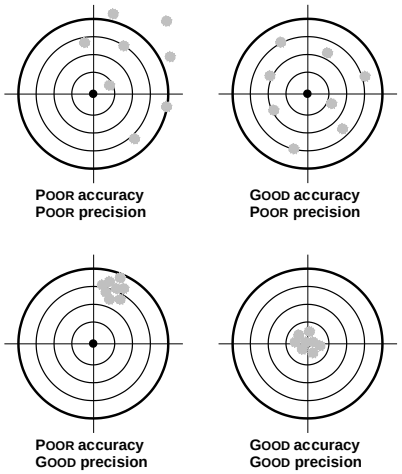
VANCOUVER ISLAND UNIVERSITY

CHEM 311
ENVIRONMENTAL CHEMICAL ANALYSIS
LABORATORY MANUAL



Prepared by Dr. Erik Krogh, Dr. Chris Gill,
Shelley Gellein, and Peter Diamente

Department of Chemistry, 2018

ENVIRONMENTAL CHEMICAL ANALYSIS
2018 LAB SCHEDULE CHEMISTRY 311

Sept. 7th	**Introduction to a Chemical Analysis Laboratory:** Good Laboratory Practices, Data Analysis, Technical Reports and Full Lab Reports.	
Sept. 14th	**Introduction to Metering Devices** (pH, Turbidity, Conductivity and DO) Calibration, Precision and Data Reporting Data Tables	**Due: Sept. 20th**
Sept. 21st	**Field Trip** – TBA Sample Collection/Field Analysis Assignment: Principle of Method, Data and Results	**Due: Oct. 4th**
Sept. 28th	**Alkalinity of Natural Waters** Volumetric Analysis Technical Report - Data, Calculations and Results	**Due: Sept. 27th**
Oct. 5th	**Carbon Dioxide in Air** Gravimetric Analysis and Back Titration Technical Report - Data, Results and Discussion	**Due: Oct. 11th**
Oct. 12th	**Dissolved Oxygen in Surface Waters** Winkler Titration (azide modification) Full Lab Report	**Due: Oct. 23rd**
Oct. 19th	**Nitrites/Nitrates in Drinking Water** Spectrophotometry/Calibration Curves Technical Report – Data, Calculations, and Results	**Due: Oct. 30th**
Oct. 26th	**Ortho-Phosphates in Wastewater** Spectrophotometry/Standard Additions Full Lab Report	**Due: Nov. 6th**
Nov 2nd	**Fluoride in Groundwater and Toothpaste** Ion Selective Electrode Technical Report – Data, Calculations, and Results	**Due: Nov. 13th**

Group Rotations Next Four Weeks (Two Week Labs)
Lab start dates: Nov. 9th and Nov. 23rd
One Full Report, One Technical Report due: **Nov. 22nd** and **Dec. 4th**

Group I	**Heavy Metals in Sediment** Digestion, Atomic Absorption Spectroscopy	
Group II	**Organic Contaminant Analysis** Sample Preparation, Chromatography/Internal Standards	

Full Lab and Technical Reports *are due 11 calendar days following the completion of the lab. A late penalty of 10% per week applies for reports up to two weeks, after which they will NOT be accepted.*

TABLE OF CONTENTS

INTRODUCTION **Page**

List of Experiments iv
Lab Reports v
Typical Marking Scheme vi
Cheating and Plagiarism vii
General Laboratory Procedures viii
How to Read an Analytical Method ix
Laboratory Safety xi
General Laboratory References xii
Introduction to Good Laboratory Practices xiii
LAB 0 – Good Laboratory Practices Exercise xxvii

EXPERIMENTS

LAB 1 – Introduction to Metering Devices 1

LAB 2 - Alkalinity of Natural Waters 13

LAB 3 - Carbon Dioxide in Air 19

LAB 4 - Sample Collection and Field Analysis Trip 23

LAB 5 - Dissolved Oxygen in Surface Waters 27

LAB 6 - Nitrates in Drinking Water 31

LAB 7 - Ortho-Phosphates in Wastewater 37

LAB 8 - Fluoride Ion in Groundwater and Toothpaste 41

LAB 9 - Metals: Cu and Fe in Marine Sediments 45

LAB 10 - Organic Contaminants: Caffeine in Water 53

APPENDICES

Glossary of Terms 65

Basic Statistics Review for Analytical Chemistry 67

Comments on Student Lab Reports 79

Summary of Canadian Drinking Water Guidelines back cover

LIST OF EXPERIMENTS

One Week Labs (Wet Chemical Techniques)

Lab Orientation, Introduction to GLPs and GLP Exercise
(no marks)

1. **Introduction to Metering Devices**
(Data Tables/5)

2. **Alkalinity of Natural Waters**
(Data, Calcs and Results Tables/10)

3. **Carbon Dioxide in Air**
(Data, Calcs, Results, Discussion/15)

4. **Sample Collection and Field Analysis Trip**
(Rationale, Principles, Results/10)

5. **Dissolved Oxygen in Surface Waters**
(Full Report/20)

6. **Nitrates in Drinking Waters**
(Full Report/15)

7. **Ortho-Phosphate Analysis in Wastewater**
(Full Report/20)

8. **Fluoride Ion in Groundwater and Toothpaste**
(Full Report/15)

Two Week Labs (Sample Prep and Instrumental Analysis)

9. **Metals in Sediment**
(Technical Report/20)

10. **Organic Contaminants**
(Technical Report/20)

FULL LAB REPORTS

CHEM 311 Lab Reports are submitted as stand-alone formal reports (unless otherwise noted) that are to be written in an impersonal voice in typed format. Your lab report should outline the principles of the chemistry and/or instrumentation employed, calibration techniques, data handling, an estimate of experimental uncertainty and a general awareness of the context and significance of the results.

