2025年臺灣國際科學展覽會
優勝作品專輯

作品編號　030029

參展科別　化學

作品名稱　Glass Coloring by the production of Colloidal Hydroxide

得獎獎項　三等獎

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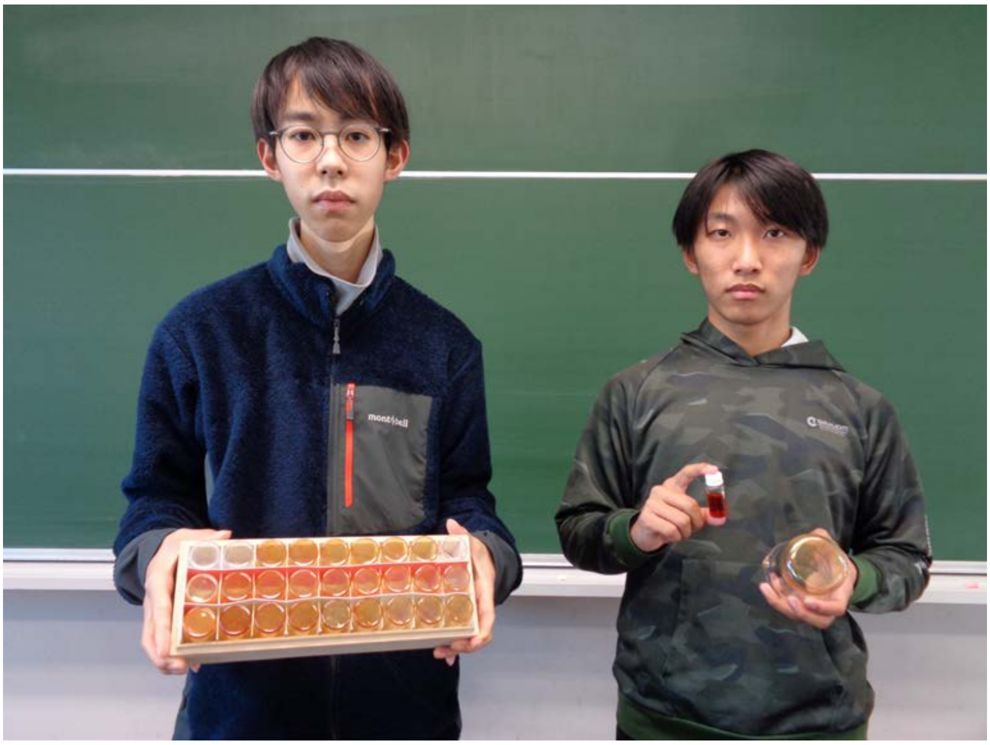

Glass Coloring by the production of Colloidal Ferric Hydroxide

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Abstract

When doing an experiment to produce colloidal ferric hydroxide, the bottom of the beaker used was colored in yellow-brown with thin film interference. This phenomenon is well-known, but the cause has not been clearly studied. As a result of the research, the coloration on the bottom of the beaker is caused by β-FeOOH forming a thin film which is chemically bonded with Si-OH on the glass surface. Also, the amount of β-FeOOH depends on the number of experiments, the area of the bottom of the beaker, and the concentration of $FeCl_3$ aq. We found that it can be possible to determine the amount of β-FeOOH from the formula m=knsc and the adhesion constant was found to be 6.8×10^{-3} (L/m^2). In addition, from machine learning we predicted that the thin film thickness becomes thicker as it moves away from the center.

1. Backgrounds and Objectives

It has been known that when doing an experiment to produce colloidal ferric hydroxide, the bottom of the beaker used is colored in yellow-brown with thin film interference (Fig. 1). But the cause of this phenomenon was never clarified. The production of colloidal ferric hydroxide is a common experiment in high school chemistry, in which an iron(III) chloride aqueous solution is added to boiling water to produce colloidal ferric hydroxide and hydrochloric acid (reaction formula : $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$) (Fig. 2). When we actually conducted an experiment to produce colloidal ferric hydroxide, we were surprised to find that the beaker was colored after only one experiment. We searched for literature of colloidal ferric hydroxide, but the occurrence state of colloidal ferric hydroxide is unclear and we couldn't find a clear answer of why the beaker was colored. Therefore we were interested in this phenomenon and started this study.

Fig. 1 Colored beaker

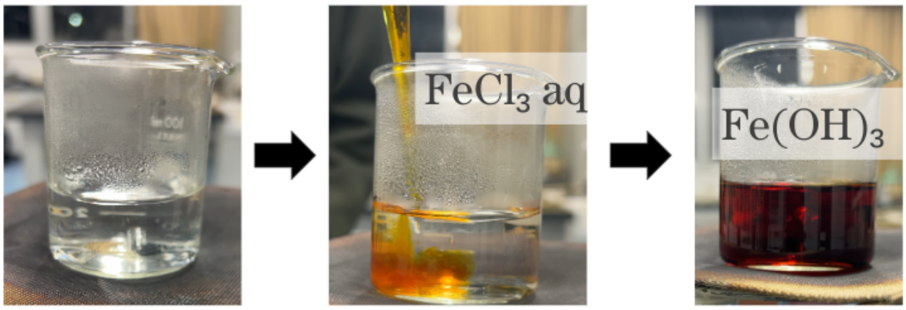


Fig. 2 Production of colloidal ferric hydroxide

The objectives of this study are shown below.

