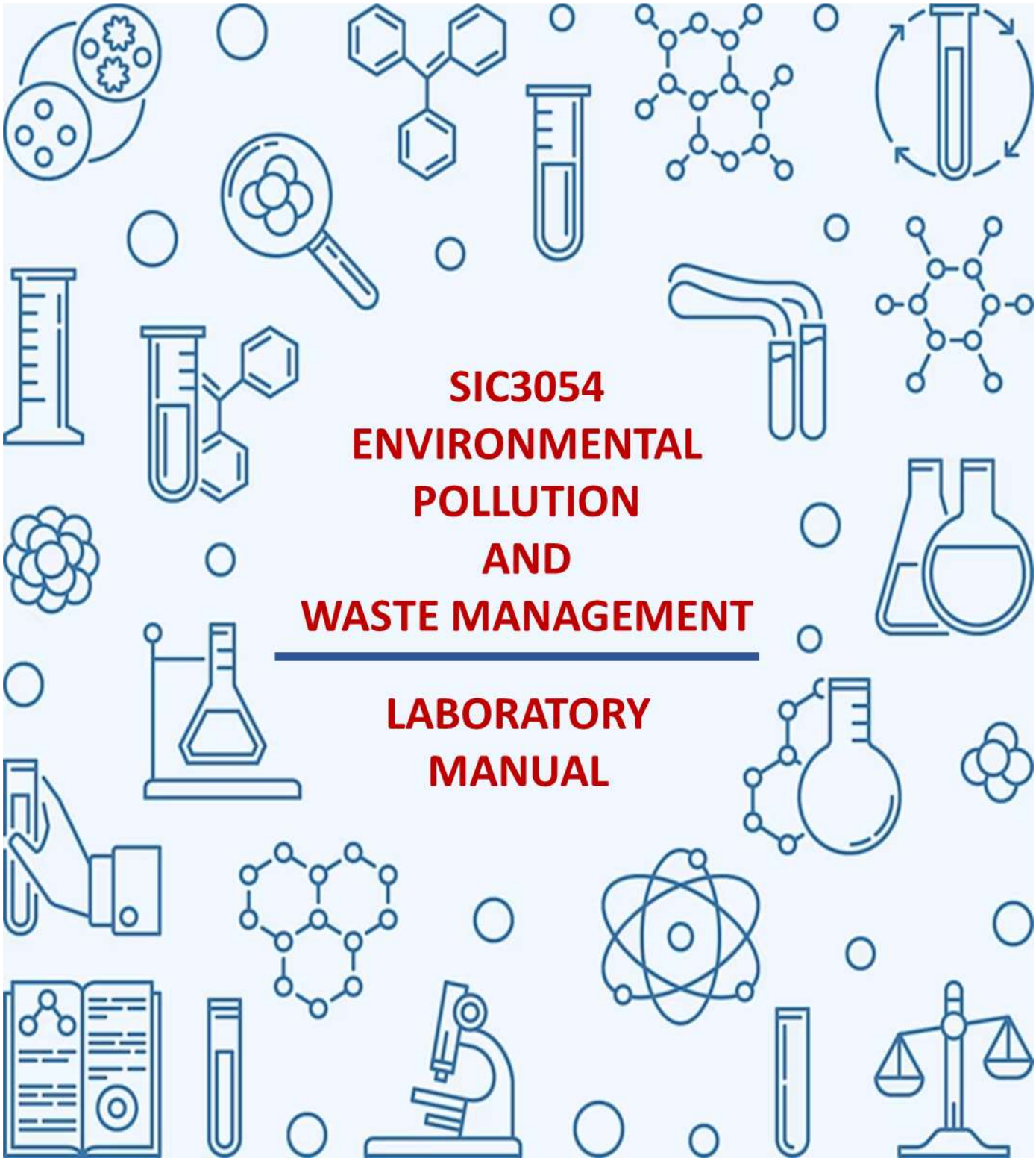
UNIVERSITI MALAYA

## CHEMISTRY DEPARTMENT
## FACULTY OF SCIENCE



# SIC3054 ENVIRONMENTAL POLLUTION AND WASTE MANAGEMENT

## 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:**

- 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

(The numbers given above are working telephone numbers, as of 28th August 2023)

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 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 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 of 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 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 comprise complete sentences. The overwhelming majority of scientific reports are written using the impersonal Third Person / Past Simple Tense / Passive Voice form, acoiding, if possiblem the use of the personal pronounce (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.

