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Stepwise Inquiry into Hard Water in a High School Chemistry Laboratory

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Ⓢ *Supporting Information*

ABSTRACT: This study focuses on the design of a learning program to introduce complexometric titration as a method for determining water hardness in a high school chemistry laboratory. Students are introduced to the different properties and reactions of hard water in a stepwise manner so that they gain the necessary chemical knowledge and conceptual understanding of the basic principles of complexometric titration. This approach involves investigating the performance of soap and household laundry detergent in hard water and using a colorimetric method to semiquantitatively determine the concentration of calcium ions in hard water by a test kit. The stepwise inquiry and learning are promoted using coordinated experimental work, logical thinking, and discussion with the aid of demonstrations and explanations. As each inquiry and learning step is completed, students develop models that describe the observed chemical properties and reactions of hard water. Using the simple models that they develop, students finally propose the basic principles of complexometric titration for determining water hardness. Based on their experimental principles, practical titration experiments are performed and the experimental data are analyzed to determine water hardness. Throughout the learning program, students actively apply preliminary knowledge and acquire new chemical knowledge and conceptual understanding from the laboratory exercises. Therefore, the students experience the process of scientific inquiry accompanied by the development of their understanding of chemical concepts. This paper reports that the developed learning program may be introduced as a suitable laboratory learning exercise in high school chemistry courses.

KEYWORDS: *High School/Introductory Chemistry, Analytical Chemistry, Environmental Chemistry, Collaborative/Cooperative Learning, Inquiry-Based/Discovery Learning, Aqueous Solution Chemistry, Water/Water Chemistry*

Determination of water hardness using complexometric titration is a laboratory exercise routinely taught as part of the general and analytical chemistry courses in universities.[1−5] Many different pedagogical methodologies for the student exercise have been proposed and trialled,[1,3,5] and several different experimental methods for determining water hardness in teaching laboratories have been proposed, including redox titration and absorption spectrometry.[6,7] The determination of water hardness is also included as a study item for the investigation of water in the environment and drinking water by students,[3,8] where a semiquantitative colorimetric analysis using a test paper or a test kit may be performed in a field study.[9] Laboratory exercises for determining water hardness also appear to be useful in high school chemistry courses,[8] because water may be used to study the different properties and chemical reactions of aqueous solutions and the subject can be related closely with daily life and the environment. However, in general, the chemical principles of analytical techniques are advanced topics for high school students. Therefore, a carefully designed learning program is necessary to implement the determination of water hardness into high school chemistry classes as a student exercise that is fully supported by chemistry learning.

Softening of hard water is another promising learning topic in chemistry courses in high schools and universities,[4,10−14] through which precipitation reactions, complexing reactions, ion exchange, and deionization can be studied. Osorio et al.[10] proposed a demonstration of soap foaming in hard water by softening using a complexation reaction. This experiment seems to be suitable for high school students, because the phenomena can be related to the chemistry of soap and household detergents, which is another useful subject in high school chemistry.[15,16] In addition, the reaction of Ca^{2+} in hard water with the chelating agent contained in the household detergent can be used to introduce the concept of complexation reactions,

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which are fundamental to understanding the experimental principle of complexometric titration.

Based on the studies described above, this study focuses on the development of a learning program for high school chemistry courses for determining water hardness through step-by-step learning about the properties and reactions of hard water. The aim of this study is to enable students to develop an understanding of the basic experimental principles of complexometric titration based on the ideas they acquire from the different learning steps in the program. Here, the learning program developed is presented, together with the results of an educational trial conducted in a high school chemistry class.

