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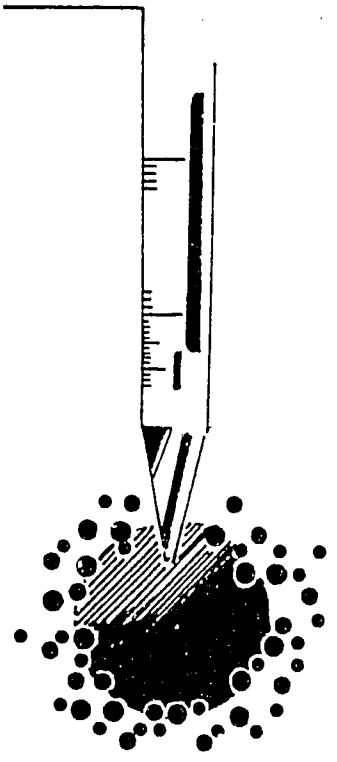
WATER ANALYSIS

USER-FRIENDLY FIELD/LABORATORY MANUAL



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IFS-NAREPP/IRG-USAID PROJECT
QUALITY ASSESSMENT OF SURFACE WATER

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Preface

Methodologies used on quality assessment of water, changes rapidly over time along with technological inventions and analytical advancements. Nonetheless, it takes time to accept a new technique for sampling or a method of analysis as being a standard method. Meaningful and object oriented water quality assessment programmes are at present based on trend analysis. Comparison of data is valid only when similar methods are employed. Therefore, it is a prerequisite to agree with initiate methodologies during sampling processing and analysis when quality assessment programmes are launched by different laboratories. Different methods can be used in accordance with the availability of resources and cost-effectiveness. However, these techniques and methods should satisfy regional and global standards.

A careful survey on available literature on water quality in many instances reveal that the techniques used in sampling and the methods employed in analysis are not well- defined. Several methods have been employed to analyse the same constituent by different laboratories or individuals. Use of similar methods is extremely important when precision analysis is undertaken for constituents such as trace elements, micro nutrients and organic-residues.

The number of state, non-government and private sector organizations involved in water analysis in Sri Lanka shows a rapid increase today. However, outdoor sampling and bench work are always carried out by technological level field assistants and laboratory analysts respectively. It is quite clear that analytical techniques in many manuals are complicated with technical jargon and difficult to understand at a quick glance, especially for technical level analysts. Therefore, to full-fill basic need for unified methodology in sampling and analysis and to make it convenient for technical level analysts, an attempts has been made to prepare this user-friendly field laboratory manual under the IFS-NAREPP/IRG-USAID funded project on Quality Assessment of Surface Water.

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Foreword

This User-friendly Field/Laboratory Manual is a major contribution made by the Department of Environmental Science of the Institute of Fundamental Studies in the field of hydrogeochemistry. Sri Lanka still has no proper standards in water quality. Application of correct and appropriate analytical techniques is most important in the implementation of programmes aimed at monitoring water quality.

This manual should be of extreme use, not only to students of analytical chemistry, but to all those engaged in routine measurements of water quality parameters. Analysis of errors in chemical analysis and the use of statistics form an important part of the manual. As shown by several previous studies, inter-laboratory comparisons of analytical results are most essential, if any meaning needs to be attached to the final results.

Simple techniques, both in the laboratory and in the field, are an asset in a water quality monitoring programme, and this manual should, therefore, find a place in our laboratories as a reference volume.

Professor C.B. Dissanayake
Director

Background

Hydrological cycle is the cohesive link between three major components of the earth (i.e. biosphere, lithosphere and troposphere). Thus water constitutes a continuum with different stage ranging from glacial ice to marine salt water. Lakes and rivers are considered as athalassic surface water since they are only confined to the land mass. In addition there are several intermediate forms of surface water bodies which are either natural (i.e. estuaries, lagoons, flood plains, waterfalls, streams, brooks, creeks pools) or a man made (e.g. reservoirs, tanks, canals etc) in origin.

Surface waters either natural or man made are essentially solutions of chemicals of various concentration and diversity. Water also provides living habitats for aquatic organisms from microorganisms to huge mammals. The constitute or concentration of chemical species occurrence of aquatic organisms in natural waters are varying due to the type and the location of the water body. In general, chemical species and organisms found in natural clean waters are not harmful or detrimental for other organisms and human being as well. The nature and types of constituents in water exhibit the quality of water. The quality of the aquatic environment shows temporal and spatial variations due to factors internal and external to the water body. However, quality of the water can be changed by man directly or indirectly by introducing substances or energy which results in such deleterious effects on biodiversity, human health and aquatic resource utilization.

Apparently at present water is in general, not clean and not suitable for human consumption without prior treatment. Since, water is being contaminated with human wastes, agrochemicals or heavy metals or un-biodegradable organic compounds there in this urge for a prior assessment of water for its chemical species, and biological communities.

The process of water quality assessment is an evaluation of the physical, chemical and biological nature of water in relation to natural quality, human effects and intended uses, particularly uses which may affect human health and aquatic biodiversity. Therefore, quality assessment of water provides basic information on the present status for detecting trends enabling the establishment of regulatory measures and mitigatory plans.

CHAPTER 1: ANALYTICAL TECHNIQUES - PRINCIPLES AND PROCEDURES

1.1 Introduction

All analytical techniques applied in water analysis are based on the measurement of a physical, chemical or a biological characteristic that is specific to the parameter sought for. The quantification procedure of the parameter, at one stage or another, depends on the measuring potential of an instrument/equipment which is either simple or complex in functionality. Hence, a basic yet thorough understanding of the principles involved in analytical techniques recommended for water analysis and instrumentation applied therein is a prerequisite for a water analyst in order to perform his task with confidence and to generate reliable as well as meaningful data that exhibits high accuracy.

This chapter presents brief notes on major analytical techniques applicable to water quality parameters described in this manual. It is divided into sub chapters each of which deals with a single analytical technique describing the its principle, the design, technical aspects and the general experimental procedure. Critical points where errors can be introduced into analysis are also highlighted in the remarks section.

1.2 Analytical Balance (weighing technique)

1.2.1 Principle

There are two types of analytical balances: Mechanical and electronic. The conventional mechanical balance consists of a beam suspended on a knife edge and two weighing pans hanging on to the ends of the beam. The weighing is based on the phenomenon that the moment of force on the two sides of the center of gravity are equal at perfect balance. Normally the distances between the center of gravity and the two pans of the balance are equal. Thus, the weight of an object is straightforwardly given by the total weight of the standards placed in the other pan to counter balance it. The sensitivity of this balance ceases at 1 mg.

The more common mechanical balance is the single pan, semi micro type one which generally has a weighing capacity of 100-200 g and a sensitivity of 0.1 mg. In this

balance, some removable weights are attached to the pan side and the total weight of the pan side is counter balanced by a standard non-removable weight fixed to the other end of the beam. Thus, when an object is placed on the pan, that side becomes heavier and in order to bring the balance back to the previous position, movable weights are removed from the pan side. Any remaining imbalance is indicated on the optical scale of the balance. The weight of the object placed on the pan is given by the sum of the weight removed plus the reading on the optical scale.

The electronic balance operates on a more complex mechanism which is based on electromagnetic principles. Therefore, unlike mechanical balances errors may occur when weighing materials with magnetic properties. Electronic balances are calibrated at the factory so that recalibration may be necessary if the gravity in the laboratory differs considerably.

1.2.2 Procedure

Basic steps involved in the weighing procedure of the electronic analytical balance is given below:

1. Switch on the balance and allow sufficient time to warm up (usually 60 minutes)
2. Calibrate the balance with the weighing chamber doors closed
3. Place the container (e.g. weighing boat, watch glass) on the pan and close the doors
4. Tare the container weight
5. Fill the container with the substance upto the targeted weight, close the door and record the weight
6. Repeat steps 3 to 5 for the next weighing
7. Turn off the switch after weighing

1.2.3. Remarks

1. Locate the balance at a vibration free place (e.g. on a marble or a concrete slab) which is away from direct sunlight and large temperature fluctuations

2. Make sure to check whether the balance is in levelled position before making any weighing. If not, level it first
3. Always close the weighing chamber doors before taking the weight
4. Never touch the weighing vessel or the pan. Use forceps or a piece of good quality tissue to hold the vessel
5. Never put material to be weighed directly on the weighing pan. Always use a container

1.3 Gravimetry

1.3.1 Definition of Symbol

Symbol	Definition	Unit
A	Analyte to be determined	--
P	Product (precipitate) formed by the chemical reaction between the analyte and the reagent	--
a/p	Molar (stoichiometric) ratio between the analyte and the product of the chemical reaction	--
[A]	Concentration of analyte	M
W_p	Weight of the product	g
V	Sample volume used in the analysis	l
M_p	Molecular weight of the product	g

1.3.2 Principle

In gravimetry, the analyte of interest which is normally dissolved in the sample is converted to a solid product (precipitate) of known chemical composition by means of a chemical reaction. The precipitate is separated quantitatively from the solution and weighed after drying. The mass (quantity) of the analyte is calculated by using the weight of the precipitate and the stoichiometry of the chemical reaction.

e.g. $aA + \ldots \Rightarrow pP + \ldots$

$$[A] = \frac{W_p}{V} \times \frac{1}{M_p} \times \frac{a}{p} \quad \text{mol/l}$$

1.3.3 Procedure

The general procedure of gravimetric analysis includes steps given below. Analyte specific procedures are given in the analytical procedure section of the manual.

1. Measure a known volume of the sample into a beaker.
2. Add precipitate forming reagent as instructed in the analytical procedure while mixing the solution.
3. Filter the sample through a pre-weighed filter paper.
4. Rinse the beaker with the filtrate several times and add to the filter paper.
5. Thoroughly wash the precipitate with the same solvent as that of the sample to remove impurities adhered to it.
6. Dry the precipitate to a constant weight in an oven maintained at the temperature specified in the analytical procedure.
7. Cool the precipitate in a desiccator to room temperature.
8. Weigh the precipitate by using an analytical balance.
9. Calculate the concentration of the analyte using the weight of the precipitate and chemical data such as reaction stoichiometry and molecular weights as illustrated above.

1.3.4 Remarks

1. To improve formation of large crystals which facilitates easy filtration add the reagent to the sample slowly with vigorous mixing. Also use a large volume of the sample in the analysis and maintain the temperature at an elevated level during precipitate formation step.
2. Keep the precipitate in the mother liquor at the elevated temperature (digestion) for a short period to improve the purity of the product and to promote formation of large crystals.
3. Some gravimetric methods require the ignition of the precipitate prior to weighing in order to achieve a reproducible, stable and constant composition. In such cases, use ashless filter papers for separating the precipitate from the mother liquor.

4. To minimize weighing errors, always bring the temperature of the weighing vessel to room temperature in a desiccator before weighing. Do not touch the vessel by hand. Instead use tongs pairs or forceps. While weighing keep the glass doors of the analytical balance closed.

1.4 Volumetry

1.4.1 Definition of Symbols

Symbol	Definition	Unit
M_A	Molarity of analyte (A)	mol/l
M_T	Molarity of titrant (T)	mol/l
a/t	Stoichiometric (molar) ratio between A and T	--
V_A	Volume of the sample used in the titration	l
V_T	Volume of the titrate used in the titration	l

1.4.2 Principle

Volumetry involves incremental addition of a reagent of known concentration to a fixed volume of a sample containing the analyte of interest until the reaction between the analyte and the reagent is complete. The completeness of the reaction is determined by an abrupt change in a physical property (usually color) of a third compound (indicator) added to the titration vessel at the beginning of the titration. As the indicator also has to react with the titrant to cause the change in physical property, the titration end point always surpasses the equivalent point causing a slight error in the reading (titration error).

Most of the instances, the titration error can be estimated by conducting a blank titration. Normally the estimated error is subtracted from sample titration data to improve the accuracy of the results. The quantity of the analyte in the sample is calculated using the titrant and sample volumes, molarity of the titrant and the stoichiometry of the chemical reaction pertaining to the titration.

e.g. for general reaction

$$aA + tT \Rightarrow \text{products}$$

Moles of T at end point = $M_T V_T$

Moles of A at end point = $M_A V_A$

at equivalent point

$$M_A V_A = \frac{a}{t} M_T V_T$$

$$M_A = \frac{a}{t} \frac{M_T V_T}{V_A} \text{ mol/l}$$

1.4.3 General Procedure

Given below are the main steps involved in volumetric analysis. Specific procedures may vary depending on the nature of chemical reaction between the analyte and the titrant and the physical property utilized for end point detection. The analyst is therefore requested to be familiar with the procedure that he intends to follow prior to analysis.

1. Prepare a standard solution of the titrant by dissolving an accurate weight (use analytical balance for weighing) of a primary standard in a known quantity of distilled water. If the titrant is not a primary standard, standardize the solution against a primary standard.
2. Rinse a clean burette with the titrant three times and fill in upto the top.
3. Open stopcock and remove all air bubbles.
4. Take the initial reading to two decimal points (second decimal is your own estimate).
5. Rinse a clean pipette with small portions of the sample three times and pipet a fixed volume of sample into a clean erlenmeyer flask.
6. Add a few drops of the appropriate indicator to the flask and titrate with the reagent while swirling the flask.
7. Wash down the walls of the flask with distilled water occasionally during titration.
8. When the end point is approaching, add small increments from the buret until the slightest but the permanent change in color results.

9. Note down the final buret reading.

10. Repeat the experiment at least twice more and calculate the analyte concentration.

1.4.4 Remarks

1. Never rinse erlenmeyer flask with the reagent or sample to be pipetted in
2. Add only the recommended volume of the indicator to minimize titration error.
3. Never try to bring liquid level of the burette down so as to coincide with a line of the burette as it is a useless and cumbersome endeavour.
4. Never wash down the burette tip to the flask with distilled water. If there is a small droplet hanging onto the tip, deliver it into the flask by touching the tip on the inner wall of the flask and rinsing down with distilled water.
5. Always run a blank titration to improve the accuracy of titration.

1.5 Potentiometry - pH Measurement

1.5.1 Definition of Symbols

Symbol	Definition	Unit
$[H^+]$	Hydrogen ion concentration of the sample	mol/l
pH	$pH = -\log[H^+]$	No units
E_{cell}	Cell potential - potential difference across the H+ sensitive (glass) membrane	V
C	Constant	V

1.5.2 Principle

pH is a measure of hydrogen ion concentration. When a pH electrode is immersed in a solution, a potential difference is built up across the glass membrane due to a difference in hydrogen ion concentrations of the internal and the external solutions. This potential difference is measured by two reference electrodes immersed in the two solutions and is related to hydrogen ion concentration of the external solution (sample) as follows:

$$\text{at } 25^{0}C,\ pH = \frac{1}{0.0591}(E_{cell} - C)$$

1.5.3 Instrument Design

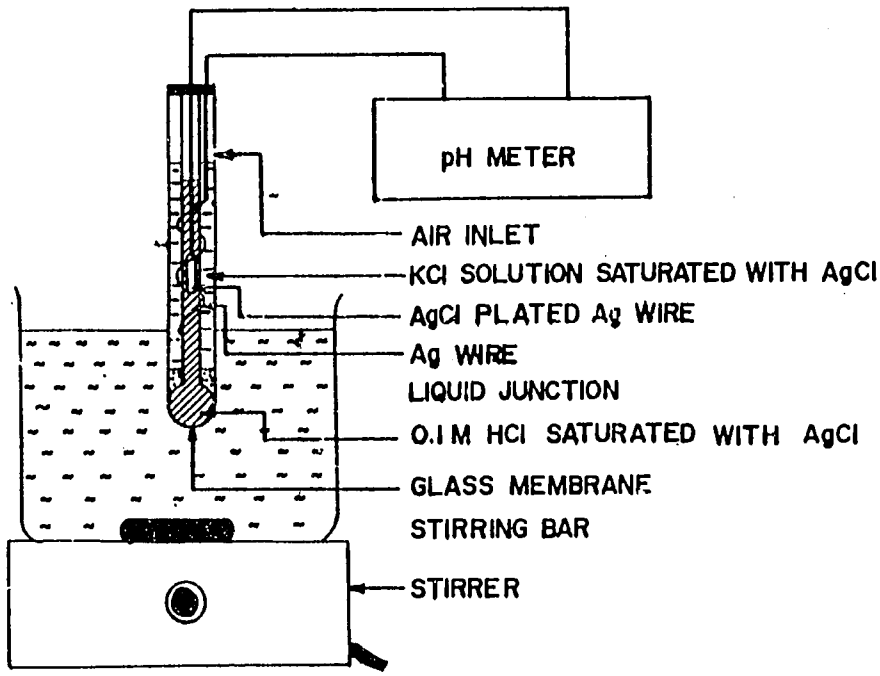

Figure 1.1

Basic components of a pH measuring system (i.e. pH meter) is given in Figure 1.1. The functions of these components are as follows:

1. pH electrode (combination type)

   The combination pH electrode consists of two components.

   a. A glass membrane (bulb) sensitive to hydrogen ion which is filled with a standard hydrogen ion solution (e.g. 0.1 M HCl) and consists of a Ag wire immersed in it as an internal reference electrode.

   b. An external reference electrode (e.g. Ag/AgCl electrode) fixed as outer compartment of the electrode body which is connected to the external (sample) solution through a liquid junction (a membrane that permits the movements of ions).

   (Note: In older models, pH (glass) electrode and reference electrode are found as two separate units).

2. Potentiometer (pH meter)

   This unit measures the potential difference across the glass membrane by means of internal and external reference electrodes, converts it into pH units and displays the value on analogue or digital scale. It also consists of components needed for the calibration of the instrument (i.e. STANDBY, READ, CAL (calibration) and SLOPE knobs).

3. Stirrer

   Stirring the sample solution improves the accuracy and the precision of pH measurement. A magnetic stirrer is suitable for this purpose.

1.5.4 Calibration

The general procedure for calibration and sample pH measurement is given below. The analyst is, however, advised to refer to the instruction manual of the pH meter at his disposal as specific procedure may vary depending on the make and the model.

1. Check the pH electrode (combination type) for reference electrode filling solution level and if the level is low, fill in with the filling solution. If there are air bubbles inside, shake the electrode to remove them.
2. Connect the pH electrode to the meter and uncover the filling hole plug.
3. Rinse the electrode with distilled water and shake off excess water. Blot the electrode dry with a tissue. Do not rub or wipe the electrode with any material.
4. Immerse the electrode in pH 7 buffer while stirring the solution and turn the meter to READ position.
5. Select temperature mode and measure the temperature of the buffer using in build temperature probe (if available) or measure it manually using a thermometer.
6. Switch to pH mode
7. Turn the meter to READ position and wait for a stable reading.
8. If the display value is different from the standard pH value for the measured temperature adjust the reading with the CAL knob.
9. Turn the meter back to STANDBY position.
10. Remove the electrode, rinse with distilled water and blot dry.

11. Place the electrode in pH 4 or 9 buffer depending on the range of pH anticipated in the samples and stir the solution.
12. Turn to READ position and wait for a stable reading. Adjust the reading to the pH value for that measured temperature using SLOPE knob.
13. Turn to STANDBY position, rinse the electrode with distilled water and blot dry.
14. Place the electrode in the sample, turn to READ position of the meter and wait for a stable reading while stirring the sample.
15. Record the pH and turn to STANDBY for the next measurement after rinsing and drying the electrode.
16. After use rinse the electrode with distilled water, blot dry and store in electrode storage solution or pH 7 buffer.

