Department of Chemistry

UNIVERSITI MALAYA

FAKULTI SAINS
Faculty of Science

SIC3005

Advanced Environmental Chemistry

Laboratory Manual

Safety in the Laboratory

Further information in the details of the safety and health practice in the Universiti Malaya can be found at:

Occupational Safety & Health and Environment (OSHREC), Universiti Malaya	Universiti Malaya Safety Handbook	Manual Keselamatan & Kesihatan Pekerjaan dan Alam Sekitar, Universiti Malaya

The University has a statutory obligation to comply with the safety requirements and you, as a student, have a duty to abide by the regulations. The following notes are to guide you in good laboratory practice and to familiarize yourself with the safety aspects of your laboratory work.

Emergency Telephone Numbers (as of 28th August 2023):

- National Emergency Number 999 (Mobile phone, dial 112)
- Universiti Malaya Security Office +603 7967 7070
- Universiti Malaya Medical Centre (UMMC) Emergency Department +603 7949 2500
- Universiti Malaya Students' Health Clinic +603 7967 6445
- Occupational Safety & Health, Risk and Environment Centre (OSHREC) +603 7967 6597
- Radiation Protection Service Unit (UPPS) +603 7967 6962/6963
- Department of Chemistry Office +603 7967 4204
- Pantai Fire Station (Jalan Pantai Baharu) +603 2282 4444
- Pantai Police Station (Jalan Pantai Baharu) +603 2282 2222

Safety is the primary concern in any chemical laboratory. Chemicals, particularly organic chemicals, are almost all potentially hazardous. Fortunately, with sensible and correct precautions, the risks can be minimized if basic safety practices are followed. The responsibility for laboratory safety lies with everyone working in the laboratory. Sensible laboratory conduct does not mean memorizing a list of rules! The true test is the actual conduct in the laboratory and safety rules apply to all laboratory activities. Individual safety is affected by the actions of fellow workers in the laboratory. Therefore, it is in everyone's best interest to follow safety work practices.

Laboratory Report Writing

(From: William, I., 2001.Environmental Chemistry: A modular approach, West Sussex, John Wiley & Soms, Ltd)

1. Introduction

As a student, you will be required to submit essays, laboratory, and project reports to your lecturers for assessment. In future years, as a researcher, technician, teacher, academic, industrialist, civil servant, media correspondent, author, salesperson, or politician, you may be required to write a range of scientific text targeted at a specific audience. This prospect may terrify you; many people regard writing as difficult, and something to be delayed or avoided. In fact, scientific writing is a skill, which, like tying your shoelaces or performing titration, can be mastered with practice and perseverance. Like any other skill, scientific writing can be developed into something that will give you confidence, satisfaction, and pleasure.

At undergraduate level, laboratory reports are very important components of assessed work, and consequently, it is worth trying to produce good quality reports. As a chemist, laboratory reports are written for several reasons. One reason is to communicate the laboratory work to management. In such situations, management often bases company decisions on the results of the report. Another reason to write laboratory reports is to archive the work so that the work will not have to be done in the future. Laboratory reports are intended to demonstrate some or all the following:

- you have performed and understood an experiment;
- you have some knowledge of the theoretical basis of the experiment;
- you can process/interpret the data obtained from an experiment;
- you can relate fundamental or derived laws to the outcome of the experiment;
- you can present these ideas/results in an appropriate context and can evaluate their significance.

2. Effective Scientific Writing

1. Remember the purpose of your writing – communicate clearly, concisely, and accurately.
2. Consider your audience (tutor/lecturer) and the assessment criteria.
3. Use appropriate format.
4. Plan and arrange your ideas in a logical order.
5. Treat what you write first as a draft.
6. Make sure your grammar, spelling and punctuation are correct.
7. Ensure the first draft is clear enough.
8. Re-read and edit your first draft as necessary.
9. Proof-read the final draft, correcting any remaining mistake.

3. Grammar and Style

All the text in your report should be grammatically correct, properly punctuated and comprised of complete sentences. The overwhelming majority of scientific reports are written using the impersonal Third Person / Past Simple Tense / Passive Voice form, avoiding, if possible, the use of the personal pronouns (I, we, or you). The following examples illustrate what is intended:

Preferred "The samples were stored at 0 °C"
Not preferred "I stored the samples at 0 °C"

4. Presentation

Laboratory reports should be good to look at; a well-presented report will please the reader, give him/her confidence in the report, and will aid assessment. A cover page will aid the presentation of your work, as well as providing important information to your assessor. The cover page should have (Figure 1):

- Course title and code;
- Number of experiment;
- Your report title;
- Your name and matric number;
- Name of your group members
- Date of submission;
- Name of Lecturer / Tutor.

SIC3005

Advanced Environmental Chemistry

Experiment 1

WATER SAMPLING, TOTAL DISSOLVED SOLIDS AND TOTAL SUSPENDED SOLIDS

Name: _____

Matric No: _____

Group member: (1) _____

(2) _____

Date of Submission: _____

Lecturer: _____

Figure 1: Example of cover page.

Laboratory reports should always use SI units. Unit is very important for all measurement. Without units much of our work as scientists would be meaningless. We need to express our thoughts clearly and units give meaning to the numbers we calculate. Knowing the units of measurement that correspond with a number can give you so much more information than a digit sitting there by itself. Units can:

- Help to show another person the exact amount you have;
- Assist in solving a mathematical problem, especially in chemistry, where you can follow the units to get to the answer;
- Show which measurement system the person is using (i.e., metric or standard).

Proper pagination of your reports will assist you to structure your work, as well as being good practice. It will also assist the reader / assessor to 'navigate' your report, thus making it easier to find relevant sub-sections, table, figures, etc. Pages containing preliminary information (e.g., cover page) are paginated in small Roman numerals (I, ii, iii, etc.), whereas pages of the main body of the report are given in Arabic numerals (1, 2, 3, etc.).

5. Structure of the Laboratory Report

Basic structure for laboratory reports:

- Cover page (refer to section 4)
- Aims / Objectives of the Experiment
- Introduction
- Materials and Methods (Experimental)
- Results
- Discussion
- Conclusions
- References
- Appendices (if related)

5.1 Aims / Objectives of the Experiment

The aims or objectives of the experiment should clearly and briefly state the purpose of undertaking the experiment. They usually include specific overall aims of the experiment. For example, in Experiment 4 that measures the oxygen content of water, the principal objective may be:

- *To determine* the *dissolved oxygen* content of samples of *tap water* and *river water* using Winkler method.

You should always refer to your aims in the Conclusions section of your report and comment upon whether they have been achieved satisfactorily.

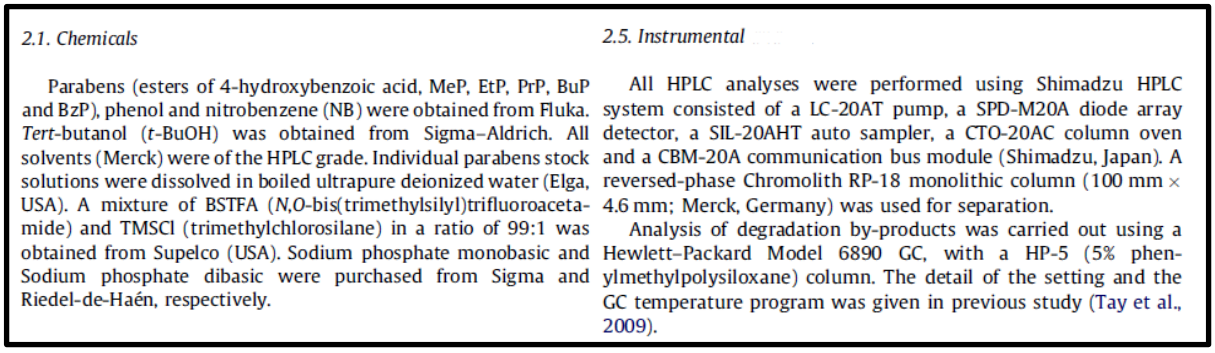
5.2 Introduction

The introduction should establish the context of the experiment, and explain the rationale for undertaking it (i.e., why is it worth doing at all). Here, you should provide some background information on the problem under investigation, such as the source of the pollutant under investigation and any potential health/environmental effects. This section can also involve a description of the theory relating to the experiment and the experimental technique(s) to be used. It should leave the reader with the feeling that the report has a general relevance and that to read on would be worthwhile.

5.3 Materials and methods

This section should contain a concise but adequate description of all your experimental materials and procedures so that your results can be verified independently. Materials too should be as fully described as is necessary for replication. The details of the apparatus / instrument (e.g., UV-Vis Spectrophotometer; GC-FID, AAS, etc.) used should be included in this section. There is also no need to repeat routine instructions for using apparatus or equipment where they are well-known or available in manufacturers' instruction. Figure 2 shows the example of the description for chemicals and instruments.

Any form of sampling procedures must be very fully described – both the sampling techniques and the sampling strategy. Sampling is usually undertaken to obtain some estimate relating to a population. Similarly, locations and study areas should be described well enough for a reader to duplicate, locate, or visualize.



2.1. Chemicals

Parabens (esters of 4-hydroxybenzoic acid, MeP, EtP, PrP, BuP and BzP), phenol and nitrobenzene (NB) were obtained from Fluka. *Tert*-butanol (*t*-BuOH) was obtained from Sigma–Aldrich. All solvents (Merck) were of the HPLC grade. Individual parabens stock solutions were dissolved in boiled ultrapure deionized water (Elga, USA). A mixture of BSTFA (*N,O*-bis(trimethylsilyl)trifluoroacetamide) and TMSCl (trimethylchlorosilane) in a ratio of 99:1 was obtained from Supelco (USA). Sodium phosphate monobasic and Sodium phosphate dibasic were purchased from Sigma and Riedel-de-Haén, respectively.

2.5. Instrumental

All HPLC analyses were performed using Shimadzu HPLC system consisted of a LC-20AT pump, a SPD-M20A diode array detector, a SIL-20AHT auto sampler, a CTO-20AC column oven and a CBM-20A communication bus module (Shimadzu, Japan). A reversed-phase Chromolith RP-18 monolithic column (100 mm × 4.6 mm; Merck, Germany) was used for separation.

Analysis of degradation by-products was carried out using a Hewlett–Packard Model 6890 GC, with a HP-5 (5% phenylmethylpolysiloxane) column. The detail of the setting and the GC temperature program was given in previous study (Tay et al., 2009).

Figure 2: Example of writing the description for chemicals and instruments.

5.4 Reporting Results

Clearly, the Results are an exceptionally important part of your report and great care should be taken in their presentation. Over the years, several conventions have developed in the reporting of results. It is important to open your Results section with appropriate text rather than by just presenting tables of data. A table must follow, and never precede, the first

reference to it in the text. You should not leave it to the reader to interpret tables – that is your job. An acceptable format is of the type, 'The data presented in Table 1 show that ……'. Indeed, the reader should be able to appreciate the significance of the result without reference to any table of data; the data are evidence to support your statements. While tables are used to present the data, figures can be helpful in interpreting them.

Tables

Tables are the main vehicles for conveying data to the reader. A table can be considered as a complete entity, in a sense, should be able to exist separately in the text. A well-constructed table does not need a lengthy explanation of how it is to be interpreted but should be self-explanatory and be characterized by its simplicity and unity. The caption (on top of the table) is clearly important if the table is to stand as a separate entity. Table 3 is a well laid out and clear example.

Table 3. Characterization of the leachate collected from the Gramacho Metropolitan Landfill used in this work (n = 4 samples).

