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Integrating Mobile Phones into Science Teaching To Help Students Develop a Procedure To Evaluate the Corrosion Rate of Iron in Simulated Seawater

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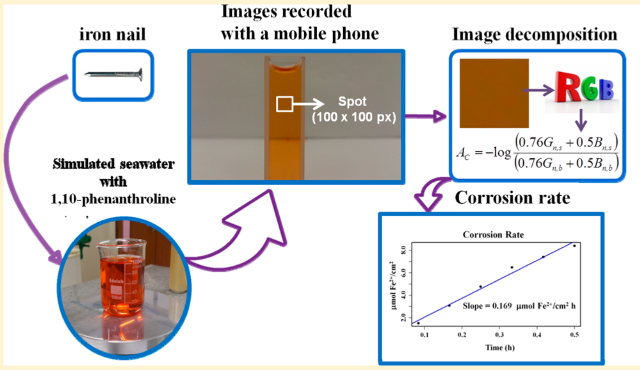
S Supporting Information

ABSTRACT: This article proposes an indirect method to evaluate the corrosion rate of iron nail in simulated seawater. The official procedure is based on the direct measurement of the specimen's weight loss over time; however, a highly precise scale is required and such equipment may not be easily available. On the other hand, mobile phones equipped with good built-in cameras have become an essential part of everyday lives of students and educators. With the built-in cameras, students followed the formation of the colored complex from the reaction between released iron ions and 1,10-phenanthroline. The images were then decomposed into the RGB channels that were converted into absorbance. Another point worth mentioning is that rather than providing students with a step-by-step procedure, the instructor used a problem-based approach that enabled students to develop the experimental procedure themselves. This project-driven interdisciplinary experiment engaged students into thinking and producing the experiment. Finally, bringing cell phones into science teaching was very helpful as it made learning more inviting and meaningful.



KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Interdisciplinary/Multidisciplinary, Student-Centered Learning, Electrochemistry, Inquiry-Based/Discovery Learning, Applications of Chemistry*

■ INTRODUCTION

Chemistry is an experimental science by its very nature. It is intrinsically inquiry-based; however, school science has been traditionally constructed around well-defined problems, such as calculating equilibrium constants by measuring equilibrium quantities, or following a "chemistry lab cookbook" to selectively remove cations from a solution. Students are provided with the "experiment recipe" that must be followed during the class. As we ourselves have observed and it has also been pointed out by Dershimer et al.,[1] this approach only teaches the students to follow instructions instead of stimulating creativity and critical thinking.[2] With the present laboratory experiment, we attempted to shift this paradigm by engaging the students into the development of the problem. We chose to explore the theme of corrosion due to its clear impact on the daily life and the possibility of synergy between two branches of Chemistry: physical chemistry (electrochemistry) and analytical chemistry. The former is concerned with the mechanism of corrosion and the latter focuses on measuring the amount of metallic ions (Fe^{2+}, in the present case) in a given matrix (in this case simulated seawater). The main idea is to show the students that there are not "different chemistries" and real problems usually involve a multidisciplinary approach.

The goal of the experiment was to determine the corrosion rate of iron in seawater. A common way of determining the corrosion rate is to measure the weight loss of the metallic specimen at different times.[3] However, at least a semi microbalance with a precision of 0.01 mg is required since the weight loss is quite small in the time frame of the experiment. Such equipment is quite expensive (US$ 3,000.00 to US$ 10,000.00), thus not available in every high school laboratory. Therefore, the approach to this problem must be different. As corrosion takes place, iron ions are released in the solution. The ions may then be colorimetrically determined through UV−vis spectroscopy with 1,10-phenanthroline,[4,5] a molecule that reacts with iron to form a red-to-orange ferrous triphenanthroline complex ion. Again, a UV−vis spectrophotometer may not be at students' disposal. On the other hand, mobile phones equipped with good built-in cameras are available everywhere and nowadays have become an essential part of everyday lives of students and educators. Why not make use of such devices in chemistry classes? In the present case, the

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mobile phone is used as the detector and captures images (it plays the role of the spectrophotometer) of the tris(1,10-phenanthroline)iron(II) complex ion whose color intensity is directly dependent upon iron concentration. Moraes et al.[6] used cell-phone cameras to capture the color intensities of flames sprayed with solutions containing distinct sodium concentrations and measured the concentration of sodium in seawater and coconut water. Kehoe and Penn,[7] with the help of camera phones, quantified the concentrations of different compounds in blue food dye, lemon-lime sports drinks, and iron(III) chloride solutions. Roberson and Hagevik[8] argued that mobile phones may be extremely helpful for educational uses since they blend real life and school life making learning more inviting and meaningful.