1.5.5 Remarks

1. pH measurement is sensitive to changes in temperature. Therefore, calibration buffers and the samples should be at approximately the same temperature. If they are different use temperature compensation (as described in your manual) to minimize error in the reading.
2. If the slope falls below about 90% during the calibration step or the readings in pH buffers drift with time, the electrode may have become dirty. Then follow the cleaning procedure given in maintenance section.
3. Standard buffer solutions should be selected such that the range of the pH value expected in the samples is covered.

1.6 UV/visible Spectrophotometry

1.6.1 Definition of Symbols

Symbol	Definition	Unit
P_o	Radiant power (incident) - energy of radiation impinging on one cm^2 of the sample	$ergs/cm^2$
P	Radiant power (transmitted)-energy of radiation transmitted from one cm^2 of the sample	$ergs/cm_2$

A	Absorbance (A = log Po/P)	No units
T	Transmittance (T = P/Po)	No units
b	Path length - distance radiation travels through solution	cm
c	Concentration of the radiation absorbing molecule	mol/l
Σ	Molar absorbtivity (Σ = A/bc)	$cm^{-1}mol^{-1}l$

1.6.2 Principle

When ultra violet/visible radiation travels through a solution, the power of incident radiation may be attenuated from Po to P as a result of absorption by molecular species. The attenuation of radiation, expressed in terms of absorbance is directly proportional to path length (b) and concentration of light absorbing molecule (c). Mathematically, it is expressed as

$$A = \Sigma bc$$

Where Σ is water absorbtivity which is a constant for a particular analyte species at a given wavelength. This relationship is known as Beer's law. At constant path length (b), absorbance holds a linear relationship with analyte concentration (c).

Thus, $A = \Sigma bc = Kc$ ($K = \Sigma b$ = constant)

UV visible spectrophotometry is based on this fundamental relationship.

1.6.3 Design of instrument

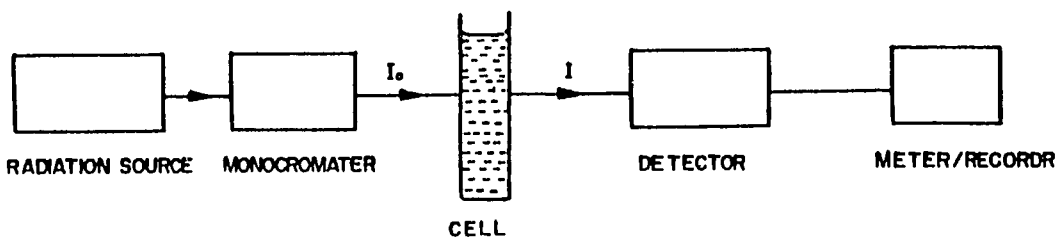

Figure 1.2

Figure 1.2 depicts a single beam UV/visible spectrophotometer. The functions of the basic components of the instrument are as follows:

1. Radiation source'

   Generates UV/visible radiation by two sources

   (i) deuterium lamp - UV range (190 - 350 nm)

   (ii)tungsten lamp - visible range (350 - 850 nm)

2. Monochromator

   Selects the wavelength of interest by means of a complex optical system.

3. Cell

   Holds the standard or the sample of interest for absorption measurement. There are two types of cells (cuvettes) used in analysis depending on the wavelength.

   (i) quartz or fused silica cell - for ultraviolet region (i.e. below 350 nm)

   (ii)silicate glass or plastic cell- for visible region (above 350nm)

4. Detector

   Consists of a photocell system to measure the power of the radiation transmitted through standard/sample.

5. Meter/recorder

   Displays the reading in analogue or digital form and records it (if recorder is available)

1.6.4 Calibration

Basic steps in the calibration of UV/visible spectrophotometer are given below. However, you must read the manual of your instrument before commencing measurements as calibration procedure may vary depending on the make and model.

1. Switch on the instrument and allow sufficient time (which is usually indicated in the manual, if not, 15-30 minutes) for warm up of optical and electronic systems.
2. Select the desired wavelength (which is given in the analytical procedure of interest). At this point, you may have to switch to relevant radiation source manually.

3. Fill up the cuvette with the blank solution upto 1 cm from the top, wipe the transparent surface with a soft tissue and insert in the cell compartment such that the light passes through transparent surfaces (caution:- make sure to hold the cuvette by coarse surfaces only).
4. Close the sample chamber lid and adjust absorbance to 0.
5. Insert the cuvette(s) containing the standard(s) and record absorbance.
6. Construct a calibration graph by plotting concentration of standards against absorbance.
7. Measure absorbance of the sample and calculate the analyte concentration from the graph.

1.6.5 Remarks

1. The Beer's law is valid only for dilute solutions. Therefore, you must always prepare a calibration graph covering the concentration range of interest to verify the linearity.
2. Spectrophotometric reading may vary with time due to electronic drift. To ensure accuracy in measurements, few points of the calibration graph should be rechecked occasionally during the analysis of samples. If there is a significant deviation, calibration graph should be corrected accordingly.

1.7 Atomic Absorption Spectrophotometry

1.7.1 Definition of Symbols

As of UV/visible spectrophotometry (Section 1.5.1).

1.7.2 Principle

A solution containing the analyte of interest is aspirated into a flame where after atomization, the analyte absorbs incident radiation. The attenuation of the radiant power of incident radiation obeys Beer's law as described in Section 1.5.2.

i.e. $A = \Sigma bc$

At constant path length $A = Kc$ (K = constant)

1.7.3 Design of instrument

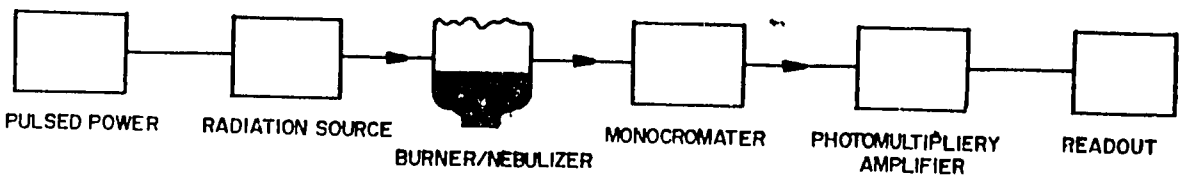

Figure 1.3

Figure 1.3 depicts basic components of a single beam (flame) atomic absorption spectrophotometer. The functions (components are as follows.

1. Pulsed power supply

   The power supply provides a high voltage to the radiation source in a particular pulse form.

2. Radiation source

   Widely used radiation source is hollow cathode lamp which consists of a cathode made of the element of interest and an anode made of tungsten. Pulsed power supply ionizes the filler gas and the positive ions formed during process bombards on the cathode. This process generates a vapour of excited atoms of the element inside the lamp. During de-excitation of the atoms, a radiation characteristic of the element of interest is emitted which follows the same pulse pattern as of the power supply.

3. Nebulizer/burner

Nebulizer converts a liquid sample into fine aerosol and aspirates it into the flame through the burner. Generally, pre mixed burners are used where aerosols are mixed with the fuel and oxidant gases first and only the fine droplets are allowed to enter the burner.

In the flame, molecules are vaporized and dissociated into elements. Part of the resulting atoms then becomes excited by absorption of radiation receiving from the hollow cathode lamp of the same element. The atomization efficiency of a compound and therefore, the sensitivity of measurement depends on the temperature of the flame (ability to dissociate molecules). Various fuel/oxidant combinations are used in AAS as illustrated below.

Fuel gas	**Oxidant**	**Flame temp. ^0C**
Acetylene	Compressed air	2100 - 2400
Acetylene	N_2O	2600 - 2800
Acetylene	O_2	3050 - 3150
H_2	O_2	2550 - 2700
H_2	Compressed air	2000 - 2100

Alternatively, electrothermal atomizers (graphite furnace) can be used to improve detection limit.

4. Monochromater

Selects the wavelength that is characteristic to the element of interest and ensures that the photomultiplier receives only this radiation.

5. Photo multiplier/amplifier

Photo multiplier converts the optical signal into an electrical current. The amplifier enhances the current to a measurable level. Photo multiplier is tuned to the pulse pattern generated by the power supply in order to distinguish between the radiation emitted from the hollow cathode lamp and that generated during deexcitation of the element in the flame.

6. Readout

Indicates the magnitude of the signal numerically either as a direct reading or, if a printer is available, as a printout.

1.7.4 Calibration

The general operational procedure for calibrating AAS is summarized below. However, as there may be model specific differences in operational procedure, you are advised to be conversant with the operation of your instrument by carefully reading the manual before attempting any measurement.

1. Air/acetylene flame

   (a) Make sure that the right burner head is installed, if not change the burner head.

   (b) Make sure that the waste water tube is not folded or blocked and its end is submerged in water inside the plastic waste bottle.

   (c) Load the hollow cathode lamp of interest into the turret of the instrument.

   (d) Switch on the instrument and allow sufficient time for warm up of electronic and optical systems as specified in the manual, if not, 15-30 minutes.

   (e) Set the lamp current and slit width corresponding to the element of interest.

   (f) Set the wavelength indicated in the procedure and optimize wavelength setting and lamp alignment.

   (g) Turn on the fan of the exhaust system.

   (h) Open the gas flow at air and acetylene cylinders and adjust the desired gas flow rate at the instrument using flow meters (if compressed air is used as oxidant, turn on the air compressor and allow sufficient time to build up adequate pressure).

   (i) Ignite the flame and continue aspirating distilled water.

   (j) Select absorbance mode

   (k) Set desired background correction

(l) Aspirate the standard with the highest concentration and optimize absorbance reading by making burner adjustment

(m) Aspirate the reagent blank and set zero absorbance.

(n) Aspirate standards and record absorbance.

(o) Construct a calibration by plotting absorbance against concentration.

(p) Aspirate samples and record absorbance.

(q) Calculate analyte concentrations using the calibration curve.

(r) After use, aspirate distilled water for a few minutes.

(s) Extinguish the flame by closing the fuel toggle.

(t) .Close the fuel regulator at the cylinder and open the fuel toggle of the instrument to bleed the fuel gas completely and then shut it off.

(u) Turn off the air compressor (or cylinder).

(v) Turn off the AAS and the exhaust fan.

2. Nitrous oxide/acetylene flame

(a) Install nitrous oxide/acetylene burner head.

(b) Perform (b) to (i) of the previous procedure.

(c) Open N_2O gas flow at the cylinder and adjust deserved gas flow rate using flow meter.

(d) After burner head is warmed up for a few minutes and if the flame is even push the N_2O button to change the oxidant from air to N_2O.

(e) If necessary, make minor adjustments to the flame by changing gas flow rates.

(f) Perform analytical measurements following steps (j) to (r) of previous procedure.

(g) Switch N_2O gas flow back to air.

(h) Extinguish the flame by closing acetylene valve.

(i) After closing acetylene and N_2O regulators, open acetylene value of the AAS until the fuel is drained off and then close it.

(j) Turn off air compressor (or cylinder)

(k) Turn off the AAS and the exhaust fan.

1.7.5 Remarks

1. Beer's law is valid only for low concentrations. Therefore, the calibration curve should cover the concentration range of interest to verify the linearity.
2. To ensure the accuracy of measurements, the drift of the instrument must be checked by reanalyzing a few standards occasionally during the analysis of samples. If there is a significant deviation in the readings, calibration curve should be corrected accordingly.
3. Always be on alert about gas leaks (some model have in built gas leak checking facilities).
4. Always maintain waste water level above the end of the water tube to avoid accidental fires.
5. Make sure all gas supplies are closed when the instrument is not in use.
6. Always keep the exhaust system operating while the flame is on.
7. Replace acetylene cylinder when the pressure drops below 5.26 Kg/cm^2 (75 psi).
8. Keep ventilated the area where AAS is installed and gas cylinders (specially N_2O) are stored.
9. Keep the gas lines free of oil to avoid spontaneous combustion or explosion.
10. When being used heat the N_2O pressure regulator to avoid freezing.
11. When the AAS flame is on always keep the burner compartment door closed (otherwise wear tinted safety glasses).
12. Do not use acetylene/N_2O flame for the elements which are best determined be acetylene/air flame.
13. If organic solvents are aspirated, discard the waste solvent get collected in the bottle immediately after analysis.

CHAPTER 2: USER MAINTENANCE - BASIC LABORATORYWARE

2.1 Introduction

Analytical instruments require constant attention of the user for them to function properly. Therefore, the instruction manual of any instrument contains a section on user maintenance. Proper care of instruments not only improve the sensitivity, accuracy and the reliability of the readings obtained by the instrument but also prolong its life time avoiding unnecessary expenses on new equipment.

This chapter describes, in general, the user maintenance procedures pertaining to the analytical instruments used in the water testing methods presented in this laboratory manual. The user is, however, strongly advised to read the relevant chapter in the instruction manual of the instrument before attempting any maintenance work. Also, please note that maintenance of certain components of the instrument can be done only by the manufacturer or by an instrument specialist. The instruction manuals usually specify such components. Do not try any maintenance work of those parts.

2.2 Analytical balance

1. Whenever necessary, clean the weighing pan and the housing of the balance with some soapy water. Wipe out moisture completely with a clean and dry cloth.
2. To remove any dust particles from the weighing chamber use a small artist's brush. Never blow air through the chamber

2.3 pH electrode and meter

Inspect the pH electrode regularly for scratches, cracks, salt crystal build ups or visible deposits. If there are cracks or scratches replace the electrode. To remove salt or other deposits follow the procedure given below. After cleaning the pH (combination type) electrode, remember to

1. drain the reference electrode solution, flush the chamber with new filling solution and refill.
2. soak the electrode in storage solution for at least two hours
3. recalibrate the electrode

2.3.1 *General cleaning of the electrode*

1. Soak the electrode in 0.1 M HCl or 0.1 M HNO_3 for half an hour and rinse with distilled water
2. If unsuccessful, soak the electrode in a 1: 10 dilution of household laundry bleach in a 0.1-0.5% liquid detergent solution prepared in hot water. Stir vigorously for 15 minutes. Rinse the electrode with distilled water.

2.3.2 *Protein removal*

1. Soak the electrode in 1% pepsin in 0.1 M HCl for few minutes to remove protein from the glass membrane or liquid junction. Rinse with distilled water.

2.3.4 *Removal of inorganics*

1. Rinse the electrode with 0.1 M tetra sodium EDTA solution and rinse with distilled water.

2.3.5 *Removal of grease and oil*

1. Rinse with a mild detergent or methanol and rinse with distilled water.

2.3.6 *Removal of hard deposits*

If all above cleaning procedures failed, immerse the electrode tip in 0.1 M NH_4HF_2 (ammonium bifluoride) for one minute and thoroughly rinse with distilled water. Check the slope of the electrode after refilling the reference electrolyte and soaking in storage solution for two hours. If the electrode slope is still unsatisfactory, discard the electrode.

2.3.7 *Storage of electrode*

For short term storage (upto one week), store the electrode in storage solution supplied by the manufacturer or in pH 7 buffer/KCl system (1 g of KCl to 200 ml buffer)

For long term storage, refill the reference electrolyte and cover the filling hole. Put a few drops of storage solution into the protective cap and cover the electrode tip with it.

2.4 UV/Visible Spectrophotometer

1. Keep the instrument in a clean and dry place which is free from dust. When not in use, always keep the instrument disconnected from the main power supply and cover with the dust cover.
2. Clean cuvettes before and after use with high quality (analytical or HPLC grade) methanol and allow to dry. Never dry cuvette in oven or under flame.

2.5 Atomic Absorption Spectrophotometer

2.5.1 Burner cleaning

An uneven flame may indicate that the burner slot needs cleaning. When dilute solutions are aspirated the burner may require only occasional cleaning. If high concentration of Ag, Cu and Hg salts are aspirated into air/acetylene flame, the burner mixing chamber requires immediate cleaning. After analyzing samples containing high levels of solids or those prepared in organic matrices (e.g. MIBK extraction) clean the burner immediately.

(a) General cleaning

1. If uneven flame is noticed, turn off the flame and carefully work along and through the slot with a single edge razor blade. Be careful not to nick the edges of the slot. This will remove deposits lightly adhered to the burner slot.
2. It above is unsuccessful, disconnect the burner head and carefully work through the slot with a razor blade. Remove scrapings from inside and outside the burner head.
3. For further cleaning (if necessary) soak the burner head overnight in a detergent solution and rinse with deionized water and blow dry with a clean air flow.

(b) Cleaning after analysis of organic samples

(1) Aspirate for 5 minutes in an organic solvent known to be miscible with the samples aspirated previously.

(2) Aspirate acetone for 5 minutes.

(3) Aspirate 1% HNO_3 for five minutes.

(4) Inspect the burner chamber and if deposits are to be seen clean the chamber using burner mixing chamber cleaning procedure.

2.5.2 *Burner mixing chamber cleaning*

(a) General cleaning

(1) Remove the burner head from the burner chamber and keep it aside.

(2) First try to clean the burner chamber without dismantling it by pouring about 50 ml of water through the neck.

(3) If unsuccessf l, remove the burner chamber from the instrument and dismantle it according to instructions given in the manual.

(4) Clean the burner head and the chamber with a detergent solution and a bottle brush. Do not use acid solution or strong cleaning agents.

(5) After cleaning rinse thoroughly with deionized water and reassemble the burner chamber.

(b) Cleaning after use of high concentration of acetylide forming metals (e.g. As, Cu, Hg)

(1) Immediately after analyzing acetylide forming metals thoroughly flush the burner mixing chamber with distilled water until all traces of residues are removed.

2.5.3 *Cleaning the nebulizer*

A lower than expected reading in absorbance for a standard may be due to an obstruction in the nebulizer. Clean the nebulizer in the following manner.

(1) Aspirate pure water (or solvent) until absorbance reading is satisfactory for a subsequent standard.

(2) If it fails, insert a thin wire into the capillary from the inlet side and move it in and out.

(3) If the nebulizer path is still obstructed, disassemble the nebulizer according to manufacturer's instructions and clean the components with soap and water.

2.5.4 *Care of optics*

(1) Do not make fingerprints on the surface of the hollow cathode lamp or on the light transmitting windows in the sample compartment of the instrument.

(2) When the covers are removed, never touch the reflecting surfaces of mirrors and gratings.

(3) If dust gets collected on optical surfaces, blow it off carefully by using a clean and dry air flow. Do not rub the surfaces with a cloth.

(4) Window surfaces may be cleaned with a tuft of cotton moistened with a dilute solution of a mild liquid detergent followed by several rinsings with deionized water.

(5) Cleaning of mirror surfaces and the gratings should be done only by a skilled service engineer.

2.6 Glassware

2.6.1 *Glassware cleaning*

The classical glassware cleaner is chromic acid solution which is prepared as follows:

Dissolve 100 g of $K_2Cr_2O_7$ in 1L of distilled water. Add slowly with great care and while stirring 1L of H_2SO_4. Allow the glassware to soak in chromic acid solution overnight. This mixture is hygroscopic and caustic so the container should be covered. Chromic acid is dangerous and for many purposes, the safer modern preparatory glassware cleaner may be suitable. They are complex chemical mixtures. So it is essential to make sure that they do not interfere with analysis. Ordinary detergents are less effective and more likely to cause interference. They may have disastrous effects on phosphorous analysis.

CHAPTER 3: STATISTICS IN WATER ANALYSIS

3.1 Introduction

Water laboratories around the world generate large amount of information every day. Much of that information is in the form of a value for a given water quality parameter. When we report a test data for any water quality parameter two questions are always asked about the experimental data:

1. How reliable is the result?
2. How can we assure the quality of data?

It is also important to note that all measurements contain certain experimental errors. In other words, it is impossible to be completely precise of a result. Understanding some basic statistics helps us to answer both of these questions and provides confidence in the laboratory data we furnish for a variety of purposes.