SIC3006 Analytical Chemistry II

Experiment 1

ANION ANALYSIS USING ION CHROMATOGRAPHY

Name: _____

Matric No:_____

Group member: (1) _____ (2) _____

Date of Submission: _____

Lecturer: _____

Tutor: _____

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 experiment. They usually include specific overall aims of the experiment. For example, in Experiment 1 that determine the concentration of anions in different types of tea leaves.

- To determine the concentration of anions in different types of tea leaves using ion chromatography.

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

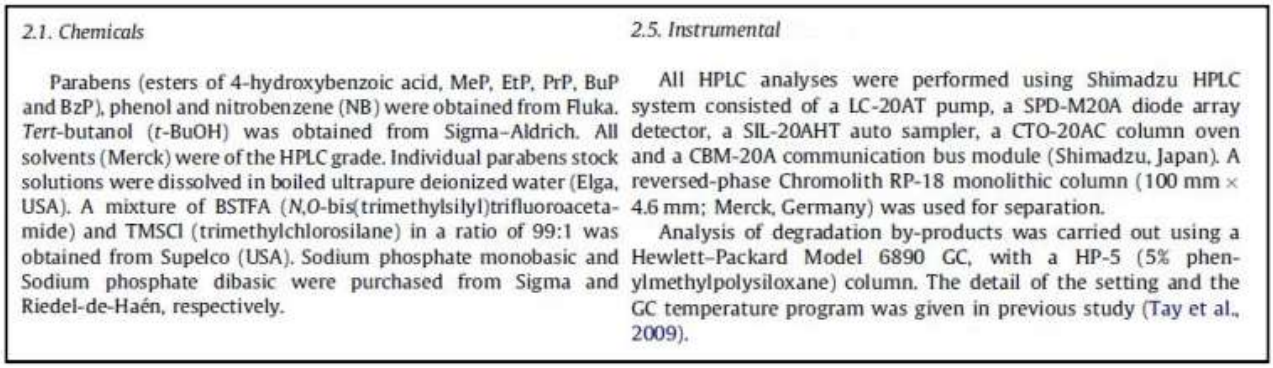
## 5.2 Introduction

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 iv 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 of your experimental materials and procedures so that your results could 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 at 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 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, a number of 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 frist 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 talbe 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 on how it is to be interpreted but should be selfexplanatory and be characterized by its simplicity and unity. The caption (on top of the table) v 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 oftern 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.

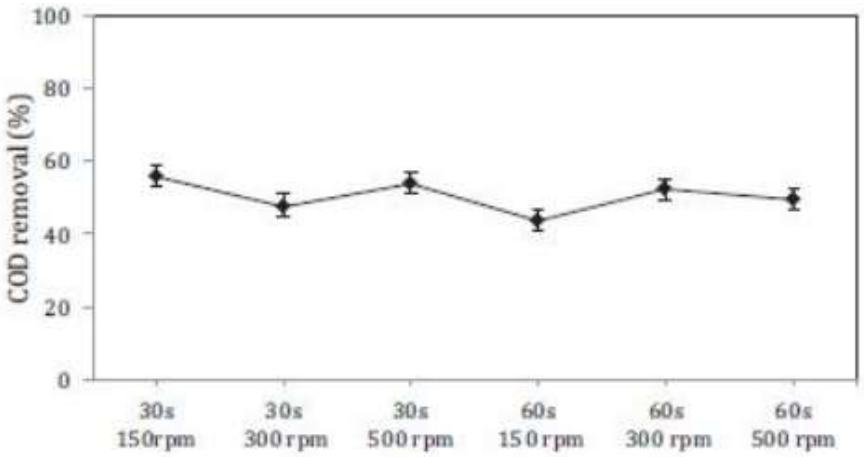



**Fig. 3.** Removal of COD for various mixing times and stirring speeds (experimental conditions: pH = 4.0, $FeCl_3$ dosage = 1400 mg $L^{-1}$ and temperature = 23°C).