TITLE PAGE AND IDENTIFICATION: Course number. Name of student. Name of partner. Date. Unknown #. The title should provide the reader with both the analyte and the matrix studied and give some indication of the technique employed. E.g., The Analysis of Fluoride Ion in Toothpaste Using an Ion Selective Electrode.

PRINCIPLE OF METHOD: Describe the principles involved in relating the *measured quantity* (e.g., volume of titrant, absorbance, potential etc.) to the *analyte concentration*. For wet chemical techniques, include the stoichiometry of chemical reactions that will be used in the calculation of results. For instrumental techniques, describe the principle of operation of the instrument itself. Schematic diagrams may be useful for instrumental methods**. *Do not describe details of the procedure here.***

PROCEDURE: Reference the Lab Manual and specify modifications.

DATA: Tabulate data with descriptive headings and footnotes providing details. Data tables should be able to stand alone providing enough information that the reader could carry out necessary calculations without having to go hunting for additional information. For example, in a data table summarizing titration volumes, be sure to include the titrant concentration and the sample volume.

CALCULATIONS AND RESULTS: Show a representative calculation used to convert measured quantities into reported results. Include calculations used to estimate uncertainties. Figures and graphs must be properly labeled. Use spreadsheets (such as Excel) to carry out repetitive calculations and generate calibration curves (include equation of best fit line and correlation coefficients). In most experiments you will be expected to estimate the experimental uncertainty either as a standard deviation or with a 95% confidence limit.

DISCUSSION: State your result/s and give some context for the magnitude (high, medium or low). For example, report the levels of Fluoride ion in commercial toothpaste, other foodstuffs or drinking water. Be sure to convert to common concentration units, if necessary. Comment on the precision (RSD) and/or accuracy (% bias) of the method using your data and the reported values given in *Standard Methods*. Discuss possible interferents and other sources of error. Conclusion paragraph should clearly report final results for all samples with 95% CL and *n* (# of replicates).

LITERATURE COMPARISON: Briefly summarize one alternative method of analysis used to measure the same analyte. Explain how the analyte is quantified and summarize any advantages/disadvantages of the alternate method. You may use the primary literature such as *Analytical Chemistry* or secondary sources such as *Standard Methods* or an Analytical Chemistry textbook.

REFERENCES: All references cited in the report should be listed as numbered endnotes in the style adopted by *Analytical Chemistry*.

TYPICAL MARKING SCHEME (Full Report)

The following represents a typical marking scheme. Actual marking schemes for a particular lab may vary.

	Mark	Max. Mark
Technique/Preparation – preparedness, timeliness and ability to work carefully in a clean an organized manner.		**1**
Principle of Method – explain the type of analysis, include relevant chemical equations and/or theory of instrumental operation, including calibration technique. Addresses the theory that relates the measured signal to a meaningful quantitative result. Does not include procedural details.		**3**
Data – complete, clearly presented tables including all pertinent information and uncertainty in measurements.		**3**
Calculations – correct, organized, clearly presented including error analysis to give uncertainty in the final result. Include calibration curves, if any.		**3**
Results – level of agreement between your result/s and the known or true value for an unknown or environmental sample.		**3**
Discussion – clearly state your result/s and give some context for the magnitude (high, medium or low). Comment on the precision (RSD) and/or accuracy (% bias) of the method using your data and the reported values given in *Standard Methods*. Discuss possible interferents and other sources of error. Conclusion paragraph should clearly report final results for all samples with 95% CL and *n* (# of replicates).		**4**
Literature Comparison – include brief overview of essential aspects of an alternate method for the same analyte or alternate analyte using the same method. Use *Standard Methods*, text or library references.		**2**
Layout/Organization – includes pertinent information on title page, proper section headings, labelled figures and/or graphs, all sources of information (references) properly cited as end-notes.		**1**
TOTAL		**20**

		Conc. F (ppm)	Uncertainty (ppm)	Slope
Unknown	Reported			
	True Value			
SRM	Reported			
	True Value			

GENERAL LABORATORY PROCEDURES

General Procedures

1. Labs are conducted in pairs. You will need to be organized and divide tasks to complete the labs in the allocated time.

2. Glassware will be provided on an as needed basis during the lab period. Students should come to the lab prepared with a list of required glassware and an organized work plan.

   Note: You may need to pre-rinse some glassware prior to use.

3. In order to avoid contaminating supplied chemical reagents, a sufficient quantity of reagents should be transferred to an appropriate receptacle, e.g. small beaker or weigh boat. A reagent bottle should always be returned to its allocated place after use.

   Note: NEVER RETURN A CHEMICAL TO THE REAGENT BOTTLE.

   Note: ALWAYS HANDLE PRIMARY STANDARDS AND STOCK SOLUTIONS WITH CARE. CONTAMINATION WILL LEAD TO POOR RESULTS FOR YOU AND OTHERS.

4. At the end of the laboratory period: All glassware should be thoroughly washed (including a final rinse with deionized water) and left on the return cart. All electrical apparatus should be switched off and unplugged. All taps should be turned fully off and all waste should be placed in the appropriate waste container.

5. No student should attempt unauthorised experiments in the laboratory. Students may, on occasion, schedule laboratory work provided permission from an instructor has been obtained. A student must not use the laboratory in the absence of the laboratory supervisor or technician.

6. No chemicals or equipment should be removed from the laboratory at any time.

HOW TO READ AN ANALYTICAL METHOD

Preparing Standard Solutions

The procedure for a particular experiment states "make up a series of standards from your stock solution, from X to Y concentration." How do you proceed?

There are several important pieces of information hidden in the above instructions.

