SAULT COLLEGE OF APPLIED ARTS & TECHNOLOGY

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COURSE OUTLINE

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EXPERIMENT 1

THE DENSITIES OF LIQUIDS AND SOLIDS

One of the fundamental properties of any sample of matter is its density, which is its mass per unit of volume. In terms of the base units of the International System, the density of water is 1000.00 kg/m^3 at $4^{\circ}C$. In more common units it is expressed as 1.00000 g/cm^3. Densities of liquids and solids range from values less than that of water to values considerably greater than that of water. Osmium metal has a density of 22.5 g/cm^3 and is probably the densest material known at ordinary pressures. The densities of liquids and solids change with changes in temperature, in general decreasing slowly with increasing temperature, and slightly increasing with increasing pressure under ordinary conditions. Any change in the density of a given sample results from a change in volume, since the mass of a sample is not a function of temperature or pressure. The densities of gases can vary considerbly with either pressure or temperature changes. Gas densities will be the subject of a later experiment.

In any density determination, two quantities must be determined - the mass and the volume of a given quantity of matter. The mass can easily be determined by finding the "weight" of the substance on a balance. The quantity we usually think of as "weight" is really the mass of a substance. In the process of "weighing" we find the mass, taken from a standard set of masses, that experiences the same gravitational force as that experienced by the given quantity of matter we are"weighing". The mass of a sample of liquid in a container can be found by taking the difference between the mass of the container plus the liquid and the mass of the empty container.

The volume of a liquid can easily be determined by means of a calibrated container. In the laboratory a graduated cylinder is often used for routine measurements of volume. Accurate measurement of liquid volume is made by using a pycnometer, which is simply a container having a precisely definable volume. The volume of a solid can be determined by direct measurement if the solid has a regular geometrical shape. Such is not usually the case, however, with ordinary solid samples. A convenient way to determine the volume of a solid is to measure accurately the volume of liquid displaced when an amount of the solid is immersed in the liquid. The liquid used in such an experiment should not react with or dissolve the solid and, as you may readily surmise, should have a lower density than the solid.

PART A: WEIGHING OPERATIONS

After you are shown how to operate the analytical balance in your laboratory, obtain a sample (about 1.5 g) of metal eg. copper and/or nickel shot (or slug). Place it in a weighing bottle that has been pre-weighed to the nearest 0.001 g. Weigh the bottle plus metal sample also to the same degree of precision. Record the mass of each on the data sheet in your laboratory notebook immediately. Then calculate the mass of the metal sample obtained from the mass of the weighing bottle and the mass of the bottle plus metal.

Repeat the weighing, if necessary, to satisfy yourself that you have mastered the weighing technique and recognize the limitations of uncertainty or precision associated with the balance.

Most of the experiments you will perform have directions which will enable you to obtain as precise results as your equipment will allow.

PART B: DENSITY OF A LIQUID

If your flask is not clean and dry, clean it with soap and water, rinse it with a little acetone, and dry it by letting it stand for a few minutes in the air or by gently blowing compressed air into it for a few moments.

Weigh the dry flask with its stopper on the analytical balance, or the toploading balance if so directed, to the nearest milligram. Fill the flask with distilled water until the liquid level is nearly to the top of the ground surface in the neck. Put the stopper in the flask in order to drive out all the air and any excess water. Work the stopper gently into the flask, so that it is firmly seated in position. Wipe any water from the outside of the flask with a towel and soak up all excess water from around the top of the stopper.

Again weigh the flask, which should be completely dry on the outside and full of water, to the nearest milligram. Given the density of water at the temperature of the laboratory and the mass of water in the flask, you should be able to determine the volume of the flask very precisely. Empty the flask, dry it, and fill it with your unknown liquid. Stopper and dry the flask as you did when working with the water and then weigh the stoppered flask full of the unknown liquid, making sure its surface is dry. This measurement, used in conjunction with those you made previously, will allow you to find accurately the density of your unknown liquid.

PART C: DENSITY OF A SOLID

Pour your sample of liquid from the flask into its container. Rinse the flask with a small amount of acetone and dry it thoroughly. Add small chunks of the metal sample to the flask until the flask is about half full. Weigh the flask, with its stopper and the metal, to the nearest milligram.

Leaving the metal in the flask, fill the flask with water and then replace the stopper. Roll the metal around in the flask to make sure that no air remains between the metal pieces. Refill the flask if necessary, and then weigh the dry, stoppered flask full of water plus the metal sample. Properly done, the measurements you have made in this experiment will allow a calculation of the density of your metal sample that will be accurate to about 0.1 per cent.

Pour the water from the flask. Put the metal in its container. Dry the flask and return it with its stopper and your metal sample to the stockroom.

Name_____ Class_____ Date_____
Section_____

DATA AND CALCULATIONS: Densities of Liquids and Solids

Metal slug no._____ Mass of slug_____

Unknown liquid no._____ Unknown solid no._____

Density of unknown liquid

Mass of empty flask plus stopper _____ g

Mass of stoppered flask plus water _____ g

Mass of stoppered flask plus liquid _____ g

Mass of water _____ g

Volume of flask (density of H_2O at 25°C, 0.9970 g/cm^3, at 20°C, 0.9982 g/cm^3) _____ cm^3

Mass of liquid _____ g

Density of liquid _____ g/cm^3

To how many significant figures can the liquid density be properly reported? _____

Density of unknown metal

Mass of stoppered flask plus metal _____ g

Mass of stoppered flask plus metal plus water _____ g

Mass of metal _____ g

Mass of water _____ g

Volume of water _____ cm^3

Volume of metal _____ cm^3

Density of metal _____ g/cm^3

Would you expect the per cent error in the metal density to be higher or lower than the per cent error in the liquid density as obtained in this experiment?

_____

Why?

