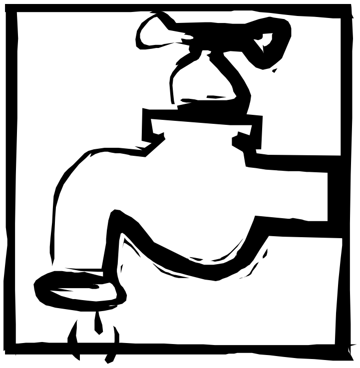
What's in Your Water Besides H_2O?

A Drinking Water Analysis Module

Chemistry 210 • Spring 2014



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Water Module: An Overview

Introduction

Few resources are more important to the functioning of a modern industrial society than a reliable, safe domestic water supply. A remarkable number and variety of other substances besides H_2O are present in drinking water. Though considerable latitude is possible in the exact composition of such supplies, the range of acceptable concentrations for many commonly found salts and organic impurities is fairly narrow. The absence of disease causing organisms is even more critical.

A report on the complete analysis of a municipal water supply would list the identity and concentration of all cations and anions, as well as the identity and concentrations of all organic compounds found in the water. Clearly such a complete analysis is beyond the scope of an introductory chemistry course, but the concentrations of the most important anions and cations can be determined reliably by a combination of titrimetric, spectroscopic, electrochemical and chromatographic techniques. In some cases, these techniques have already been introduced in the course; in many cases, however, interest in the composition of the water samples themselves provides the incentive to master the techniques (and the underlying principles) required for the determinations.

Carrying out the chemical analysis of domestic water sources will be the major objective of this module. The focus of the module is the analytical laboratory where these determinations are made, but both underlying theory and the specific procedures will be examined. Though the chemical analysis of the water samples, and the principles involved in the techniques employed, will occupy much of our class and laboratory time in this investigation, the close examination of the results of these analyses and the insights that we can derive from that examination provide the ultimate justification for the effort. Finally, the requirement that we describe our techniques and communicate our results to a broader community should contribute to a more thorough mastery of the material and to a most interesting project.

Objectives and Organization of the Module

The Goal

To become thoroughly familiar with the ionic composition, method(s) of analysis, and treatment of the drinking water supply of four selected communities in the US and of the community in which each student lives.

Case Studies of Four Water Sources

A case history approach will be used to examine the geological source, the chemical composition, and the method(s) of treatment of four US domestic water supplies. Four samples from the following quite different water sources, which illuminate a good range of chemistry and geology, will be employed in initial experiments:

- **Grinnell, IA**, with deep wells drilled into the Cambrian-Ordovician aquifer (450-540 million year old sandstones and dolomites), which lies approximately one half-mile beneath the surface;
- **Des Moines, IA**, with water obtained from the rivers and associated shallow alluvial aquifers which collect runoff water from intensively farmed areas;
- **Chicago, IL**, which uses the relatively soft water of Lake Michigan and an engineering plan that insures that the waste water flows away from the city and its drinking water source.

- **Bottled/spring water (e.g., Dasani, bottled by Coca Cola Corp.**) available in individual bottles at the local grocery store; typical of such bottled water which accounts for an increasing percentage of the water drunk by American consumers.

Scope of Project

Informed by the comparative examination of these samples, each student group will be expected to generate a similar description of other water systems (preferably samples from their home city, though the college home community area well that serves single residents, etc. are also possible sources for this comparison). The final report and poster session will then include a comparison of the range of samples examined by the group.

Structure

The module will be heavily laboratory oriented and cooperative learning will be emphasized. Students will be expected to work cooperatively to set up an analytical chemistry lab to carry out a range of analyses on the water samples that each group is examining. Each group will be responsible for preparing solutions and testing specific methods. That group will do all of the analyses of all of the samples brought in by class members. After the first week, class members will also be responsible for presentations on specific topics included in the module. Both written and oral reports on the project will be required.

Class Sessions/Problems

Class sessions will be devoted to discussions of general principles involved in the analyses of a water sample and to details of the specific methods actually employed in our laboratory--and included in the lab manual. The material is organized into 11 class sessions (Session 1, 2, etc.). Each in-class session is devoted to a single major topic, which is introduced by a specific question which the session is designed to answer. A series of more specific questions are provided to focus of the class discussion. In most cases, problems, demonstrations, or simple in-class lab exercises are also included in the session description. A separate problem set is included at the end of the session descriptions.

Some of the background material included in these 11 sessions may have already been considered earlier in the term, but it is included here to make the module relatively self-contained. Your instructor will probably choose to devote fewer than 11 class meetings to the material, either by combining portions of two or more sessions into a single session or by simply calling attention to material that you have covered earlier in the term.

Behavioral Aspects

In addition to mastery of the subject matter content, the module also includes the following behavioral objectives:

- to learn how to formulate a question and to identify procedures and carry out experiments to answer that question;
- to learn to work effectively and efficiently as part of a group with a common goal;
- to learn to report technical information to a general audience.

Session 1: Formulating the Questions and Limiting the Exploration
What's in your water besides H2O?

Exploration 1A.	What is your current attitude toward the quality of public water supplies and of bottled water?
Exploration 1B.	What is in the water that comes from our taps (besides H2O)?
Exploration 1C.	What methods can be used to determine quantitatively the composition of water samples?
Exploration 1D.	What criteria are used to evaluate drinking water quality?
Exploration 1E.	Closure.

Session 1: Formulating the Questions and Limiting the Exploration

What's in your water besides H_2O?

Exploration 1A. What is your current attitude toward the quality of public water supplies and of bottled water?

Each of us uses about 100 gallons of water a day for drinking, bathing, toilet, etc. The immediate source of that water is the tap at the sink or tub, but for most of us the ultimate source of that water is a municipal water supply system. With proper use of modern technology, that supply--whether it comes from deep underground wells or surface reservoirs--should be safe and reliable. The tremendous growth of the bottled water industry in the U.S. in the past decade suggests that many of us do not find the municipal water supply satisfactory. Some simple questions will be used to help us clarify our current views on the quality of the water we drink and the bases of those views.

Exploration 1B. What is in the water that comes from our taps (besides H_2O)?

We need to know both what other substances are in the water and what effects those substances have on human health, water taste, etc. The assignment is to work in groups of 3-4 to compile a list of at least 10 specific substances that one might expect to find in a domestic water supply. After compiling your list, reorganize the list to group the individual substances into broader categories. After lists have been compiled by each group, we will select the categories and individual substances which are most significant to assessing the quality of the water for drinking.

Exploration 1C. What methods can be used to determine quantitatively the composition of drinking water samples?

Prior to this module you have spent much of a semester using several different techniques to determine quantitatively the chemical composition of a variety of samples. **Make a list of these techniques and consider which ones might be most applicable to each of the substances identified in 1B.**

The rest of this module will be devoted to examining in detail techniques that are applicable to determining the concentrations of the components that have been identified as important constituents of typical drinking water samples. In many cases, more than one technique can be used to determine the concentration of a particular species. The choice of method to use depends on the availability of equipment, reagents, etc. and other circumstances, including the degree of accuracy required, the number of samples which must be determined, etc. The techniques actually employed in the lab will be the ones emphasized in the classroom discussions and exercises.

Exploration 1D. What criteria are used to evaluate drinking water quality?

Chemical analysis can be used to determine the presence and concentration of substances present in drinking water samples, but the question of the safety of the water for drinking is one that requires in addition some criterion of safety. In short, how much of substance X in our drinking water is too much? What criteria are used to set these standards? And who (or what agency) has the authority either to set or to enforce the standards? In the United States, the U.S. Environmental Protection Agency (EPA) promulgates drinking water standards. Regulations are divided into two broad categories: 1) primary and 2) secondary standards. Primary standards are enforceable by law and are the acceptable limits for biological, chemical, or radiologic agents that pose risk to human health. Secondary standards are non-enforceable guidelines for maintaining the aesthetic quality of water (e.g., clarity, taste, and odor). Up–to-date information on drinking water standards in the United States can be found at:

http://water.epa.gov/drink/contaminants/index.cfm, (accessed, 2/27/14).

Exploration 1E. Closure.

After the examination of 1A-D we should be in a position to establish the limits of our experimental investigation of drinking water samples in order to be able to set up the laboratory to carry out the analyses. Clearly any such analysis is incomplete in some sense. It is not feasible to carry out a complete analysis for all possible contaminants that might be considered; however, we would like to carry out enough analyses to be able to provide an answer — even - if incomplete — to the module question: What's in your water besides H_2O and *why*?

Session 2. Dissolved Ionic Solids
Which ionic salts are present in typical water samples and how did they get there?

Exploration 2A. What substances contribute to total dissolved ionic solids (TDS)?

Exploration 2B. What properties reflect the concentration of TDS?

Exploration 2C. What simple alternatives are available for determining TDS?

Exploration 2D. What might TDS tell us about the source of our water?

Exploration 2E. Closure.

Session 2: Dissolved Ionic Solids

Which ionic salts are present in typical water samples and how did they get there?

Exploration 2A. What substances contribute to total dissolved ionic solids (TDS)?

No ground water or surface water sample consists only of pure water. Even freshly precipitated rainwater contains small concentrations of dissolved particles and gases that accumulated in falling through the atmosphere. Familiarity with the solubility properties of typical inorganic substances and the composition of the earth's crust can enable us to make reasonable guesses about the likely composition of dissolved minerals in water samples. Substances which are very soluble in water would be expected to be found at a high concentration in ocean water, but would no longer be present to dissolve in fresh rainwater. Sodium chloride is, therefore, the principal dissolved substance in the ocean. Clearly the specific composition of a given sample will depend on the local geological conditions. High salt concentrations can also be found in water from geysers and hot springs. Normal drinking water samples have much lower concentrations of dissolved salts; however, some cations and anions are certain to be present in almost any ground water sample--at measurable concentrations.

From a list of common anions and cations, identify those that are likely to be present at significant concentrations in drinking water samples. (Recall Exploration 1B.)

Exploration 2B. What properties reflect the concentration of TDS?

Any property which depends in a predictable way on the concentration of dissolved solids potentially can be used as the basis of an analytical technique for measuring the concentration. Some techniques might be more convenient than others (or more reliable than others), but a useful exercise is to compile a list of possibilities.

A demonstration: A simple light bulb in series with a pair of wires that can be immersed in a water sample lights up when the solution contains ions to make it conductive.

Exploration 2C. What simple alternatives are available for determining TDS?

On the basis of the properties identified in 2B, suggest methods to determine quantitatively the total concentration of dissolved solids in a water sample. One obvious method is to determine the mass of solid that remains when a large volume of water is evaporated. Discuss the advantages and disadvantages of this approach.

Suggest ways to employ the electrical conductivity property to establish the concentration of dissolved solids in water samples. What assumptions are required to use this technique for a quantitative characterization of TDS?

Exploration 2D. What might TDS tell us about the source of our water?

The presence of dissolved ionic solids in a water sample can be quite revealing about the history of the water. Freshly precipitated rainwater or the deionized water from a reverse osmosis or distillation apparatus will have a very low concentration of dissolved solids. By contrast, seawater is essentially 3 weight % sodium chloride (approximately 0.5 M NaCl) with smaller amounts of other salts. This is much, much more concentrated than typical drinking water samples, for which most ion concentrations are less than 5 mM = 0.005 M. Bottled “mineral water” may contain much higher concentrations of dissolved solids than typical domestic water supplies, and water from sources near the ocean that have been infiltrated by ocean water will have higher than normal concentrations of NaCl.

Exploration 2E. Closure.

Though the total dissolved solids (TDS) level is only a rough indicator of water quality, it is a property that is important and easy to measure. In preparation for carrying out subsequent determinations of concentrations of specific ions, knowledge of the TDS level reveals readily whether one is dealing with very dilute solutions or more concentrated solutions. This can be particularly useful in estimating sizes of samples and concentrations of reagents to use in subsequent analytical determinations. Though described last in the lab manual which is part of this module, the TDS level is often the first quantity to be determined.

An example which involves concentration levels that might be regarded as typical is the following: Calculate the concentration in moles/L (M) and millimoles/L (mM) of all of the ions in a water sample which contains 400 ppm = 400 mg/L of TDS if the TDS consists (a) entirely of sodium chloride, NaCl (58.5 g/mol), (b) entirely of sodium sulfate, Na_2SO_4 (144g/mol), (c) 200 ppm of each of the two salts.

Session 3. Major species vs. minor species
Why are so many different concentration units employed to describe concentration levels of the several species present in water samples?

Exploration 3A. What concentration scales should we employ in our descriptions?

Exploration 3B. How much is a part per million (ppm); part per billion (ppb)?

Exploration 3C. What methods can be used to determine major components?

Exploration 3D. What methods can be used to determine minor components?

Exploration 3E. Closure.

Session 3: Major species vs. minor species

Why are so many different concentration units employed to describe concentration levels of the several species present in water sample?

Exploration 3A. What concentration scales should we employ in our descriptions?

The choice of a concentration scale to use to specify the composition of a solution is somewhat arbitrary; however, over time conventions emerge, and workers in a particular field come to use particular units that make sense for the solution they are describing. In general, the preferred concentration unit to use for a given solute is one for which typical values reported are of the order of 1-10. This avoids use of lots of zeros or exponential notation in reporting the data.

For the chemist, the molar concentration scale, **M, defined as the number of moles of solute per liter of solution**, is often the most convenient scale to use, since equal volumes of solutions with the same molar concentrations would contain equal numbers of moles (and molecules) of solute. For drinking water samples, which are quite dilute (with molar concentrations of ions in the 0.0001-0.0100 range), it is often more convenient to specify the concentration in **millimoles/L = mM**, or even **micromoles/L = μM**. Again the scale which yields concentration values in the 1-10 range is usually chosen.

The molar concentration is not widely employed in conventional reporting of the composition of drinking water samples; the mass of a given solute dissolved in a given volume of water (usually 1 L) is much more often specified. Because drinking water samples are typically very dilute, the mass is usually specified in mg, so the concentrations are in mg/L. Since 1 L of water contains 1000 g = 10^6 mg, the concentration in **mg/L is equivalent to the concentration in parts per million, ppm**. With the increase in sophistication and sensitivity of modern analytical techniques, concentrations as low as 0.001 mg/L can often be determined reliably. Such concentrations are often specified in **parts per billion, ppb, which is equivalent to micrograms/L, μg/L.**

An additional complication must be considered in reading and evaluating reported analytical data. The value specified may be for a portion of the solute or in terms of another substance which is equivalent to the substance actually determined. Nitrate in water samples is typically reported, for example, as 8.5 ppm **nitrate (N).** This is to be interpreted as 8.5 mg **nitrogen in the form of nitrate anion per liter**. Since nitrate is NO_3^-, the actual concentration of **nitrate** would be (8.5 mg N/L)(62 mg NO_3/14 mg N) = 37.6 mg NO_3/L. Similarly, the magnesium hardness of water is conventionally ppm of $CaCO_3$. In this reporting, one mol of Mg^{2+} corresponds to one mol of $CaCO_3$ (because one mol of Mg^{2+} reacts with one mol of CO_3^{2-} to produce $MgCO_3$). For example, a sample containing 7.2 mg Mg^{2+}/L would be reported as containing 30 mg $CaCO_3$/L:

$$\left(\frac{7.2\text{ mg Mg}^{2+}}{\text{L}}\right)\left(\frac{1\text{ mmol Mg}^{2+}}{24\text{ mg Mg}^{2+}}\right)\left(\frac{1\text{ mmol CaCO}_3}{1\text{ mmol Mg}^{2+}}\right)\left(\frac{100\text{ mg CaCO}_3}{1\text{ mmol CaCO}_3}\right)=\frac{30\text{ mg CaCO}_3}{\text{L}}$$

Exploration 3B. How much is a part per million (ppm); part per billion (ppb)?

One consequence of the use of concentration scales which are chosen to match the analyte being described is that one can lose appreciation of the huge range of concentrations involved in the total description. This exercise should help to give you a better feel for the differences among the commonly employed concentration scales.

Exercise: Consider the following containers:

1) a 100 mL volumetric flask
2) a 100 L fish tank
3) a million L swimming pool

Calculate how much sodium sulfate, Na_2SO_4 (142 g/mol), must be added to each of these vessels to yield a solution with each of the following concentrations:

i. 0.100 M sulfate ion
ii. 1.0 mM sodium ion
iii. 1.0 ppm sodium sulfate
iv. 1.0 ppb sulfate ion

Exercise: Work in groups of 3-4 to propose analogies to help someone unfamiliar with these matters understand what it means for a solution to contain 1 ppm or 1 ppb of a dissolved solute. (For example, a grain of sand in a bucket of sand is ??? ppm.)

Exploration 3C. What methods can be used to determine major components?

As we consider which analytical methods we could employ to determine the concentration of a specific analyte, it is useful to think about the distinction between minor components and major components. In general, the classical wet chemical methods, titrations and gravimetric methods, give satisfactory results for the determination of major components, i.e., those whose concentrations are of the order of 0.01 M or greater. Gravimetric determinations must yield enough material to determine the mass accurately and titrations with very dilute solutions are often not reliable.

Exercise: Review the list of substances generated earlier (1B) and identify which of these species is a major component. Suggest a specific technique to determine the concentration of each of these species.

Exploration 3D. What methods can be used to determine minor components?

Many of the techniques introduced in a formal analytical chemistry course are able to detect very low concentrations of analyte. Three widely used techniques that are in this category are **potentiometric methods** (the pH meter for the determination of $[H^+]$ is a familiar example), **photometry** to determine the concentration of light absorbing (or emitting) substances, and **chromatography**, which can be used in several variations to determine a wide range of species from hydrocarbons and pesticides to metal ions in solution. Some of these techniques can be used in combination. For example, a glass electrode equipped pH meter can be used to plot a titration curve to determine the end-point in a titration of an acid with standard base.

Exercise: Review the list of substances generated earlier (1B) and identify which of these species is a minor component. Suggest a specific technique to determine the concentration of each of these species.

Exploration 3E. Closure.

A wide range of techniques are required to completely characterize the dissolved species in a typical water sample. Some techniques are simple and convenient, but require fairly high concentrations of analyte; other techniques can be employed to determine concentrations that are several orders of magnitude below the level required for the classical methods to work. Knowing the approximate concentrations of the species to be determined enables the analyst to make a sound choice regarding method to use.

Because the range of concentrations of species is so great, several different concentrations units are routinely used to report data. It is essential to be able readily to interconvert between these units.

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Session 4. Carbon dioxide and dissolved carbonates
Why do virtually all fresh water samples contain bicarbonate as a principal species?

Exploration 4A. What is the pH of rainwater?

Exploration 4B. Why do rocks dissolve?

Exploration 4C. What can a pH titration reveal about a water sample?

Exploration 4D. What is the difference between alkalinity and pH?

Exploration 4E. Closure.

Session 4: Carbon dioxide and dissolved carbonates

Why do virtually all fresh water samples contain bicarbonate as a principal species?

Exploration 4A. What is the pH of rainwater?

The key to understanding the mineral composition of drinking water lies in understanding the composition of freshly precipitated rainwater. A variety of processes contribute to unusually high acidity for rainwater in some regions. This unusually high acidity (referred to as **acid rain** or acid precipitation) can often be attributed to air pollution from industrial or geological processes. But it is usually not the principal source of acidity in rainwater. Whether or not there is significant air pollution, the ambient concentration of carbon dioxide in air and its finite solubility in water insures that the pH of rainwater will always be less than 7.0, the pH of pure water. The reaction of CO_2 with water yields the weak acid carbonic acid, H_2CO_3; and the dissociation of the carbonic acid lowers the pH of the water appreciably, i.e.,

$$CO_2(g) \;+\; H_2O(l) \text{ ------->} \; H_2CO_3(aq) \text{ ------->} \; H^+(aq) \;+\; HCO_3^-(aq)$$

Because carbonic acid is a weak acid, the second step in this process does not go very far, but any increase in $[H^+(aq)]$ lowers the pH of the water below 7.0.

Exercise: **The pH of rainwater**. The solubility of gases in liquids can be described quantitatively by Henry's Law, $c = K_H P$, where the concentration of dissolved gas (c) is proportional to the partial pressure of the gas above the liquid (P), K_H being the proportionality constant.

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3(aq) \qquad K_H = \frac{[H_2CO_3]}{P_{CO_2}} = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$$

For $CO_{2\,in}$ the atmosphere at 25 degrees C, $k_H = 3.4 \times 10^{-2}$ mol L^{-1} atm^{-1} and the partial pressure of CO_2 is .000398 atm (398.03 ppm by volume in the atmosphere).

a. Use these data to calculate the concentration of dissolved $H_2CO_3(aq)$ in air-saturated rainwater at 25°C.

b. Once we know the concentration of $H_2CO_3(aq)$, we can determine the pH of rainwater. While H_2CO_3 is a diprotic acid ($pK_{a1} = 6.35$ and $pK_{a2} = 10.33$ at 25°C), recall that if we are interested in calculating the pH of a solution containing the fully protonated form of diprotic acid, we can treat the diprotic acid as a monoprotic acid. Based on the calculated concentration of H_2CO_3 from (a), calculate the pH of rainwater in equilibrium with the CO_2 in the atmosphere.

The presence of sulfur dioxide, SO_2, in the air--typically from burning high sulfur coal--leads to the similar weak acid sulfurous acid, $H_2SO_3(aq)$, when it dissolves in rainwater. More importantly, either the sulfur dioxide or the sulfurous acid is usually oxidized under atmospheric conditions to +6 sulfur, which ends up as sulfuric acid. Since the latter is a strong acid, it has even more effect on the pH than an equivalent concentration of the weak acids carbonic or sulfurous acid.

In regions where photochemical smog from auto exhaust fumes contains significant concentrations of gaseous nitrogen oxides, nitric acid formed by reaction of NO_2 with water droplets also contributes importantly to acid rain. Nitric oxide, NO, formed in the high voltage discharge of a lightning bolt, is another source of NO_2 and thereby the strong acid HNO_3, nitric acid.

The reactions by which the strong acids sulfuric and nitric acids are formed and contribute to acid precipitation can be abbreviated:

$$S(s) + O_2(g) \longrightarrow SO_2(g) \xrightarrow{H_2O\ +\ O_2} H_2SO_3(aq) \longrightarrow H_2SO_4(aq)$$

$$N_2(g) + O_2(g) \longrightarrow NO(g) \xrightarrow{O_2\ +\ H_2O} NO_2(g) \longrightarrow HNO_3(aq)$$

Exploration 4B. Why do rocks dissolve?

The dissolved minerals in a drinking water supply originated as solids in the soil or subterranean rocks. Even the salty water that infiltrates wells in coastal areas near the ocean accumulated slowly by rainwater washing over deposits of water soluble sodium chloride, etc. Very deep wells and wells in areas where there is significant geothermal activity often accumulate high concentrations of water soluble salts, simply because they have had more opportunity to dissolve such salts over time, especially when the water is hot. The less soluble carbonate and silicate minerals, however, dissolve in water only with the assistance of acidic substances in the water.

The carbonate minerals warrant particular attention. Limestone deposits, which are near the surface in much of the country, are essentially calcium carbonate or calcium/magnesium carbonate (dolomite). Though carbonates are not significantly soluble in neutral water, the reaction of CO_2-saturated water with $CaCO_3$ yields an aqueous solution of calcium bicarbonate; i.e.:

$$CO_2 + H_2O + CaCO_3(s) \longrightarrow Ca^{2+}(aq) + 2HCO_3^{-}(aq)$$

Acid/base properties of domestic water supplies are important for the users, whether home owners or commercial enterprises. The reverse of reaction (1) is responsible for filling up water heaters, boilers, tea kettles, and distribution pipes with lime deposits, essentially $CaCO_3(s)$, when the water is heated or boiled to drive off CO_2. The reverse reaction is also responsible for the formation of stalactites and stalagmites in caves in limestone rich areas.

