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Acid–Base Titration: Analysis of Phosphoric Acid Anodizing Solutions. A Problem-Based Learning Approach

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Abstract: Phosphoric acid anodizing solutions are routinely titrated to monitor their concentrations; however, after successive anodizations of aluminum metal, increasing amounts of dissolved aluminum interfere with the neutralization titration. The true concentration of phosphoric acid is determined by a correction factor based on the concentration of the dissolved aluminum, which is determined industrially by flame atomic absorption spectrometry. The academic determination of a correction factor for aluminum as well as copper can be designed as a traditional or a problem-based learning exercise.

Introduction

Industrial Application. Phosphoric acid anodizing solutions (PAAS) are used to create an aluminum oxide layer suitable for bonding with an adhesive primer. PAAS contain increasing amounts of dissolved aluminum (Al) with successive anodizations of Al metal. The phosphoric acid reacts with the Al metal during the anodizing process and, thus, it is consumed and produces dissolved Al. The concentration of phosphoric acid decreases and the concentration of dissolved Al increases over time. However, the concentration of phosphoric acid must be maintained at a high level in order to properly anodize the Al metal; therefore, acid–base titration is used in industry to determine the concentration of PAAS.

The industrial documentation from the Boeing Specification Support Standard (BSS 7245) is entitled "Analysis of Phosphoric Acid Anodizing Solutions" [1]. It "involves the acidimetric titration of phosphoric acid with a correction for error introduced by dissolved aluminum" [1]. In the industrial titration of phosphoric acid, dissolved Al interferes due to its acidic nature; thus, more base is required to reach a pH value of 4.2, a value close to the first equivalence point of 4.7 [2]. The true concentration of phosphoric acid is determined by subtracting a correction factor based on the concentration of the dissolved Al determined industrially by flame atomic absorption spectrometry (FAAS).

Academic Application of an Industrial Problem – A Problem-Based Learning Approach [3]. Rather than performing the typical phosphoric acid titration in a quantitative analysis laboratory course, the titration of PAAS provides real-world situation for the application of the titration technique for students. A problem-based learning approach can also be used for this exercise. Students are provided with the above information and asked to determine the correction factor. The students must devise the experimental procedure. This experiment allows students to develop the correction factor for the interference of Al in the titration of phosphoric acid by titrating PAAS of known phosphoric acid and Al concentrations. By providing the experimental procedure as

seen below, however, the exercise can be performed in the "classical" format [3].

Dissolved copper, Cu, also in the PAAS as confirmed by FAAS, does not interfere with the industrial titration at the low concentrations found. At higher concentrations, however, Cu does interfere; thus, although it is not industrially relevant, a correction factor for Cu can also be developed as a problem-based learning exercise.

This experiment brings an industrial relevance to the acid–base titration technique taught in a quantitative analysis laboratory. It includes both individual and group work and can be conducted in the classical mode of providing the experimental procedure or in the new problem-based learning mode [3] where the experimental procedure is not provided. It is unique due to the fact that students also learn that metals such as Al and Cu also produce acidic solutions and thus interfere in acid–base titrations.

Experimental Procedure

Create diluted phosphoric acid by placing 60.0 mL of concentrated phosphoric acid (14.7 M) into a 100.0-mL volumetric flask and diluting to volume. Add 5.00 g Al in the form of aluminum chloride hexahydrate to a 250-mL beaker and dissolve with 50 mL of deionized water. Transfer 10.00 mL of diluted phosphoric acid to the beaker and label it "with Al." Dilute the "with Al" quantitatively to 100.0 mL using a volumetric flask. Transfer 10.00 mL of the diluted phosphoric acid to a second 100.0-mL volumetric flask, dilute to volume and label it "without Al." These two solutions are 0.9 M in phosphoric acid.

Take 10.00 mL of the "without Al" phosphoric acid as the sample. Titrate with 1.00 M NaOH to pH 9.5, recording the volume for pH changes of every 0.2 pH units with a pH meter. Repeat the titration, by taking 10.00 mL of the "with Al" phosphoric acid as the sample. Analyze each in triplicate. The titration may be stopped at a pH of 4.2 if time does not permit the titration to proceed to a pH of 9.5.