Name_____ Class_____ Date_____
Section_____

ADVANCE STUDY ASSIGNMENT: Densities of Solids and Liquids

1. In an experiment a student was asked to measure the densities of an organic liquid and a metal. He was given a small flask with a ground-glass stopper, which he found weighed 31.601 g when empty. He filled the flask with water and weighed the full, stoppered flask, recording a mass of 60.735 g in a room at about 25°C. He dried the flask, filled it with organic liquid, and found that the flask then weighed 56.796 g. Then he dried the flask again and added some of the metal to it; the flask plus the metal weighed 99.323 g. He filled the flask with water, leaving the metal in the flask, and found that after he had removed all the air bubbles the flask with the metal and the water weighed 120.827 g. From the data the student obtained, calculate the volume of the flask, the density of the metal, and the density of the organic liquid.

Volume of flask _____ cm^3

Density of organic liquid _____ g/cm^3

Density of metal _____ g/cm^3

2. Give the effects of the following errors on the value of the density of the metal as obtained in Problem 1. Explain your reasoning in each case.

a. The flask was not quite dry when weighed the first time.

b. The value recorded for the mass of the flask plus the metal was 98.323 g. rather than 99.323 g.

DILUTION OF SAMPLES (i)

EXPERIMENT 2

INTRODUCTION

Occasionally, when conducting tests on water obtained from natural sources, it is necessary to dilute the sample prior to analysis. This procedure is particularly used in water samples taken for bacterial counts.

Often individual bacteria colonies in a given water sample are too numerous to count accurately. As a result, a series of dilution is necessary. Dilution in effect produces a lower bacterial population density for a given sample volume.

As required for a good dilution technique, the invetigator creates a homogenous solution by shaking the water sample vigorously. Agitation combined with careful use of a clean pipette allows the investigator to bring bacterial counts as well as some chemical concentrations down to a manageable level.

A process called serial dilutions is a progressive dilution technique that takes a volume of sample through a series of progressive dilutions to produce a desired final concentration.

SERIAL DILUTION MODELS

NO. OF ML TO START	DILUTION	FINAL CONCENTRATION	
50	450	$1X10^{-1}$	(A)
50	450	$1X10^{-2}$	(B)
10	90	$1x10^{-}3$	(C)
50	450	$1X10^{-4}$	(D)
5	495	$1X10_{-5}$	(E)
1	999	$1X10^{-6}$	(F)

DILUTION OF SAMPLES (ii)

LAB 2...CONTINUED

PURPOSE: To acquaint the student with the technique of serial dilution.

APPARATUS: (PER GROUP)

1. 4-500 ml volumetric flasks.
   1-1000 ml volumetric flask.

2. 1-100 ml volumetric flask.

3. Masking tape or labels.

4. 1-5 ml pipette.
   1-1 ml pipette.
   1-10 ml pipette.
   1-50 ml pipette.

5. Wash bottle.

6. Stock sample (available at front desk)

***N.B.** Be sure to rinse the pipettes with distilled water between each stock sample withdrawal.

PROCEDURE

1. Shake stock sample (1 M KCl) vigorously 25 times.

2. Immediately using a 50 ml pipette, withdraw 50 ml of the stock sample into a 500 ml volumetric flask. Label 1 x 10^{-1}. **[SOLUTION A]**. Top off this and all following dilutions with distilled water to the line indicated on the flask.

   Note: Use a wash bottle to fill flask when approaching the line, to control the filling.

3. Shake stock sample 25 times and immediately withdraw 50 ml of the stock sample into a 500 ml volumetric flask. Label 1 x 10^{-2}. **[SOLUTION B]**. Fill.

4. Shake the 1 x 10^{-1} dilution (#A) vigorously 25 times and immediately withdraw 5 ml into a 500 ml flask. Label $1x10^{-3}$. **[SOLUTION C]**. Fill.

5. Shake the 1 x 10^{-2} dilution and withdraw 50 ml into a 500 ml flask. Label 1 x 10^{-4}. **[SOLUTION D]**. Fill.

6. Shake the 1 x 10^{-3} (#C) dilution and withdraw 5 ml into a 500 ml flask. Label 1 x 10^{-5}. **[SOLUTION E]**. Fill.

DILUTION OF SAMPLES (iii)

7. Shake the 1 x 10^{-4} (#C) dilution and withdraw 1 ml into a 1000 ml flask. Label 1 x 10^{-6}. **[SOLUTION F]**. Fill.

8. Measure the conductivity of each of the dilutions. Be sure to rinse the conductivity bridge beaker/container with distilled water prior to each measurement.

9. Record conductivity readings.

10. Determine percent errors using the following formula:

$$\frac{\text{observed conductivity - expected conductivity}}{\text{expected conductivity}} \times 100$$

QUESTIONS FOR DISCUSSION

1. Briefly discuss the importance of serial dilutions. Give some other practical examples of when serial dilutions are used.

   N.B. Be sure to give reasons for any discrepancies in your results from those expected.

CONDUCTIVITY UNITS

British Units: Micromhos per centimetre (umhos/cm)

S.I. Units: Millisiemens per Metre (m^S/m)

1 $m^S/m = \frac{1}{100}$ m^S/cm = 10 umhos/cm OR

1 m^S/cm = 100 m^S/cm = 1000 umhos/cm

E.G. a reading of 3.11 m^S/cm = 311 m^S/m = 3110 umhos/cm

DILUTION OF SAMPLES (iv)

TABLE 2

EXPERIMENT 3

ACIDS, BASES, BUFFERS AND pH

GOAL: To observe how acidic, basic and buffer solutions relate to the pH scale.

APPARATUS AND REAGENTS:

- small dropper bottles of the following solutions: 0.1 M HCl, 1 M NaOH, 1 M HCl, 1 M NH_4OH, and 1 M $HC_2H_3O_2$
- pH hydrion paper (range 1 to 12)
- distilled water
- a buffer solution
- antacid tables such as Alka-Seltzers, Tums or Rolaids
- white vinegar
- urine
- soap solution
- mortar and pestle
- stirring rods
- test tube rack
- graduated cylinders (10 mL)
- pH metre

BACKGROUND:

The acid-base balance is a critical factor for many solutions. This balance in blood must be maintained at a fairly narrow range for life to be sustained. The acid-base balance of processed food must be controlled to prevent spoilage. This balance is monitored in such processes as corrosion prevention, electroplating, photography and agricultural to produce optimum results.