If there is significant sulfuric acid from dissolved sulfur dioxide in the water, some limestone can dissolve to form a solution of calcium sulfate with the release of carbon dioxide into the air; i.e.:

$$H_2SO_4(aq) + CaCO_3(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) + CO_2(g) + H_2O$$

This is the reaction that is resulting in premature destruction of limestone sculptures and artifacts in areas of heavy air pollution.

A demonstration: Crush pieces of chalk, essentially calcium carbonate. Add portions of the powdered chalk to open 250 mL beakers of water and of 1 M sulfuric acid. Discuss the differences observed in terms of acid strength and competing acid-base and solubility equilibria.

Exploration 4C. What is the pH of a typical ground and surface water sample?

The pH of most domestic water sources is rarely exactly 7.0. As we have seen, dissolved carbon dioxide (and other non-metal oxides) lowers the pH below 7, but reaction of part of that acid with carbonate rocks can raise the pH to 8.34, where bicarbonate is the principle species. The pH of ~8.3 derives from the fact that CO_2 reacts with $CaCO_3(s)$ to produce HCO_3^-. The pH of a solution of the intermediate species HCO_3^- is given by:

$$pH = \tfrac{1}{2}\ (pK_{a1} + pK_{a2}) = \tfrac{1}{2}(6.35 + 10.33) = 8.34$$

The pH of the water is important. If it is too low, the rate of corrosion of pipes is increased. If it is too high, precipitation of $CaCO_3(s)$ is increased. So, for many domestic suppliers, the pH is controlled carefully, by addition of NaOH if necessary, to obtain a pH about 8.3, where HCO_3^- is the principal carbonate species.

Exploration 4D. What is the difference between alkalinity and pH?

Two terms that are commonly used to describe the acid-base properties of water samples are **alkalinity** (and/or **acidity**) and **pH**. The relationship between the two is like the relationship between heat and temperature. The first involves a **capacity** while the second involves only the **intensity** of a related property. The alkalinity of a water sample is measured by the amount of strong acid required to titrate a sample completely. It is conventionally measured by specifying the concentration of bicarbonate in the sample, or by specifying the concentration of $CaCO_3$ in ppm that would have the same neutralizing power. By contrast, the pH is simply an indicator of hydrogen ion concentration in a specific solution. Two solutions can have the same pH (for example 8.3) but drastically different neutralizing powers, i.e., different alkalinities (for example 0.10 and 2.00 mM bicarbonate). For carbonate solutions, the **pH** reflects the **ratio** of concentrations of principal species while the **alkalinity** reflects the total concentration of unprotonated forms. These distinctions are discussed more fully in Session 8, page 27, and in Section L3:6 of the lab manual. For carbonate containing waters,

$$\text{Alkalinity} = [\text{Alk}] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

Note the multiplier 2 in front of $[CO_3^{2-}]$ because each mole of CO_3^{2-} can consume 2 mole of H^+. An alternative definition of alkalinity is as the imbalance between other cations (excluding H^+) and anions (excluding carbonate species and OH^-). This definition derives from consideration of the electroneutrality equation. For a typical water sample, considering major species only, the electroneutrality equation would be:

$$[H^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] = [OH^-] + 2[CO_3^-] + [HCO_3^-] + 2[SO_4^{2-}] + [Cl^-]$$

This equation can be rearranged:

$$\{2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+]\} - \{2[SO_4^{2-}] + [Cl^-]\} = [OH^-] + 2[CO_3^-] + [HCO_3^-] - [H^+]$$

Giving:

$$\{2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+]\} - \{2[SO_4^{2-}] + [Cl^-]\} = [\text{Alk}]$$

Given this definition, it is relatively easy to see how dissolution of geologic materials will contribute to the alkalinity of a water sample. Dissolution of $CaCO_3$ or $MgCO_3$ produces Ca^{2+} and Mg^{2+} but no Cl^- or SO_4^{2-}, so dissolution of these rocks will increase the alkalinity and increase the buffering capacity of the water. Dissolution of gypsum ($CaSO_4 \cdot 2H_2O$), in contrast releases equal amounts of Ca^{2+} and SO_4^{2-} and thus no net alkalinity; gypsum dissolution thus provides no buffering capacity in the water.

Exploration 4E. Closure.

Unusual geological conditions or major pollution events can lower or raise the pH of surface or ground water significantly. For example, relatively high pressures of carbon dioxide gas trapped in underground deposits produce a natural carbonation of area water, like Perrier water from France. This natural carbonation (excess carbonic acid) lowers the pH of the water significantly and leads to the fizziness of Perrier water when a bottle is opened. However, for most natural waters, the pH lies in the mid-range where HCO_3^- is the dominant species. The ability of this water to neutralize strong acids leads to an emphasis on the alkalinity of the water, which is readily determined by titration with standard HCl, as discussed in Session 8: Potentiometric Titrations on page 27.

Session 5. Hard Water
What is meant by hard water and why does degree of hardness matter?

Exploration 5A. What happens to soap dissolved in hard water?

Exploration 5B. Why is ground water typically harder than surface water?

Exploration 5C. Why does EDTA bind to metal ions?

Exploration 5D. How is hardness determined and expressed quantitatively?

Exploration 5E. Closure.

Session 5: Hard Water

What is meant by hard water and why does degree of hardness matter?

Exploration 5A. What happens to soap dissolved in hard water?

The term hard water appears to be an inappropriate term to apply to a liquid which is clearly not hard in the usual sense of being "solid and firm to the touch." Of course, hard has many meanings, and the property of hard water which gave rise to the label can probably best be appreciated by a demonstration of the effect of dissolved calcium on soap.

A Demonstration. Show effects of [Ca^{2+}] on soap solutions.

Exploration 5B. Why is ground water typically harder than surface water?

The superiority of rainwater for washing dishes and clothes, for bathing and showers, etc. has been well established for many years. At the turn of the century, many houses were equipped with cisterns to collect the rainfall runoff from roof drains, and this soft water was used for all washing and bathing. A separate ground water well typically was used as the source of drinking water. Since the well water had seeped through soil and rocks, it was much harder than the rainwater.

The surface water in lakes and streams is usually not as hard as the water in deep wells. It has not had much chance to dissolve minerals from the soil and rocks in the area. The composition will also vary with the season. Dilution by spring runoff and heavy rains reduces the hardness in proportion to the dilution factor.

Exploration 5C. Why does EDTA bind to metal ions?

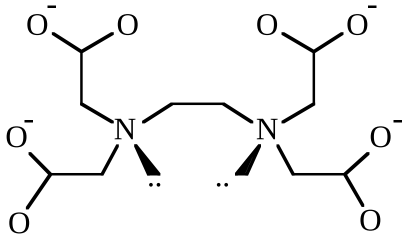
One of the ways to minimize the deleterious effects of hard water is to add a substance to the water that ties up the calcium or magnesium ion so that the $Ca(soap)_2$ precipitate does not form. One of the most effective of such reagents is EDTA, a polyfunctional synthetic amino acid which forms quite stable 1:1 complexes with almost all 2^+ cations. The EDTA anion (**1**) is a hexadentate complexing agent, so it forms stable, water soluble anionic complexes with calcium and magnesium cations. These complexes are more stable than complexes of simpler bidentate chelating agents, like the naturally occurring amino acids glycine and alanine.

Structures of Metal Chelates. Use a ball and stick modeling kit or computerized structure building program (like Spartan, CAChe, etc.) to construct models of octahedral complexes of the following ligands with a general metal cation M^{2+}:

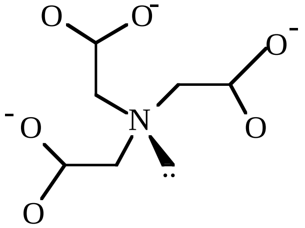
- oxalate (3:1 complex)
- ethylenediammine = en (3:1 complex)

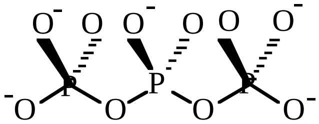
- glycinate (3:1 complex)
- EDTA (1:1 complex)

EDTA is sometimes added to cleaning agents to improve their effectiveness in hard water. Other less expensive anionic species which are commonly used in substantial quantities in commercial cleaning products include the sodium salt of nitrilotriacetic acid (NTA), a tridentate amino acid (**2**), and sodium tripolyphosphate (**3**).



Structure 1





Structure 2 and 3

Exploration 5D. How is hardness determined and expressed quantitatively?

The hardness of water has often been estimated by noting how much of a standard soap solution is required to produce suds after shaking with a given volume of hard water. However, a more reliable reagent to employ as a titrating reagent for the calcium and magnesium ions that are responsible for water hardness is a standard solution of EDTA (The EDTA $^{4-}$ anion is commonly denoted Y^{4-}). The equilibrium constant for the titration reaction at pH 10 is,

$$Ca^{2+} + HY^{3-} \text{ -------> } CaY^{2-} + H^+$$

is large, so the reaction goes to completion, and appropriate indicators are available to signal the end-point of the titration. The titration usually involves complexing with both calcium and magnesium ions, but it can be done at high pH where $Mg(OH)_2$ is not soluble and only the calcium is available for reaction with EDTA. The former titration yields **total hardness** while the latter is referred to as **calcium hardness**. (See Water Module L2, page 63, for additional details.)

The total concentration of calcium + magnesium, the **total hardness**, can be specified in moles/L (M) or millimoles/L (mM), which can readily be calculated from the volumes determined in an EDTA titration experiment. For comparison with standard reports and accepted practice, it is also useful to report the mg of $CaCO_3$/L (ppm $CaCO_3$), which would produce the observed hardness if it were soluble in the given water sample. Since 1 millimole of Ca^{2+} is available for each millimole of $CaCO_3$ and 1 millimole $CaCO_3$ is 100 mg $CaCO_3$, hardness in ppm $CaCO_3$ = 100 x hardness in mM (Ca^{2+} + Mg^{2+}).

The same conversion applies to both **total hardness** (which includes Mg and Ca) and to **calcium hardness**.

Exploration 5E. Closure.

Ground water or surface water in any area that contains limestone rocks inevitably contains some dissolved calcium and magnesium ions from dissolution of limestone by acidic precipitation. This dissolved calcium contributes positively to the taste of water and is a significant source of this nutritionally essential mineral. Water hardness, if excessive, has a variety of undesirable effects, so the specification of the hardness of a drinking water sample is an important part of its characterization. Metal complexing by multidentate chelating agents accounts for their addition to cleaning products to reduce undesirable effects of excessive hardness and for their use in the design of reagents to determine water hardness. An alternative strategy for dealing with excessive hardness is to reduce the hardness of a domestic water supply, either at the water treatment plant, before it is distributed to users, or--on a smaller scale--in homes or businesses by the individual users. A total hardness of 50-100 ppm $CaCO_3$ is considered to be an appropriate level for municipal supplies in the U. S. The chemistry and the effects of such water softening are examined in detail in Water Module Session 6, page 19, and the lab manual, Laboratory Manual for Water Module.

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Session 6. Sodium and Yellow Flames
How can we determine how much sodium is in the water?

Exploration 6A	Why is there so much sodium in the ocean and so little in fresh water?
Exploration 6B	How is hard water softened?
Exploration 6C	What is the difference between atomic emission and atomic absorption spectroscopy?
Exploration 6D	How can concentrations be determined from emission intensities?
Exploration 6E	Closure.

Session 6: Sodium and Yellow Flames

How can we determine how much sodium is in the water?

Exploration 6A. Why is there so much sodium in the ocean and so little in fresh water?

Why is the sea salty? According to one popular legend, the sea became salty when a salt mill kept on churning out salt after it had fallen into the ocean. Though we recognize the absurdity of this explanation for the saltiness of the sea, we are all well aware that the concentration of sodium chloride in seawater is very high. At about 3% by mass NaCl, the concentration of sodium and chloride ions in seawater is about 0.5 M. By contrast, the concentration of sodium in fresh water from wells and lakes (with the exception of lakes in arid regions which have no drainage, like Great Salt Lake and the Dead Sea) is usually about a thousand times less, often of the order of 0-1 mM.

A trip to the stockroom. An inspection of the reagent shelves of a typical chemical stockroom gives one a valuable clue to understanding the high concentration of sodium in the sea. A disproportionate fraction of the salts on the shelves are sodium or potassium salts. Similarly, the latest Aldrich Chemical Co. Catalog lists almost twenty pages of sodium compounds vs. approximately four pages of compounds of iron, another abundant metal. Of course, the reason for the widespread use of sodium (and potassium) reagents is that such salts are generally soluble in water. Similarly almost all chloride salts are soluble in water. This high solubility of sodium and chloride salts insures that any such salts that had been deposited by geological activity earlier in the earth's history have largely been dissolved by water flowing to the sea over the ages. Evaporation from the sea leaves the salt behind and provides the source for more fresh water to dissolve still more sodium and chloride salts, etc.

Question for discussion: It is easy to understand why sodium and chloride accumulate in the sea. We have also established that surface waters often contain significant concentrations of calcium and magnesium. Why do these ions not build up in the ocean to a greater extent than sodium?

Exploration 6B. How is hard water softened?

Since most soluble sodium salts have already been leached from top layers of soil, why do we often find significant concentrations of sodium in domestic water supplies? One possible answer is that salty water – either from the ocean or from another mineral rich source, like a hot spring, for example – is infiltrating (leaking into) the aquifer. This is often the case for shallow aquifers near the ocean. In this case, high sodium is always balanced by high chloride, the principal anion in ocean water.

Survey of Home Water Softeners: Is a water softener used in your home? If so, describe the operation and servicing of that water softener.

Several methods are available to soften hard water. Since the hardness is caused by calcium and/or magnesium cations, any process which removes those cations, or which replaces those cations by less troublesome cations, like sodium or potassium, can be employed. Here is a partial listing, with brief comments.

1) **Cation exchange resin softening**. Either synthetic polymers or naturally occurring insoluble minerals called zeolites can be used to exchange the calcium cation which causes hardness for another cation, typically sodium. The process, which can be carried out readily by simply allowing the water to flow over a bed of the resin in a cylinder or large chamber (depending on the scale), can be reversed by passing a sodium chloride solution over the calcium form of the resin. The softening and recharge are represented by the equation:

   $$2Na^+R^-(s) + Ca^{2+}(aq) \text{ -------> } Ca^{2+}R^-_2(s) + 2Na^+(aq)$$

   and its reverse:

   $$Ca^{2+}R^-_2(s) + 2Na^+(aq) \text{ -----------> } 2Na^+R^-(s) + Ca^{2+}(aq)$$

   where $R^-(s)$ represents the anion form of the solid resin. Water softened in this way contains a relatively high concentration of sodium ion, which is generally matched by a corresponding concentration of bicarbonate anion formed when $CaCO_3$ dissolved in CO_2-saturated rainwater.

2) **Ion-exchange demineralizing**. If the cation-exchange resin is initially in the H^+ form (by flushing with HCl(aq)), passing water through the resin effectively converts Ca^{2+} to H^+ and the water becomes quite acidic. Subsequent passage of that water through an anion exchange resin which has been prepared in the OH^- form removes the other anions and yields mineral free water, since the OH^- released combines with the H^+ from the cation exchange resin treatment to form water. A single passage of water through a mixed bed of cation and anion resin beads yields the same result, but the resins cannot be recharged. Such mixed bed resins, packed in disposable cartridges are often used to remove the last trace of ions after **reverse osmosis** or **distillation** units are used to remove most of the dissolved salts.

3) **Soda-lime softening process**. An alternative to the ion-exchange softening process is the soda-lime process, which has the advantage that the total salt concentration is reduced. If the water contains only calcium bicarbonate, the addition of slaked lime, $Ca(OH)_2$, leads to precipitation of both the calcium and the original bicarbonate (as calcium carbonate) by the neutralization of bicarbonate with OH^- ion, i.e.,

   $$Ca^{2+} + 2HCO_3^- + Ca(OH)_2(aq) \text{ ---------> } 2CaCO_3(s) + 2\,H_2O$$

   If the water contains additional calcium ion, not balanced by bicarbonate, some sodium carbonate (Na_2CO_3 = soda) is added to precipitate the remaining calcium. In this way, the water can be softened without adding significant sodium ion.

Exploration 6C. What is the difference between atomic emission and atomic absorption spectroscopy?

Emission spectrum demonstration. Atomic spectroscopy, in one of its several forms, can be used to identify and to determine the concentration of any element, especially the metals. The basis of the method can be understood readily by noting the effect of salts of the alkali metals on the color of a Bunsen burner flame. This can be illustrated by sprinkling salts from salt shakers filled with LiCl, NaCl, KCl, and $CaCl_2$ and noting the colors of the flames produced by the vaporized salts.

The demonstration of the effects of metal salts on flame colors emphasizes that each element emits a characteristic spectrum of frequencies when its atoms are excited by the input of energy from some source, in this case the high temperature flame. The block diagrams in Figures 6.1 and 6.2 show the two distinct ways that this phenomenon can be adapted to the determination of the concentration of an element in a sample. For atoms like sodium that are readily excited by the high temperatures of a flame, the intensity of **atomic emission** at a wavelength (selected by the monochrometer) emitted by the atoms can be amplified and measured directly. An aspirator is used to release a constant flow of the solution being analyzed while the emission intensity is recorded. Under these conditions, the intensity of emission is related to the concentration of atoms in the solution being aspirated.

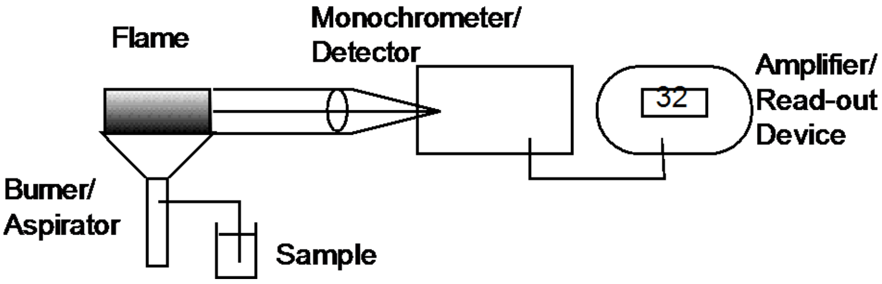

Figure 6.1: Block diagram of atomic emission spectrometer with flame excitation

For elements which are not so easily excited in a flame, the alternative **atomic absorption** approach shown in Figure 6.2 can be employed to obtain reliable measurements for quite dilute solutions of an element. The light source is a hollow-cathode lamp which contains the element being investigated. The source emits light at wavelengths which are just the wavelengths absorbed by unexcited atoms of the same element vaporized into the flame by an aspirator as in the emission method. The extent of reduction of light intensity is then related to the concentration of atoms of the element in the flame. Sodium can be determined by either method. The emission method is simpler in not requiring a sodium lamp light source.

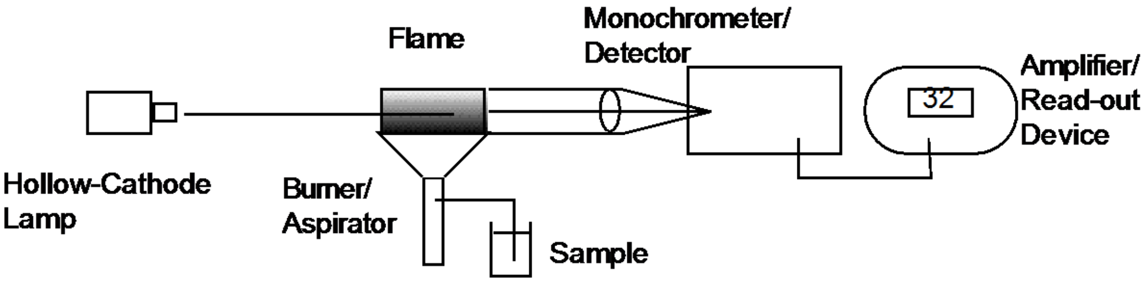

Figure 6.2: Block diagram of atomic absorption spectrometer with flame atomization

Exploration 6D. How can ion concentrations be determined from emission intensities?

The determination of sodium ion concentrations in a water sample from the intensity of emission of the characteristic yellow 589 nm radiation in an atomic emission spectrometer requires the construction of a standard curve of intensity vs. concentration. Over a narrow concentration range this curve could be expected to be nearly linear. However, for a hundred-fold range of concentrations, such a plot normally deviates significantly from linearity. Even if the plot of intensity, I, vs. concentration deviates from linearity, a smooth curve can be drawn through the points and this calibration curve can be used to estimate the concentration of a sample from its measure emission intensity.

The question of what salt to use to prepare solutions for the calibration curve is not a trivial one. For most drinking water samples, bicarbonate is the principal anionic species, so sodium bicarbonate is a good candidate for the preparation of standard solutions. An alternative experimental approach that eliminates the specific medium effects associated with all the other ions in the solution is the **standard addition method**. In this approach, small increments of a standard of known concentration are added to a series of beakers or flasks each containing a fixed volume of the sample. A plot of I vs. mL added is constructed, and a straight line is drawn through the experimental points. The line is extrapolated back to the I = 0 axis to obtain the mL of standard that contains as much sodium as was present in the original sample. This value can then be used to determine the concentration of sodium in the original sample. The major disadvantage of the standard addition approach, of course, is that it is labor intensive as multiple standard-amended solutions must be prepared and analyzed for every sample of interest.

Exercise. Addition of 0, 0.10, 0.20, 0.40, and 1.00 mL of 1000 mg/L sodium standard to five identical 25.0 mL samples of water gave the following intensities of sodium (589 nm) emission in an atomic emission spectrometer: 42.0, 47.8, 53.5, 64.8, and 98.4. Plot the data to determine the concentration of sodium in ppm and in mM in the water sample.

The plotted intensity vs. mL of 1000 mg/L sodium standard data yield a straight line of the form I = 0.5631 mL + 42.1. So when I = 0, mL = -42.1/0.5631 = -0.748. So the concentration of Na is (0.748 mL)(1000 mg Na/L)(1 L/1000 mL)/(0.025 L) = 29.9 mg Na/L = (29.9 mg Na/L)(1 millimole Na/23.0 mg Na) = 1.30 mM Na.

Exploration 6E. Closure.

The concentration of sodium in drinking water samples is often a good indicator of the geochemistry of the water source and/or the subsequent treatment of the water before it is distributed to users. High sodium is often associated with generally high mineral concentrations, whether from seawater infiltration or from leaching from mineral beds. It is also often an indication of ion-exchange softening of relatively hard water from ground water sources. Some sodium is also a result of pH adjustment to about 8 with NaOH before the water is introduced into the distribution system.

The flame emission method of analysis for sodium suggested here is fast, convenient, and reliable. The atomic absorption method is similarly effective for a wide range of metals, including those metals like lead and cadmium that are of concern at very low concentrations.

The unfavorable effects of high salt diets for people with heart problems has been well publicized in the last few years. The effect seems mainly to be associated with high sodium levels. If sodium levels in drinking water are very high, the sodium ingested with a gallon of water a day can be a significant fraction of recommended daily intake from salting of food. So the sodium concentration in drinking water is of more than academic interest.

A Problem. Suggest an inexpensive and convenient way to reduce the sodium ion concentration in the water used for drinking by a household. Such a procedure would be of interest to anyone who depends on a high sodium drinking water supply.

Session 7. Galvanic Cells and Ion Concentrations
How can galvanic cells be used to determine ion concentrations?

Exploration 7A. How can a digital multimeter be used to measure cell voltage?

Exploration 7B. What is required to construct a galvanic cell?

Exploration 7C. How does the potential (voltage) of a cell depend on its makeup?

Exploration 7D. How does the potential of a cell depend on ion concentrations?

Exploration 7E. Closure.

Session 7: Galvanic Cells and Ion Concentrations

How can galvanic cells be used to determine ion concentrations?

Exploration 7A. How can a digital multimeter be used to measure cell voltage?