Parameters	*Average value*	*Standard deviation*
pH	8.3	0.3
Total alkalinity (mg $CaCO_3$ L^{-1})	8857	1480
Carbonate alkalinity (mg $CaCO_3$ L^{-1})	450	490
Bicarbonate alkalinity (mg $CaCO_3$ L^{-1})	8374	1917
Total ammonia nitrogen (mg [N-NH_3] L^{-1})	1998	387
Chloride (mg L^{-1})	3196	862
Dissolved Reactive Phosphorus (mg L^{-1})	7.5	1.3
Total Solids (mg L^{-1})	9390	2087
Total Suspended Solids (mg L^{-1})	53	31
DOC – dissolved organic carbon (mg L^{-1})	935	71
COD chemical oxygen demand (mg L^{-1})	3332	523
BOD - biochemical oxygen demand (mg L^{-1})	141	45

Figures / Graphs

Laboratories exercises will often involve the production of graphs from the data collected. A graph can provide much more information than a set of data. It gives a visual representation of trends and relationships and permits the prediction of what happens between the known points. Graphs are commonly labeled as Figure in lab reports. As tables, appropriate captions (or titles) should be added at the bottom of the graph (refer to Fig. 3). Well-drawn graphs can greatly enhance the effectiveness of display and interpretation of the results presented in a report.

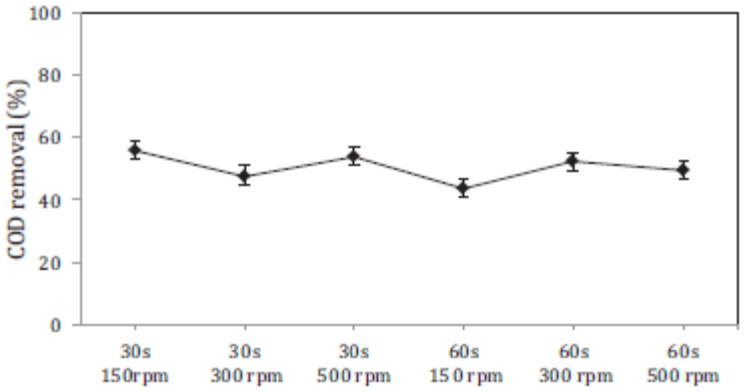


Fig. 3. Removal of COD for various mixing times and stirring speeds (experimental conditions: pH = 4.0, $FeCl_3$ dosage = 1400 mg L^{-1} and temperature = 23°C).

5.5 Discussion

The Discussion should draw all the threads of the report together and is, arguably, the most important part of the report. The discussion offers the widest scope for individual freedom of expression, and may include items such as the following:

- A comparison of the results with those obtained or published elsewhere;
- A discussion of the significance of the data in an appropriate context;
- Comments on the value of the results in a wider scientific, environmental or even commercial context.
- A discussion of the possible limitations of the methods;
- Comments upon the precision, reproducibility, or repeatability) of the results, as well as on the accuracy, if known.
- A discussion of effectiveness and limitations of the experiment and any statistical treatment of the data.

Attention should be drawn to any fault/problems with the chemicals or equipment used and to any deficiency in the assumptions upon which the experiment is based. Modifications and improvements should be included if appropriate.

5.6 Conclusions

The Conclusion section should summarize the main findings of the experiment. It is not a summary of your work programme, or a description of the research carried out. It is often helpful to use ‘bullet points’, each no more than two or three lines, to summarize your results. This enables you, lecturer, and tutor to see at glance, whether you have addressed all the important areas and helps you to check that you have covered everything that you wanted to and listed in the objectives.

5.7 References

Citing references

References may be cited in the text in several ways, depending upon your style of writing or the context of your reference. However, there are conventions that should be followed, as shown below – note the use of brackets.

- Natural levels of carbon monoxide are low, typically in the range 20 – 200 ppb (Grimes and Clement, 1993).
- Kinnear (1998) describes a system for sampling PM10 on an hourly basis, while Hegarty et al. (2001) describe a system for the continuous sampling of PM10. [Note: "Hegarty, Scanlon and Chan (2001) are written as Hegarty et al. (2011)]

If reference has two authors or less, the family name of all author(s) should be mentioned in the reports. If a reference has more than two authors, only the first is mentioned with "et al." "et al. translates as "and others".

You may want to cite an official or company report, or government paper, where there is no specified author, or the authorship belongs to a committee. In such cases, you normally cite the body responsible for publishing the paper or report. Thus, in the text, the body responsible for publishing the paper is cited with the year of publication, e.g. (EvironTech Ltd, 2000).

The Reference Section

The Reference section must include details of all references ***that have been cited in the text***. It does not include peripheral reading. The details of each reference include the following: name(s) of the author(s) (surname first, with a comma), the year of publication, and the title of the publication. In the case of books and reports, the name of the publisher and place of publication is also given, there is more than one way of presenting this information; the following example illustrate the use of upper- and lower-case letters, italics, punctuation marks and general layout.

Books

Example: Roberts, M.B.V. (1984). Biology: A Functional Approach (3rd Edn). Nelson Publishers, London.

Book Chapters

XYZ, F.M. (Year Published). Title of chapter In F.M. XYZ Editor (Ed.), Title of book/anthology (pp. Pages). Publisher City, State: Publisher.

Article in Journals

XYZ, F. M., & ABC, F. M. (Year Published). Article title. Journal Name, Volume (Issue), Pages.

Websites

Satalkar, B. (2010, July 15). Water aerobics. Retrieved from http://www.buzzle.com.

6. PLAGIARISM

Plagiarism is the representation of another person's published or unpublished work or ideas as your own by using an extensive unacknowledged quotation. In academia, plagiarism carries heavy penalties; your mark for any assessed work may be significantly reduced and you may be open to accusations of academic misconduct. However, this does not mean that all your work must be completely original; expressing views that are influenced by other authors is a consequence of shared knowledge and reflection of wide reading. To avoid accusations of plagiarism, you should clearly reference sources by using the conventions outlined.

Suggested Detailed Rubrics for Level II and III Laboratory Classes

Section A: Attendance and Responsibility (Total 20%)

1. Attendance (5%)

Score	Criteria
0	Student did not attend without any valid reasons.
5	Student is present.

2. Pre-entering lab (5%)

Score	Criteria
0	No preparation of experimental procedure.
3	Summary of procedures too brief, lack of details and confusing.
5	Presents easy to follow steps in lab experimental, logical and adequately detailed.

3. Proper attire (5%)

Score	Criteria
0	No proper attire – covered shoes, safety goggles and lab coat.
3	Covered shoes and lab coat available but no safety goggles.
5	Safety attire checked.

4. Promptness (5%)

Score	Criteria
0	Student is late for more than 15 minutes without any valid reasons.
3	Student is late for not more than 15 minutes without any valid reasons.
5	Student is always prompt.

Notes:

1. The student MUST attend the laboratory session to be eligible to obtain marks. NO marks will be given at all if the student did not attend any laboratory sessions without valid reasons.

2. If the student did not attend any of the laboratory session, there MUST be an official explanation (i.e., if Covid-19: MySejahtera Screenshot; Sick: MC from doctor; representing UM in activities: Official Letter from the Department/Faculty/University, etc.; Family reasons: Death of family member, etc.).

Section B: Lab Performance − Skills and Technique (Total 20%)

Score	Criteria
0-5	No skill is demonstrated.

6-10	Wrong glassware used, wrong technique, spillage and wasting of chemicals.
11-15	Right glassware used, incorrect or lack of lab technique.
16-20	Presents correct lab skill, clean and tidy.

Section C: Lab Jotter (Total 10%)

Score	Criteria
0	No jotter or student did not show raw data to the lecturer-in-charge; student exhibit evidence of data forging and/or plagiarism.
1-3	Raw data are out-of-place; major data or observations missing; no proper labelling.
4-6	Some key data or observations missing. Presentation need major improvement.
7-8	Almost all raw data and key observations written. Presentation can still be improved.
9-10	Raw data and observations tabulated/written in a clear and tidy manner, with correct units and no evidence of data forging and/or plagiarism.

Section D: Lab Report (Total 40%)

(I) Short Report

Section	Score	Criteria
Title **(5 marks)**	0	No title.
	1	Too brief (e.g. “Lab Report”, “Mercury in Fish”, “Synthesis of Cinnamic Acid” or “Boiling Point of Water”).
	2-3	Too long or does not identify the complete subject of study (e.g. “Determination of iron”, “Determination of lead”, etc.).
	4-5	Identify the complete subject of study and encapsulates the purpose of the report/study (e.g. “Kinetics of the hydrolysis of *t*-butyl chloride at 30 ^{o}C”, “Synthesis of triphenylcarbinol via Grignard reaction” or “Determination of iron in red meat via spectrophotometry”).
Results	0	Section missing completely.

(Data, figures, graphs, tables, observations, % yield, etc.) **(35 marks)**	1-10	No flow of results. Figures, graphs, tables contain errors or are poorly constructed, have missing titles, captions or numbers, units missing, or incorrect, numerical data did not have correct significant figures, etc.
	11-20	Most figures, graphs, tables OK, some still missing some important or required features.
	21-30	All figures, graphs, tables are correctly drawn, but some have minor problems (e.g. incorrect significant figures, incomplete observation) or could still be improved.
	31-35	All figures, graphs, tables are correctly drawn, are numbered and contain titles/captions. Observations clearly stated. Numerical data contains correct significant figures and units.
Discussion **(35 marks)**	0	Section missing completely.
	1-10	Lack of attempt to relate experimental findings and data with contemporary theories. Very incomplete or incorrect interpretation of trends and comparison of data indicating a lack of understanding of results.
	11-20	Some attempt to relate experimental findings and data but using inaccurate theories. Some of the results have been correctly interpreted and discussed; partial but incomplete understanding of results is still evident.
	21-30	Almost all of the results have been correctly interpreted and discussed, only minor improvements are needed.
	31-35	All of the important trends and data comparisons have been interpreted correctly and discussed; good understanding of results is conveyed.
Safety Precautions **(5 marks)**	0	Section missing completely.
	1	Sentences are incomplete, focusing on minor points or lack important steps.
	2-3	State only 1-2 major and most important safety precautions.
	4-5	State at least 3 major and most important safety precautions.
Conclusions	0	Section missing completely.

(10 marks)	1-3	Conclusion missing the important points or is not supported by the experimental results.
	4-6	Conclusions regarding major points are drawn, but many are misstated, indicating a lack of understanding.
	7-8	All important conclusions have been drawn, could be better stated.
	9-10	All important conclusions have been clearly made, student shows good understanding.
References **(5 marks)**	0	Section missing completely.
	1-3	Incomplete references to the books or any other sources used in report.
	4-5	Correct in-text citations and the references in the reference list conform to all respects of the formatting convention (e.g. APA format). Complete references to the books or any other sources used in report. References in text are matched with references in reference list (e.g. no missing references).
Appearance and Formatting **(5 marks)**	1	Sections out of order, too much handwritten copy, sloppy formatting.
	2	Sections in order, contains the minimum allowable amount of handwritten copy, formatting is rough but readable.
	3	All sections in order, formatting generally good but could still be improved.
	4-5	All sections in order, well-formatted, very readable.

Total section D marks = **(x/100) × 40%**

(II) Full Report

Section	Score	Criteria
Title **(5 marks)**	0	No title.
	1	Too brief (e.g. “Lab Report”, “Mercury in Fish”, “Synthesis of Cinnamic Acid” or “Boiling Point of Water”).