Objective 1: Find out why the beaker is colored

Objective 2: Identify the amount of coloration in conditions

To achieve these objectives, we decided to conduct the following experiments.

1. Solubility of colored parts
2. Discrimination of coloration substance
3. Observation of coloration by scanning electron microscopy

4. Identification of coloration substance
5. Identification of adhered form
6. Amount of coloration adhered under different conditions
7. Prediction of thin film thickness

Colloidal ferric hydroxide is produced by adding 2.0 mL of 1.0mol/L iron(III) chloride aqueous solution to 50mL of boiling water resulting in hydrolysis according to the following reaction formula [I].

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl \qquad [\,I\,]$$

2. Methods to achieve objective 1

2.1 Solubility of colored parts

Since the coloration could not be removed physically, such as by scrubbing with a brush, we decided to first try to dissolve the coloration by using chemicals. Concentrated hydrochloric acid, dilute sulfuric hydroxide, 2.0mol/L sodium hydroxide, 2.0mol/L potassium hydroxide, acetone, and ethanol were each added to a 50mL colored beaker, and left at room temperature for 3 days. There was no basis for the concentration of chemicals at this time, and it was done anyway to test for solubility.

Category	Acid		Base		Organic	
Chemicals	HCl	H_2SO_4 aq	NaOH aq	KOH aq	Ethanol	Acetone
Result	○	○	○	○	×	×

Table. 1 Solubility in various chemicals

The results are shown in Table. 1. The coloration on the bottom of the beaker dissolved in concentrated hydrochloric acid, dilute sulfuric acid, 2.0mol/L sodium hydroxide, 2.0mol/L potassium hydroxide and did not dissolve in ethanol and acetone. This means, the coloration on the bottom of the beaker was found to be an amphoteric substance that exhibited solubility in both acidic and basic solutions. Hereafter, the substance that is causing the coloration will be referred to as the “coloration substance”.

2.2 Discrimination of coloration substance

In the experiment to produce colloidal ferric hydroxide (reaction formula $FeCl_3+3H_2O \rightarrow Fe(OH)_3+3HCl$), both reactants and products contained Fe(III) compounds. Also, when the coloration substance was dissolved in hydrochloric acid, the solution showed a yellow color as shown in Fig. 3. The yellow color of the solution is inferred to be Fe(III) ions. Therefore, we considered that the coloration substance might be a Fe(III) compound. To confirm this, we added potassium ferrocyanide $K_4[Fe(CN)_6]$ to the solution in which the coloration substance was dissolved in concentrated hydrochloric acid.

Fig. 3 HCl which dissolved coloration

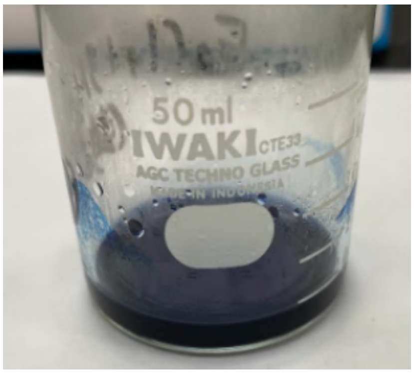


Fig. 4 Dark blue precipitate

The result is shown in Fig. 4, a dark blue precipitate was formed. This indicates that the solution in which the coloration substance was dissolved contains Fe(III) ions and the coloration substance is a Fe(III) compound.

2.3 Observation of coloration by scanning electronic microscopy

When observing the coloration, we noticed that the coloration is very similar to thin film interference like soap bubbles. Thin film interference is a phenomenon in which the refractive index of light is changed by a thin film existing on the surface, making it appear to shine in various colors. Therefore, we made a hypothesis that a thin film of the Fe(III) compound may be formed on the glass surface. We observed the glass surfaces of the beaker before and after coloration by using the scanning electron microscopy (SEM).

