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WATER ANALYSIS

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I. OBJECTIVES:

- To learn procedures useful for analyzing water quality.
- To use these procedures to test previously-collected water samples and/or various water samples available in the lab.

II. BACKGROUND:

In Biology 112, you learned how to test water samples for coliform bacterial count. There are, however, a number of other factors which affect water quality, several of which can be fairly easily determined. In this lab, you will be testing water for temporary hardness (= CaCO₃ concentration), acidity, chloride content (normally related to salt content), and dissolved oxygen content.

Temporary hardness of water is caused by the following chemical reactions:

$$\text{mL HCl added} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.01 \text{ m HCl}}{1 \text{ L HCl}} \times \frac{1 \text{ m CaCO}_3}{2 \text{ m HCl}} \times \frac{100 \text{ g CaCO}_3}{1 \text{ m CaCO}_3} = \text{g CaCO}_3$$

or mL HCl added $\times 5.0 \times 10^{-4} = \text{g CaCO}_3$ present in a 100 mL sample of H₂O. Remember that the density of water is 1 g/mL. Thus,

$$\text{mL HCl added} \times \frac{5.0 \times 10^{-4} \text{ g CaCO}_3}{100 \text{ g H}_2\text{O}} \times \frac{10^4}{10^4} = \frac{\text{mL HCl added} \times 5.0 \text{ g CaCO}_3}{10^6 \text{ g H}_2\text{O}}$$

or mL HCl added $\times 5.0 = \text{ppm}$ (parts per million) of CaCO₃ present (10⁶ = 1 million).

Quantitative determination of the chloride content of water samples (or various other salt solutions, including body fluids) can be done by titration with silver nitrate (AgNO₃). Caution: AgNO₃ crystals or solution will turn your skin black wherever it touches--this does not wash off. A small amount of potassium chromate (K₂CrO₄) is added to the solution as an indicator. This

H₂O + CO₂ → H₂CO₃ (carbonic acid) and either Ca⁺⁺ or Mg⁺⁺ + HCO₃⁻ → Ca(HCO₃)₂ or Mg(HCO₃)₂ (Ca or Mg bicarbonate) or Ca⁺⁺ or Mg⁺⁺ + CO₃⁻⁻ → CaCO₃ or MgCO₃ (Ca or Mg carbonate).

The titration you will be doing in this lab tests for dissolved CO₂/bicarbonate/carbonate ions by the following reaction: 2HCl + CaCO₃ → CaCl₂ + H₂O + CO₂↑.

The carbonate content can be calculated as follows:

titration proceeds by the following reaction: AgNO₃ + Cl⁻ → AgCl↓ + NO₃⁻. The AgCl is not water-soluble and precipitates out as a white material. When all of the Cl⁻ is used up, the Ag⁺ will start to react with the chromate (CrO₄⁻⁻) to form Ag₂CrO₄ which is red, thus indicating the endpoint of the reaction when this red color barely starts to show up. The chloride content can be calculated as follows:

$$\text{mL of AgNO}_3 \text{ added} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.1 \text{ m AgNO}_3}{1 \text{ L AgNO}_3} \times \frac{1 \text{ m Cl}^-}{1 \text{ m AgNO}_3} \times \frac{35.45 \text{ g Cl}^-}{1 \text{ m Cl}^-} = \text{g Cl}^-$$

so,

$$\frac{\text{mL AgNO}_3 \text{ added} \times 3.545 \times 10^{-3} \text{ g Cl}^-}{\text{mL of H}_2\text{O in sample} \div 10^3 \text{ mL/L}} = \frac{\text{mL AgNO}_3 \text{ added} \times 3.545 \text{ g Cl}^-}{\text{mL of H}_2\text{O in sample} \times 1 \text{ L H}_2\text{O}}$$

III. MATERIALS NEEDED:

HARDNESS	ACIDITY	CHLORIDE	D I S S O L V E D
0.01 M HCl	pH meter	0.1 M AgNO ₃	OXYGEN
indicator soln:		(=16.988 g q.s. to 1 L soln)	dissolved O ₂ (DO) meter and/or see separate list & write-up
0.02 % methyl red		sat. K ₂ CrO ₄ --approx. 6-7 g per 100 mL of dH ₂ O	
0.1 % brome cresol green in 95% EtOH		buret & glassware	