	2-3	Too long or does not identify the complete subject of study (e.g. “Determination of iron”, “Determination of lead”, etc.).
	4-5	Identify the complete subject of study and encapsulates the purpose of the report/study (e.g. “Kinetics of the hydrolysis of *t*-butyl chloride at 30 ^{o}C”, “Synthesis of triphenylcarbinol via Grignard reaction” or “Determination of iron in red meat via spectrophotometry”).
Introduction (Including objectives) **(10 marks)**	0	Section missing completely.
	1-3	Very little background information provided, or information is incorrect.
	4-6	Some introductory information, but still missing some major points.
	7-8	Introduction is nearly complete, missing some minor points.
	9-10	Introduction complete and well-written; provides all necessary background principles for the experiment with evidence of extra reading.
Experimental Procedure **(10 marks)**	0	Section missing completely.
	1-3	No sub-sections, missing several important experimental details or not written in paragraph format. Parts have been included under the wrong sub-section.
	4-6	Written in paragraph format, still missing some important experimental details.
	7-8	Written in paragraph format, important experimental details are covered, some minor details missing.
	9-10	Well-written in paragraph format, all experimental details are covered.
Results (Data, figures, graphs, tables, observations, % yield, etc.) **(25 marks)**	0	Section missing completely.
	1-7	No flow of results. Figures, graphs, tables contain errors or are poorly constructed, have missing titles, captions or numbers, units missing or incorrect, numerical data did not have correct significant figures, etc.
	8-15	Most figures, graphs, tables OK, some still missing some important or required features.

	16-20	All figures, graphs, tables are correctly drawn, but some have minor problems (e.g. incorrect significant figures, incomplete observation) or could still be improved.
	21-25	All figures, graphs, tables are correctly drawn, are numbered and contain titles/captions. Observations clearly stated. Numerical data contains correct significant figures and units.
Discussion **(25 marks)**	0	Section missing completely.
	1-7	Lack of attempt to relate experimental findings and data with contemporary theories. Very incomplete or incorrect interpretation of trends and comparison of data indicating a lack of understanding of results.
	8-15	Some attempt to relate experimental findings and data but using inaccurate theories. Some of the results have been correctly interpreted and discussed; partial but incomplete understanding of results is still evident.
	16-20	Almost all of the results have been correctly interpreted and discussed, only minor improvements are needed.
	21-25	All of the important trends and data comparisons have been interpreted correctly and discussed; good understanding of results is conveyed.
Safety Precautions **(5 marks)**	0	Section missing completely.
	1	Sentences are incomplete, focusing on minor points or lack important steps.
	2-3	State only 1-2 major and most important safety precautions.
	4-5	State at least 3 major and most important safety precautions.
Conclusions **(10 marks)**	0	Section missing completely.
	1-3	Conclusion missing the important points or is not supported by the experimental results.
	4-6	Conclusions regarding major points are drawn, but many are misstated, indicating a lack of understanding.
	7-8	All important conclusions have been drawn, could be better stated.

	9-10	All important conclusions have been clearly made, student shows good understanding.
References **(5 marks)**	0	Section missing completely.
	1-3	Incomplete references to the books or any other sources used in report.
	4-5	Correct in-text citations and the references in the reference list conform to all respects of the formatting convention (e.g. APA format). Complete references to the books or any other sources used in report. References in text are matched with references in reference list (e.g. no missing references).
Appearance and Formatting **(5 marks)**	1	Sections out of order, too much handwritten copy, sloppy formatting.
	2	Sections in order, contains the minimum allowable amount of handwritten copy, formatting is rough but readable.
	3	All sections in order, formatting generally good but could still be improved.
	4-5	All sections in order, well-formatted, very readable.

Total section D marks = **(x/100) × 40%**

Section E: Assessment of Understanding/Revision on Conducted Experiments (10%)

Score	**Criteria**
x	Test/Quiz/Lab Presentation, etc.

* For Section E: Assessment - it is up to the lecturer in-charge to decide whether he/she wants to carry out the method of assessment (simple test, presentation, etc.). If he/she chooses not to, the 10% marks will be allocated back to Section D: Lab report (i.e., total marks/100 × 50%)

** Late Report Submission: −1 mark / day

CONTENTS

WATER SAMPLING, TOTAL DISSOLVED SOLIDS AND TOTAL SUSPENDED SOLIDS

1. INTRODUCTION

A) Water Sampling

Samples collected for analysis should be obtained in such a way as to provide the most representative sample possible. In general, samples should be taken near the center of the body of water and entirely below the surface. It is difficult to obtain a truly representative sample when collecting surface water samples. More meaningful results are commonly obtained by carrying out a series of tests with samples taken from several locations and depths and at different times. The results can then be used to establish patterns applicable to that particular body of water (Boehnke and Delumyea, 2000).

Generally, as little time as possible should elapse between collecting the sample and carrying out the analysis. Depending on the nature of the test, special precautions in handling the sample may be necessary to prevent natural interferences, such as bacterial growth or the loss of dissolved gases. Table 1-1 gives detailed information for preserving samples. When studying a particular aquatic ecosystem, an environmental scientist learns as much about the system as possible. This knowledge helps to explain results and aids in locating areas of the system thus should be studied (Boehnke and Delumyea, 2000).

B) Total Suspended Solids

The total suspended solids (TSS) test is one of the most common determinations made in wastewater treatment plants. The test is not intended to measure the concentrations of specific chemical substances, but rather give an empirical estimate of water quality by measuring the amount of suspended foreign materials present. It is determined from the weight gain of a filter after drawing a known volume of water through the filter.

All streams carry some suspended solids under natural conditions. However, if concentrations are enhanced through anthropogenic perturbations, this can lead to alterations to the physical, chemical, and biological properties of the waterbody. Physical alterations caused by suspended solids are reduced penetration of light, temperature changes, and infilling of channels and reservoirs when solids are deposited (Bilotta and Brazier, 2008). These physical alterations are associated with undesirable aesthetic effects, higher costs of water treatment, reduced navigability of channels and decreased longevity of dams and reservoirs (Bilotta and Brazier, 2008).

C) Total Dissolved Solids

Material that cannot be removed by a filter of a particular porosity is said to be "dissolved." Many, although not all of these species, are inorganic salts or weak organic acids, which ionize in water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, hydrogen carbonate, chloride, sulfate, and nitrate anions. The presence of dissolved solids in water may affect its taste. High TDS concentrations can be measured gravimetrically, although volatile organic compounds are lost by this method (WHO, 2003). The palatability of drinking water has been rated by panels of tasters in relation to its TDS level as shown in Table 1-2.

Table 1-1: EPA recommended preservation methods of water and wastewater samples (Boehnke and Delumyea, 2000).

Parameter	Preservation Method	Container*	Maximum Holding Time
Acidity/Alkalinity	Store at 4°C	P, G	14 days
Ammonia	Sulfuric acid to pH < 2	P, G	28 days
	Store at 4°C		
BOD	Store at 4°C	P, G	48 hours
COD	Sulfuric acid to pH < 2	P, G	28 days
	Store at 4°C		
Chloride	None	P, G	28 days
Residual chlorine	None	P, G	Analyze immediately
	0.6 g Ascorbic acid		
Dissolved oxygen	None	G with Glass Top	Analyze immediately
Fluoride	None	P	28 days
Mercury	Nitric acid to pH < 2	P, G	6 months
Nitrate	Sulfuric acid to pH < 2	P, G	48 hours
	Store at 4°C		
Nitrite	Store at 4°C	P, G	48 hours
Oil and grease	Sulfuric acid to pH < 2	G	28 days
	Store at 4°C		
Total organic carbon	Sulfuric acid to pH < 2	P, G	28 days
	Store at 4°C		
pH	None	P, G	Analyze immediately
Ortho-Phosphate	Filter on site	P, G	48 hours
	Store at 4°C		
Phosphorus, total	Sulfuric acid to pH < 2	P, G	28 days
Solids	Store at 4°C	P, G	7 days
Specific conductance	Store at 4°C	P, G	28 days
Sulfate	Store at 4°C	P, G	28 days
Sulfide	Store at 4°C	P, G	7 days
Turbidity	Store at 4°C	P, G	48 hours
Purgeable aromatic Hydrocarbons	Store at 4°C	G, Teflon-Lined Septum	14 days
	HCl to pH 2		
Phenols	Store at 4°C	G, Teflon-Lined Cap	7 Days until extraction
			40 Days after extraction
PCBs	Store at 4°C	G, Teflon-Lined Cap	Same as above
Phthalate esters	Store at 4°C	G, Teflon-Lined Cap	Same as above
	Store in dark		

*P is plastic and G is glass.

Table 1-2: Water quality according to TDS concentration (WHO, 2003).

Classification of water	Concentration of TDS
Excellent	< 300 mg/L
Good	between 300 and 600 mg/L
Fair	between 600 and 900 mg/L
Poor	between 900 and 1200 mg/L
Unacceptable	> 1200 mg/L

2. LEARNING OBJECTIVES

i. To introduce the methods used in water sample collection.
ii. To use the collected water samples to determine total suspended solids (TSS) and total dissolved solid (TDS).

3. METHODOLOGY

A) Water Sampling

1. Collect a sample of water from about 1 m below the surface of a river or pond, from a boat dock, or from another convenient location, into a 1 L plastic bottle. Rinse the plastic bottle with the water sample first prior to collection.
2. Device for collecting water samples is shown in Figure 1-1.
3. In your laboratory notebook record all conditions under which the sample was obtained (air and water temperatures, weather conditions, tide, etc.).
4. Store the water sample in a refrigerator at 4°C. Allow the samples to reach the room temperature before use.

Figure 1-1: Van Dorn sampler.

B) <u>Determination of Total Suspended Solids (TSS) according to EPA Method 160.2 (EPA, 2015)</u>

1. Weigh a 47 mm filter paper.
2. Assemble the filtering apparatus, as shown in Figure 1-2, and begin suction. Wet the filter paper with a small volume of distilled water to seat it against the fritted support.
3. Shake the sample vigorously and quantitatively transfer 300 mL of sample volume to the filter using a graduated cylinder.
4. Remove all traces of water by continuing to apply vacuum after sample has passed through.
5. With suction on, wash the graduated cylinder, filter, non-filterable residue, and filter funnel wall with three portions of distilled water allowing complete drainage between washing. **RECORD THE EXACT VOLUME OF DISTILLED WATER!!**
6. Remove all traces of water by continuing to apply vacuum after water has passed through.
7. Carefully remove the filter paper from the filter support. Alternatively, remove filter from membrane holder. Dry at least one hour at 103-105°C.
8. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained.