Ionic solutions and basic electrical theory and measurements have been closely intertwined since the early 19th century experiments by Franklin, Faraday, Arrhenius and others that led to a clearer understanding of both electrical phenomena and the nature of electrolyte solutions. Nowadays simple electrical measurements can be made easily and reliably with inexpensive digital devices that would have been the envy of the best equipped laboratory only a few years ago. Measurements of all three of the basic electrical quantities **resistance** (measured in **ohms**), **current** (measured in **amperes**) and **electrical potential** (measured in **volts**) can be made the basis of accurate analytical determination of ion concentrations. Sophisticated modern electrochemical techniques often involve measurement of more than one of these variables simultaneously, but much useful information can be derived from the measurement of the potential (in volts) of an electrochemical cell. So that is a good place to focus initial discussion.

A Classroom Multimeter Exercise:

Each group of 3-4 students will be provided with a **digital multimeter** and several small batteries.

Examine the multimeter carefully and note the different scales and controls. Turn the function selector knob to resistance (ohms, Ω) and have one student grip the two probe leads tightly-one in each hand. Use the scale selection knob to find the appropriate setting to determine the resistance of the student. Try the measurement on another student.

The object of this exercise is to use the multimeter to determine the voltage of the batteries and to determine which electrode is the source of the electrons that constitutes the current flow if the two electrodes were to be connected with a wire. Set the function selector switch to **DC volts** and have one student hold red and black leads to the two terminals of one of the batteries. Another student can then switch the scale knob to obtain a clear reading of the voltage of the battery. Record that voltage, including the - sign if it is present. Now interchange the leads and record the voltage, including sign, again. Repeat these measurements with each battery.

Questions for Discussion:

1) Why do the batteries not have the same voltage?
2) What is the effect of interchanging the leads?
3) Which electrode is the source of electrons for the current that flows when the two poles of the battery are connected?

Exploration 7B. What is required to construct a galvanic cell?

The batteries used in Exploration 7A are examples of galvanic (or voltaic) cells. Such cells are widely used in laboratories to measure ion concentrations. The ubiquitous pH meter to measure hydrogen ion concentrations is the most familiar example of such a device in common use. It employs a fairly complicated voltage measuring probe, but any **galvanic cell** consists of a **cathode**, at which **reduction** occurs, and an **anode**, at which **oxidation** occurs. The two electrodes must also be physically separated. Otherwise direct electron transfer from reducing agent to oxidizing agent will short circuit the flow of electrons from one pole to the other. The simplest galvanic cell consists of two different metals, each immersed in a solution containing cations of the metal. A zinc/copper cell is shown below. Because a complete circuit is required for any electrical device, the two electrodes, called **half-cells**, must be connected by a conducting medium. In a laboratory setting, this connection is often a **salt bridge**, a tube filled with a concentrated salt solution. Because the human body is a relatively good conductor of electricity, it can serve as a satisfactory salt bridge to make a complete circuit to permit voltage measurements.

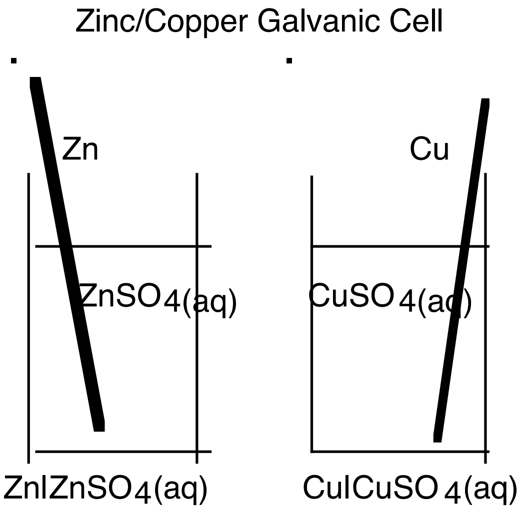

Figure 7.1 Zinc/Copper Galvanic Cell

Make Your Own Cell:

Use the metal strips, solutions, and meter provided to construct a galvanic cell consisting of two metals and solutions containing the same metal cations. Use one student's hand as the salt bridge, with two fingers immersed in the two separate solutions close the circuit. Determine the cell voltage, and note carefully the sign of the voltage.

Questions for Discussion:

1) If the cell you constructed were encased in a box with only the two wire leads protruding, which lead would be labeled as positive (+) and which as negative (-)?
2) Which way would the electrons flow if a wire connected the two electrodes to allow current to flow?
3) Write out the cell reaction that occurs when the cell discharges.
4) How would you construct a battery to generate 12 volts with the cell you were using?

Exploration 7C. How does the potential (voltage) of a cell depend on its makeup?

The simple cell examined in 7B can be constructed of different metals and corresponding salts. In general, the voltage of such a cell depends on the identity of the metal. Measurement of the voltages of a series of cells can be used to arrange the metals in order of increasing strength as **reducing agents** (or of the metal ions as **oxidizing agents**). This series is often referred to as the activity series or emf (electromotive force) series.

Exercise to determine the emf series for three metals:

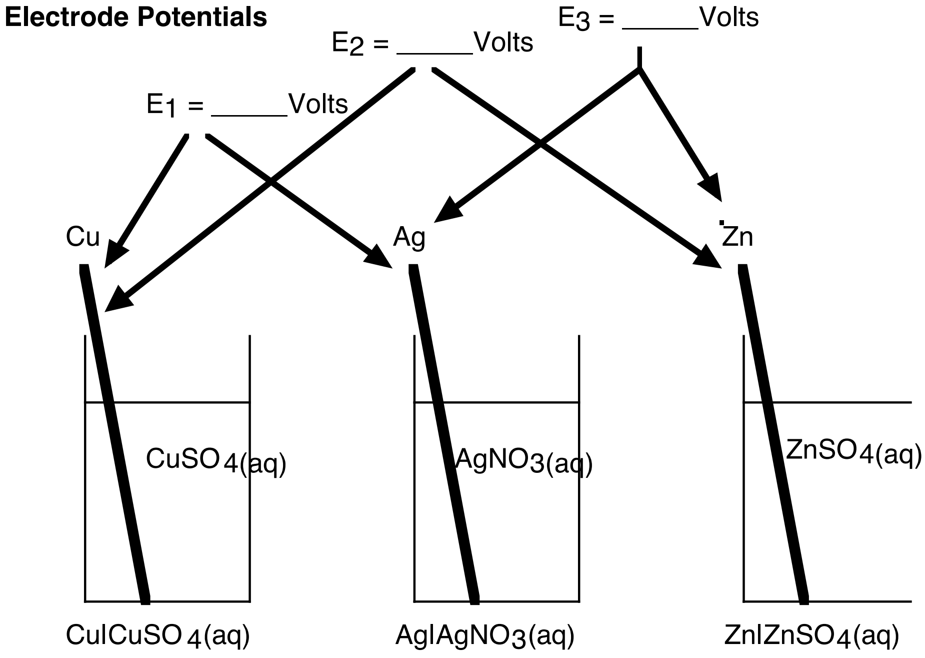

Figure 7.2: Electrode Potentials

Work in groups of 3-4. Set up the three half-cells shown in Figure 7.2, using the metal strips (or wires) and solutions provided. Use your digital multimeter to determine the magnitude of the cell voltage for each combination of two half-cells. Is there any pattern in the values recorded? Then record the potential, including the sign, of each half-cell relative to the Cu|$CuSO_4$(aq) half-cell. On the basis of your values, which metal (Zn, Ag, or Cu) is the best reducing agent? Which is the poorest reducing agent?

Exploration 7D. How does the potential of a cell depend on ion concentrations?

We have found that the potential (voltage) of a galvanic cell depends on the identity of the materials employed to construct the electrodes. However, if either the oxidized or reduced form of the substance involved in the half-cell reaction is a dissolved species, the potential will also depend on the concentration of that ionic species. This is the basis of all potentiometric methods for measuring ion concentrations.

Exercise to explore the effect of ion concentrations on cell potentials:

A version of a cell that we have already examined, a copper-silver cell, can be constructed from readily available materials in a compact form that permits its use as a probe of silver ion concentrations in solutions held in a simple test tube or beaker. The cell, along with the cell diagram, cell reaction, and the Nernst Equation, which relates the cell voltage to the standard cell voltage and the concentration of ionic species, are shown below:

Cell to monitor [Ag^+]

$Cu|CuSO_4(aq)||AgNO_3(aq)|Ag$

Cell Reaction:

$Cu + 2\,Ag^+ \text{------>} Cu^{2+} + 2Ag$

Nernst Equation:

$$E\text{ (volts)} = E^o - (0.059/2)\log[Cu^{2+}]/[Ag^+]^2$$

$$= E' + 0.059\log[Ag^+]$$

$$E(mV) = E' + 59\log[Ag^+]$$

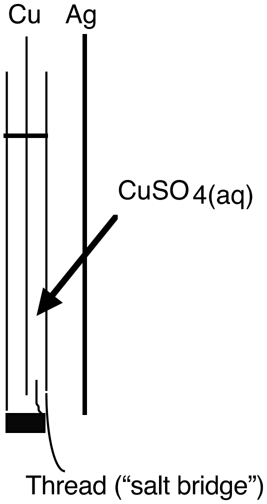

Figure 7.3: Copper-Silver Cell

The effect of ion concentrations on the cell potential is given by the Nernst Equation. For the cell shown, the concentration of Cu^{2+} ions bathing the copper wire is constant. If the probe is immersed in a series of solutions which contain varying concentrations of silver cations, the potential of the cell will depend on the silver ion concentration. Use the silver nitrate solutions provided to prepare a series of solutions which vary from 0.100 to 0.0010 M silver nitrate. Starting with the most dilute solution, immerse the electrodes in each of the solutions in turn (rinsing the electrodes carefully with water between solutions), and record the potential of each solution to the nearest mV. How do your results compare with the predictions of the Nernst Equation?

Exploration 7E. Closure.

Ion-selective electrodes (ISE) are used widely to determine the concentration of ions in solution. We will be using four different ion-selective electrodes in our water analysis laboratory. In order to understand the behavior of such electrodes, it is essential to examine closely the measurement of electrical potential and the properties of simple galvanic cells. We always require a pair of electrodes, connected by a salt bridge, for such a cell. One of the electrodes is an **indicator electrode** (a simple silver wire in our example), whose potential depends on the concentration of the species being examined; the other electrode is a **reference electrode** (the copper wire immersed in copper sulfate solution in our example), whose potential is independent of the solution being examined. Because of the logarithmic relation between concentration and cell potential, ion selective electrodes can often be used effectively to determine the concentrations of very dilute solutions, e.g., a pH meter which is capable of determining [H^+] with good accuracy from 0.1 to 10^{-12} M. Specific properties of other ion-selective electrodes will be examined in connection with the determinations of the corresponding ion concentrations.

Session 8. Potentiometric Titrations
How do ion concentrations change in the course of a titration?

Exploration 8A. How does the pH change in the titration of acetic acid with NaOH?

Exploration 8B. How does the [Cl^-] change in the titration of Cl^- with $AgNO_3$?

Exploration 8C. How can the $Ag/Ag^+//Cu^{2+}/Cu$ cell be used to follow [Cl^-]?

Exploration 8D. How does the pH vs. mL HCl titration curve reveal alkalinity?

Exploration 8E. Closure.

Session 8: Potentiometric Titrations

How do ion concentrations change in the course of a titration?

Exploration 8A. How does the pH change in the titration of acetic acid with NaOH?

Concentrations of major species in solution can often be determined most conveniently by carrying out a **titration**, in which the volume of a reagent which reacts with the dissolved species is determined. By contrast, species which are present at very low concentrations cannot usually be determined in this way. Measurements of the potentials of appropriate electrochemical cells can be employed to determine concentrations of dissolved species in both cases. In the first case, the cell is used as a probe to follow the changing concentration of the analyte (or a related species) in the course of the titration in order to reveal the **equivalence point of the titration**. In the second case, the cell is used to determine the **concentration** of the dissolved species directly, but only after some **calibration** or **standardization** of the meter/cell combination. This session is devoted to the titration applications, and the following session will be devoted to the direct determination of ion concentrations from cell potential measurements.

The titration curve for the plot of pH vs. volume of standard acid or base, shown in Figure 8.1 for the titration of 20.0 mL of a solution of a weak acid, HA, with 0.100 M NaOH, is a typical example of the use of cell potential measurements to follow the course of the titration. The inflection point at 30 mL corresponds to the equivalence point at which one mole of NaOH has been added per mole of initial acetic acid.

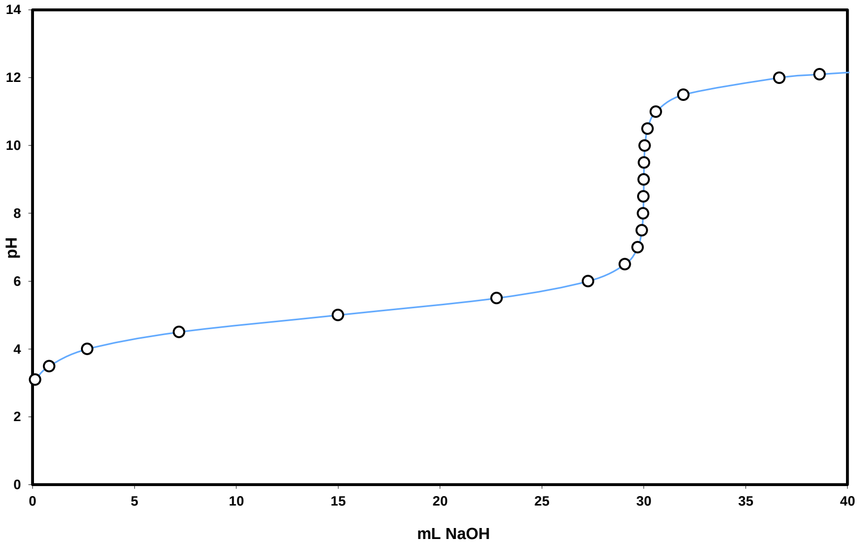

Figure 8.1: The titration curve for the titration of 20.0 mL of a solution of a weak acid, HA, with 0.100 M NaOH

In this case, convenient indicators are also available to signal the equivalence point by a color change of the solution. The pH meter is here serving the same function as a color indicator. In fact using the meter to determine the equivalence point for this titration is more tedious than using an indicator. However, the titration curve often reveals subtle details (like the pK_a determined from the mid-point of the titration or the diprotic nature of an acid being titrated) that are not available from an indicator-based titration. In addition, titration curves that show only gradual changes near the equivalence point can still give reliable equivalence points, even when no indicator method is available for the titration.

Exercise. 8.1: Calculate (a) the initial molar concentration and (b) the pK_a of the weak acid HA from the data given in the text and the titration curve shown above.

Exploration 8B. How does the $[Cl^-]$ change in the titration of Cl^- with $AgNO_3$?

A titration curve shows how the concentration of the analyte changes with added titrant. Because the changes are usually several orders of magnitude, the logarithm of the concentration (or -log [ ], to keep the quantity positive) vs. volume of titrant is what is usually displayed. The approximate titration curve for the precipitation titration of a chloride sample with silver nitrate can be generated quickly as follows:

To make the example specific, consider titrating 100 mL of 0.010M chloride with 0.100 M silver nitrate.

Initial pCl: Since $[Cl^-] = 0.01 = 10^{-2}$, $pCl = -\log[Cl^-] = -\log(10^{-2}) = 2.00$.

Equivalence point: Since the reaction is $Ag^+ + Cl^- \text{---->} AgCl(s)$, the equivalence point lies at **10.00 mL** where mmols Ag^+ = mmol Cl^- = 1.00. The chloride concentration at this volume is just $(K_{sp})^{1/2}$, where K_{sp} for AgCl is 1.8×10^{-10}. So, pCl = 4.87.

Half-titration point: At 5.0 mL added, half of initial chloride has been precipitated and the volume has been increased from 100 to 105 mL, so the free chloride concentration is 0.50 mmol/105 mL = 4.8×10^{-3} M and pCl = 2.32.

Beyond the equivalence point: Here it is most convenient to calculate the concentration of excess silver ion, which determines the concentration of free chloride, since $[Ag^+][Cl^-] = K_{sp}$. For example, at 15 mL, $[Ag^+]$ = 0.50 mmol/115 mL = 0.0043 M, and $[Cl^-] = K_{sp}/[Ag^+] = (1.8 \times 10^{10})/(0.0043) = 4.14 \times 10^{-8}$ M. So pCl = 7.38.

The complete curve, calculated in this way, is shown in Figure 8.2. The inflection point at the equivalence point volume (10.0 mL) is clearly evident. For more dilute chloride solutions and correspondingly more dilute titrants, the change in pCl would be smaller, but the inflection point would still lie at the equivalence point.

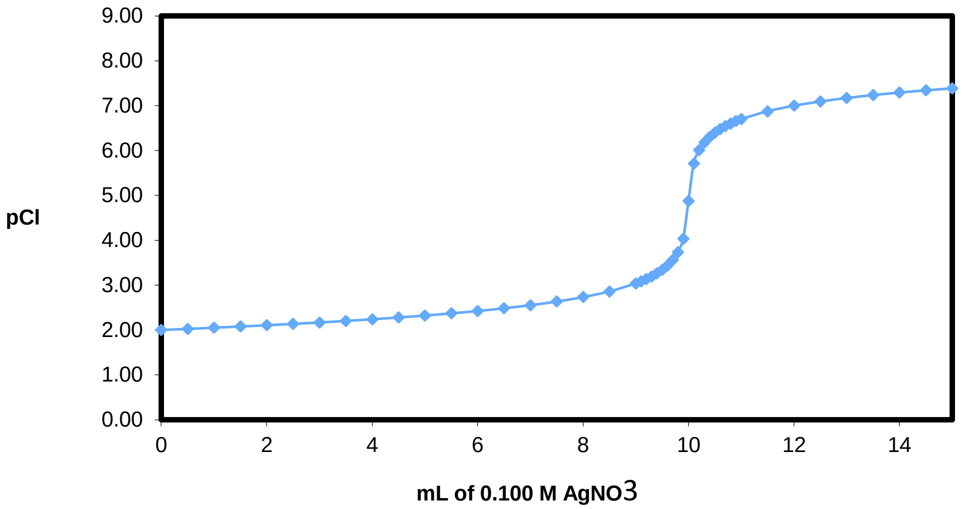

Figure 8.2. The pCl vs. ml $AgNO_3$ titration curve for the titration of 100 mL of 0.0100 M chloride with 0.100 M silver nitrate.

Exploration 8C. How can a $Ag/Ag^+//Cu^{2+}/Cu$ cell be used to follow $[Cl^-]$?

In the previous section, we have seen how the chloride ion concentration varies in the course of the titration of a chloride sample with silver nitrate. In section 7D we saw how the $Ag/Ag^+//Cu^{2+}/Cu$ cell could be used to monitor the silver ion concentration in a solution. Because the silver and chloride ion concentrations in any solution which is in equilibrium with solid silver chloride are related by the solubility product expression, any device which records changes in $[Ag^+]$ also responds to changes in $[Cl^-]$.

The specific relation between the cell potential and pCl can be derived as follows:

$$\text{Since} = [Ag^+][Cl^-] = K_{sp}, [Ag^+] = Ksp/[Cl^-] = 1.8 \text{ x } 10\text{-}10/[Cl\text{-}] \text{ and}$$

$$\log[Ag^+] = \log K_{sp} - \log[Cl^-] = -9.74 + pCl.$$

The potential for the $Ag/Ag^+//Cu^{2+}/Cu$ cell with $[Cu^{2+}]$ constant varies linearly with $\log[Ag^+]$, i.e., E (mV) = $E^o + 59 \log [Ag^+]$ (see session 7) = $(800\text{-}340) + 59 \log[Ag^+]$ for 1 M Cu^{2+}. So,

$$E\ (mV) = 460 + 59(-9.74 + pCl) = -115 + 59\ pCl$$

Thus, we see that the variation in the cell potential with volume of titrant is parallel to the variation in pCl with volume of titrant, so a plot of cell potential vs. mL titrant, Figure 8.3, parallels exactly the calculated plot of pCl vs. mL titrant, Figure 8.2. In each case, the equivalence point is at the inflection point in the plot.

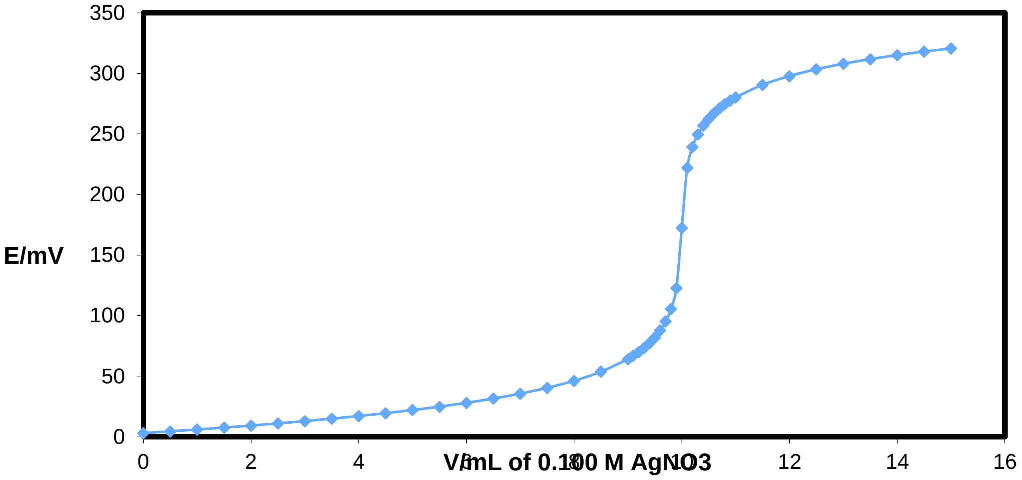

Figure 8.3. Potentiometric titration of 100 mL of 0.0100 M chloride with 0.100 M silver nitrate monitored with silver wire vs Cu/$CuSO_4$ electrodes

Exploration 8D. How does the pH vs. mL HCl titration curve reveal alkalinity?

The **pH** and **total alkalinity** of a water sample are typically included in a report of the composition of the water. The pH is determined with a commercially available **pH meter** equipped with a pH-sensitive electrode (usually a glass electrode) and a reference electrode. Since the actual potential between the pair of electrodes depends on the identity and conditions of the individual electrodes, the meter-electrode set-up must be standardized before each use. With the electrodes immersed in a standard buffer solution whose pH is close to the pH of the solution to be investigated, the meter is adjusted to that known pH. For measurements over a range of pH values, the meter should be standardized with two solutions that span the approximate range (e.g., 7 and 4).

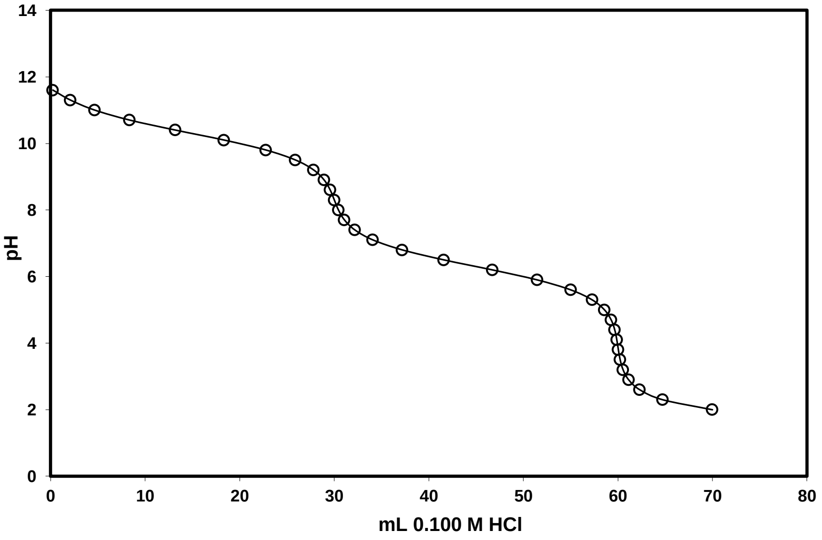

Figure 8.4. Titration of 30 mL of 0.100 M carbonate with 0.100 M HCl

The **total alkalinity** reflects the capacity of the water sample to neutralize a strong acid, like HCl. The total alkalinity of a water sample is determined by titrating the sample with standard HCl solution to an end point that is signaled by the color change of an appropriate indicator. More complete information about the nature of the species responsible for the alkalinity can be obtained from a full pH vs. mL HCl titration curve. The curve is essentially a portion of the titration curve for the titration of the basic carbonate anion (CO_3^{2-}) with HCl as shown in Figure 8.4. The initial pH depends on the distribution of carbonate species in the water at the start of the titration, and the equivalence point of the titration depends on the total concentration of those species.