This section describes the basic statistical calculations which should be performed routinely on any water quality laboratory. The description will also include step-wise approach of calculation of statistical data and some limitations and the use of these parameters in data quality control. Basic statistics include methods which may be viewed as suitable for pencil-and-paper approach on small data sets. We strongly recommend to be conversant with hand calculations before using scientific calculators.

3.2 Basic statistics required in analysis of data

3.2.1 Mean and Standard Deviation

Mean value is the average of all measurements in the data set. Value of standard deviation indicates the spread of the individual measurements around the mean value. Small standard deviation signals very little variation of individual measurements around the mean.

Calculation

A. Mean (x)

$x = \sum x_i / n$

$x_i \Rightarrow$ ith measurement value

n number of measurements

B. Standard Deviation (s)

$s = \sqrt{(\sum (x_i - X)/(n-1))}$

$x_i \Rightarrow$ ith measurement

$X \Rightarrow$ mean of measurements

$n \Rightarrow$ number of measurements

Note: * Standard deviation is always positive.

* The square of the standard deviation is called variance.

3.2.2 Comparison of Means (Student-t Test)

In order to apply this test to compare means of two data sets, the standard deviations of the samples should be same (statistically, not significant at the confidence levels of interest). Therefore, before performing t-test, always perform F-test to check the significance of standard deviations of two sets.

Calculation:

Case 1 When the true mean is known

$t = |(X-\mu)/s|\ n^{1/2}$

Case 2 General case (with two means ?)

$t = |(X-Y)/s|\ |nm/(n+m)|^{1/2}$

X mean of data set, sample 1

μ true mean, sample 1

s Standard deviation, sample 1

n number of observations, sample 1

m number of observations, sample 2

Y mean of data set sample 2

Confidence Interval

The calculated mean and standard deviation of a data set are only approximates (You may never get a true value). By calculating **confidence interval** we suggest a range in which the **true mean** (μ) resides. The probability (the chance) level of the confidence interval should always be given.

Calculation

$\mu = X \pm ts/\sqrt{n}$

μ ⇒ true mean

X ⇒ mean (calculated)

t ⇒ Student t values (refer table x)

n ⇒ number of measurements

Note * The true mean (μ) is called the population mean.

* (n-1) is called degrees of freedom.

3.2.3 *Comparison of Precision* (F-test)

The F-test is used to compare the standard deviations of two sets of measurements. Since standard deviation is directly related to precision, by this way the precision of two sets of data can be compared for their differences.

Calculation:

F-test

$F_{calculated}$ S_A^1 ⇒ standard deviation of data set 1

S_B^2 ⇒ standard deviation of data set 2

$F_{tabulated}$ ⇒ get from the F-table for the degrees of freedom of data sets 1 and 2 for 95% confidence limit

If $F_{calculated} > F_{tabulated}$ ⇒ no difference in standard deviations = no difference in precision.

Note: * Always plug-in larger standard deviation value in the numerator of the formula

* Degree of freedom (n-1)

3.2.4 *Reliability of Results* (Q test)

Always reject the result of any analysis in which a known error has occurred. You may not, however, reject data arbitrarily. Do a Q test to make a decision on data rejection.

Calculation:

1. To apply a Q test arrange the data in order of increasing values
2. Calculate the **range** (the difference between lowest and highest values)
3. Determine the **gap** (the difference between the questionable point and the nearest value)
4. Calculate **Q = gap/range.**
5. If $Q_{calculated} > Q_{tabulated}$ reject the questionable point

Q table

Q(at 90% level)	0.94	0.76	0.64	0.56	0.51	0.47	0.44	0.41
n	3	4	5	6	7	8	9	10

3.2.5 *Accuracy and Precision*

The **true value** for a measurement remains unknown except when a standard sample is being analyzed. **Accuracy** is the nearness of a measurement or result to the true value. It is not defined in statistics. However, by estimating the related term, **standard error** (σ_μ) of a series of measurements, you can get a feeling of the accuracy of the results.

Precision indicates how close each measurements are to one another. **Unlike accuracy, precision can be defined statistically.** It is obtained by calculating the standard deviation of the data set. For better indication of the precision of your data set, always calculate the related term, **coefficient of variation** (CV).

Calculation

A Standard Error

$\sigma_\mu = X/\sqrt{n}$

$\sigma_\mu \Rightarrow$ Standard error of means

$X \Rightarrow$ mean of analysis

$n \Rightarrow$ number of measurements

B Coefficient of Variation

$CV\ (\%) = (s/X) \times 100$

$CV \Rightarrow$ coefficient of variation

$s \Rightarrow$ standard deviation

$X \Rightarrow$ mean of measurements

Note: * When standard error of data set gets smaller, the measurements become accurate (accuracy is high).

* When the coefficient of variation gets smaller, the measurements become more precise (precision is high).

* It is not possible to have accuracy without precision. However, you may have good precision without accuracy (see figure x).

3.2.6 *Rounding off Numbers*

When you perform mathematical operations with your raw data (i.e., instrument readings) to find out the quantity of a desired parameter in the sample, you have to maintain a certain number of digits in the answer in accordance with the rules of significant figures (Rules governing significant figures are discussed in the next section). If your answer carries more digits than that are allowed by the rules of significant figures, you have to round off extra digits such that the rules are obeyed. For rounding off numbers, you should follow the rules given below.

(i) If the segment to be rounded off is more than half way to the next higher digit, add 1 to the last number to be retained.

e.g. If 3 numbers are to be retained,

segment to be round off

↓	↓	↓	↓
67.0501	67.4501	67.5501	67.9501
↓	↓	↓	↓
67.1	67.5	67.6	68.0

(ii) If the segment to be rounded off is less than half way to the next higher digit, add 0 to the last number to be retained.

e.g. If 4 numbers to be retained,

segment to be rounded off

↓	↓	↓	↓
1.480499	1.482499	1.483499	1.489499
↓	↓	↓	↓
1.480	1.482	1.483	1.489

(iii) If the segment to be rounded off is exactly halfway to the next higher digit, round off the segment such that the last number to be retained becomes an even digit.

e.g. If 3 numbers to be retained,

segment to be rounded off

↓	↓	↓	↓
7.10500	7.13500	7.14500	7.19500
↓	↓	↓	↓
7.10	7.14	7.14	7.20

3.2.7 *Significant figures*

Let us consider a portion of a 50 ml buret as shown in Figure 3.1. On this buret, a 1 ml segment is divided into 10 small graduation each representing 0.1 ml. Therefore, you can take the reading upto the first decimal point exactly. For example, any one can read the liquid level in the buret exactly as 36.4 ml. However, you may notice that you are able to estimate the second decimal place between the small graduations (between 36.4

and 36.5) by your eye. By doing so, you are improving the accuracy of your reading and the ultimate result of your titration/experiment. In this case, the second decimal place, of course, is not exact (i.e. contains some un-certainty). Different analysts may read the second decimal place differently.

Figure 3.1

You may take the above reading as 36.44 ml. Another analyst may read it as 36.43 or 36.45 or even 36.46 ml. Hence, the buret reading has at least ± 1 uncertainly in the last digit. Here, you cannot possibly take the reading upto the third decimal place. Therefore, a reading such as 36.442 deviates from accurate reading as the third decimal place (i.e. 2) is <u>insignificant</u> when taking the reading by this particular buret. You may now understand that the third decimal place is significant only if, in addition to 0.1 ml graduations, 0.01 ml graduations are marked on the buret as in the case of some micro burets.

Now we can define the term <u>significant figures</u>. The number of significant figures in a reading obtained from an analytical instrument is the number of digits that are needed to express the reading without loss of accuracy. Therefore, a reading expressed in accordance with the concept of significant figures should contain all the certain digits and one uncertain digit. In the above example, 36.43, 36.44, 36.45 and 36.46 ml all contain correct significant figures (i.e. 4 figures) although the uncertainty in the last digit is different. Readings such as 36.4 ml and 36.442 ml do not comply with the concept of significant figures as the former does not include the first uncertain digit and the latter has one additional uncertain digit. If you are using a micro buret with 0.01 ml graduations, a reading like 36.442 ml obeys the concept of significant figures and

therefore carrier 5 significant figures.

You must follow the some rules when taking readings from any instrument with an analogue or digital scale. In the case of digital scales, the digit next to the last stable digit of the reading (i.e. first uncertain figure) should be taken as the last significant figure of the reading.

You must also understand that sometimes you can find the number of significant figure in a value only if the value is reported in scientific notation. For example, the number 80,400 is ambiguous with regard to significant figures. You should write above number in scientific notation to find out number of significant figures.

Number	**Scientific notation**	**Measurement upto**	**Number of significant figures**
80400	8.04×10^4	2 decimals	3
80400	8.040×10^4	3 decimals	4
80400	8.0400×10^4	4 decimals	5

Significance of zero digit in a number

Let us consider the level of significance of the following numbers

Number	**Scientific notation**	**Measurement upto**	**Number of significant figures**
2.000102	2.000102×10^0	6 decimals	7
0:000102	1.02×10^{-4}	2 decimals	3
0.0001020	1.020×10^{-4}	3 decimals	4

You should now understand that zeros are significant when they occur (a) in the middle of a number (b) at the end of a number on the right hand side of the decimal point. However, they are not significant when they appear before the first non zero digit on the left as they are merely holding decimal places.

Mathematical operations

You must follow the concept of significant figures through all mathematical operations that follow the initial experimental measurements. There are different rules governing addition and subtraction, multiplication and division and logarithm and antilogarithm.

Addition and subtraction

For addition and subtraction, express all the numbers by the same exponent and align them with respect to decimal point. Perform addition or subtraction and round off the answer so as to give same number of decimal places as of the number with fewest decimal place.

e.g.

(1)

$$\begin{array}{rl} & 2.562 \times 10^{5} \\ + & 1.035 \times 10^{3} \\ + & 5.12 \times 10^{6} \\ \hline & 5.377235 \times 10^{6} \end{array} \quad \Rightarrow \quad \begin{array}{rl} & 0.2562 \times 10^{6} \\ + & 0.001035 \times 10^{6} \\ + & 5.12 \times 10^{6} \\ \hline & 5.38 \times 10^{6} \end{array}$$

(2)

$$\begin{array}{rl} & 8.015 \times 10^{-1} \\ - & 5.1 \times 10^{-3} \\ \hline & 7.964 \times 10^{-1} \end{array} \quad \Rightarrow \quad \begin{array}{rl} & 8.015 \times 10^{-1} \\ & 0.051 \times 10^{-1} \\ \hline & 7.964 \times 10^{-1} \end{array}$$

Multiplication and Division

In these mathematical operations you should retain the number of digits contained in the number with the fewest significant figures in your answer. Here the exponent has no influence on the figure that should be retained

e.g.

$$\begin{array}{c} 5.46 \times 10^{5} \\ \times\ 3 \\ \hline 16.38 \times 10^{5} \\ \downarrow \\ 1.638 \times 10^{6} \\ \downarrow \\ 2 \times 10^{6} \end{array} \qquad \begin{array}{c} 4.3179 \times 10^{12} \\ \times\ 3.6 \times 10^{-19} \\ \hline 15.54444 \times 10^{-7} \\ \downarrow \\ 1.554444 \times 10^{-6} \\ \downarrow \\ 1.6 \times 10^{-6} \end{array} \qquad \begin{array}{c} 1234.6 \\ \div\ 2.482 \\ \hline 497.4214343 \\ \downarrow \\ 497.421 \\ \downarrow \\ 497.4 \end{array}$$

Logarithms and antilogarithms

Consider the logarithm of number 584. Since the number contain 3 significant figures the logarithm value should also contain 3 significant figures

e.g. log 584	=	log 5.84 x 10^2	=	2.766412847	=	2.766
		3 significant digits		3 significant digits		2 significant digits

Remember the first digit (2) in the answer is not significant. It only corresponds to exponent in 5.84 x 10^2. Therefore, here 2.766 (which is a log value) has only three significant figures. The rule is that the number of digits in the mantissa of log value should equal the number of significant figure in the number of which the log value was taken.

In converting a logarithm to antilogarithm, number of figures in the mantissa of the logarithm should equal the significant figures in the antilogarithm value.

e.g. antilog (-3.42)	=	$10^{-3.42}$	=	3.801893963 x 10^{-4}	=	3.8 x 10^{-4}
		2 significant digits		2 significant digits		2 significant digits

3.2.8 Signal and Noise

Electronic signals will be produced by all equipments even when a blank sample is being analyzed. This electronic signal is called **noise**. The **Signal/Noise** (S/N) ratio is a measure of **equipment resolution**. See the manual of particular equipment for this value. **Detection limit** is the smallest concentration that can be detected from a given procedure and with a given degree of confidence. We have three types of detection limits in water analysis.

Calculations

Instrument Detection Limit (IDL)

The concentration of analyte that produces a signal greater than **five times the S/N ratio**

of the equipment. This is same as "**critical level**"

IDL_x = 5 x S/N where S ⇒ signal, N ⇒ noise & IDL_x ⇒ Instrument detection limit for x analyte.

Detection Limit (DL)

The analyte concentration in reagent water that produces a signal of **2(1.645)s** above the means of blank analysis.

LDL_x = 2 x 1.649 x s where s ⇒ standard deviation, LDL_x ⇒ lower limit of detection or detection limit.

Method Detection Limit (MDL)

Add a analyte of interest to the water, to make a concentration near the estimated MDL. Analyze seven portions of this solution. Calculate standard deviation (s).

MDL_x = 3.14 x s where s⇒standard deviation of seven portions,

MDL_x ⇒ method of detection limit of solute x.

3.2.9 Regression and correlation

Regression

Imagine that two variables are linearly related (as judged by correlation coefficient), you can predict the value of one variable from the value of the other variable. You can plot a straight line by eye to show linear relationship.

We have formal ways of plotting this line, which is called **the line of regression**. The normal way is called the method of least squares. In this section we deliberately by pass the derivation procedure and the theoretical justification for the best line. We shall use the required formulas in calculating the coefficients a and b of the straight line y= a + bx and try to explain the term "**method of least square**"

Method of least square

Assumptions:

1. The errors in the y values are larger than the errors in the x values.
2. The uncertainties in y values are similar.

Correlation

Correlation is the term in statistics when looking for links or connections between two variables. The degree of correlation is measured by the **correlation coefficient (r).**

$-1 \leq$ correlation coefficient (r) $\leq +1$

Case I:

$r=+1 \Rightarrow$ perfect linear positive relationship between the variables (figure 1.x).

Case II:

$r=-1 \Rightarrow$ perfect linear negative relationship between the variables (figure 1.y).

Case III:

$r=0 \Rightarrow$ no linear correlation at all!

Case IV:

When $r < +1$ or $r < -1$ none of these data points lie exactly on the line, but on the whole the line fits fairly well (figure 1.z).

Note: * In both cases the all data points lie exactly on a straight line (How accurate you are?)

Calculation of correlation coefficient

$$r \qquad \frac{n\Sigma xy - \Sigma x\Sigma y}{\sqrt{[n\Sigma x^2 - (\Sigma x)^2]\,[n\Sigma y^2 - (\Sigma y)^2]}}$$

1. Tabulate observations according to the following format.
2. Calculate Σx, Σy, Σxy, Σx^2, Σy^2 from the table.
3. Plug-in the formula given for r.

CHAPTER 4: SAMPLING, PROCESSING AND PRESERVATION

4.1 Introduction

Meaningful assessment of water quality depends on a variety of factors such as monitoring design, sampling, processing, pre-treatment, shipment to laboratory and laboratory analysis. This is particularly crucial for some physical, chemical and biological analysis undertaken on water samples such as, pH, trace elements, micro-nutrients (e.g. nitrate, phosphate, ammonia). Errors can occur from field operations to laboratory analysis. Contamination in common errors occurs during sampling, filtration and laboratory analysis. In the case of field measurements (e.g. pH, conductivity, temperature, salinity, etc.), uncalibrated operations will provide erroneous results. Understanding of hydrological regime also fairly important to ensure meaningful field operations. Loss of labels and break of containers are also commonly occurring sources of errors in the water quality assessment processes.

It is also necessary to follow recommended procedures to avoid collection of unrepresentative samples. Each method or sampling gear (apparatus) has appropriate procedures which should be followed accurately at every sampling occasion. In addition, simple basic rules such as avoiding any unnecessary disturbances of the site prior to sampling (e.g. by standing in water and washing hands before sampling) must be followed. It is important to note that the sampling procedures depend largely on the nature of the monitoring programme and the site to be sampled.

4.2 Sampling Strategies

Water sampling is fairly straightforward although certain factors must always be taken into account. For example:

a. obtaining an adequate volume of samples

b. cleanness of samplers and containers

c. collection of samples into a container with respective analysis (e.g. determination of oxygen)

d. filteration samples in the case of dissolved constituents

e. appropriate method of storage and

f. quick shipment to the laboratory

4.3 Surface Water

True surface water bodies in Sri Lanka are mainly rivers, estuaries and lagoons. Villus in the floodplain and marshes are also natural in form but transitional or seasonal in nature. It should be noted that Sri Lanka has no lakes. Reservoirs are anthropogenic in origin and intermediate forms between rivers and lakes. Shallow irrigation tanks are fairly different from reservoirs. Smaller irrigation tanks which are commonly known as village tanks are rain fed shallow pools. Several perennial pools can be seen in Hortan Plains, the highest altitudanal place of the country, and their origin is unknown. A unique trope of surface water in rock pools popularly known as "Kema" is located in the southeastern part of the country.

4.4 Samplers

Bottle samplers:

1. Friedinger
2. Van Dorm
3. Ruttner

Suitable for open waters. Enables sampler to be collected from discrete depths. However, these samplers are expensive unless manufactured in house.

4.5 Sampling

4.5.1 *Sampling for physico-chemical analysis*

Samples for physico-chemical analysis (i.e. temperature, conductivity, pH and oxidation reduction potential) will seldom create problems. However, attention must be paid here to changes caused by access or escape of gases.

4.5.2 *Sampling for chemical analysis*

The choice of bottle material and bottle size to suit the intended purposes of the analysis in important variable components such as Fe^{++} and cyanide, oxygen and free CO_2 must be determined at the time of sampling.

4.5.3 *Sampling for Microbiological analysis*

Secondary infection or technical errors in sampling can falsify the accuracy of the entire microbiological investigation. It is therefore of decisive ..... that sampling should be carried out expertly.

* As a rule sterilized glass-stoppered bottles covered with aluminum foils should be used to collect samples
* Bottles used for sampling chlorinated water must be treated (0.25 ml of 0.01 m thiosulfate for 250 ml .....) with sodium thiosulfate before sterilization
* In the case of drinking water, taps must be initially cleaned mechanically and subsequently be flamed until it is completely dry
* In order to prevent changes in microbiological quality of the water, samples must be transported in insulated boxes
* The samples should be examined immediately on arrival at the laboratory. If this is not possible in exceptional circumstances the samples should be stored at 4 ^{0}C. However, storage time should be minimum
* If the time span between sampling and investigation is too long the bacteriological tests will have to be carried out in situ

4.6 Sample treatment and storage

Collected samples can be contaminated by inadequately or inappropriately cleaned glassware, filters filter apparatus, chemicals used for preservation etc. Thus care must be taken in the cleaning of equipment and in the checking for purity of chemicals used. Water quality variables which should be determined in the field immediately after sampling need individual ..... which cannot be used for further analytical work. In

addition field analytical operations should follow a defined sequence in order to avoid contamination. For example conductivity must not be determined after measurements of pH in the same water sample. Because concentration of electrolytes from the reference electrode used in the pH determination may enter the sample and affect the conductivity measurement.