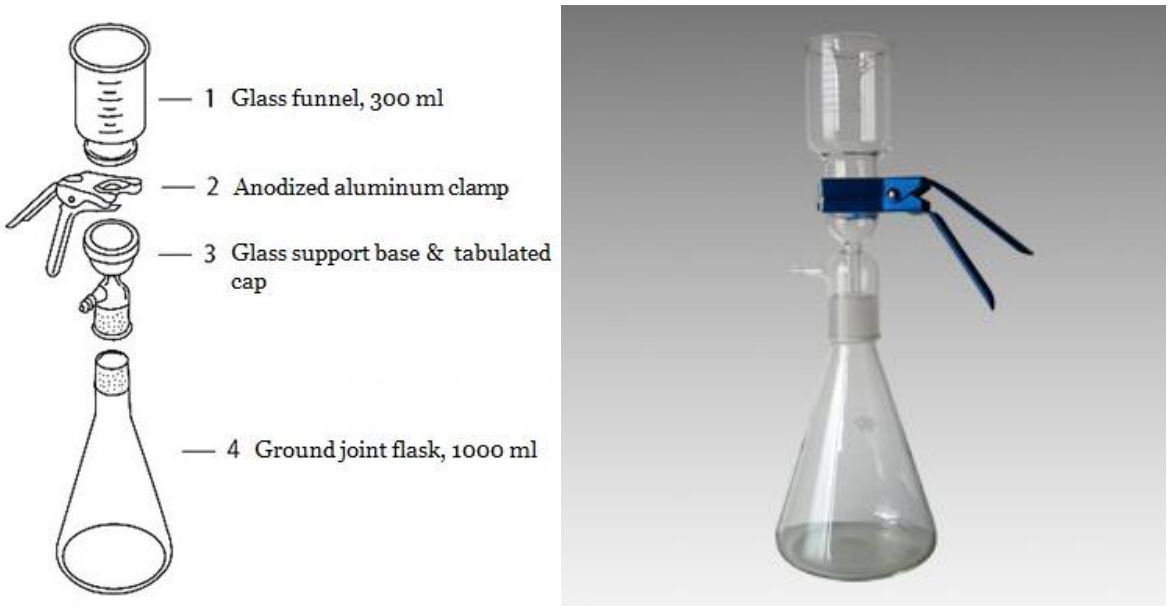


Figure 1-2: Suction filtration system with membrane holder.

C) Determination of Total Dissolved Solids (TDS) according to ASTM D5907-03 (Environmental Express, 2016)

1. Weigh an empty evaporating dish on a balance to the nearest 0.0001 g and record the weight.
2. Mix the filtrate (from Section B) thoroughly and measure out a portion expected to contain between 2.5 and 200 mg residue.
3. Transfer the portion (containing filtrate and the washings) to your evaporating dish and record the sample volume.
4. Evaporate the sample to dryness in a drying oven (103-105 °C).
5. Dry the dish for at least one hour at 180 ± 2 °C.
6. Remove dish from the oven and place in a desiccator until at room temperature.
7. Weigh the dish on a balance to the nearest 0.0001 g and record the weight.

REPORT

Calculate the concentration of TSS and TDS in the unit of mg/L.

4. REFERENCES

Bilotta GS, Brazier RE, 2008. Understanding the influence of suspended solids on water quality and aquatic biota, Water Research 42, 2849-2861.

Boehnke DN, Delumyea RD, 2000. Laboratory Experiments in Environmental Chemistry, Prentice Hall, New Jersey.

Environmental Express, 2016. Understanding Total Dissolved Solids (TDS), http:// http://www.envexp.com/labmatters/235-understanding-total-dissolved-solids-tds (Accessed on 18/10/2016)

World Health Organization (WHO), 2003.Total dissolved solids in Drinking-water: Background document for development of WHO guidelines for drinking water quality. Geneva, Switzerland.

US Environmental Protection Agency (EPA), 2015. Total Suspended Solids (TSS): EPA Method 160.2 (Gravimetric, Dried at 103-105 °C), http:// https://www.epa.gov/quality/total-suspended-solids-tss-epa-method-1602-gravimetric-dried-103-105-degrees-c (Accessed on 18/10/2016).

The pH, Buffer Capacity and Alkalinity of Environmental Waters

1. INTRODUCTION

The Origin of Natural Acidity (Boehnke and Delumyea, 2000)

In this section, we examine factors that affect the pH of natural waters, which are often somewhat basic. Most acidity in natural waters is due to carbon dioxide which dissolved in water and produces hydronium ion:

$$CO_2\,(g) + H_2O\,(1) \leftrightarrow H^+\,(aq) + HCO_3^-\,(aq)$$

This reaction can be considered to occur in two stages. **Stage I** is the establishment of equilibrium between atmospheric and aqueous carbon dioxide. The amount of carbon dioxide that dissolves in water is governed by Henry's law, which takes the form

$$[CO_2(aq)] = K_H P(CO_2)$$

where K_H is the Henry's law constant and $P(CO_2)$ is the partial pressure of carbon dioxide. For carbon dioxide at 25°C, $K_H = 3.4 \times 10^{-2}$ mol/L•atm. The concentration of CO_2 in the atmosphere is about 350 ppm. In the gaseous state, 350 ppm of CO_2 means 350 molecules per 1×10^6 molecules of air, and since moles and molecules are proportional,

$350/1000000 \equiv$ mol CO_2/ mol $\equiv$ air mol fraction CO_2 = pressure fraction CO_2 = $P(CO_2)$/ P(air)

Thus $P(CO_2) = 3.5 \times 10^{-4}$ atm when Pair = 1.0 atm and $[CO_2(aq)] = 1.2 \times 10^{-5}$ mol/L at 25°C from Stage I.

Stage II is the dissociation of dissolved carbonic acid, according to

$$H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO^-\,(aq) \qquad K_{a1} = 4.5 \times 10^{-7}$$

$$HCO_3^-\,(aq) \leftrightarrow H+\,(aq) + CO_3^{2-}\,(aq) \qquad K_{a2} = 4.7 \times 10^{-11}$$

Since $K_{a1} >> K_{a2}$, the pH of the system is primarily due to the first equilibrium. Therefore, $K_{a1} = [H^+][HCO^-]/[H_2CO_3] = [H^+]^2/1.2 \times l0^{-5} = 4.5 \times 10^{-7}$, and $[H^+] = 2.3 \times 10^{-6}$, giving a pH of 5.63. This is the expected pH for pure water in equilibrium with atmospheric carbon dioxide at 25°C.

Although the pH of a natural water is affected by the carbon dioxide acidity of rain, a third factor to be considered is the background carbonate level that is due, in part, to the dissociation of calcium carbonate in soil. When rain falls on land, it first percolates through topsoil, where its pH may drop by another unit due to the large quantity of carbon dioxide produced by bacteria. However, much of the earth's crust contains calcium carbonate (ultimately derived from marine organisms). The effect of calcium carbonate on the pH of environmental waters is due to three factors: (1) calcium carbonate is sparingly soluble in water; (2) the carbonate ion is a moderately strong base, where bicarbonate is only a weak base, and (3) dissolved carbonate is in equilibrium with carbon dioxide in some gases and in bodies of water. The net result of these factors is that the pH of natural waters will be somewhat basic instead of the acidic pH from dissolved CO_2 alone. To illustrate, first consider the dissociation of calcium carbonate,

$$CaCO_3\,(s) \leftrightarrow Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$$

where $K_{sp}= [Ca^{2+}][CO_3^{2}-] = 4.6 \times 10^{-9}$ at 25° C. If this were the only process to occur, the pH would remain unchanged.

However, since carbonate ion is a Bronsted-Lowry base, according to

$$CO_3^{2-}\,(aq) + H_2O\,(l) \leftrightarrow HCO_3^{-}\,(aq) + OH^{-}\,(aq)$$

the observed pH is due to not only atmospheric carbon dioxide, but also to the carbonate from the hydrolysis of $CaCO_3$(s), which increases pH.

The hydrolysis constant for the last reaction is found as follows:

$$K_h = K_w / K_{a2} = [HCO_3^{-}][OH^{-}]/[HCO_3^{2}]$$

$$=1.0 \times 10^{-14}/ 4.7 \times 10^{-11} = 2.1 \times 10^{-4}$$

When the solubility product equilibrium is combined with the hydrolysis equilibrium, the net result is

$$CaCO_3\,(s) + H_2O\,(l) \leftrightarrow Ca^{2+}\,(aq) + HCO_3^{-}\,(aq) + OH^{-}\,(aq)$$

Because when equilibrium is added the new equilibrium constant is the product of the individual equilibrium constants, the equilibrium constant for the last equilibrium is $K' = Ksp \times K_h = 4.6 \times 10^{-9} \times 2.1 \times 10^{-4} = 9.7 \times 10^{-13}$. Since $[Ca^{2+}][HCO_3^{-}][OH^{-}]\,[OH]^3 = 9.7 \times 10^{-13}$, $[OH^{-}] = 9.9 \times 10^{-5}$ and pH = 10.00. Thus, without atmospheric carbon dioxide, the pH of natural waters in contact with calcium carbonate would be quite high. Now consider both equilibria simultaneously,

$$H_2CO_3\,(aq) \leftrightarrow H^+\,(aq) + HCO_3^-\,(aq)$$

$$CaCO_3 + H_2O \leftrightarrow Ca^{2+}\,(aq)\; HCO_3^-\,(aq) + OH^-\,(aq)$$

where K_{a1} = 4.5 x 10^{-7}, K' = 9.7 x 10^{-13}, and K= 1/K_w = 1.0 x 10^{14}, respectively for the three equilibria. The overall description of the three simultaneous processes is found by summing the equilibria to give,

$$CaCO_3\,(s) + H_2CO_3\,(aq) \leftrightarrow 2HCO_3^-\,(aq) + Ca^{2+}\,(aq)$$

for which K'' = K_{a1} x K' x K = 4.4 x 10^{-5}.

Now, since [HCO_3^-] = 2 x [Ca^{2+}], [Ca^{2+}](2 x [Ca^{2+}])^2/ 1.2 x 10^{-5} = 4.4 x 10^{-5}, then [Ca^{2+}] = 5.1 x 10^{-4} mol/L. In terms of ppm $CaCO_3$, the calcium level is (5.1 x 10^{-4}mol/L) (100 g/mol)(1000mg/g) = 51 ppm — a reasonable value based on actual levels found. Finally, to calculate the expected pH, the last equilibrium is used, and we examine the bicarbonate produced to see if it is a stronger acid or a stronger base.

As an acid,

$$HCO_3^-\,(aq) \leftrightarrow H^+\,(aq) + CO_3^{\,2-}\,(aq) \qquad K_{a2} = 4.7 \times 10^{-11}$$

and as a base,

$$HCO_3^-\,(aq) + H_2O\,(l) \leftrightarrow H_2CO_3\,(aq) + OH^-\,(aq) \qquad K_b = 2.2 \times 10^{-8}$$

since K_b = K_h = K_w / K_{a1}. Since K_h >> K_{a2}, K_{a2} can be ignored, and the pH is calculated using the expression for K_b.

Then, K_b = [H_2CO_3][OH^-]/[HCO_3^-] = 2.2 x 10^{-8}. From Henry's law we found that [H_2CO_3] = 1.2 x 10^{-5} and we also showed that [HCO_3^-] = 2 x [Ca^{2+}] = 2(5.1 x 10^{-4}) = 1.0 x 10^{-3}. Since K_b is so small, we can use (1.2 x 10^{-5})[OH^-] / 1.0 x 10^{-3} = 2.2 x 10^{-8}. This gives [OH^-] = 1.8 x 10^{-6}, and finally pH equals 8.26. This is remarkably close to the pH of many natural waters. Over a 10-year period in a major stream in the southeastern United States, Boehnke and Delumyea (2000) found an average pH close to 8.0, with little variation, except after periods of substantial rainfall.

<u>Alkalinity and Buffering Capacity of Natural Water (Ibanez et al., 2008)</u>

This experiment will allow the determination of the alkalinity and buffering capacity of water samples from different natural sources. The buffering capacity is the ability to neutralize the pH and the resistance to change in it due to the small acidic or basic inputs or discharges. When a system is poorly buffered, the addition of even small amounts of an acid or a base will noticeably alter its pH, but when a system is

well buffered, the same addition barely modifies its pH (i.e., it becomes relatively insensitive to the addition of small amounts of acids or bases). The buffering capacity of a system is defined as the moles/L of strong acid (or strong base) needed for a change in one pH unit of a solution. A typical buffer is formed by a combination of a weak acid (or base) with its corresponding salt. For example:

$$HA \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

The equilibrium (acidity) constant is:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

from which we can derive the equation of pK_a (= -log K_a) with respect to the pH:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

This is known as Henderson-Hasselbalch equation and it is built under the assumption that $[H^+]$ or $[OH^-]$ « [HA] and $[A^-]$, where HA = weak acid, and A^- = the corresponding anion generated from the salt. In a well-buffered system, the greatest resistance to changes in pH will occur when the ratio of concentrations of the acid and its salt are approximately equal and therefore the pK_a will be equal to its pH. From the above equation this occurs at $[A^-]/[HA] = 1$.