## 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; vi
- 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 'bullt points', each no more than two or there lines, to summarize your results. This enables you, lecturer and tutor to see, at glance, whether you have addressed all of 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 a number of ways, depending upon your style of writing or the context of your reference. However, there are convention 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) is 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 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 assessd work may be significantly reduced and you may be open to accusations of academic misconduct. However, this does not mean that all of 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. In order to avoid accusations of plagiarism, you should clearly reference sources by using the conventions outlined above

# Laboratory Report Marking Scheme

**Section 1: Lab Performance (Total 20%)**

1. Pre-entering lab (5%)

| Score | Criteria |
|---|---|
| 0 | No preparation of experimental procedure, no proper attire-shoes; goggle; lab coat. |
| 1-2 | Summary of procedures too brief, lack of details and confusing; incomplete safety attire. |
| 3-5 | Presents easy to follow steps in lab experimental, logical and adequately detailed; safety attire checked. |

2. Skill & Techniques (15%)

| Score | Criteria |
|---|---|
| 0 | No skill is demonstrated. |
| 1-5 | Wrong glassware used, wrong technique, spillage and wasting of chemicals. |
| 6-10 | Right glassware used, incorrect or lack of lab technique. |
| 10-15 | Presents correct lab skill, clean and tidy. |

**Section 2: Lab report (Total 60%)**

| Section | Total Mark | Rubric | |
|---|---|---|---|
| Title | 5 | 0-1 | • No title, or<br>• Too brief (e.g. “Lab report”; “Mercury in fish”; Ascobic acid in fruits”, etc). |
| | | 2-3 | • Too long, or<br>• Does not identify the complete subject of study (E.g “Determination of mercury”; “Determination of lead”, etc). |
| | | 4-5 | • Identify the complete subject of study and encapsulates the purpose of the report/study. |
| Objective | 15 | 0 | • Section missing completely. |
| | | 1 - 7 | • Be too vague, ambitious or broad in scope.<br>• Just repeat each other in different terms.<br>• Just be a list of things related to the topic.<br>• Contradict with methods.<br>• Does not identify subject of study. |
| | | 8 - 15 | • Concise and brief.<br>• Be interrelated and describes how to achieve that objective.<br>• Clearly identify the subject of study.<br>• Related to the experiment that has been done. |
| Introduction | 10 | 0 | • Section missing completely. |
| | | 1 - 5 | • Background info only from lab manual. |
| | | 11 -15 | • Clearly written, well structured, with evidence of extra reading.<br>• Clear outline of study’s hypotheses.<br>• Does show something novel in it as compared to the supplied handout/laboratory manual.<br>• Does include the rationale for performing the experiment. |

| | | | |
|---|---|---|---|
| Experimental | 10 | 0 | • Section missing completely. |
| | | 1 - 5 | • One or more subsections (e.g. chemicals or instrumentation) are missing.<br>• Confusing statement.<br>• Parts have been included under the wrong sub-section. |
| | | 6 - 10 | • Contains all of the relevant information about the method used; clearly and systematically described in such a way that a reader could replicate the study from the description. |
| Results | 20 | 0 – 5 | • Graphs or tables are included without caption and any written explanation,<br>• Has some writing without tables and graphs.<br>• Very poor presentation of the collected data. |
| | | 6 – 10 | • Has included the raw data in tables<br>• Poor presentation of data (e.g. no graphs; wrong graphs; irrelevant graphs, no label and caption)<br>• Inaccurate explanations. |
| | | 11 – 15 | • Has presented the data in a logical format (e.g. graphs, tables)<br>• Show some understanding with explanation, but some relevant information has been omitted<br>• Graphs and tables are not label accordingly/correctly.<br>• Standard deviations or standard errors missing from the presented data (if related). |
| | | 16 – 20 | • Logical sequence,<br>• Clear presentation with relevant and clear explanation,<br>• Figures and tables are well labeled. |
| Discussion | 20 | 0 – 5 | • No attempt to relate results to relevant theoretical and empirical research<br>• Does not understand of what the study was about. |
| | | 6 – 10 | • Poor structure, wrong order, shows little understanding of the experiment. |
| | | 11 – 15 | • Poor structure, but contains essential elements, or<br>• Good structure with some missing elements. |
| | | 16 – 20 | • Well organized and clearly written<br>• Clearly summarize the obtained results<br>• Does show attempt to relate the findings to previous research<br>• Does show ability to evaluate the weakness and limitations of the study<br>• Does include sensible suggestion for possible improvement. |
| Safety caution | 5 | 0-1 | • Section is not presented |
| | | 1-3 | • Sentences are not in complete, focusing on minor or lack important steps. |
| | | 4-5 | • Tabulated at least 3 major and most important safety caution. |
| Conclusions | 10 | 0 | • Section missing completely |
| | | 1 – 5 | • Conclusion is drawn but not supported by experimental evidence.<br>• No sensible conclusion is drawn.<br>• No clear evidence of a thorough understanding of the |