■ LEARNING PROGRAM AND STUDENT ACTIVITY

Overview

This learning program is designed for students in high school chemistry classes under the assumption that the students have already completed units covering the properties of solutions, chemical reaction stoichiometry, and acid−base reactions (including neutralization titration). The learning program introduces different properties and chemical reactions of hard water in a step-by-step manner via five consecutive learning steps:

- Step 1: Discrimination of water samples
- Step 2: Foaming of household laundry detergent in water
- Step 3: Semiquantitative determination of the molar concentration of Ca^{2+}
- Step 4: Quantitative determination of total molar concentration of Ca^{2+} and Mg^{2+}
- Step 5: Calculation of water hardness

For each learning step, different student exercises and introductions by an instructor are arranged, and as a result of the exercises, the students develop simple models of solutions, which form the basis of the subsequent learning steps. On the basis of the models developed in steps 1−3, students propose the experimental principle of complexometric titration by refining the previously developed models. The experimental principles illustrated using the simple models are utilized in steps 4 and 5 for the practical application of complexometric titration and the calculation of water hardness, respectively. The frameworks of the learning program and the student activities are summarized in Table S1 in the Supporting Information, illustrating the objectives and learning content of each step and the overall flow of the learning program, together with approximate times required for each learning step.

This learning program was developed through trials in high school chemistry classes and introductory chemistry classes at our university over a five-year period and has been improved continuously based on the results of the educational trials. The newest version of the learning program presented in this article was also implemented for students in 3−4 member groups in a high school chemistry class and in an introductory chemistry class at our university. A total of 5 h was allotted to complete the learning program. The student handout provided in the Supporting Information was supplied in a step-by-step manner to students. The progress of the individual students was evaluated by assessing the models developed (and improved after discussions in groups and in class) for each learning step, as presented in the students' records sections of the student handout. Video recordings taken during the course of the laboratory classes were also used to assess the efficacy of the program.

Step 1: Discrimination of Water Samples

To introduce this learning topic in the student laboratory, four different water samples labeled A−D, the contents of which are unknown to students, are provided to each student group (see Table S2 in the Instructor Information section of the Supporting Information). The samples are (A) distilled water, (B) bottled water (hard water), (C) bottled water (soft water), and (D) tap water. Students are asked to propose possible experimental methods to distinguish these water samples. Students propose several methods informed by their experiences in the school laboratory and their households, which typically involve smell testing, taste testing, and pH testing. Then, the students attempt to distinguish the water samples using the methods they have proposed, but they are usually unsuccessful. After the student activity, the instructor proposes the addition of a small amount of natural soap to the water samples and observation of the foaming behavior with stirring. Through this simple experiment, students identify the water sample that does not produce foam and instead produces precipitates, that is, (B) bottled water (hard water), and thus distinguish the hard water sample from the others. Typical results of the soap-foaming experiment in water samples A−D are shown in Figure S3 in the instructor information section of the Supporting Information.

The causes for the unique behavior of water sample B are then discussed among the students. They usually consider the possibility of contaminations in water sample B and propose evaporation to dryness and flame testing. Through the discussion of the experimental procedures, students are also made aware of the necessity for comparative experiments using a foaming, nonprecipitating water sample as a control, for example, water sample A. Students only observe a solid product as the result of evaporation to dryness for water sample B, and the water sample produces an orange flame in a flame test. From these results, the students ascertain that water sample B contains calcium ions (Ca^{2+}). This conclusion is subsequently confirmed by adding oxalic acid solution to water sample B, upon which a precipitation reaction is observed. Once the students are aware of the existence of Ca^{2+} in water sample B, the concept of hard water is introduced to the class. Typical experimental results in this learning step are shown in Figure S4 in the instructor information section of the Supporting Information.

At the end of step 1, students are asked to draw simple models of water sample B and the precipitation of calcium oxalate in water sample B using symbolic labels for calcium ion and oxalate ion. Figure 1 shows typical models for water sample B (Figure 1a) and the precipitation of calcium oxalate (Figure 1b) drawn by students. On the basis of the students' models of the precipitation reaction, the instructor introduces the precipitation reaction between Ca^{2+} and soap as observed when natural soap is added to water sample B.