By contrast, for the titration of pure bicarbonate, HCO_3^-, the initial pH is approximately the average of the two pKa values for carbonic acid, 1/2(6.35 + 10.33) = 8.34. As shown in Figure 8.5, titration with standard HCl then converts the bicarbonate to carbonic acid, with the equivalence point being at pH approximately 4.0. If the initial pH is greater than 8.3, significant CO_3^{-2} is also present and it must first be titrated to HCO_3^- (to pH 8.3). On the other hand, if the pH is much below 8.3, significant carbonic acid is present. Its concentration could be determined by titrating the sample with standard base to pH 8.3.

The determination of the concentration of the basic species, HCO_3^- and CO_3^{-2}, from the full titration curve is straightforward, but it can be confusing. If the initial pH is greater than 8.3, the volume of HCl used to go from the initial pH to 8.3 is used to calculate the mmoles and concentration of CO_3^{-2}. The volume used to titrate from pH 8.3 to 4.0 includes the volume required to titrate the HCO_3^- that was originally CO_3^{-2}, so that volume should be subtracted from the volume to go from pH 8.3 to 4.0 to determine the mmoles and concentration of original CO_3^{2-}

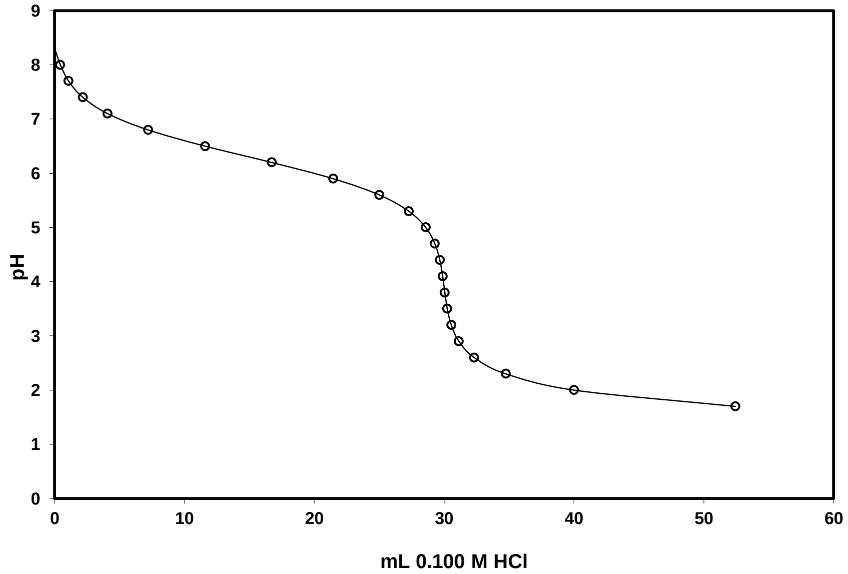

Figure 8.5. Titration of 30 mL of 0.100 M bicarbonate with 0.100 M HCl

Exploration 8E. Closure.

Any cell in which the cell reaction involves an ion of interest can, in principal, be used to monitor the changes in the cell potential that accompany changes in ion concentration in the course of the titration. We have here examined just two systems that are commonly used in the determination of two important ionic species in drinking water. An alternative approach that is particularly convenient for determining directly the concentration of ions from measured potentials is treated in Session 9, which follows.

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Session 9. Ion-Selective Electrodes and ppm Concentrations
How can we determine ion concentrations at the 1 ppm level?

Exploration 9A. What is the Nernst Equation? Nernstian response for an electrode?
Exploration 9B. What does the [NO_3^-] reveal about a drinking water source?
Exploration 9C. What does the [F^-] reveal about a drinking water source?
Exploration 9D. Why are NO_3^- and F^- levels of particular concern?
Exploration 9E. Closure.

Session 9: Ion-Selective Electrodes and ppm Concentrations

How can we determine ion concentrations at the 1 ppm level?

Exploration 9A. What is the Nernst Equation? Nernstian response for an electrode?

The potential of a galvanic cell depends on the composition of the electrodes and on the **concentrations** of the ions that are involved in the electrode reactions. The concentration dependence can be employed as the basis of an analytical technique that is sensitive to quite low concentrations of ions and is very convenient to use in the laboratory. The basic principle was introduced in Exploration 7D with the copper/silver electrode pair which could be used to determine the concentration of Ag^+ cations in solution from the measured potential of the cell. Other half cells can be designed to respond to changes in concentration of anions. One that is commonly employed as an internal element in pH electrodes is the silver/silver chloride electrode, which can be represented Ag|AgCl|Cl^-(aq), for which the half-cell reaction can be written:

$$AgCl(s) + e^- \text{ ----> } Ag(s) + Cl^-(aq)$$

Regardless of the detailed design of the cell employed in such measurements, two electrodes are required, **a reference electrode**, whose potential does not change in a series of measurements, and an **indicator electrode**, whose potential changes in a predictable way with changes in the concentration of the ion being investigated. With standard hydrogen electrode (which is used as the arbitrary zero reference for tabulation of electrode potentials) employed as the reference electrode, the potential of the silver/silver chloride electrode at 25°C can be expressed as:

$$E = E^o - 0.059 \log [Cl^-]$$

where E^o is the standard potential of the silver/silver chloride electrode, 0.222 V, and [Cl^-] is the molar concentration of chloride ion in solution. This logarithmic relation between the potential and the chloride ion concentration is called the **Nernst Equation** after Walter Nernst the 19th century physical chemist who introduced it. The Nernst Equation predicts that the potential for the silver/silver chloride half-cell will change by 0.059 volts (59 mV) for a change in chloride ion concentration of one order of magnitude. So for $[Cl^-] = 0.010$, $E = 0.222 - 0.059 \log (0.010) = 0.340$ V, while for $[Cl^-] = 0.00010$, $E = 0.222 - 0.059 \log (0.00010) = 0.458$ V, etc. In practice, a more convenient reference electrode than the standard hydrogen electrode is employed in practical cells. The absolute voltage of the cell will therefore be different, but the change in voltage between 0.0100 and 0.00010 M will be 0.118 V = 118 mV.

The range of concentrations over which the potential changes with ion concentration in the logarithmic manner suggested by the Nernst Equation is limited. Even for well-behaved systems, the range may be only 5-6 powers of 10 (from 0.10 to 10^{-6} M, for example). In practical applications, the range is typically determined experimentally by diluting a standard solution by several powers of 10 and plotting the measured potential vs. the logarithm of the concentration of ions involved in the cell reaction. The plot should be linear with slope -.059 V. Such a **calibration curve** can be used to estimate concentrations from measured potentials, even when the plot is no longer yielding a Nernstian (i.e., linear) response.

One additional phenomenon complicates the use of these devices. The potential of half-cells also depends on the total concentration of ions as well as on the concentration of the ion specifically involved in the cell reaction. When solutions are simply diluted with water, both the specific ion concentration and the **ionic strength** (related to the sum of the concentration of all ions in the solution) change.

While it is convenient to write all potentials in terms of concentrations, formally their relationships depend on activities. Activity, A, is related to concentration by:

$$A = [ion]\,\gamma_{ion}$$

Where γ is the activity coefficient for the ion. Table 12-1 in Harris lists the values for the activity coefficients for F^- and NO_3^-:

Ionic Strength, μ, M						
Ion	Ion size (pm)	0.001	0.005	0.01	0.05	0.1
F^-	350	.964	.926	.900	.81	.76
NO_3^-	300	.964	.925	.899	.805	.755

Daniel C. Harris, "Exploring Chemical Analysis" Third Edition, Pg. 248, Table 12-1, W.H. Freeman & Company, 2005

As the ionic strength, μ, increases, the activity coefficients decrease and the difference between activity and concentration increases. In lab, we will be measuring changes in F^- or NO_3^- with the ion selective electrodes. So long as the activity coefficients remain constant, potential measurements will indicate concentration differences. A relatively high concentration of an inert salt electrolyte is added to all solutions, including all standards used to prepare a calibration curve, so that all measurements are made on solutions of nearly the same ionic strength and same activity coefficients. If salt is not added to the solution to keep the ionic strength constant, the calibration curve will not be linear. Lower concentrations would have a higher relative activity producing a disproportionately higher potential change than solutions of higher concentrations.

An electrode which responds to fluoride ion concentration changes, a **fluoride ion-selective electrode**, consists of a silver/silver chloride conducting element immersed in a solution containing both sodium chloride and sodium fluoride and separated from the sample solution by a LaF_3 crystal doped with a small amount of EuF_2. The response of this electrode to changes in fluoride ion concentration is reliably Nernstian down to 10^{-6} M.

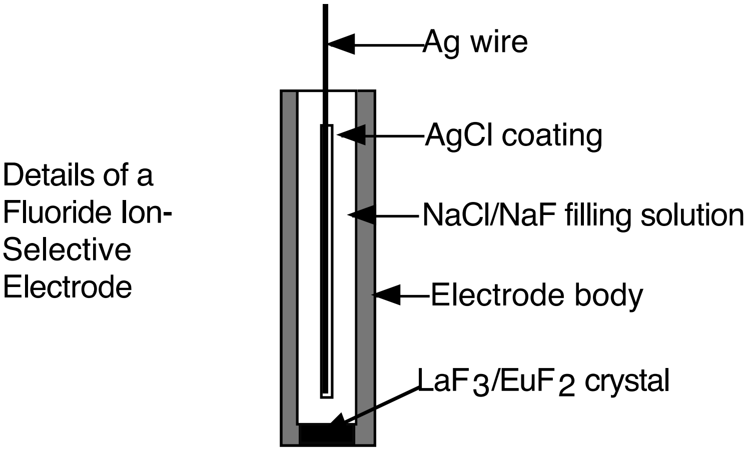
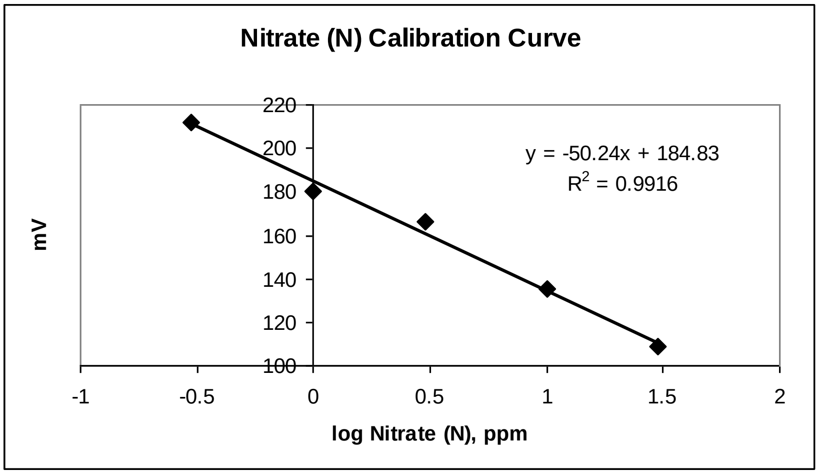


Figure 9.1: Details of construction of a fluoride ion-selective electrode.

The **nitrate ion-selective electrodes** can be similar to the fluoride in that a nitrate ion-selective electrode is used with a reference electrode. Also commercially available are combined electrodes which incorporate both the nitrate probe and a reference electrode. The potential developed between the two electrodes gives a Nernstian response to changes in the nitrate concentration over several orders of magnitude and is sensitive to concentrations as low as 0.1 ppm nitrate.

Figure 9.2: A laboratory calibration curve for a nitrate ion selective electrode.



Class Exercise. Distribute several electrodes for close examination by the class. Include pH, fluoride, and nitrate probes, as well as the Cu|CuSO4||Ag+|Ag cell.

Exploration 9B. What does the [NO_3-] reveal about a drinking water source?

The City of Des Moines, IA obtains significant quantities of water for municipal water supply from the Des Moines and Raccoon Rivers. These rivers drain land with intense agricultural production and are subject to significant nitrate contamination due to fertilizer applications. For approximately three months of 2013, the Raccoon and Des Moines Rivers each had nitrate concentrations well above the 10 ppm N as NO_3^- EPA standard for drinking water. These high nitrate concentrations in the water supply necessitated the operation of Des Moines Water Works' expensive nitrate removal facility and a switch to alternative lower-nitrate water supplies. See the Des Moines Register online posting about the issue online at:

http://blogs.desmoinesregister.com/dmr/index.php/2013/05/10/record-nitrate-levels-in-raccoon-des-moines-threaten-des-moines-area-tap-water/article, (accessed 2/28/14)

This a good place to discuss the **nitrogen cycle**, the variable oxidation states of nitrogen, and the role of bacteria in nitrogen fixing, oxidation, and denitrifying. The **anion exchange process**, by which nitrate is removed from a portion of the Des Moines water, can be discussed and compared with the **cation exchange process** by which Grinnell reduces the hardness of its water.

Exercise on Nitrogen Oxidation States

1) Nitrogen can assume a number of oxidation states. Assign oxidation numbers to nitrogen in each of the following nitrogen species.

ammonia	N_2	N_2O	NO_2	NH_2-NH_2
N_2O_4	nitrate ion	nitrous acid	nitrite ion	NO
HO-NH_2	N_2O_3	NH_4^+	HNO_3	N_2O_5

2) Write a balanced equation for the oxidation of ammonium ion by atmospheric oxygen to nitrate ion in an acidic medium. Note that there are microorganisms (e.g., ammonia oxidizing bacteria) that efficiently carry out this reaction in natural waters.

Exploration 9C. What does the $[F^-]$ reveal about a drinking water source?

Fluoride ion is a minor component of some ground water sources, but it is rarely found in measurable concentration in surface waters. In general, the higher the total concentration of dissolved salts (TDS), the higher the concentration of fluoride ion. In the U. S., the measured concentration of fluoride in the drinking water is often unrelated to the actual concentration of fluoride in the water source.

Beginning in 1950, when it became clear that low levels of fluoride provides substantial protection from tooth decay, the U. S. Public Health Service encouraged municipal water works to add fluoride, if necessary, to bring the concentration to 1 ppm. Most major U. S. cities now fluoridate their water, and it is estimated that about 57% of the U. S. population currently uses drinking water that is so treated.

Questions for discussion: Is the water in your hometown fluoridated? Has fluoridation been the source of public debate or discussion in your community?

Exploration 9D. Why are NO_3^- and F^- levels of particular concern?

Although both NO_3^- and F^- are typically present in drinking water at quite low levels, where monitoring by specific-ion electrodes is particularly convenient, it is important to insure that their levels are monitored carefully. For both nitrate and fluoride, high concentrations in drinking water can have significant adverse health effects.

Fluoride concentrations in excess of 2 ppm cause perceptible mottling of teeth in children. It was the investigation of this phenomenon, in fact, that led to the discovery that fluoride levels that led to mottling also protected teeth against decay. The **EPA Maximum Contaminant Level (MCL)** for fluoride is set at 4 ppm to protect against both dental mottling and crippling skeletal fluorosis, a rare (but serious) condition. For water systems that add fluoride, regular monitoring is essential to insure that the metering equipment used to add the sodium fluoride to the water is operating properly. In 2011, the U.S. Department of Health and Human Services and the EPA reviewed the data on fluoride in water and recommended lowering the dosing from the range of 0.7—1.2 mg F^-/L to 0.7 mg F^-/L for municipal drinking water.

High levels of nitrate in drinking water are particularly harmful to infants. In infants younger than about three months, ingested nitrate is converted in the gastro-intestinal tract to nitrite which reacts with hemoglobin to form methemoglobin, which cannot transport oxygen. This leads to a condition called **methemoglobinemia** or, more commonly, blue baby syndrome, which can be fatal. The MCL for nitrate, established by the EPA, reflects the fact that no fatalities have been reported for infants who consumed water containing up to 10 ppm nitrate(N). The actual hazard for adults is substantially less than for young infants, since the reduction of nitrate to nitrite that is responsible for the blue baby syndrome does not occur in older children or adults.

Exploration 9E. Closure.

The convenience of making electrical measurements and the ease of using a simple probe has encouraged the development of a wide range of ion-selective electrodes for the analysis of aqueous solutions, ranging from water supplies, to industrial processes, to body fluids. Microelectrodes permit the examination of single cells and the investigation of brain function. Electrodes have been designed to respond to specific single molecules, including drugs and antibiotics. **Ion chromatographic** methods have been developed to permit the simultaneous determination of the concentrations of essentially all of the ions in a water sample, but simple, relatively portable devices to measure the concentration of a single species easily and simply will still have wide applicability.

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Session 10. Conservation of Mass and Charge
Does it all add up?

Exploration 10A. After Sessions 2-9, which ion(s) has (have) not yet been determined?

Exploration 10B. How are the total concentrations of all cations and anions related?

Exploration 10C. How can the total concentration of all ions be used to determine TDS?

Exploration 10D. What combination of simple salts would yield a given composite analysis?

Exploration 10E. Closure.

Session 10: Conservation of Mass and Charge

Does it all add up?

Exploration 10A. After Sessions 2-9, which ion(s) has (have) not yet been determined?

Up to this point we have examined potential sources and methods of analysis for several ionic species that one might expect to find in typical drinking water samples. We could continue in this fashion to consider other possible ions and their methods of analysis. However, we anticipate that experimental determinations on real samples has been going on in concert with these more theoretical discussions. It is time to take stock of the situation and to determine whether any significant species remain unaccounted for.

Exercise 10.1. Bring to class your lab data (or lab data provided by your instructor) on the concentrations of all species in a particular sample that has been investigated. List the anions and cations separately and tabulate the concentrations (in mM) of each ion. Use the formula mass of each ion to calculate the ppm concentration of that ion. This tabulation will provide the basis for further discussion and analysis in the following sections. The table below is one way to summarize the data conveniently:

Source			
Ion	**Concentration, mM**	**FW g/mole**	**Concentration, ppm**
Na+		23	
Ca2+		40	
Mg2+		24	
HCO3-		61	
Cl-		35.5	
F-		19	
NO3-		62	
(SO4)2-		96	
pH			
Total anions		TDS calc	
Total cations		TDS expt	

Sample data for ion concentrations/mM:
Na^+, 10.2; Ca^{2+}, 0.85; Mg^{2+}, 0.15; HCO_3^-, 6.41; Cl^-, 0.70; F^-, 0.06; NO_3^-, 0.30, SO_4^{2-}, 1.9

Exploration 10B. How are the total concentrations of all cations and anions related?

For any aqueous solution, the total charge associated with the cations must equal the total charge associated with the anions. For example, for a 0.100 M solution of $CaCl_2$, the molar concentrations of Ca^{2+} and Cl^-, respectively are 0.100 M and 0.200 M. However the total concentration of positive charges and of negative charges is 0.200 M. Formally, this condition can be written:

$$\sum C_c Z_c = \sum C_a Z_a$$

where C_i and Z_i are the molar concentrations and the magnitude of the charges, respectively, of the cationic species (c) and anionic species (a), and the sum includes a term for each cation or anion.

Exercise 10.2. Calculate the total millimolar concentration of cationic charges and of anionic charges for the data listed in 10A. Are they equal? If not, which one is larger? Suggest possible species to account for the difference, and calculate the millimolar concentration of each such species required by the conservation of charge condition.

Exploration 10C. How can the total concentration of all ions be used to determine TDS?

Once the millimolar concentration of all of the significant species has been determined, the mass concentration of total dissolved solids (TDS) in ppm can be calculated by converting each mM concentration into ppm concentration and summing the separate contributions to obtain the total ppm concentration. Some uncertainty would be associated with this value, since the identity of all ions might not be unambiguously determined. However, this should give a reasonably accurate value for the total dissolved solids.

Exercise 10.3. Calculate the concentration of total dissolved solids (TDS) in ppm from the data in 10A and 10B. If the total dissolved solids concentration has been determined independently (by evaporation of the liquid water or from conductivity measurements, for example), compare the values obtained by the two methods.

Exploration 10D. What combination of simple salts would yield a given composite analysis?

Once the concentrations of all significant ions have been established, we are in a position to speculate about ways in which that particular combination of ion concentrations could have originated. For example, a mixture containing Na^+, Ca^{2+}, Cl^- and HCO_3^- could have come from a mixture of NaCl and $Ca(HCO_3)_2$ or from a mixture of $NaHCO_3$ and $CaCl_2$ or from other combinations of these four salts. More than one combination may be possible, but some combinations are ruled out by the data while some combinations are more likely than others.

Exercise 10.4. Propose a mixture of specific salts and determine the mass (in mg) of each of these salts that should be dissolved in one liter of water to yield the concentrations of cations and anions described in Exercises 10.1-10.3.

Exploration 10E. Closure.

Session 11. What does it all mean?
What does the complete chemical analysis reveal about the source and treatment of our water samples?

Exploration 11A. Which ion concentrations are most revealing about the geological history of a water sample?

Exploration 11B. Which ion concentrations of a water sample are most revealing about human activity in the area or of specific chemical treatment of the source?

Exploration 11C. What is revealed by the concentration patterns?

Exploration 11D. Closure.

Session 11: What does it all mean?

What does the complete chemical analysis reveal about the source and treatment of our water samples?

Exploration 11A. Which ion concentrations are most revealing about the geological history of a water sample?

With the complete profiles of the chemical composition a set of water samples in hand we are in a position to draw some conclusions about the geological history and the subsequent chemical treatment of the water samples. For surface and ground water samples, both the total concentration of ionic species and the distribution of those ions reflect that history. The effects of geology and of subsequent chemical treatment cannot always be cleanly separated, but a few key indicators can usually be attributed mainly to one or the other of these factors.

The simplest comparison is one based on the total concentration of dissolved solids. Clearly fresh rainwater will have essentially zero TDS and a correspondingly low electrical conductivity. Water from clear mountain streams that have been in contact only with insoluble granite bedrock for a short time since falling as rain or as last winter's snow will not have had much opportunity to dissolve soluble minerals. So its conductivity and TDS level will also be very low. By contrast, water from aquifers near the seacoast that have been infiltrated by seawater will have high TDS values. So will water samples from hot springs and other "mineral water" sources. Most domestic sources lie between these extremes, so there may be little difference in conductivity among the samples drawn from several different sources. In general, the deeper the well, the higher the TDS level of the water from that well.

Some of the specific ion concentrations are also typical of particular geological situations. Water that contains only low concentrations of calcium (or magnesium) cations and bicarbonate anions owes its simple composition to rather limited contact with limestone deposits. If the water contains significant excess carbon dioxide, the pH will also be significantly less than 8.3. A high concentration of natural fluoride ion (1 ppm and greater) is almost always associated with high TDS levels. Therefore, fluoride levels near 1 ppm along with low TDS levels strongly suggests that fluoride has been added to the water in the treatment process. The nitrate concentration of surface waters and shallow aluvial aquifers is often high, especially in the spring and early summer, but tends to be very low in deeper lying aquifers and in rocky mountain streams, where decaying vegetation is the only significant source.

Exploration 11B. Which ion concentrations of a water sample are most revealing about human activity in the area or of specific chemical treatment of the source?