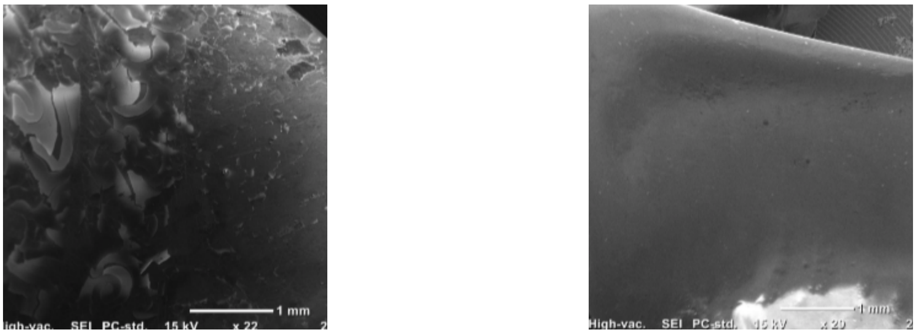


Fig. 5 SEM photographs of the glass surface (left: before coloration, right: after coloration)

The results are shown in Fig. 5. While many irregularities existed on the glass surface before the coloration, the glass surface after coloration was smooth. From this, it was determined that the coloration phenomenon of the beaker was caused by the Fe(III) compound forming a thin film on the glass surface.

2.4 References of colloidal ferric hydroxide

A review of literature revealed that colloidal ferric hydroxide are not simple substances as described in textbooks and other sources, but are quite profound. $Fe(OH)_3$ reacts with condensation to form colloidal particles, and further condensation results in iron oxide hydroxide FeO(OH). The process of $Fe(OH)_3$ becoming FeO(OH) by condensation reaction is considered to be as follows. First, Fe(III) is basically a six-coordinated octahedral structure, and in water it is in a state $\{[Fe(OH_2)_6]^{3+}\}$ in which six OH_2 are coordinated. Depending on the acidity of the water, the hydrolysis reaction (reaction formula II) occurs in which H_3O^+ is removed and OH is coordinated, as shown in Fig. 6 below.

$$[Fe(OH_2)_6]^{3+} + H_2O \rightarrow [Fe(OH)(OH_2)_5]^{2+} + H_3O^+ \qquad [\ II\ ]$$

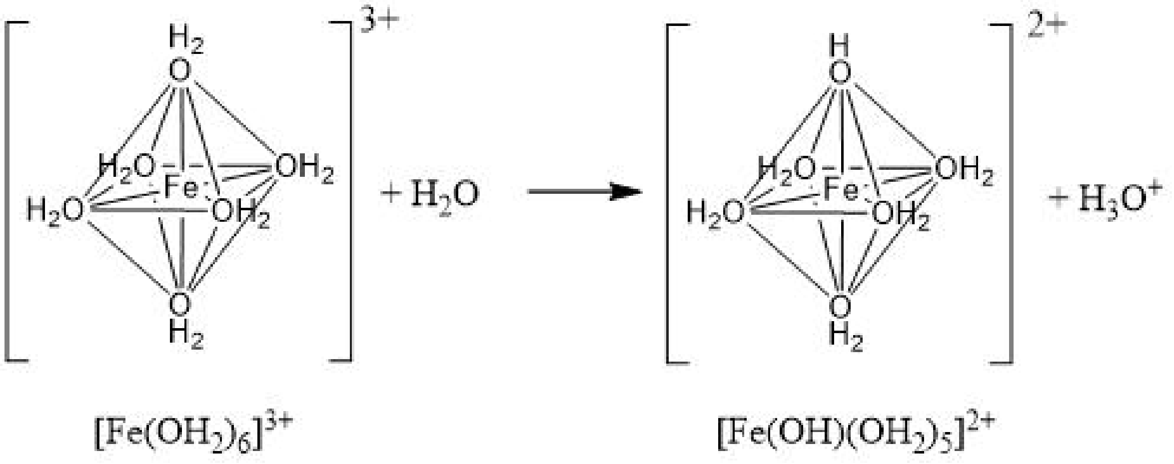


Fig. 6 Hydrolysis reaction of Fe(III)

The OH and (OH_2) formed here share an octahedral edge, and when a dehydration-condensation reaction (−H_2O) occurs, they dimerize. When these dimers develop by further condensation and are arranged in a belt shape, they form a precipitate, iron oxide hydroxide γ-FeOOH (lepidocrocite) crystals as shown in Fig. 7.