Step 2: Foaming of Household Laundry Detergent in Water

The instructor proposes an investigation of the foaming of a household laundry detergent in water sample B, that is, hard water. The sufficient foaming of the detergent observed in hard water (Figure S1 in the instructor information section of the Supporting Information) leads students to the next inquiry. Students learn the components of the detergent from the label on the detergent bottle. They identify alkaline and chelating

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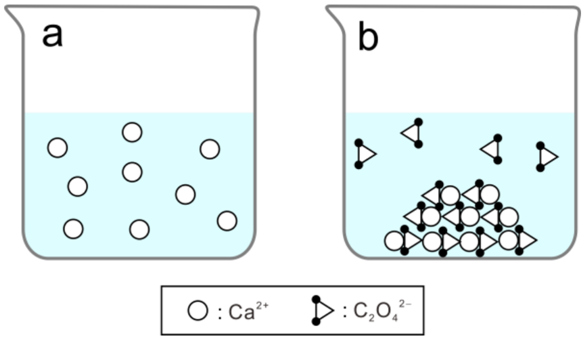

Figure 1. Typical models proposed by students for (a) hard water (MODEL 1) and (b) precipitation of CaC_2O_4 in hard water (MODEL 2).

agents as the chemicals potentially responsible for the foaming of the detergent in hard water. With regard to the alkaline agent, the students initially test the influence of the pH of the aqueous solution on the foaming behavior of the soap and interpret the results through instruction with reference to the acid dissociation equilibrium of soap molecules in aqueous solution. Then, students test the foaming of natural soap in hard water with the addition of alkaline and chelating agents. They find that both alkaline and chelating agents are required for the production of foam. Typical results for the foaming of natural soap in water sample B under different alkaline and chelating agent conditions are shown in Figure S5 in the instructor information section of the Supporting Information. At this point, the instructor introduces the concept of complex formation between chelating agents and metal ions under alkaline conditions by considering the roles of alkaline and chelating agents in the observed phenomena. As an example of a chelating agent, the instructor introduces ethylenediaminetetraacetate (EDTA) and discusses its molecular structure, its acid dissociation equilibrium, and the stoichiometry of EDTA–metal ion complex formation. Then, the students are asked to draw a simple model of the complex formation between EDTA and Ca^{2+} in alkaline-adjusted hard water, as shown in Figure 2.

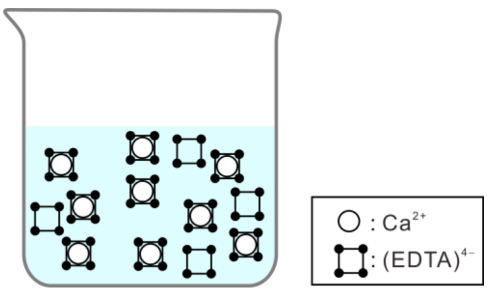

Figure 2. Typical model proposed by students for complex formation between Ca^{2+} and $(EDTA)^{4-}$ under alkaline conditions (MODEL 3).

Step 3: Semiquantitative Determination of the Molar Concentration of Ca^{2+}

To introduce students to the next step of inquiry, the instructor introduces the concept of water hardness. Then, the students' inquiry proceeds to the semiquantitative determination of Ca^{2+} concentration using a commercially available test kit, in our case a PACKTEST WAK-Ca (KYORITSU Chemical-Check Lab. Co., Japan).[17] Students ascertain the Ca^{2+} concentrations of water samples A–D to be 0–5, > 50, 5–10, and 5–10 mg L^{-1}, respectively (Figure S6). During this activity, the instructor reveals the contents of the PACKTEST, that is, sodium tetraborate decahydrate as the alkaline buffer agent and phthalein complexone as the metal indicator, and introduces the principle of colorimetric analysis. Students draw a simple model for the coloration reaction observed in the PACKTEST experiment, as shown in Figure 3a.