Acids in solutions yield hydronium ions (H_2O^+). The following equation describes the reaction for hydrogen chloride dissolved in water to yield hydronium ions.

$$HCl + HOH \dashrightarrow H_3O^+ + Cl^-$$

Since all acid solutions contain H_3O^+ ions; a system to measure the concentrations of H_3O^+ ions in solution known as the pH scale, ranging from 0 to 14, has been devised. Table 3-2 illustrates how the scale relates to the concentration of H_3O^+. The pH of a water solution containing H_3O^+ ions is defined as:

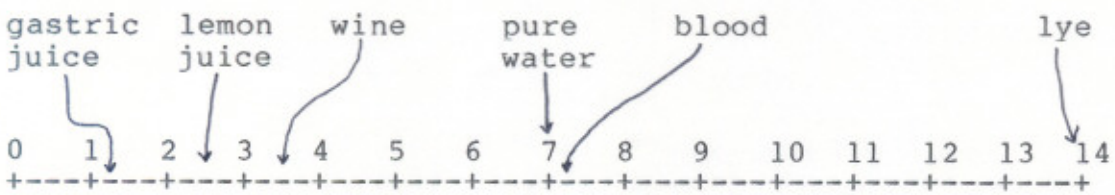
$$pH = -\log[H_3O^+]$$

Note that the product of the $[OH^-]$ and the $[H_3O^+]$ is a constant value, $1.0 * 10^{-14}$.

The pH of some common substances is shown in Table 3-1 along with the conditions for acidic, basic and neutral solutions to exist.

Table 3-1

Acidic Solutions	Neutral Solutions	Basic Solutions
$[H_3O^+] > [OH^-]$	$[H_3O^+] = [OH^-]$	$[H_3O^+] < [OH^-]$
$pH < 7$	$pH = 7$	$pH > 7$



ACIDS/BASES (iii)

Table 3-2

The pH Scale for Water Solutions

$[OH^-]$	$[H_3O^+]$	$\log[H_3O^+]$	$-\log[H_3O^+]$	pH	
$1.0 * 10^{-14}$	$1.0 * 10^{0}$	0	0	0	
$1.0 * 10^{-13}$	$1.0 * 10^{-1}$	-1	1	1	
$1.0 * 10^{-12}$	$1.0 * 10^{-2}$	-2	2	2	increas-
$1.0 * 10^{-11}$	$1.0 * 10^{-3}$	-3	3	3	ingly
$1.0 * 10^{-10}$	$1.0 * 10^{-4}$	-4	4	4	acidic
$1.0 * 10^{-9}$	$1.0 * 10^{-5}$	-5	5	5	
$1.0 * 10^{-8}$	$1.0 * 10^{-6}$	-6	6	6	
$1.0 * 10^{-7}$	$1.0 * 10^{-7}$	-7	7	7	neutral
$1.0 * 10^{-6}$	$1.0 * 10^{-8}$	-8	8	8	
$1.0 * 10^{-5}$	$1.0 * 10^{-9}$	-9	9	9	
$1.0 * 10^{-4}$	$1.0 * 10^{-10}$	-10	10	10	increas-
$1.0 * 10^{-3}$	$1.0 * 10^{-11}$	-11	11	11	ingly
$1.0 * 10^{-2}$	$1.0 * 10^{-12}$	-12	12	12	basic
$1.0 * 10^{-1}$	$1.0 * 10^{-13}$	-13	13	13	
$1.0 * 10^{0}$	$1.0 * 10^{-14}$	-14	14	14	

PROCEDURE:

pH Hydrion Paper - pH hydrion paper includes a variety of dyes which give a predominant color at definite pH levels. To determne the pH of a solution, use a stirring rod to touch a drop of the solution to t a strip of pH hydrion paper and match the resulting color to the color code shown on the hydrion paper container. Use this procedure to test for pH of a solution throughout the experiment.

1. **The pH of Common Substances** - add about 1 mL of the following substances to small test tubes: tap water, vinegar, urine, saliva, a pinch of antacid tablets ground and added to water, 1 M HCl, 1 M $HC_2H_3O_2$, 1 M NaOH and 1 M NH_4OH. Determine and record the pH of each solution.

2. **$[H_3O^+]$ and the pH Scale** -

A. Label four small tst tubes in $[H_3O^+]$ as 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4}. Add 3 mL of 0.1 M HCl to the first test tube.

B. Using a graduated cylinder, add 1 mL of 0.1 M HCl soltuion to 9 mL of distilled water and mix. Pour 3 mL of this solution into a second test tube and save the remaining solution for Step C.

C. Add 1 mL of the remaining solution above to 9 mL of distilled water in a clean, dry graduated cylinder and mix. Add 3 mL of this soltuion to the third test tube. Save the remaining solution for Step D.

D. Add 1 mL of the remaining solution above to 9 mL of distilled water and mix. Add 3 mL of this solution to the fourth test tube.

E. Determine and record the pH values in your data table. Save the samples for part 5.

3. **Neutralization** -

A. To a small test tube add 5 mL of distilled water and 2 drops of 1 M NaOH. Record the pH. Next, to the same test tube, add dropwise, while counting, 1 M HCl until the pH equals 7. Record the number of drops needed for neutralization.

B. To five mL of distilled water, add 2 drops of 1 M NaOH. Note the pH. Next, to the same test tube add, while counting drops, 0.1 M HCl until the pH equals 7. Record the number of drops needed for neutralization.

4. Buffer Action -

A. Add 10 mL of distilled water to a small beaker and record the pH. Add 1 drop of 1 M $HC_2H_3O_2$ and note the pH in the data table. Continue with this procedure until 5 drops of acid have been added.