In the laboratory, students can analyze the diluted phosphoric acid with a range of dissolved Al. Thus, a class can analyze a series of "with Al" at concentrations of Al ranging from 1 to 25 g L^{-1} Al. Higher concentrations of phosphoric acid such as 1.1 and 1.3 M (obtained by taking 75.0 or 90.0 mL of concentrated phosphoric acid diluted to 100.0 mL) should also be evaluated with varying amounts
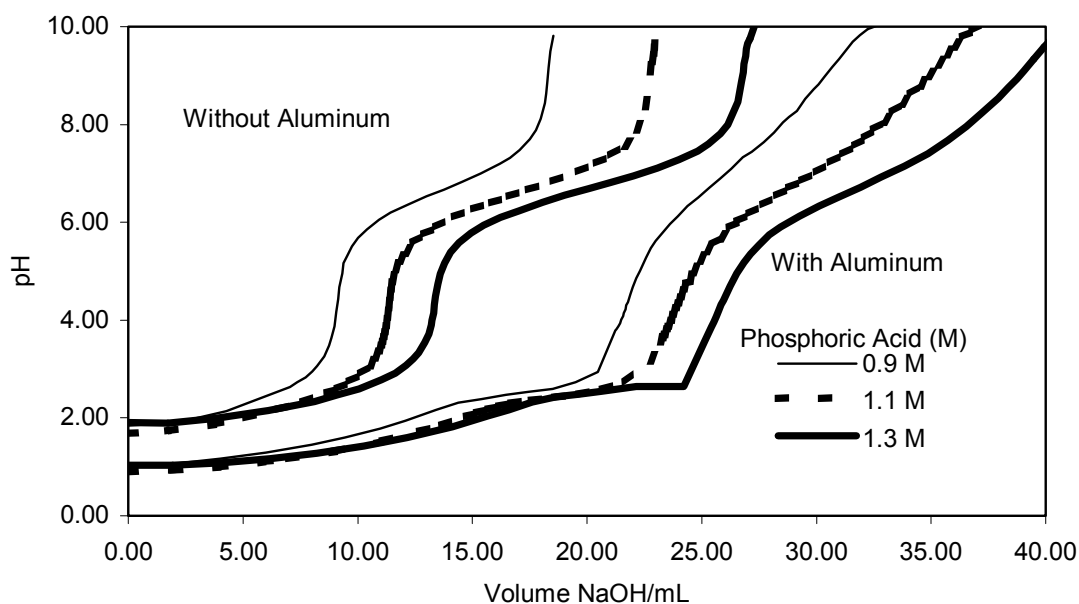
Figure 1. Acid–Base Titration of phosphoric acid with 1.00 M NaOH. The six titrations shown represent phosphoric acid with and without 17 g/L Al.

of Al. In addition, varying amounts of Cu in the form of copper (II) chloride dihydrate can be used instead of Al.

In the laboratory, the concentration of Al is known, and thus its determination by FAAS is not necessary; however, if actual phosphoric acid anodizing solutions are obtained from industry, their concentrations of Al need to be determined by FAAS.

Hazards

Gloves should be worn at all times. Phosphoric acid is a corrosive chemical and contact can severely irritate and burn the skin and eyes. The vapors can irritate the nose, throat and lungs. Prepare the phosphoric acid solutions in a ventilated hood. Sodium hydroxide is a corrosive chemical and contact can cause skin irritations and burns. Copper (II) chloride dihydrate can cause skin, eye and respiratory irritations.

Results and Discussion

Figure 1 illustrates the shift in the amount of base required to neutralize phosphoric acid and Al in the titration of 17 g L^{-1} Al added to 0.9, 1.1, and 1.3 M phosphoric acid. With increasing phosphoric acid concentration, the shift remains constant for the same concentration of Al. The unusual-shaped curve obtained for the "with aluminum" sample is due to the precipitation of aluminum hydroxide causing deviations in the pH.

Figure 2 illustrates the titration correction of phosphoric acid based on the g L^{-1} of Al. By subtracting the molarity determined for the "without Al" solution from the molarity determined for the "with Al" solution, the titration correction (in molarity phosphoric acid) is determined for a given g L^{-1} Al. By doing a series of these titrations at different concentrations of Al, Figure 2 can be created. As the concentration of Al increases the correction required increases linearly. It is clear that without correcting for Al in the phosphoric acid titration, incorrect concentrations of phosphoric acid, which are higher than the true value, are

obtained. The students must produce Figure 2 in order to determine their correction factor. The equation of the line can be used subsequently for all calculations.

The true concentration of phosphoric acid in anodizing solutions is determined by (1) obtaining the amount of Al in g L^{-1} by a FAAS analysis, (2) titrating the anodizing solution for its "apparent" molarity, and (3) subtracting the titration correction obtained by using the equation in Figure 2 from the "apparent" molarity of phosphoric acid.

Dissolved Cu is also found in true anodizing solutions. The titration of phosphoric acid in the presence of varying amounts of copper is seen in Figure 3. The Cu also has acidic character and shifts the titration of the phosphoric acid similar to Al. The dips in pH occur due to the sudden precipitation of copper(II) hydroxide during the titration.

The industrial titration to determine the concentration of phosphoric acid in anodizing solutions is only taken to a pH of 4.2. Because the contamination of Cu in the anodizing solution will not be greater than 1.0 g L^{-1}, an amount that does not interfere with the titration up to a pH of 4.2, no industrial correction for Cu is needed; however, academically, titrations of phosphoric acid with added Cu could be performed instead of using added Al.

Questions for discussion with the students or for their laboratory reports would be "Why does Al interfere?," "Write the chemical reactions to show how Al causes an acid–base reaction," and "Explain why Al does not form a precipitate with phosphate, because aluminum phosphate is not very soluble?"