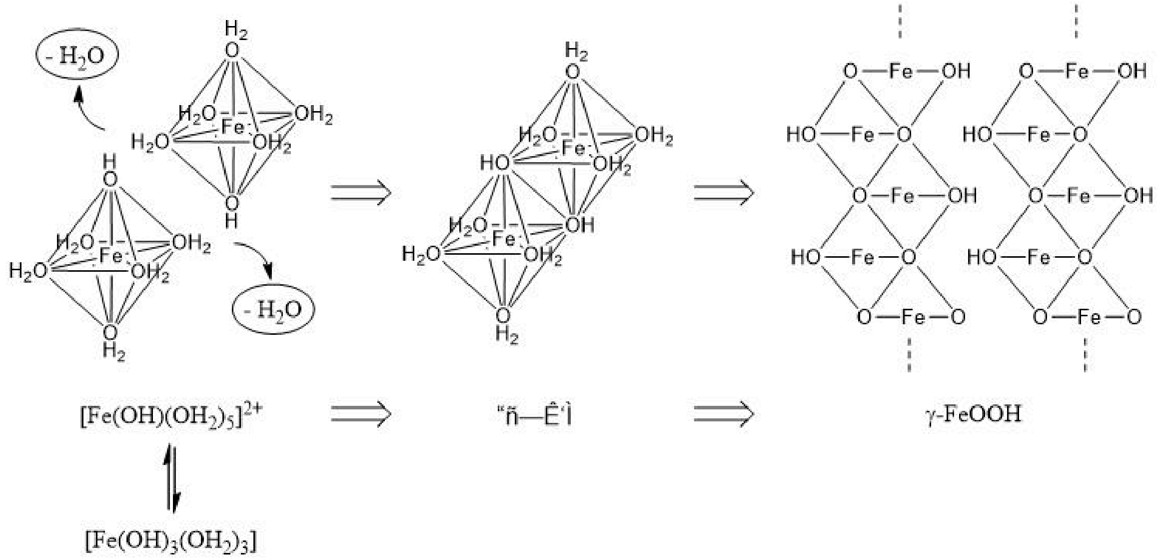


Fig. 7 Structure of iron(III) hydroxide and iron(III) oxide hydroxide

Also iron ions in solution transform into various substances by different pathways depending on the conditions (Fig. 8). Colloidal ferric hydroxide is formed by adding an aqueous solution of iron(III) chloride in boiling water. The iron ion in water is in the state $\{[Fe(OH_2)_6]^{3+}\}$ with six OH_2 coordination, which is synonymous with $Fe^{3}+(OH_2)_6$ in Fig. 8. From Fig. 8, it is known that heating $Fe^{3}+(OH_2)_6$ in the figure in the presence of chloride ions results in β-FeOOH. Therefore, the coloration substance is considered to be β-FeOOH formed by heating Fe(III) in the presence of chloride ions.

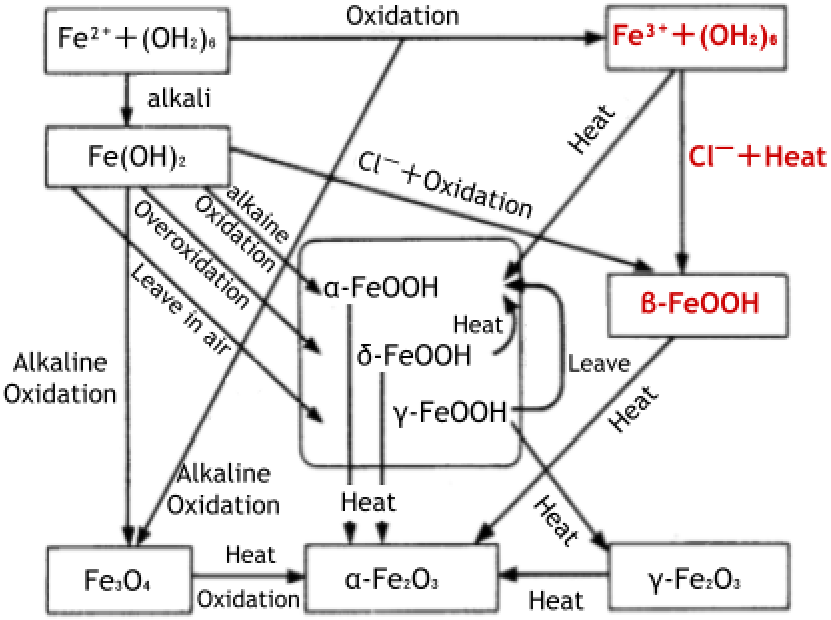


Fig. 8 The formation pathway of “iron oxide” starting from iron ions

2.5 Identification of Fe(Ⅲ) compound

From references (Fig. 8), it was suggested that the Fe(III) compound is β-FeOOH, which is formed by heating Fe(III) ions in the presence of chloride ions. In order to confirm that the Fe(III) compound is β-FeOOH, we conducted experiments under the following conditions A~C.

Condition A **No heating process**

50mL each of 1.0mol/L iron(III) chloride aqueous solution and colloidal ferric hydroxide were placed in a beaker and left still in room temperature for 24 hours.

Condition B **No chloride ions**

Heating 50mL of colloidal ferric hydroxide, which has been dialyzed to remove chloride ions.

Condition C **No chloride ions (Influence of other negative ions)**

Produced colloidal ferric hydroxide by adding 1.0mol/L aqueous solutions of iron(III) sulfate and iron(III) nitrate to 50mL of boiling water.

In all conditions, the presence or absence of coloration was determined by the presence or absence of dark blue precipitation (same method as **2.2**).