B. Repeat the above procedure substituting 1 M NH_4OH for the acid solution.

C. Repeat Step A above substituting 10 mL of buffer of pH 7 for the water.

D. Repeat Step B above substituting 10 mL of buffer of pH 7 for the water.

5. Measure the pH of the samples in part 2 using a pH meter. Record your results.

ACIDS/BASES (vi)

EXPERIMENT 3

NAME _____

SECTION _____

1. The pH of Common Substances

Substance	pH
tap water	
vinegar	
urine	
saliva	
antacid tablet	
1 M HCl	
1 M $HC_2H_3O_2$	
1 M NaOH	
1 M NH_4OH	

2. $[H_3O^+]$ and the pH Scale

$[H_3O^+]$	10^{-1}	10^{-2}	10^{-3}	10^{-4}	Test Method
pH					Papers
					Meter

3. Neutralization

Solution	Neutralized by:
2 drops NaOH	____ drops of 1 M HCl
2 drops NaOh	____ drops of 0.1 M HCl

4. Buffer Action

Using Buffer pH 7 as the Solvent

# drops acid	pH	# drops base	pH
1		1	
2		2	
3		3	
4		4	
5		5	

Using Water as the Solvent

# drops acid	pH	# drops base	pH
1		1	
2		2	
3		3	
4		4	
5		5	

QUESTIONS:

1. What is the ratio of the concentration of H_3O^+ in solutions of pH 3 and pH 4?

2. Find the $[OH^-]$ in each of the four solutions in Part 3.

   Solution 1:

   Solution 2:

   Solution 3:

   Solution 4:

3. How do you account for the difference in pH of a 1 M HCl solution as compared to a 1 M $HC_2H_3O_2$ solution?

4. How do you account for the differences in pH of a 1 M NaOH solution as compared to a 1 M NH_4OH solution?

5. What generalization can you make about the volume and concentrations of acid needed to neutralize the base solution in Parts 3-A and 3-B?

6. How does pH of a buffered solution change upon the addition of acid or base compared to an unbuffered solution? Why do you think a buffer is included in certain medications such as aspirin?

EXPERIMENT 4 - TOTAL INFLECTION POINT ALKALINITY

INTRODUCTION (From Environmental Dynamics Section Fisheries Branch, Ont. Min. of Nat. Res., Toronto, March, 1980)

In recent years serious concern has arisen for the potential consequences of acidic precipitation on aquatic and terrestrial ecosystems. The widespread occurence of this phenomenon has now been well documented throughout North America and Europe. However, at this time, the number and distribution of waters susceptible to acidification in Ontario is not known with any degree of accuracy. To address this deficiency the Ontario Ministry of Natural Resources initiated a water chemistry monitoring program in 1979 as part of a larger Ontario program entitled "Acidic Precipitation in Ontario Studies" (A.P.I.O.S.).

The susceptibility of a lake or stream to acidification is primarily a function of the loading of acid it receives, and its buffering capacity (ability to neutralize acids). Total inflection point alkalinity (TIP) is perhaps the best single measure of a lake's residual capacity to neutralize acidic inputs. This exercise has been selected from a M.N.R. manual for field personnel who are carrying out the sampling and field titrations necessary for the determination of TIP alkalinity.

APPARATUS:

N.B. DO NOT USE ACID RINSE ON GLASSWARE

1. 1-pH meter and electrode.
2. 2-400 ml beakers. Label one "Waste Water" and one "Sample".
3. 1-wash bottle.
4. pH 4 buffer and 100 ml beaker labelled "pH 4".
5. pH 7 buffer and 100 ml beaker labelled "pH 7".
6. 1-100 ml volumetric flask.
7. Stirrer and stir bars.
8. Buret.
9. Gran Titration Alkalinity Form.
10. Thermometer.

REAGENTS:

1. 1 liter 0.010 N H_2SO_4.

PREPARATION OF pH METER

1. **Power Source**

   A.C. - for line operation, slide power switch at rear of instrument to "A.C." and connect the A.C. line cord to the line receptacle.

   BATT. - for battery operation, slide power switch to "BATT". Battery installation is covered in the Sargent Welch manual provided.

2. **Electrode Connection**

   a) Remove the universal glass electrode and the reference electrode from the storage boxes. Insert glass electrode in holder and tighten plastic thumb screw gently. Do not overtighten or the electrode will break. Before inserting reference electrode, remove cap. Next, slide rubber sleeve up, exposing the hole in the side of the probe or remove small cap to expose hole in the side arm projection. Place in the holder as per instructions for glass electrode. Be careful not to knock either electrode against the holder. Avoid touching glass especially the glass tips. This will help prevent contamination and scratches which will ruin the electrodes.

   N.B. If crystals are present in the reference probe or the level of electrolyte is low (i.e., 10mm below hole), see instructions in Section 4.1 "Maintenance of Probes".

b) Plug the pin connector of the reference probe into the black jack marked "REF" on the rear panel, and the connector of the glass electrode into the jack marked "GLASS". Note the socket for the glass electrode is spring loaded. Push the plug in and hold while tightening the thumb screw so it locates the groove on the plug.

3. Standardizing the Meter

The pH meter must be standardized each day it is used, but does not have to be standardized for each sample. With the operation switch at "OFF", the meter should read 7.00. If it does not, adjust the reading. Turn the screwdriver adjustment directly below the meter needle. This is called the 'ZERO POINT ADJUSTMENT' (mechanical).

a) Slide the electrode holder to the top of the stand. Place the beaker marked "Waste Water" under the electrodes. Using the deionized water bottle, rinse each electrode and the stirring rod. Dry each with a Kimwipe.

   N.B. It is essential that all rinsing be done with deionized water.

b) Add at least 100 mL of pH buffer "7" to the appropriate beaker marked "7". Do not mix up beakers. Always use the same beakers for same buffers.

c) Immerse the probes into the buffer so that the probe tips and the stirrer are covered sufficiently but not touching bottom or sides. Turn on the stirrer by attaching clips to battery. It should not splash or hit the sides of the beaker or probes.

d) Turn the operation switch to "STDBY". No warm-up time is necessary.

e) Measure the temperature of the pH 7 buffer with a clean thermometer and set the temperature dial of the meter accordingly. (Should be approximately room temperature). Allow 30 seconds for the temperature reading to stabilize.

