

Potentiometric Determination of Chloride in Natural Waters: An Extended Analysis

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S Supporting Information

ABSTRACT: Fully functional and inexpensive electrodes assembled by students have previously been described for use in potentiometric titrations. A detailed analysis of graphs generated from titration data obtained with such electrodes can offer students greater insight into the nature of solubility and practical use of the Nernst equation. These titration data can also be used by students to calculate the solubility product of the precipitant formed by the chemical reaction between the analyte and titrant.

KEYWORDS: *Second-Year Undergraduate, Analytical Chemistry, Environmental Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Aqueous Solution Chemistry, Electrochemistry, Potentiometry, Titration/Volumetric Analysis*

There have been a number of publications in this *Journal* describing inexpensive but fully functional electrodes^{1–5} readily constructed by students. This communication expands the pedagogy of an engaging experiment in a paper presented by Lisenksy and Reynolds.⁶ These authors describe a simple electrode that students assemble to determine chloride in natural waters using potentiometric titration with silver nitrate. In our analytical chemistry laboratory, we have used this electrode to determine the chloride content in the urban Muddy River in Boston, MA, that is frequently contaminated by stormwater runoff;⁷ the study of this river is of great interest to many students. The electrodes in this experiment are easy to assemble, and the students gain first-hand experience with the inner workings of an analytical electrode. The experimental procedure is a modification of that used by Lisenksy and Reynolds and is described in detail in the Supporting Information. A more extensive analysis of the titration data yields not only the chloride concentration, but also a deeper understanding of solubility.

■ ANALYSIS

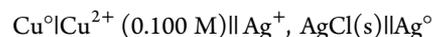
During the titration, students observed that the solution turns milky as silver nitrate is added due to the formation of silver chloride and at the end point the solution clears and black metallic silver forms in the solution. This is an important pedagogic moment, because it is an opportunity to “picture” what is happening in solution. Figure 1A is a typical student potentiometric titration curve for a 100 mL sample of the 50 mg/L “standard” chloride solution. Figure 1B is a typical student potentiometric titration curve for a 100 mL sample of filtered Muddy River water. The students should observe that the initial voltage readings of the Muddy River sample (~40 mV) is significantly lower than that of the 50 mg/L chloride solution (~80 mV).

Students also prepare first derivative curves, which allow more accurate end point determinations. The end point is chosen as the maximum rate of change of electrochemical potential with added silver nitrate. For both titrations, the end point potentials are approximately 190 (±10) mV. Using the

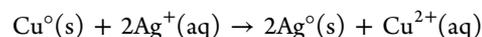
end point, students calculate the amount of Ag⁺ added, which is equivalent to the initial chloride concentration of the sample. With these results, the environmental significance of the high chloride concentrations in rivers can be discussed. However, the titration curves contain significantly more chemical information. The significance of the initial voltages and the end point voltages is discussed in the Supporting Information. An analysis of these data offers an opportunity to extend an environmental investigation of chloride content of natural water into a study of solubility by employing the Nernst equation.

■ DETERMINATION OF THE SOLUBILITY PRODUCT OF AgCl

Students are surprised to find that they can calculate the solubility product of silver chloride from the titration curve. At the equivalence point, the solution consists of a saturated solution of silver chloride with no excess Ag⁺ or Cl⁻ ions. The Nernst equation can be used to solve for the solubility product, K_{sp} , for AgCl. At the equivalence point the relevant shorthand notation for the electrochemical cell is



The balanced relevant electrochemical reaction is



and the overall standard electrochemical potential, E_{cell}° is

$$E_{\text{cell}}^\circ = E_{\text{red}(\text{Ag}^+/\text{Ag})}^\circ - E_{\text{red}(\text{Cu}^{2+}/\text{Cu})}^\circ = +0.462 \text{ v}$$

The Nernst equation describes this electrochemical potential at nonstandard concentrations:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{2} \log \left[\frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \right]$$

Before the equivalence point where there is an excess of chloride, [Ag⁺] is determined by the equilibrium