1. "make up … from your stock solution": all of your standards will originate from this solution. In some cases, where a wide range of concentrations is required, you may need to prepare a 'sub-stock' solution (diluted stock), which you will then use to make your most dilute standards.
2. "a series of standards": in some cases you will be told to make a certain number of standards; in others it is left to your discretion. Generally, four or five standards are used to prepare a calibration curve. You must prepare at least three standards.
3. "standards … from X to Y": this is the concentration range that your standards will cover. Your most dilute standard will have a concentration of X. Your most concentrated standard will have a concentration of Y. Units will depend on the experiment.
4. the dilutions you use to make your standards must be calculated to 'fit' the glassware available. You will have access to 1, 2, 5, 10, 20, 25 and 50 mL volumetric pipettes. You also have 25, 50, 100, 200, 250, 500 and 1000 mL volumetric flasks. Calculate your dilutions so they 'fit' this equipment. (e.g., 1.5 mL into a 150 mL flask is an impossible dilution with your equipment. How else could you get the same dilution factor?)
5. All dilutions used to make standards are done using volumetric glassware.

Analytical Shorthand

Rather than spell out exactly how quantities should be measured every time, analytical chemists use a shorthand based on the precise use of language and significant figures. Read through the following examples and 'translate'. If you can't see the difference between the instructions, ask your lab instructor!

"weigh 1 gram of sample"
"weigh exactly 1.0000 gram of sample"
"weigh about 1 g of NaCl exactly"
"add 1 mL of reagent"
"add 1.00 mL of reagent"
"dilute to 1 L in a volumetric flask"
"dilute to 75 mL"

Your translation should include: the type of equipment used, the technique used, and the amount of reagent used.

Units

A word on units: you will spend a lot of your time as an analytical chemist converting between units. If you have worked in an analytical lab, you already know about it. Set up a list of conversions for yourself or create an Excel spreadsheet to do this for you. It will save you a lot of time and needless errors later.

mg/L
μg/mL
moles/L
mg/kg
mg/g
wt/wt %
mg/L
ng/mL

Hint: use scientific notation and base SI units.
For example, mg/L = 10^{-3}g/L ≅ 10^{-3} g / 1000 g solution ≡ 'parts per million' by mass.
The symbol ≅ indicates that these quantities are not exactly equal, but are often used that way.

The Plan

You will need to have an experimental plan organized prior to arriving in the lab.

1. The information you have in the lab manual must be reprocessed to create an "analytical method", i.e., a plan. Some of that reprocessing is described above, for example preparing calibration standards.
2. Create your plan using numbered steps or a flow chart, so you can track where you are. Set it up, if you like, so you can check off each step you complete.
3. Number the steps so you can make the most efficient use of your time in the lab.
4. Be aware of time requirements. For example, if your standard will be made from a chemical in the drying oven, it will take some time for it to cool. This might be your first step.

"I can't figure this out …"

Take pity on your Instructor and all the students around you. Ask this question BEFORE your lab period. No, not just 10 minutes before - at least the day before! The more planning you do, the less time you will need in the lab. Planning requires a pen and paper, writing out your sequence of steps, analyzing and modifying as you go. Hint: highlighters are nice, but by the time your whole page is yellow it doesn't really help you much. Rewrite the methods for yourself in point form in your lab book.

LABORATORY SAFETY

A chemical laboratory is a potentially dangerous environment; the hazards of fire, cuts, burns and poisoning being most prevalent. It is a safe practice to assume all chemical reagents are potentially hazardous. While the use of particularly toxic or carcinogenic reagents is generally avoided, some of the reagents in this lab are dangerous. Check the MSDS and consult your instructor for more information. The first line of defence for skin contact is to flush with plenty of water. Two eyewash stations are provided for the immediate flushing of eye splashes. In the event of an accident, contact your instructor immediately. Safety rules will work only if you obey them and encourage others to obey them. Please familiarise yourself with the following regulations.

Personal Safety

- There must be no smoking or eating in the laboratory.
- Students must wear safety glasses at all times. Safety glasses are available. Contact lenses should be removed prior to entering the laboratory. Prescription glasses may be worn, but should be covered with safety glasses.
- Students are recommended to wear laboratory coats in the laboratory.
- Many of the chemicals in the laboratory are poisonous whether taken orally or absorbed through the skin. If any chemical is swallowed the supervisor should be summoned immediately. If any chemical comes into contact with the skin it should be washed off immediately with plenty of water.
- While heating a substance in a test tube, care should be taken to ensure that the mouth of the test tube is not pointing at anyone. A student should never look down into a test tube that is being heated.
- Concentrated acids and bases; strong oxidising and reducing agents; flammable solvents and toxic chemicals should be treated with respect.
- Always wash your hands prior to existing the lab and before eating.

Fire

- In the event of fire, the flames should be extinguished with one of the extinguishers in the laboratory and the supervisor notified immediately.

Spillages and Fumes

- All breakages and minor spills of chemicals should be reported immediately to the supervisor or technician without delay.
- A receptacle in the laboratory is reserved solely for broken glassware.
- Any experiment involving the evolution of pungent odours or fumes must be carried out in the fume hood.
- Students are accountable for their own actions in the laboratory and this Department will not accept liability for accidents that occur due to irresponsibility on the part of a student or students.

Material Safety Data Sheets (MSDS)

- Material Safety Data Sheets summarize physical and chemical properties of all chemical reagents used in this laboratory. In addition, the MSDS sheets contain information on the hazards and toxicity effects. MSDS can be found in the prep room and should be consulted if there is any question regarding the safety of materials encountered.

MSDS contain information in the following nine categories:

1. product information
2. hazardous ingredients
3. physical data
4. fire and explosion data
5. reactivity data
6. toxicological properties (health effects)
7. preventive measures
8. first aid measures
9. preparation data of MSDS

GENERAL LABORATORY REFERENCES

1. Standard Methods for the Examination of Water and Wastewater (21st Ed.), APHA, 2005.
2. Water Analysis Handbook, (2nd Ed.), Hach Co., Loveland, 1992.
3. Environmental Sampling and Analysis for Technicians, M. Csuros, Lewis Publishers, Boca Raton, 1994.
4. Drinking Water Chemistry: A Laboratory Manual, B.A. Hauser, Lewis Publishers, Boca Raton, 2001.
5. Laboratory Manual for the Examination of Water, Wastewater and Soil (3rd Ed.), H.H. Rump, Wiley-VCH, New York, 1999.
6. Water Quality and Pond Soil Analysis for Aquaculture, C.E. Boyd, C.S. Tucker, Auburn University, 1992.