   N.B. Rinse off the thermometer with deionized water. Dry with a Kimwipe.

f) Rotate the operation switch to the "READ" position.

g) Use the standardization control to set the meter reading to exactly 7.00. Align needle with its mirror image.

h) Slide the electrode holder up so that the probes are clear of the top of the beaker. Remove the beaker with the pH 7 buffer. Replace the beaker marked "Waste Water". Rinse the electrodes and stirrer with deionized water allowing water to run into beaker. Dry electrodes and stirrer with Kimwipes.

i) Remove beaker. Replace with pH 4 beaker containing 100 mL of pH 4 buffer.

j) Immerse probes into buffer solution and turn on the stirrer. Set temperature dial to temperature of pH 4 buffer (should be the same temperature as pH 7 buffer. If not, follow instructions as in "e)" above.

k) Turn the operation switch to "READ" and set the Buffer adjust control (screw driver control at right rear of instrument) until the meter indicates the exact value of the buffer, i.e., 4.00.

l) Turn the operation switch to "STDBY". Turn off stirrer. Rinse and dry probes as per "g)" and "h)".

THE METER IS NOW STANDARDIZED

N.B. If the meter is not to be used immediately (i.e., more than one minute), the probes should be immersed in deionized water to avoid drying out. If the meter is to be stored for a greater length of time, (i.e., several hours), the probes must be immersed in pH 7 buffer.

THE TITRATION PROCEDURE

1. PREPARATION OF TITRATION SAMPLE

a) Rinse "Sample Beaker" with deionized water. Dry thoroughly with Kimwipe.

b) Using a pipette, measure out 50 mL of sample water from the sample bottle. Transfer the sample into the sample beaker, allowing the pipette to drain thoroughly. (Do not blow out small portion in tip.)

N.B. Never put sample in a beaker which has previously contained a buffer.

2. INITIAL pH MEASUREMENT

a) Immerse dry probes into sample and turn stirrer on.

b) Measure the temperature of the sample with a clean, dry thermometer. Adjust the temperature dial to the sample temperature.

N.B. The temperature should be between 15-25^{o} C and no more than 5^{o}C different from the buffer temperature. If the sample temperature is too cool, leave the sample with stirrer on and allow it to come up to room temperature. This should only take a few minutes. It is better, however, to leave sample in capped volumetric flask to "warm up" if the sample is obviously too cool to start preparation.

c) Turn operation switch to "pH". The instrument will now indicate the pH of the sample.

N.B. Read the meter to an accuracy of 2 decimal digits. e.g., 6.95.

d) Record this initial pH on the Gran titration form opposite to where volume of acid added equals zero.

3. TITRATION OF SAMPLE

The next steps involve titrating the sample with acid from the buret which will cause the pH of the sample to decrease. The amount of acid added each step is recorded as well as the resultant pH change. Follow the methodology described below very carefully.

The critical range in which total inflection point (T.I.P.) alkalinity is determined is from pH 5.5 to 3.5. Twenty points minimum are required in this range, therefore a maximum change of 0.10 pH units per addition of acid is permitted. The pH will change most rapidly in the range closest to the inflection point, therefore the smallest acid additions are advised in this range - pH 5.25 - 4.50. Note as well, that no less than 0.02 mL acid (approximately one drop) should be added at any one time. The following chart recommends the maximum permitted volumes of acid that should be added in different pH ranges.

pH	Maximum Volume of Acid Aliquot (mL)
greater than 7.5	2.0
7.5 - 5.5	1.0
5.5 - 5.25	0.5
5.25 - 4.50	0.2
4.50 - 3.75	0.5
3.75 - 3.50	0.75
3.50 & less	1.0

These are recommended guidelines. Only additions less than or equal to these are acceptable; none should be greater .

N.B. Before titrating the sample, make sure that the buret is primed and contains no air bubbles.

a) Record titration starting time and date on Gran titration form.

b) Add acid to sample. N.B. Buret should be positioned so that acid is not released onto side of beaker, probes or stirrer.

c) Read pH value on meter after needle has stabilized (usually several seconds).

d) Record volume of acid added and resultant pH on Gran titration form. Accumulative volume of acid added is entered after complete titration of sample.

e) Continue to titrate by following instructions in "b)" and "c)" above until pH reaches 5.5 + 0.1.

N.B. If pH starts to drop rapidly, it will be necessary to decrease the amount of each acid solution.

f) When pH 5.5 is reached, reduce the volume of acid to 0.1 or less regardless of previous rate of change of pH.

g) Continue to titrate and record pH readings as in steps above, keeping to the recommended acid aliquots as outlined at the beginning of this section.

N.B. Keep a close watch on rate of change of pH. At least 30 readings should be obtained between the range 5.5-3.5.

The size of the volume increments of acid added can be changed to smaller or larger amounts at any time but should not be more than the maximum allowd for each pH range. If a drop of acid is left on the tip of the buret, do not attempt to knock it off.

h) When pH 3.5 is obtained, do not stop titrating. Continue making additions and taking readings until curve flattens out. Complete form including the accumulative total of acid added.

i) Draw a graph of pH on the vertical axis versus volume of acid added on the horizontal axis.

j) From the graph, determine the end point and record the volume of acid added to neutralize the alkalinity to the specific pH.

k) Calculate total alkalinity in mg of $CaCO_3$/Liter.

$$T.A. = \frac{A \times N \times 50\,000}{\text{mL of sample}}$$

where: A = mL of titrant to specific pH end point
N = Normality of Acid Titrant

QUESTIONS FOR DISCUSSION

1. Define alkalinity and pH of natural aquatic systems.
2. What are the environmental ranges of alkalinity and pH for natural waters?
3. What is acid rain and generally how do reduced pH levels affect a lake ecosystem? (Consult literature.)
4. What factors determine a lake's susceptibility to acid precipitation? (i.e., What factors determine a lake's alkalinity?)

Gran Titration - Alkalinity

Aliquot of Acid Added	Accumulative Volume	pH

Gran Titration - Alkalinity

Aliquot of Acid Added	Accumulative Volume	pH

EXPERIMENT 5 - PELLET PREPARATION/CALORIMETRY

INTRODUCTION

The caloric value of ecological materials is an important determination in understanding the energy dynamics of individual populations. Energy content of many plants and animals can be obtained using an oxygen bomb calorimeter.

