

Experiment 9**USING ION-SELECTIVE ELECTRODES TO MEASURE THE CHLORIDE CONTENT IN WATER AND ALCOHOLIC BEVERAGES**

2 lab periods

Reading: Chapter 14 and Chapter 5 (pg 106-108). Quantitative Chemical Analysis, 8th Edition, Daniel C. Harris. (7th Edition: Chapter 15 and Chapter 5, pg 87-90).

Objective

This lab will introduce you to the use of ion-selective electrodes. You will use ion-selective electrodes to measure the chloride content of water and of white wine.

Suggested Schedule

Lab Services has a limited number of ion-selective electrodes. Chloride ion-selective electrodes will be set up at several measurement stations in the lab. Prepare your standards and samples at your bench area, check out a Vernier LabQuest, and make your measurements when one of the stations becomes free. Note your electrode number. Be sure to use the same electrode for all your measurements.

Lab 1 Prepare your standard solutions and the ionic strength adjustment buffer (ISAB). Familiarize yourself with the care and use of the ion-selective electrodes and meter. Begin analyses of tap water and reclaimed water.

Lab 2 Finish your water analyses and start your wine analyses.

There are many methods which can be used to determine the concentrations of cations and/or anions in solutions. Methods which you have used (or will use) in this class include spectrophotometry, complexation titrations, and gravimetric analysis. *Ion-selective electrodes* represent yet another frequently used method to measure solution concentrations of certain analyte ions. Common analyte ions for which ion-selective electrodes are commercially available are listed below:

Cations: NH_4^+ , K^+ , Ca^{2+} , Ba^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} , Hg^{2+} , Na^+ , Ag^+
 Anions Br^- , Cl^- , I^- , NO_3^- , NO_2^- , F^- , CN^- , SCN^- , S^{2-} , ClO_4^-

Ion-selective electrodes fall into one of the following types:

- 1) Glass membrane— the pH electrode is an important example of this type.
- 2) Solid-state electrodes are based on an inorganic salt crystal— the chloride electrode is an example.
- 3) Liquid-based electrodes are based on a hydrophobic polymer membrane saturated with a hydrophobic liquid exchanger— the calcium electrode is an example.
- 4) Compound electrodes, such as the CO_2 gas-sensing electrode (this is a very cleverly-designed electrode, which actually responds to H^+).

In this class we will use a membrane-based ion-selective electrode which has a solid state

membrane that is selective for Cl^- . This electrode is a *combination electrode*, meaning that it contains an internal Ag/AgCl reference electrode. A schematic of this type of electrode is shown in Figure 1.

Analyte ions in solution equilibrate with the ion-selective membrane, creating a potential difference across the membrane. The voltage developed between the sensing and the reference electrodes is a measure of the activity of the ion being measured. We can use a calibration curve to relate this potential difference to analyte concentration. While an ideal ion-selective membrane would be one capable of binding only one particular target analyte ion (A), in reality, a membrane will have some response to ions other than the target ion (i.e. ion X). The relative response of the electrode to different species having the same charge is given by the selectivity coefficient, $k_{A,X}$.

$$k_{A,X} = (\text{response to X})/(\text{response to A})$$

The response of an ion-selective electrode for the case where X and A have the same charge is given by:

$$E = \text{const} + \beta(0.05916/n) \log \{ \mathcal{A}_A + \Sigma(k_{A,X}\mathcal{A}_X) \}$$

Where E is the electrode potential, n is the charge on the analyte ion A, \mathcal{A}_A is the activity of the analyte ion A, and \mathcal{A}_X is the activity of interfering ion X. Interfering ions for the chloride ISE we will use in this class are Br^- , I^- , CN^- , and S^{2-} . Significant concentrations of these ions are unlikely to be present in our samples.