During the field operations, periodic blank samples (one blank for every ten water samples) are required to determine errors arising from contamination. Usually for this purpose a distilled water sample is subjected to all the operations undertaken for the environmental sample such as filtration, storage and preservation. The blank is shipped with the other samples to the laboratory for analysis. When blank tests show evidence of contamination, additional investigations must be need during the next round of sampling.

Preservation of samples may be necessary in individual case. The best form of preservation of a sample is a rapid investigation of the water sample after sampling. This should take place in the laboratory as far as possible not later than 2 days after sampling. During the transportation and until commencement of the investigation the water sample should be stored in cool condition at around 4 ^{0}C.

CHAPTER 5: ANALYTICAL PROCEDURES

5.1 Introduction

There are a number of important points related to water analysis which are rarely mentioned in analytical manuals. Firstly, when a method is tried for the first time or when it is restarted after a break of some time, the precision (reproducibility) and accuracy are unsatisfactory. Simply repeating the procedure with no deliberate changes will often restore the earlier reliability. But it is wise to assume that the first batch of measurements will not be satisfactory and to avoid including samples which cannot be repeated. Secondly, it should be constant practice when new standard solution is made to check it against the old one and sufficient amount of the old one should be kept for this purpose. This is necessary even when commercial standard solutions are used.

Thirdly, the analyst should constantly be seeking to match the precision and accuracy of his analysis to the needs of his problems and limitations of the sampling programme. It is usually waste of money to strive for accuracy ± % if the samples are unrepresentative or have the standard deviation of 10% or if the problem involves the comparison of two samples which differ in concentration by a factor of 10.

Even within a single procedure there is a scope for judgement.

The standard solution may have to be made with accuracy ± 0.1% and the HCl used to make the solution acid may need to be a accuracy no better than ± 10% but it may have to be dispensed in amounts which have precision (reproducibility) ± 0.5%.

The acid should be made up rapidly in a measuring cylinder and dispensed with an automatic dispenser. But if the laboratory needs stocks of both 0.1M and 0.100 m HCl then using the more accurate 0.100 M solution for all purpose may cool less and cause few mistakes.

5.2 Physical Parameters

COLOR **Spectrophotometric**

Interferences Slight amounts of turbidity may interfere

1. Background

   1.1 The method is applicable to drinking, surface and saline waters, domestic and industrial wastes

2. Apparatus

   2.1 Spectrophotometer

   2.2 Filtration system

      2.21 Filtration flasks, 250 ml with side tubes

      2.22 Crucible holder

      2.23 Filter crucible

      2.24 Vacuum system

3. Reagents

   3.1 Filter aid- Celite No.505 or equivalent

4. Procedure

   4.1 Use two 50 ml samples, one at the original pH and the other at 7.6 pH at room temperature (use sulfuric acid or sodium hydroxide to adjust the pH)

   4.2 Remove excessive quantities of suspended materials by centrifuging

   4.3 Treat each sample as follows

      4.31 Thoroughly mix 0.1 g filter aid in a 10 ml portion of centrifuged sample and filter to form a precoat in the filter crucible

      4.32 Direct filtrate to waste flask

      4.33 Mix 40 mg filter aid in a 35 ml portion of centrifuges sample

      4.34 With vacuum still on filter through the precoat and pass filtrate to waste flask until clear

4.35 Direct clear filtrate flow to clean flask and collect 25 ml for the transmittance determination

4.4 Thoroughly clean 1 cm absorption cells with detergent and rinse with distilled water

4.5 Rinse twice with filtered sample

4.6 Fill cell with filtered sample

4.7 Determine transmittance values at certain selected wavelengths

5. Calculation

5.1 Express color characteristics in terms of dominant wavelength (Refer the table)

Wavelength Range (nm)	Colour
400-465	Violet
465-482	Blue
482-497	Blue-green
497-530	Green
530-575	Greenish yellow
575-580	Yellow
580-587	Yellowish orange
587-598	Orange
598-620	Oragne-Red
620-700	Red

Note: * Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible.

* Refrigeration of samples at 4°C is recommended.

Reference

1. Standard methods for the examination of water and wastewater, 17th Edition, 1989.

2. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

1. Background

   1.1 The method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

2. Apparatus

   2.1 Mercury-filled celsius thermometer

   2.2 Thermometer should have a scale marked for every 0.1°C

3. Reagents

   Not required

4. Procedure

   Direct measurement from the instrument

Note: * Measuring device should be routinely checked against a precision thermometer

Reference

1. Standard methods for the examination of Water and Wastewater, 17thEdition, 1989.

TURBIDITY **Nephelometric**
NTU

Linear range	0 to 40 NTU
Detection limit	0.02 NTU
Interferences	Presence of floating debris and coarse sediments which settle out rapidly will give low readings Finely divided air bubbles will affect the results The presence of true color that is the color of water which is due to dissolved substances which absorb light will cause turbidities to be low
Precision and Accuracy	For surface water samples at levels of 26 and 41 NTU the precision was reported as 2%

1. Background
   1.1 The method is applicable to drinking, surface and saline waters
2. Summary of method
   2.1 The method is based upon a comparison of the intensity of light scattered by the sample with the intensity of the light scattered by a standard reference suspension
   2.2 The higher the intensity of light scattered, the higher the turbidity
3. Apparatus
   3.1 Turbidimeter consisting of a nephelometer with light source and a photoelectric detector
   3.2 Clear, colorless glass sample tubes
4. Reagents
   4.1 Turbidity free water
   4.2 Stock formazin turbidity suspension
   4.3 Standard formazin turbidity suspension
   4.4 Alternate standards
5. Preparation of standards
   5.1 Turbidity free water

5.11 Pass distilled water through a 0.45 u pore size membrane filter

5.2 Stock formazin turbidity suspension

5.21 Solution I- Dissolve 1.00 g hydrazine sulfate in distilled water

5.22 Dilute to 100 ml in a volumetric flask

5.23 Solution II - Dissolve 10.00 g hexamethylene - tetramine in distilled water

5.24 Dilute to 100 ml in a.volumetric flask

5.25 Mix 5.0 ml solution I with 5.0 ml solution II in a 100 ml volumetric flask

5.26 Allow to stand 24 hours at 25 $\pm$ 3^{0}C, then dilute to the mark and mix

5.3 Standard formazin turbidity suspension

5.31 Dilute 10.00 ml stock turbidity suspension to 100 ml with turbidity-free water

5.32 Dilute portions of the standard turbidity suspension with turbidity-free water as required

6. Calibration

6.1 Follow the manufacturer's operating instructions

6.2 Check accuracy of any supplied calibration scales on a precalibrated instrument by using appropriate standards

6.3 Run at least one standard in each instrument in the range to be used

7. Procedure

7.1 Turbidities less than 40 units

7.11 Shake the sample thoroughly to disperse the solids

7.12 When air bubbles disappeared, pour the sample into the turbidimeter tube

7.13 Read the turbidity directly from the instrument

7.2 Turbidities exceeding 40 units

7.21 Dilute the sample with one or more volumes of turbidity free water until the turbidity falls below 40 units

7.22 The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor

8. Calculation

8.1 Multiply sample readings by appropriate dilution to obtain the final reading

$$\text{Nephelometric turbidity units (NTU)} = \frac{A \times (B + C)}{C}$$

Where, A = NTU found in diluted sample

B = Volume of dilution water, ml

C = Sample volume taken for dilution, ml

Reference

1. Standard Methods for the examination of water and wastewater, 17th Edition, 1989.
2. EPA/600/4-79/020 Methods for chemical analysis of water and wastes.

Precision and accuracy Precision of salinity ± 0.0002

1. Background

   1.1 The method responds only to ionic solutes. For all dissolved solutes use density method

2. Summary of method

   2.1 An indirect method involving the measurement of conductivity

2. Apparatus

   2.1 Conductivity bridge, range 1 to 1000 μmhos/cm

   2.2 Conductivity cell, cell constant 1.0 or micro dripping type cell with 1.0 constant

   2.3 Thermometer

3. Reagents

   3.1 Conductivity water

   3.2 Standard Potassium chloride solution (0.01 M)

4. Preparation of standards

   Refer conductivity

5. Calibration

   Refer conductivity

6. Procedure

   Refer conductivity

7. Calculation

   Salinity S

$$S_{pss} = \frac{a_0}{1 + 1.5X + X^2} - \frac{b_0 f(t)}{1 + Y^{1/2} + Y^{3/2}}$$

Where,

S_{pss}	=	value determined from the practical salinity scale
a_0	=	0.008
b_0	=	0.0005
X	=	400 R_t
Y	=	100 R_t
f(t)	=	(t-15)/{1 + 0.0162 (t-15)}
t	=	temperature in celcius

Reference

1. Standard methods for the examination of water and wastewater, 17th Edition, 1989.

TOTAL HARDNESS
mg/l as $CaCO_3$

Titrimetric

Linear range	All concentration ranges
Interference	Metals may interfere
Percision and Accuracy	For synthetic water samples containing increments of 31 and 444 mg/l $CaCO^3$, the precision was reported as 9% and 2% respectively The accuracy was reported as -0.87% and -3.23% respectively for the above two samples

1. Background

   1.1 The method is applicable to drinking, surface and saline waters, domestic and industrial wastes

2. Summary of method

   2.1 Calcium and magnesium ions in the sample are titrated upon the addition of disodium ethylenediamine tetraacetate

   2.2 The end point is detected by means of Eriochrome Black indicator

3. Apparatus

   3.1 Standard laboratory titrimetric equipment

4. Reagents

   4.1 Buffer solution

   4.2 Inhibitors

   4.3 Indicators

   4.4 Standard EDTA titrant

   4.5 Ammonium Hydroxide

5. Preparation of standards

   5.1 Buffer solution

      5.11 If magnesium EDTA is available, dissolve 16.9 g NH_4Cl in 143 ml conc. NH_4OH in a 250 ml volumetric add 1.25 g of magnesium salt of EDTA

and dilute to the mark with distilled water

5.12 If magnesium EDTA is unavailable, dissolve 1.179 g disodium EDTA and 780 mg $MgSO_4.7H_2O$ in 50 ml distilled water. Add this solution to a 250 ml volumetric flask containing 16.9 g NH_4Cl and 143 ml conc. NH_4OH with mixing and dilute to the mark with distilled water

5.13 Store these solutions in tightly stoppered plastic bottles (discard this solution when 1 or 2 ml face to produce a pH of 10.0 ± 0.1 at the end point).

5.2 Inhibitor

5.21 Inhibitor I - NaCN powder

5.22 Inhibitor II - Dissolve 5.0 g $Na_2S.9H_2O$ or 3.7 g $Na_2S.5H_2O$ in 100 ml distilled water. Exclude air with tightly fitted rubber stopper

5.23 Inhibitor III - Dissolve 4.5 g hydroxylamine hydrochloride in 100 ml of 95% ethanol or isopropanol

5.3 Indicator - use a commercially available indicator such as Calamagite

5.4 Standard EDTA titrant (0.02 N)

5.41 Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate $Na_2H_2C_{10}H_{12}O_8N_2.2H_2O$ in a 1 liter volumetric flask

5.42 Dilute to the mark with distilled water

5.43 Standardize the solution with standard calcium solution by a titration

5.44 Store in polyethylene bottles

5.5 Ammonium Hydroxide solution (1 N)

5.51 Dilute 70 ml of conc. NH_4OH to 1 liter with distilled water

6. Procedure

6.1 Place 25.0 ml sample in titration vessel, neutralize with 1N ammonium hydroxide

6.2 Dilute to about 50 ml

6.3 Add 1 or 2 ml buffer solution

6.4 If end point is not sharp (as determined by practice run), add inhibitor at this point

6.5 Add 1 or 2 drops indicator solution

6.6 Titrate slowly with continuous stirring with standard EDTA titrant until last reddish tint disappears. Solution is normally blue at end point

7. Calculation

$$\text{Hardness (EDTA) as mg } CaCO_3/l = \frac{A \times B \times 1000}{\text{ml sample}}$$

Where, A = volume of EDTA titrant for sample in ml

B = mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant

Note: * For low hardness, a large sample, propotionately larger amounts of buffer, inhibitor and indicator must be used.

* Inhibitors are used to reduce the metallic interferences.

* To avoid large titration volumes, use a sample aliquot containing not more than 25 mg $CaCO_3$

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

2. Standard methods for the examination of water and wastewater, 17th Edition, 1989.

pH
pH units

Potentiometric

Interferences: Dissolved gases such as CO_2, H_2S or NH_3 may contribute acidity
Solids and oily matter may coat the glass electrode
Presence of oxidizable or hydrolyzable ions may interfete
Na may interfere at pH levels greater than 10

Precision & Accuracy: A precision of ± 0.02 pH unit and an accuracy of ±0.05 pH units can be achieved.

1. Background

   1.1 This method is applicable to drinking, surface and saline waters domestic and industrial wastes and acid rain

2. Summary of method

   2.1 The pH is determined by electrometrically using either a glass electrode in combination with a reference electrode

3. Apparatus

   2.1 pH meter laboratory or field model

   2.2 Glass electrode

   2.3 Reference electrode - calomel, silver-silver chloride or other reference electrode

   2.4 Magnetic stirrer and Teflon-coated stirring bar

   2.5 Thermometer

4. Reagents

   4.1 Saturated Potassium Chloride solution

   4.2 Standard potassium chloride solution

   4.3 Potassium hydrogen phthalate solution (pH-4.004)

   4.4 Sodium borate decahydrate solution (pH-9.183)

   4.5 Saturated Calcium hydroxide solution (pH-12.454)

5. Preparation of standards

5.1 Standard Potassium chloride solution

5.11 Boil and cool distilled water (conductivity less than 2 μmhos/cm)

5.12 To 50 ml of water add 1 drop of saturated Kcl solution

5.13 If the pH is between 6.0 and 7.0 use it to prepare all standard solutions

5.2 Potassium hydrogen phthalate solution (pH-4.004)

5.21 Dissolve 10.12 g of potassium hydrogen phthalate in distilled water

5.22 Dilute to 1000 ml

5.3 Sodium borate decahydrate solution (pH-9.183)

5.31 Dissolve 3.80 g of sodium borate decahydrate (borax) in distilled water

5.32 Dilute to 1000 ml

5.4 Saturated Calcium hydroxide solution

5.41 Dry $Ca(OH)_2$ at 110^{0}C cool and pulverize to uniformly fine granules.

5.42 Vigorously shake an excess of fine granules with distilled water in a stoppered polyethylene bottle.

5.43 Let temperature come to 25^{0}C after mixing

5.44 Filter supernatant under suction through a sintered glass filter of medium porosity and use filtrate as the buffer solution.

6. Calibration

6.1 Each instrument/electrode system must be calibrated with minimum of 2 buffer solutions having pH values approximately three pH units apart from the expected pH of the sample.

7. Procedure

7.1 Keep electrode wet by returning them to storage solution (std. Kcl solution) whenever pH meter is not in use

7.2 Standardize the meter and electrode system as outlined in Chapter 1.5.

7.3 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes

7.4 If the sample temperature differs by more than 2^{0}C from the buffer solution the measured pH values must be corrected.

7.5 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample and stir at a constant rate to provide homogeneity and suspension of solids

7.6 Note and record sample pH and temperature

7.7 Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient

8. Calculation

8.1 pH meters read directly in pH units

8.2 Report pH to the nearest 0.1 unit and temperature to the nearest ^{0}C.

Note: * Electrode coatings can be removed by gentle wiping or detergent washing followed by distilled water rinsing. An additional treatment with hydrochloric acid may be necessary to remove any remaining film.

* Interference by sodium can be eliminated by using a low Sodium error electrode

Reference

1. Standard methods for the Examination of Water and Waste Water,. 17th Edition, 1989.

2. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

CONDUCTIVITY
Micromhos/cm

Interferences	No significant interferences
Precision and Accuracy	For synthetic water samples containing increments of inorganic salts with specific conductance of 100 and 1710, the precision was reported as 8% and 7% respectively The accuracy was reported as -2.02% and -5.08% respectively for the above two samples

1. Background

   Method is applicable to drinking, surface and saline waters, domestic and industrial wastes

2. Summary of method

   2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Weastone type or equivalent

3. Apparatus

   3.1 Conductivity bridge, range 1 to 1000 μmhos/cm

   3.2 Conductivity cell, cell constant 1.0 or micro dipping type cell with 1.0 constant

   3.3 Thermometer

4. Reagents

   4.1 Conductivity water

   4.2 Standard potassium chloride solution (0.01 M)

5. Preparation of standards

   5.1 Dissolve 0.7456 g of pre dried (2 hours at 105^{0}C) Kcl in distilled water and dilute to 1 liter at 25^{0}C.

6. Calibration

   6.1 Instrument must be standardized with KCl solution before use

   6.2 Accuracy of the cell constant and conductivity bridge should be checked with the standard potassium chloride solution

7. Procedure

7.1 Rinse cell with one or more portions of sample

7.2 Adjust temperature of a final portion to 25.0 ± 0.1 °C

7.3 Measure sample resistance or conductivity and note temperature

Note: * Temperature variations and corrections represent the largest source of potential error.

References

1. Standard methods for the examination of water wastewater, 17th edition, 1989.

2. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

SUSPENDED SOLIDS **Gravimetric**
mg/l

Linear range	4 mg/l to 20,000 mg/l
Interferences	Samples high in dissolved solids may cause a positive interference
Precision and Accuracy	Preeision data are not available

1. Background

   1.1 The method is applicable to drinking, surface and saline waters, domestic and industrial wastes

2. Summary of method

   2.1 A well mixed sample is filtered through a glass fiber filter and the residue retained on the filter is dried to constant weight at 103-105^{0}c

3. Apparatus

   3.1 Glass fiber filter discs without organic binder

   3.2 Filtering apparatus with reservoir and a coarse (40 -60 microns) fritted disc as a filter support

   3.3. Suction flask

   3.4 Drying oven 103-105^{0}C

   3.5 Desiccator

   3.6 Analytical balance capable of weighing to 0.1 mg

4. Procedure

   4.1 Preparation of glass fiber filter disc

      4.11 Place the glass fiber filter on the membrane filter aparatus or insert into bottom of a suitable Gooch crucible with the wrinked surface facing upwards

      4.12 While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water

      4.13 After water has passed through,remove all traces of water by continuous application of vacuum

4.14 Remove the filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105°C for one hour

4.15 Remove to desiccator and store until needed

4.16 Repeat the drying cycle until a constant weight is obtained

4.2 Selection of sample volume

4.21 For a 4.7 cm diameter filter, filter 100 ml of sample

4.22 If weight of captured residue is less than 1.0 mg the sample volume must be increased to provide at least 1.0 mg of residue

4.23 If other filter diameter are used, start with a sample volume equal to 7 ml/cm^2 of filter area and collect at least a weight of residue propotional to 1.0 mg

4.3 Assemble the filtering apparatus and begin suction

4.4 Shake the sample vigorously and quantitatively transfer the pre-determined sample volume selected in 4.2 to the filter using a graduated cylinder

4.5 Remove all traces of water by continuing to apply vaccum

4.6 With suction on, wash the graduated cylinder, filter, non filterable residue and filter funnel wall with three volume portions of distilled water allowing complete drainage between washing

4.7 Remove the filter from the filter support. Remove crucible and filter from crucible adapter

4.8 Dry at least for one hour at 103-105°C in an oven

4.9 Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained

5. Calculation

$$\text{Non filterable residue, mg/l} = \frac{(A-B) \times 1000}{C}$$

Where, A = weight of filter (or filter + crucible) + residue in mg

B = weight of filter (or filter + crucible) in mg

C = volume of sample filtered in ml

Note: * Non representative particulates such as leaves, sticks, fish and lumps of facal matter should be excluded from the sample if their inclusion is not desired in final result.