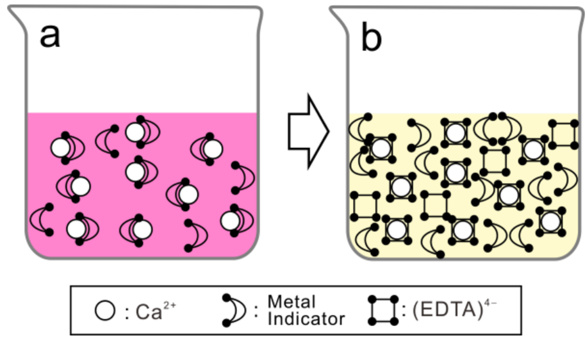

Figure 3. Typical models proposed by students for (a) complex formation between Ca^{2+} and a metal indicator under alkaline conditions (MODEL 4) and (b) the ligand displacement reaction (MODEL 5).

Here, the instructor demonstrates discoloration of the colored hard water in the PACKTEST solution upon the addition of EDTA, which causes the purplish red coloration of the solution to change to light yellow (Figure S2). Following this demonstration, students discuss the cause of the discoloration and draw a simple model for the discoloration reaction that describes the ligand displacement reaction, as shown in Figure 3b. Although a complete explanation of the ligand displacement reaction requires quantitative understandings of chemical equilibrium and equilibrium constant related to complex formation reactions, the quantitative understanding is an advanced chemistry learning usually treated in university analytical chemistry. In this program, students advance to the next learning step with the phenomenological understanding of the ligand displacement reaction based on the model shown in Figure 3.

Step 4: Quantitative Determination of Total Molar Concentration of Ca^{2+} and Mg^{2+}

Owing to the semiquantitative nature of the Ca^{2+} concentration determination using the PACKTEST kit, students are asked to propose possible methods to determine the concentration quantitatively and to describe their proposal by drawing simple models. After 15 min of group discussions, the students propose the experimental principles of complexometric titration by simply refining the simple models they have already developed in previous inquiry steps. Figure 4 shows models of the experimental principles of complexometric titration proposed by the students. The proposed experimental methods are reviewed in the class, with any necessary advice for the practical application of the experiments being provided by the instructor, which involves explanation of the apparatus, chemicals, and safety procedure. Furthermore, guidance concerning the required amount of metal indicator for the titration experiment is provided because the model for the coloration of hard water by the metal indicator proposed previously by the students involves an excess amount of the metal indicator, but only a minimal amount is required for the

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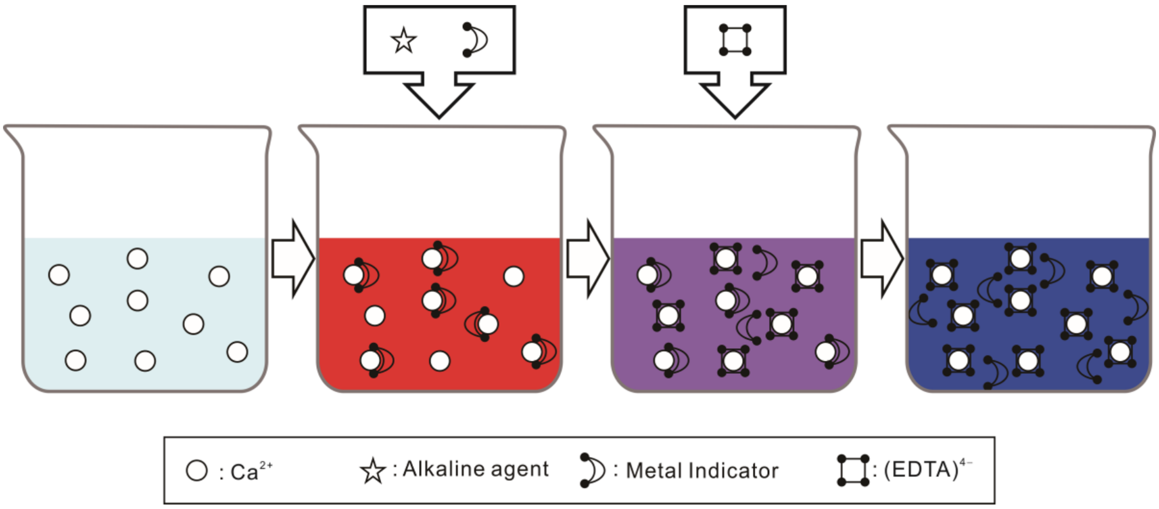