INTRODUCTION TO GOOD LABORATORY PRACTICES (GLPs)

The following notes on proper experimental technique and use of equipment are collectively known as GLPs. It is assumed that the student is familiar with and always practices the following procedures outlined in this section. Your laboratory instructor will be evaluating your experimental technique. Failure to practice the following will lead to poor results and poor technique. Both of these are graded. Exceptions to standard GLPs must be noted in your lab report.

1. Cleaning and Storing Glassware

Care must be taken to ensure that glassware is thoroughly clean before use. However, recognize that soap can be a serious chemical contaminant. Do not clean your glassware with soap unless specifically instructed. In general, glassware will be supplied clean, acid washed and thoroughly rinsed with deionized water. Properly cleaned glassware is indicated by the presence of an unbroken film of water on the surface. It is seldom necessary to dry glassware before use; in fact this practice should be discouraged because it wastes time, can be a cause of contamination and result in changes in volumetric glassware.

Always pre-rinse burets and volumetric pipettes with the titrant or solution to be transferred prior to use. Note that rinsing is most effectively accomplished with a greater number of small portions, rather than a smaller number of large portions.

Rinse all glassware with tap and distilled water after use. **Never let reagents dry in volumetric glassware.**

2. Housekeeping

Good housekeeping is important for the **safety** and convenience of everyone, including the cleaning staff, who are not chemists. The analytical lab is a shared space. It is a busy place, and any mess you don't clean up will inconvenience many people. A mess will not impress your lab instructor and you certainly won't impress any future employers with poor, unsafe work habits.

Don't leave equipment and chemicals scattered over the benchtop; return them when you are finished using them. This allows others to use the same equipment, and prevents any accidents involving or resulting from your mess. Fumehood space is often at a premium, so clear out as soon as you no longer need to work there. When you are finished working, in the fumehood especially, clean the entire area with a damp paper towel. Clean up all chemical spills immediately, especially when the balances or other instruments are involved. Wash the outside of reagent bottles when you are finished using them. Drips and small spills may go unnoticed until they have had some time to react and cause a burn, at which point it is too late.

Never leave experiments unattended. If you must, especially in the case of reactions and digestions or anything that involves the use of hotplates and stirrers, inform your lab instructor

and have them or another student keep an eye on your experiment. Even if you have to leave the lab for only a minute to go to the bathroom, inform your lab instructor.

When using chemicals and supplies, use all of one container before opening another one, unless specifically directed to do otherwise by your lab instructor. Inform your lab instructor of any chemicals or supplies that are running low, including cylinders of compressed gases and printer supplies, so that there will be enough for the next student to complete their experiment. Also inform your lab instructor as soon as possible if anything is missing or if anything is broken, so that replacements can be obtained as quickly as possible.

Dispose of all refuse in the appropriate waste container as soon as possible; if in doubt ask your lab instructor. Questions are not 'stupid'; unlike endangering the lives and health of others. At the end of the lab, return all chemicals and equipment where they belong and clean up your work area. Double-check everywhere you worked, make sure that all equipment and supplies are returned, and all waste appropriately disposed (including any bench and fumehood space, the balances, instruments and sinks where you worked). As far as possible, shut down and turn off all equipment that you have worked with as soon as you have finished.

3. Use of Tap, Distilled and Deionized Water

There are three grades of water available for use in the lab:

- tap
- distilled/ reverse osmosis
- deionized

The three grades of water are progressively more expensive to produce. In general, *use only the minimum purity of water necessary* and do not waste water, particularly the more expensive grades. Distilled water will suffice for most uses.

4. Handling Reagents and Solutions

Successful analytical work depends on the purity and quality of the available reagents. A freshly opened reagent container can be used with confidence; whether or not the stated assay values for purity and impurities remain valid depends entirely on how the container has been handled since being opened. The purity of the chemical reagents available (and the quality of your results and, therefore, your marks) depends on strict adherence to the following rules.

Use small pre-cleaned beakers (in 10 and 20 mL sizes) for pouring out reagents. Any solid or liquid not used should be disposed of appropriately.

1 The possibility of contamination can be minimized by choosing the smallest bottle that will supply the required quantity of reagent. Ensure that the purity of the reagent is sufficient to prevent contamination and interferences and to reduce the blank to a minimum. In general, try to use only reagents whose purity you can be certain of (check assay values on the label).
2 Replace the top of the reagent container immediately after removal of the reagent.
3 Hold stoppers between the fingers; stoppers should never be set down on the bench or anywhere else except in the neck of the appropriate flask or reagent bottle.
4 Unless specifically directed to the contrary, never return any excess reagent or solution to a reagent bottle. Contamination of the entire bottle by returning excess reagent is a false economy - considerable time can be spent determining the source of any contamination (and consequent poor results), and the entire bottle then has to be disposed of and a new bottle obtained.
5 Before taking a bottle of chemical to the weighing room, first clean your spatula with deionized water. Scrub it dry with a Kimwipe. Now take your solid chemical to the weighing room and weigh it.
6 Keep reagent storage areas and the balances clean. Clean up any spilled chemicals immediately.
7 Do not use a new or unopened bottle of reagent without first obtaining the permission of the lab instructor.

5. Handling Solids

5.1 Balances

Both analytical and top-loading balances are available. Use the top-loading balances wherever possible, i.e., whenever the weight does not have to be exact or where an uncertainty of 0.01 g will suffice. For all work where the weight has to be known as exactly as possible, use the analytical balances.