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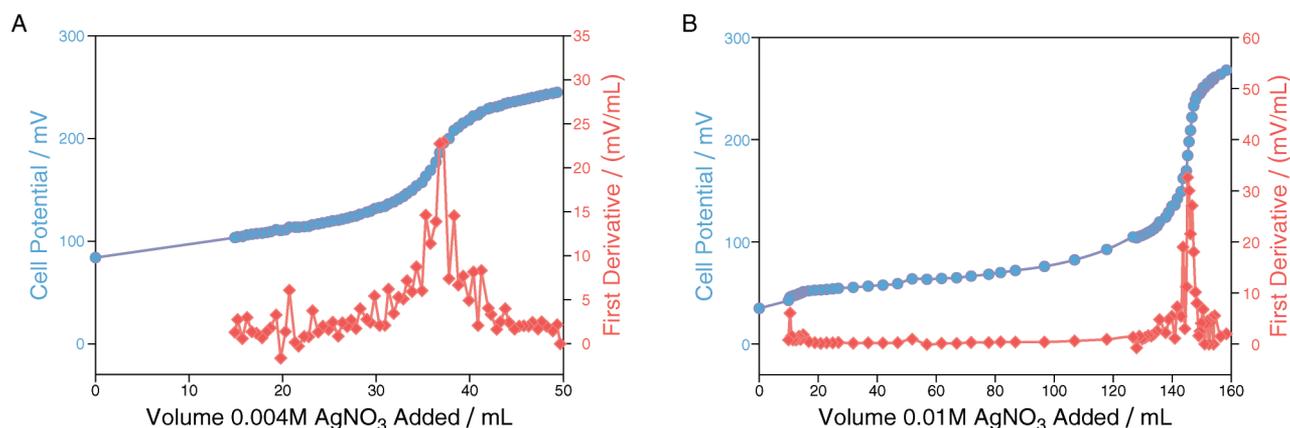
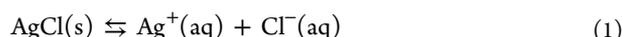


Figure 1. (A) Student potentiometric titration curve for a “standard” chloride solution. (B) Student potentiometric titration curve for a sample of filtered Muddy River water.



and is described by the solubility constant, $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$. At the equivalence point, excess chloride has been precipitated as $\text{AgCl}(s)$, and the concentrations of Ag^+ and Cl^- arising from eq 1 are equal, so $[\text{Ag}^+]^2 = K_{\text{sp}}$. With $[\text{Cu}^{2+}] = 0.100 \text{ M}$, the Nernst equation can now be written as

$$E_{\text{cell}} = 0.462 - \frac{0.0592}{2} \log \left[\frac{(0.100)}{K_{\text{sp}}} \right] \quad (2)$$

E_{cell} can be experimentally determined from the titration curves and the first derivative graphs as the potential at the equivalence point: estimated to be 190 (± 10) mV for titrations of the 50 mg/L chloride standard and Muddy River water. Thus

$$0.190 = 0.462 - \frac{0.0592}{2} \log \left[\frac{(0.100)}{K_{\text{sp}}} \right]$$

Solving for K_{sp} yields a value of 6.4×10^{-11} compared to the literature value of 18×10^{-11} . Note the sensitivity of K_{sp} to E_{cell} at the equivalence point: $\pm 10 \text{ mV}$ uncertainty gives values for K_{sp} ranging from $(3 \text{ to } 14) \times 10^{-11}$.

Students were asked to comment on (i) the higher initial millivolt reading for the 50 mg/L standard chloride solution ($\sim +80 \text{ mV}$) compared to that of the Muddy River water ($\sim +35 \text{ mV}$). On the basis of the author’s measurements, the Muddy River water usually contains significant concentrations of sulfate anions, from 20 to 40 mg/L. (ii) Students were asked to address the following question: Is sulfate a significant source of interference in the titration? These questions are addressed in the Supporting Information.

CHEMICAL HAZARDS

Silver nitrate is an oxidant and should be stored away from organic compounds. It is also toxic and corrosive requiring the use of protective gloves while handling silver nitrate solutions. Copper sulfate causes skin irritation and may cause skin burns, allergic eczema, and eye irritation. Care is required when handling these chemicals.

CONCLUSION

This experiment integrates a wide range of topics that can interest and inform students: environmental pollution, electro-

des, relative solubility, solubility products, and the uses of the Nernst equation.

ASSOCIATED CONTENT

Supporting Information

Procedures used in this experiment as well as a discussion of the use of the Nernst equation and solubility considerations. This material is available via the Internet at <http://pubs.acs.org>.

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REFERENCES

- Bendikov, T.; Harmon, T. *J. Chem. Educ.* **2005**, *82*, 439–441.
- King, D.; Friend, F.; Kariuki, J. *J. Chem. Educ.* **2010**, *87*, 507–509.
- Thomas, J. *J. Chem. Educ.* **1999**, *76*, 97–98.
- Williams, H. *J. Chem. Educ.* **1994**, *71*, 162–163.
- Riyazuddin, P. *J. Chem. Educ.* **1994**, *71*, 167.
- Lisenky, G.; Reynolds, K. *J. Chem. Educ.* **1991**, *68*, 334–335.
- McCauley, R.; *Limnol. Oceanogr.* **1966** *11* (4) 475; http://www.aslo.org/lo/toc/vol_11/issue_4/0475.pdf (accessed Apr 2012).