■ THEORETICAL BACKGROUND

Seawater is an excellent electrolyte since it contains a large amount of dissolved salts such as sodium chloride. The chloride ion is particularly aggressive because most of chloride compounds are soluble, which hampers the formation of passivating films. Passivation is a process that involves the shielding of the base material by a protective layer, such as a metal oxide, that prevents further oxidation.

In the seawater there is enough oxygen to be reduced in the cathodic reaction. The whole process is as follows:

$$\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{2+}(aq)} + 2\mathrm{e^-} \tag{1}$$

$$\mathrm{O_2(g)} + 2\mathrm{H_2O(l)} + 4\mathrm{e^-} \rightarrow 4\mathrm{OH^-(aq)} \tag{2}$$

Iron ions then react with the hydroxyl ions to form a precipitate that is quickly oxidized to produce rust

$$\mathrm{Fe^{2+}(aq)} + 2\mathrm{OH^-(aq)} \rightarrow \mathrm{Fe(OH)_2(s)} \tag{3}$$

$$4\mathrm{Fe(OH)_2(s)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{Fe_2O_3{\cdot}H_2O(s)} + 3\mathrm{H_2O(l)} \tag{4}$$

When 1,10-phenanthroline (phen) is added to the seawater in the beginning of the process, the iron ions will react with it to produce the soluble tris(1,10-phenanthroline)iron(II) complex ion $[\mathrm{Fe(phen)_3}]^{2+}$, also known as ferroin:

$$\mathrm{Fe^{2+}(aq)} + 3\mathrm{phen} \rightarrow [\mathrm{Fe(phen)_3}]^{2+} \tag{5}$$

As a consequence, the intensity of tris(1,10-phenanthroline)-iron(II) complex ion color in the solution will be proportional to the amount of iron released from the sample[9,10] (a commercial iron nail, for example). The intensities of the Red, Green, and Blue channels (RGB channels) in the digital images will change with the augment of iron concentration. As a result, RGB responses can be directly related to iron concentration in our experiments.

■ EXPERIMENTAL DETAILS

Materials

Ammonium iron(II) sulfate hexahydrate (>99.5%), 1,10-phenanthroline (>99.5%), sulfuric acid (95−99%), and ascorbic acid (99%) were obtained from Vetec Química Fina (Duque de Caxias, Brazil). Sodium chloride (>99.5%) was purchased from Dinâmica Química Contemporânea (Diadema, Brazil). All the standard solutions and samples were prepared with distilled water.

Determination of the Corrosion Rate

The construction of the calibration curve is fully described in the Experimental Procedure of the Supporting Information. It involves acquiring images of solutions containing known concentrations of $\mathrm{Fe^{2+}}$ for posterior image processing.

The corrosion rate was determined for commercial iron nails cut to 1.6 $\mathrm{cm^2}$-area specimens and treated according to ASTM G1-90 Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. The shape of the nail is approximately a cylinder whose area is the sum of the areas of two circles (bottom and top) and of one rectangle (one of its sides is the length of the circles and the other the height of the cylinder). As the radius of the nails is fixed, a desired area is achieved by cutting them at the correct height. The treatment comprised polishing the specimens with a wet 1200-grit sandpaper followed by ultrasonic degrease in acetone for 10 min. Alternatively, an acetone-wet paper tissue may be used for degreasing. A specimen was then air-dried and immersed in 100 mL of a solution containing 3.5% NaCl, 1% ascorbic acid, and 0.25% 1,10-phenanthroline. At this moment the students started the chronometers. The color of the solution turned orange with time. The experiment took place onto a magnetic stirrer to ensure solution homogenization. Since the iron nail sample is magnetic, it itself functioned as a stir bar. Aliquots of the solution were sampled every 5 min, transferred into a glass cuvette, and had their pictures captured with the student's mobile phones. The arrangement of the experiment can be seen in Figure AC1 of the Supporting Information. For comparison, the same above-described procedure was applied to a stainless steel nail with pictures taken 3 weeks apart. The images were then processed according to the Data Treatment section of the Supporting Information.