Electronic Balances:
Most of you will have used the self-taring electronic balances in other courses. In general:

- Keep the balance pan and surrounding areas clean.
- Weigh solids into a container that is as light as possible.
- An initial tare weight is usually unneeded, since you can tare the container to zero.
- CLEAN UP when you are done

Detail: weighing solids
Ensure that the solid is of fairly uniform texture and will readily pour. If necessary, shake the capped reagent bottle and/or tap it on a wooden surface to break up any large lumps to allow the reagent to pour freely. Remove the cap and pour a slight excess into a clean, dry beaker or weighing boat. Immediately replace the cap on the reagent bottle and tighten it. Weigh reagent from the beaker or weighing boat into the desired container(s). If necessary, obtain additional solid from the reagent bottle as described above. When finished, return the sealed reagent bottle and properly dispose of the excess reagent.

5.2 Quantitative Transfers

After weighing a solid, it usually must be transferred in its entirety to a volumetric flask or beaker. This process is referred to as a quantitative transfer.

- Take your notebook, wash bottle, funnel and receiving vessel (beaker or flask) into the weighing room.
- After weighing your solid and recording the mass, rinse it from the weigh boat through a funnel into the receiving flask.
- Make sure all of the solid has been rinsed from the weigh boat and the funnel into the receiving flask.
- Remove the funnel while rinsing the stem into the flask.

5.3 Ovens and Desiccators

Most solids absorb atmospheric moisture and, as a consequence, change in composition. This effect can be substantial when a large surface area is exposed to a humid atmosphere, as with a reagent that is a fine powder. It is ordinarily necessary to dry such solids before weighing to free the results from dependence upon the atmospheric humidity. Oven drying is the most convenient method for removing absorbed moisture from a solid. This technique, of course, is not appropriate for samples that change composition at the temperature of the oven. Furthermore, with some solids the temperatures attainable in ordinary drying ovens are insufficient to completely remove bound water.

While cooling, dried material is stored in a desiccator to prevent the uptake of atmospheric moisture. The base of the desiccator contains a chemical drying agent. Samples are placed on a perforated plate that is supported by a constriction in the desiccator wall. Lightly greased ground-glass surfaces provide a tight seal between the lid and the base of the desiccator. Whether it is being replaced or removed, the lid of the desiccator is properly moved by a sliding, rather than a lifting, motion. An airtight seal is achieved by slight rotation and direct downward pressure on the positioned lid.

When handling heated objects manipulations should be practiced first, if necessary, to assure that adequate control can be maintained with the implements to be used. If using tongs, always place them on surfaces so the grips are in the air rather than resting on the surface (prevents contamination). When a heated object is placed in a desiccator, the increased pressure of the enclosed air may be sufficient to break the seal between the lid and the base, causing the lid to slide off and break. Upon cooling, the opposite effect is

likely to occur, the interior of the desiccator now being under a partial vacuum. Both of these conditions can cause the contents of the desiccator to be physically lost or contaminated. Although it defeats the purpose somewhat, it may be best to allow some cooling to occur before finally sealing the lid. It also helps to break the seal several times during cooling to relieve any vacuum that may be forming.

6. Measurement of Liquids

The reliable measurement of volume is usually performed with the pipet, the buret and the volumetric flask (weighing is accurate but time-consuming). Pipets and burets are ordinarily designed and calibrated to deliver specified volumes, whereas volumetric flasks are calibrated on a "to contain" basis. Volumetric equipment is marked by the manufacturer to indicate not only the manner of calibration (usually with a TD for "to deliver" or a TC for "to contain") but also the temperature for which the calibration strictly refers. The volume occupied by a given mass of liquid varies with temperature, as does the volume of the container holding the liquid. As a general rule, volumetric glassware should not be heated because the calibration can be permanently altered.

6.1 Dispensing liquid reagents

Estimate the total volume of liquid reagent required, including any needed for rinsing of pipets or other volumetric glassware. Pour a slight excess of the reagent into a clean, dry beaker. *(Note: If the beaker is clean but not dry, pour into the beaker enough reagent to rinse the inside of the beaker by tilting the beaker and swirling the reagent. Dispose of this reagent. Repeat this rinsing at least two more times, for a total of at least 3 rinsings, and then pour a slight excess of the liquid reagent into the clean, rinsed beaker*). For pipetting, you will want to take sufficient excess to ensure that no air is taken up into the pipet, probably 15% - 30%.

6.2 Pipets

There are different types of pipets. Most of the work in this course involves the use of volumetric pipets which deliver a fixed volume of liquid and graduated pipets. Carefully inspect graduated pipets to see if the graduations extend to the tip of the pipet - if they do not then the volume of the tip is not calibrated and the pipet should be drained only as far as the lowest calibration line. Liquids are drawn into pipets through the application of a slight vacuum. ***Never* pipet anything by mouth**, use a pipet bulb.

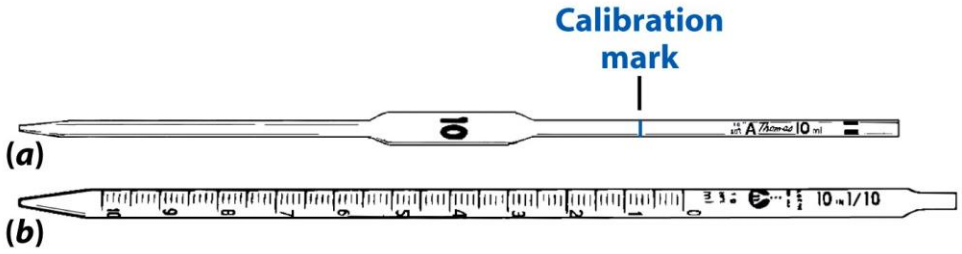


Figure 2-11
Quantitative Chemical Analysis, Seventh Edition

Carefully inspect the pipet for damage, especially the tip. Consult your lab instructor if in doubt about damaged pipets.