The ion concentrations that are most affected by human activity include those which influence the source of the water and those which have been systematically altered by the water treatment process. In the first category are nitrate anion, which tends to be high in water sources that are fed by runoff from agricultural land that has been treated with nitrogen fertilizer to improve crop yields. The nitrate concentration typically rises and falls with the seasons, reaching a maximum in spring and early summer (see Exploration 9B, page 35). A relatively high concentration of sodium is often found in mineral rich water, whatever the source. A high concentration of sodium in water that does not have much calcium or magnesium suggests strongly that the water may have been softened by an ion exchange process. The pH of water from most wells and surface sources tends to be less than the 8.3 of a bicarbonate solution. So if the pH is near 8.3, sodium hydroxide has probably been added to the water to adjust the pH.

Exploration 11C. What is revealed by the concentration patterns?

Close examination of the pattern of ion concentrations is often more revealing than the concentration of any single ion. High concentration of both sodium and chloride suggests salt-water infiltration from the sea. Since dissolved calcium carbonate is the source of both calcium (and magnesium) and bicarbonate, the bicarbonate concentration should be close to twice the sum of the calcium and magnesium concentrations. A relatively low concentration of these ions and few other ions then reflects water that has had limited contact to a limestone deposit. On the other hand, if the bicarbonate concentration is substantially higher than twice the sum of the calcium plus magnesium concentrations and the sodium ion concentration is high, the water has almost certainly been softened by a cation exchange process.

Exploration 11D. A Case Study: Grinnell groundwater and regional geology.

The city of Grinnell extracts its groundwater from a number of deep wells (2,000 ft. deep or more) tapping the Cambrian-Ordovician aquifer. A profile-view of the subsurface geology of Iowa is shown in Figure 11.1; Grinnell is roughly in the center of this transect. The Cambrian-Ordovician Aquifer is a formation of 450 – 540 million year old rocks consisting of three units: the Jordan Sandstone (oldest unit), the Prairie du Chien Group (middle unit; dolomite (a Mg/Ca-carbonate) and sandstone), and the St. Peter Sandstone (youngest unit). During this period of Earth history, Iowa was at the margin of a warm shallow sea that covered the interior portion of the North American continent, leading to thick accumulations of sand and shallow marine deposits (e.g., the dolomite). The Cambrian-Ordovician aquifer is bracketed by underlying and overlying shale formations that are relatively impermeable, making the Cambrian-Ordovician a *confined* aquifer. The Cambrian-Ordovician aquifer recharges in southern Minnesota and Northern Iowa, where water flows vertically through overlying formations (for example, evaporate deposits containing appreciable gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$)).

The water quality of groundwater in the Cambrian-Ordovician reflects both the interaction of water with the aquifer rock (principally sandstone and dolomite) as well as interaction of water with rocks along the flow path of water from the recharge zone to the extraction area.

Examining the data for the Grinnell water sample, how is the geologic setting of the aquifer reflected in the concentration and distribution of the ions you observe? How would you expect the composition of groundwater extracted from a shallow well from the unconsolidated sediments along riverbanks to differ? In what ways has the water treatment process likely altered the concentrations and distributions of ions for the Grinnell water sample?

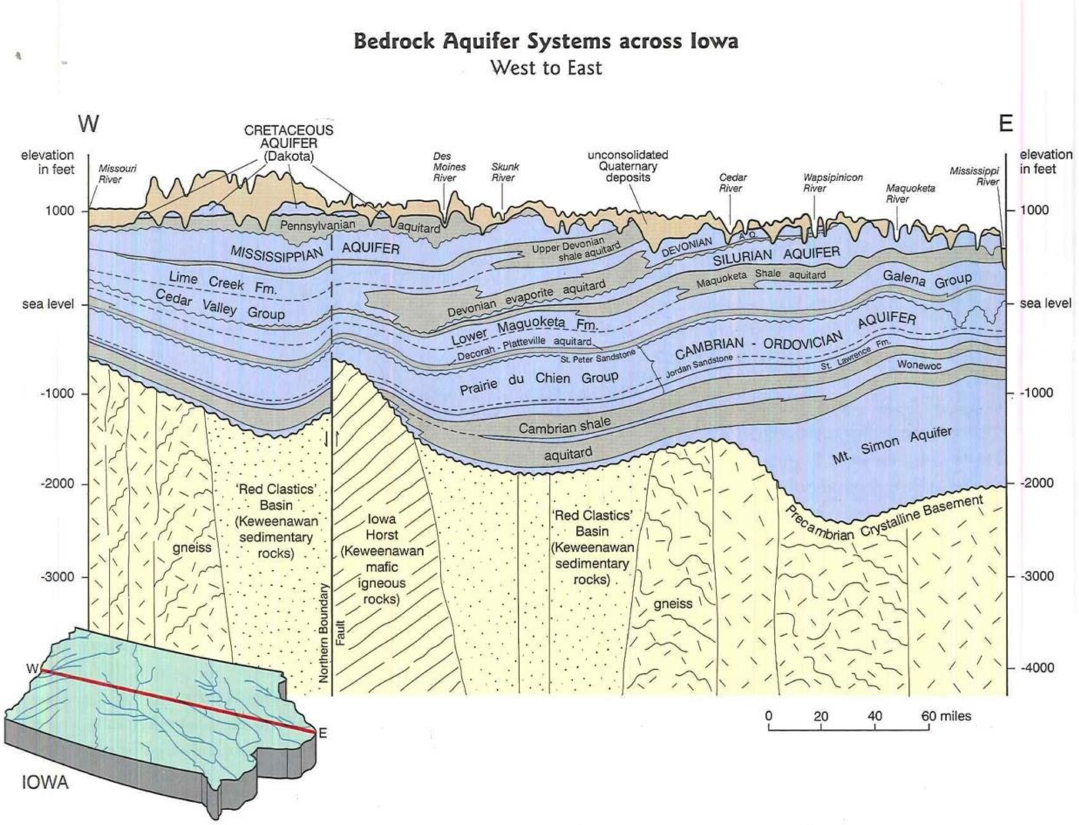

Figure 11.1: Subsurface geology of Iowa along an east-west transect.
Figure reproduced from Prior, J.C., Boekhoff, J.L., Howes, M.R., Libra, R.D., and VanDorpe, P.E. 2003. Iowa's Groundwater Basics. Iowa Department of Natural Resources.

Exploration 11E. Closure.

The complete analysis of the inorganic constituents in a drinking water sample gives us useful information about its geological history and subsequent treatment. This information by itself does not insure that the water is safe to drink. The presence of organic compounds from industrial or agricultural activity can be significant. More importantly, disease-causing microorganisms are the principal threat to human health and are thus the most important factor in determining whether a given source provides water that is safe to drink. Nevertheless, the proper management of a municipal water supply requires the careful adjustment of the concentrations of the dissolved minerals that are the major components of the precious liquid that comes from our taps. Though H_2O is the major constituent of drinking water, it is not the only substance in the water.

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Problem Set

Water Module Problem Set

Problems and questions related to the composition, methods of analysis, and chemical treatment of drinking water supplies

A. Problems related to the acid/base and solubility properties of the carbon dioxide/water/calcium carbonate system and to methods used to determine and to adjust the water hardness and alkalinity levels.

The initial pH of your water samples varied from 7.4 to 9.2, the concentrations of bicarbonate varied from 0.6 to 6.4 mM, and the hardness from 0.29 to 1.34 mM. Can these values be understood on the basis of known equilibrium constants for the system?

1. **The pH of rainwater.** The solubility of gases in liquids can be described quantitatively by Henry's Law, $c = k_H P$, where the concentration of dissolved gas (c) is proportional to the partial pressure of the gas above the liquid (P), k_H being the proportionality constant. For CO_2 in the atmosphere at 25 degrees C, k_H = 3.4 x 10-2 mol L-1 atm-1 and the partial pressure of CO_2 is .000398 atm.

(398.03 ppm by volume in the atmosphere; per NOAA, measured at the Mauna Loa Observatory http://www.esrl.noaa.gov/gmd/ccgg/trends/; accessed 3/5/14).

   a) Use these data to calculate the concentration of dissolved $H_2CO_3(aq)$ air-saturated rainwater.

   b) Use the result in a. to determine the pH expected for rainwater on the basis of the first dissociation constant of the carbonic acid, $H_2CO_3(aq)$, from the dissolved CO_2. The pK_a values of carbonic acid are $pK_{a1} = 6.35$ and $pK_{a2} = 10.33$ at 25 C.

2. The **solubility of limestone ($CaCO_3$) in water; the simplest view considering only the solubility of the salt in H_2O:** Calcium carbonate (limestone) is not very soluble in water. This low solubility is reflected in its small K_{sp} value (4.6×10^{-9}).

   a) Use this value for K_{sp} to calculate the solubility in millimoles/L, mM, for $CaCO_3(s)$, assuming simple dissociation into the two ions for the dissolved $CaCO_3(s)$.

$$CaCO_3(s) \text{ -------> } Ca^{2+}(aq) + CO_3^{2-}(aq)$$

   b) How does this value compare with the calcium ion concentrations found in the water samples the class analyzed? If data are not yet available, you may compare with historical data for some water samples (See Table PS-1 in units of mg/L).

Typical Results for 3 of 4 Benchmark Samples

(Grinnell, Des Moines, and Fareway Bottled Spring Water).
Values are mean ± standard deviation for 3-4 years of data.

Analyte	**Grinnell**	**Des Moines**	**Fareway Bottled Water**
Total Dissolved Solids (mg/L)	1200±100	380±80	400±100
Na^+ (mg/L)	220±40	30.0±20	8.0±2
Ca^{2+} (mg/L)	33.0±20	38.0±10	120±80
Mg^{2+} (mg/L)	14.0±5	21.0±8	13.0±8
HCO_3^- (mg/L)	350±40	80±33	200±70
Cl^- (mg/L)	27.0±2	35.0±8	14.0±7
F^- (mg/L)	1.1±0.1	0.90±0.2	0.25±0.10
NO_3^- (NO_3^- as N, mg N/L)	3.0±5	4.0±2	3.8±0.7
SO_4^{2-} (mg/L)	300±100	80±40	60.0±50
pH	8.5±0.4	7.9±0.6	7.2±0.2

Table PS-1

3. **The solubility of limestone ($CaCO_3$) in water; a more realistic model that considers pH a bit:** The carbonate anion, $CO_3^{\ 2-}$, is a relatively strong base, so a better representation of the dissolution reaction for $CaCO_3$(s) in water is

$$CaCO_3(s) + H_2O \text{ -------> } Ca^{2+}(aq) + \underbrace{HCO_3^-(aq)}_{\textit{weak base}} + \underbrace{OH^-(aq)}_{\textit{strong base}}$$

The equilibrium constant, K', for the above reaction can be expressed as $K_{sp}K_w/K_{a2}$, where K_w is the ion product of water = 10^{-14}. This result can be obtained by adding reactions together (multiplying K's)

$$CaCO_3(s) \text{ -----------} \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp}$$

$$CO_3^{2-}(aq) + H_2O \text{ --------} \rightarrow HCO_3^-(aq) + OH^-(aq) \quad K_{b1}$$

When we add these reactions together, the CO_3^{2-} cancels. When we add reactions together, we can get the K for the new reaction by simply multiply the K's of the reactions we added together:

$$CaCO_3(s) + H_2O \text{ -------> } Ca^{2+}(aq) + HCO_3^-(aq) + OH^-(aq) \quad K' = K_{sp}K_{b1}$$

The last step is to recognize that $K_w = K_{b1}K_{a2}$ so $K_{b1} = K_w/K_{a2}$

Substituting this relationship into our equation for K', we have:

$$K' = \frac{K_{sp}K_w}{K_{a2}} = [Ca^{2+}][HCO_3^-][OH^-]$$

Note that neither $CaCO_3$(s) or H_2O appears in the equilibrium expression.

a) Use this equilibrium constant to calculate a more realistic value for the pH and the concentration of Ca^{2+}(aq) = HCO_3^-(aq) = OH^-(aq) in a saturated solution of $CaCO_3$(s), if the basic properties of carbonate are considered in this way.

b) How does this value compare with the Ca^{2+}(aq) concentrations found for the water samples?

4. **The solubility of limestone ($CaCO_3$) in CO_2- saturated water: an even better model where all the acid/base characteristics of carbonate and carbonic acid are included.** When the acidity provided by the dissolved carbon dioxide and the basicity provided by the solid $CaCO_3$ are both considered, the single reaction that best represents what happens when solid $CaCO_3$ dissolves in water in contact with atmospheric carbon dioxide at a partial pressure P is the following:

$$CaCO_3(s) + CO_2(g) + H_2O \text{ -------> } Ca^{2+}(aq) + 2HCO_3^-(aq)$$

a) Using the approach of adding reactions, show that the equilibrium constant for the above reaction is given by:

$$K' = K_{sp}k_HK_{a1}/K_{a2}$$

where the equilibrium constants have been defined in the earlier problems 1-3; calculate a numerical value for K' from the numerical values at 25° C that have been given.

b) Use the value calculated for K' to determine the concentration of Ca^{2+}(aq) and HCO_3^-(aq) in water that is in equilibrium with solid $CaCO_3$ and water that is exposed to the nominal partial pressure of atmospheric carbon dioxide, 0.000398 atm.

c) Compare the solubility calculated by this approximation with the values found for the water samples analyzed by the class.

5. pH and species distribution in actual water samples.

a) What pH is expected for a water sample that contains only $Ca(HCO_3)_2$ from the reaction of $CaCO_3$ with H_2CO_3 (CO_2-saturated rain water)? (Recall the pH vs. mL HCl titration curve for the dibasic carbonate anion and the pH at each equivalence point.)

b) Using the measured HCO_3^- concentration as the total carbonate concentration and measured pH, prepare a table of fractional populations and mM concentrations of each of the three carbonate species (H_2CO_3, HCO_3^- and CO_3^{2-}) for each of the benchmark samples. If data are not yet available, you may use the data for the Grinnell, Des Moines, and Fareway samples provided.

6. **Water softening methods: cation exchange.** Grinnell water is softened by the cation exchange process using a cation exchange resin to replace the Ca^{2+} and Mg^{2+} ions responsible for the hardness with Na^+ ions from sodium chloride. The process, which is reversible, can be written

$$2Na^+Res^-(s) + M^{2+}(aq) = M^{2+}Res_2^-(s) + 2Na^{2+}(aq)$$

Note that the process does not remove any other anions or cations, so bicarbonate remains high. With the ground water containing about 3.5 mM Ca^{2+} + Mg^{2+} and the city using about 1,000,000 gal/day (about 100 gal/day person x 10,000 persons) calculate the quantity (in moles and kg) of NaCl that is required to regenerate the resins after the water has been softened to about 1 mM Ca^{2+} + Mg^{2+}.

7. **Water softening methods: soda/lime process.** An alternative process, that is employed by the Des Moines waterworks to soften its water, is to add quick lime, CaO, to titrate all of the HCO_3^- to CO_3^{2-}, which then precipitates as the calcium (or magnesium) carbonate. The reaction can be written

$$Ca^{2+}(aq) + 2HCO_3^-(aq) + CaO(s) \text{------>} 2CaCO_3(s) + H_2O$$

If the initial calcium concentration is more than half of the bicarbonate, some will remain after this titration, so soda, Na_2CO_3 is then added to precipitate the remaining calcium as $CaCO_3$.

a) For the Grinnell water, the total hardness of the well water is equivalent to about 3.5 mM Ca^{2+} before softening. Calculate how much CaO, in kg, is required to reduce this level to 1.0 mM, approximately the level in the distributed water. For this calculation, use the volume of water given in question 6.

b) Calculate the mM concentration of Na^+ for the Grinnell water if this method, rather than the ion exchange method, were used to soften the water.

B. Problems related to the chemical analysis of the water samples and electrochemistry

8. **EDTA water hardness titrations**. The "hardness" of water is associated with Ca^{2+} and Mg^{2+} ions in the water. The total concentration of these ions can be determined readily by titration with the metal complexing agent EDTA, which forms a stable 1:1 complex with the ions. The molar concentration of these ions is a suitable--and chemically the most meaningful--index of hardness, but the hardness is conventionally expressed in ppm $CaCO_3$ = mg $CaCO_3$/L, where the total Ca^{2+} + Mg^{2+} concentration is reported as the equivalent concentration of $CaCO_3$.

a) Noting that the formula mass of $CaCO_3$ is 100.0 g/mol (or 100 mg/mmol), show that the hardness, in ppm $CaCO_3$, can be calculated conveniently from the volume of 0.0100 M EDTA solution, mL_{EDTA}, used to titrate 100 mL of a water sample as:

$$\text{ppm } CaCO_3 = 10 \times mL_{EDTA}$$

b) Starting with the mM concentrations reported for the Ca^{2+} + Mg^{2+} ions, calculate the ppm $CaCO_3$ hardness and the volume of 0.0100 M EDTA solution required to titrate 100-mL portions of each of the four water samples examined by the class.

9. **Titration curve for a precipitation titration**. The titration curve, a plot of concentration of the species being titrated vs. mL titrant, is a particularly useful tool to employ to analyze the changes that occur in the course of the titration, the basis of indicator selection, and the differences observed between different analyte samples. The concentrations required to generate the curve can be readily calculated from the equilibrium constant for the titration reaction and the concentrations and amounts of analyte and titrant. The use a computer spreadsheet greatly simplifies the calculations

and the preparation of the titration curve itself. Use this approach to generate a table of concentrations and a graph of the titration curve for each of the following:

a) The titration of 100 mL of 0.001 M chloride with 0.0100 M $AgNO_3$. Calculate $[Cl^-]$ and $pCl = -\log[Cl^-]$ at 0.50 mL increments from 0 to 15 mL. For the first 9.5 mL, assume that each mmol of added Ag^+ removes one mmole of Cl^-; at the equivalence point volume (10 mL), calculate $[Cl^-] = [Ag+]$ from the solubility product of AgCl; beyond the equivalence point, calculate the [Ag+] from the quantity of excess $AgNO_3$ added and $[Cl^-]$ from the solubility product. The K_{sp} of AgCl is 1.8×10^{-10}. The following spreadsheet set-up will facilitate convenient display of intermediate quantities required for the simulation:

mL $AgNO_3$	Mmol Ag^+	Mmol Cl^- added	Mmol Ag	$[Cl^-]$ left	pCl excess

b) Use an appropriately modified version of the spreadsheet employed in a. to prepare a table of concentrations at 0.5 mL intervals and a titration curve for the titration of 100 mL of 1.00 mM bromide solution with 0.0100 M $AgNO_3$ $Ksp=5.0 \times 10^{-13}$.

10. Electrochemical cells, E° values and the Nernst Equation. Given the following diagram for a galvanic cell,

$$Cu \mid CuSO_4(0.010\ M) \| AgNO_3(0.30\ M) \mid Ag$$

a) Prepare a sketch of the cell.

b) Write balanced equations for the half-cell reactions and for the over-all reaction that occurs when the copper and silver wires are connected

c) Calculate E°_{cell} and show on your diagram the direction of flow of electrons between the half cells.

d) Use the Nernst equation to calculate E_{cell} from E°_{cell} and the concentrations of the electrolytes.

11. **Potentiometric titration with electrochemical monitoring.** The cell described in 10 can be used to monitor the concentration of Ag^+ ion in the titration of a soluble chloride or bromide with $AgNO_3$. The potential of a silver wire immersed in the chloride solution, measured relative to a $Cu|CuSO_4(1\ M)$ reference electrode which makes contact with the analyte solution through a porous thread (see sketch), is given by

$$E(\text{volts}) = 0.46 - 0.059\ pAg$$

where $pAg = -\log[Ag^+]$.

a) Derive the above equation from the Nernst equation and the E° values of the $Cu^{2+}|Cu$ and $Ag^+|Ag$ half-cells (question 10).

b) Calculate the potential of the cell at the equivalence point in the precipitation titration of a soluble chloride with silver nitrate.

c) Add columns to the spreadsheet in problem 9 for $[Ag^+]$, pAg, and the cell potential at each of the volumes for which the silver ion concentration can be calculated and prepare a graph of the measured E vs. mL silver nitrate.

12. **Potentiometric determination of concentrations from cell potentials with specific ion electrodes**. Electrodes which yield a Nernstian response (59 mV change for every power of 10 change in concentration) have been developed for several ionic species. The glass electrode used to measure pH values between 1 and 14 is a familiar example. Similar electrodes have also been developed to respond to changes in nitrate and fluoride concentrations at the low concentration levels typical of these ions in water samples. When the Nernst Equation is obeyed, the measured cell voltage should be a linear function of the logarithm of the ion concentration (compare problem 10 and 11). Like the pH measurement, a calibration of the meter response is required. Data are given below for voltages and concentrations measured for fluoride and nitrate standards and for a water sample. Prepare a plot of E vs. log[ion] to test the Nernstian response of the electrode and estimate from the plot the concentration of the water samples in ppm and in mM in each case:

    Data for fluoride ion-selective electrode vs. reference electrode:

solution	ppm F	E/mV
standard	2.0	188
standard	1.0	205
standard	0.50	223
standard	0.20	244
Grinnell water		200
Des Moines water		209
Chicago water		211
Sesqui/spring water		266

13. **Redox chemistry of nitrogen**. Although the source of most of the nitrogen that finds its way into surface and ground waters is nitrogen in its reduced form (ammonia and organic amines), bacterial action in an oxygen rich atmosphere leads to rapid oxidation to the most oxidized form, nitrate = NO_3^-. Furthermore, it is usually reported as ppm NO_3^- (N), which is read to mean ppm nitrogen in the form of nitrate. (Concentrations in excess of 10 ppm NO_3^-(N) are regarded as unsafe in drinking water.)

    The only one of our four water samples that contained a significant level of nitrate was the Des Moines water. Express the concentration of this water in the following terms: ppm NO_3^- (N), ppm NO_3, mg $NaNO_3$/L, moles of N/L. In November, 2004, the average NO_3^- as N reported by the Des Moines Water Works was 2.1 mg/l NO^-_3 (N).

14. **The Redox Chemistry of Nitrogen**. Decomposition of plant and animal wastes produces soluble nitrogen compounds (ammonia, urea, etc.), which finds their way into the soil and ground water to provide the nutrients used by the next generation of plants. In our oxygen-rich atmosphere these compounds are oxidized to nitrite and ultimately to nitrate, NO_3^-.

    a) Write balanced equations for the half-cell reactions and for the overall reaction that converts ammonium ion (the predominant form at pH 7 and lower) to nitrate.

    b) The E° value for the half reaction reducing nitrate to ammonium is:

$$NO_3^- + 10H^+ + 8e^- \text{----->} NH_4^+ + 3H_2O \qquad E° = 0.875\ V$$

    Locate the half-cell (acid conditions) reaction for the reduction of oxygen to water and calculate $E°_{cell}$ for the emf (galvanic) cell in part (a) where ammonium is converted to nitrate in an oxygen rich, aqueous environment.

15. **Electrical Conductivity and Ion Concentrations.** The electrical conductivity, L (in mhos), of water is very low and its electrical resistance, R (in ohms), is very high. By contrast, the conductivity of an aqueous solution of dissolved strong (completely dissociated) electrolytes is very high and, for dilute solutions, is proportional to the concentration of the electrolyte. The conductivity of a liquid, in mhos/cm, is typically measured with a probe of fixed dimensions immersed in the liquid after first calibrating the cell and meter with a solution of known conductivity.

    a) Typical conductivity vs. concentration (in mM $NaHCO_3$) data are given below for aqueous solutions of $NaHCO_3$ and for our four water samples at room temperature. Plot the conductivity vs. concentration (in mM) for the standards and obtain the slope and intercept of the best linear fit of the data. Use these parameters to calculate the mM concentration of salts (in units of mM $NaHCO_3$)in each of the four water samples for which data are given in the table **or** for comparable benchmark samples that you have been analyzing in the lab.