* Preservation of sample is not practical.

* Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter minimize the potential interference.

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

2. Standard methods for the examination of water and wastewater, 17th Edition, 1989.

TOTAL DISSOLVED SOLIDS **Gravimetric**
mg/l

Linear range	10 mg/l to 20,000 mg/l
Interferences	Highly mineralized water and samples high in bicorbanate may interfere Excessive residue in the dish may form a crust which entraps water that will not be driven off during drying
Precision and Accuracy	Precision data are not available

1. Background

   1.1 The method is applicable to drinking, surface and saline waters, domestic and industrial wastes.

   1.2 The method can be used for the solids capable of passing through a glass fiber filter and dried to constant weight at 180°C

2. Summary of method

   2.1 A well mixed sample is filtered through a standard glass fiber filer. The filterate is dried to constant weight at 180°c.

3. Apparatus

   3.1 Glass fiber filter disks without organic binder (4.7 cm or 2.1 cm)

   3.2 Filter holder, membrane filter funnel or Gooch crucible adapter

   3.3 Suction flask, 500 ml

   3.4 Gooch crucible, 25 ml (if 2.1 cm filter is used)

   3.5 Evaporating dishes (porcelain, 100 ml volume)

   3.6 Steam bath

   3.7 Drying oven, 180°C ± 2°C

   3.8 Desiccator

   3.9 Analytical balance capable of weighing to 0.1 mg

4. Procedure

   4.1 Preparation of glass fiber filter disc

4.11 Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible

4.12 While vacuum is applied wash the disc with three successive 20 ml volumes of distilled water

4.13 After water has passed through, remove all traces of water by continuous application of vacuum. Discard washings

4.2 Prepartion of evaporating dishes

4.21 Heat the clean dish to 180 $\pm 2^0$C for one hour

4.22 Cool in desiccator and store until needed

4.3 Assemble the filtering apparatus and begin suction

4.4 Shake the sample vigorously and rapidly, transfer 100 ml to a funnel by means of a 100 ml graduated cylinder

4.5 Filter the sample through the glass fiber filter

4.6 Rinse with three 10 ml portions of distilled water and continue to apply vacuum for about 3 minutes

4.7 Transfer 100 ml of the filterate to a weighed evaporating dish

4.8 Evaporate to dryness on a steam bath

4.9 Dry the evaporated sample for at least one hour at 180 $\pm$ 2^{0}C in an oven

4.10 Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg

5. Calculation

$$\text{Filterable residue, mg/l} = \frac{(A-B) \times 1000}{C}$$

Where, A = weight of the dried residue + dish in mg

B = weight of the empty dish in mg

C = volume of sample used in ml

Note: * Preservation of the sample is not practical, analysis should begin as soon as possible

* Refrigeration or cooling to 4^{0}C, to minimize microbiological decomposition of solids is recommended

* Highly mineralized and samples containing high concentrations of bicarbonate will require prolonged drying at 180°C

* Total residue in the evaporating dish should be limited to about 200 mg

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

2. Standard methods for the examination of water and wastewater, 17th Edition, 1989.

5.3 Metals

ALUMINUM
μg/l

Chelation Extraction-Atomic Absorption
Instrument parameters
Aluminum hollow cathode lamp
Wavelength - 309.3 nm
Fuel - acetylene
Oxidant - Nitrous oxide
Type of flame -

Linear range	10 μg/l to 300 μg/l
Detection limit	0.1 mg/l
Interferences	Iron cocentrations above 10 mg/l will interfere Magnesium forms an insoluble quinolate at pH 8
Precision and accuracy	For reagent water samples containing 50 and 300 μg/l aluminum, the precision was reported as 12% and 10% respectively The accuracy was reported as +5.8% and -3.5% for the reagent water samples containing 40 and 275 μg/l of aluminum respectively

1. Background
   - 1.1 The method is applicable to reagent and natural waters
   - 1.2 Limited to waters containing less than 10 mg/l of iron
2. Summary of method
   - 2.1 Aluminum is extracted after chelation with 8-Hydroxyquinoline into methylisobutyl ketone
   - 2.2 The extract is aspirated directly into a nitrous-oxide-acetylene flame
3. Apparatus
   - 3.1 Atomic absorption spectrophotometer (for use at 309.3 nm) and associated equipment.
4. Reagents
   - 4.1 Aluminium solution, standard

4.2 Aluminium solution, working

4.3 Concentrated ammonium hydroxide

4.4 Ammonium hydroxide-ammonium acetate buffer

4.5 Concentrated hydrochloric acid

4.6 8-hydroxyquinoline solution

4.7 Methylisobutyl ketone (MIBK)

4.8 Concentrated nitric acid

4.9 Nitrous oxide

4.10 Air

4.11 Acetylene

5 Preparation of standards

5.1 Aluminum solution, standard (1 ml = 100 μg Al)

5.11 Dissolve 1.758 g of aluminum potassium sulfate in water

5.12 Add 1 ml of nitric acid

5.13 Dilute to 1 litre

5.2 Aluminum solution, working (1 ml = 1.0 μg Al)

5.21 Dilute 10 ml of aluminum standard solution, adding 1 ml of nitric acid to 1 litre with water

5.3 Ammonium hydroxide ammonium acetate buffer

5.31 Dissolve 200 g of ammonium acetate in water

5.32 Add 70 ml of concentrated ammonium hydroxide

5.33 Dilute to 1 litre

5.4 8-hydroxyquinoline solution

5.41 Dissolve 20 g of 8-hydroxyquinoline in a mixture of 57 ml of glacial acetic acid and 200 ml of reagent water

5.42 Dilute to 1 litre with water

5.5 Methylisobutyl ketone (MIBK)

5.51 MIBK saturatd water in a separatory funnel mix equal volumes of MIBK and water, separate phases carefully

5.52 Water saturated MIBK use MIBK phase from 5.51

6 Calibration

6.1 Prepare a blank and standards ranging in concentration from 10 $\mu g/l$ to 300 $\mu g/l$ by appropriate dilution of the working aluminum solution

6.2 Extract 100 ml of each standard and a blank as in procedure

6.3 Plot absorbance versus concentration of aluminum

7 Procedure

7.1 Soak all glassware in hot HCl (1+1) for 2 h. Drain and rinse at least 5 times with water. Drain and flush with methyl alcohol, ethyl alcohol or isopropyl alcohol

7.2 Measure a well mixed acedified volume upto a maximum of 100 ml into a 125 ml beaker

7.3 Add 0.5 ml of nitric acid and 5 ml of hydrochloric acid

7.4 Heat the samples on a hot plate until the volume has been reduced to 10 to 15 ml (do not boil the samples)

7.5 Adjust the pH to 8 with concentrated ammonium hydroxide

7.6 If necessary filter the samples into a 200 ml volumetric flask

7.7 Wash the filter paper several times and bring the volume approximately to 100 ml

7.8 Add 2 ml of 8-hydroxyquinoline solution and mix

7.9 Add 10 ml of buffer solution to 1 sample and immediately add 10 ml of water saturated MIBK

7.10 Shake vigurously for 15 seconds

7.11 Treat samples and standards alike

7.12 After the layers have separated add MIBK saturated water to raise the ketone layer completely into the neck of the flask

7.13 Aspirate the ketone layer into the nitrous oxide acetylene flame and determine its absorbance from the calibration curve (aspirate water saturated MIBK between samples)

8 Calculation

Aluminum, $\mu g/l$ = C x (100/V)

where: C = concentration from the curve in $\mu g/l$

V = volume used in ml

Note:* Interference caused by magnesium can be avoided if the samples are extracted immediately after they are buffered to pH 8

Reference

1. Annual Book of ASTM Standards. Vol. 11.01 Water (1), 1993.

CADMIUM μg/l	**Chelation Extraction-Atomic Absroption** Instrument parameters Cadmium hollow cathode lamp Wavelength 228.8 nm Fuel-acetylene Oxidant-air Type of flame
Linear range	5 - 200 μg/l
Detection limit	0.002 mg/l
Interferences	Calcium concentrations above 1000 mg/l suppress the cadmium absorption High concentrations of other metals and sulfate chloroide and nitrate may interfere
Precision and Accuracy	For natural water samples containing 30 and 160 μg/l cadmium, the precision was reported as 23% and 13% respectively The accuracy was reported as -3.6% and -3.1% for the natural water samples containing 77 and 29 μg/l of cadmium respectively

1. Background

   1.1 Method is applicable to surface and groundwater, domestic and industrial wastewater

2. Summary of method

   2.1 Cadmium is chealated with pyrolidine dithiocarbomic and extracted with chloroform

   2.2 The extract is treated with nitric acid to destroy organic matter and is dissolved in hydrochloric acid

   2.3 Total cadmium is then determined by aspirating a portion of the resulting solution following hydrochloric nitric acid digestion and filtration

3 Apparatus

   3.1 Atomic absorption spectrophotometer (for use at 228.8 nm) and associated equipment

4 Reagents

4.1 Bromphenol blue indicator solution

4.2 Cadmium solution, intermediate

4.3 Cadmium solution, standard

4.4 Cadmium solution, stock

4.5 Chloroform

4.6 Concentrated hydrochloric acid

4.7 Hydrochloric acid (1+2)

4.8 Hydrochloric acid (1+49)

4.9 Concentrated nitric acid

4.10 Pyrrolidine dithiocarbamic acid chloroform reagent

4.11 Sodium hydroxide solution

4.12 Air

4.13 Acetylene

5 Preparation of standards

5.1 Bromphenol blue indicator solution (1 g/l)

5.11 Dissolve 0.1 g of bromphenol blue in 100 ml of 50% ethanol or isopropanol

5.2 Cadmium solution stock (1 ml = 1 mg Cd)

5.21 Dissolve 1 g of cadmium metal in a minimum quantity of nitric acid

5.22 Dilute to 1 litre

5.3 Cadmium solution intermediate (1 ml = 50 μg Cd)

5.31 Dilute 50 ml of stock solution (5.2) and 1 ml of nitric to 1 litre with water

5.4 Cadmium solution standard (1 ml = 0.5 μg Cd)

5.41 Dilute 10 ml of Cd intermediate solution (5.3) and 1 ml of nitric acid to 1 litre with water

5.5 Hydrochloric acid (1+2)

5.51 Add 1 volume of HCl to 2 volumes of water

5.6 Hydrochloric acid (1+49)

5.61 Add 1 volume of HCl to 49 volumes of water

5.7 Pyrrolidine dithiocarbamic acid chloroform reagent

5.71 Add 36 ml of pyrrolidine to 1 litre of chloroform

5.72 Cool the solution and add 30 ml of CS_2 in small portions

5.73 Dilute to 2 litres with chloroform

5.8 Sodium hydroxide solution (100 g/l)

5.81 Dissolve 100 g of Sodium hydroxide in water

5.82 Dilute to 1 litre

6 Calibration

Refer sodium

7 Procedure

7.1 Measure a volume of (100 ml maximum) well mixed acidified sample into a 125 ml beaker

7.2 Adjust the volume to 100 ml with water if necessary

7.3 Add 5 ml of HCl

7.4 Heat the sample on a steam bath or hot plate until the volume has been reduced to 15 to 20 ml (do not boil the sample)

7.5 Cool and filter the sample into 250 ml separatory funnel

7.6 Wash the filter paper with water and adjust the volume approximately to 100 ml

7.7 Add 2 drops of bromphenol blue indicator and mix

7.8 Adjust the pH until a blue colour persists by adding sodium hydroxide solution

7.9 Add HCl (1+49) dropwise until the blue colour disappears

7.10 Add 2.5 ml of HCl (1+49) in excess (pH should be 2.3).

7.11 Add 10 ml of pyrrolidine diothiocarbamic acid chloroform reagent and shake for few minutes

7.12 Plug the tip of the separatory funnel with cotton, allow the phases to separate, drain the chloroform layer into a 100 ml beaker

7.13 Repeat the extraction with 10 ml of chloroform and drain the chloroform layer into the same beaker

7.14 Evaporate the solution to near dryness

7.15 Remove beaker from heat and allow residual solvent to evaporate without further

heating

7.16 Add 2 ml nitric acid dropwise and mix well

7.17 Evaporate the solution to near dryness

7.18 Add 2 ml of HCl (1+2) to the beaker, and heat while swirling for 1 minute

7.18 Cool and transfer the solution quantitatively to a 10 ml volumetric flask and adjust the volume with water.

7.19 Aspirate the sample to the flame and record the absorbance

7.20 Determine the concentration of cadmium from the calibration curve

8 Calculation

Cadmium, $\mu g/l = (1000/A) \times B$

where: A = volume of original sample in ml

B = weight of cadmium in the sample in μg

Note: * Pyrrolidine dithiocarbamic acid chloroform reagent is highly toxic

* Carbon disulfide is highly flammable

Reference

1. Annual Book of ASTM Standards. Vol. 11.01 Water (1), 1993.

CALCIUM
mg/l

Atomic Absorption
Instrument parameters
Calcium hollow cathode lamp
Wavelenght 422.7 nm
fuel- acetylene
oxidant- Air
type of flame - reducing

Linear range	0.2 -.7 mg/l using a wavelength of 422.7 nm
Detection limit	0.003 mg/l
Interferences	chemical interferences
Precision and Accuracy	For distilled water samples containing 9 and 36 mg/l calcium, the precision was reported as 3% and 2% respectively with 99% recoveries

1. Background

   1.1 The method can be used for drinking, surface and saline waters and domestic and industrial wastes

2. Apparatus

   2.1 Atomic absorption spectrophotometer and associated equipment

3. Reagents

   3.1 Air

   3.2 Acetylene

   3.3 Metal free water

   3.4 Calcium solution, stock

   3.5 Calcium solution, standard

   3.6 Lanthanum chloride solution

4. Preparation of standards

   4.1 Calcium solution, stock

      4.11 Dissolve 1.250 g of $CaCO_3$ (dried at 180^{0}C for one hour before weighing) with a minimum of deionized water

      4.12 Dilute to 1000 ml with deionized distilled water

4.2 Calcium solution, standard

4.21 Prepare dilutions of the stock solution

4.22 To each 10 ml volume of calibration standard and sample alike add 1.0 ml of the Lanthanum chloride solution

4.3 Lanthanum chloride solution

4.31 Dissolve 29 g of La_2O_3, slowly and in small portions in 250 ml conc.HCl

4.32 Dilute to 500 ml with deionized distilled water

5. Calibration

Refer sodium

6. Procedure

Refer sodium

7. Calculation

Refer sodium

Note: * Phosphate, sulfate and aluminium interferneces can be eliminated by the addition of Lanthanum

* Concentrations of magnesium greater than 1000 mg/L cause low calcium values

* The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences

* The 239.9 nm line may also be used which has a relative sensitivity of 120

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

2. Standard methods for the examination of water and wastewater, 17th Edition, 1989.

3. Annual Book of ASTM standards,vol.11.02,1993

CHROMIUM **Colorimetric**
mg/l

Linear range	0.01 to 0.5 mg/l
Interference	Interferences from permanganate iron in concentrations greater than 1 mg/l may produce a yellow color. Molybdinum, Vanadium, iron and copper may interfere
Precision and Accuracy	For a synthetic water sample containing 110 μg/l chromium, the precision was reported as 47.8% with a relative error of 16.3%

1. Background

   1.1 The procedure measures only hexavalent chromium in natural or treated water intended to be potable

2. Summary of Method

   2.1 All the chromium is converted to the hexavalent state by oxidation with potassium permanganate

   2.2 The hexavalent chromium will be determined colormetrically by reaction with diphenylcarbazide in acid solution

   2.3 Then a red violet color will be produced

3. Apparatus

   3.1 Spectrophotometer for use at 540 nm with a light path of 1 cm or longer

   3.2 Separating funnels, 125 ml

4. Reagents

   4.1 Stock chromium solution

   4.2 Standard chromium solution

   4.3 Nitric acid conc.

   4.4 Sulfuric acid (1+1)

   4.5 Methyl orange indicator solution

   4.6 Hydrogen peroxide (30%)

   4.7 Redistilled water

4.8 Ammonium hydroxide conc.

4.9 Potassium permanganate solution

4.10 Sodium azide solution

4.11 Diphenelcarbazide solution

4.12 Chloroform

4.13 Cupferron solution

4.14 Phosphoric acid conc.

4.15 Sulfuric acid (0.2 N)

5. Preparation of standards

5.1 Stock chromium solution

5.11 Dissolve 141.4 mg $K_2Cr_2O_7$ in distilled water

5.12 Dilute to 1000 ml

5.2 Standard chromium soltuion

5.21 Dilute 10.0 ml stock chromium solution to 100 ml

5.3 Potassium permanganate solution

5.31 Dissolve 4 g $KMnO_4$ in 100 ml distilled water

5.4 Sodium azide solution

5.41 Dissolve 0.5 g of NaN_3 in 100 ml distilled water

5.5 Diphenylcarbazide solution

5.51 Dissolve 250 mg 1,5-diphenylcarbazide in 50 ml acetone

5.52 Store in a brown bottle

5.6 Cupferron solution

5.61 Dissolve 5 g $C_6H_5N(NO)ONH_4$ in 95 ml distilled water

5.7 Sulfuric acid 0.2 N

5.71 Dilute 17 ml 6N H_2SO_4 to 500 ml with distilled water

6. Calibration

6.1 Pipet out measured volumes of standard chromium solutions (5.2), to give standards for 10 to 100 μg Cr, into 250 ml beakers (volumes ranging from 2.00ml to 20.0 ml)

6.2 Depending on pretreatment used for samples (7.1), proceed with subsequent treatment of standards and cupfferon treatment if required

6.3 Develop color as for samples, transfer a portion of each colored solution to 1 cm absorption cell

6.4 Measure absorbance at 540 nm

6.5 Correct absorbance readings of standards by subtracting absorbance of a reagent blank

6.6 Construct a calibration curve by plotting corrected absorbance values against micrograms of chromium in 102 ml final volume