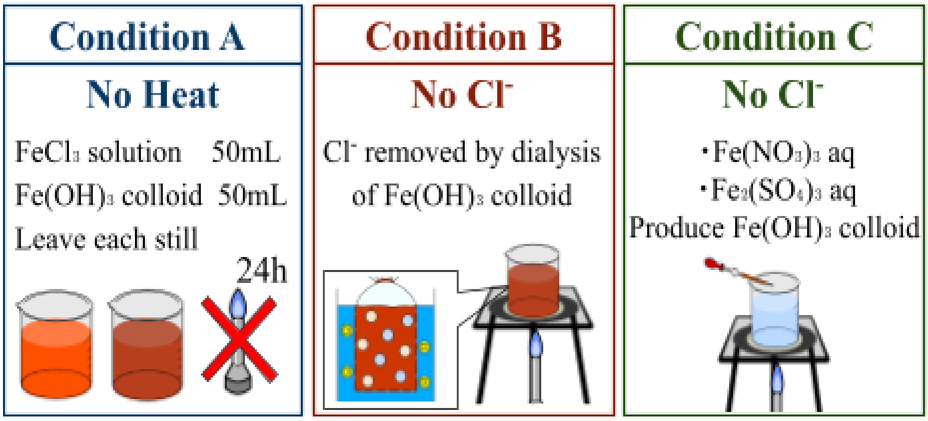


Fig. 9 Images of condition A~C

Conditions	Fe(III)	Heat	Chloride ions (Cl^-)	Dark blue precipitation
A	○	×	○	×
	○	×	○	×
B	○	○	×	×
C	○	○	×	×
	○	○	×	×

Table. 2 Presence or absence of dark blue precipitation in conditions A~C

The results are shown in Table. 2. Since dark blue precipitation was not observed under condition A, it was understood that the heating process is necessary for the coloration. We also understood that chloride ions are necessary for the coloration, since no dark blue precipitation was observed under condition B and C.Therefore, the coloration requires Fe(III) heating in the presence of chloride ions, it follows that the Fe(III) compound which is causing the coloration is β-FeOOH.

2.6 Identification of Adhered form

From 2.1, coloration dissolved in chemicals, but couldn't dissolve by physical ways such as rubbing it with a brush. This made us think that β-FeOOH and the glass surface are chemically bonded together. To confirm this we conducted production experiments using materials beside glass to see if the coloration only occurs on glass surfaces. We conducted production experiments of colloidal ferric hydroxide using glass, plastic(PMP), and metal (copper) containers. The presence of coloration was determined visually because the material of the containers made it difficult to dissolve with concentrated hydrochloric acid.

Materials	Glass	Plastic (PMP)	Metal (copper)
Presence of coloration	○	×	×

Table. 3 Presence or absence of coloration in the container material

The results are shown in Table. 3. The coloration only occurred on glass surfaces, suggesting that β-FeOOH and the glass surface may be attached to each other through a specific reaction. From 2.1 it was found that the coloration is soluble in acids and bases. However, there are only a few amphoteric substances in the iron compound system, and β-FeOOH is known to not show amphoteric properties. However in the case of silicon - oxygen - metal bonding (Si-O-M bond), it is known to dissolve in base, and cleavage reactions occur one after another. Therefore, β-FeOOH is considered to be chemically bonded to the glass surface. The detailed reaction is considered to be as follows (Fig. 10).

