution was dropped into the conical flask with a measuring pipette, and the beaker was covered with a dark box and allowed to stand for 10 min. Thereafter, 20 mL of 3.0% potassium iodide solution was added. The mixture was titrated with 5.00×10^{-2} mol/L sodium thiosulfate standard (0.5% starch solution was used as indicator). Near the endpoint, the titration was performed while stirring with a glass rod, and it was confirmed that the solution had become clear when the filter paper returned to white (Figure 6).

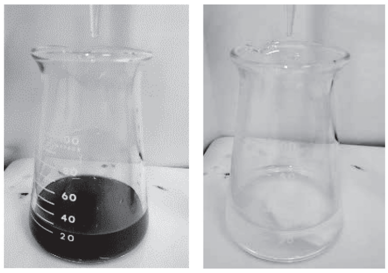


Fig. 6 Titration with sodium thiosulfate solution.
(Left: during titration, right: end point).

The iodine value was calculated by Wijs' method as follows [9]:

$$\text{Iodine value} = 0.635 \times (A - B)/C$$

A: Amount of 5.00×10^{-2} mol/L sodium thiosulfate standard solution used in blank test (mL)

B: Amount of sodium thiosulfate standard solution used in this test (mL)

C: Sample collection volume (g)

In this experiment, 2.00 mL of Wijs' solution was used. The volume (A) of the sodium thiosulfate standard solution reacting with this solution was 7.70 mL. The mass of oil or fat contained in 0.50 ml of the 2.00×10^{-2} g cyclohexane solution applied to the filter paper was defined as C.

3.5 Results and discussion

Table 1 presents a comparison of the iodine values obtained by Wijs' Method with those obtained by the official method [7-8] and the filter paper method. The filter paper method was used to measure the iodine value 20 times, and the average value and the range of the measured values are shown.

The iodine value calculated by the filter paper method was within 10% deviation from that obtained by the official method. It is reported that the matrix components of the fats do not interfere with the titration by Wijs' method; however, upon inquiry, the manufacturer of linseed oil and fish oil indicated that vitamin E is added as an antioxidant. [9]

Table 1 Comparison of iodine value obtained with the official method and filter paper method.

Types of Oils and Fats	Iodine value		
	Range	Official method	Filter Paper Method (10 minutes)
Salad oil (Soybean Rapeseed)	94–139	128	137 ± 3
Canola oil	94–126	118	129 ± 5
Linseed oil	170–200	201	187 ± 9
Fish oil	150–200	198	183 ± 8

4 Changes in oxidation state of oils and fats over time by filter paper method

4.1 Introduction

In the oxidation of oils and fats, peroxides are formed by radical reactions between oxygen molecules in the air and the hydrocarbon groups of fatty acids in the oils and fats, as shown in the Figure 7. This is followed by dimerization through hydroperoxide radicals to form a cross-linked structure (-COOC- or -COC-) [10].

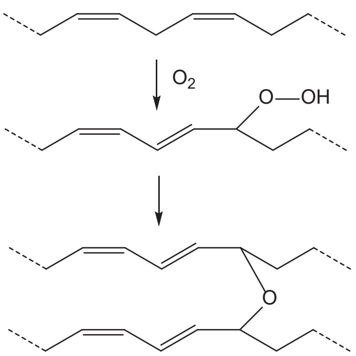


Fig. 7 Oxidation of oils and fats (model).

The iodine value indicates the degree of unsaturation of oils and fats, and the change in the iodine value with time can be used as an index of the oxidation of oils and fats. In this study, air oxidation of oils and fats was examined using the filter paper method. Factors such as temperature, light, and heavy metals affect the deterioration of fats and oils, and copper(II) salts are known to accelerate oxidation and reduce the shelf-life of oils and fats by half at 0.05 ppm [11]. With this in mind, we applied aqueous copper acetate (II) solution as a catalyst to promote the oxidation process and used dried filter paper.

4.2 Measurement of air oxidation and iodine value of oils and fats by the filter paper method

A 2.0 mL aliquot of 0.10% aqueous copper(II) acetate solution was applied in advance to the filter paper, which was dried at room temperature and then quartered. As shown in Section 3.3, a cyclohexane solution of oils and fats was applied to the filter paper, dried, and left in a room at 25 ° C to oxidize the oils and fats. After a predetermined time, the iodine value was determined by Wijs' Method, as described in Section 3.4. The results of the blank test (equivalent to 0.18 mL of aqueous sodium thiosulfate solution) were not used for correction, taking into account the circumstances in which the data will be utilized in the student experiments.