IV. PROCEDURE:

A water analysis test kit may be available for use to test water samples in the field. Water specimens should also be brought back to the lab for use in the following analyses:

HARDNESS

- Measure out a 100 mL sample of water as carefully as possible (use volumetric flask) and put all of it into an Erlenmeyer flask or beaker.
- Add a couple drops of indicator solution.
- Titrate with HCl (remember to record before and after readings) until the water starts

to show a faint pink color. (**Note: we are using a slightly different indicator solution which turns yellowish, not pink!**)

- Multiply the mL HCl added by 5 to determine the ppm of CaCO₃.
- If your water sample is large enough, titrate three aliquots and average your results.

ACIDITY

After standardizing the pH meter with the buffer solutions, measure the pH of your water sample.

CHLORIDE

1. If not previously prepared, mix up the reagents:

a. Dissolve 16.988 g AgNO₃ (come as closely as possible for most accurate results) in dH₂O and q.s. to 1 L to make a 0.1 M solution.

b. Saturated K₂CrO₄ solution--this will contain approximately 6-7 g of K₂CrO₄ per 100 mL dH₂O. Add as much as the solution will hold, indicated by the presence of a few left-over crystals on the bottom.

2. The titration should be carried out as closely as possible to 20° C, as temperature can affect the chloride content.

3. For fresh water, use a 50.0 mL aliquot and for salt water use a 10.0 mL aliquot (titrate in triplicate and average if your water sample is large enough). Make sure you use a white background under your flask/beaker. Measure

your aliquot(s) as accurately as possible and transfer all to the flask/beaker.

4. Add 2 to 3 drops K₂CrO₄ solution.

5. Titrate with AgNO₃, remembering to take before and after readings. Swirl vigorously to release chloride ions that may be trapped in the AgCl precipitate. The endpoint is when the red color first becomes permanent.

6. Calculate the chlorosity of the water (gm Cl⁻/L H₂O @ 20° C) = mL AgNO₃ added $\times 3.545 \div \text{sample size}$ (of 50 or 10 mL).

Note: body fluids can also be tested by this method by measuring 1 mL with a pipet, diluting to 10 mL, then titrating. When doing calculations, remember the 10 \times dilution--your actual sample will be 10 \times more concentrated than as calculated in step 6.

DISSOLVED OXYGEN

Chemistry's DO meter may be available for our use to test water samples in the field. If not, we'll use the Winkler Iodometric method (which is vaguely like our vitamin C titrations in Biology 112).

Unfortunately, this method requires that the water samples be collected just prior to being tested -- we can't collect them one week and test them another week. A separate explanation follows.

V. DATA:

Take notes on procedures, write down all numbers, and perform requested calculations.

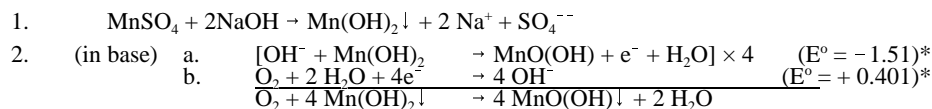
WINKLER IODOMETRIC DETERMINATION OF O₂ CONTENT

I. BACKGROUND:

Since you may not have had this in chemistry yet, portions of this explanation may be beyond your present understanding. The detail is here mostly to show you it's not "magic" -- I'm not pulling numbers out of thin air. File this in your lab notebook for future reference as you never know what you may need to refer to twenty years from now (as I'm finding out now). If you've had this in

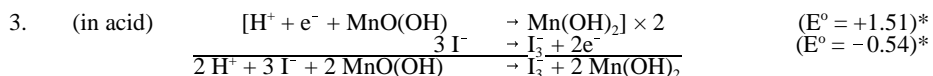
chemistry (redox reactions, valence states, etc.) it will make a lot more sense.