Figure 4. Principles of complexometric titration proposed by students using the simple models they developed (MODEL 6).

titration experiment. The instructor proposes the use of Eriochrome Black T (BT) as the metal indicator, which forms a complex with Ca^{2+} and Mg^{2+} that produces a reddish-purple color under alkaline conditions. Here, the existence of magnesium ions in hard water is introduced through a demonstration using a test kit for magnesium ions (PACKTEST WAK-Mg). It is also demonstrated that BT indicates a reddish-purple color both in the alkaline solutions of calcium and magnesium ions. The NH_4Cl/NH_3 buffer solution (pH ~10) is introduced, and a standard EDTA solution (1.00×10^{-2} M) is provided. The color change of the water sample upon addition of the metal indicator, and the subsequent discoloration by titration with the standard EDTA solution, are demonstrated by the instructor. The solution titrated to the end point by the instructor is provided as a reference for the students to determine the end point of the titration. While reviewing the experimental principles, students are made aware of the experimental method for determination of the total concentration of Ca^{2+} and Mg^{2+} in their water samples.

Then, in groups, students perform the complexometric titration of water sample B according to their own manual, as described using their simple models (Figure 4). The standard procedure for the complexometric titration is also described in the student handout. At high schools that are located close to karstic areas, mineral water taken from river caves may also be subjected to complexometric titration. The titration is repeated at least four times for each sample, and the average titration volume is calculated by the students.

Step 5: Calculation of Water Hardness

Students are taught to calculate the water hardness using their average titration volume by a stepwise calculation involving (1) the amount of EDTA used in the titration, (2) the total amount of Ca^{2+} and Mg^{2+} in the 10 mL water sample, (3) the total molar Ca^{2+} and Mg^{2+} concentration of the water sample, and (4) the mass of total Ca^{2+} and Mg^{2+} as $CaCO_3$ in a 1.0 L water sample (that is, water hardness). Typical results reported by student groups following this learning program in a high school chemistry course are listed in Table 1. The total water hardness of sample B (Evian) is 304 mg/L from the description on the label of the bottle. Natural water taken from karst cave has been determined to be 141 ± 2 mg/L by the instructor prior to the course. The experimental values for the water hardness reported by the students are close to these reference values.

Table 1. Typical Results for Total Water Hardness Reported by Student Groups in the Present Learning Program

	Total Water Hardness (mg/L)	
Group	Water Sample B	Natural Water
1	307	154
2	303	143
3	338	130
4	313	129
5	302	131
6	325	147
7	313	149
8	312	130
Average	314 ± 5	139 ± 4

Students classify the water samples into hard and soft water with reference to the WHO reference value.[18] Students also discuss the possible origins of Ca^{2+} and Mg^{2+} dissolved in the water samples. When natural water taken from a karst cave is used, students quickly recognize that the origin is related to the geological characteristics of the karst area. This idea is expanded to water sample B by an Internet investigation of the geological conditions in the area in which Evian is produced. The learning program is concluded by assigning several daily topics related to the learned chemical knowledge and concepts to students for further discussion. Examples of the topics are listed in further discussion section at the end of the student handout provided in the Supporting Information.

■ HAZARDS

Students are required to wear safety goggles and protective gloves throughout the experimental work. The aqueous solution of oxalic acid is a deleterious substance. The NH_4Cl/NH_3 buffer solution (pH ~10) has an irritating odor. These materials are hazardous in cases of skin contact, eye contact, aspiration, or ingestion. The buffer solution should be added to the water samples in a fume hood. During the titration experiment, air ventilation of the laboratory is necessary. The waste solutions should be disposed of according to laboratory rules.