Conclusion

This experiment provides a real-world application for students by developing the correction factor that is used in industry for the titration of PAAS. This can be accomplished by using a problem-based learning format or the classical laboratory format. The presence of Al does interfere in the
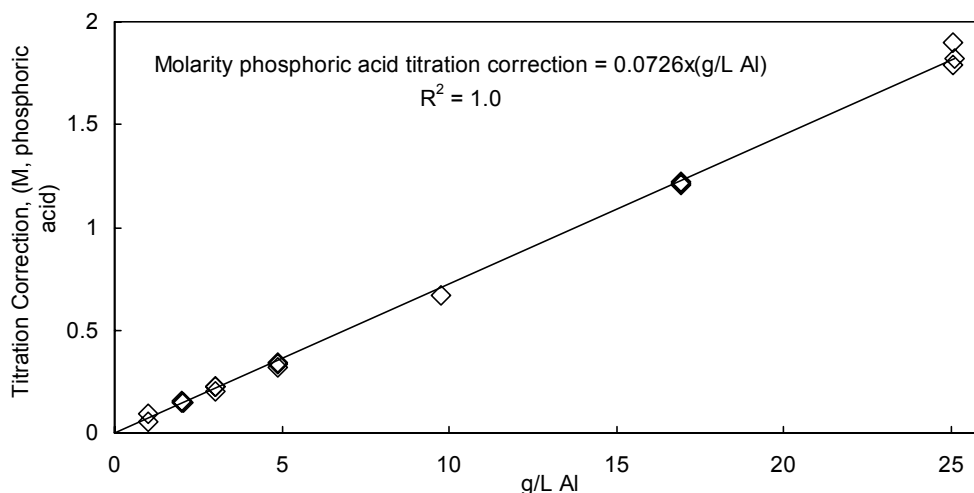
Figure 2. Titration correction (M, phosphoric acid) versus g L^{-1} Al. Subtraction of the titration correction based on g L^{-1} Al present in the PAAS corrects for the presence of Al.
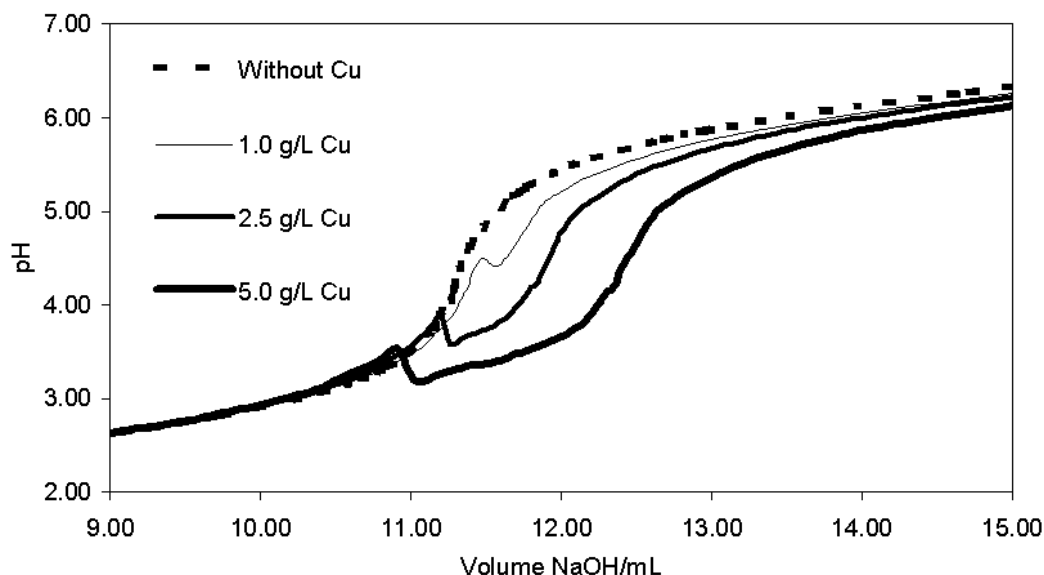
Figure 3. Acid–Base Titration of phosphoric acid with 1.00 M NaOH. The four titrations shown represent phosphoric acid (1.1 M) with (0, 1.0, 2.5, and 5.0) g L^{-1} Cu.

titration of phosphoric acid, and, thus, in industry it is not apparent that the concentration of phosphoric acid has decreased. Deriving the correction factor may require a group effort so that sufficient data is obtained at a number of different concentrations of Al. Students learn to work independently, as well as in a group setting, to derive the equation of the line from the results of many titrations. Students have found this exercise challenging, due to the data analyses involved, but they appreciated the real-world application and the need for teamwork.

References and Notes

1. Boeing Specification Support Standard 7245. *Analysis of Phosphoric Acid Anodizing Solutions*, Boeing Airlines: Seattle, 1993.

2. Harris, D. C. *Quantitative Chemical Analysis*, 5th ed.; Freeman: New York, 1999; p AP24.

3. Wenzel, T. J. *Anal.Chem.* **2001**, *73*, 501A-502A.