The first step is the addition of a divalent manganese (Mn⁺⁺) solution and strong alkali (base) to your sample in a glass-stoppered glass bottle. Dissolved oxygen (DO) oxidizes Mn⁺⁺ in Mn(OH)₂ ppt to Mn⁺³ in MnO(OH) ppt. by the following chemical reactions:



The mixture is then acidified with sulfuric acid (H₂SO₄) and in the presence of previously-added iodide ions (I⁻) the Mn⁺³ is reduced

back to Mn⁺⁺ with the liberation of iodine which combines with I⁻ in the solution to form I₃⁻ by the following reaction:

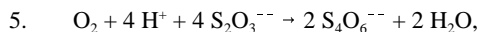


The iodine is then titrated with a solution of thiosulfate ions ($\text{S}_2\text{O}_3^{2-}$), and the following reaction occurs:



* = Don't worry about these numbers unless you've had chemistry and know all about something called the Nernst Equation.

Anyway, if you combine the whole thing, the overall reaction is:

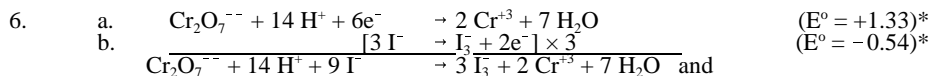


which means that for every molecule (or mole) of O_2 that is dissolved in the water, it takes 2 molecules (or moles) of thiosulfate to react with it.

Because we are trying to measure the DO, special care must be taken in acquiring and handling the sample so that extra O_2 is not added to the water. The sample must not come into contact with air for very long or be agitated. Air must not be allowed to bubble through the sample when collecting it. Samples should be collected in 300 mL glass bottles with glass stoppers. Also, it is very important that the bottles be full before placing the stopper in so there is no air bubble

at the top. Photosynthetic algae in the sample could increase O_2 content and bacteria could decrease it, so DO must be determined immediately on all samples with a large amount of O_2 in them. Samples with less O_2 should have all reagents up through the sulfuric acid added, and can then be kept for a few hour in the dark. Unfortunately, this makes it impossible to collect water samples in the field one day and analyze them another day--you need to have time to do it all at once within a very short period of time.

In standardizing the thiosulfate ($\text{S}_2\text{O}_3^{2-}$) with the dichromate ($\text{Cr}_2\text{O}_7^{2-}$) the following reactions are occurring:



4. The same $\text{I}_3^-/\text{S}_2\text{O}_3^{2-}$ reaction as above, so the following calculations are possible:

$$20 \text{ mL aliquot of } \text{Cr}_2\text{O}_7^{2-} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{\text{actual gm } \text{Cr}_2\text{O}_7^{2-}}{0.0500 \text{ L } \text{Cr}_2\text{O}_7^{2-}} \times \frac{1 \text{ m } \text{Cr}_2\text{O}_7^{2-}}{294.129 \text{ g } \text{Cr}_2\text{O}_7^{2-}}$$

$$\times \frac{3 \text{ m } \text{I}_3^-}{1 \text{ m } \text{Cr}_2\text{O}_7^{2-}} \times \frac{2 \text{ m } \text{S}_2\text{O}_3^{2-}}{1 \text{ m } \text{I}_3^-} = \text{actual gm } \text{Cr}_2\text{O}_7^{2-} \times 8.158 \times 10^{-4} \text{ m } \text{S}_2\text{O}_3^{2-} \text{ used.}$$

To find the concentration of the $\text{S}_2\text{O}_3^{2-}$, divide this by the volume used to titrate the dichromate, or:

$$\frac{\text{actual gm } \text{Cr}_2\text{O}_7^{2-}}{\text{mL } \text{S}_2\text{O}_3^{2-} \text{ used}} \times \frac{8.158 \times 10^{-4}}{10^{-3} \text{ L/mL}} = \frac{\text{actual gm } \text{Cr}_2\text{O}_7^{2-}}{\text{mL } \text{S}_2\text{O}_3^{2-} \text{ used}} \times 0.8158,$$

which should come very close to 0.025 M.