    Conductance Data for Standard Solutions and Four Water Samples

mM $NaHCO_3$	L/micromhos/cm	Sample	L/micromhos/cm
14.00	1367	Grinnell	1218
10.00	980	Des Moines	452
8.00	802	Chicago	298
5.00	489	Sesqui spring	85
3.00	289		
1.50	147		
0.75	74		
0.00	2		

    b) Since ions have different mobilities in an applied electric field, the concentrations calculated in this way would generally differ from the directly determined sum of the concentrations of all cations or anions. **If data are available**, compare these values with the total ion concentrations of the samples determined by adding up the ion concentrations (in meq/L) of the major cations, Na^+, Ca^{2+} and Mg^{2+}.

16. **Concentration of missing anions by conservation of charge.** If a drinking water sample has the following concentrations of ions, determine the concentration of **sulfate** in **ppm** and **mM**, assuming that all of the missing anionic charge is due to the presence of sulfate anion: bicarbonate, 81 ppm; chloride, 1.16 mM; nitrate(N), 4.2 ppm; fluoride, 1.1 ppm; calcium, 1.32 mM, magnesium, 0.28 ppm; sodium, 84.2 ppm.

    In solving this problem, it is essential to take into account the charge on the ions and to express all ion concentrations in the same units, meq/L = milliequivalents/L. For singly charged ions, 1 meq = 1 mmole, but for doubly charged ions, 1 mmole = 2 meq.

17. **The description of water composition in terms of equivalent component salts.** The major ion composition of any water sample can be described in terms of a specific mixture of simple salts that would yield the observed analytical composition. If non-zero concentrations are known for 6 ions, 5 individual salts are required to reproduce this composition. Electro neutrality of the solution insures that the 6th ion concentration is determined by specifying the other 5.

    Determine the number of millimoles and milligrams of each of the following 5 salts which must be added to one liter of deionized water to yield the concentrations observed for the 6 major ions (Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, Cl^- and SO_4^{2-}, neglecting the minor components nitrate and fluoride) in one of the benchmark water samples: NaCl(58.5 mg/mmol), $MgSO_4$(120 mg/mmol), $CaSO_4$(136mg/mmol), $NaHCO_3$(84 mg/mmol), Na_2SO_4(142 mg/mmol).

18. **Water Disinfectants**. Even relatively pure drinking water is typically treated with a disinfectant to prevent the growth of pathogenic organisms in the water distribution system. All of the widely used disinfectants (chlorine, chlorine dioxide, chloramine, and ozone) are strong oxidizing agents. Calculate the quantity (in kg/day; see problem 6 for details) of compressed chlorine gas that would be required to bring the free chlorine content of Grinnell water to a level of 1 ppm.

Laboratory Procedures

Laboratory Procedures

Lab Session and Organization

Organization of Lab

The class is divided into groups, with 4-5 students in each group. A section of 24 would ideally consist of 6 groups of 4. As shown in Figure 1, within each group, a given student(s) is (are) responsible for a particular determination. The group as a whole is responsible for the complete analysis and interpretation of the data for their samples. In addition, the students who are doing a particular determination in each group are expected to share their expertise and to assist each other in developing the techniques, preparing the solutions, carrying out the measurements, and in completing the calculations required to interpret the data most fruitfully. So each student is a member of two groups: The first is based on the breakdown of samples; the second on the technique being employed.

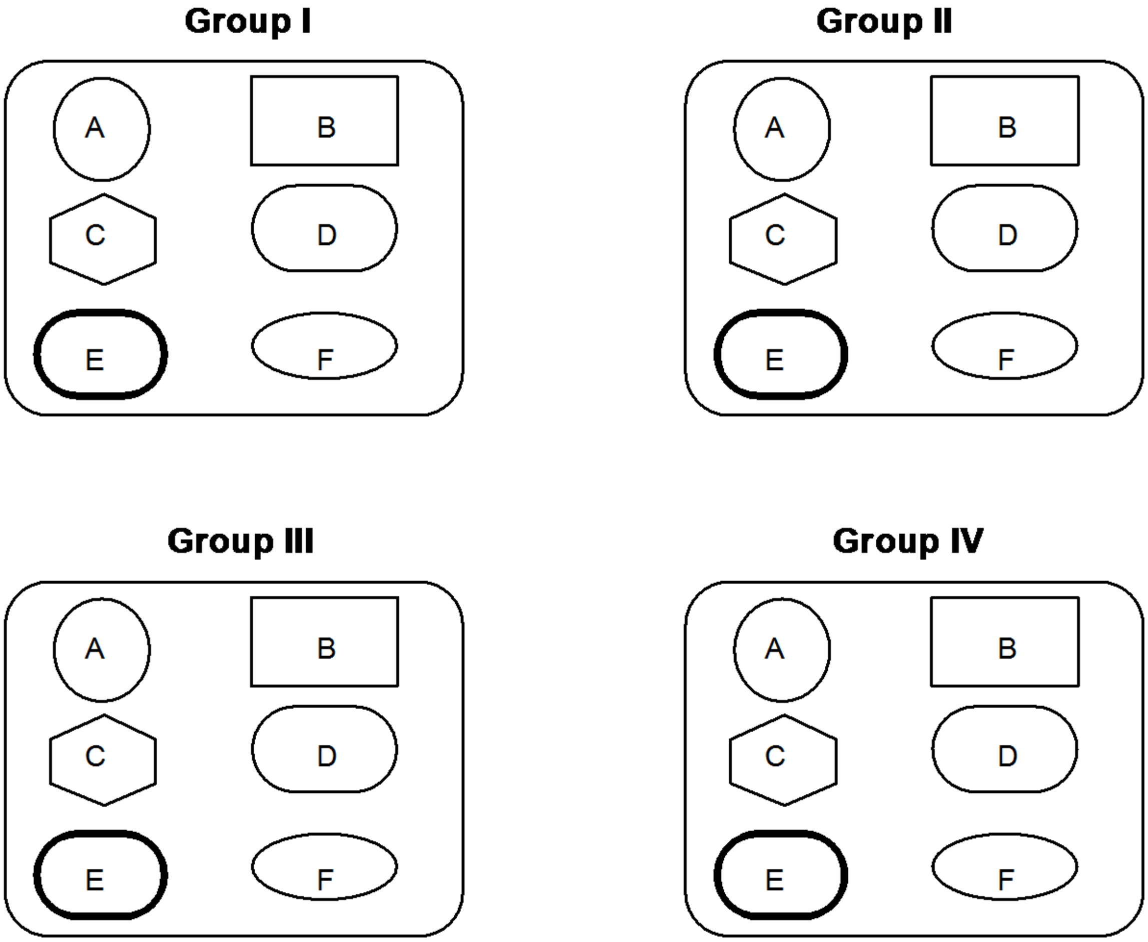


Figure 1: Suggested organization of lab for analysis of water samples by group.

Each lab group is required to analyze each of the 3-4 benchmark samples and each of the individually provided samples (= number in the group). Each student is expected to be familiar with the principles and procedures employed by all of the other members of the group. Three weeks are available for completion of the analyses and data compilation.

Equipment required for each section of 24 students

- **pH meters** (4; 1 per group) with pH electrode and buffers for pH and alkalinity determinations
- **second pH or ISE meter** (4; 1 per group): 4 fluoride + reference electrodes; standard solutions and other reagents for fluoride determinations [nitrate in previous years]
- **digital VOM** (4; 1 per group) with Cu/Cu2+ reference and Ag-wire indicator electrodes for chloride titrations
- **Conductivity meter** (4; 1 per group) with probe for estimate of total dissolved solids
- **Atomic Absorption Spectrometer** (ideally 2; 1 for each two groups) and reagents for Na calibration and determination
- **Burets, stir plates, beakers, and flasks** (standard items, as required)
- **Ion Chromatography unit** and filters, vials and standard reagents

L1: Water Hardness by EDTA Titration

References

1. D. C. Harris, *Exploring Chemical Analysis*, (W. H. Freeman, New York, 1997), Chapter 15.
2. T.L. Brown, H.E. LeMay, B.E. Burtsen, *Chemistry the Central Science* (Prentice Hall, Upper Saddle Rivers, NJ, 1997), Chap. 18-24.

Introduction

Source and effects of hard water. Ground water obtained from wells and springs and the surface water contained in lakes and streams contains substantial concentrations of dissolved salts that have been leached from rock and soil particles over which the water has flowed. The major component in most ground water and surface water in this part of the country is $Ca(HCO_3)_2$ formed by the dissolution of limestone, $CaCO_3$, or dolomite, $CaCO_3/MgCO_3$, by rainwater that is saturated with CO_2 from the atmosphere. The reaction with $CaCO_3$can be written

(1) $CaCO_3(s) + H_2O + CO_2(aq)$ ------------------> $Ca^{2+}(aq) + 2HCO_3^-(aq)$

A certain amount of dissolved minerals is nutritionally important and contributes to the taste of ground water. However, water that contains very high concentrations of dissolved calcium and magnesium ions is referred to as "hard water." Excessive hardness of water contributes to excessive clogging of water pipes, water heaters, and boilers, and to the reduced effectiveness of soap and detergents. It also contributes to a lowering of the taste quality of water for drinking. So the water hardness, as measured by the concentration of calcium and magnesium cations, Ca^{2+} and Mg^{2+}, is an important water quality index.

Effect of water softening on water composition. In areas where the ground water source yields very hard water, the water is often treated to reduce the hardness before it is distributed to the users. The **ion exchange process** replaces most of the calcium and magnesium in the water with sodium ions that are initially attached to a solid cation-exchange resin, denoted Na^+R^-. The process can be represented as

(2) $2Na^+R^-(s) + Ca^{2+}(aq)$ ----------> $Ca^{2+}R^{-2}(s) + 2Na^+(aq)$

to indicate that the dissolved calcium ions are retained by the solid resin while the sodium on the resin is released into the water. The effect of the process is to decrease the concentration of calcium and magnesium (the hard water ions) and to increase the concentration of sodium ion. In order to continue to operate the system day after day, the resin must be recharged regularly by back washing the resin with concentrated NaCl(aq) solution.

(3) $Ca^{2+}R^{-2}(s) + 2NaCl(aq)$ -----------> $2Na^+R^-(s) + CaCl_2(aq)$

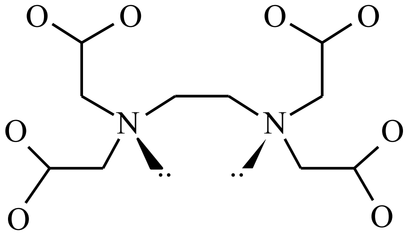
The calcium chloride and excess sodium chloride from this backwash process is added to the waste stream before it enters into the sewage treatment plant. It remains in that stream until the treated liquid fraction is released into the drainage system that accepts the treated wastewater.

Complexometric Titrations with EDTA: Many synthetic polydentate chelating agents, which form very stable complexes with metal ions, have been developed and employed in a wide variety of applications, ranging from water softening to treatment for lead poisoning. The great stability of the complexes formed also provides the basis for **complexometric titrations**, a convenient technique for the quantitative determination of a significant fraction of the metal ions. The most popular of these complexometric methods employs EDTA, ethylenediamine tetraacetic acid, a hexadentate polyfunctional amino acid, which forms very stable complexes with almost all of the metal ions (except the alkali metal cations like Na^+, K^+ and ammonium ion, NH_4^+). Because EDTA is a polyfunctional acid, the principal species present in solution depends strongly on the pH of the solution. Only at pH>11(above the highest pK_a) is the anionic species, denoted Y^{4-} (**I**), the predominant species present in solution. Reaction with metal cations then involves competition between M^{2+} and H^+ for the basic sites on the anionic ligand. The calcium titration is typically carried out at pH about 10 where the monodentate species, denoted HY^{3-}, is the predominant species of free EDTA. Under these conditions, the reaction with Ca^{2+} is therefore most appropriately abbreviated

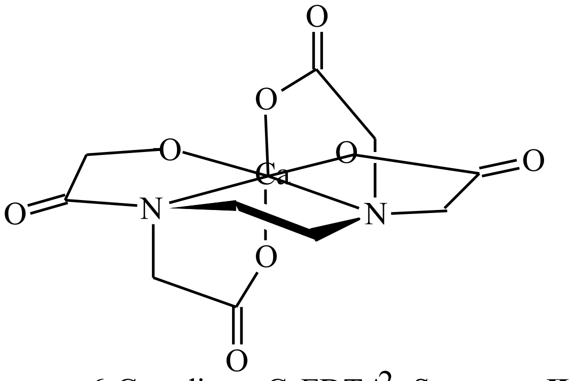
(4) $Ca^{2+} + HY^{3-}$ ------------> $CaY^{2-} + H^+$

where CaY^{2-} is the 1:1 calcium complex whose structure is shown in **II**, however, the most convenient form of the reagent is the disodium salt, $Na_2H_2Y{\cdot}2H_2O$ (372.24 g/mol), which is available in high purity for the direct preparation of reliable, stable **standard solutions** for use in titrations.

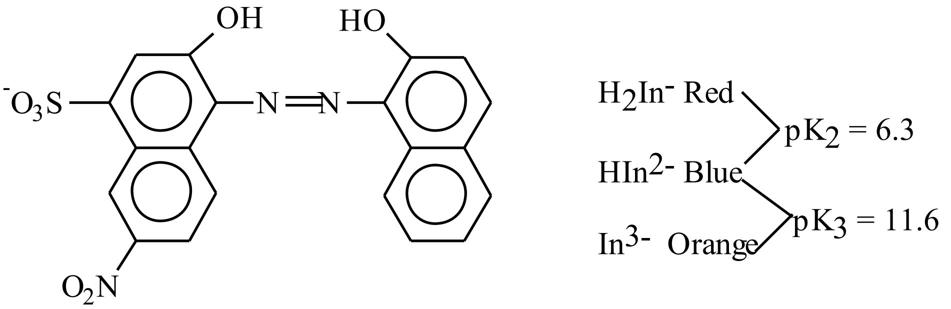
Structures:



Y^{4-} = EDTA Anion Structure,**I**



6-Coordinate $CaEDTA^{2-}$ Structure, **II**



Eriochrome Black T Indicator Dye,**III** , for EDTA Titration

The end-point of the EDTA titrations can be detected readily by using an appropriate indicator, which is itself a metal complexing agent. Eriochrome black T (abbreviated erio T), **III**, forms red complexes, denoted MIn^-, with most metals. The protonated indicator ligand, denoted H_2In^-, is also red. However, at pH > 7, where HIn^{2-} is the predominant species, the free ligand is blue. Thus, the addition of EDTA (primarily in the form HY^{3-}) to a solution of a metal containing the Erio T indicator in a buffered solution at pH 10 produces the following reaction and color change at the end-point:

(5) MIn^-(red) + HY^{3-} -----------------> HIn^{2-}(blue) + MY^{2-}

The formation constant of the MIn^- complex for most metals is large enough to insure that the MIn^- persists until a slight excess of EDTA has been added, so the end-point is typically quite sharp.

Procedure

Stock Solutions and Titration Procedure

- **Standard EDTA Solution.** The purity of reagent grade $Na_2H_2EDTA{\cdot}2H_2O$ is high enough to permit the preparation of a standard solution by careful weighing of the solid and quantitatively diluting an accurately measured mass, using volumetric glassware. A solution which is about 0.0100 M = 2.722 g/L (but accurately prepared, of course) is convenient for titrating typical water samples. (Provided in lab).
- **Buffer solution for pH control**. A pH 10 buffer solution can be prepared by adding 142 mL of concentrated NH_3 reagent (28%) to 17.5 grams of NH_4Cl and diluting to 250 mL with water. (Provided in lab).
- **Erio T indicator solution.** Dissolve 0.2 grams of erio-T solid in 15 mL of triethanolamine plus 5 mL of absolute ethanol. Store the solution in a refrigerator between lab periods. (Provided in lab).
- **Calconcarboxylic acid**: This indicator is convenient to titrate for calcium at high pH.
- **Hydroxynaphthol Blue Indicator.** This alternative indicator is available as a water soluble solid.
- **Sampling and titration: total hardness.** After running a titration on a standard calcium chloride solution (about 0.01 M) to be able to recognize the color change from red to pure blue at the end-point, a 50.0 mL sample of water should be titrated. Each titration should be made after about 3-4 mL of the pH 10 buffer and several (5-10) drops of recently prepared erio-T indicator have been added. A second titration of the same sample should be carried out to determine the concentration more accurately. The volume of water sample used for this second sample, which could be larger or smaller than the original sample, should be determined on the basis of the initial titration.
- **Sampling and titration: calcium hardness**. Carry out duplicate titrations of appropriate volumes of water samples as before, but this time add 10 mL of 10 % aqueous NaOH to each solution to precipitate $Mg(OH)_2$ before carrying out the titration. Allow 3-4 minutes after the NaOH addition to permit the precipitate to form before titrating (it is usually not visible for low amounts of magnesium). It is not necessary to add the pH=10 buffer to the solutions since they will be quite basic from the hydroxide added. Use about 0.1 grams of calconcarboxylic acid, instead of erio-T, as the indicator. Add the solid directly to your water sample and swirl to dissolve. In basic solution a calcium containing solution will be pink-red. At the endpoint when the calcium is complexed by the EDTA, the solution will be blue. Since there is less calcium than the total amount of calcium and magnesium, the volume of EDTA should be less (for the same volume of water sample) in the calcium only titration than in the titration for total hardness.

Analysis of Data

Depending on the use of the data, either molar (M) or millimolar (mM) concentrations may be the more convenient scale, so both should be calculated and reported. Since the stoichiometry of the reaction is 1:1, the molar concentration of the calcium + magnesium (**total hardness**) or just calcium (**calcium hardness**) in the water can be calculated readily from the volumes of water and EDTA and the known molar concentration of the standard EDTA reagent, e.g.,

$$[Ca^{2+}] = (mL_{EDTA} \text{ x } M_{EDTA})/mL_{sample}$$

from which the mass concentration in mgCa/L (=ppm Ca) can be calculated as

$$\text{mgCa/L} = [Ca^{2+}] \text{ (1000 mmoles/mole)(40 mg Ca/mmole).}$$

It is also conventional to report **hardness** of water in **ppm $CaCO_3$**, as if it had been $CaCO_3$ in the water. Since the formula mass of $CaCO_3$ is:

$$100 \text{ g/mol,}$$

$$\text{ppm } CaCO_3 = \text{mg } CaCO_3/L = (\text{mmoles } Ca^{2+}/L)(1 \text{ mmole } CaCO_3/\text{mmole } Ca^{2+}) \text{ x}$$

$$(100 \text{ mg } CaCO_3/\text{mmole } CaCO_3)$$

$$= 100 \text{ x mM } Ca^{2+}$$

So, for example, a 1.5 mM solution of Ca^{2+} (or of Ca^{2+} + Mg^{2+}) would have a hardness of 150 ppm $CaCO_3$. If the Ca^{2+} charge is balanced by $2HCO_3^-/Ca^{2+}$, the **alkalinity in units of ppm $CaCO_3$** and the **hardness in ppm $CaCO_3$** would be identical.

L2: Total Dissolved Solids by Electrical Conductivity

References

1. Solution Conductivity: *Instruction Manual Digital Conductivity Meter Model 1054* (Amber Science, Inc. Eugene, OR, 1996).
2. T.L. Brown, H.E. LeMay, B.E. Burtsen, *Chemistry: The Central Science* (Prentice Hall, Upper Saddle Rivers, NJ, 1997), Chap. 13, 18.

Introduction

Total Dissolved Solids (TDS).

The total concentration of dissolved ionic solids is often used as a rough indicator of the composition of a drinking water sample. For example, deionized water has essentially zero for the concentration of dissolved solids, whereas ocean water contains about 3 % by mass dissolved salts (mainly NaCl), and “mineral water” from brackish sources is required by the International Bottled Water Association (IBWA) to contain at least 500 ppm (0.05 % by mass) of total dissolved solids (TDS). Of course, the total concentration by itself gives no indication of the specific chemical composition of the dissolved solids. By contrast, if the concentration of all significant cations and anions in the water has been determined, that data can be used to calculate the total concentration of dissolved solids. So the specification of total dissolved solids typically complements other indices of drinking water quality.

Electrical Conductivity of Ionic Solutions.

In the 19th century, measurements of the electrical conductivity of aqueous solutions played a major role in clarifying our understanding of the ionic nature of dissolved salts in such solutions. Such measurements still provide the most convenient way to determine the **approximate** concentration of dissolved ionic salts. The method is rapid, reproducible, and non-destructive of the sample. The obvious alternative of weighing the solid residue obtained by evaporating a known mass of water is more direct, but it is time consuming, subject to substantial error for dilute solutions, and tedious. One limitation of the electrical conductivity method is that there is no unique relation between the concentration of ionic species and the conductivity. A 0.0100 M solution of KCl does not have exactly the same electrical conductivity as a 0.0100 M solution of $NaHCO_3$. On the other hand, the range of ion conductivities for equivalent concentrations is only a few percent, so a measured conductivity can be expressed as the equivalent concentration of some arbitrarily chosen salt, often KCl which is commonly used in the preparation of standard solutions for the calibration of the equipment used to make the measurements.

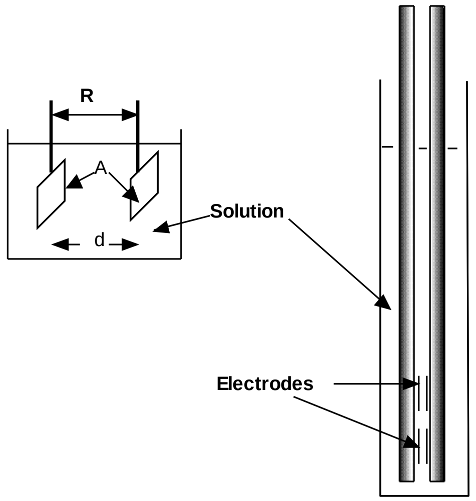


Figure L2.1: Cell for measurement of electrolyte conductivity of aqueous solutions.

Definition and Determination of Electrolyte Conductance.

The measurement of electrolyte conductance is accomplished by measuring the electrical resistance R (in ohms) between two metal plates that are immersed in a solution of the electrolyte, as shown in Figure L2.1. The resistance of such a set-up varies directly as the distance, d, between the plates and inversely as the cross-sectional area of each plate, A. For a cell with a fixed distance and area, the resistance will have a specific value for a solution of a given composition and concentration. The quantity which varies directly with concentration is the conductance L = 1/R, in mhos. In practice, the area and distance for a cell of rigid dimensions are combined into a cell constant, k_{cell}, and the relation between L and the measured R is given by Equation (1).

(1) $L = k_{cell}/R$

Convenient hollow, pencil-shaped dip probes, also shown in Figure L2.1, are commonly employed with water monitoring equipment. A standard solution of known conductivity is used to calibrate the meter. The probe is subsequently immersed in other solutions to obtain a direct reading of conductivity, which can then be converted to the equivalent concentration of KCl, or other arbitrary reference substance.

Procedure

Standard solutions for calibration of instrument.

Since the measured conductivity depends on the properties of the probe as well as the solution being examined, the instrument must first be standardized with a solution of known conductivity. A 0.00500 M = 5.00 mM KCl solution is usually used for this standardization. At 20°C, this solution has a conductance of 718 micromhos (0.718 millimhos). On the assumption that conductivity is directly proportional to concentration, the equivalent KCl concentration of any subsequent sample can be calculated as (meter reading in micromhos) x (5.00/718) mM.

Typical drinking water samples contain mainly bicarbonate anion, with a mixture of alkali metal and alkaline earth cations. A more appropriate substance to use as a reference substance, therefore, is sodium bicarbonate. A series of solutions from 0 to 1000 ppm $NaHCO_3$ can be prepared readily by serial dilution of a 0.100 % (1000 ppm = 13.4 mM $NaHCO_3$) standard solution. These solutions can be used to prepare a calibration curve to test the linearity of response of the instrument and to approximate more closely the total mM concentration of dissolved salts in water samples subsequently investigated.