7. Procedure

7.1 Treatment of sample

7.11 If only hexavalent chromium is desired, no treatment is necessary

7.12 If total chromium is desired and there are molybdenum, vanadium, copper or iron present remove them as in 7.2

7.13 If the above metals are not present do the oxidation of trivalent chromium as in 7.3

7.2 Removal of molybdenum, vanadium iron and copper with cupferron

7.21 Pipet a portion of digested sample containing 10 to 100 μg Cr into a 125 ml separating funnel

7.22 Dilute to about 40 ml with distilled water and chill in an ice bath

7.23 Add 5 ml ice-cold cupferron solution, shake well and let stand in ice bath for 1 min.

7.24 Extract in separating funnel with three successive 5 ml portions of $CHCl_3$

7.25 Shake each portion thoroughly with aqueous solution let layers separate, and discard $CHCl_3$ extract

7.26 Transfer extracted aqueous solution to a 125 ml conical flask

7.27 Wash the funnel with a small amount of water to flask and boil for about 5 min. and cool

7.28 Add 5 ml HNO_3 and a minimum of 3 ml H_2SO_4 acid

7.29 Boil samples to the appearance of SO_3 fumes

7.30 Cool and add 5 ml HNO_3, again boil to complete decomposition of organic matter. Cool again and add 25 ml water

7.3 Oxidation of trivalent chromium

7.31 Pipet a portion of digested sample containing 10 to 100 μg Cr into a 125 ml conical flask

7.32 Using methyl orange as indicator, add conc.NH_4OH until solution is just basic to methyl orange

7.33 Add 1+1 H_2SO_4 dropwise until it is acidic plus 1 ml in excess

7.34 Adjust volume to about 40 ml and heat to boiling

7.35 Add 2 drops $KMNO_4$ solution to give a dark red color

7.36 If fading occurs, add $KMNO_4$ dropwise to maintain an excess of about 2 drops

7.37 Boil for about 2 min. Add 1 ml NaN_3 solution and continue boiling gently

7.38 If red color does not fade after boiling for 30 seconds add another 1 ml NaN_3 solution

7.39 Continue boiling for 1 min. after color has faded completely, cool and add 0.25 ml H_3PO_4

7.4 Color development and measurement

7.41 Use 0.2N H_2SO_4 and a pH meter to adjust solution to pH 1.0 $\pm$ 0.3

7.42 Tranfer solution to a 100 ml volumetric flask, dilute to the mark and mix

7.43 Add 2.0 ml diphcylcarbazide solution, mix and let stand for 5 to 10 min. for full color development

7.44 Transfer an appropriate protion to a 1 cm absorption cell and measure its absorbance at 540 nm (use distilled water as reference)

7.45 Correct absorbance of the sample by subtracting absorbance of a blank

7.46 From the corrected absorbance, determine micrograms of chromium present by reference to the calibration curve

8. Calculation

mg Cr/l $\frac{\mu g \text{ Cr(in 102 ml final volume)}}{A \times B} \times 100$

Where, A = volume of original sample in ml

B = volume portion from 100 ml digested sample in ml

Note: * Potential interferences from permanganate is eliminated by prior reduction with azide

Reference

1. Standard method for the examination of water and wastewater, 17th edition, 1989

COBALT
μg/l

Chelation Extraction-Atomic Absroption
Instrument parameters
Cobalt hollow cathode lamp
Wavelength 240.7 nm
Fuel-acetylene
Oxidant-air
Type of flame

Linear range	10 - 1000 μg/l
Detection limit	0.03 mg/l
Interferences	Nitrate interferes at 1 mg/l by suppressing the absorption of the cobalt High concentrations of sodium, potassium, magnesium, nickel, lead, copper, zinc, cadmium, chromium and sulfate may interfere
Precision and Accuracy	For surface water samples containing 100 and 700 μg/l cobalt, the precision was reported as 12% and 8% respectively The accuracy was reported as +4.0% and +1.1% for the surface water samples containing 100 and 700 μg/l of cobalt respectively

1. Background

   1.1 Method is applicable to surface and groundwater, domestic and industrial wastewater

2. Summary of method

   2.1 Cobalt is chealated with pyrolidine dithiocarbomic and extracted with chloroform

   2.2 The extract is treated with nitric acid to destroy organic matter and is dissolved in hydrochloric acid

   2.3 Total cobalt is then determined by aspirating a portion of the resulting solution following hydrochloric nitric acid digestion and filtration

3 Apparatus

   3.1 Atomic absorption spectrophotometer (for use at 240.7 nm) and associated equipment

4 Reagents

4.1 Bromphenol blue indicator solution

4.2 Cobalt solution, intermediate

4.3 Cobalt solution, standard

4.4 Cobalt solution, stock

4.5 Chloroform

4.6 Concentrated hydrochloric acid

4.7 Hydrochloric acid (1+2)

4.8 Hydrochloric acid (1+49)

4.9 Concentrated nitric acid

4.10 Pyrrolidine dithiocarbamic acid chloroform reagent

4.11 Sodium hydroxide solution

4.12 Air

4.13 Acetylene

5 Preparation of standards

5.1 Bromphenol blue indicator solution (1 g/l)

5.11 Dissolve 0.1 g of bromphenol blue in 100 ml of 50% ethanol or isopropanol

5.2 Cobalt solution stock (1 ml = 1 mg Co)

5.21 Dissolve 4.0372 g of cobaltous chloride in reagent water

5.22 Dilute to 1 litre

5.3 Cobalt solution intermediate (1 ml = 0.1 mg Co)

5.31 Dilute 100 ml of the stock solution (5.2) to 1 litre with water

5.4 Cobalt solution standard (1 ml = 1 μg Co)

5.41 Dilute 10 ml of Co intermediate solution (5.3) and 1 ml of nitric acid to 1 litre with water

5.5 Hydrochloric acid (1+2)

5.51 Add 1 volume of HCl to 2 volumes of water

5.6 Hydrochloric acid (1+49)

5.61 Add 1 volume of HCl to 49 volumes of water

5.7 Pyrrolidine dithiocarbamic acid chloroform reagent

5.71 Add 36 ml of pyrrolidine to 1 litre of chloroform

5.72 Cool the solution and add 30 ml of CS_2 in small portions

5.73 Dilute to 2 litres with chloroform

5.8 Sodium hydroxide solution (100 g/l)

5.81 Dissolve 100 g of Sodium hydroxide in water

5.82 Dilute to 1 litre

6 Calibration

Refer sodium

7 Procedure

7.1 Measure a volume of (100 ml maximum) well mixed acidified sample into a 125 ml beaker

7.2 Adjust the volume to 100 ml with water if necessary

7.3 Add 5 ml of HCl

7.4 Heat the sample on a steam bath or hot plate until the volume has been reduced to 15 to 20 ml (do not boil the sample)

7.5 Cool and filter the sample into 250 ml separatory funnel

7.6 Wash the filter paper with water and adjust the volume approximately to 100 ml

7.7 Add 2 drops of bromphenol blue indicator and mix

7.8 Adjust the pH until a blue colour persists by adding sodium hydroxide solution

7.9 Add HCl (1+49) dropwise until the blue colour disappears

7.10 Add 2.5 ml of HCl (1+49) in excess

7.11 Add 10 ml of pyrrolidine diothiocarbamic acid chloroform reagent and shake for few minutes

7.12 Plug the tip of the separatory funnel with cotton, allow the phases to separate, drain the chloroform layer into a 100 ml beaker

7.13 Repeat the extraction with 10 ml of chloroform and drain the chloroform layer into the same beaker

7.14 Evaporate the solution to near dryness

7.15 Remove beaker from heat and allow residual solvent to evaporate without further heating

7.16 Add 2 ml nitric acid dropwise and mix well

7.17 Evaporate the solution to near dryness

7.18 Add 2 ml of HCl (1+2) to the beaker, and heat while swirling for 1 minute

7.18 Cool and transfer the solution quantitatively to a 10 ml volumetric flask and adjust the volume with water

7.19 Aspirate the sample to the flame and record the absorbance

7.20 Determine the concentration of cadmium from the calibration curve

8 Calculation

Cobalt, $\mu g/l = (1000/A) \times B$

where:

A = volume of original sample in ml

B = weight of cobalt in the sample in μg

Note: * Interference by nitrate can be eliminated by adding ammonium chloride to blanks, standards and samples

Reference

1. Annual Book of ASTM Standards. Vol. 11.01 Water (1), 1993.

COPPER
μg/l

Chelation Extraction-Atomic Absroption
Instrument parameters
Copper hollow cathode lamp
Wavelength 324.7 nm
Fuel-acetylene
Oxidant-air
Type of flame

Linear range	2 - 500 μg/l
Detection limit	0.01 mg/l
Interferences	High concentrations of metals may interfere
Precision and Accuracy	For surface water samples containing 9 and 36.3 μg/l copper, the precision was reported as 77% and 25% respectively The accuracy was reported as +4.0% and +4.3% for the surface water samples containing 9 and 36.3 μg/l of copper respectively

1. Background

   1.1 Method is applicable to surface and groundwater, domestic and industrial wastewater

2. Summary of method

   2.1 Copper is chealated with pyrolidine dithiocarbomic and extracted with chloroform

   2.2 The extract is treated with nitric acid to destroy organic matter and is dissolved in hydrochloric acid

   2.3 Total copper is then determined by aspirating a portion of the resulting solution following hydrochloric nitric acid digestion and filtration

3 Apparatus

   3.1 Atomic absorption spectrophotometer (for use at 324.7 nm) and associated equipment

4 Reagents

   4.1 Bromphenol blue indicator solution

   4.2 Copper solution, intermediate

   4.3 Copper solution, standard

4.4 Copper solution, stock

4.5 Chloroform

4.6 Concentrated hydrochloric acid

4.7 Hydrochloric acid (1+2)

4.8 Hydrochloric acid (1+49)

4.9 Concentrated nitric acid

4.10 Pyrrolidine dithiocarbamac acid chloroform reagent

4.11 Sodium hydroxide solution

4.12 Air

4.13 Acetylene

5 Preparation of standards

5.1 Bromphenol blue indicator solution (1 g/l)

5.11 Dissolve 0.1 g of bromphenol blue in 100 ml of 50% ethanol or isopropanol

5.2 Copper solution stock (1 ml = 1 mg Cu)

5.21 Dissolve 1 g of electrolytic copper contained in a 250 ml beaker in a mixture of 15 ml nitric acid and 15 ml water

5.22 Slowly add 4 ml of sulfuric (1+1) and heat until SO_3 fumes evolve

5.23 Cool, wash down the beaker with water and dilute to 1 litre

5.3 Copper solution intermediate (1 ml = 10 μg Cu)

5.31 Dilute 10 ml of stock solution (5.2) and 1 ml of nitric to 1 litre with water

5.4 Copper solution standard (1 ml = 1 μg Cu)

5.41 Dilute 10 ml of Cu intermediate solution (5.3) to 100 ml with water

5.5 Hydrochloric acid (1+2)

5.51 Add 1 volume of HCl to 2 volumes of water

5.6 Hydrochloric acid (1+49)

5.61 Add 1 volume of HCl to 49 volumes of water

5.7 Pyrrolidine dithiocarbamic acid chloroform reagent

5.71 Add 36 ml of pyrrolidine to 1 litre of chloroform

5.72 Cool the solution and add 30 ml of CS_2 in small portions

5.73 Dilute to 2 litres with chloroform

5.8 Sodium hydroxide solution (100 g/l)

5.81 Dissolve 100 g of Sodium hydroxide in water

5.82 Dilute to 1 litre

6 Calibration

Refer sodium

7. Procedure

7.1 Measure a volume of (100 ml maximum) well mixed acidified sample into a 125 ml beaker

7.2 Adjust the volume to 100 ml with water if necessary

7.3 Add 5 ml of HCl

7.4 Heat the sample on a steam bath or hot plate until the volume has been reduced to 15 to 20 ml (do not boil the sample)

7.5 Cool and filter the sample into 250 ml separatory funnel

7.6 Wash the filter paper with water and adjust the volume approximately to 100 ml

7.7 Add 2 drops of bromphenol blue indicator and mix

7.8 Adjust the pH until a blue colour persists by adding sodium hydroxide solution

7.9 Add HCl (1+49) dropwise until the blue colour disappears

7.10 Add 2.5 ml of HCl (1+49) in excess

7.11 Add 10 ml of pyrrolidine diothiocarbamic acid chloroform reagent and shake for few minutes

7.12 Plug the tip of the separatory funnel with cotton, allow the phases to separate, drain the chloroform layer into a 100 ml beaker

7.13 Repeat the extraction with 10 ml of chloroform and drain the chloroform layer into the same beaker

7.14 Evaporate the solution to near dryness

7.15 Remove beaker from heat and allow residual solvent to evaporate without further heating

7.16 Add 2 ml nitric acid dropwise and mix well

7.17 Evaporate the solution to near dryness

7.18 Add 2 ml of HCl (1+2) to the beaker, and heat while swirling for 1 minute

7.18 Cool and transfer the solution quantitatively to a 10 ml volumetric flask and adjust the volume with water

7.19 Aspirate the sample to the flame and record the absorbance

7.20 Determine the concentration of cadmium from the calibration curve

8 Calculation

Copper, $\mu g/l = B/A$

where:

A = volume of original sample in litre

B = weight of copper in the sample in μg

Note: * Pyrrolidine dithiocarbamic acid chloroform reagent is highly toxic

* Carbon disulfide is highly flammable

Reference

1. Annual Book of ASTM Standards. Vol. 11.01 Water (1), 1993.

IRON
mg/l

Atomic Absorption
Instrumental parameters
Iron hollow cathode lamp
Wavelength - 248.3 nm
Fuel - acetylene
Oxident - air
type of flame-oxidizing

Linear range	0.3-5 mg/l
Detection limit	0.02 mg/l
Interference	chemical interferences
Precision and Accuracy	For a synthetic water sample containing 435 and 855 μg/l iron, the precision was reported as 42% and 20% with a relative error of -0.7% and 1.8% respectively

1. Background

   1.1 The method can be used for drinking, surface and saline waters and domestic and industrial wastes

2. Summary of method

   Refer sodium

3. Apparatus

   3.1 Atomic absorption spectrophotometer and associated equipments

4. Reagent

   4.1 Air

   4.2 Acetylene

   4.3 Metal free water

   4.4 Iron solution stock

   4.5 Iron solution standard

5. Preparation

   5.1 Iron solution stock

   5.11 Weigh 1.000 g of pure iron wire

   5.12 Dissolve in 5 ml redistilled HNO_3 warming if necessary

5.13 When dissolving is complete, dilute up to 1 liter with dionized distilled water

5.2 Iron solution standard

5.21 Prepare dilutions of the stock solution

6. Calibration

Refer sodium

7. Procedure

Refer sodium

8. Calculation

Refer sodium

Note: * The following lines may also be used 248.8 nm relative sensitivity

2271.9 nm relative sensitivity 4

302.1 nm relative sensitivity 5

252.7 nm relative sensitivity 6

372.0 nm relative sensitivity 10

Reference

1. EPA/600/4-79/020 Method for Chemical analysis of water and wastes

2. Standard method for the examination of water and wastewater, 17th edition, 1989

LEAD $\mu g/l$	**Chelation Extraction-Atomic Absroption** Instrument parameters Lead hollow cathode lamp Wavelength 283.3 nm Fuel-acetylene Oxidant-air Type of flame

Linear range	100 - 1000 $\mu g/l$
Detection limit	0.05 mg/l
Interferences	High concentrations of calcium may interfere
Precision and Accuracy	For reagent water samples containing 100 and 800 $\mu g/l$ lead, the precision was reported as 18% and 16% respectively The accuracy was reported as -13.9% and -15.8% for the reagent water samples containing 100 and 800 $\mu g/l$ of lead respectively

1. Background

   1.1 Method is applicable to surface and groundwater, domestic and industrial wastewater

2. Summary of method

   2.1 Lead is chealated with pyrolidine dithiocarbomic and extracted with chloroform

   2.2 The extract is treated with nitric acid to destroy organic matter and is dissolved in hydrochloric acid

   2.3 Total lead is then determined by aspirating a portion of the resulting solution following hydrochloric nitric acid digestion and filtration

3 Apparatus

   3.1 Atomic absorption spectrophotometer (for use at 283.3 nm) and associated equipment

4 Reagents

   4.1 Bromphenol blue indicator solution

   4.2 Lead solution, intermediate

   4.3 Lead solution, standard

4.4 Lead solution, stock

4.5 Chloroform

4.6 Concentrated hydrochloric acid

4.7 Hydrochloric acid (1+2)

4.8 Hydrochloric acid (1+49)

4.9 Concentrated nitric acid

4.10 Pyrrolidine dithiocarbamac acid chloroform reagent

4.11 Sodium hydroxide solution

4.12 Air

4.13 Acetylene

5 Preparation of standards

5.1 Bromphenol blue indicator solution (1 g/l)

5.11 Dissolve 0.1 g of bromphenol blue in 100 ml of 50% ethanol or isopropanol

5.2 Lead solution stock (1 ml = 200 μg Pb)

5.21 Dissolve 0.3198 g of lead nitrate in water containing 1 ml of nitric acid

5.22 Dilute to 1 litre

5.3 Lead solution intermediate (1 ml = 2 μg Pb)

5.31 Dilute 10 ml of stock solution (5.2) and 1 ml of nitric to 1 litre with water

5.4 Lead solution standard (1 ml = 0.2 μg Pb)

5.41 Dilute 10 ml of lead intermediate solution (5.3) and 1 ml of nitric acid to 100 ml with water

5.5 Hydrochloric acid (1+2)

5.51 Add 1 volume of HCl to 2 volumes of water

5.6 Hydrochloric acid (1+49)

5.61 Add 1 volume of HCl to 49 volumes of water

5.7 Pyrrolidine dithiocarbamic acid chloroform reagent

5.71 Add 36 ml of pyrrolidine to 1 litre of chloroform

5.72 Cool the solution and add 30 ml of CS_2 in small portions

5.73 Dilute to 2 litres with chloroform

5.8 Sodium hydroxide solution (100 g/l)

5.81 Dissolve 100 g of Sodium hydroxide in water

5.82 Dilute to 1 litre

6 Calibration

Refer sodium

7 Procedure

7.1 Measure a volume of (100 ml maximum) well mixed acidified sample into a 125 ml beaker

7.2 Adjust the volume to 100 ml with water if necessary

7.3 Add 5 ml of HCl

7.4 Heat the sample on a steam bath or hot plate until the volume has been reduced to 15 to 20 ml (do not boil the sample)

7.5 Cool and filter the sample into 250 ml separatory funnel

7.6 Wash the filter paper with water and adjust the volume approximately to 100 ml

7.7 Add 2 drops of bromphenol blue indicator and mix

7.8 Adjust the pH until a blue colour persists by adding sodium hydroxide solution

7.9 Add HCl (1+49) dropwise until the blue colour disappears

7.10 Add 2.5 ml of HCl (1+49) in excess

7.11 Add 10 ml of pyrrolidine diothiocarbamic acid chloroform reagent and shake for few minutes

7.12 Plug the tip of the separatory funnel with cotton, allow the phases to separate, drain the chloroform layer into a 100 ml beaker

7.13 Repeat the extraction with 10 ml of chloroform and drain the chloroform layer into the same beaker

7.14 Evaporate the solution to near dryness

7.15 Remove beaker from heat and allow residual solvent to evaporate without further heating

7.16 Add 2 ml nitric acid dropwise and mix well

7.17 Evaporate the solution to near dryness

7.18 Add 2 ml of HCl (1+2) to the beaker, and heat while swirling for 1 minute

7.18 Cool and transfer the solution quantitatively to a 10 ml volumetric flask and adjust the volume with water

7.19 Aspirate the sample to the flame and record the absorbance

7.20 Determine the concentration of cadmium from the calibration curve

8 Calculation

Lead, $\mu g/l = (1000/A) \times B$

where:

A = volume of original sample in ml

B = weight of lead in the sample in μg

Note: * Pyrrolidine dithiocarbamic acid chloroform reagent and lead salts are highly toxic

* Carbon disulfide is highly flammable

Reference

1. Annual Book of ASTM Standards. Vol. 11.01 Water (1), 1993.

MAGNESIUM
mg/l

Atomic Absorption
Instrument parameters
Magnesium hollow cathode lamp
Wavelenght 285.2 nm
Fuel- acetylene
Oxidant- Air
Type of flame - oxidizing

Linear range	0.02-0.5 mg/l using wavelength of 285.2 nm
Detection limit	0.0005 mg/l
Interference	Chemical interference
Precision and Accuracy	In a single laboratory, for distilled water samples containing 2.1 and 8.2 mg/l magnesium, the precision was reported as 5% and 2% respectively with a 100% recovery