4.3 Results and discussion

The change in the iodine value of edible oils over time using the filter paper method is shown in Figure 8. The oxidation of linseed oil and fish oil progressed over time, and the iodine value reached a minimum in approximately 24-48 h. Wijs' Method measures iodine produced from unreacted reagents, as well as iodine produced from peroxides. Therefore, an experiment to measure the change in the peroxide values with time was also carried out separately [12]. This experiment indicated a correlation between the decrease in the iodine value and the increase in the peroxide value of linseed oil and fish oil. However, the amount of sodium thiosulfate consumed in the measurement of the peroxide value was minimal (~0.2 mL maximum of sodium thiosulfate solution). Therefore, the purpose of the student experiment employing Wijs' method was ‘to make students realize that the oxidation of oils and fats progresses with time and that unsaturated bonds are lost’ [13].

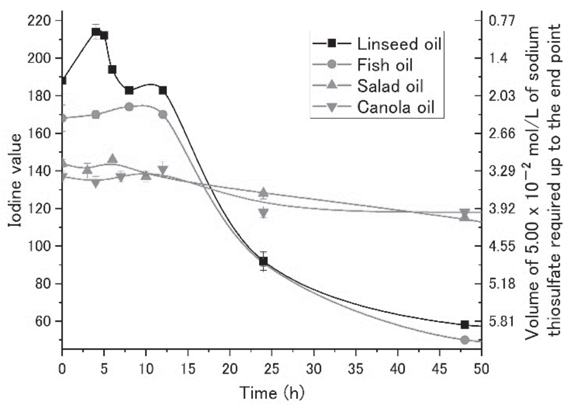


Fig. 8 Evaluation of change in iodine value over time by the filter paper method.

4. 4 Student experiments to learn about the oxidation of oils and fats

We conducted an experimental class for students taking the Advanced Lecture on Chemistry Education at the university to which the authors belong (July 2021, 90 minutes, for 2 consecutive days), and each student performed the experiment individually. In this experiment, the aim was to treat paper as potato chips, and to associate the oxidation of oil and fat with the deterioration of food flavor. In the student experiment, instead of calculating the iodine value, the students were asked to consider the decrease in unsaturated bonds due to the oxidation of oils and fats in relation to the change in the volume of sodium thiosulfate solution.

First, the properties of the oils and fats were studied in relation to unsaturated bonds and the experimental principle was introduced. Thereafter, the concentration of ICl in Wijs' solution was calculated by iodometric titration using sodium thiosulfate solution. The oil and fat solutions were then applied to six quartered sheets of filter paper (with catalyst). Oil and fat were applied using a disposable plastic dropper graduated pipette (1 mL), with the choice of linseed oil or fish oil. The volume of the sodium thiosulfate solution was determined by titration using Wijs' Method with three sheets of filter paper. In the next lesson the following day, oxidation of the oil and fat and loss of the unsaturated bonds were evaluated by titration using Wijs' method and comparing the values with the titer values from the previous day. Finally, a watch tray with a cured membrane of linseed oil was circulated, and we highlighted the fact that curing oil is also used as a binder for oil paints.

In the discussion by the students, there were some comments such as:

"The number of C=C double bond decreases when oxidized in air, and the volume of the sodium thiosulfate solution becomes larger".

"The results were almost the same for linseed oil and fish oil, so the oxidation progressed to the same extent for both oils".

"Double bonds are invisible, but it was easy to understand because I could actually see the reaction".

"Although I am currently studying theoretical matters, I felt that I had returned to the starting point of my desire to study science".

The results of the experiments (mean values) are shown in Table 2; these values are slightly larger than those from the authors' experiments (Figure 8), which may be due to the individual differences in the disposable pipette.

Table 2 Volume (mL) of aqueous sodium thiosulfate solution used in student experiments.