| | | | |
|---|---|---|---|
| | | | experiment and/or theory behind the experiment. |
| | | 6 – 10 | • Conclusion is drawn and supported by experimental evidence.<br>• Sensible conclusion is drawn.<br>• Shows clear evidence of a thorough understanding of the experiment and/or theory behind the experiment. |
| References | 5 | 0 | • Reference not included in the report |
| | | 1 - 3 | • Incomplete references to the books or any other sources used in report. |
| | | 4 - 5 | • References in the text and in the reference list conform in all respects to the formatting convention (e.g. APA format)<br>• Complete references to the books or any other sources used in report.<br>• References in text are matched with references in reference list (e.g. no missing references) |
| Total Mark | 100 | | |

**Section 3 Assessment of Understanding/Revision on conducted experiments (20%)**

**For Section 3 Assessment-it is up to the lecturer in-charge to decide whether want to carry out a simple test or not. If choose not to, the 20% marks will be allocated back to Section 2- Lab report*

| **Score** | **Criteria** |
|---|---|
| 0 | Unable to answer any questions. |
| 1-5 | Very little attempt to answer question correctly. |
| 6-10 | Most answers are incorrect, and some are irrelevant to the question type. |
| 11-15 | Some answers maybe very short or incomplete. |
| 16-20 | Questions are answered to the best of abilities and answers match the question types. |

Late Report: -1 marks / day

# Contents

# EXPERIMENT 1(a)

## 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 such as 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.

*Source*: EPA-600/4-82-0129, Handbook for Sampling and Sample Preservation in Various Waters and Wastewaters.

**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) Determination of Total Suspended Solids (TSS) according to EPA Method 160.2 (EPA, 2015)

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.