Caloric value of any given plant or animal is a function of its:

1. Genetic constitution
2. Nutritive condition
3. Life history

Because these factors may vary with species, seasons and environmental conditions, the investigator making intensive measurements of energy flow through natural systems cannot depend on caloric constants or equivalents.

APPARATUS/MATERIAL

1. plant and animal samples
2. shears, sieves (No. 40)
3. air-tight containers
4. mortar and pestle
5. measuring boats (3)
6. pellet press with punch and die
7. benzoic acid
8. scupula, tweezers
9. drying oven
10. petri dishes with lids
11. dessicating chamber
12. accurate balance

PELLET PREPARATION/CALORIMETRY (ii)

METHOD

1. All materials on which the calorimetric determination is to be made are to be collected at least two weeks prior to the pellet preparation lab. They should be clearly labelled and placed in a drying oven for at least a week at approximately 50°C. (Skip to #6 if browse have already been ground.)

2. Materials to be made into pellets should be removed from the drying oven just prior to the laboratory and stored in an air-tight container.

3. Each sample should be carefully selected so as to be representative of the material to be selected. For example, if browse from different species of plants is used, twigs of equal length containing an equal quantity of various parts (buds, lateral buds, etc.) should be used throughout.

4. All samples should then be carefully cut up with pruning shears or by other appropriate method into small parts. Be careful not to lose any parts as they are brittle at this stage. Note that while only a one-gram pellet is used in the final analysis, a much larger quantity (perhaps 10 g) must be prepared in order to obtain representative samples for determination.

5. After the samples have been cut into small pieces, grind the sample into a powder with a ceramic mortar and pestle. Certain parts will be difficult to grind up. These should be separated from the powdered portion by sieve and further ground until all parts of the sample are reduced to powder form. Once all of your sample is ground up, you will be ready to make up a pellet.

6. Weigh out approximately 1.1 g of sample and approximately 2.3 g of benzoic acid. Record weights accurately. Put both in a mortar and mix well for five minutes.

7. Measure out approximately 1 g of mixture and form a pellet using the pellet press and die. (0.9990-1.0010 g) (See instructor for demonstration.)

8. If pellet is loose and crumbling, weigh out and then add more benzoic acid to mixture and form another pellet.

9. <u>DO NOT HANDLE PELLET WITH HANDS</u>, use tweezers to place pellet in a pre-weighed measuring boat for accurate weighing. Determine weight of benzoic acid in each pellet using the weight ratio of the orignal mixture. Be accurate.

PELLET PREPARATION/CALORIMETRY (iii)

10. Acceptable pellets should be placed in separate petri dishes. Student group, date, type of sample and benzoic acid content is recorded on dish. Place dishes in dessicating chamber.

11. Proceed with calorimetric determination in a subsequent class.

EXPERIMENT 5 - OXYGEN BOMB CALORIMETRY TECHNIQUE

PURPOSE

To assess the energy value (in calories) of different common foods of wildlife and fish species and to relate these calorific values to energy-consumng activities.

MATERIALS

Oxygen Bomb Calorimeter
Balance
Dissecting Kit
Kimwipes
1.0 ml. Pipette
Pelletized food samples
1000 ml graduated cylinder

Parts of the Calorimeter

The oxygen bomb calorimeter consists of: a) the bomb or container in which the combustible sample is ignited; b) the oval bucket which holds a measured quantity (2 litres) of distilled water and in which the bomb, the thermometer and the stirrer are immersed; c) the jacket which insulates and protects the bucket from temperature variations.

PROCEDURE

A. Assembling the Bomb:

1. Remove the bomb head carefully from the bomb and place it on the support stand. There are two electrodes hanging below the bomb head; one has a loop which holds the sample container and fuel pellet. A piece of fuse wire must be attached between the two electrodes as indicated in the attached sketch (Figure 1). This fuse wire must be cut to approximately 10 cm and its initial weight must be recorded.

2. At the balance, weight the small sample container provided and record its weight. Remove a fuel pellet from the dessicator, remembering to handle the pellet only with the forceps, and place it in the sample container. Record the total weight and subtract the two values to find the actual weight of the pellet.

3. Place the sample container with the fuel pellet on the loop electrode, making sure that the fuse wire touches the top of the pellet. The fuse wire must touch the pellet in order to ignite it. Make sure the wire does not touch the side of the sample container or the wire will be shorted out and you will have to start over.

4. Using a pipette, put 1.0 ml of distilled water in the bottom of the bomb. The head of the bomb can now be replaced on the bomb. Screw the retainer ring down adequately to secure it temporarily. The entire bomb should now be clamped into its holder on the bench using a wrench to tighted it securely. Using both hands, firmly screw down the retaining ring on the head of the bomb. Don't forget you have to get the top off later.

B. Pressurizing the Bomb:

The procedure that follows must be performed carefully to avoid accidents. The correct process will be demonstrated to you and must be followed during each and every test that you perform. It is necessary to subject the bomb to about 30 atmospheres of pressure of oxygen to ensure complete combustion of the fuel. To do this:

1. Turn the main oxygen tank valve on by turning it counter-clockwise, the black needle on the small dial will move indicated the volume of air present in the air cylinder.

2. Connect the threaded hose coupling from the oxygen pressure tank to the top of the bomb calorimeter.

3. Now turn the black secondary valve slowly in the counter-clockwise direction. Watch the larger dial closely - it indicates the bomb pressure level. As the pressure reaches 30 atmospheres, it should automatically turn off. Do not allow the pressure of the bomb to exceed about 32 atmospheres under any circumstances. If this should occur, you will hear a loud noise - the air inside the bomb will have to be released using the relief valve situated on the top of the bomb, and the bomb will have to be refilled properly. In order to remove the threaded coupling from the top of the bomb, the pressure from the hose must be released using the black valve located below the larger dial. Once the hose is removed, replace the removable thumb nut. The bomb is now pressurized.