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EVALUATION OF LEARNING ACTIVITY

The students' learning process was tracked by evaluating models developed by the individual students in each learning step. The level of the models was graded as "perfect", "incomplete", or "wrong". Figure 5 shows the ratio of perfect/incomplete/wrong for each model developed by individual students at the first instruction for drawing the model at the respective steps of the learning program as practiced in a high school class (N = 30). At the individual student level, the number of "perfect" scores gradually decrease as the program progresses. Many models graded as "incomplete" were missing the necessary consideration of the quantitative relationship between the species. For example, an excess amount of metal indicator is required for the colorimetric analysis in MODEL 4 (Figure 3a). The models graded as "wrong" usually involve a misunderstanding of the reaction stoichiometry. It was confirmed from the video recordings that the incomplete students' understanding of each model is improved in each respective step through discussions, both in groups and as a whole class, as well as through introduction of the relevant chemical concepts by the instructor. It was also noted that the refinement processes of each individually proposed model through discussions were very important activities in the learning program, through which each student explained the chemical background of the proposed model and correlated more closely the model with chemical knowledge and concepts for improving their models. Overall, the stepwise learning design in this program is successful, as shown by the step-by-step rearrangement of the models as the program progresses. As a result, all the students were able to propose the fundamental experimental principles of complexometric titration at the individual student level, although some points require further clarification in order that the students' understanding is completed, most notably the amount of metal indicator to be added. This point is also refined through discussions in groups and reinforced by the instructor through discussions as a whole class.

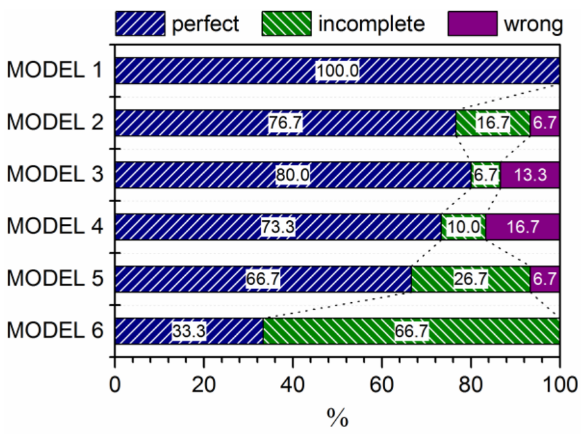

Figure 5. Evaluation of models proposed by individual students (N = 30) at the first instruction for drawing the model in each step in the proposed learning program as applied in a high school chemistry class.

During the development of the learning program, suitable learning step to introduce the existence of magnesium ions in hard water was examined through educational trials. For example, the existence of magnesium ions was confirmed by students in the learning step of semiquantitative determination of cation concentrations (Step 3) in some educational trials. However, the introduction of magnesium ions in earlier learning step in this program made the model developments difficult for students in many cases, because they must consider two different kinds of cations in the models. In the reported version of the learning program, students were made aware of the existence of magnesium ions in the sample water after they developed the fundamental model for complexometric titration in Step 4 when BT was introduced as a metal indicator. They also noted that the comparable chemical behavior of Ca^{2+} and Mg^{2+} in an alkaline solution when reacting with BT and EDTA before the titration experiment.

MODEL 6 developed by the students is effectively utilized during the complexometric titration experiment and calculation of water hardness. The students performed the complexometric titration experiment according to the procedure illustrated by the model without any support from the instructor. The students also derived the relevant method required for calculation of the water hardness, and no practical support from the instructor was required for determining its value.

CONCLUSIONS

Through a strategically arranged experimental approach to investigating the properties and reactions of aqueous solutions, students develop simple models that rationalize the phenomena observed for hard water. In this process, they actively apply the chemical knowledge and conceptual understanding acquired in the preceding steps to the new step. Simultaneously, the learning program provides many opportunities to engage in logical thinking suitable to high school students and to introduce novel chemical knowledge and concepts, including chemical properties of soap in a solution, complex formation reactions, and ligand displacement reactions. On the basis of the results of this stepwise approach to hard water, students develop the basic experimental principles of complexometric titration by themselves and use their methodology in titration experiments and the calculation of water hardness. Over the course of the learning program, students experience the fundamentals of scientific inquiry in a laboratory. This makes it possible to integrate the determination of water hardness, which is usually utilized in the basic chemistry laboratory courses in universities, into high school chemistry courses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00217.