In general, when planning dilutions, attempt to use the largest volumetric pipet that is practical. For example, making a 1/10 dilution with a 5 mL pipet and 50 mL flask will be less accurate than making the same dilution using a 10 mL pipet and a 100 mL flask. For even better accuracy, you could use a 25 mL pipet and a 250 mL flask! These guidelines apply primarily to your standard solutions, and particularly to any that will be used for subsequent dilutions. If in doubt about your 'dilution plan', speak to your instructor before the lab.

1. Use volumetric transfer pipets to carry out dilutions of standard solutions.
2. Rinse the pipet: Draw a small quantity of the liquid to be pipetted into the pipet. Tip the pipet nearly horizontal, and rotate to thoroughly wet the interior surface, up to above the mark. Discard the liquid and repeat rinsing at least twice more, for a total of at least three rinsings.
3. Carefully fill the pipet somewhat past the mark. Quickly place a forefinger over the upper end of the pipet to hold the liquid. Ensure that there are no bubbles in the bulk of the liquid or foam at the surface.
4. Tilt the pipet slightly from the vertical, and wipe the exterior free of adhering liquid.
5. Slowly allow the sample to drain into a waste beaker by partially releasing the forefinger.
6. Halt further flow when the bottom of the meniscus touches the top of the graduation mark.
7. Place the tip of the pipet well into the receiving vessel, and allow the liquid to drain. When free flow ceases, rest the tip of the pipet against the inner wall or bottom of the receiving vessel for 10 s.
8. Finally, withdraw the pipet with a rotating motion to remove any droplet still adhering to the tip. The small volume remaining **is not** blown out or rinsed into the receiving vessel.

Thoroughly rinse the pipet with distilled water after use.

Note that only the upper part of the pipet should be handled. Do not touch or hold the bottom of the pipet to avoid contaminating the liquid being pipetted (and yourself!).

Table 1: Tolerances of Class A transfer (volumetric) pipets

Volume (mL)	Tolerance (mL)	Tolerance as a % of total volume
0.5	± 0.006	1.2
1	± 0.006	0.6
2	± 0.006	0.3
3	± 0.01	0.33
4	± 0.01	0.25
5	± 0.01	0.2
10	± 0.02	0.2
15	± 0.03	0.2
20	± 0.03	0.15
25	± 0.03	0.12
50	± 0.05	0.1
100	± 0.08	0.08

6.3 Micropipettors

Micropipettors are commercially available in various sizes; some deliver a fixed volume while others are adjustable within a given range. Common volumes for micropipettors in an analytical lab are 5 uL to 2000 uL. Micropipettors use disposable plastic tips. To prevent contamination of these tips, insert the clean pipettor (not your hand) into bag containing the tips and using your hand on the outside of the bag, slide a tip into place.

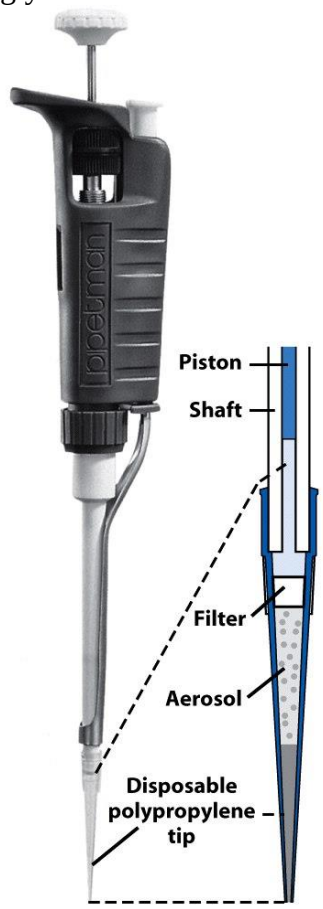


Figure 2-12ab
Quantitative Chemical Analysis, Seventh Edition

Once the disposable tip is firmly in place, the micropipettor is ready for use. Depress the button at the top of the micropipettor to the first stop position and place the tip into the liquid to be transferred. Release the button to pull up the solution and then remove the micropipettor. Place the tip into the receiving vessel and then depress the button at the top of the micropipettor to the second stop position. Depressing to the first stop ejects most of the solution drawn up, while the second stop 'blows out' the remaining solution. Some micropipettors have a third stop position which ejects the tip.

Fixed volume micropipettors are more accurate than the adjustable micropipettors. Typical values for accuracy and precision are given for Eppendorf™ brand micropipetteor.

Table 2: Fixed volume micropipettor specifications

Pipette volume (μL)	Accuracy (%)	Precision (%)
5	± 1.5	< 0.8
10	± 1.0	< 0.5
50	± 0.7	< 0.3
> 100	± 0.6	< 0.2

6.4 Measurement of liquids using a graduated cylinder

If the reagent bottle is small and/or easy to handle, the amount of reagent required may be poured directly into the graduated cylinder. Immediately replace the cap or stopper on the reagent bottle. Clean up any spills as noted above and return the reagent bottle. Any excess reagent can be removed from the graduated cylinder using a pasteur pipet; this excess is then disposed of. If the reagent bottle is large, difficult to handle or if you are worried about spillage (especially if the reagent is a concentrated caustic, for example) the reagent should be poured into a clean beaker and then from the beaker into the graduated cylinder. In this instance, excess reagent from the graduated cylinder is returned to the beaker. Since graduated cylinders are not used for exacting analytical measurements, the small amount of water remaining after cleaning normally does not need to be removed by drying or rinsing.

6.5 Volumetric Flasks

Fill the flask until the bulb of the flask is almost full. Stop and swirl the solution to achieve adequate mixing. Bring the liquid level almost to the mark and allow time for solutions to drain from the neck of the flask (and for thermal expansion to room temperature, if necessary). Use a pasteur pipet to carefully dilute to the mark. Firmly stopper the flask, and invert repeatedly (do not shake) to assure uniform mixing. For storage beyond one day, transfer the contents to a clean, dry storage bottle or one that has been thoroughly rinsed with several portions of the solution from the flask. If you are using aqueous solvents, it is unnecessary to dry glassware; rinse glassware with deionized water. In general, volumetric glassware (pipets and volumetric flasks) should not be placed in a hot oven to dry as the thermal expansion may distort accuracy.