C. Assembling the Calorimeter

1. The oval bucket should be prepared next. Using the 1 litre graduated cylinder, measure two litres of distilled water and pour it into the bucket. The distilled water should be cool. Grasp the bomb valve between the thumb and forefinger and lower the bomb into the water, taking care to avoid jarring or disturbing the contents. Set the bomb with its feet spanning the locating boss and turned so that the electrode terminal

is near the insulated ignition wire. Attach the thrust terminal to the bomb electrode and shake back into the bucket all drops of water adhering to the fingers. Now set the filled bucket in the jacket with the long axis of the oval bucket in line with the operator, making sure that the bucket is secure between the four supports in the bottom of the jacket. Place the cover on the jacket with the thermometer toward the operator. Lower the cover into position, using care to avoid striking the thermometer against anything. The locating pin at the rear of the cover should fall into the hole in the top rim of the jacket, thereby properly aligning the assembly. Put in the rubber drive belt and start the motor.

D. Recording Temperature:

1. Allow the stirrer to run for five minutes to equalize water temperature throughout.
2. Read and record temperatures to the nearest $0.01^{\circ}F$ at one minute intervals for five minutes.
3. At the beginning of minute six, press the button on the ignition unit to fire the charge.
4. Record temperature every 15 seconds for the first three minutes. The rate of rise will be rapid during the first few minutes and decreases as the calorimeter approaches a maximum temperature.
5. Record temperature every minute until the recordings have remained constant for three successive readings. The temperature rise curve should be similar to the one illustrated in Figure 2.

E. Opening the Calorimeter:

After the readings are completed, stop the motor, remove the belt and lift the cover from the jacket. Wipe the thermometer bulb with a clean cloth to remove any water and set the cover on its stand. Disconnect the firing connection from the bomb terminal and lift the bucket and bomb out of the jacket. Lift the bomb out of the bucket and fasten it securely in the bench clamp. Relieve all residual pressure from the bomb by slowly turning the relief valve on the top of the bomb until the air begins to leak out at a uniform rate. After the pressure has been relieved, remove the screw cap. Lift out the bomb head and place it on the support stand. Evidence of soot inside the bomb indicates incomplete combustion and therefore results should be discarded.