β is a type of “fudge factor”. An electrode with a Nernstian response will give a calibration curve with a slope of $0.05916/n$ ($\beta = 1$). Each of the chloride ion-selective electrodes used in this class may have a unique value for β . *Thus, you must use the same electrode for all your measurements.*

Ion-selective electrodes have numerous advantages over other analytical methods. They are relatively easy to use, have a fast response time, and respond linearly to the logarithm of analyte activity over four to six orders of magnitude. However, ion-selective electrodes also have several weaknesses. For example, they are fragile, expensive, have a limited shelf life, may be easily fouled or poisoned, and their precision is rarely better than 1%. One other limitation of ion-selective electrodes is that they measure the activity of an ion, not concentration. Activity is dependent on the total ionic strength of the analyte solution, and may deviate quite a bit from concentration as the ionic strength of the solution changes. For this reason, an ionic strength adjusting buffer (ISAB) is added to the solution before measurement in order to keep the ionic strength high and constant. If ionic strength and activity coefficients are kept constant, the electrode potential can be directly related to analyte concentration.

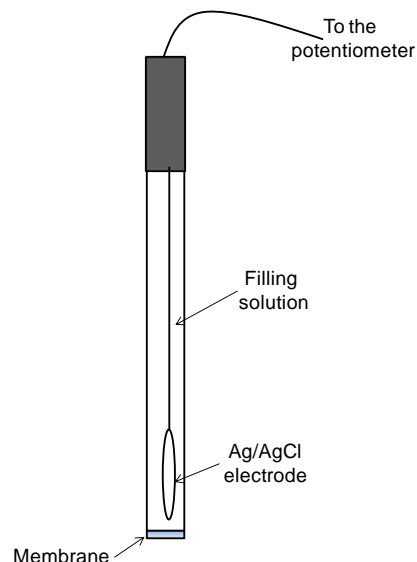


Figure 1. Schematic of a combination-style ion-selective electrode

It is important that the composition of the standard solutions and the composition of the sample solutions be closely matched when using ion-selective electrodes. In situations where the composition of the sample solution and the standard solutions cannot be matched, (i.e. when the sample matrix is a complex one), the *method of standard additions* must be used. This method simply involves immersing the electrode in the sample solution and sequentially adding several small aliquots of a standard solution. The electrode potential is measured after the addition of each aliquot of standard added, and a graphical method is used to determine the concentration of the unknown. The use of standard additions with ion-selective electrodes is described on pg 330-331 of *Quantitative Chemical Analysis*, 8th Edition.

In the first part of this experiment, you will use a chloride ion-selective electrode to measure the potential due to chloride of a series of chloride standards, a sample of tap water, and a sample of reclaimed water. You will generate a calibration curve, which you will use to determine the chloride content of the tap water and reclaimed water samples. In the second part of this experiment, you will use the method of standard additions to determine the chloride content of a sample of white wine.

Reclaimed water is a mix of domestic wastewater, industrial process water and stormwater that has been taken through a multi-step treatment process at a wastewater treatment plant. In many areas of the US, water demand is beginning to outstrip supply. Thus, many cities have turned to the use of reclaimed water for such uses as irrigation, industrial process and cooling water, toilet flushing, and dust control. Reclaimed water is also used to create or restore wetlands, recharge groundwater supplies and increase water flow in rivers and streams. In some areas, local governments are contemplating “indirect potable reuse” of reclaimed water. The University of Idaho uses reclaimed water for irrigation, and has done so since the 1970’s. Currently, more than 90% of campus irrigation uses reclaimed water, and this saves as much as 120 million gallons of water per year. One drawback to the use of reclaimed water for irrigation is that it has a higher chloride content than tap water.

Prelaboratory Assignment

The following data were obtained when a calcium ion selective electrode was immersed in standard solutions to which an ionic strength adjusting buffer had been added.

Ca ²⁺ , M	E (mV)
2.0 x 10 ⁻⁵	-73.0
2.0 x 10 ⁻⁴	-46.0
2.0 x 10 ⁻³	-17.1
2.0 x 10 ⁻²	+12.0
2.0 x 10 ⁻¹	+39.0

Prepare a calibration curve using Excel or another plotting program, and find the slope and the intercept. Hint: look at Figures 14-21 and 14-27 in your text for examples of what your plot should look like. Your plot should have a title, and axes must be appropriately labeled. Determine β for this electrode. Watch your units!

The above electrode was used to analyze a well water sample to which an ionic strength adjusting buffer had been added. The electrode gave a reading of (-30.2 ± 0.3) mV in four replicate measurements. Find the concentration of calcium in the water sample in ppm.