■ HAZARDS

Wear safety goggles and rubber gloves when manipulating the chemicals. According to the respective Material Safety Data Sheet, 1,10-phenanthroline, ascorbic acid, and ammonium iron(II) sulfate hexahydrate are irritant upon skin or eye contact. Sulfuric acid is very hazardous in case of skin contact (corrosive, irritant, permeator) or eye contact.

■ RESULTS

Recording devices are intrinsically susceptible to noise. In electronic recording apparatus, heat causes electrons to stray from their designated path. The stray electrons influence the voltage of the output signal leading to detectable noise that is essentially corrupted pixels. As seen in Figure 1, the raw images (upper row) contain a considerable amount of speckling noise that completely disappears upon applying the median filter (lower row).

The filter algorithm runs through the signal pixel by pixel replacing each one with the median of neighboring pixels (the filtering procedure is described in the Data Treatment section of the Supporting Information). This process is important to remove pixels that do not reflect the true intensities of the real scene. RGB values were then extracted from the filtered images and inserted in eq 6 in order to generate the absorbances for the construction of the analytical curve

$$A_{\mathrm{C}} = -\log \frac{(0.76G_{\mathrm{n,s}} + 0.5B_{\mathrm{n,s}})}{(0.76G_{\mathrm{n,b}} + 0.5B_{\mathrm{n,b}})} \tag{6}$$

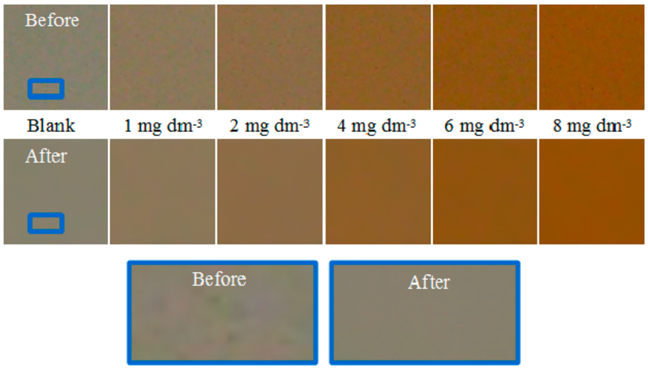

Figure 1. Effect of the median filtering on the calibration-curve images.

where $G_{n,s}$ and $B_{n,s}$ are the normalized values from equations (AC1) and (AC2) (see Data Treatment in the Supporting Information) for the samples and $G_{n,b}$ and $B_{n,b}$ are those for the blank (distilled water). The calibration curve observed in Figure 2 showed a linear correlation between the colorimetric absorbance (A_C) and Fe^{2+} concentration with R^2 (variance explained by the model) close to 1. LOD for Fe^{2+} was 0.26 mg dm^{-3}. The results obtained with mobile phones' cameras were quite similar to those from the UV−vis method (see Figure AC4 in the Supporting Information), which attests the validity of the herein proposed method.

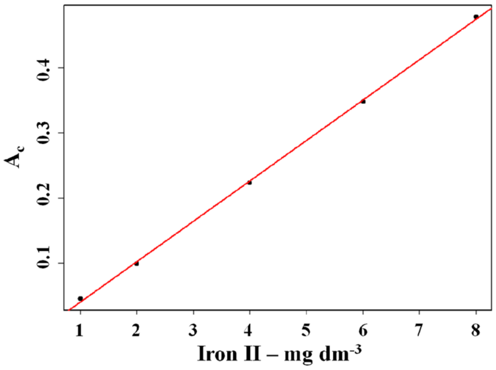

Figure 2. Calibration curve acquired from the image colorimetric absorbances of simulated seawaters at distinct Fe(II) concentrations. Adjusted R^2 = 0.9993.

Figure 3 presents the amount of released Fe^{2+} over area and time determined with the mobile phone. The method was linear (R^2 = 0.9821) in the time frame of the experiment and gave a corrosion rate of 0.169 μmol $Fe^{2+}/(cm^2\ h)$, which is comparable to the value of 0.173 μmol $Fe^{2+}/(cm^2\ h)$ obtained with UV−vis (R^2 = 0.9986) found in Figure AC4 of the Supporting Information. McCafferty[11] reported the value of 0.665 μmol $Fe^{2+}/(cm^2\ h)$ for the corrosion rate of iron in simulated seawater, thus in the same order of magnitude of the value found in the present work. A reason for the discrepancy may be different amounts of carbon present in the samples.