By knowing the pK_a of the buffering acid, one can estimate the pH at which its greatest buffering capacity will be centered. The pH of a buffer solution is affected by two factors: the concentration ratio, [A-]/[HA] (i.e., the inverse ratio of the acid to the conjugate base), and the strength of the parent acid or base. The stronger the parent acid or base in the buffer solution, the more extreme will the buffer's pH value be.

The buffering capacity depends on the concentration of the buffer, and on the type and concentration of the acid or base to be added to the buffered solution. In selecting the right working buffer for a specified pH, it is common to consider that its pK_a must be at least one pH unit above or below the working pH.

The buffering capacity in natural waters is mainly due to the carbonate system and its equilibria. Therefore, it is important to know the alkalinity of the system, because this will provide the capacity for neutralizing an acid. The expression for alkalinity (i.e., dissolved species only) or acid neutralizing capacity (ANC) (i.e., the whole sample) is generally based on the carbonate system:

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

and this property is expressed as mg/L (or in eq/L, in the case of ANC) of the equivalent calcium carbonate. The ANC of natural water systems depends on the composition of the watershed. If there are minerals with poor solubility in the surrounding soil, the ANC will be low, whereas if calcareous minerals are present, there will be a high ANC. Some dissolved organic substances derived from decaying plant materials may also contribute to the ANC capacity of the water.

2. LEARNING OBJECTIVES

i. Making pH measurements on environmental waters.
ii. To determine the buffer capacity of environmental waters.
iii. To determine the alkalinity of environmental waters.

3. METHODOLOGY

A) pH and Buffer Capacity of Environmental Water

1. Collection of water samples: In this experiment, you will use water sample (filtrate) collected in Experiment 1(B) and rainwater. Collect a sample of rainwater, if possible, using a standard rain collector. After collection, store all water samples in a refrigerator at 4°C. Allow the samples to reach the room temperature before use.
2. Use 100 mL of one environmental sample to determine buffer capacity. Select a sample expected to exhibit high buffer capacity. Set up a clean burette and a magnetic stir plate. Fill the burette with 0.01000 M HCl and take the initial volume reading. Add the sample to the titration beaker (250 mL) and measure the initial pH of the sample. Add 1 mL increments of 0.01000 M HCI. Measure the pH after each addition, stirring with a magnetic stir bar. Continue to a pH of about 4.0.
3. If the volume needed to reduce the pH by 1 unit is too small, increase the sample size and repeat the titration. Add either 0.5 or 1.0 mL increments of titrant at a time. It is advantageous to plot pH versus volume of titrant as the titration progresses to determine where less (or greater) volume increments should be used.

B) Alkalinity

I. Standardization

1. Prepare a 0.1 M sodium hydroxide solution. Quickly weigh about 4 g of sodium hydroxide pellets using a small beaker and transfer to a 1 L plastic bottle. Fill the bottle with 1 L of DI water and mix thoroughly. An alternative procedure is to dilute 8 g (about 5-6 mL) of 50% (w/w) sodium hydroxide to 1 L with DI water, whereby this procedure eliminates sodium carbonate as an impurity since it is insoluble in the concentrated base.
2. Prepare 0.1 M HCl (for alkalinity greater than 20 mg/L). In a fume hood, measure out 8.3 mL of concentrated HCl using a 10 mL graduated cylinder

and dilute to 1 L in a glass or plastic bottle. Mix well.

3. Prepare 0.02 M HCl (for alkalinity lesser than 20 mg/L). Dilute 200 mL of the 0.1 M HCl to 1 L using volumetric flasks.
4. Standardize the 0.1 M NaOH against primary standard potassium acid phthalate (KHP). Weigh accurately (to 0.1 mg) three samples of KHP (previously dried) weighing about 0.5 g each (0.49-0.51 g). Quantitatively transfer the KHP to 250 mL Erlenmeyer flasks and dissolve in about 75 mL DI water. Add 3 drops of phenolphthalein indicator and titrate with the 0.1 M NaOH until the faintest pink persists for 30 seconds. You must rinse the burette with three 10 mL portions of the sodium hydroxide before use. If there is no prepared phenolphthalein indicator, it shall be prepared by dissolving 0.5 g of phenolphthalein in 50 mL of ethanol in a 100 mL volumetric flask, followed by addition of DI water up to the calibration mark.
5. Use the standardized 0.1 M NaOH solution to titrate 25.00 mL (pipetted) aliquots of the 0.1 M HCl diluted to about 75 mL with DI water. Do three determinations of the molarity of the HCl and use the average value in subsequent calculations.

II. Indicator Titration for Alkalinity

1. Do not filter, dilute, or concentrate the selected water samples before testing. Since a large range of alkalinity is possible, made a rough measurement using 0.1 M HCl titrant. This allows for adjusting sample size so that the titration volume is greater than 10 mL, but less than 50 mL. For sample with titrant volume used is very small, a 0.02 M HCl solution is used with an appropriate sample size. Thus, the “test titration” with 0.1 M HCl is a guess to see what concentration of acid is needed.
2. Pipet 100 mL of sample (or the appropriate amount determined in a test titration) into a 250 mL Erlenmeyer flask. Add 3-5 drops of methyl orange. If there is no prepared methyl orange indicator, it shall be prepared by dissolving 1 g of methyl orange in 20 mL of ethanol in a 100 mL volumetric flask, followed by addition of DI water up to the calibration mark.
3. Rinse a burette with three 10 mL portions of 0.1 M HCI. Fill with the acid and record the initial volume. Titrate the sample with the standardized 0.1 M HCI to the endpoint (which is orange to red) and record the final volume.
4. If the alkalinity is less than 20 mg/L, as determined by the test titration, use 0.02 M HCl and adjust the sample size if necessary.
5. Do two additional titrations on the same sample according to Steps 1 and 2.
6. Repeat Steps 1-3 for rainwater sample.

III. Potentiometric Titration

1. Choose one of the environmental samples studied by indicator titration to examine in this part of the experiment. Use pipet to measure out 100 mL of sample into a 250 mL beaker. Lower the pH electrode into the sample, being certain that the bulb of the glass electrode is completely covered.

2. Using a magnetic stir bar and plate, obtain a potentiometric titration curve by adding standard 0.1 M HCl from a burette in either 0.5 mL or 1.0 mL increments, stirring and measuring the pH, until a pH of 4.0 is obtained. Record the pH after each addition of titrant.

4. REPORT

A) pH and Buffer Capacity of Environmental Water

1. Tabulate your pH values, the type of sample, and expected pH values as presented in Introduction. Explain any differences between measured pH values and expected values.
2. Prepare a plot of pH versus volume of titrant for the environmental samples studied. Submit a copy of the titration curve.
3. Use the titration curve to determine the volume of titrant needed to decrease the initial pH by 1.00 unit. Use this volume to calculate the buffer capacity. The buffer capacity is the number of moles of the acid needed per liter of sample needed for this change in pH. Compare your result with the buffer capacity of a carbonate/bicarbonate system. You can obtain the buffer capacity of a carbonate/bicarbonate system through literature search.

B) Alkalinity

1. The molarity of sodium hydroxide can be obtained from the stoichiometric titration reaction, NaOH + KHP $\longrightarrow$ H_2O + KNaP. At the endpoint, the moles of base are equal to the moles of acid. Also, mol NaOH = [(mL)/1000](M) and mol KHP = mass/molar mass. Therefore, the molarity of NaOH is given by,

$$M = (mass\ KHP / 204.23)/(mL\ NaOH\ / 1000)$$

Report each individual molarity and the average of the values for NaOH.

2. Report the titration volumes and the calculated molarities of the 0.1 M HCl and report the mean molarity.
3. If the 0.02 M HCl was used, report its molarity (from standardization or by calculation from the dilution of a standard solution).
4. The alkalinity for both the indicator and potentiometric methods is given by

$$[Alk] = 1/2(mL\ HCl)(M_{HCL})(100.0\ mg/mmol\ )/L\ of\ sample$$

where the alkalinity is expressed in mg $CaCO_3$/L. The volume of titrant is the

volume of HCl needed to achieve a pH of 4.3 and 100.0 mg/mmol is the molar mass of $CaCO_3$ (g/mol = mg/mmol). Report the alkalinity of the water samples. Compare the alkalinity values obtained from both indicator and potentiometric methods.

5. Discuss the alkalinities for the two sample types and discuss their differences.

5. REFERENCES

Boehnke DN, Delumyea RD, 2000. Laboratory Experiments in Environmental Chemistry, Prentice Hall, New Jersey.

Ibanez JG, Doria-Serrano MHC, Singh AFMM, 2008. Environmental Chemistry: Microscale Laboratory Experiments, Springer, New York.

DETERMINATION OF WATER HARDNESS OF ENVIRONMENTAL WATERS – CONVENTIONAL EDTA COMPLEXOMETRIC TITRATION

1. INTRODUCTION

The hardness of water is originally defined in terms of its ability to precipitate soap. Calcium and magnesium ions are the principal causes of hardness in water, although iron, aluminum, manganese, strontium, zinc, and hydrogen ions are also capable of producing the same effect. The total hardness of water is now defined as the amount of calcium and magnesium present and is expressed as ppm calcium carbonate.

The procedure for determining both calcium and magnesium, when present together, is found in many schemes of applied analysis, including the analysis of minerals, blood serum, and food, and is the standard method for determining water hardness.

The hardness test is one of the most performed analyses in the water industry. High levels of hardness are undesirable and must be removed before the water is used by the beverage, laundry, metal-finishing, dying and textiles, food, and paper pulp industries. Hardness levels greater than 500 ppm calcium carbonate are undesirable for domestic use and most drinking water supplies average about 250 ppm. Table 3-1 lists the various classes of hardness.

Table 3-1 Classes of hardness based on hardness range (Boehnke and Delumyea, 2008).

Hardness Range (ppm $CaCO_3$)	Hardness Description
0 – 50	Soft
51 – 150	Moderately hard
151 – 300	Hard
> 300	Very hard

Metal ions act as Lewis acids. Anions or molecules with unshared pairs of electrons can act as Lewis bases and covalently bind to metal ions. The electron pair donors are called ligands, and the species formed in the reaction are known as complex ions if ionic or complexes (or coordination compounds) if neutral. Ligands that bind to the metal at more than one coordination site are called polydentate. The ethylenediaminetetraacetate ion (EDTA) is an important polydentate ligand. This species has six donor atoms and is thus hexadentate. It reacts with many metal ions in a 1:1 ratio to form very stable complexes, as in the equation:

$$Co^{3+} + [EDTA]^{4-} \rightarrow [Co(EDTA)]^{-}$$

EDTA is a tetraprotic acid and is frequently represented as H_4Y. The usual form of EDTA is the disodium salt, Na_2H_2Y. When this form is used as the titrant in a complexometric titration, the titration reaction is:

$$Na_2H_2Y\ (aq) + M^{2+}\ (aq) \rightarrow MY^{2-}\ (aq) + 2\ H^{+}\ (aq) + 2\ Na^{+}\ (aq)$$

Since hydronium ions are produced, a buffer is necessary since calcium and magnesium ions must be titrated at high pH for stable complexes to be formed and for the proper functioning of the indicator.