1. Background

   Refer sodium

2. Apparatus

   Refer sodium

3. Reagents

   3.1 Air

   3.2 Acetylene

   3.3 Metal free water

   3.4 Magnesium solution stock

   3.5 Magnesium solution standard

   3.6 Lanthanum chloride solution

4. Preparation of standards

   4.1 Metal free water

   Refer sodium

   4.2 Magnesium solution, stock

   4.21 Dissolve 0.829 g of magnesium oxide in 10 ml of redistilled HNO_3

   4.22 Dilute to 1 liter with deionized distilled water

4.3 Magnesium solution standard

4.31 Prepare dilutions of the stock solution

4.32 To each 10 ml volume of sample add 1.0 ml of the lanthanum chloride solution

4.4 Lanthanum chloride solution

Refer sodium

5. Calibration

Refer sodium

6. Procedure

Refer sodium

7. Calculation

Refer sodium

Note: * The interferences caused by aluminium at concentrations greater than 2 mg/L is masked by addition of lanthanum

* The line 202.5 nm may also be used with relative sensitivity of 25

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

2. Standard methods for the examination of water and wastewater, 17th Edition, 1989.

MANGANESE
mg/l

Atomic Absorption
Instrumental parameters
Manganese hollow cathode lamp
Wavelength - 279.5 nm
Fuel - acetylene
Oxident - air
type of flame-oxidizing

Linear range	0.1-3 mg/l
Detection limit	0.01 mg/l
Interferences	Chemical interferences
Percision and Accuracy	For synthetic water samples containing 104 and 432 μg/l manganese, the precision was reported as 30% and 16% respectively The accuracy was reported as -2.1% and +1.5% respectively for the above two samples

1. Background

   1.1 The method is applicable for drinking, surface and saline waters and domestic and industrial wastes

2. Summary of Method

   Refer sodium

3. Apparatus

   3.1 Atomic absorption spectrophotometer and associated equipments

4. Reagents

   4.1 Air

   4.2 Acetylene

   4.3 metal free water

   4.4 Manganese solution stock

   4.5 Manganese solution standard

5. Preparation of Standards

   5.1 Manganese solution stock

5.11 Weigh 1.000 g of manganese metal

5.12 Dissolve in 10 ml of redistilled HNO_3

5.13 When dissolving is complete, dilute to 1 liter with 1% HCl

5.2 Manganese solution standard

5.21 Prepare dilutions of the stock solution

6. Calibration

Refer sodium

7. Procedure

Refer sodium

8. Calibration

Refer sodium

Note: * The line 403.1 nm, at relative sensitivity of 10 may also be used

Reference

1. EPA/600/4-79/020 Method for Chemical analysis of water and wastes

2. Standard method for the examination of water and wastewater, 17th edition, 1989

NICKEL μg/l	**Chelation Extraction-Atomic Absroption** Instrument parameters Nickel hollow cathode lamp Wavelength 232.0 nm Fuel-acetylene Oxidant-air
Linear range	10 - 1000 μg/l
Detection limit	0.02 mg/l
Interferences	High concentrations of other metals and sulfate chloroide and nitrate may interfere
Precision and Accuracy	For natural water samples containing 399.4 and 794.4 μg/l nickel, the precision was reported as 9% and 17% respectively The accuracy was reported as -0.2% and -11.7% respectively for the above two samples

1. Background

   1.1 Method is applicable to surface and groundwater, domestic and industrial wastewater

2. Summary of method

   2.1 Nickel is chealated with pyrolidine dithiocarbomic and extracted with chloroform

   2.2 The extract is treated with nitric acid to destroy organic matter and is dissolved in hydrochloric acid

   2.3 Total nickel is then determined by aspirating a portion of the resulting solution following hydrochloric nitric acid digestion and filtration

3 Apparatus

   3.1 Atomic absorption spectrophotometer (for use at 232.0 nm) and associated equipment

4 Reagents

   4.1 Bromphenol blue indicator solution

   4.2 Nickel solution, intermediate

4.3 Nickel solution, standard

4.4 Nickel solution, stock

4.5 Chloroform

4.6 Concentrated hydrochloric acid

4.7 Hydrochloric acid (1+2)

4.8 Hydrochloric acid (1+49)

4.9 Concentrated nitric acid

4.10 Pyrrolidine dithiocarbamac acid chloroform reagent

4.11 Sodium hydroxide solution

4.12 Air

4.13 Acetylene

5 Preparation of standards

5.1 Bromphenol blue indicator solution (1 g/l)

5.11 Dissolve 0.1 g of bromphenol blue in 100 ml of 50% ethanol or isopropanol

5.2 Nickel solution stock (1 ml = 200 μg Ni)

5.21 Dissolve 0.9906 g of nickelous nitrate in water containing 1 ml of nitric acid

5.22 Dilute to 1 litre

5.3 Nickel solution standard (1 ml = 2 μg Ni)

5.31 Dilute 10 ml of Ni stock solution (5.2) and 1 ml of nitric acid to 1 litre with water.

5.4 Hydrochloric acid (1+2)

5.41 Add 1 volume of HCl to 2 volumes of water

5.5 Hydrochloric acid (1+49)

5.51 Add 1 volume of HCl to 49 volumes of water

5.6 Pyrrolidine dithiocarbamic acid chloroform reagent

5.61 Add 36 ml of pyrrolidine to 1 litre of chloroform

5.62 Cool the solution and add 30 ml of CS_2 in small portions

5.63 Dilute to 2 litres with chloroform

5.7 Sodium hydroxide solution (100 g/l)

5.71 Dissolve 100 g of Sodium hydroxide in water

5.72 Dilute to 1 litre

6 Calibration

Refer sodium

7 Procedure

7.1 Measure a volume of (100 ml maximum) well mixed acidified sample into a 125 ml beaker

7.2 Adjust the volume to 100 ml with water if necessary

7.3 Add 5 ml of HCl

7.4 Heat the sample on a steam bath or hot plate until the volume has been reduced to 15 to 20 ml (do not boil the sample)

7.5 Cool and filter the sample into 250 ml separatory funnel

7.6 Wash the filter paper with water and adjust the volume approximately to 100 ml

7.7 Add 2 drops of bromphenol blue indicator and mix

7.8 Adjust the pH until a blue colour persists by adding sodium hydroxide solution

7.9 Add HCl (1+49) dropwise until the blue colour disappears

7.10 Add 2.5 ml of HCl (1+49) in excess

7.11 Add 10 ml of pyrrolidine diothiocarbamic acid chloroform reagent and shake for few minutes

7.12 Plug the tip of the separatory funnel with cotton, allow the phases to separate, drain the chloroform layer into a 100 ml beaker

7.13 Repeat the extraction with 10 ml of chloroform and drain the chloroform layer into the same beaker

7.14 Evaporate the solution to near dryness

7.15 Remove beaker from heat and allow residual solvent to evaporate without further heating

7.16 Add 2 ml nitric acid dropwise and mix well

7.17 Evaporate the solution to near dryness

7.18 Add 2 ml of HCl (1+2) to the beaker, and heat while swirling for 1 minute

7.18 Cool and transfer the solution quantitatively to a 10 ml volumetric flask and adjust the volume with water

7.19 Aspirate the sample to the flame and record the absorbance

7.20 Determine the concentration of cadmium from the calibration curve

8 Calculation

Nickel, $\mu g/l = (1000/A) \times B$

where:

A = volume of original sample in ml

B = weight of nickel in the sample in μg

Note: * Pyrrolidine dithiocarbamic acid chloroform reagent is highly toxic

* Carbon disulfide is highly flammable

Reference

1. Annual Book of ASTM Standards. Vol. 11.01 Water (1), 1993.

POTASSIUM
mg/l

Atomic Absorption
Instrument parameters
Potassium hollow cathode lamp
Wavelenght 766.5 nm
Fuel- acetylene
Oxidant- Air
Type of flame - slightly oxidizing

Linear range	0.1-2 mg/l using wavelenght of 766.5 nm
Detection limit	0.005 mg/l
Interferences	Chemical interferences
Precision and Accuracy	In a single laboratory, for distilled water samples containing 1.6 and 6.3 mg/l potassium, the precision was reported as 13% and 8% with 103% and 102% recoveries respectively

1. Background

   1.1 The method is applicable for drinking, surface and saline waters and domestic and industrial wastes

2. Apparatus

   2.1 Atomic absorption spectrophotometer and associated equipment

3. Reagents

   3.1 Air

   3.2 Acetylene

   3.3 Metal free water

   3.4 Potassium solution, stock

   3.5 Potassium solution, standard

4. Preparation of standards

   4.1 Metal free water

   refer sodium

   4.2 Potassium solution, stock

   4.21 Dissolve 0.1907 g of KCl, dried at 110°C in deionized distilled water

   4.22 Make up to 1 liter

4.3 Potassium solution standard

4.31 Prepare dilutions of the stock solution

5. Calibration

Refer sodium

6. Procedure

Refer sodium

7. Calculation

Refer sodium

Note: * Any enhancement due to sodium can be stablized by adding excess sodium (1000 μg/ml) to both sample and standard solutions

* The 404.4 nm line may also be used. This line has a relative sensitivity of 500

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes
2. Standard methods for the examination of water and wastewater, 17th Edition, 1989.
3. Annual Book of ASTM standards,vol.11.02,1993.

SODIUM
mg/l

Atomic absorption
Instrument parameters
Sodium hollow cathode lamp
Wavelenght 589.6 nm
Fuel- Acetylene
Oxidant- Air
Type of flame - Oxidizing

Linear range	0.03 - 1 mg/l
Detection limit	0.002 mg/l
Interference	Chemical interference
Percision and Accuracy	In a single laboratory, for distilled water samples containing 8.2 and 52 mg/l sodium, the precision was reported as 1% and 1.5% with 102% and 100% recoveries respectively

1. Background

   1.1 The method is applicable for drinking, surface and saline waters and domestic and industrial wastes

2. Summary of method

   2.1 A sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp (cathode is made out of the element to be determined) is directed through the flame into a monochromator and onto a detector which measures the light absorbed

3. Apparatus

   3.1 Atomic absorption spectrophotometer and associated equipemnt

4. Reagents

   4.1 Air

   4.2 Acetylene

   4.3 Metal-free water

   4.4 Sodium solution, Stock

   4.5 Sodium solution, standard

5. Preparation of standards

5.1 Metal free water

5.11 Deionize tap water or use one of the following processes, depending on the metal concentration in the sample.

Single distillation, redistillation or sub-boiling

5.2 Sodium solution, stock

5.21 Dissolve 2.542 g sodium chloride (NaCl), dried at 140°C in water

5.22 Make up to 1000 ml

5.3 Sodium solution standard

5.31 Prepare dilutions of the stock solution

6. Calibration

6.1 Aspirate a blank consisting of deionized water or an acid solution containing the same concentration of acid in standards

6.2 Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum response

6.3 Aspirate the blank again and rezero the instrument

6.4 Aspirate a standard near the middle of the linear range

6.5 Record absorbance of the standard

6.6 Refer to the data on subsequent determinations of the same element to check consistency of instrument setup

7. Procedure

7.1 For the analysis procedure see Chapter 1.7.

8. Calculation

$$\text{concentration, mg/l} = \frac{V_1 (A_s \times C_{std})}{V_2 (A_{std} - A_s)}$$

where,

V_1 : Volume of the dilute sample, ml

V_2 : Volume of the original sample, ml

A_s : Absorbance of dilute sample

A_{std} : Absorbance of one of the standard additions

C_{std} = Concentration of the same standard addition as A_{std}^2 in mg/l

Since there are two standard additions, calculate for each, and average the two

Note: * Low temperature flames increase sensitivity by reducing the extent of ionization of the metal

* Ionization may also be controlled by adding potassium (1000 mg/l) to both standards and samples

* Chemical interferences may be eliminated by adding specific elements or compounds to the sample solution

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes
2. Standard methods for the examination of water and wastewater, 17th Edition, 1989.
3. Annual Book of ASTM standards, Vol.11 02,1993.

ZINC
μg/l

Chelation Extraction-Atomic Absroption
Instrument parameters
Zinc hollow cathode lamp
Wavelength 213.8 nm
Fuel-acetylene
Oxidant-air
Type of flame

Linear range	1 - 200 μg/l
Detection limit	0.005 mg/l
Interferences	High concentrations of other metals and sulfate chloroide and nitrate may interfere
Precision and Accuracy	For reagent water samples containing 10 and 170 μg/l zinc, the precision was reported as 160% and 14% respectively The accuracy was reported as +7.5% and +8.1% for the reagent water samples containing 172 and 75.6 μg/l of zinc respectively

1. Background

   1.1 Method is applicable to surface and groundwater, domestic and industrial wastewater

2. Summary of method

   2.1 Zinc is chealated with pyrrolidine dithiocarbomic and extracted with chloroform

   2.2 The extract is treated with nitric acid to destroy organic matter and is dissolved in hydrochloric acid

   2.3 Total zinc is then determined by aspirating a portion of the resulting solution following hydrochloric nitric acid digestion and filtration

3 Apparatus

   3.1 Atomic absorption spectrophotometer (for use at 213.8 nm) and associated equipment

4 Reagents

   4.1 Bromphenol blue indicator solution

   4.2 Zinc solution, intermediate

4.3 Zinc solution, standard

4.4 Zinc solution, stock

4.5 Chloroform

4.6 Concentrated hydrochloric acid

4.7 Hydrochloric acid (1+2)

4.8 Hydrochloric acid (1+49)

4.9 Concentrated nitric acid

4.10 Pyrrolidine dithiocarbamic acid chloroform reagent

4.11 Sodium hydroxide solution

4.12 Air

4.13 Acetylene

5 Preparation of standards

5.1 Bromphenol blue indicator solution (1 g/l)

5.11 Dissolve 0.1 g of bromphenol blue in 100 ml of 50% ethanol or isopropanol

5.2 Zinc solution stock (1 ml = 1 mg Zn)

5.21 Dissolve 1.245 g of zinc oxide in a mixture of 10 ml of nitric acid and 10 ml of water

5.22 Dilute to 1 litre

5.3 Zinc solution intermediate (1 ml = 0.1 mg Zn)

5.31 Dilute 100 ml of stock solution (5.2) and 1 ml of nitric to 1 litre with water

5.4 Zinc solution standard (1 ml = 1 μg Zn)

5.41 Dilute 10 ml of zinc intermediate solution (5.3) and 1 ml of nitric acid to 1 litre with water

5.5 Hydrochloric acid (1+2)

5.51 Add 1 volume of HCl to 2 volumes of water

5.6 Hydrochloric acid (1+49)

5.61 Add 1 volume of HCl to 49 volumes of water

5.7 Pyrrolidine dithiocarbamic acid chloroform reagent

5.71 Add 36 ml of pyrrolidine to 1 litre of chloroform

5.72 Cool the solution and add 30 ml of CS_2 in small portions

5.73 Dilute to 2 litres with chloroform

5.8 Sodium hydroxide solution (100 g/l)

5.81 Dissolve 100 g of Sodium hydroxide in water

5.82 Dilute to 1 litre

6 Calibration

Refer sodium

7 Procedure

7.1 Measure a volume of (100 ml maximum) well mixed acidified sample into a 125 ml beaker

7.2 Adjust the volume to 100 ml with water if necessary

7.3 Add 5 ml of HCl

7.4 Heat the sample on a steam bath or hot plate until the volume has been reduced to 15 to 20 ml (do not boil the sample)

7.5 Cool and filter the sample into 250 ml separatory funnel

7.6 Wash the filter paper with water and adjust the volume approximately to 100 ml

7.7 Add 2 drops of bromphenol blue indicator and mix

7.8 Adjust the pH until a blue colour persists by adding sodium hydroxide solution

7.9 Add HCl (1+49) dropwise until the blue colour disappears

7.10 Add 2.5 ml of HCl (1+49) in excess

7.11 Add 10 ml of pyrrolidine diothiocarbamic acid chloroform reagent and shake for few minutes

7.12 Plug the tip of the separatory funnel with cotton, allow the phases to separate, drain the chloroform layer into a 100 ml beaker

7.13 Repeat the extraction with 10 ml of chloroform and drain the chloroform layer into the same beaker

7.14 Evaporate the solution to near dryness

7.15 Remove beaker from heat and allow residual solvent to evaporate without further heating

7.16 Add 2 ml nitric acid dropwise and mix well

7.17 Evaporate the solution to near dryness

7.18 Add 2 ml of HCl (1+2) to the beaker, and heat while swirling for 1 minute

7.18 Cool and transfer the solution quantitatively to a 10 ml volumetric flask and adjust the volume with water

7.19 Aspirate the sample to the flame and record the absorbance

7.20 Determine the concentration of cadmium from the calibration curve

8 Calculation

Zinc, $\mu g/l$ = $(1000/A) \times B$

where:

A = volume of original sample in ml

B = weight of zinc in the sample in μg

Note: * Pyrrolidine dithiocarbamic acid chloroform reagent is highly toxic

* Carbon disulfide is highly flammable

Reference

1. Annual Book of ASTM Standards. Vol. 11.01 Water (1), 1993.

5.4 Non-metalics

ALKALINITY **Titrimetric**
mg/l,$CaCO_3$

Linear range	All concentration ranges
Interferences	Salts of weak organic and inorganic acids may interfere Oil and grease may coat the electrodes
Precision and accuracy	In a single laboratory (EMSL) using surface water samples at an average concentration of 122 mg $CaCO^3$/l, the precision was reported as 2.5%

1. Background

   1.1 The method is applicable to drinking, surface and saline waters, domestic and industrial wastes

2. Summary of method

   2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5

   2.2 The sample must not be filtered, diluted, concentrated or altered in anyway.

3. Apparatus

   3.1 pH meter (can be read to 0.05 pH units)

   3.2 Appropriate sized vessel

   3.3 Magnetic stirrer

   3.4 Pipets, flasks and other standard glassware

   3.5 Burets (50, 25 and 10 ml)

4. Reagents

   4.1 Sodium carbonate solution (0.05N)

   4.2 Standard acid (HCl or H_2SO_4) 0.1 N

   4.3 Standard acid (HCl or H_2SO_4) 0.02 N

5. Preparation of standards

   5.1 Sodium carbonate solution (0.05 N)

5.11 Place 2.5±0.2 g sodium carbonate (dried at 250°C for 4 hours and cooled in a desiccator) in a 1 liter volumetric flask

5.12 Dilute to the mark with water

5.2 Standard acid (0.1 N)

5.21 Dilute 3.0 ml concentrated sulfuric or 8.3 ml concentrated hydrochloric to 1 liter with distilled water

5.22 Standardize with 0.05 N sodium carbonate solution

5.3 Standard acid (0.02 N)

5.31 Dilute 200 ml of 0.1 N standard acid to 1 liter with distilled water

5.32 Standardize with 0.05 N sodium carbonate solution

6. Procedure

6.1 Standardization of acid

6.11 Take 40 ml of 0.05 N sodium carbonate solution with about 60 ml distilled water

6.12 Titrate with the acid potentiometrically to pH of about 5

6.13 Rinse the electrode into the beaker

6.14 Cover with a watch glass and boil the solution gently for 3 to 5 minutes

6.15 Cool to room temperature

6.16 Rinse cover glass into beaker

6.17 Continue titration to the pH inflection point

6.18 Calculate normality

6.2 Sample size

6.21 Use a sufficiently large volume of titrant (>20 ml in a 50 ml buret)

6.22 For < 1000 mg $CaCO_3$/l, use 0.02 N titrant

6.23 For > 1000 mg $CaCO_3$/l, use 0.1 N titrant

6.3 Potentiometric titration

6.31 Place sample in flask by pipetting with pipet tip near bottom of flask (use a measured volume of sample sufficient enough to cover the sensing elements of the electrode)