■ DISCUSSION

The experiment is intended to be a two-day activity. In the first day, the instructor discussed with the students the electrochemical basis for corrosion and started delineating the problem. The goal is to determine the iron corrosion rate in simulated seawater, and at this moment, the students should be familiar with the anodic reaction where iron ions leave the metallic specimen leading to its weight loss. If the students themselves do not come up with the idea of measuring the specimen's weight loss over time, the instructor should ask questions that lead students to that conclusion. In the Supporting Information (Note for Instructors), we provide a chart that is an example of how to conduct the questioning. We strongly advise instructors not to release answers whenever students ask, but rather guide them to reach the answers. This inquiry-based approach would allow the activity to reach its full potentiality in terms of learning and teaching.

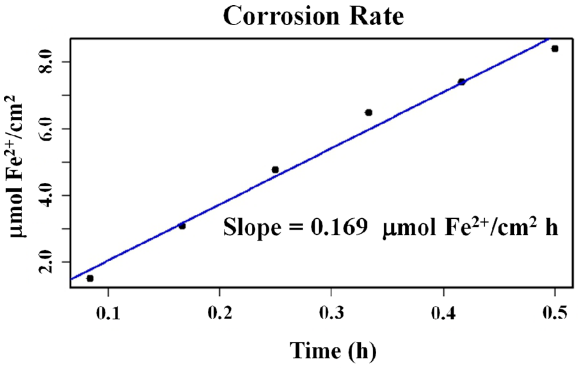

Figure 3. Corrosion rate curve produced with cell phone images of simulated seawater containing a sample of iron nail. Adjusted R^2 = 0.9821.

After reaching the weight-loss approach for the determination of the iron corrosion rate, the instructor informed the students of the unavailability of a high-precision scale to measure tiny mass changes; hence, the focus had to be shifted to the solution because, according to the anodic reaction, the iron mass loss is stoichiometrically linked to the amount of iron ions released into the solution. This change of strategy resembles real-life situations in which one may have to adapt or improvise a procedure according to available materials and equipment. At this point, the instructor discussed with students strategies to measure iron ion concentration, a field classically taught by Analytical Chemistry. The instructor briefly explained typical techniques, such as atomic absorption spectroscopy and inductively coupled plasma emission spectroscopy, which would require unavailable sophisticated instrumentation. Students were reminded they could perform a reaction with iron that would make it colored and relate the color intensity with the iron concentration in the solution, which is essentially the colorimetric method. The only difference was that the cell phone cameras would play the role of the photometer. Students were quite surprised and excited to know that an every day device such as a cell phone could be of any use in science. They were divided in two-person groups and instructed to research on the colorimetric determination of iron with 1,10-phenanthroline. The final first-day task was to draft an experimental procedure that comprised the method for the calibration curve and preparing the specimens, in addition to checking the chemicals' hazards.

On the second day, the students performed the experiment, which took around 4 h. Each group received one specimen that was submitted to the corrosion test. After the calibration curve was built, the first trial had the goal of adjusting the duration of the corrosion experiment to ensure the color of the solution fall within the calibration curve. As the areas of the iron nails were approximately equal, the groups found the same time length of about 30 min for the corrosion test. Images of the solution were taken 5 min apart and analyzed according to the data treatment section. If possible, data treatment should be carried out in the laboratory right after the end of the experiment. This is to emphasize that theory and practice are indissociable. Each group plotted moles of Fe^{2+} versus time and acquired a straight line whose slope was the corrosion rate. The representative graphic in Figure 3 gave a corrosion rate of 0.169 μmol $Fe^{2+}/(cm^2\ h)$. Deviation from this value among the groups could be discussed in terms of differences in real areas among the samples. Real areas, in contrast to geometric ones (those measured with a ruler, for example), strongly depend on the surface roughness. The latter, in turn, is greatly affected by the treatment of the sample. As the students polished the samples manually, the surface roughness was not under control and the real areas were naturally different.

CONCLUSIONS

This simple experiment was an excellent opportunity to show students that the solution of a given problem might require the integration of chemistry branches that are classically taught separately. In other words, there are no "different chemistries". In the present case Physical Chemistry and Analytical Chemistry had to work together for the completion of the experiment. In addition, students were required to learn the basics of image processing. This project-driven interdisciplinary approach reduces the teacher talking time and engages the students into thinking and producing the experiment. Furthermore, bringing cell phones into science teaching was very helpful as it made learning more inviting and meaningful.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00274.

> Experimental procedure for the calibration curve; data treatment; note for instructors; program script (PDF DOC)

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Notes

The authors declare no competing financial interest.

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