	Blank	Linseed oil	Fish oil
Immediately after application	7.6	2.0	2.3
24 h after application	-	6.1	6.1

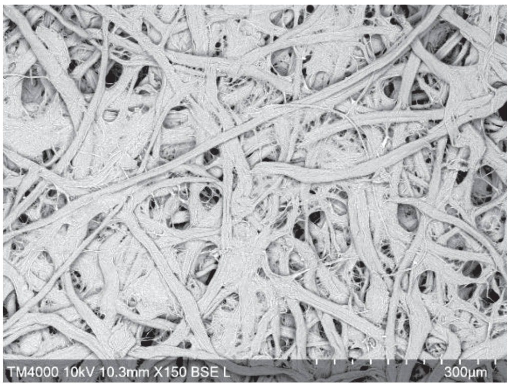
5 Experiment to synthesize pigments for oil painting

Paints are made of a pigment and a binder that holds the pigment onto the surface to be painted. In the middle ages, paintings were made on wooden boards coated with plaster and pigment mixed with egg yolk or gum Arabic. In the Renaissance period of the 15th century, canvas was invented and the method of painting with linseed oil mixed with pigments became popular [14-15].

5.1 Observation of oxidation of linseed oil by electron microscopy

Linseed oil is easily oxidized when exposed to air, which is a disadvantage in the case of food, but an advantage in the case of oil painting. The surface of the filter paper

(a) Immediately after application (× 150)



(b) 24 hours after application (× 150)

Fig. 9 Electron micrograph of filter paper coated with linseed oil.

coated with linseed oil was photographed with an electron microscope (TM4000PlusII, Hitachi High-Tech). Figure 9 shows that on the paper coated with linseed oil, a cured film is formed by oxidation of the oil and fat. It is thought that impregnating the canvas with linseed oil increased the area of the canvas exposed to the air and constrained the movement of the oil, which facilitated oxidation of the oil. This indicates that linseed oil is suitable as a pigment binder.

Oil paper is a product that uses the oxidation of oil and fat to produce a cured film. Because of its water-repellent properties, oil paper is used for packaging materials and for medical purposes. It has also been used for a long time as a material for Japanese umbrellas (Figure 10), but modern students do not know much about it; thus, it is worth introducing it in class.

Fig. 10 Japanese umbrella.

5.2 Student experiment to synthesize pigments

Malachite is a typical blue pigment that can be synthesized by adding sodium bicarbonate powder to a copper(Ⅱ) sulfate aqueous solution. Gaquere-Parker et al. developed a student experiment to synthesize this pigment, mix it with egg yolk, gum Arabic, and linseed oil respectively, and observe the color [16].

$$2\ CuSO_4 + 4\ NaHCO_3 \rightarrow CuCO_3 \cdot Cu(OH)_2 + 3\ CO_2 + H_2O + 2\ Na_2SO_4$$

A variety of pigments can be obtained by adding carbonate salts to aqueous transition metal salt solutions [17]. The reason for this is that aqueous solutions of transition metal salts show relatively strong acidity due to hydrolysis and react with carbonates. The authors took electron micrographs of the produced pigments and analyzed them with an energy-dispersive X-ray fluorescence spectrometer. As observed, these pigments are considered to be composed of transition metal salts and hydroxides adsorbed on the surface of carbonate crystals.

The authors also found that the color of the obtained pigments differed depending on the amount of carbonate salt added, and conducted an investigation. Typical results are shown below [18].

5.3 Experiments to observe the hydrolysis and adsorption of transition metal salts

A 40 mL aliquot of 0.100 mol/L aqueous copper(II) nitrate solution was placed in ten thick test tubes. Sodium bicarbonate was added in increments of 0.10 g up to 1.0 g. The solutions were stirred well and allowed to stand for 24 h after the foaming caused by the carbonate of carbon dioxide had ceased. The pH of the solution was measured and the mass of the precipitate obtained by filtration was determined.

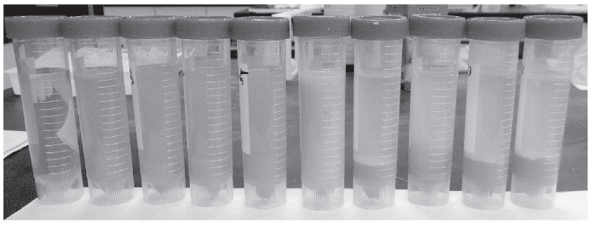


Fig. 11 Addition of sodium bicarbonate to aqueous copper(II) nitrate solution.