Instructor information and student handout (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Soriano, D. S.; Draeger, J. A. A Water Treatment Experiment (Chemical Hardness) for Nonscience Majors. *J. Chem. Educ.* **1993**, *70*, 414.

(2) Yappert, M. C.; DuPre, D. B. Complexometric Titrations: Competition of Complexing Agents in the Determination of Water Hardness with EDTA. *J. Chem. Educ.* **1997**, *74*, 1422−1423.

(3) Myers, R. L. Identifying Bottled Water: A Problem-Solving Exercise in Chemical Identification. *J. Chem. Educ.* **1998**, *75*, 1585−1587.

(4) Ceretti, H.; Hughes, E. A.; Zalts, A. The Softening of Hard Water and Complexometric Titrations. An Undergraduate Experiment. *J. Chem. Educ.* **1999**, *76*, 1420−1421.

(5) Yang, S.-P.; Li, C.-C. Using Student-Developed, Inquiry-Based Experiments to Investigate the Contributions of Ca and Mg to Water Hardness. *J. Chem. Educ.* **2009**, *86*, 506−513.

(6) Gordon, J. S.; Harman, S.; Weiss, K.; Pettegrew, B. A Microscale Spectrophotometric Determination of Water Hardness. *J. Chem. Educ.* **2001**, *78*, 1089−1090.

(7) Richardson, J. N.; Stauffer, M. T.; Henry, J. L. Microscale Quantitative Analysis of Hard Water Samples Using an Indirect Potassium Permanganate Redox Titration. *J. Chem. Educ.* **2003**, *80*, 65−67.

(8) Mandler, D.; Blonder, R.; Yayon, M.; Mamlok-Naaman, R.; Hofstein, A. Developing and Implementing Inquiry-Based, Water Quality Laboratory Experiments for High School Students to Explore Real Environmental Issues Using Analytical Chemistry. *J. Chem. Educ.* **2014**, *91*, 492−496.

(9) Sarkis, V. D. A Study of Water Pollution. An Undergraduate Chemistry Laboratory Experience. *J. Chem. Educ.* **1974**, *51*, 745−747.

(10) Osorio, V. K. L.; de Oliveira, W.; El Seoud, O. A. Hard Water and Soft Soap: Dependence of Soap Performance on Water Hardness. A Classroom Demonstration. *J. Chem. Educ.* **2005**, *82*, 257−259.

(11) Birch, E. J. H. Hardness in Water—a Demonstration. *J. Chem. Educ.* **1949**, *26*, 196−198.

(12) Sangster, A. W. Removal of Hardness and Deionization of Water by the Ion Exchange Method. *J. Chem. Educ.* **1963**, *40*, A987.

(13) Egen, N.; Ford, P. C. Hard Water, Water Softening, Ion Exchange. *J. Chem. Educ.* **1976**, *53*, 302−303.

(14) Fulkrod, J. E. The Water Softener - a Relevant, Unifying Example of Many Common Chemical Principles and Calculations. *J. Chem. Educ.* **1985**, *62*, 529.

(15) Koga, N.; Kimura, T.; Shigedomi, K. Laboratory Inquiry for Determining the Chemical Composition of a Component in a Daily Use Detergent: Sodium Sesquicarbonate. *J. Chem. Educ.* **2011**, *88*, 1309−1313.

(16) Wada, T.; Koga, N. Chemical Composition of Sodium Percarbonate: An Inquiry-Based Laboratory Exercise. *J. Chem. Educ.* **2013**, *90*, 1048−1052.

(17) *Packtest Calcium*. http://kyoritsu-lab.co.jp/english/seihin/list/instructions/wak-ca-e.pdf (accessed Mar. 2016).

(18) WHO *Calcium and Magnesium in Drinking-Water: Public Health Significance*. http://apps.who.int/iris/bitstream/10665/43836/1/9789241563550_eng.pdf (accessed Mar. 2016).

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