Originally, your water sample bottles should contain 300 mL. Since 2 mL of the MnSO_4 and 2 mL of the alkali-iodine reagent will be carefully added to the bottom of the bottle, a corresponding 4 mL of water will overflow. Thus, the actual volume of water is 296 mL (which is "diluted" to 300 mL by the addition of the 4 mL). When the bottle is inverted, the reagents precipitate out all the O_2 from the water as a solid which settles to the bottom. Thus, when the 2 mL of H_2SO_4 are added, the water that overflows doesn't

matter--the O_2 is tied up in the ppt on the bottom. The sample you will titrate should be 200 mL out of the original 296, but since that was "diluted" to 300 mL, your actual aliquot will have to be slightly larger. This can be calculated by use of a simple ratio: $X/200 = 300/296$; or $X = 300 \times 200/296 = 203 \text{ mL}$. When you actually titrate your sample, based on the previously-mentioned reactions, the amount of O_2 in the water can be calculated like this (the long way):

$$\text{mL } \text{S}_2\text{O}_3^{2-} \text{ used on sample} \times \frac{1 \text{ L}}{10^{-3} \text{ mL}} \times [\text{conc of } \text{S}_2\text{O}_3^{2-} \text{ in mL}] \times \frac{1 \text{ m } \text{I}_3^-}{2 \text{ m } \text{S}_2\text{O}_3^{2-}}$$

$$\times \frac{31.9988 \text{ g } \text{O}_2}{\text{m } \text{O}_2} = \text{g } \text{O}_2 \text{ in the 203 (= 200) mL sample.}$$

Remember that [conc of $\text{S}_2\text{O}_3^{2-}$] was just calculated above, so substituting and doing the other arithmetic:

$$\text{g of } \text{O}_2 \text{ in the 200 ml sample} = \text{ml } \text{S}_2\text{O}_3^{2-} \text{ used}_{\text{sample}} \times \frac{\text{actual gm } \text{Cr}_2\text{O}_7^{2-}}{\text{ml } \text{S}_2\text{O}_3^{2-} \text{ used}_{\text{stand.}}} \times 0.8158$$

$$\times 0.0079997 = \text{ml used}_{\text{sample}} \times \frac{\text{act. gm } \text{Cr}_2\text{O}_7^{2-}}{\text{ml used}_{\text{stand.}}} \times 0.006526.$$

Thus, to find out how many gm O_2 are in 1 L (1000 mL) of H_2O , it is necessary to multiply this by $1000/200 = 5$, so $0.006526 \times 5 = 0.3263$. Also, since the amount of O_2 in

the water is so small, milligrams ($= 10^{-3} \text{ gm}$) would be more useful to express the quantity. Combining all of this gives:

$$\text{ml } \text{S}_2\text{O}_3^{2-} \text{ sample} \times \left[\frac{\text{actual gm } \text{Cr}_2\text{O}_7^{2-}}{\text{ml } \text{S}_2\text{O}_3^{2-} \text{ stand.}} \times 32.63 \right] = \text{mg } \text{O}_2/\text{l } \text{H}_2\text{O}.$$

The quantity in the box can be combined as a "conversion factor" (which should be ≈ 1.00).

II. MATERIALS NEEDED:

CHEMICALS	EQUIPMENT
$\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$	dH ₂ O
NaOH--caution	NaI
soluble starch	KI
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	$\text{K}_2\text{Cr}_2\text{O}_7$
(salicylic acid)	conc. H_2SO_4 --caution
	heat source
	buret
	300 mL glass bottles with glass stoppers
	volumetric flasks (100s, 1 @ 500-1000)
	balance & weighing paper
	various Erlenmeyer flasks & beakers
	(drying oven at 103° C)
	pipets (10 & 2 mL)
	piece of white paper for under flask