The results are as shown in Figure 11. No precipitation occurred when the mass of sodium bicarbonate was less than 0.50 g. However, when more than 0.60 g was added, almost all of the copper(II) salt was adsorbed onto sodium bicarbonate, and the solution became transparent. As the amount of carbonate increased, the pH increased and became closer to neutral, and the blue color of the precipitate became lighter as the mass of the precipitate increased (Figure 12).

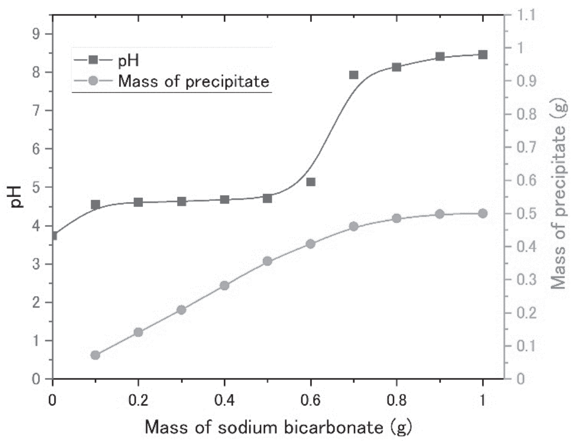


Fig. 12 Relationship between mass and pH of generated precipitate.

Figures 13 and 14 show the results from a similar method in which calcium carbonate was added to 40 mL of a 0.100 mol/L aqueous solution of iron(III) nitrate in increments of 0.10 g up to 1.0 g, and the solution was allowed to stand for 15 min after the carbon dioxide foaming had subsided. In the calcium carbonate mass range of up to 0.60 g, the reddish-brown color of the solution became darker as calcium carbonate was added (no precipitation), but when more than 0.60 g was added, almost all of the iron(III) ions were adsorbed by calcium carbonate and a reddish-brown precipitate was formed, and the solution became transparent. The reddish brown color of the solution is thought to be caused by colloids consisting of hydroxides and oxides of iron(III) ions [19].

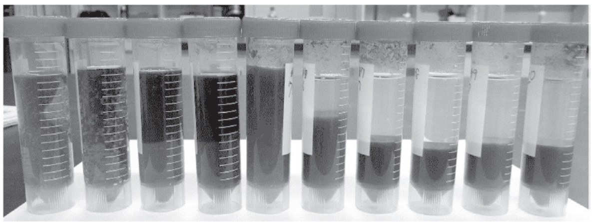


Fig. 13 Addition of calcium carbonate to aqueous iron(III) nitrate solution.

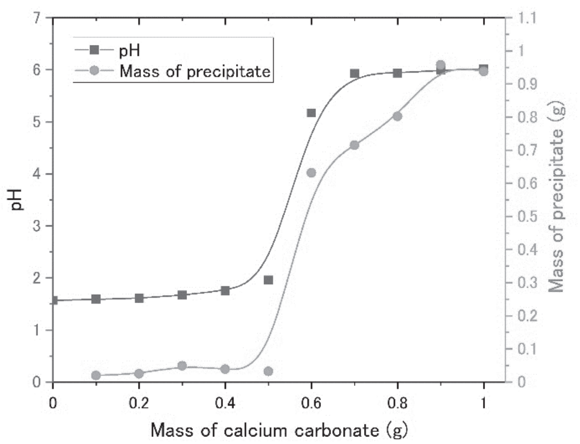


Fig. 14 Relationship between mass and pH of generated precipitate.

The fact that carbon dioxide foaming is observed when calcium carbonate powder is added to aqueous solutions of copper(II) and iron(III) salts is suitable as a student experiment to visualize the acidity that develops during the hydrolysis of salts. In addition, the phenomenon whereby a precipitate is generated and the solution becomes transparent in about 15 min when an excessive amount of carbonate is added is used industrially to remove heavy metal ions from solutions, enabling students to recognize of the importance of stable and good quality water supply and environmental conservation.

6. Conclusion

Various compounds enrich our daily life and society due to their characteristics. It is important in basic chemistry education to let students experience this through experiments and to consider the characteristics of these compounds based on scientific evidence. As an example, the authors focused on the use of oils and fats in daily life. First, we developed an experimental material focusing on the compounds dissolved in oils and fats. The filter paper method was devised for oxidizing a small amount of oils and fats quickly at room temperature. In addition, we developed an experiment to visually observe the acidity of transition metal salt solutions, focusing on pigments necessary for oil painting.

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