Conductivity measurements.

Detailed procedures for the operation of the conductivity meter are provided by the manufacturers of the instrument. Whatever the make and model, however, the following considerations apply to making the measurements: In making measurements with a hollow pencil-shaped dip cell, it is essential that the small quantity of sample between the electrodes is representative of the whole sample. A convenient way to insure this is to use three test tubes of each standard solution or sample and to move the cell from one test tube to the next to insure that it is thoroughly flushed with the sample to be measured before recording a reading with the cell in the third tube. Moving the cell up and down several times in each test tube also helps to dislodge air bubbles to insure that the solution in the electrode area of the probe is representative of the bulk sample. Solution conductivity is temperature dependent, so all measurements should be made at the same temperature. Samples which are stored and measured at room temperature should be close enough to constant temperature to insure good results.

After initial calibration of the meter with the standard KCl solution, the conductivity of each of several dilutions of a standard substance, preferably $NaHCO_3$, should be carried out to prepare a standard curve for subsequent determination of the concentration of dissolved salts in water samples. To minimize errors due to variations in the equipment, measurements on a series of solutions should all be made over a reasonably short time interval (e.g., one afternoon) with the same meter and probe. Duplicate determinations should be carried out for each water sample.

Analysis of Data

Calibration Curve.

Using Excel, or equivalent spreadsheet program, a table of measured conductivity and the corresponding sodium bicarbonate concentration should be prepared and used to create a calibration graph, a plot of mM concentration of $NaHCO_3$ vs. conductivity in mhos. The data can then be fit to a straight line or other function to obtain an analytical function of the form,

(2) $[NaHCO_3]$ (in mM) $= f(L) = a + b\,L + c\,L^2 + \ldots$

where a, b, and c are determined by the computer fitting routine. With the functional form and constants (a, b, and c ...) determined, the $NaHCO_3$-based concentration of total dissolved solids for all of the water samples can be determined readily from the measured L for each sample. Average values and average (or standard) deviations should be reported for each water sample.

It is also conventional to report the concentration of total dissolved solids in ppm. With $NaHCO_3$ as the reference substance, this value could be calculated from

(3) ppm $NaHCO_3$ = (84 mg $NaHCO_3$ /mmol)(1 mmol $NaHCO_3$/L)

So, for example, a 3.0 mM sample would be:

(84 mg $NaHCO_3$/mmol)(3.0 mmol/L) = 252 mg $NaHCO_3$/L = 252 ppm (as $NaHCO_3$)

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L3. The Determination of the pH and Total Alkalinity of Water Samples.

References

1. D. C. Harris, *Exploring Chemical Analysis,* (W. H. Freeman, New York, 1997), Chap. 11,12
2. T.L. Brown, H.E. LeMay, B.E. Burtsen, *Chemistry the Central Science* (Prentice Hall, Upper Saddle Rivers, NJ, 1997), Chap. 16-18.

Introduction

Acid/base properties of ground water and surface water.

Most domestic water supplies are obtained either from ground water from wells drilled into the earth or from surface water from lakes or rivers. Ultimately both sources are recharged by run-off of rainwater, whether from rainfall in the immediate vicinity or – in the case of some very deep wells – from some quite distant locations. The composition of the water reflects the geology, soil composition, agricultural or commercial activity, etc. of the watershed.

Attention to "acid rain" notwithstanding, by far the most important contributor to the acid/base properties of domestic water sources is the bicarbonate ion, HCO_3^-, which is generated in the reaction of CO_2-saturated water with limestone, $CaCO_3$, reaction (1).

(1) $CO_2 + H_2O + CaCO_3(s)$ -------> $Ca^{2+}(aq) + 2HCO_3^-(aq)$

Acid/base properties of domestic water supplies are important for the users, whether home owners or commercial enterprises. The reverse of reaction (1) is responsible for filling up water heaters, boilers, tea kettles, and distribution pipes with lime deposits, essentially $CaCO_3(s)$, when the water is heated or boiled to drive off CO_2.

The pH of the water is also important. If it is too low, the rate of corrosion of pipes is increased. If it is too high, precipitation of $CaCO_3(s)$ is increased. So the pH of most domestic water supplies is controlled carefully by addition of NaOH to obtain a pH about 8.3, where HCO_3^- is the principal carbonate species.

The **pH** and **total alkalinity** of a water sample are typically included in a report of the composition of the water. The pH is determined with a commercially available **pH meter** equipped with a pH-sensitive electrode (usually a glass electrode) and a reference electrode. Since the actual potential between the pair of electrodes depends on the identity and conditions of the individual electrodes, it is essential to standardize the meter-electrode set-up by adjusting the meter to the known pH of a buffer solution whose pH is close to the pH of the solution to be investigated. For measurements over a range of pH values, the meter should be standardized with two solutions that span the approximate range (e.g., 7 and 4).

The **total alkalinity** is a quantity which reflects the capacity of the water sample to neutralize a strong acid, like HCl. The total alkalinity of a water sample is determined by titrating the sample with standard HCl solution to an end point that is signaled by the color change of an appropriate indicator. More complete information about the nature of the species responsible for the alkalinity can be obtained from a full pH vs. mL HCl titration curve. The curve is essentially a portion of the titration curve for the titration of the basic carbonate anion (CO_3^{2-}) with HCl as shown in Figure L3.1. The initial pH depends on the distribution of carbonate species in the water at the start of the titration, and the equivalence point of the titration depends on the total concentration of those species.

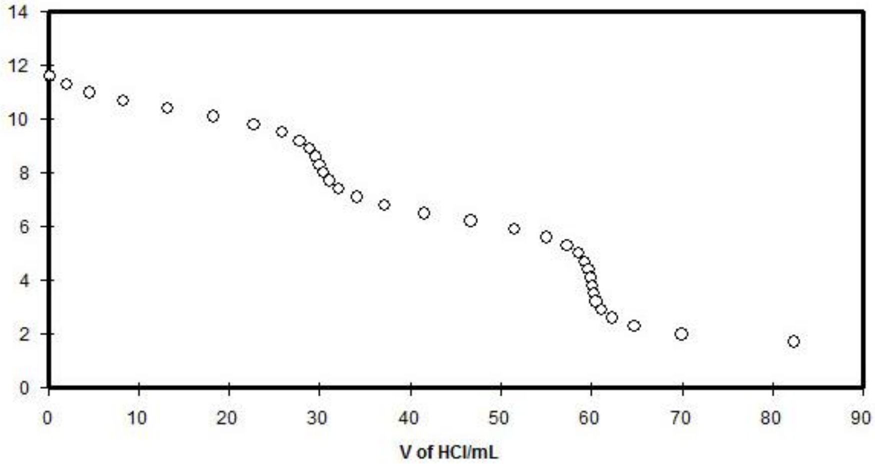

Figure L3.1: Titration of 30 mL of 0.100 M carbonate with 0.100 M HCl.

By contrast, for the titration of pure bicarbonate, HCO_3^-, the initial pH is approximately the average of the two pKa values for carbonic acid, ½(6.3 + 10.3) = 8.3. As shown in Figure L3.2, titration with standard HCl then converts the bicarbonate to carbonic acid, with the equivalence point being at pH approximately 4.0. If the initial pH is greater than 8.3, significant CO_3^{-2} is also present and it must first be titrated to HCO_3^- (to pH 8.3). On the other hand, if the pH is much below 8.3, significant carbonic acid is present. Its concentration could be determined by titrating the sample with standard base to pH 8.3.

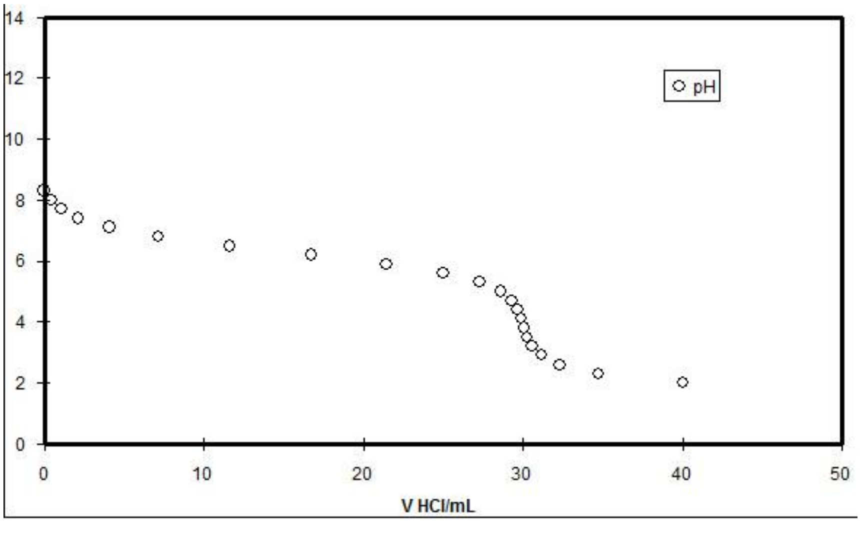

Figure L3.2: Titration of 60 mL of 0.050 M bicarbonate with 0.100 M HCl.

Indicator Titration.

An indicator which changes color at the equivalence point pH (about 4) can be used to signal the endpoint of the titration with HCI. Bromcresol green or a bromcresol green-methyl red mixed indicator are often employed in such carbonate titrations. The end point can be detected more readily by first titrating to the first detectable color change and heating the solution to the boiling point to expel the carbon dioxide produced by carbonic acid decomposition before adding the last few drops of HCI.

Procedure

Sample size and reagent concentration.

The volume of sample and the concentration of the HCl reagent depend somewhat on the likely concentration of the base to be titrated with the HCl. For the titration of 100 mL of typical drinking water samples, 0.02 M HCl might be used to get an end-point in the 5-20 mL range. A quick titration of 25 mL with an appropriate indicator can be used to determine conditions for a subsequent, more careful preparation of the full titration curve.

pH Titration.

The set-up for a potentiometric pH titration is shown in Figure L1.3. The pH meter should be standardized at pH 7 and 10 with appropriate buffers. After recording the initial buret reading and the initial pH of the water sample, add the HCl in small increments initially, recording the pH after each addition after allowing some time for pH electrode equilibration. After the first three additions, add 1-mL increments until the pH reaches about 5.0. Return to smaller increments until the pH reaches 3. Finish with three 3-mL increments.

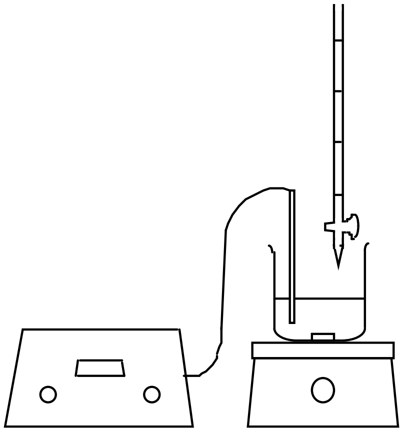

Figure L3.3: Set-up for potentiometric pH titration of an acid or base.

Analysis of Data

Plot the titration curve (pH vs. mL HCl added) to determine the **equivalence point volume** by estimating (to the nearest 0.1 mL) the volume and mmol of HCl at the inflection point in the curve (about pH 4.5). Alternatively, note the volume of HCI used to reach the end point revealed by the indicator color change.

Use the volume and concentration of the HCl solution to calculate the number of mmols of HCO_3^- that would be equivalent (in acid neutralizing capacity) to the HCl used, and calculate the initial **molar concentration of HCO_3^-** from the volume of water used. Note carefully the stoichiometry of the reaction.

If the initial pH is >8.3, the separate CO_3^{-2} and HCO_3^- concentrations can each be determined from the full titration curve. The volume of HCl titrant required to reach pH 8.3, $V_{8.3}$, can be used to calculate the **molar concentration of CO_3^{-2}** while the volume of HCl to go from pH 8.3 to the final equivalence point, $V_{4.5}$, can then be used to calculate the **molar concentration of HCO_3^-.** (Note that $V_{4.5}$ - $2V_{8.3}$ = volume to titrate the initial HCO_3^-, since one mole of HCO_3^- is also formed from the initial $CO_3^{-.2}$.)

Finally, express the total **carbonate alkalinity in ppm $CaCO_3$** by converting the molar concentration of $HCO_3^{-\ \text{and}}$ CO_3^{-2} to molar concentration of $CaCO_3$, noting that 1mmol $CaCO_3$ = 1 mmol CO_3^{-2} = 2 mmol HCO_3^- in acid neutralizing capacity, 1 ppm = 1 mg/L for water solutions, and the molar mass of $CaCO_3$ is 100 g/mol = 100 mg/mmol. Alternatively, the **alkalinity in ppm $CaCO_3$** can be calculated directly from the volume and concentration of the HCl used in the titration of a known volume of water, noting that 1 mmole of $CaCO_3$ is equivalent to 2 mmoles of HCl.

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L4. Determination of Chloride in Water by Precipitation Titration with Silver Nitrate

References

1. D. C. Harris, *Exploring Chemical Analysis,* (W. H. Freeman, New York, 1997), Chapter 6.
2. T.L. Brown, H.E. LeMay, B.E. Burtsen, *Chemistry the Central Science* (Prentice Hall, Upper Saddle Rivers, NJ, 1997), Chap. 17, 18, 20.

Introduction

Chloride in seawater and fresh water.

The most common anionic species in seawater is chloride. Seawater is essentially a solution of sodium chloride, NaCl, with lower concentrations of other ions. The concentration is high, approximately 0.5 M or about 3% by mass sodium chloride. The concentration is so high because sodium chloride is quite soluble and there are no mechanisms for precipitating either sodium or chloride from the seawater. So most of the salt that has been dissolved from rocks and soil over the centuries has found its way to the sea. The only significant quantities of NaCl that are found as solid deposits are the solids that were left behind in the evaporation of water from ancient seas.

The high solubility of NaCl in water that is responsible for its dissolution by rainwater and deposition into the sea insures that its concentration in inland lakes, streams, and wells is typically very low. However, in coastal areas or in other geological situations involving drainage through salt beds, the concentration of chloride can be quite high.

For surface waters, industrial and commercial activity, including the salting of highways to aid the flow of vehicular traffic by lowering the melting point of ice and snow, can affect the concentration of chloride substantially. As the snow melts in the spring, the runoff water dissolves the salt and carries it to the connecting drainage ditches, rivers, and lakes. So such water bodies often show large seasonal variation in chloride concentration, with peak concentration just after the spring snow melt. The concentration of chloride often reflects the severity of the winter, but the level is also strongly influenced by the dilution effect of unusually heavy spring rains and by the condition of the receiving water body before the melt begins.

Chloride from drinking water treatment.

The softening of water by an ion-exchange process (See L2) can contribute significantly to chloride concentrations in surface waters. In summary, the ion-exchange water softening process reduces the hardness of the distributed water by replacing calcium and magnesium ions by sodium ions. The anion composition is unchanged by this process; however, in the regeneration process, calcium and magnesium chloride (and some sodium chloride) are added to the wastewater stream.

For a small city which uses about a million gallons of water a day (3.8×10^6 L/day) – 100 gal/day per person x10,000 people – and whose water contains about 100 ppm Ca (100 mg/L of Ca) the softening process removes about 4×10^8 mg of Ca or 4×10^2 = 400 kg of Ca. A corresponding quantity of Na must be added to displace the removed Ca, so about a ton of salt is required each day to recharge the ion exchange resin, and all of the chloride from this process is added to the sewage treatment effluent stream every day from this process. The concentration of chloride expected from this source where it enters the waste stream is then about 100 ppm chloride = about .003 M, not a huge concentration, but enough to be detectable above the background level with appropriate analytical methods. In the backwashing process, some chloride is also added to the small quantity that is typically present in the water coming from the ground water source, so measurable levels of chloride are often present in most domestic water supplies.

Elemental chlorine (as Cl_2 gas) is often used as a disinfectant to kill bacteria and other microorganisms in drinking water. Though the added Cl_2 may end up as chloride ion when chlorine acts as an oxidizing agent, typical levels of Cl_2 used in the process (about 1 ppm) are too low to affect significantly the much higher levels of chloride from other sources.

Precipitation methods for chloride determinations.

The relatively low solubility in water of silver chloride, AgCl, can be used as the basis of a precipitation titration of any aqueous chloride sample with a standard solution of silver nitrate, $AgNO_3$. For solutions that are 0.10 to 0.01 M, a variety of indicators are available to signal the end-point of the titration. For more dilute chloride solutions, like most drinking water or surface water samples, the indicator methods are less reliable. An alternative potentiometric titration method, using a simple silver/copper electrode pair to follow the changing silver concentration, is preferable. The addition of silver nitrate to an aqueous chloride solution results in AgCl precipitate formation until all of the chloride is used up; i.e.,

(1) $Ag^+ + Cl^- \text{-------------->} AgCl(s)$

Then the silver concentration rises rapidly and the cell potential (voltage) changes sharply. For the quite dilute solutions normally encountered, however, the change is fairly gradual, so it is more accurate to determine the equivalence point in the titration by locating the inflection point in the voltage vs. mL $AgNO_3$ titration curve plot. A typical titration curve for this titration, which emphasizes the voltage changes observed near the equivalence point, is shown in Figure L4.1.

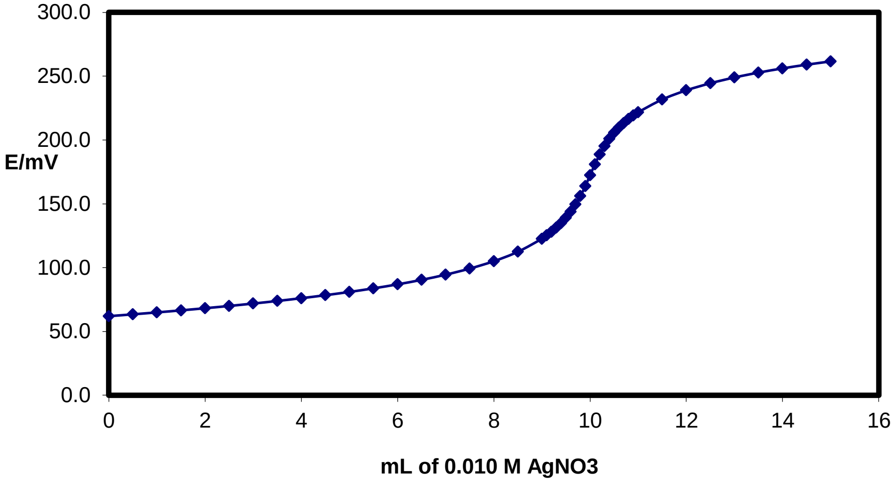

Figure L4.1: Potentiometric titration of 100 mL of 0.001 M chloride with 0.010 M AgNO3 monitored with Ag wire and Cu/Cu^{2+} electrodes.

Procedure

Potentiometric titration.

The set-up and procedure are similar to that employed in the potentiometric pH titration with HCl to determine alkalinity of water samples, Figure L3.3. The electrode pair employed in the voltage measuring system is shown in Figure L4.2, and a simple digital VOM meter is used instead of the pH meter shown in Figure L3.3.

The electrode pair consists of a copper wire/copper sulfate solution **reference electrode** and a silver wire **indicator electrode**. When immersed in a solution containing silver ions, the electrode pair gives a voltage response which is related (by the Nernst Equation) to the concentration of silver ions in solution. The copper/copper sulfate reference electrode makes contact to the silver ion solution by way of a simple thread which allows ion flow from the copper sulfate reference electrode to insure a complete circuit.

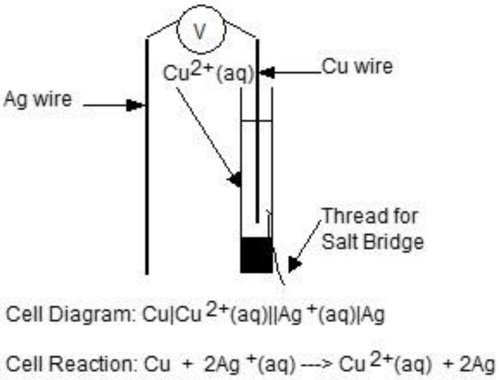

Figure L4.2: Electrode assembly for monitoring silver ion concentrations with a copper reference electrode.

Reagents.

Silver nitrate is available in relatively pure form. A 0.0100 M standard solution can be prepared readily by transferring a carefully weighed amount of dried (one hour at 110°C) $AgNO_3$to a 1-L volumetric flask and diluting to the mark. The solution should be stored in the dark to avoid photochemical decomposition.

Titration of samples.

Use 100 mL aliquots for potentiometric titration with 0.0100 M $AgNO_3$. Be sure that the electrodes are immersed enough to give reliable voltage readings when connected to the voltmeter. Add $AgNO_3$ slowly from the buret in small enough increments to be able to determine the equivalence point readily. Do one preliminary titration quickly to estimate an approximate end-point. Then repeat the titration with a second sample, taking care to obtain several points near the equivalence point where the cell potential changes most rapidly. Plot the voltage vs. mL data to determine the equivalence point volume (to the nearest 0.1 mL) as the inflection point in the curve.

Analysis of Data

The molar concentration of chloride in each sample can be calculated from the equivalence point volume, determined from the titration curve, the concentration of silver nitrate titrant, and the volume of the sample.

(2) $[Cl^-] = M_{AgNO3} (V_{AgNO3}/V_{sample})$

This concentration can also be expressed in ppm Cl, since

(3) $\text{ppm Cl} = \text{mg Cl/L} = (\text{mol Cl/L})(\text{mg Cl/mol Cl}) = [Cl^-]\,(35{,}500)$

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L5. Sodium Ion by Atomic Emission Spectroscopy

References

1. D. C. Harris, *Exploring Chemical Analysis,* (W. H. Freeman, New York, 1997), Chapter 20.
2. T.L. Brown, H.E. LeMay, B.E. Burtsen, *Chemistry the Central Science* (Prentice Hall, Upper Saddle Rivers, NJ, 1997), Chap. 6, 18.

Introduction

Effect of water softening on sodium ion concentration.

Surface water in lakes and streams typically contains quite low concentrations of sodium, but ground water sources which contain very high concentrations of salts can have high sodium levels. More commonly, the sodium added in the **ion-exchange softening process** is the principal source of sodium in domestic water supplies. Sources and effects of hard water have been identified earlier, and the ion-exchange process that is commonly employed to reduce water hardness has been outlined (L2). To summarize, the effect of the ion-exchange process is to decrease the concentration of calcium and magnesium (the hard water ions) and to increase correspondingly the concentration of sodium ions. Anion concentrations, except for a little chloride carryover from backwash of the ion-exchange resin tanks, are unaffected.

An alternative water softening method, the **soda-lime process**, removes both the calcium/magnesium cations and the bicarbonate anions by converting the calcium bicarbonate to insoluble calcium carbonate by the addition of lime (CaO) to the hard water; i.e.,

(1) $Ca(HCO_3)_2(aq) + CaO(s)$ ----------> $2CaCO_3(s) + H_2O$

If some of the initial calcium or magnesium originated from salts like $CaCl_2$ or $MgSO_4$, a quantity of Na_2CO_3 (soda) equivalent to that excess is added to precipitate additional $CaCO_3(s)$ (or $MgCO_3$); i.e.,

(2) $CaSO_4(aq) + Na_2CO_3(aq)$ -------> $CaCO_3(s) + Na_2SO_4(aq)$

So the soda-lime process removes both calcium and magnesium cations and the bicarbonate anions. Only the excess calcium and magnesium ions which require additional carbonate, added as $Na_2CO_3(aq)$, contribute to an increase in sodium ion concentration in the finished water.

Atomic Emission/Absorption Methods for Sodium.