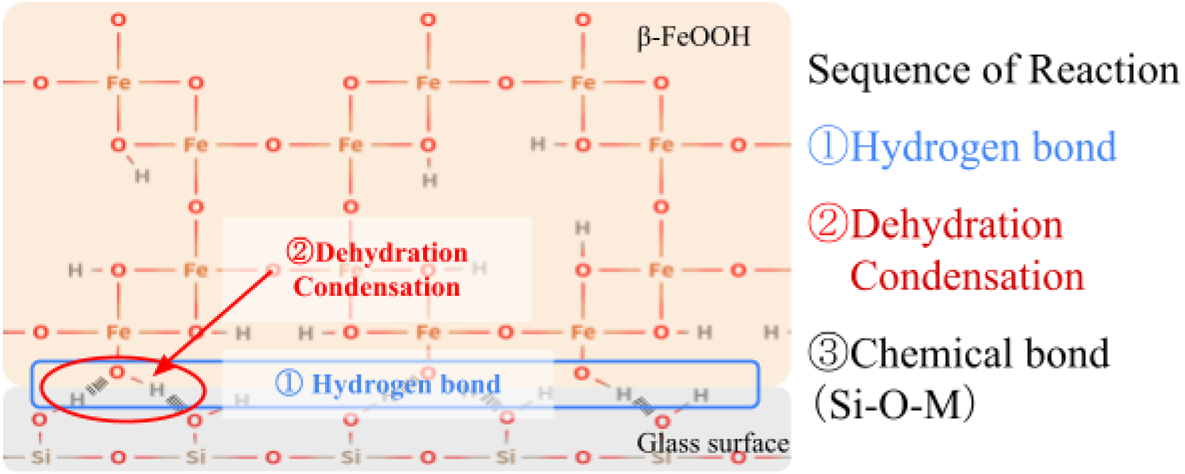


Fig. 10 Attachment morphology hypothesis

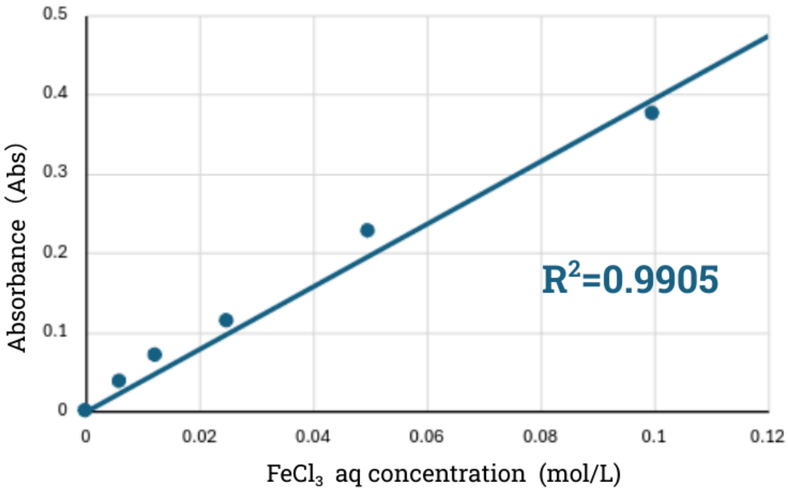
It is known that the silanol group Si-OH exists on the glass surface. In addition, hydroxyl group -OH exists on the surface of β-FeOOH. First, the hydroxyl group -OH of the silanol group Si-OH on the glass surface and the hydroxyl group -OH of β-FeOOH from hydrogen bonds, bringing them closer together. Furthermore, a dehydration condensation reaction occurs in the hydrogen bonding area to form Si-O-Fe, resulting in a silicon-oxygen-metal bond, which is thought to form a chemical bond between β–FeOOH and the glass surface. This explains why the coloration is soluble in base and occurs only on glass.

2.7 Summary so far

It was understood that the coloration phenomenon at the bottom of the beaker was caused by β-FeOOH in a thin film state. We also understood that heating in the presence of chloride ions are necessary for the coloration, and that β-FeOOH and the glass surface Si-OH undergo a hydrogen bonding followed by a dehydration condensation reaction to form a chemical bond.This has allowed us to achieve our objective : Find out why the beaker is colored.

3. Methods to achieve objective 2

To quantitatively evaluate the amount of β-FeOOH attached to the glass surface, it is necessary to accurately measure it. However, since it is difficult to measure accurately, we decided to ascertain it by the amount of Fe, assuming that Fe is contained in a certain proportion in the thin film of β-FeOOH. After dissolving β-FeOOH in 3.0mL of concentrated hydrochloric acid, the absorbance (Abs) was measured using a spectrophotometer. We made a calibration curve using an aqueous solution of iron(III) chloride by a known molar concentration at 510.5nm (Graph. 1) . We used this calibration curve to determine the amount of β-FeOOH.



Graph. 1 Calibration curve of iron (III) chloride solution at 510.5nm

3.1 Amount of β-FeOOH by the number of production experiments

We checked if the amount of β-FeOOH depends on the number of production experiments of colloidal ferric hydroxide. We also compared the amount by using new and used beakers to see if there was any difference.

Method

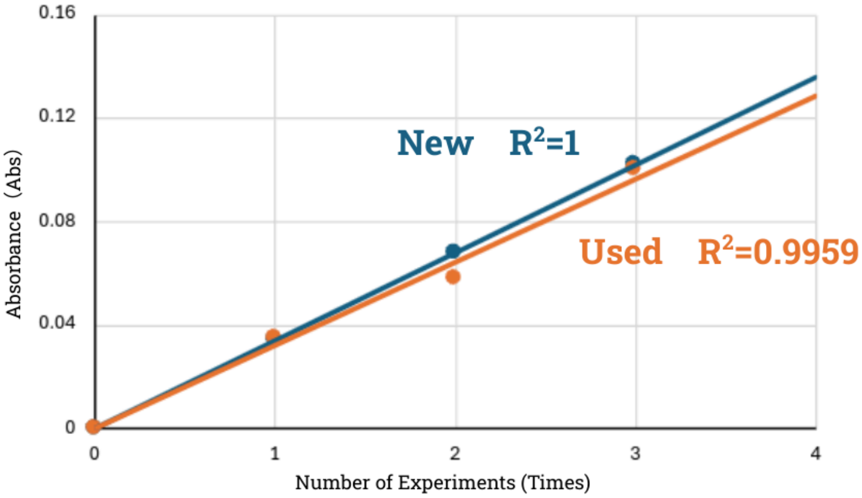
We added 2.0mL of 1.0 mol/L iron(III) chloride aqueous solution to 50mL of boiling water and left it still.We did the experiment once only, two consecutively three consecutively and used new and used beakers five each.Then, we removed the coloration by using 3.0mL of concentrated hydrochloric acid, and measured the absorbance of the solution.