The indicators used for EDTA titrations are called metallochromic indicators, and for the most part they are weakly acidic organic dyes. They include Eriochrome Black T (EBT). EBT functions by forming a colored metal complex, $MEBT^-$, at the start of the titration. As long as some metal remains unchelated by EDTA, the solution being titrated remains the color of $MEBT^-$ complex. At the equivalence point, EDTA removes the metal ion from the indicator-metal complex by chelating it, and the solution changes color:

$$Na_2H_2Y + MEBT^- \rightarrow HEBT^{2-} + MY^{2-} + H^{+} + 2\ Na^{+}$$

The hardness due to calcium and magnesium ions separately can be determined by using the fact that at very high pH, magnesium forms the insoluble hydroxide, $Mg(OH)_2$, whereas calcium remains in solution. The calcium can then be titrated with standard EDTA, and its concentration determined. If another sample is titrated with EDTA at a lower pH, both calcium and magnesium ions react. The magnesium hardness is found by the difference in titrant volume used for the two samples. Some ions, notably iron (III), block the indicator by combining irreversibly with it. In this case the interfering ion must either be removed or chemically tied up before titrating with EDTA.

2. LEARNING OBJECTIVES

i. To measure the hardness of environmental water samples using conventional EDTA complexometric titration.

3. METHODOLOGY

1. In this experiment, you will use the sample collected in Experiment 1, tap water, and rainwater. Filter 50 mL of all the water samples beforehand.
2. Prepare a 250 mL EDTA standard solution with the concentration of 0.01 M using Na_2EDTA. For more accuracy, standardize the EDTA.

3. Pipet 10.00 mL of filtered water into a 250 Erlenmeyer flask, and dilute to about 50 mL with DI water. Add 15 mL of pH 10 buffer and mix thoroughly. Add 4 drops (or a small amount) of EBT indicator and titrate with standard 0.01 M EDTA until a pure blue color, with no tinge of purple. Repeat this procedure for two additional samples, increasing the volume of sample if the titrant used is less than 10 mL.
4. Repeat step 3 for other samples.

4. REPORT

1. Report the concentration of the standard EDTA.
2. Report the total hardness, in ppm $CaCO_3$, for each determination. Since number of moles of EDTA = number of moles of metal from the titration reaction, the moles of calcium carbonate are equal to the moles of EDTA used in a titration. This is finally converted into mg $CaCO_3$/L of sample.
3. Report the mean, standard deviation and %RSD for each type of sample analyzed. Discuss the precision of this method.
4. Compare your hardness results with those given in Table 3-1 and classify the hardness of your samples accordingly.

5. REFERENCE

Boehnke DN, Delumyea RD, 2000. Laboratory Experiments in Environmental Chemistry, Prentice Hall, New Jersey.

DETERMINATION OF DISSOLVED OXYGEN AND CHEMICAL OXYGEN DEMAND OF ENVIRONMENTAL WATERS

1. INTRODUCTION

A) Dissolved Oxygen (DO)

The level of DO in water is one of the most important parameters in determining its quality, because it indirectly indicates whether there is some kind of pollution. Common processes that pollute surface waters include the discharge of organic matter derived from municipal sewage or industrial wastes, and runoff from agricultural lots and livestock feedlots. In addition, the release of warm or hot discharges from industrial cooling towers induces what is known as thermal pollution. Such discharges directly affect the level DO in water bodies, which is crucial for the survival of aerobic organisms and aquatic fauna such as fish; in fact, excessive pollution has caused massive fish deaths. In the long run, the discharges of organics or of nutrients favor the accelerated eutrophication or productivity process with algal blooms. As a consequence, there will be a lowering of the DO content (or DO level) and the "death" of the aquatic system (Ibanez et al., 2008).

The measurement of the DO is also important to determine whether a water system is predominantly aerobic or anaerobic, predict the survival of aquatic organisms, and predict whether aerobic biological processes can take place for transforming the biodegradable organic contaminants discharged in water. When there is an organic discharge, the DO decreases rapidly due to the action of the aerobic microorganisms that consume oxygen during the metabolic degradation of organic matter. Consequently, the presence of dissolved oxygen is critical for the self-cleansing of the water system, and in combination with the presence of CO_2, it is also critical for the determination of the corrosive character of water on materials such as iron and other metals (Ibanez et al., 2008).

In this experiment, DO will be determined using Winkler method. The principle of analysis is based on the oxidation of iodide ion to iodine by DO. The amount of iodine generated is then determined by titration with standard thiosulfate solution. The endpoint is determined by using starch as a visual indicator.

B) Chemical Oxygen Demand (COD)

COD is a measurement of the oxygen required to oxidize soluble and particulate organic matter in water (Real Tech Inc, 2015). COD is a common parameter used to measure the amount of organic compounds in water. Most applications of COD

determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in mg/L, which indicates the mass oxygen consumed per liter of solution. The method used in this experiment involves using an excess amount strong oxidizing reagent, potassium dichromate $Cr_2O_7^{2-}$, to oxidize the organic matter in solution to carbon dioxide and water under acidic conditions. The test also involves a silver sulfate to encourage oxidation of certain organic compounds and mercury (II) sulfate to reduce the interference from oxidation of chloride ions (Real Tech Inc, 2015). The sample is reflux for 45 min. The remaining $Cr_2O_7^{2-}$ is determined using titration method. The amount of oxygen required is calculated from the quantity of chemical oxidant consumed.

2. LEARNING OBJECTIVES

i. To determine the dissolved oxygen (DO) of water samples by using Winkler Method.
ii. To determine the chemical oxygen demand (COD) of water.

3. METHODOLOGY

A) Determination of DO

1. **Collection of sample —** Collect 2 different environmental water samples using a narrow necked 200-300 cm^3 glass bottle having an accurately fitting ground glass stopper. If the water from a tap, pass the water down a glass tube to the bottom of the bottle and allow water to overflow for 2-3 minutes before insertion of the stopper. When sampling stream water, displace the water in the bottle several times, before collecting the sample. Avoid inclusion of air bubbles in the sample bottle.

2. **Standardisation of Sodium Thiosulphate —** Mix 5 cm^3 of 10% w/v aqeuous potassium iodide solution and 10 cm^3 of dilute sulphuric acid (1:3 v/v) and add 2 cm^3 of 0.025 mol dm^{-3} potassium iodate solution in that order in a glassstoppered flask. Add about 100 cm^3 of distilled water. Titrate immediately with sodium thiosulphate solution until the colour is pale yellow. Add 2 to 3 drops of starch solution and continue the titration until the blue colour just disappears. Freshly prepare the starch solution by dissolving 0.25 g of starch in 50 mL of near boiling water in a 100 mL beaker, and leave the solution to cool.

3. **Procedure for the Determination of DO in Water —** Carefully remove the stopper from the sample bottle and add 1 cm^3 of 0.5 mol dm^{-3} manganous sulphate solution followed by 1 cm^3 alkaline-iodide-azide solution. When introducing various reagents into the full bottle of sample, the tips of the pipettes should be well below the surface of the liquid. Replace the stopper carefully after each addition so as to avoid inclusion of air bubbles. Thoroughly mix the contents by inversion and rotation until a clear supernatant water is obtained.

Add 1 cm^3 concentrated sulphuric acid with the trip of the pipette below the level of solution and again replace the stopper. Mix well by rotation until the precipitate has completely dissolved. Pipette into a 250 cm^3 conical flask 100 cm^3 of the solution and immediately titrate it against 0.0125 mol dm^{-3} standard sodium thiosulphate using freshly prepared starch solution as the indicator (add when solution becomes pale yellow). Carry out the titration in duplicate.

B) Determination of COD

1. **Collection of Sample —** Use 2 different environmental water samples.

2. **Standardization of Ammonium Iron (II) Sulphate —** Add 10 cm^3 concentrated sulphuric acid carefully to 20 cm^3 water and cool. Add 2 cm^3 of 0.02 mol dm^{-3} potassium dichromate and titrate with 0.025 mol dm^{-3} ammonium iron(II) sulphate using drops of ferroin as indicator. The colour changes from bluish-green to reddish-brown.

3. **Procedure for Determination of COD —** Introduce 10.0 cm^3 of the water sample into 100 cm^3 round-bottomed flask, and add 2 cm^3 of 0.02 mol dm^{-3} potassium dichromate, 2.5 cm^3 mercuric sulphate solution, 10-15 cm^3 concentrated sulphuric acid containing silver sulphate, and an anti-bumping rod. Heat to gentle, but steady boiling over an electric hot plate or heating mantle and under a reflux condenser. After exactly 45 minutes boiling, allow to cool briefly, wash 20 cm^3 distilled water through the condenser into the flask and the cool completely in cold water. Add 2 drops of ferroin solution and titrate the excess potassium dichromate with ammonium iron (II) sulphate until the colour changes from bluish-green to reddishbrown. Determine a blank with 10.0 cm^3 distilled water under exactly the same conditions.

4. REPORT

1. Explain the reaction involved in the determination of dissolved oxygen in water using Winkler methods. Establish the relationship: 10 cm^3 of 0.0125 mol dm^{-3} sodium thiosulphate = 1 mg O_2.
2. Report the result in mg dm^{-3} of COD and DO as well as percentage of O_2 saturation by refering to the following table:

Table 4-1 Oxygen content in Air-Saturated Water.

Temperature (°C)	**10**	**15**	**20**	**25**	**30**	**35**
O_2 content (mg/kg)	**11.2**	**10.2**	**9.1**	**8.3**	**7.6**	**7.1**

5. REFERENCE

Ibanez JG, Doria-Serrano MHC, Singh AFMM, 2008. Environmental Chemistry: Microscale Laboratory Experiments, Springer, New York.

Real Tech Inc., 2015. Chemical Oxygen Demand (COD). http://realtechwater.com/chemical-oxygen-demand/ (accessed on 20/10/2016).

SPECTROPHOTOMETRY, COLORIMETRY, AND ABSORPTION SPECTRA: DETERMINING IRON IN ENVIRONMENTAL WATERS

1. INTRODUCTION

Background of Colorimetric and Spectrophotometric Analysis

Colorimetric and spectrophotometric methods are perhaps the most frequently used and important methods of quantitative analysis. These methods are based on the absorption of light by a sample. The amount of radiant energy absorbed is proportional to the concentration of the absorbing material, and by measuring the absorption of radiant energy it is possible to determine quantitatively the amount of substance present.

Colorimetric and spectrophotometric methods of analysis have been worked out for most of the elements and for many types of organic compounds. Methods based on the absorption of light are well suited to the determination of sample constituents from trace levels up to amounts of 1-2% but are not as frequently used for the analysis of larger (macro) quantities of substances.

The fundamental law on which colorimetric and spectrophotometric methods are based is the Bouguer-Beer or Lambert-Beer law, usually referred to simply as Beer's law. In mathematical form this Law is

$$A = abc$$

where *A* is the absorbance, a is the absorptivity, *b* is the internal cell length, and c is the concentration of the solution. When the concentration is expressed in mol/L, Beer's law is written

$$A = \varepsilon bC$$

where ε is called the molar absorptivity, or the extinction coefficient, and C is the molarity. Typically, *b* is measured in cm, and therefore ε has units of $M^{-1}cm^{-1}$.