The concentrations of most elements in a sample can be determined by quantitative measurement of either the emission or the absorption of light in the visible or ultraviolet portion of the spectrum from a suitably excited sample of the material. The concentration of cations in aqueous solutions can most conveniently be determined by measuring the intensity of either **atomic absorption** or **atomic emission** of a sample vaporized in the flame of a high temperature burner. For sodium and other alkali metal cations, which readily undergo electronic

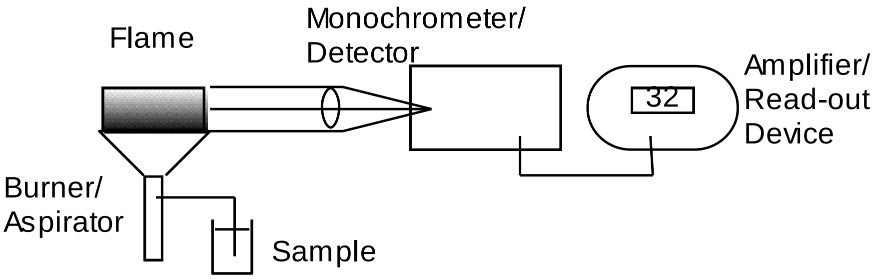

Figure L5.1. Block diagram of atomic emission spectrometer.

excitation at flame temperatures, atomic emission measurements are most often employed. The measurement is essentially a quantitative version of the familiar yellow flame test commonly used for qualitative identification of sodium in a solution. A block diagram of an atomic emission spectrometer, which uses the high-temperature flame of a burner for excitation, is shown in Figure L5.1.

Over a modest concentration range, the emission intensity is proportional to the concentration of sodium in the solution that was vaporized. So a calibration curve, a plot of intensity (I) vs. the known concentration of Na (ppm Na) in a set of standard solutions, can be constructed and used subsequently to determine the concentration of samples to be analyzed. The **standard addition method**, in which the sample is spiked with increased amounts of standard solution, has the advantage that the concentration of other species in the solutions is only slightly perturbed, so deviation from a linear fit is minimized. For the wide range of concentrations expected for a random set of drinking water samples, the standard curve should not be expected to be linear, but the curve fitting features of a typical spreadsheet program (Excel, etc.) can be employed to fit the data to a power series or other simple function. The resultant analytical function can then be employed to calculate the concentration of any sample from its measure emission intensity.

Procedure

Standard solutions of sodium for standardization of instrument.

A series of dilutions of a concentrated standard solution should be prepared for use in preparing a standard curve of ppm Na vs. emission intensity, I. Since bicarbonate is the most common anion in drinking water, sodium bicarbonate is a good choice of compound to use for this standard. Serial dilution of a 10 ppm (or more concentrated) Na standard can be employed to obtain a good range of standard solutions with concentrations ranging from 10 to 0.5 ppm, or lower.

Wavelength selection and emission measurements.

Detailed procedures for the operation of atomic emission spectrometers are provided by the manufacturers of the instruments. Whatever the make and model, however, the following steps are required to determine the concentration of a given metal ion by the technique: The burner, which typically employs acetylene as fuel and compressed oxygen gas as the oxidizer, is turned on, ignited, and adjusted to get a smoothly burning flame. The wavelength is adjusted to match the wavelength of characteristic emission lines of the element sought (589 nm for sodium). Pure water is aspirated into the flame and the scale is adjusted to read zero (using the appropriate knob or button). A solution of the most concentrated standard is then aspirated into the flame and the sensitivity (or gain control) is adjusted to give an emission intensity reading near the maximum on the scale. This measurement should be repeated to give three readings which can be averaged to improve the precision of the data. The emission intensity of each of the other standards should then be determined in triplicate, with the instrument re-zeroed with deionized water between samples. Without making any changes in the sensitivity or gain control, triplicate determinations of the intensity of each of the water samples is then determined.

Analysis of Data

Calibration Curve.

A table of emission intensity and corresponding sodium concentration is prepared and used to prepare a calibration graph, a plot of ppm Na vs. intensity of emission, I, at the wavelength employed in the measurements. The data are then fit to a straight line or other function to obtain an analytical function of the form

(1) $\text{ppm Na} = f(I) = a + b\,I + c\,I^2 + \ldots$

where a, b, and c are determined by the computer fitting routine. With the functional form and constants (a, b, and c …) determined, the concentrations of all of the water samples can be determined readily from the measured I for each. Average values and average (or standard) deviations should be reported for each water sample.

It is also convenient to report the concentration of Na^+ in M and mM. Since 1 mmol = 23 mg Na and 1 ppm = 1 mg/L, the millimolar concentration of sodium for each sample is given by

(2) mM Na = (mg Na/L)(1 mmol Na/23 mg Na)

So, for example, a 40 ppm = 40 mg/L Na sample would be (40 mg Na/L)(1 mmol Na/23 mg Na) = 1.74 mM Na^+.

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L6/L7. The Determination of Fluoride and Nitrate by Potentiometric/Ion-Selective Electrode Methods

References

1. D. C. Harris, *Exploring Chemical Analysis*, 4th Ed. (W. H. Freeman, New York, 1995), Chapter 14.
2. Hach Company, *Instruction Manuals for Nitrate Electrode* (Model 48680) and *Fluoride Electrode* (Model 44500-1)
3. T.L. Brown, H.E. LeMay, B.E. Burtsen, *Chemistry the Central Science* (Prentice Hall, Upper Saddle Rivers, NJ, 1997), Chap. 16-18.

Introduction

The most significant anion in most domestic water supplies is bicarbonate, HCO_3^-, produced – along with Ca^{2+} – by the action of CO_2-saturated rainwater on limestone, $CaCO_3(s)$. Typically sulfate and chloride are also found at lower, but still readily measurable, levels. Considerable latitude in the range of concentrations of these principal anions is acceptable in domestic water supplies. By contrast, the concentrations of two other minor component anions in the water supply, fluoride and nitrate, is of more concern and requires careful monitoring.

Nitrate ion sources and effects.

Nitrate in surface waters typically comes from decay of plant and animal matter and from the bacteria-promoted oxidation of ammonia and organic amines. The nitrate concentration in surface waters (lakes and streams) often varies sharply with the season. In streams that drain heavily fertilized watersheds, the nitrate level reaches a peak following summer rains after the crop has been planted and fertilized. Deep underground aquifers, on the other hand, contain quite low levels of nitrate, so the presence of high levels of nitrate is a clear indication that the water source is from shallow aluvial aquifers. Unfavorable health effects of high nitrate concentrations are most severe with infants who are susceptible to a condition known as methemoglobinemia (blue baby), The current EPA limit on nitrate in US public water supplies is 10 ppm nitrogen in the form of nitrate, conventionally reported as $NO_3(N)$. An anion exchange resin treatment has been used by some municipal water plants to reduce higher levels to meet this criterion.

Fluoride ion sources and effects.

Though low nitrate concentrations are a source of health concern, fluoride in levels of about 1 ppm has been found to be very beneficial to the development of healthy teeth by preventing tooth decay. Since water from surface sources or shallow aquifers seldom contains measurable fluoride, many municipal suppliers add a fluoride salt to the water supply to provide this benefit for its users. It is important to monitor this addition carefully, since somewhat higher concentrations can produce significant mottling of teeth. Fortunately, very few domestic water sources have fluoride concentrations which exceed 1 ppm.

Potentiometric Methods for the Determination of Nitrate and Fluoride.

A potentiometric method, comparable to the glass electrode determination of pH and silver electrode monitoring of Ag^+ concentration, is available for both fluoride and nitrate determinations. In each case, the determination requires the preparation of a standard curve of cell potential vs. the log [conc]. Over several orders of magnitude of concentration, the cell potential variation with concentration is Nernstian; i.e., the potential (in mV) at 25°C varies as

(1) $E = E_{ref} - 59 \log[F^-]$

for the fluoride electrode, and

(2) $E = E_{ref} - 59 \log [NO_3^-]$

for the nitrate electrode, where the response of the reference electrode, E_{ref}, depends on its identity and the details of its construction, but is constant for a given reference electrode.

Like commercial pH meters used for measurement of hydrogen-ion concentrations, meters for use with specific-ion electrodes can be arranged to read directly the log of the concentration of the ion under investigation. Since the range of linearity of such electrodes is typically less than that of available pH electrodes, a procedure that employs a series of solutions to construct a calibration curve is recommended. Any available pH meter with appropriate plugs to accommodate the terminals of the electrodes can be used to determine the cell potential, and the concentrations of fluoride and nitrate ions, with this setup.

Procedure and Analysis of Data

Calibration of Electrodes with Standard Solutions.

The most reliable way to use the potentiometric method for concentration determinations is to construct a calibration curve by obtaining the potential between reference and ion-selective electrodes as a function of concentration over at least one order of magnitude of ion concentrations surrounding the anticipated concentration of the samples to be analyzed. Because the potential difference is also influenced by the ionic strength (the total concentration of dissolved ions), it is necessary to add an inert salt to all samples to insure that they all have nearly the same high ionic strength before the potential is determined. A series of standard solutions is prepared by quantitatively diluting a more concentrated nitrate or fluoride standard solution. The procedure outlined in the Hach instruction manual for nitrate and fluoride electrodes employs pre-packaged ionic strength adjustment packets (called powder pillows) which are dissolved in each standard solution before the potential is determined.

The choice of concentrations of standard solutions depends somewhat on the anticipated concentration of the samples to be analyzed. A broad range for nitrate standards that would span the range of almost all routine drinking water samples would be 30, 10, 3, 1, and 0.3 ppm. Such a set can be prepared readily by careful dilution of a 100 ppm standard solution. Since fluoride concentrations seldom exceed 1 ppm, a more useful set of standards for fluoride electrode calibration would be 10, 3, 1, 0.3, 0.1 ppm, which could be prepared readily from a 100-ppm or a 10-ppm standard solution. Because the potential varies linearly with the log of the concentration, these sets would each be expected to yield nearly equal increments in cell potential between solutions.

The potential of each solution should be measured carefully, allowing some time for the potential to equilibrate after the electrodes have been immersed in the solution. The electrodes should be rinsed with deionized water and blotted dry carefully with a tissue between measurements. After the measurements have been completed, a calibration curve can be constructed by plotting E (y axis) vs. log [concentration] (on x axis) as suggested by Equation (1) or Equation (2). The concentration units are arbitrary, but are typically ppm (or mg/L) for these low concentration species. It is convenient to fit the data to a linear equation and to use the slope and intercept ($=E_{ref}$) of that plot in subsequent use of the calibration data. If the electrode response is ideal, the slope of the plot should be -59 mV (at 25°C), but the curve is still useable if the slope is not exactly -59 mV. A typical calibration curve for a fluoride vs. silver-silver chloride reference electrode is shown in Figure L6.1.

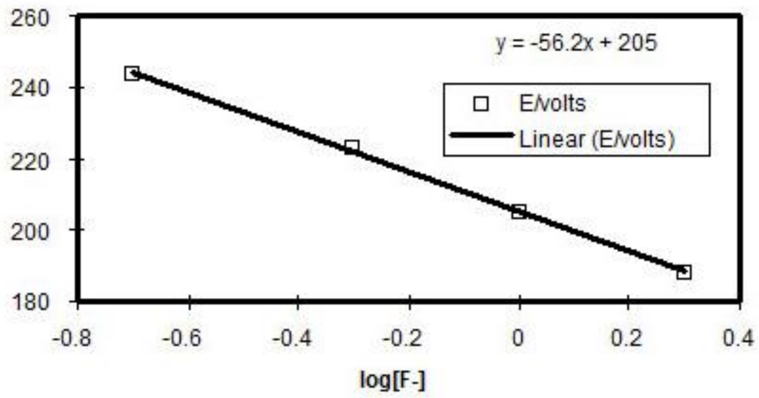

Figure L6.1: Calibration curve for fluoride electrode.

Determination of Concentration of Analytical Samples.

After a calibration curve has been prepared, the concentration of nitrate or fluoride in your unknown samples can be determined readily by measuring the potential of each solution **with the same electrode pair and meter**, after the ionic strength of each sample has been adjusted.

For the **fluoride measurements**, ionic strength is adjusted by dissolving the contents of a powder pillow in 25 mL of each sample. For the fluoride determination, the ionic strength packet also contains a buffer to insure that the pH is high enough to prevent protonation of the F^- to the weak acid HF (pK_a = 3.16). For **nitrate measurements**, a liquid ionic strength solution should be added to each sample to achieve the same ionic strength for all the samples.

For both fluoride and nitrate measurements, the presence of chloride in the water sample will produce some AgCl turbidity or precipitate, but this does not interfere with the response of the electrodes. The concentration of the anion, [ion], can then be calculated from the slope and intercept, since

(3) E_{sample} = intercept - slope x log [ion]

With the concentration of standard solutions given in ppm mg/L fluoride or nitrate (N), the results of these determinations can also be expressed in those units. However, the concentration in moles/L and in mmol/L, mM, should also be determined to permit more convenient comparisons with concentrations of other anions. For fluorides and nitrates (N), these conversions are:

(4a) (mg F/L) x (1mmole F/19mg F) = mM F

and

(4b) (mg NO_3(N)/L) x (1mmole NO_3(N)/14mg NO_3(N)) = mM NO_3(N)

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L8: Anion Exchange Chromatography of Drinking Water Samples

References

1. Harris, 3rd Edition, pp. 499-504; Reeve, *Introduction to Environmental Analysis*, John Wiley & Sons: West Sussex, England, **2002**. pp. 69-75.

Introduction

The sulfate anion was assumed to be in many of the drinking water samples analyzed in the water module. The goal of this experiment is to measure the concentrations of sulfate, phosphate, bromide, nitrite, chloride, fluoride, and nitrate by a liquid chromatographic method. For ions such as sulfate, this may be the best experimental method for measuring the ion concentration.

There are a wide range of liquid chromatographic techniques. These techniques are classified by the solid phase and liquid phases used in the chromatography. For this experiment we will be using an anion exchange resin as the solid phase in a column and an aqueous bicarbonate solution as the mobile phase. We will use a conductivity detector to measure the elution of the anions in the water samples. This type of chromatography is called anion exchange chromatography and is a type of ion chromatography. A typical chromatogram is shown below (reproduced from Harris, p. 503).

Since anions elute from the column at characteristic times, we can identify and quantify the concentrations of the anions by their elution times and peak areas. Modern instruments do most of these calculations with custom software provided by the instrument manufacturer and produce a data table for the user.

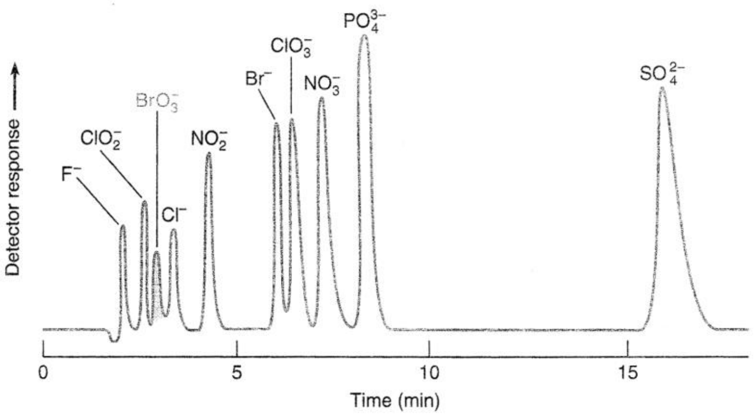

Figure 23-4 Converting one human hazard into another. Chlorination of drinking water converts some organic compounds into potential carcinogens, such as $CHCl_3$. To reduce this risk, ozone (O_3) has replaced Cl_2 in some municipal purification systems. Unfortunately, O_3 converts bromide (Br^-) into bromate (BrO_3^-), another carcinogen that must be monitored. The figure shows an anion chromatographic separation of ions found in drinking water. With preconcentration of the water, the detection limit for bromate is ~2 ppb. [From R. J. Joyce, *Am. Environ. Lab.*, May 1994, p. 1.]

Procedure

Equipment.

- 0.2 µ filter cartridge (1 per water sample)
- Clean, labeled vial (20 ml capacity, 1 per water sample)
- 10 ml disposable syringe (1 per water sample)
- Latchat ion chromatography instrument (Biology Dept.)

Sample Preparation.

Samples for liquid chromatography must be filtered before injection onto the column. Use about 20 ml of the water sample from the water module. If any of the anion concentrations for the water sample exceed the maximum level of the calibration standards, then dilute the sample to get the ion in the range of the calibration curve. (A five-fold dilution of the Grinnell water sample is recommended.) Draw up 10 ml of the water into a disposable plastic syringe. Place a 0.2 µ filter on the syringe (in place of a syringe needle or on the luer lock) and push the water sample through the filter into a clean, labeled vial. Do this 2 or 3 times until 15-20 ml of the water sample fills the vial. *Note: Use the same syringe and filter for the subsequent filterings*. Cap the vial.

If you have used a syringe needle, then dispose of it in a ‘sharp box’, a specific waste container for sharp objects.

Concentration ranges for calibration standards for anions:

Bromide: 0.05 to 5 ppm

Chloride: 0.5 to 50 ppm

Fluoride: 0.05 to 5 ppm

Nitrate as Nitrogen (NO_3^-(N)): 0.05 to 5 ppm

Nitrite as Nitrogen (NO_2^-(N)): 0.05 to 5 ppm

Phosphate: 0.05 to 5 ppm

Sulfate: 1 to 100 ppm

Running the Chromatograms.

We will take all the samples down to the Biology department’s instrument room (Noyce 1601) where the instrument is located. Professor P. Jacobsen will load our samples into the automated sample changer for the measurement of the chromatographic results. Each chromatographic run takes about 13 minutes, so the chromatograms for the class will be recorded into the evening by the computer. The next day you will get a data table of your results (for one chromatogram of your water sample and each anion measured).

Using this Data: Questions to address in your presentation on your drinking water sample.

1) Report the sulfate concentration measured by ion chromatography for your water sample in your presentation.
2) For the other anions (chloride, fluoride, nitrate) that we have measured during the water module, do the chromatographic results agree with the water module results? Explain any differences.

3) Should we be analyzing for other anions during the water module that were found chromatographically (bromide, nitrite, phosphate)?

4) Does the sum of the cationic charges and anion charges balance? What might be responsible for any difference?

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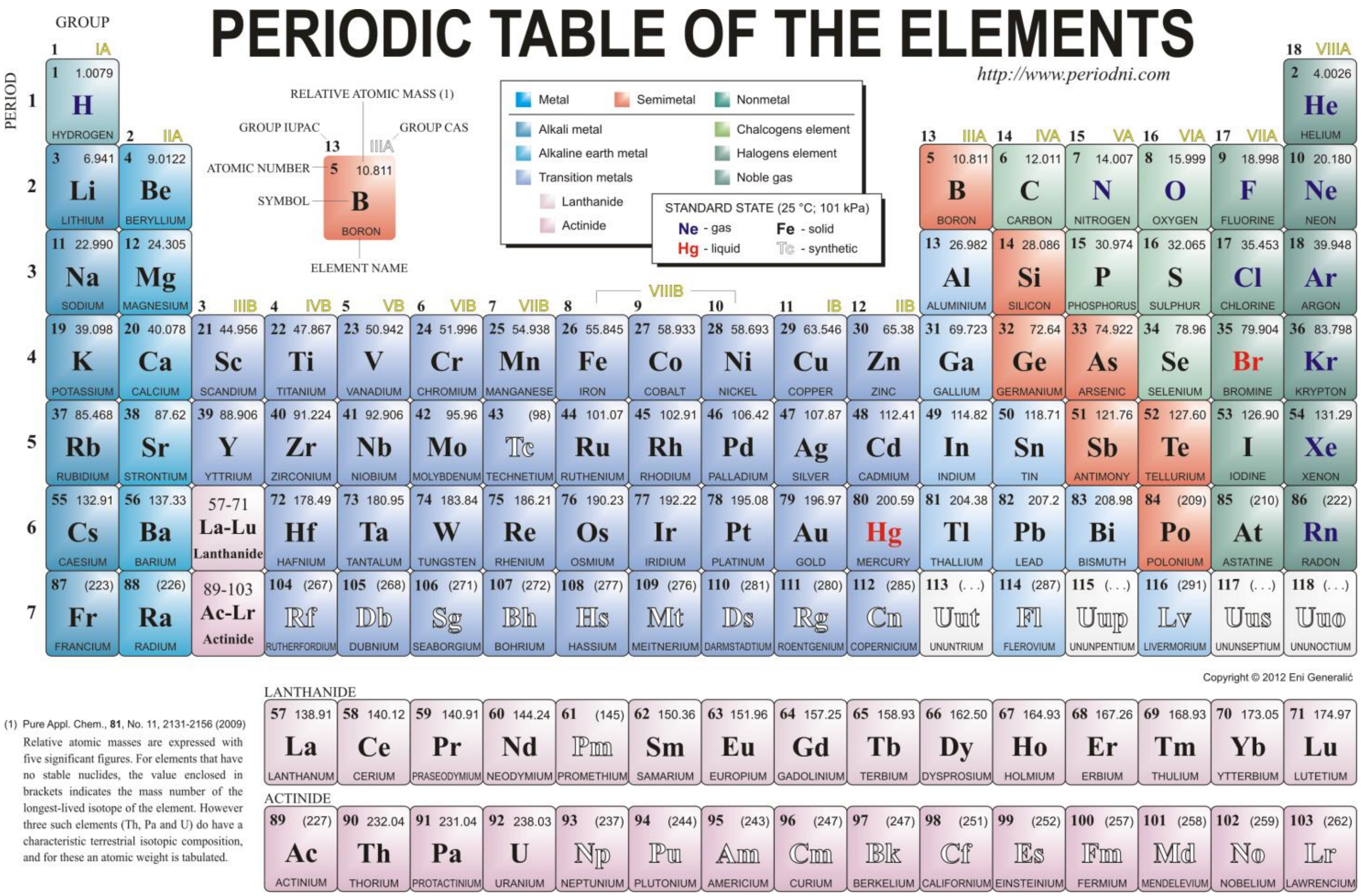

PERIODIC TABLE OF THE ELEMENTS

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.798 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.96 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt MEITNERIUM	110 (281) Ds DARMSTADTIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (. . .) Uut UNUNTRIUM	114 (287) Fl FLEROVIUM	115 (. . .) Uup UNUNPENTIUM	116 (291) Lv LIVERMORIUM	117 (. . .) Uus UNUNSEPTIUM	118 (. . .) Uuo UNUNOCTIUM

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.05 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., **81**, No. 11, 2131-2156 (2009)
Relative atomic masses are expressed with five significant figures. For elements that have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element. However three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

This is a free, downloadable color Periodic Table available from Generalic, Eni. "Download printable materials." EniG. Periodic Table of the Elements. 18 Oct. 2013. KTF-Split. Accessed, 12/16/13 <http://www.periodni.com/download.html>

Conversion Factors	Constants		
1 inch = 2.54 cm	Avagadro Number	N_O	6.023 x 10^{23} particles/mol
1 lb. = 453.6 g	Absolute Zero		-273.15ºC
1 Angstrom = 10^{-10}m	Planck constant	h	6.625 x 10^{-34} J sec
1 liter = 1.06 qt.	Velocity of light	c	3.00 x 10^{8} m/sec
1 cal = 4.184 joules (J)	Mass electron	m_e	9.11 x 10^{-28} g
1 amu = 1.66053 x 10^{24} g	Charge of electron	e	1.602 x 10^{-19} coulomb
ln x = 2.303 log x	Faraday constant	F	96,485 coulomb/mole 96,485 kJ/volt mole
2.303 RT/F = 0.0592 volts			
1 electron volt			
= 96,485 J/mole	Gas Constant	R	0.0821 liter − atm/mole 8.317 Joules/mole 8.317 kg m^2/sec^2 mol k
= 23.06 kcal/mole			
= 1.602 x 10^{19} J			
1 atm = 760 torr (mm Hg)			
14.7 lb/in^2			