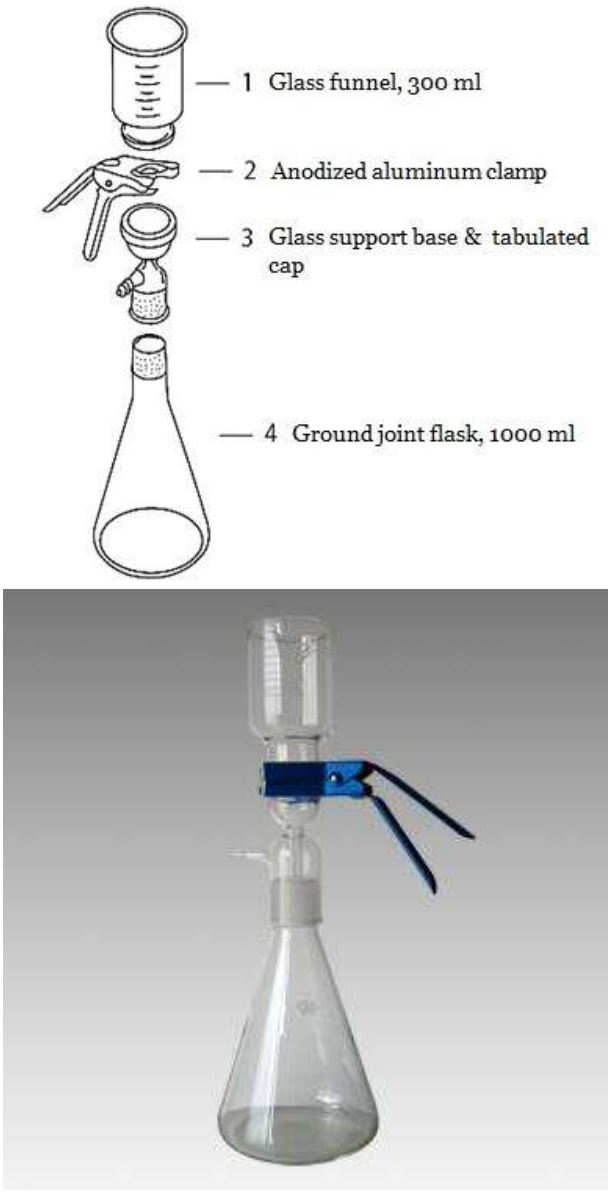



**Figure 1-2: Suction filtration system with membrane holder**

**C) <u>Determination of Total Dissolved Solids (TDS) according to ASTM D5907-03 (Environmental Express, 2016)</u>**

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.

4. **REPORT**

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

## 5. 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)

# EXPERIMENT 1(b)

## 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 $1 \times 10^6$ molecules of air, and since moles and molecules are proportional,

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

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 $K_{a1} = 4.5 \times 10^{-7}$, $K' = 9.7 \times 10^{-13}$, and $K = 1/K_w = 1.0 \times 10^{14}$, 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 $K'' = K_{a1} \times K' \times K = 4.4 \times 10^{-5}$.

Now, since $[HCO_3^-] = 2 \times [Ca^{2+}]$, $[Ca^{2+}](2 \times [Ca^{2+}])^2 / 1.2 \times 10^{-5} = 4.4 \times 10^{-5}$, then $[Ca^{2+}] = 5.1 \times 10^{-4}$ mol/L. In terms of ppm $CaCO_3$, the calcium level is $(5.1 \times 10^{-4}$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, $K_b = [H_2CO_3][OH^-]/[HCO_3^-] = 2.2 \times 10^{-8}$. From Henry's law we found that $[H_2CO_3] = 1.2 \times 10^{-5}$ and we also showed that $[HCO_3^-] = 2 \times [Ca^{2+}] = 2(5.1 \times 10^{-4}) = 1.0 \times 10^{-3}$. Since $K_b$ is so small, we can use $(1.2 \times 10^{-5})[OH^-] / 1.0 \times 10^{-3} = 2.2 \times 10^{-8}$. This gives $[OH^-] = 1.8 \times 10^{-6}$, 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.

## Alkalinity and Buffering Capacity of Natural Water (Ibanez et al., 2008)

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 it is clear that this occurs at $[A^-]/[HA] = 1$.

By knowing the pKa 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 pKa 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 HCl

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 HCI and report the mean molarity.
3. If the 0.02 M HCI 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

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

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

# EXPERIMENT 2

## 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 $Na_2$EDTA. 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 not 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.

# EXPERIMENT 3

## DETERMINATION OF DISSOLVED OXYGEN (DO) AND CHEMICAL OXYGEN DEMAND (COD) OF ENVIRONMENTAL WATERS

## 2. INTRODUCTION

### A) Dissolved Oxygen

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 Dissolved Oxygen 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 tip 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)

# EXPERIMENT 4

## REMOVAL OF METHYLENE BLUE USING ACTIVATED CARBON IN WATER SAMPLES PRIOR TO UV-VIS SPECTROPHOTOMETER ANALYSIS

### 1. INTRODUCTION

Dyes find widespread applications across various industries, including textiles, rubber, plastics, printing, leather, cosmetics, and more. They are crucial for imparting colour to products, and their demand is driven by consumer preferences for a wide range of vibrant colours. The global market for textile dyes was valued at USD 10.7 billion in 2021 and is projected to reach USD 14.0 billion by 2027. It is estimated that the global market produces about 7 X 10^5 dyes annually, and about 2% of these dyes are discharged into the water system, with most of the sources generated from textile industries.