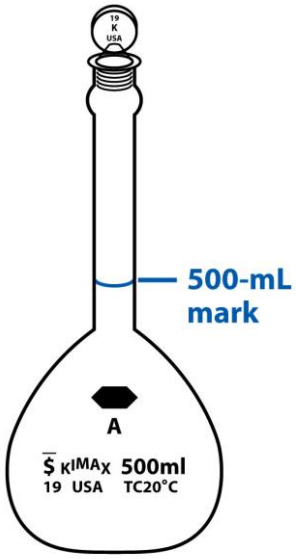


Figure 2-9a
Quantitative Chemical Analysis, Seventh Edition

Table 3: Tolerances of Class A volumetric flasks

Volume (mL)	Tolerance (mL)	Tolerance as a % of total volume
1	± 0.02	2
2	± 0.02	1
5	± 0.02	0.4
10	± 0.02	0.20
25	± 0.03	0.12
50	± 0.05	0.1
100	± 0.08	0.08
200	± 0.1	0.05
250	± 0.12	0.048
500	± 0.2	0.04
1000	± 0.3	0.03
2000	± 0.5	0.025

6.6 Burets

Burets are designed to deliver liquids primarily for the purpose of volumetric titrations. They are still widely used in an analytical laboratory and considered a 'reference' method for many analytes. A standard 50 mL buret is divided into 1 mL graduations with 0.1 mL sub-divisions. Leveling the eye with the bottom of the meniscus, an analyst should be able to interpolate volume readings to within 0.02 mL with a high degree of reproducibility.

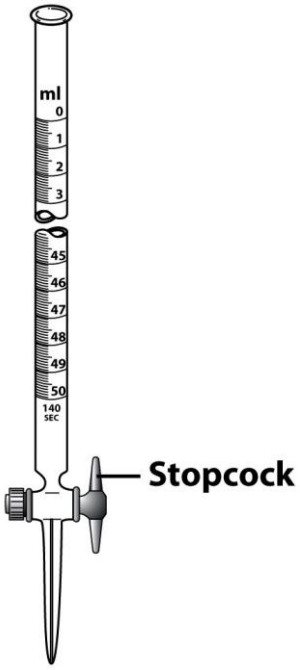


Figure 2-6a
Quantitative Chemical Analysis, Seventh Edition

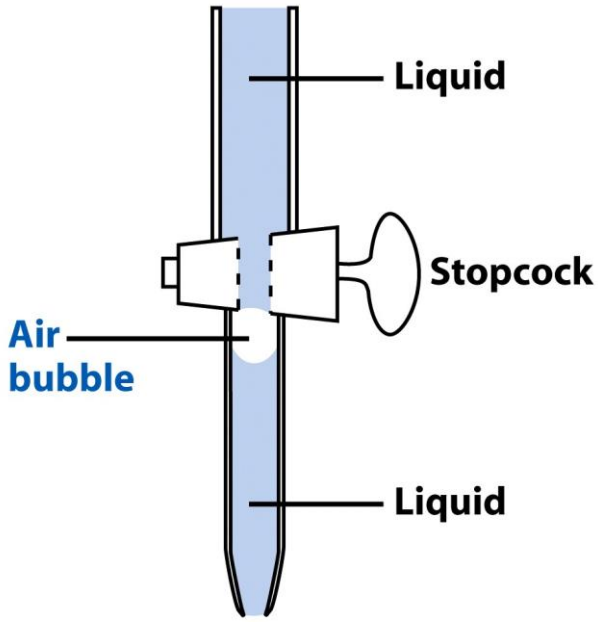


Figure 2-8
Quantitative Chemical Analysis, Seventh Edition

Filling burets

- Load 50 mL burets using a funnel.
- Rinse inside of buret including the valve and tip, with three small portions of titrant to be used.
- Fill the buret and run some titrant into a waste beaker checking for air bubbles in the tip.
- Make sure all air bubbles have cleared.
- Let the solution level stabilize and record the initial volume to nearest ±0.02 mL.

Titrating

- Control the stopcock valve with your non-dominant hand. This allows for finer control of the valve and swirling of the receiving flask with your dominant hand.
- If you know (by calculation or experience) the approximate volume to be delivered, you can add ~80% quickly and then slow down as you approach the endpoint.
- If the endpoint is to be determined by a colour change, you will observe a temporary change which disappears with swirling as you get close to the endpoint.
- To add less than a drop of titrant as the endpoint approaches, carefully adjust the stopcock valve until titrant just begins to flow. Close the valve and wash the hanging drop into the receiving flask with a wash bottle.
- Repeat the above step until the endpoint colour change is just barely visible and

permanent for more than 30 sec.

6.7 Digital titrators

Digital titrators are small portable devices designed to deliver minute volumes of titrant. They are convenient for field measurements (although less precise).