Apparatus

- Stir plate and stir bar, or Vernier stirring station and stir bar
- Vernier LabQuest
- Chloride ion-selective electrode (ISE)
- 100-mL beakers
- 100-mL volumetric flasks; larger sizes are OK
- Plastic disposable dropper with calibration to 1 mL
- 1-, 5-, 10-, and 25-mL volumetric pipets
- 50-mL graduated cylinder
- Bottles for storage of the chloride standards (if necessary)

Chemicals

- Primary standard grade sodium chloride
- ISAB solution for the chloride ISE: 5 M NaNO₃
- Tap water and reclaimed water samples (~300 mL each)
- White wine sample (~300 mL)

Procedure

The chloride ion-selective electrodes you will use in this experiment are very expensive. Please handle them with care! The shiny black membrane at the bottom of the electrode is the sensing element. This membrane is very fragile, and one must be careful not to damage it. If you use a stir bar in your solution during your titration, be sure the electrode is in a location to one side of

the beaker where it cannot be damaged by the stir bar. It is best if the electrode is somewhat high in the beaker, but make sure both the sensing element and the small white reference contact are below the level of the solution. Make sure no air bubbles are trapped below the ISE. Do not touch the membrane, and never allow the bottom of the electrode to rest on the bottom of the beaker, the counter, or anything else. To dry the electrode, carefully wick the excess liquid away using a Kim Wipe. The TA's will demonstrate this technique.

The chloride ion-selective electrode has most likely been soaking in a chloride storage solution prepared by lab services. Leave it in this solution until you are finished preparing your standards and samples for analysis.

Important! Use the same ISE for all your measurements!

I Preparing standards.

In order for the ISE to give accurate measurements, it must be calibrated with standards having known chloride concentrations. Remember to use DI water to prepare your standards.

1. Use dried primary-standard-grade NaCl to prepare a chloride standard that is ~0.3 M in chloride. Remember to record your weights to 4 places after the decimal point. This will be your top standard.
2. Use your top standard to prepare solutions ranging in concentration from 3×10^{-5} M to 0.03 M. The easiest way to do this is to perform a series of serial dilutions.

Hint: The first step in making a serial dilution is to use a volumetric pipet to deliver a known volume (perhaps 10 mL) of your top standard into an appropriately-sized volumetric flask (perhaps 100 mL), which you then bring to volume with DI water.

3. Place 50 mL of your lowest standard into a 100 mL beaker (you may use a graduated cylinder for this part). Use the calibrated plastic dropper to add 1 mL of the ISAB solution to each beaker. Measure the chloride concentration as described below.

Using the Vernier LabQuest with the chloride ISE to acquire data for a calibration curve.

1. Plug the cable of the ISE into the Vernier LabQuest. Write down the number of your chloride ISE. You must use the same ISE for all your measurements.
2. Wash the ISE carefully with DI water by directing a stream of water from a squirt bottle at the area which has been submersed in the chloride storage solution and which will be submersed in your sample. Wick away excess liquid using the procedure demonstrated by the TA.
3. Place the beaker containing your lowest concentration standard on a stir plate and add a stir bar to it. Begin stirring the solution. Carefully place the electrode in your standard, making sure that the sensing element and the reference contact are both submersed. On the screen of the Lab Quest, press “sensors” → “calibrate” → “Chloride ISE” → “calibrate now”. You will see a small, inconspicuous box containing the voltage reading. Ignore everything else on the screen. Write down the voltage reading once it stabilizes.
4. Remove the electrode from the solution, rinse the electrode with DI water, wick away excess liquid, and place it in the beaker containing the next highest standard. Again, swirl

or stir the solution while taking the reading. Repeat until you have made measurements on all your standards up to the 0.03 M standard. Remember to rinse and dry the electrode before immersing it in the next solution.

5. Add 50 mL of your tap water sample to a 100 ml beaker. Add 1 mL ISAB to the beaker using the plastic dropper. Record the voltage reading.
6. Repeat step 5 until you have three readings for the tap water sample (from individually prepared samples).
7. Repeat steps 5 and 6 for the reclaimed water sample.

II Using the Vernier LabQuest with the chloride ISE for standard additions.

You will use the method of standard additions to measure the chloride concentration in a sample of an alcoholic beverage.