Dyes can exert inhibitory effects on bacterial growth and attenuate photosynthesis in aquatic plants by reducing incident solar radiation reaching water bodies. This has significant implications for both human health and water quality. The acute and chronic repercussions on human skin include allergic responses, dermatitis, skin irritations, carcinogenesis, genetic mutations, and other adverse effects. Therefore, it is important to tackle the issue of dye pollution.

Methylene blue (MB) is a widely used dye that occupies a key role in a variety of industries. It plays a significant role in the textile industry by adding brilliant colours to materials including silk, wool, cotton, and paper. MB is used in the food business, in addition to the textile industry, to assess the freshness of dairy products, particularly milk. A large part of dyes, about 15%, are eventually released into the environment during production and processing, which raises environmental concerns.

Researchers have studied the toxicity of MB and investigated possible techniques for removing it from wastewater. Among these, the adsorption technique is found to be the most prominent method to remove MB by using activated carbon from water samples.

### 2. LEARNING OBJECTIVES

i) To familiarise with Ultraviolet-visible spectrophotometer (UV-VIS).
ii) To investigate the efficacy of activated carbon as an adsorbent for removing Methylene Blue dye from water samples.
iii) To quantify the concentration of Methylene Blue dye in water samples before and after adsorption using UV-VIS.

### 3. METHODOLOGY

**Preparation of Standard Solution**

Prepare 6 standard solutions with concentrations varying from 1mg/L to 7mg/L from the methylene blue stock solution. Using a pipette, transfer the appropriate volume of the stock solution into separate 10 mL volumetric flasks based on the desired final concentration. Fill each volumetric flask to the mark with distilled water, ensuring that the bottom of the meniscus aligns precisely with the mark on the flask. Fill up the concentration data in the table below:

| Standard concentration (mg/L) | Flask volume (mL) | Pipette volume (mL) |
|---|---|---|
| 1.5 | 10 | |
| 2.5 | 10 | |
| 3.5 | 10 | |
| 4.5 | 10 | |
| 5.5 | 10 | |
| 6.5 | 10 | |

**Measurement process by using UV-VIS**

Pipette an aliquot (around 3 mL) of each standard solution into a glass cell. With the UV-Vis spectrophotometer, determine the absorbance of each standard solution at the selected wavelength (664nm) by using the photometric method. For each measurement, make sure to use a clean glass cell. Note the absorbance values that were measured for each standard solution. Plot a graph with concentration vs. absorbance using the data obtained.

**Removal of Methylene Blue from Water sample for UV-VIS Analysis**

Prepare a 5 mg/L methylene blue solution and add 60 mg of activated carbon to a 10 mL solution. Shake the solution for 30 minutes using a shaker. Prior to analysis with a UV-Vis spectrophotometer, filter the solution using a nylon filter. Measure the concentration of the solution before and after removal using a UV-Vis spectrophotometer at 664nm. Repeat this entire procedure in triplicate for 3 different types of water samples. Calculate the removal efficiency for each type of water using the formula:

$$\textbf{Removal Efficiency}\ (\%) = \frac{(\textbf{Initial Concentration} - \textbf{Final Concentration})}{\textbf{Initial Concentration}} \times 100\%$$

**4. REPORT**

Report the removal efficiency (%) for each water sample.

## 5. QUESTIONS

1. What part does activated carbon play in the removal procedure, and how does it adsorb Methylene Blue?
2. Why is it required to experiment again with various types of water samples? What variances in outcomes could you anticipate?

## 6. REFERENCE

Abdelali, G., Abdelmalek, C., Réda, Y. A., Ammar, S., & Boubekeur, N. (2019). Removal of methylene blue using activated carbon prepared from date stones activated with NaOH. Global Nest J, 21, 374-380.

Samal, D. P. (2014). Characterization of activated carbon and study of adsorption of methylene blue dye using activated carbon (Doctoral dissertation).