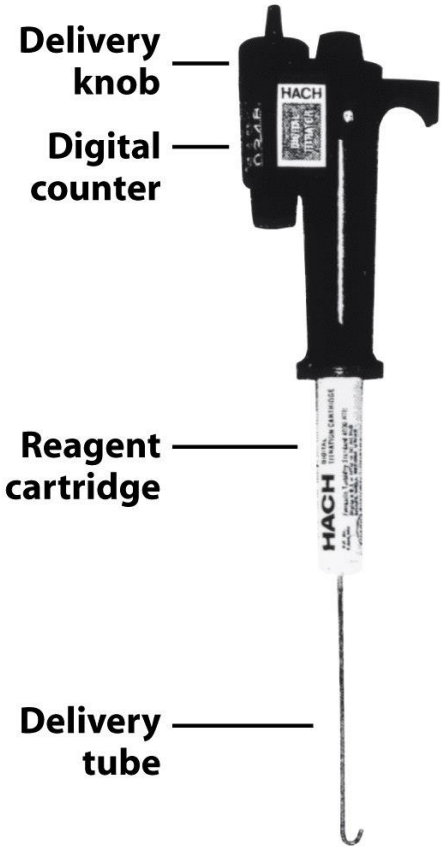


Figure 2-6b
Quantitative Chemical Analysis, Seventh Edition

Follow the instructions below for the use of digital titrators:

1. Choose the appropriate titrant Reagent Cartridge for the analyte and method chosen. Be sure to check both the titrant identity and concentration. Record the sample volume and the digit multiplier to be used.
2. With the titrator plunger fully retracted, slide the Reagent Cartridge into place.
3. Remove the Reagent Cartridge tip cap and replace with a Delivery Tube.
4. Depress the button on the plunger slider and slide the plunger until it meets resistance.
5. With the titrator in the vertical position (tip up) continue to slide the plunger by hand or by cranking the Delivery Knob to remove all air bubbles from the Reagent Cartridge and the Delivery tube. This will require wasting some of the titrant.
6. Wipe the outside of the Delivery Tube with a Kimwipe™ to remove excess titrant.
7. Re-set the Digital Counter to zero.
8. Titrate the sample to the specified endpoint.
9. Record the number on the Digit Counter and convert this to concentration of analyte using the multiplier appropriate for the particular method.

7. Quality Control Program

For most experiments, a 'quality control' sample, or QC, will be available and labeled as either a Certified Reference Material (CRM) or a Standard Reference Material (SRM). You will determine the concentration of analyte in the QC and compare that value to the known value. Accuracy is expressed as a % bias or % error and gives insight into the experimental method and/or the analyst.

Replicates are required or recommended in most cases to assess precision and are typically reported as relative standard deviations (RSD) or 95% confidence limits (CL's)

8. Sample Sequencing

Analytical laboratories have strict guidelines for sample analysis, which are required to meet various quality control standards. For CHEM 311, you will use the following sequence in all experiments, unless otherwise noted. In some cases, you may not have separate calibration and method blanks. Try to run at least one sample in triplicate; this will allow you to calculate precision estimates.

Table 4. GLP Order for Sample and Standard Analysis

Run #	Sample	Reason
1	calibration blank	set the instrument zero, or check for impurities
2	most conc. standard	make sure the instrument range is set properly
3	least conc. standard	rinse well before running this one!
4	remaining standards	
5	calibration blank	make sure instrument zero hasn't drifted
6	method blank	check sample preparation for contamination
7	samples ('unknown')	run the samples!!
8	QC sample	use to confirm the instrument is working properly, and standards are made correctly.
9	most conc. standard	make sure instrument response hasn't drifted

LAB 0: GOOD LABORATORY PRACTICES EXERCISE

OBJECTIVE

a) to prepare a *stock* and *standard* solution by volumetric dilution and

b) to standardize a solution of unknown concentration using the standard solution.

EXPERIMENTAL PROCEDURE

An accurately weighed quantity of sulfamic acid (a primary standard) is provided in a 100 mL volumetric flask. Prepare your stock solution of sulfamic acid (HSO_3NH_2) by diluting this solid to the 100.00 mL mark with deionized water. Ensure complete mixing of this solution with a minimum of 15-20 inversions. Using the mass information provided on the flask, determine the molarity of stock sulfamic acid.
(Molar Mass of HSO_3NH_2 = 97.10 g/mol)

$[HSO_3NH_2]_{Stock}$ =

Next, prepare a ~0.1M standard solution of sulfamic acid by diluting the appropriate volume of stock solution with deionized water in another 100 mL volumetric flask. Note: the final concentration should be known as precisely as possible (it is a standard solution), but need not be exactly 0.1000M (i.e., 0.09981 M or 0.1022 M are completely acceptable values).

$[HSO_3NH_2]_{Standard}$ =

Finally, *standardize* the unknown sodium hydroxide solution provided by titrating a 25 mL aliquot of standard sulfamic acid with the NaOH solution. Use 3 drops of indicator solution (phenolphthalein) to visualize the endpoint of the titration by the appearance of a persistent light pink color. The stoichiometry of the reaction is:

$$NaOH\ (aq) + HSO_3NH_2\ (aq) \rightarrow NaSO_3NH_2\ (aq) + H_2O\ (l)$$

Calculate the concentration of NaOH in the unknown, and if time permits, repeat the titration several times. How do your values for [NaOH] compare with each other and with other groups?

[NaOH] =

Summary of Student Results from previous year for reference.

STANDARDIZATION OF NaOH (INTRO LAB EXERCISE)

Concentrations of NaOH in moles/L*

student group	**[NaOH] (mol/L)**			**group mean**	**group std dev**	**group 95% CI**
	trial 1	trial 2	trial 3	**(M)**	**(M)**	**(M)**
1	0.1100	0.1288	0.1194	**0.1194**	**0.0094**	**0.0233**
2	0.1320	0.1314	0.1322	**0.1319**	**0.0004**	**0.0010**
3	0.1295	0.1329	0.1328	**0.1317**	**0.0019**	**0.0048**
4	0.1318	0.1326	0.1333	**0.1326**	**0.0008**	**0.0019**
5	0.1327	0.1337	0.1346	**0.1337**	**0.0010**	**0.0024**
6	0.1283	0.1326	0.1332	**0.1314**	**0.0027**	**0.0066**
7	0.1297	0.1323	0.1310	**0.1310**	**0.0013**	**0.0032**

overall mean (M)	**0.1302**
std dev (M)	**0.0049**
95% CI (M)	**0.0045**

Final Reported [NaOH] = 0.130_2 +/- 0.005 moles/L

* from the titration of 25.00 mL of ~0.1 M sulfamic acid standard solutions using a phenolphthalein endpoint