1. Pipet 100 ml of the wine sample into a 250 mL beaker. Place the beaker on a stir plate and add a stir bar to it. Measure the voltage as above. *Use the same ISE you used in part I.*
2. Use a volumetric pipet to add 1 mL of the top standard (~0.3 M standard) to the beaker containing the sample. Measure the voltage. Add a second and third 1-mL aliquot of the top standard to the beaker, taking a voltage reading after each addition.
3. Repeat steps 1 and 2 twice more, using a fresh sample each time.

III Chloride Unknown

1. Obtain a performance evaluation sample and determine its chloride concentration and repeat the procedure I.5.

Report (100 pts)

A typed report is required for this experiment. Pay attention to the quality of your writing. This report should contain:

- 1) A title page with the title of the experiment, the date, and your name.
- 2) A short introduction, which includes the experimental and educational objectives of the experiment, a description of your samples, the measurements you made and the technique you used.
- 3) A brief *summary* of the experimental procedures you used, with enough detail so that one of your fellow students could repeat your work.
- 4) Results. For the results and discussion section you should consider/complete/discuss the following:

Results, Part I

- a. Prepare a table similar to that in the prelab assignment. In your table, provide your measured potentials for your standards and for your water samples.
- b. Using Excel, or another plotting program, create a standard curve by plotting the electrode potential vs. the log of the chloride concentration of your standards. Show the equation of the calibration line and the R^2 value on the plot. Give your plot a title and

make sure the axes are labeled appropriately and have units. Does your plot contain a nonlinear region? What should you do if it does? Determine the R^2 value for the linear region only and include this on your plot as well.

- c. Determine β , the electromotive efficiency, for your electrode using your plot above.
- d. Calculate the concentration of chloride in the tap water and reclaimed water samples from the equation of the calibration line determined using Excel. If you diluted your samples, do not forget to consider the dilution factor in your calculations. Calculate the uncertainty in the chloride concentration in the tap water and reclaimed water samples. Report your chloride ion concentrations and associated uncertainties in ppm.

Results, Part II

- a) Prepare a table containing the data you obtained from your standard additions study. Note the chloride ion concentration of the standard solution you used (in M) and the volume (V_0) of wine sample you used in mL. The table should have columns for the volume of standard added (V_S) in mL and the voltage measured after each addition (E) in volts. Calculate $(V_0+V_S)10^{E/S}$ for each data point, where S is $\beta(0.05916)/n$ V, and place the results into yet another column.
- b) Using Excel, or another plotting program, create a standard additions graph similar to that shown on page 331 of your text (Figure 14-30). Show the equation of the calibration line and the R^2 value on the plot. Make sure you show the point where the calibration line intersects with the x axis of your plot. Give your plot a title and make sure the axes are labeled appropriately and have units. Does your plot contain a nonlinear region? What should you do if it does? Determine the R^2 value for the linear region only and include this on your plot as well. Use your plot to determine the concentration of chloride in the wine sample. The method for determining the chloride concentration from your plot is discussed on page 330-331 of your text. Calculate the uncertainty in the chloride concentration, based on your three analyses. Report your chloride ion concentrations and associated uncertainties in ppm. Use the appropriate number of significant figures when reporting your results.

You may wish to include examples of the various calculations you performed for Parts I and II. These may be neatly handwritten.

5) Discussion

- a. Discuss, interpret and comment on your results from parts I and II of the experiment.
- b. You have previously used a gravimetric method for determination of chloride in this class. Compare and contrast the potentiometric and the gravimetric methods for analysis of chloride in terms of precision and accuracy, ease of analysis, amount of sample required for each method, etc. Describe a third method that can be used for chloride analysis. If you were the manager of a water quality laboratory, which method would you choose for the measurement of chloride in water and wine, and why?
- c. Comment on the precision you were able to obtain using the ion selective electrode. Is this precision adequate for measurement of chloride concentration in water?
- d. Discuss any problems you had in this experiment and how you addressed these problems. How would you change the experiment to improve the quality of the data?
- e. Discuss the advantages and disadvantages of the method of standard additions for the

analysis of chloride in wine. Include both a general discussion of this method and specific comments about the application of standard additions to ion selective electrodes.

- 6) Conclusions. What conclusions can you draw from your data? Is the ISE an appropriate tool for the measurement of chloride in water? For the measurement of chloride in other beverages, such as wine? Defend your conclusions.