Results

The results are shown in Table. 4 and Graph. 2 below. The amount of β-FeOOH showed a proportional relationship between the number of production experiments. This means that the amount of β-FeOOH per experiment is constant.

Number of production experiments	Absorbance (Abs)	
	New beakers	Used beakers
1	0.034	0.035
2	0.068	0.058
3	0.102	0.1

Table. 4 The absorbance by the number of production experiments



Graph. 2 Relationship between the number of experiments and the absorbance

3.2 Amount of β-FeOOH by different bottom areas

We checked if the amount of β-FeOOH depends on the base area of the beaker.

Method

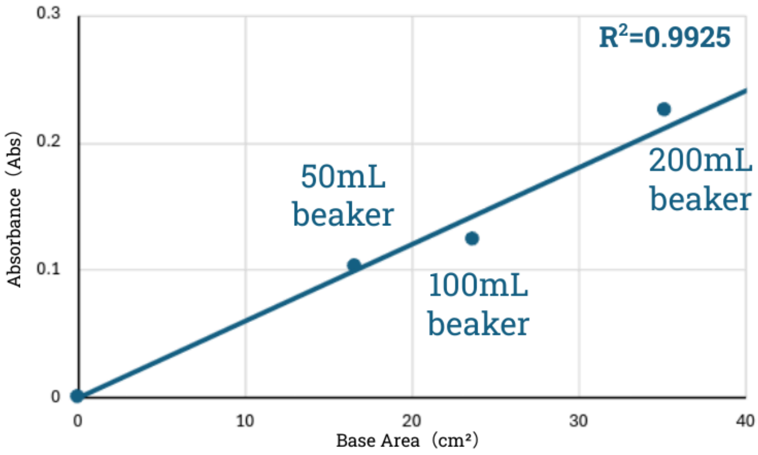
We added 2.0mL of 1.0 mol/L iron(III) chloride aqueous solution to 50mL of boiling water and left it still.We did the experiment 3 times consecutively and used beakers 50mL, 100mL, 200mL, five each. Then, we removed the coloration by using 3.0mL of concentrated hydrochloric acid, and measured the absorbance of the solution.

Results

The results are shown in Table. 5 and Graph. 3 below. The amount of β-FeOOH showed a proportional relationship between the base area of the beaker. This means that the amount of β-FeOOH depends on the base area of the beaker.

	Absorbance (Abs)	Absorbance raito	Base Area (cm^2)	Base area raito
50mL beaker	0.102	1	5.29 π	1
100mL beaker	0.123	1.205	7.56 π	1.429
200mL beaker	0.225	2.205	11.22 π	2.121

Table. 5 The absorbance by the base area of the beaker



Graph. 3 Relationship between the base area and the absorbance

3.3 Amount of β-FeOOH by the concentration of iron (III) chloride aqueous solution

We checked if the amount of β-FeOOH depends on the concentration of iron(III) chloride of aqueous solutions.

Method

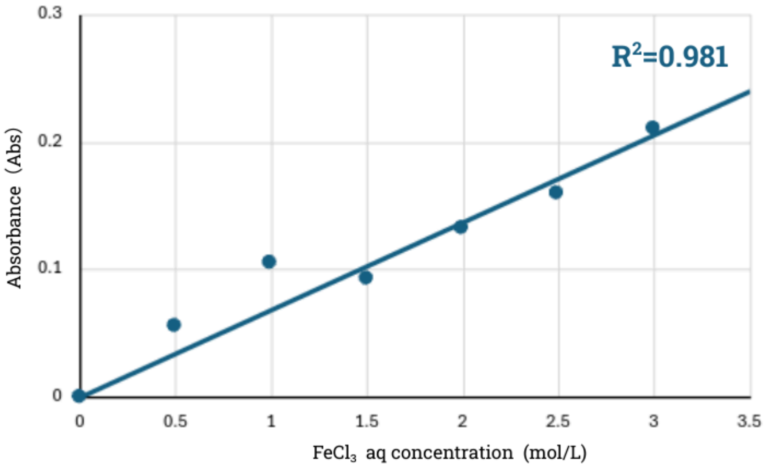
We added 2.0mL of iron(III) chloride aqueous solution to 50mL of boiling water and left it still.We changed the concentration from 0.5 ~ 3.0 mol/L and did the experiment 3 times consecutively and used beakers five each. Then, we removed the coloration by using 3.0mL of concentrated hydrochloric acid, and measured the absorbance of the solution.

Results

The results are shown in Table. 6 and Graph. 4 below. The amount of β-FeOOH showed a proportional relationship between the concentration of iron(III) chloride aqueous solutions. This means that the amount of β-FeOOH depends on the concentration of iron(III) chloride aqueous solutions.