# EXPERIMENT 5

## SIMULTANEOUS DETERMINATION OF NITRATE AND PHOSPHATE IN ENVIRONMENTAL SAMPLES BY ION CHROMATOGRAPHY

### 1. INTRODUCTION

Nitrogen and phosphorus are essential elements for all living organisms. They are used in DNA and chemical processes in the body. Most nitrogen is found in the air and most phosphorus is bound up in rocks and sediments, making them unavailable to organisms. This makes them "limiting factors" – they can limit the amount of growth, particularly of plants. When nitrogen and phosphorus are readily available in a form plants can use, such as nitrate and phosphate, plant growth can explode. Anthropogenic activities causing a transformation of the natural nitrogen and phosphorus cycle are considered as one of the most fundamental environmental issues. When nitrate and phosphate ions concentrations in shallow waterbodies are in excess, there is overgrowth of water plants leading to the formation of algal bloom. This causes a high consumption of dissolved oxygen in the water. Dissolved oxygen in the waterbody reduces drastically leading to the suffocation and death of aquatic plants and animals. The dead plants and animals decay creating deterioration of water quality. This process is termed eutrophication (Moshoeshoe and Obuseng, 2018; Agbazue et al., 2015).

Methods applied in analyzing nitrates and phosphates include electroanalytic techniques such as amperometry, polarography, potentiometry and voltammetry. Other methods include electrophoresis, gas chromatography, high performance liquid chromatography and ion chromatography. In this experiment, ion chromatography will be used. It offers a possibility of simultaneous determination of a few ions in a short time, good reproducibility of results, high sensitivity, possibility of simultaneous determinations of anions and cations, small sample volume required and the possibility of using different detectors from the most popular conductometric to mass spectrometry (Michalski, 2006).

### 2. LEARNING OBJECTIVES

1. To develop practical skill in stock & calibration standards preparation and sample preparations.
2. To introduce one of the chromatography method (ion chromatography) in analyzing nitrates and phosphates in environmental samples.
3. To gain basic knowledge from handling ion chromatography, sample analysis to data interpretation.

### 3. METHODOLOGY

### A. SOLUTION PREPARATION

1) **1000 ppm stock solution (100 mL)**

The anion stock solution consisting nitrate and phosphate can be prepared by dissolving _____ grams of _____, and _____ grams of _____, in ultrapure water to obtain a 100 mL final volume.
** show full calculations in your report*

2) **Calibration standard solution (25 mL)**
Prepare five standard solutions with various concentrations of the anions from the stock solution ranging from 0 to 25 ppm. The solutions can be prepared by pipetting various volumes of the stock solution into a series of five 25 mL volumetric flasks.

## B. SAMPLE PREPARATION

1) Filter the water samples through a 0.45 µm syringe membrane filter into a 100 mL volumetric flask.
2) Prepare the samples in triplicates.
3) Analyse the solution using an ion chromatography (IC).

## 4. REPORT

1. Prepare a calibration plot of absorbance versus concentration of each selected anion.
2. Use the calibration plots to calculate the concentration of nitrate and phosphate (in ppm).
3. Do your values fall within expected values, or are they much higher than normal background levels? Discuss.

## 5. REFERENCES


Cummins, P. M., Rochfort, K. D., & Connor, B. F. (2016). Ion-exchange chromatography: Basic principles and application. Protein Chromatography, 209-223. DOI:10.1007/978-1-4939-6412-3_11

Frenzel, W., & Michalski, R. (2016). Sample Preparation Techniques for Ion Chromatography. Application of IC-MS and IC-ICP-MS in Environmental Research, 210–266. doi:10.1002/9781119085362.ch8

Thermo Fisher Scientific Inc. (2012). Dionex ICS-1100 Ion Chromatography System Operator's Manual

M.N. Moshoeshoe, V. Obuseng. (2018). Simultaneous determination of nitrate, nitrite and phosphate in environmental samples by high performance liquid chromatography with UV detection. S. Afr. J. Chem., 71 (2018), pp. 70-85

V.E. Agbazue, N.R. Ekere, Y. Shaibu. (2015). Assessment of the levels of phosphate in detergents samples. Int. J. Chem. Sci., 13 (2) (2015), pp. 771-785

# EXPERIMENT 6

## ANALYSIS OF CARBON CONTENT IN SEDIMENT AND WATER

### 1. INTRODUCTION

Environmental pollution is not a new phenomenon, but it has become the most serious concern in the world. This is because environmental pollution could lead to the unfavourable alteration of our surroundings, threatening human life or other living things including animals and plants. This happens due to the natural and anthropogenic activities that occur in the environmental system .The production of pollution in the environmental system will continuously increase with the passage of time because of the rapid development and population growth and thus create a greater concern to the environmental quality (Shaw, 1989).