ASSEMBLING AND PRESSURIZING THE BOMB

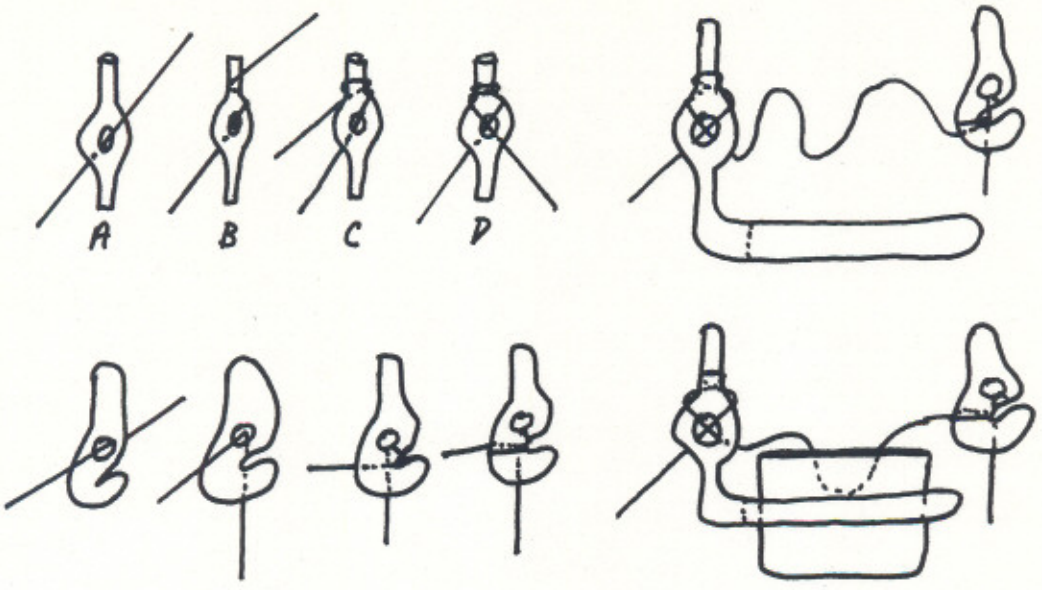


FIG 1 ATTACHING FUSE WIRE

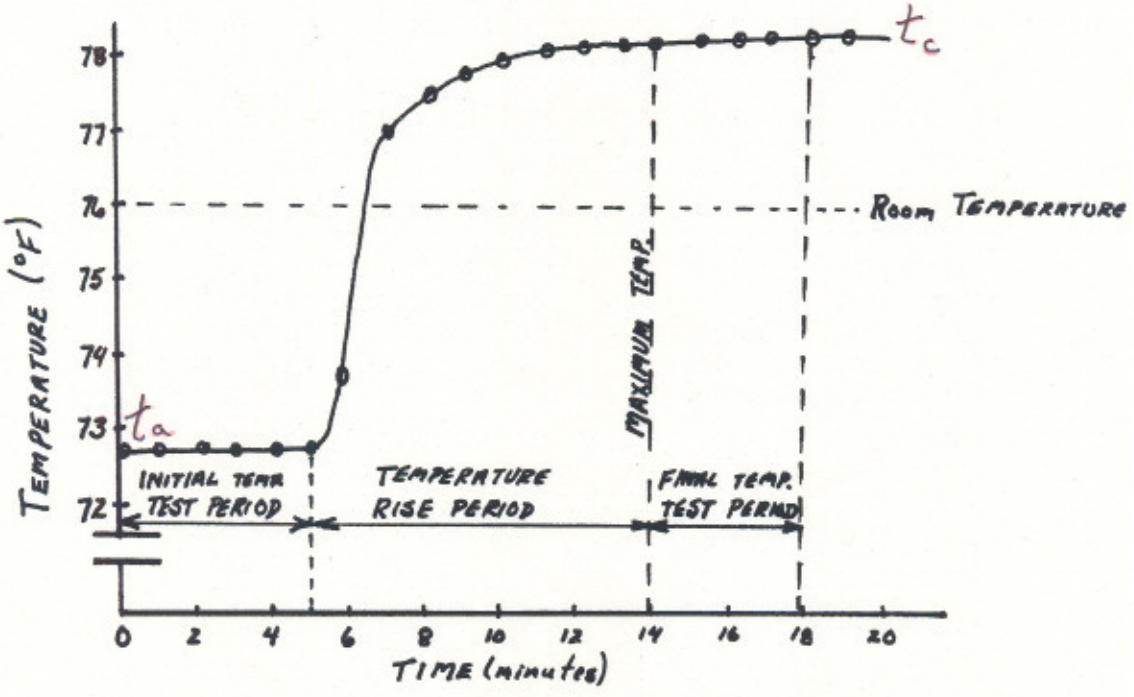


FIG 2 TEMPERATURE CURVE

F. Calculations and Correction Factors:

1. Acid Titration: Reactions during the combustion of the fuel may result in the formation of acidic products (eg. HNO_3) which consume heat energy. This must be accounted for by calculating the amount of acid produced by titrating it against 0.0705 N NaOH. Wash all interior surfaces of the bomb with a jet of distilled water and collect all the washings in a 250 mL flask. Titrate with 0.07225 N NaOH, using phenolphthalein as an indicator. Record the number of mLs needed for the titration. **[Note: This procedure may be omitted at the discretion of the instructor.]**

2. Fuse Correction: Remove all unburned pieces of fuse wire from bomb electrodes, weigh them and subtract this value from the initial fuse wire weight. Enter the difference as net weight of fuse wire burned on the data sheet.

3. Sulfur Correction: Factor is disregarded because it is negligible.

4. Calculate the gross heat of combustion for each prepared pellet using the formulae and sample calculation below as a guide:

STANDARD FORMULA:

$$Hg = \frac{(\text{change in temp.})(W) - (e_3 + e_4)}{\text{mass of sample}}$$

Where: Hg is the calorific value of sample

W is the energy required to increase the temperature of the bomb by one Celcius degree (2465 cal/^{o}C)

Change in temperature is the initial temperature minus the final temperature

e_3 is mass of the fuse wire multipled by the calorific value of the wire (1400 cal/g.)

e_4 is the correction for benzoic acid. The mass of benzoic acid in the pellet multiplied by the calorific value of benzoic acid

Mass of the sample is the mass of the pellet minus the mass of benzoic acid in the pellet

[Sample Run]

Sample #: 204-2-W Name: Faye Frank

Determination #: 1 Date: July 18 /85

DATA:

Mass of sample:	1.3005 g
Mass of benzoic acid:	2.6002 g
% benzoic acid in mixture:	66.66 %
Mass of pellet:	1.0165 g
Mass of sample in pellet:	0.3389 g
Mass of benzoic acid in pellet:	0.6776 g
Std. calorific value of benzoic acid:	6338 cal/g
Initial mass of fuse wire:	0.0161 g
Final mass of fuse wire:	0.0090 g
Mass of fuse wire consumed:	0.0071 g
Std. calorific value of fuse wire:	1400 cal/g

Time (minutes)	Temp. (°C)	Time (minutes)	Temp. (°C)
at stabilization:	19.30	8	21.80
1	19.50	9	
2	20.90	10	
3	21.45	11	
4	21.65	12	
5	21.78	13	
6	21.80	14	
7	21.80	15	

[Sample...continued]

CALCULATIONS:

Standard Formula: $Hg = \dfrac{(\text{change in temp.})(W) - (e_3 + e_4)}{\text{mass of sample in pellet}}$

change in temp. = Final - Initial =

$W = 2465.18$ cal /°C

e_I = omit

$e_3 = 1400\ \text{cal/g} \times 0.0071\ \text{g} = 9.94\ \text{cal}$

$e_4 = 6338\ \text{cal/g} \times 0.6776\ \text{g} = 4294.63\ \text{cal}$

m(sample) = 0.3389 g

$$Hg = \frac{(2.50\ ^\circ\text{C})(2465.18\ \text{cal}/^\circ\text{C}) - (9.94\ \text{cal} + 4294.63\ \text{cal})}{0.3389\ \text{g}} = 5469.62\ \text{cal/g}$$

Where:

W = energy equivalent of calorimeter in calories per degree Farenheit of Centigrade

e_3 = correction for heat of combustion of firing wire, in calories
= mass of fuse wire x std. calorific value of wire

e_4 = correction for heat of combustion of benzoic acid in the pellet, in calories
= mass of benzoic acid in pellet x calorific value of benzoic acid

Sample #:_____ Name:_____

Determination #:_____ Date:_____

DATA:

Mass of sample: ----------

Mass of benzoic acid: ----------

% benzoic acid in mixture: ----------

Mass of pellet: ----------

Mass of sample in pellet: ----------

Mass of benzoic acid in pellet: ----------

Std. calorific value of benzoic acid: ----------

Initial mass of fuse wire: ----------

Final mass of fuse wire: ----------

Mass of fuse wire consumed: ----------

Std. calorific value of fuse wire: ----------

Time (minutes)	Temp. (°C)	Time (minutes)	Temp. (°C)
at stabilization:	_____	8	_____
1	_____	9	_____
2	_____	10	_____
3	_____	11	_____
4	_____	12	_____
5	_____	13	_____
6	_____	14	_____
7	_____	15	_____

CALCULATIONS:

Standard Formula: $$Hg = \frac{(\text{change in temp.})(W) - (e_3 + e_4)}{\text{mass of sample in pellet}}$$

change in temp. = Final - Initial =

W =

e_I =

e_3 =

e_4 =

m(sample) =

Hg =

Where:

W = energy equivalent of calorimeter in calories per degree Farenheit of Centigrade

e_3 = correction for heat of combustion of firing wire, in calories
= mass of fuse wire x std. calorific value of wire

e_4 = correction for heat of combustion of benzoic acid in the pellet, in calories
= mass of benzoic acid in pellet x calorific value of benzoic acid