III. PROCEDURE:

MIXING REAGENTS

- MnSO₄**
Dissolve 48.0 g of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in dH₂O and q.s. to 100 mL. (Note: because the molecular weight of this is 223.06 g/m, this solution is 2.152 M.)
- Alkali-Iodine Reagent**
Dissolve 50.0 g NaOH (caution: will burn skin) and 13.5 g NaI in dH₂O and q.s. to 100 mL. (Note: MW of NaOH is 39.99 g/m, so [OH⁻] is 12.5 M and MW of NaI is 149.89 g/m so [I⁻] is 0.901 M.)
- conc. H₂SO₄**
Have this on hand--caution: will burn skin.
- Starch Solution**
Heat about 80 mL dH₂O to boiling. Dissolve 0.5 g of soluble starch in a little cold dH₂O. Add, with stirring to the boiling H₂O, q.s. to 100 mL, and boil a few minutes longer. (For best results, although not necessary, let settle overnight and use only the clear supernate. Also, it is suggested that 0.125 g of

salicylic acid be added as a preservative if you're going to be keeping it.)

- Na₂S₂O₃**
Dissolve 6.205 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in (freshly boiled & cooled) dH₂O and q.s. to 1 liter. Add 5 mL of chloroform or 0.4 gm NaOH to preserve if you're going to be keeping it. The more accurately you can weigh this, the easier your calculations will be. (Note: MW of this is 248.18 g/m, so if properly made up, concentration should be 0.025 M)
- Standard 0.025 M K₂Cr₂O₇**
Be very precise when weighing the dichromate (for best results dry first at 103° C for 2 hr). Weigh out 0.613 g--record exact amount weighed--dissolve in dH₂O in 500 mL volumetric flask and q.s. to exactly 500 mL (or 1.226 g/l L or 0.1226 g/100 mL). (Note: MW is 294.1918 g/m so this solution is 0.004167 M)

STANDARDIZING THE THIOSULFATE

- Preferably, do three samples and average the results.
- In a large Erlenmeyer flask, put about 100 to 150 mL dH₂O.

- Dissolve about 2 gm potassium iodide (KI).
- Add 1 mL conc H_2SO_4 ? (Original protocol says "10 mL of 1 + 9 H_2SO_4 .")

5. Add exactly 20 mL (10 mL pipet 2×) dichromate.
6. Place in dark 5 min., then dilute to about 400 mL.
7. Titrate with thiosulfate, recording initial and final volumes

TITRATING THE WATER SAMPLE(S)

The assumption is that samples were collected in 300 mL glass bottles with glass stoppers. When you add reagents to the bottle(s) it/they will overflow, so plan to catch the spill.

1. With a pipet, add 2 mL of MnSO_4 solution (to each sample). Add this gently with tip of pipet under the surface of the H_2O and so it sinks to the bottom.
2. With a clean/different pipet, add 2 mL alkali-iodide solution, also with tip of pipet under the surface and so it sinks to the bottom.
3. Stopper carefully so there are no air bubbles in the jar. Mix by inverting at least 15 times. When ppt settles, invert again to mix some more. When at least 2 min. of settling time has produced at least 100 mL of clear supernate, continue.
4. Remove stopper. With pipet, add 2.0 mL conc. H_2SO_4 by letting it run down the neck of the bottle. Replace stopper, avoiding air.

8. If three samples were done, average the three volumes of $\text{S}_2\text{O}_3^{--}$ used.
9. Calculate the conversion factor: $\text{CF} = \text{gm Cr}_2\text{O}_7^{--} \text{ actually weighed} \times 32.63 / (\text{X}) \text{ mL S}_2\text{O}_3^{--} \text{ used to titrate.}$

5. Invert until all ppt is dissolved. Solution will turn brownish as iodine forms. Distribute iodine evenly throughout the solution before using.
6. Measure, as exactly as possible, a 203 mL sample into an Erlenmeyer flask.
7. Record initial volume of thiosulfate and titrate until a pale straw-yellow color is reached (most, but not all, of the iodine has been used up). Use white paper underneath to see the color better.
8. Add 1-2 mL of starch solution. Solution should turn the familiar blue color.
9. Continue titration (not much farther to go, now) until blue color goes away. The color may return later on due to contaminants in the water, but don't worry about it. Take final reading. You only get one try per H_2O sample--there's not enough for an average--so make it a good one.
10. Do the calculation: $\text{mL S}_2\text{O}_3^{--} \text{ used} \times \text{CF} = \text{mg O}_2/\text{L H}_2\text{O.}$