In recent years, there are a lot of parameters that are used to indicate the quality of water and soils systems. Carbon content is one of the parameters that help to identify the condition of soil and water quality at a given place. This is because carbon content can be found practically over all the earth's surface, in both terrestrial and aquatic habitats (Schnitzer, 1978). Carbon contents found in soils and sediments range from simple sugars and carbohydrates to more complex proteins, fats, waxes, and organic acids. Moreover, it has the characteristic to be able to form water-soluble and water-insoluble complexes with metal ions and hydrous oxides, interact with clay minerals and bind particles together, sorb and desorb both naturally occurring and anthropogenically-introduced organic compounds, absorb and release plant nutrients, and hold water in the soil environment (Schumacher, 2002). The carbon content is used as a chemical component indicating the presence of organic matter in water and soil systems. Carbon contents include TIC and TOC are important parameters for the environmental status estimation of terrestrial and aquatic ecosystems. The proportion of carbon content in water and soil are a good proxy for water and soil quality checking as high carbon levels indicate a high level of contamination (MacDonald & Ingersoll, 2010). In earlier sediment geochemical-related research studies, TOC was found to be a prominent governing factor, manipulating the distribution of other components in the aquatic environment, including chemical and biological components (LAZĂR et al., 2012). Organic and inorganic chemical pollutants in sediments, such as hydrophobic organic compounds and total mercury, were found to have a strong relationship with TOC (Kwaansa-Ansah et al., 2012)

### 2. LEARNING OBJECTIVES

To introduce a method for the determination of carbon and nitrogen in sediments

### 3. METHODOLOGY

## A. CALIBRATION STANDARD SOLUTION PREPARATION

TC standard solution

Prepare a 1000ppm total carbon stock solution by adding _____ g of potassium phthalate, $C_8H_5KO_4$ to a volumetric flask with a capacity of 1000 mL.

IC standard solution

(Note: If the solution has been prepared by our laboratory staff, dilute 1000 ppm of NaHCO3 solution to 100 ppm prior to TOC analysis)

1) Prepare a 1000 ppm inorganic carbon stock solution by adding _____ g of anhydrous sodium carbonate ($Na_2CO_3$) and _____ g of sodium hydrogen carbonate ($NaHCO_3$) to a volumetric flask with a capacity of 1000 mL.
2) Dissolve both solutions with ultrapure water to 1000 mL marker of volumetric flask.
3) Stir the solution until no more precipitate present.
4) Then, close the volumetric flask tightly with a stopper.
5) Prepare one standard solutions (the highest concentration selected) from the stock solution.

## B. SAMPLE PREPARATION

Soil samples

1) Pulverise the air dried samples with mortar and pestle.
2) Pass the soil samples through a 2mm size sieve to remove large particles
3) Sieve the soil samples again using a smaller mesh (1mm).
4) Keep the samples at 4$^{o}$C freezer, prior to TOC analysis.

Water samples

1) In this experiment, you will use the sample collected in Experiment 1, tap water, and rainwater.

## 4. REPORT

1. Discuss your results thoroughly.

## REFERENCES

Yalcin, M. S., Geçgel, C., & Battal, D. (2016). Determination of bisphenol A in thermal paper receipts. Journal of the Turkish Chemical Society, Section A: Chemistry, 3. doi:10.18596/jotcsa.21345

Shimadzu LC-10/20 System Clarity Control Module. (2020). Data Apex, Prague, The Czech Republic.

Meyer, V. R. (2010). Practical high-performance liquid chromatography (Fifth Edition). A John Wiley and Sons, Ltd., Publication