The colorimeter, or spectrophotometer, is an important analytical instrument that makes possible a quantitative measurement of the light that passes through a solution. The first step in an analysis is the determination of the optimum wavelength to use for the analysis. The analyte must appreciably absorb light at the wavelength chosen. In a colorimeter exact wavelength is not used, but rather small bands of wavelengths and the wavelength chosen for analysis must be such that the absorbance does not change rapidly with the wavelength. If all the wavelengths in this narrow band are absorbed to nearly the same extent, the result is the same as if we isolated a single wavelength to use. Therefore, for an analysis have chosen a flat portion of the absorption spectrum (a

plot of absorbance versus wavelength). Absorption spectra for metal analysis is shown in **Figure 5-1**.

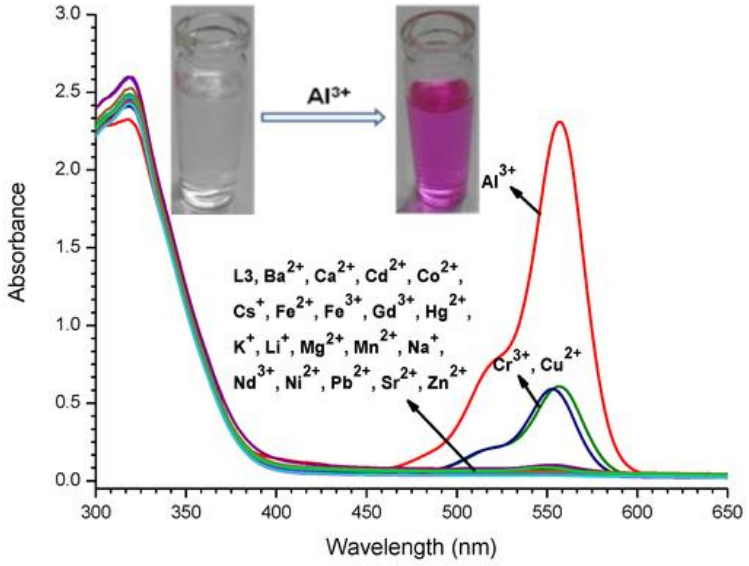


Figure 5-1 Absorption Spectra for the determination of metals (Mergu et al., 2015).

Instruments that measure the absorption of radiant energy, spectrophotometers, have five essential components, as shown in **Figure 5-2**. For instruments that are used in the visible region of the spectrum, tungsten filament bulb is used as the source. The **wavelength** of light that enters the system is limited by means of a filter or a monochromator. The **amount** of light that enters the system is controlled with a variable slit or other means. The light then passes through the sample solution held in a glass cell called **cuvette** (quartz must be used in the ultraviolet region). Finally, the transmitted light strikes a phototube or other transducer (such as a photodiode), that converts it into an electric current. The current produced is a function of the radiant power of the light striking the transducer. The current is amplified and is then measured by a meter or a digital readout.

The advantage of a colorimeter is its relatively low cost and simplicity of operation. However, most colorimeters are not able to automatically change wavelength. The output from the source is not constant for all wavelengths, and this necessitates an adjustment in slit width or the sensitivity whenever they wavelength is changed. Also, colorimeters are single-beam instruments and therefore cannot automatically correct for the intensity changes in the light source and variations in detector sensitivity when the wavelength is changed.

The absorbance of a "reagent blank" must be determined at the start of an analysis to correct for any light absorption by the solvent or reagents.

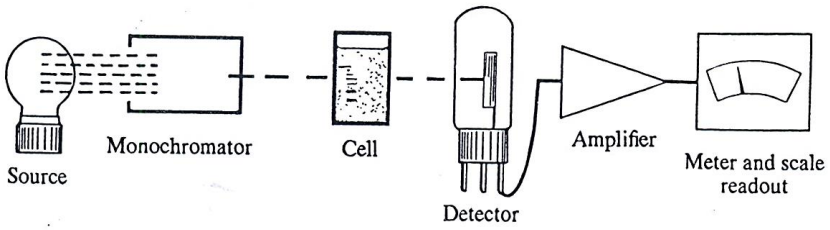


Figure 5-2 Block Diagram of a Generic Spectrophotometer (Boehnke and Delumyea, 2000).

Steps in an Analysis

If the analyte is colored, a colorimeter is used for the analysis and the cuvettes can be made of optical glass. If the analyte is not colored, but has an absorption in the ultraviolet, an ultraviolet spectrophotometer is used for the analysis and the cuvettes must be made of quartz or fused silica. In either case, the procedure for an analysis is the same, with the exception of the wavelength region scanned. In the visible region the wavelength range scanned is 760-400 nm, whereas in the ultraviolet region the wavelength range scanned is 400-200 nm.

1. *Formation of a Light-Absorbing Species* - When a species to be analyzed is not colored and must be analyzed using a colorimeter, it is transformed into a light-absorbing species. (Alternatively, if an ultraviolet spectrophotometer is available and if the species has a functional group that absorbs in the ultraviolet, the use of this instrument may be the easiest way to analyze the sample.) One straightforward way to obtain a colored species is to form a complex. Some metals form highly colored complexes with thiocyanate, r for example. A second way to produce a colored species is to transform a metal from a low oxidation state to a higher oxidation state by using an oxidizing agent. Chromium(III), which is only faintly colored, is - transformed by oxidizing agents into chromate, CrO_4^{2-} or dichromate, $Cr_2O_7^{2-}$, both of which are intensely colored. Some other types of reactions also produce colored species.

2. *Measuring the Absorption Spectrum* - The absorbance of the analyte solution is determined as a function Off of wavelength. The results are plotted (if a recording instrument is not used), preferably using computer software. Ideally, the most intense peak is chosen for the analysis, since it would be the most sensitive to the lowest concentrations. However, if the most intense peak is also sharp, it is better to choose a smaller, broader peak. The solutions should not contain suspended matter or colloids, which scatter light and distort absorbance measurements.

3. *Preparation of a Calibration (Beer's Law) Plot* - A series of standard solutions of the analyte is prepared spanning the concentrations expected. The instrument is

adjusted to the wavelength chosen for the analysis, 7 and the absorbance of each standard is measured. A plot of absorbance (ordinate) versus concentration is made, preferably using a computer. A least-squares analysis is carried out to obtain the equation of a straight line from which solution concentrations are calculated from measured absorbances. The correlation 7 coefficient from this analysis indicates the precision of the results. Curvature of the plot may indicate a change of equilibrium position of the analyte species with dilution and may have to be taken into account. A Beer's law plot is illustrated in **Figure 5-3**.

4. *Measuring the Sample* - The absorbance of the sample is measured at the wavelength used for the calibration. The concentration of the analyte is found from the Beer's law plot (either by estimating directly from the plot or by calculation using the straight-line Beer's law equation). The analyte concentration should be between the extreme limits of the plot; if not, its concentration or the concentrations of the standards should be adjusted accordingly.

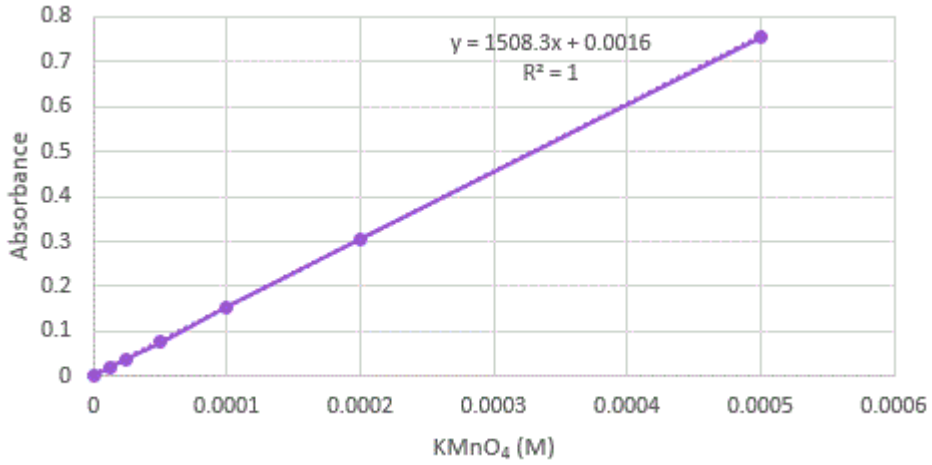


Figure 5-3 Beer's Law Plot for Permanganate at 500 nm.

Determining Iron in Natural Waters

Iron is found throughout the environment, often in large amounts. It enters the hydrosphere through the weathering of iron salts and minerals. Both iron(II) and iron(III) are found dissolved in water, often in colloidal form, or as inorganic and organic iron complexes. There are many industrial sources of iron, including canneries, tanneries, textile mills, shipping, and metal-cleaning operations.

Large concentrations of iron discharged into a stream or lake may have deleterious effects on aquatic life. A limit of 0.3 mg/L of iron is recommended for food and dairy product processing, soft drink manufacture, rind brewing, mainly because of taste.

Iron is a vital element in the respiratory processes of many animals, including humans. The human body has a great demand for iron, and 4 grams are found in the

average human. Iron-containing proteins transport oxygen, catalyze the decomposition of peroxides, and play an essential role in the body's energy-generating processes. It is possible to ingest too much iron, which may cause liver damage. Thus, iron vitamin supplements contain cautionary statements.

A simple but sensitive procedure for the colorimetric determination of iron entails chelating ferrous iron with three molecules of 1,10-phenanthroline (phen) in a solution buffered at low pH,

$$Fe^{2+} + 3\ phen \rightarrow [Fe(phen)_3]^{2+}$$

The orange-red complex has an absorption maximum at 510 nm.

A preliminary acid digestion of the sample is carried out in a fume hood to destroy organic matter and also to remove cyanide and nitrate which interfere with the analysis. Hydroxylamine hydrochloride is then added to reduce all iron(III) to iron(II), which is the effective complexing species. Then an excess of phen is added to the sample at a pH between 3.5 and 4.5. The low pH prevents other metals from precipitating rand provides rapid reaction and color development. The concentration range of this method is 0.025-3.0 mg/L. Concentrations greater than 3.0 mg/L can be determined after diluting.

An advantage of the 1,10-phenanthroline method is its use of slightly acidic media. This prevents not only the precipitation of hydroxides, but also the phosphates and other anions of many metals. It is necessary that iron be present in a form that reacts completely with 1,10-phenanthroline in a reasonable period of time. This means that iron must not be bound to pyrophosphates or other ligands that form stable complexes; also, phosphate precipitates that contain iron must be prevented from forming. Therefore, the usual procedures in which sodium acetate is used to adjust the pH to 3.5-4.5 are not adequate for biological samples due to the possibility of precipitating ferric and aluminium phosphates. This is avoided by using sodium citrate.

2. LEARNING OBJECTIVES

i. To illustrate the general principles of absorption spectrophotometry by demonstrating Beer's law.
ii. To measure the concentration of iron in water.

3. METHODOLOGY

Preliminary Work

1. Attempt to form a complex between thiocyanate ion and iron(II) by mixing together 5 mL each of 0.01 M KSCN and 0.01M $Fe(NO_3)_2$.

2. Repeat Step 1, this time using 0.01 M $Fe(NO_3)_3$ in acid in place of 0.01 M ferrous ion.

3. Use a colorimeter or a recording spectrophotometer to measure the absorption spectrum of the solution prepared in Step 1 and 2, scanning from 760 to 400 nm. If necessary, dilute the solution to bring its absorbance within the range of the instrument. Use water as the reference.

4. Repeat Steps 1 and 3 using 5 mL each of 0.01M $Fe(NO_3)_2$ and 0.3%(w/v) 1,10-phenanthroline solution instead of thiocyanate.

Procedure for Iron in Water

1. Preparation of Standard 100 ppm Iron Solution - Weigh 351 mg of high quality ferrous ammonium sulfate hexahydrate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, and quantitatively transfer to a 500 mL volumetric flask. Add 50 mL DI water followed by 1 mL of concentrated sulfuric acid. Dilute to the mark with DI water and mix thoroughly.