$FeCl_3$ (mol/L)	0.5	1.0	1.5	2.0	2.5	3.0
Absorbance (Abs)	0.055	0.105	0.092	0.132	0.159	0.210

Table. 6 The absorbance by the concentration of iron(III) chloride aqueous solutions



Graph. 4 Relationship between the concentration of iron(III) chloride aqueous solution and the absorbance

3.4 Amount of β-FeOOH in conditions

From 3.1~3.3 we understood that the amount of β-FeOOH depends on the number of experiments, the base area of the beaker, and the concentration of iron(III) chloride aqueous solutions. Therefore, we thought that we could compute the amount of β-FeOOH from a formula multiplying the number of production experiments, the base area, and the concentration of iron(III) chloride aqueous solutions. The formula became m=knsc, and adhesion constant “k” was found to be 6.8×10^{-3} (L/m^2). (“m” amount of β-FeOOH (mol), “n” number of production experiments, “s” the base area (m^2), “c” the concentration of iron (III) chloride aqueous solution).

3.5 Prediction of thin film thickness trend

It is known that there is a relationship between thin film thickness and interference colors. By using machine learning for the relationship between thin film thickness and the RGB value of interference color, we thought it is possible to predict the thin film thickness trend. We used python and made a 3D model of the trend of thin film thickness.

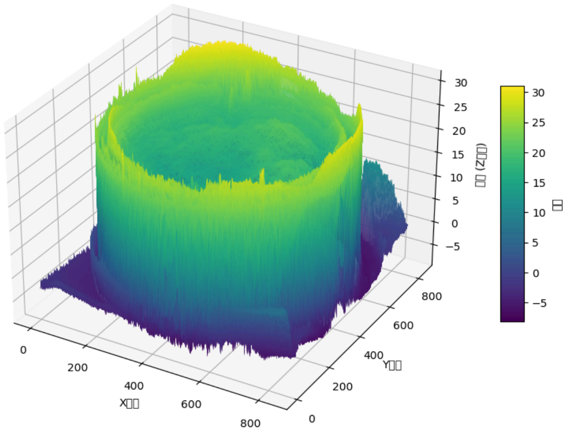


Fig.11 3D model of thin film thickness trend

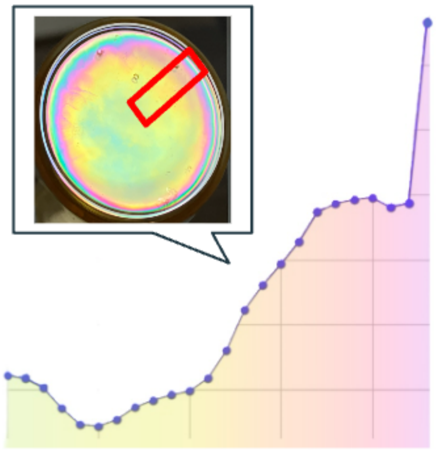


Fig. 12 Cross sectional view of 3D model

The results are shown in Fig. 11 and Fig. 12 is a cross sectional view of the 3D model. From this 3D graph we can see that the thickness of the thin film becomes thicker as it moves away from the center.

4. Conclusion

The cause of the coloration of the bottom of the beaker caused by the production of colloidal ferric hydroxide was found to be β-FeOOH forming a thin film on the glass surface.The coloration phenomenon does not occur if only colloidal ferric hydroxide are present, but the hydrolysis process is necessary when an aqueous solution of iron(III) chloride is added to boiling water. Also, it is suggested that the glass surface Si-OH and β-FeOOH are chemically absorbed. Therefore we achieved goal 1 : Find out why the beaker is colored. It became possible to determine the amount of β-FeOOH from the formula m=knsc, and the adhesion constant “k” was found to be 6.8×10^{-3} (L/m^2). By using machine learning it is predicted that the film thickness becomes thicker as it moves away from the center. Therefore we achieved goal 2 : Identify the amount of coloration in conditions.

5. Acknowledgements

In conducting this study, we would like to express our deepest gratitude to teachers and seniors, especially to Mr. Yusuke Sugawara & Mr. Yuunosuke Kudo for their kind and constructive suggestions. We deeply appreciate their contributions.

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【評語】030029

The objectives of this study are to find out why the glass beaker is colored and to identify the amount of coloration in conditions. The cause of the coloration of the bottom of the beaker caused by the production of colloidal ferric hydroxide was found to be β-FeOOH forming a thin film of silicon-oxygen-metal binding on the glass surface. They summarized the production of β-FeOOH in a single equation and succeed in creating a 3D image to visually show how the thin film adheres to the glass surface using machine learning in python. The authors need to explain the difference in structural definition of and form. It will also be helpful if atomic spectroscopy such as AA or AE can be used to confirm the presence of Fe in the coloration rather than simply using UV absorbance. The authors have outlined a list of 18 actions and they completed up to 8 items in the year one; 9-18 items were completed this year. This is a good work and worth recommendation.