2. Preparation of Standard Solutions - Prepare five standard solutions of iron(II) having the following concentrations: 0.5, 1.0, 2.0, 3.0 and 5.0 ppm. Pipet 0.5, 1.0, 2.0, 3.0 and 5.0 mL of 100 ppm stock solution into 100 mL volumetric flasks and dilute to the mark with DI water.

3. Obtaining a Beer's Law Plot - Transfer a 5 mL aliquot of the 0.5 ppm iron standard to a 125 mL Erlenmeyer flask and test the pH with test paper. If greater than 4.5, add enough 0.2 M sulfuric acid dropwise by using a buret to bring the pH to about 3.5, record the volume of sulfuric acid. Add sodium citrate (259 g/L) buffer dropwise to bring the pH to about 4.5 and again record the volume of sodium citrate buffer. Pipet 1 mL of 10%(w/v) hydroxylamine hydrochloride and 3 mL of 0.3%(w/v) 1,10-phenanthroline into the sample, mix, and allow 5 minutes for color development. Use the same volume of sulfuric acid and sodium citrate for the remaining four standard solutions, followed by 3 mL of 0.3%(w/v) 1,10-phenanthroline and 1 mL of 10%(w/v) hydroxylamine hydrochloride. Mix well. After adjusting the 0 and 100%T on the colorimeter at 512 nm, use water as the reference and measure the absorbance of each standard. (A reagent blank can also be used if desired. This consists of all substances added to the sample, is treated the same way as the sample, and accounts for any absorbance due to these materials.)

4. Analysis of Samples - Natural and tap water samples often have less than 0.5 ppm iron. A water faucet that has not been used for some time may furnish a good sample for iron analysis. Some well waters are high in iron content as well. However, even very dilute samples are within the range of this experiment. Determine the iron in several environmental water samples. Treat samples the same way as the standards, adding sulfuric acid initially, if necessary, followed by citrate buffer, reducing agent and the indicator. Use 5 mL samples and adjust the pH for each sample individually.

4. REPORT

1. Submit the two absorption spectra. From the iron-phenanthroline absorption spectrum decide what wavelength(s) can be used for analysis. Which particular peak, if there is more than one, would be best for an iron analysis?
2. Briefly discuss the effect of the ligand on the wavelength and the maximum absorbance of the peaks.
3. Calculate the extinction coefficient for the largest peak in the absorption spectrum of the iron-phenanthroline complex. (An excess of 1,10-phenanthroline was used.) The cell path length is exactly 1.0 cm. What quantitative information does this provide?
4. Prepare a Beer's law plot for the standard solutions (absorbance as ordinate versus concentration as T abscissa). Carry out a least-squares analysis and determine the slope, the y-intercept, and the correlation coefficient for the best straight line; comment on the linearity of the plot.
5. Use your Beer's law plot to determine the concentration (in mg/L) of iron in each sample studied. The concentration of a sample can be obtained directly from the Beer's law plot. Alternatively, the equation of a straight line can be obtained from the slope and y-intercept and the concentration calculated from the sample's absorbance. If duplicate determinations were done, report average values and the individual values of concentration and discuss the reproducibility.
6. Discuss the magnitude of the iron levels with respect to the sampling site.

5. REFERENCE

Boehnke DN, Delumyea RD, 2000. Laboratory Experiments in Environmental Chemistry, Prentice Hall, New Jersey.

Mergu N, Singh AK, Gupta VK, 2015. Highly Sensitive and Selective Colorimetric and Off-On Fluorescent Reversible Chemosensors for Al3+ Based on the Rhodamine Fluorophore, Sensors 15, 9097-9111.

DETERMINATION OF TRACE AMOUNTS OF METALS BY ATOMIC ABSORPTION SPECTROSCOPY

1. INTRODUCTION

Background of Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy (AAS) is an important analytical technique for the quantitative and qualitative analysis of metal ions. It is useful for measuring the presence and amounts of toxic metal cations in environmental samples, as well as for interrogating the metal content of ores in the mining industry to evaluate the economical worth of pursuing their extraction. With proper sample preparation method, the metal content of various samples such as minerals biological samples, agricultural samples, petroleum, air particulate matters and water can be determined using AAS. This experiment is intended to illustrate the basic procedures used to analyse real samples for metals at the low part per million level.

Free atoms cannot undergo rotational or vibrational energy transitions, as molecule can. Only electronic transitions can occur when energy is absorbed or emitted. Because electronic transitions are discrete (quantized), line spectra are observed.

There are various ways of obtaining free atoms and measuring the radiation they absorb or emit. In flame spectrometry, a solution is aspirated into a flame and the compounds present are thermally dissociated into atomic vapour. The heat of the flame first causes the solvent to evaporate. The micro-crystals produced are partially (or wholly) dissociated into the elements in the gaseous state. Some of the atoms thus produced can absorb radiant energy of a particular wavelength and become excited to a higher electronic state. When these atoms fall back to lower energy levels and emit light, this provides the basis for a very sensitive analytical technique, atomic emission spectroscopy. In this method, high-temperature electric arcs or plasmas are used to maximize the production of excited atoms.

The term “Atomic absorption” refers to the absorption of energy from a light source, with a consequent decrease in the radiant power transmitted through the flame. The measurement of this absorption corresponds to AAS.

The majority of atoms in a flame are in the ground state; thus, most electronic transitions originate from this state. A partial energy-level diagram for sodium is shown in Figure 6-1. There are several possible transitions for sodium, but the primary line is at 589 nm.

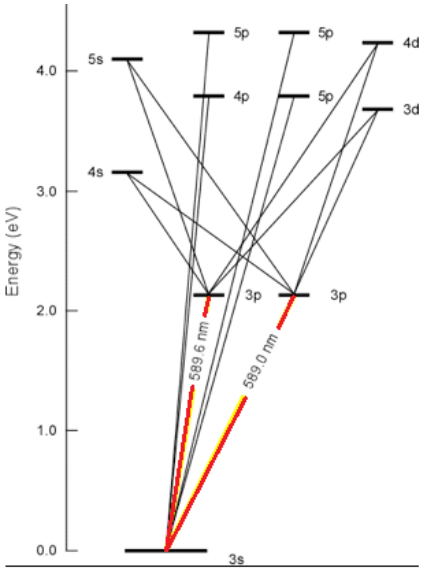


Figure 6-1 Partial energy level diagram for the sodium atom.

More than 60 elements can be determined by AAS, many at the part per billion level. Only metals and metalloids can be determined directly by usual flame methods because the resonance lines for non-metals occur in the vacuum ultraviolet region of the spectrum. Table 10-1 lists the atomic absorption detection limits and wavelengths used for several environmentally important elements. For analytical measurements, the concentrations should be at least 10 times the detection limit since, by definition, the precision at the detection limit is no better than ±50%.

Table 6-1 Wavelengths and Detection Limits for Various Elements.

Element	Wavelength (nm)	Detection limit (ppb)
Ag	328.07	1
Ca	422.67	2
Cd	228.80	1
Co	240.72	2
Cr	357.87	2
Cu	324.75	4
Fe	248.33	4
Hg	253.65	500
K	766.49	3
Mg	285.21	3
Mn	279.48	0.8
Na	589.00	0.8
Ni	232.00	5
Pb	283.31	10
Sn	235.48	50
Zn	213.86	1

Atomic absorption essentially uses monochromatic radiation to excite vaporized atoms in their ground state. The instrument consists of a light source, a cell (consisting of the aspirated sample), a monochromator, and a detection system. The instrument is shown in Figure 6-2.

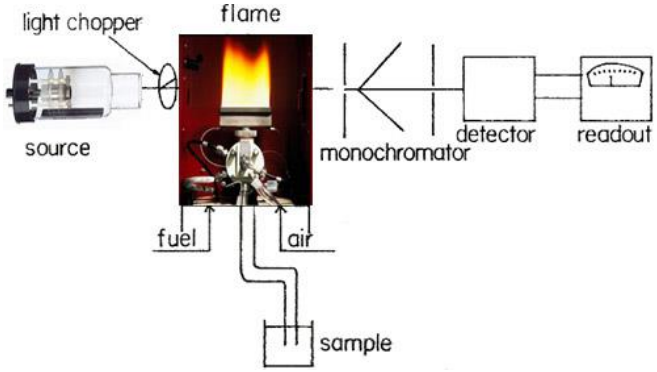


Figure 6-1 Schematic diagram for a basic AAS.

The source, usually a hollow cathode tube, emits essentially line radiation of the same wavelength as that being absorbed by the element under study. This is accomplished by making the source out of the sample element. Thus, if iron is to be determined, a lamp having an iron cathode is used. The sample is nebulized into a premixed gas-air burner designed for a long path length. The radiation then passes into a monochromator and is measured at the detector. The amount of radiation absorbed is proportional to the concentration of the element in the sample. A calibration curve is obtained by measuring the absorbance of a series of standard solutions.

2. LEARNING OBJECTIVES

i. To introduce one of the most important methods of environmental chemistry, atomic absorption spectroscopy. This instrumental method is used to detect metals and metalloids down to the ppb level. The method is fast and accurate and can be made to be essentially free of interferences.

3. METHODOLOGY

1. Collect two soil samples. Dry the samples at 110 °C for 3 hours.
2. Tare a labeled 150 mL beaker on an analytical balance and scoop in 10 g of soil sample. Weigh the sample to the nearest 0.1 mg. Repeat for a different environmental sample.
3. In a fume hood, add 10 mL of DI water and 10 mL of high-purity (for trace metal analysis) concentrated nitric acid to each sample, Add the acid slowly if there is frothing.
4. Prepare blank by adding 10 mL of DI water and 10 mL of high-purity concentrated nitric acid to another 150 mL beaker. Treat the blank identically to the samples.
5. Cover the beakers with watch glasses and gently swirl to mix. Heat on a hotplate to just below the boiling point and continue heating for 30 minutes. If necessary, add

an additional 10 mL of acid if it appears that organic matter has not decomposed. Also add additional water if there is much evaporative loss. ***NO_2 fumes (brown colour fumes) given off by decomposing nitric acid are extremely toxic. Avoid breathing in any of these fumes.**

6. Remove the beakers from the hotplate, add 10 mL DI water to each sample, and allow to cool to room temperature. Filter each sample, including blank, using filter paper, catching the filtrate in a 100 mL volumetric flask. Rinse the beaker twice with small portion of DI water, adding the rinses to the funnel. Finally, rinse the funnel twice, using small amounts of DL water from a squeeze bottle. Bring the volume in the flask up to the mark, stopper, and mix thoroughly. The solution should be clear and devoid of any particles. Transfer the samples and blank to plastic bottles if they are not going to be immediately analyzed.
7. Select 3 metals. For each of the selected metals, prepare five standard solutions having concentration of 1, 2, 3, 5, 10 ppm. Prepare 50 mL of each standard and transfer to plastic containers for storage if samples and standards are not going to be immediately analyzed.
8. Analyze the samples and standard solutions with AAS.
9. Analysis of soil samples should be performed in triplicate.

4. REPORT

1. Prepare a calibration plot of absorbance versus concentration of each selected metal.
2. Use the calibration plots to calculate the concentration of metals (in ppm).
3. Calculate the (mg of metal)/(kg of sediment) for each metal and for each sample.
4. Do your values fall within expected values, or are they much higher than normal background levels? Discuss.

5. REFERENCE

Boehnke DN, Delumyea RD, 2000. Laboratory Experiments in Environmental Chemistry, Prentice Hall, New Jersey.