6.32 Measure pH of the sample

6.33 Add standard acid while stirring

6.34 Titre to pH of 4.5

6.35 Record volume of the titrant

6.4 Potentiometric titration of low alkalinity

6.41 For alkalinity of <20 mg/l, titrate 100 to 200 ml as in 6.32 using a 10 ml microburette and 0.02 N acid solution

6.42 Stop titration at pH in the range of 4.3 - 4.7

6.43 Record volume and exact pH

6.44 Very carefully, add titrant to lower pH exactly 0.3 pH units and record volume

7. Calculation

Normality of acid = A*B / 53.00*C

Where, A = Na_2CO_3 weighed into 1 liter

B = volume of Na_2CO_3 solution in ml

C = volume of acid used to inflection point in ml

$$\text{Alkalinity, mg/l } CaCO_3 = \frac{A*N*50,000}{\text{ml of sample}}$$

Where, A = volume of standard acid in ml

N = normality of acid

Reference

1. EPA/600/4-79/020 Method for Chemical analysis of water and wastes

2. Standard method for the examination of water and wastewater, 17th edition, 1989

CHLORIDE **Titrimetric**
mg-Cl/l

Linear range	8.0 to 250 mg/l Cl^-
Detection limit	10 to 150 mg of chloride
Interference	Sulfide, bromide, iodide, thiocyanate, Cyanide, Phosphate, sulfite, carbonate, hydroxide and iron may interfere
Precision and Accuracy	For water samples containing 8.0 and250 mg/l Cl., the precision was reported as 10% and 1.6% respectively The accuracy was reported as -6.13% and -0.80% for the above two samples

1. Background
   1.1 The method is applicable to drinking and surface water
2. Summary of method
   2.1 The chloride reacts with the silver ion before any silver chromate forms, due to the lower solubility of silver chloride
   2.2 The potassium chromate indicator reacts with excess silver ion to form a red silver chromate precipitate
3. Apparatus
   3.1 Laboratory glassware
   3.2 Buret, 25 ml capacity
4. Reagents
   4.1 Standard silver nitrate solution
   4.2 Hydrogen peroxide (30%)
   4.3 Potassium chromate, indicator solution
   4.4 Standard sodium chloride solution
   4.5 Sodium hydroxide solution
   4.6 Sulfuric acid (1+19)

5. Preparation of standards

5.1 Potassium chromate solution

5.11 Dissolve 50 g of potassium chromate in 100 ml of water

5.12 Add silver nitrate until a slight red precipitate is produced

5.13 Allow the solution to stand at least 24 hours (in a dark place)

5.14 Filter to remove the precipitate

5.15 Dilute to 1 liter

5.2 Standard solution, silver nitrate (0.025 N)

5.21 Dissolve 4.2473 g of silver nitrate (crushed and dried to constant weight at 40°C) in some water

5.22 Dilute to 1 liter

5.23 Standardize against the sodium chloride solution (follow the procedure 6.2 to 6.6)

5.3 Standard solution, sodium chloride (0.025 N)

5.31 Dry several grams of sodium chloride for 1 hour at 60°C

5.32 Dissolve 1.4613 g of the dry salt in water

5.33 Dilute to 1 liter in a volumetric flask

5.4 Sodium hydroxide solution (10 g/l)

5.41 Dissolve 10 g of sodium hydroxide in water

5.42 Dilute to 1 liter

5.5 Sulfuric acid (1+19)

5.51 Add one volume of concentrated sulfuric acid to 19 volumes of water, while mixing

6. Procedure

6.1 Pour 50 ml or less of the sample containing not more than 20 nor less than 0.25 mg of chloride ion into a porcelain dish

6.2 If sulfite ions are present add 0.5 ml of hydrogen peroxide to the sample, mix and let stand for 1 minute

6.3 Dilute approximately to 50 ml with water if necessary

6.4 Adjust the pH to 8.3 using H_2SO_4 or NaOH

6.5 Add approximately 1.0 ml of K_2CrO_4 indicator and mix

6.6 Add standard silver nitrate solution dropwise from a 25 ml buret until the appearance of a permanent brick-red color

6.7 Repeat the procedure from 6.1 to 6.6 using exactly one half as much original sample, diluted to 50 ml with water

7. Calculation

Chloride,mg/l = $[(V_1-V_2)*N*70\ 906]/S$

where V_1 = Silver nitrate standard solution added in titrating the sample prepared in 6.1 in ml

V_2 = Silver nitrate standard solution added in titrating the sample prepared in 6.7 in ml

N = Normality of standard silver nitrate solution

S = Original sample in the 50 ml test specimen prepared in 6.1, in ml

Note: * Compounds which precipitate at pH 8.3 may cause error

* Orthophosphate and polyphosphate interfere if present in concentration greater than 200 and 25 mg/l respectively

* Sulfite and objectionable color or turbidity must be eliminated

Reference

1. Annual Book of ASTM standards,vol.11.01,1993

CYANIDE **Titrimetric**
mg CN/l

Linear range	> 1 mg/l
Interferences	Sulfides will adversely affect
	Fatty acids will distill from soaps under alkaline conditions
Precision and Accuracy	Precision data are not available

1. Background

   1.1 The method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes

2. Summary of Method

   2.1 CN^- in the alkaline distillate is titrated with standard silver nitrate to form the soluble cyanide complex, $Ag(CN)_2^-$

   2.2 The excess Ag^+ is detected by the silver-sensitive indicator, p-dimethylaminobenzalrhodanine, which immediately turns the color from yellow to salmon

3. Apparatus

   3.1 Koch microburette, 10 ml capacity

4. Reagents

   4.1 Indicator solution

   4.2 Standard silver nitrate titrant

   4.3 Sodium hydroxide dilution solution

5. Preparation of standards

   5.1 Indicator solution

      5.11 Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 ml acetone

   5.2 Standard silver nitrate titrant

      5.21 Dissolve 3.27 g $AgNO_3$ in 1 liter distilled water

      5.22 Standardize against standard NaCl solution

5.23 Dilute 500 ml $AgNO_3$ solution according to the titer found, so that 1.00 ml is equivalent to 1.00 mg CN

5.3 Sodium hydroxide dilution solution

5.31 Dissolve 1.6 g NaOH in 1 liter distilled water

6. Procedure

6.1 Take a measured volume of the sample that will require approximately 1 to 10 ml $AgNO_3$ titrant

6.2 Dilute to 250 ml using the NaOH dilution solution. For samples with low cyanide concentrations dilution is not necessary

6.3 Add 0.5 ml indicator solution

6.4 Titrate with standard $AgNO_3$ titrant to the first change in color from canary yellow to salmon hue

6.5 Titrate a blank containing the same amount of alkali and water

7. Calculation

$$\text{mg CN/l} = \frac{(A-B) \times 1000}{\text{ml original sample}} \times \frac{250}{\text{ml portion used}}$$

Where, A = volume of standard $AgNO_3$ for sample in ml

B = volume of standard $AgNO_3$ for blank in ml

Note: * If titration shows that CN is below 1 mg/l examine another portion colorimetrically or potentiometrically. The indicator is sensitive to about 0.1 mg Ag/l

Reference

1. Standard method for the examination of water and wastewater, 17th edition, 1989

AMMONIA **Spectrophotometric**

NH_3- N mg/l

Linear range	0.05 to 1.0 mg NH_3- N/l
Interferences	A number of aromatic and aliphatic amines as well as other organic and inorganic compounds will cause turbidity Cyanate will hydrolyze to some extent Volatile alkaline compounds may cause an off-color upon nesslerization
Precision and Accuracy	For an increment of 0.26 mg N/l and 1.92 mg N/l, precision was reported as 27% and 15% respectively The accuracy was reported as -18.12% and -2.01% respectively for the above samples

1. Background

   1.1 The method is applicable to drinking, surface and saline waters, domestic and industrial wastes

2. Summary of Method

   2.1 The sample is buffered at a pH of 9.5 in order to decrease hydrolysis of cyanates and organic nitrogen compounds

   2.2 Then distilled into a solution of boric acid

   2.3 The ammonia in the distillate can be determined colorimetically by nesslerization

3. Apparatus

   3.1 An all glass distilling apparatus with a 800-1000 ml flask

   3.2 Spectrophotometer for use at 425 nm

   3.3 Nessler tubes

   3.4 Erlenmeyer flasks marked at 350 ml and 500 ml volumes

4. Reagents

   4.1 Ammonia free distilled water

   4.2 Boric acid solution (20g/l)

4.3 Nessler reagent

4.4 Borate buffer

4.5 Sodium hydroxide (1N)

4.6 Dechlorinating reagents

5. Preparation of Standards

5.1 Ammonia free distilled water.

5.11 Prepare by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.

5.2 Boric acid solution (20 g/l)

5.21 Dissolve 20 g H_3BO_3 in distilled water

5.22 Dilute to 1 liter

5.3 Nessler reagent

5.31 Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water

5.32 Add this mixture slowly,(while stirring) to a cooled solution of 160 g of NaOH in 500 ml of water

5.33 Dilute the mixture to 1 liter

5.4 Borate buffer

5.41 Add 88 ml of 0.1 N NaOH solution to 500 ml of o.625 M sodium tetraborate solution (5g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7.10H_2O$ per liter) and dilute to 1 liter

5.5 Sodium hydroxide (1 N) solution

5.51 Dissolve 40 g NaOH in ammonia free water

5.52 Dilute to 1 liter

5.6 Dechlorinating reagent

5.61 Dissolve 3.5 g $Na_2S_2O_3.5H_2O$ in distilled water

5.62 Dilute to 1 liter

6. Procedure

6.1 Preparation of equipment

6.11 Add 500 ml of distilled water to a 800 ml of Kjeldahl flask

6.12 Steam out the distillation apparatus until the distillate shows no trace of ammonia with nessler reagent

6.2 Sample preparation

6.21 Remove the residual chlorine in the sample by adding a dechlorinating agent equivalent to the chlorine residual

6.22 To 400 ml of sample add 1 N NaOH until the pH is 9.5 (use a pH meter or short range pH paper)

6.3 Distillation

6.31 Transfer the samples (pH 9.5) to an 800 ml Kjeldahl flask

6.32 Add 25 ml of the borate buffer

6.33 Distill 300 ml at the rate of 6-10 ml/min into 50 ml of 2% boric acid

6.34 Dilute the distillate to 500 ml with distilled water

6.35 Nesslerize an aliquot to obtain an approximate value of the ammonia nitrogen concentration

6.4 Determination of ammonia in distillate

6.41 Prepare a series of Nessler tube standards as follows

ml of standard	mg NH_3-N/50 ml
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

6.42 Dilute each tube to 50 ml with distilled water

6.43 Add 2.0 ml of Nessler reagent and mix

6.44 After 20 min. read the absorbance at 425 nm against the blank

6.45 From the values obtained plot absorbance Vs. NH_3-N in mg for the standard curve

6.46 Determine the ammonia in distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm for the standards

6.47 Ammonia nitrogen content is read from the standard curve

7. Calculation

$$\text{mg/l } NH_3\text{-N} = \frac{A \times 1000}{D} \times \frac{B}{C}$$

Where,

A = mg, NH_3-N read from standard curve

B = volume of total distillate collected including boric acid and dilution in ml

C = volume of distillate taken for nesslerization in ml

D = volume of original sample taken in ml

Note:

* For determination of NH_3-N, from 1.0 to 25 mg/L titrimetric procedure and from 0.05 to 1400 mg/L electrode method should be used
* Samples may be preserved with 2 ml of conc.H_2SO_4 per liter and stored at 4^0c
* Volatile alkaline compounds may be eliminated by boiling off at a low pH (2 to 3) prior to distillation and nesslerization

Reference

1. EPA/600/4-79/020 Method for Chemical analysis of water and wastes

2. Standard method for the examination of water and wastewater, 17th edition, 1989

KJELDAHL NITROGEN
mg/L

Nesslerization

Linear range	Below 1 mg N/l
Interferences	High nitrate concentrations result low TKN values.
Precision and Accuracy	For-sample having an increment of 0.31 Nitrogen, Kjeldahl mg/l, the precision was reported as 80% with +5.45% accuracy

1. Background

1.1 The method is applicable for drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes

2. Summary of Method

2.1 The sample is heated in the presence of conc. H_2SO_4 acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained then the solution becomes colorless or pale yellow.

2.2 The residue is cooled, diluted and and made alkaline with a hydroxide-thiosulfate solution.

2.3 The ammonia is distilled and determined after distillation by Nesslerization.

3. Apparatus

3.1 Digestion apparatus - A Kjeldahl digestion apparatus with 800 or 100 ml flasks and suction take off to remove SO_3 fumes and water.

3.2 Distillation apparatus - The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected.

3.3 Spectrophotometer for use at 400 and 425 nm, with a light path of 1 cm or longer.

4. Reagents

4.1 Ammonia free distilled water.

4.2 Mercuric sulfate solution.

4.3 Sulfuric acid - mercuric sulfate - potassium sulfate solution.

4.4 Sodium hydroxide - Sodium thiosulfate solution.

4.5 Boric acid solution.

4.6 Ammonium chloride stock solution.

4.7 Ammonium chloride standard solution.

4.8 Nessler reagent.

5. Preparation of standards

5.1 Ammonia free distilled water

5.11 Prepare by the passage of distilled water through an ion-exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.

5.2 Mercuric sulfate solution.

5.21 Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10.0 ml conc. H_2SO_4:40.0 ml distilled water).

5.22 Dilute to 100 ml with distilled water.

5.3 Sulfuric-Mercuric sulfate-potassium sulfate solution.

5.31 Dissolve 267 g K_2SO_4 in 1300 ml distilled water and 400 ml conc. H_2SO_4.

5.32 Add 50.0 ml mercuric sulfate (5.2) solution.

5.33 Dilute to 2 liters with distilled water.

5.4 Sodium hydroxide-sodium thiosulfate solution.

5.41 Dissolve 500 g NaOH and 25 g $Na_2S_2O_3.5H_2O$ in distilled water.

5.42 Dilute to 1 liter.

5.5 Boric acid solution.

5.51 Dissolve 20 g boric acid, H_3BO_3 in water.

5.52 Dilute to 1 liter with distilled water.

5.6 Ammonium chloride, stock solution.

5.61 Dissolve 3.819 g NH_4Cl in water.

5.62 Make up to liter in a volumetric flask with distilled water.

5.7 Ammonium chloride, standard solution.

5.71 Dilute 10.0 ml of the stock solution (5.6) with distilled water to 1 liter in a volumetric flask.

5.8 Nessler reagent.

5.81 Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water.

5.82 Add this mixture slowly, with stirring to a cooled solution of 160 g of NaOH in 500 ml of distilled water.

5.83 Dilute the mixture to 1 liter.

6. Procedure

6.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution until the distillate is ammonia free.

6.2 Macro-Kjeldahl system.

6.21 Place a measured residue from the distillation in an 800 ml Kjeldahl flask. The sample size can be determined from the following table.

Kjeldahl Nitrogen in sample, mg/L	Sample Size, ml
0 - 5	500
5 - 10	250
10 - 20	100
20 - 50	50.0
50 - 500	25.0

6.22 Dilute the sample, if required, to 500 ml with distilled water

6.23 Add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate (5.3)

6.24 Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow

6.25 Continue heating for 30 additional minutes, cool the residue and add 300 ml distilled water

6.26 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide thiosulfate solution (5.4) without mixing

6.27 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution in the receiving flask

6.28 Distill 300 ml at the rate of 6-10 ml/min into 50 ml of 2% boric acid contained in a 500 ml Erlenmeyer flask

6.29 Dilute the distillate to 500 ml in the flask

6.30 Determine the ammonia concentration colorimetrically

6.3 Determination of ammonia in distillate..

6.31 Prepare a series of Nessler tube standards as follows

ml of Standard	**mg NH_3-N /50 ml**
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

6.32 Dilute each tube to 50 ml with ammonia free water, add 1 ml of Nessler reagent and mix

6.33 After 20 min. read the absorbance at 425 nm against the blank

6.34 From the values obtained for the standards plot absorbance vs mg NH_3-N for the standard curve

6.35 Develop color in the 50 ml diluted distillate in exactly the same manner and read mg NH_3-N from the standard curve

7. Calculation

$$\text{TKN, mg/L} = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where, A = mg NH_3-N read from curve.

B = total volume of distillate collected including the H_3BO_3 in ml

C = volume of distillate taken for nesslerization in ml

D = volume of original sample taken in ml

Note: * When high concentration of nitrate is present, the reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin to remove the nitrate prior to the analysis

* For concentrations above 1 mg N/l, the titrimetric method is used
* For the range of 0.05 to 1400 mgN/L, potentiometric method may be used
* Samples may be preserved by addition of 2 ml conc. H_2SO_4 per liter and stored at 4^0c.

References

1. EPA/600/4-79/020 Methods for Chemical Analysis of Water and Wastes.
2. Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.
3. Annual Book of ASTM standards,vol.11.02,1986

NITRATE
mg/l

Spectrophotometric

Linear range	0.01 to 1.0 mg/l
Interference	Build up of suspended matter in the reduction column will restrict the sample flow High concentration of iron, copper or other metals may interfere. Large concentrations of oil and grease will coat the surface of the cadmium
Precision and Accuracy	In a single laboratory, using sewage samples containing 0.04 and 0.24 mg/l $NO^3 + NO^2$ the precision was reported as 12.5% and 1.6% respectively In a single laboratory,using sewage samples at concentrations of 0.24 and 0.55 mg $NO^3 + NO^2$ N/l, the recoveries were reported as 100% and 102% respectively

1. Background

   1.1 The method is applicable to the determination of nitrite singly or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes

   1.2 If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure without the reduction step

2. Summary of method

   2.1 Sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite

   2.2 The nitrite is determined by diazotizing with sulfanilamide and coupling with N-(1.naphthyl) ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically

3. Apparatus

3.1 Reduction column (The column may be constructed from a 100 ml pipet by removing the top portion)

3.2 Spectrophotometer for use at 540 nm

4. Reagents

4.1 Granulated Cd (40-60 mesh)

4.2 Copper-Cadmium

4.3 Ammonium chloride - EDTA solution

4.4 Dilute Ammonium chloride - EDTA solution

4.5 Color reagent

4.6 Zinc sulfate solution

4.7 Sodium hydroxide solution

4.8 Ammonium hydroxide conc

4.9 Dilute hydrochloric acid, 6N

4.10 Copper sulphate solution

4.11 Stock nitrate solution

4.12 Standard nitrate solution

4.13 Stock nitrite solution

4.14 Standard nitrite solution

4.15 Standard solutions

5. Preparation of standards

5.1 Copper Cadmium

5.11 The cadmium granules are cleaned with dilute HCl and copperized with 2% solution of copper sulfate(5.8) in the following manner

5.12 Wash the cadmium with dilute HCl and rinse with distilled water. The color of the Cadmium should be silver

5.13 Swirl 25 g cadmium in 100 ml of 2% copper sulfate solution (5.8) for 5 minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms

5.14 Wash the copper-cadmium with distilled water to remove all the precipitated copper. The color of the Cd should be black

5.2 Ammonium chloride - EDTA solution

5.21 Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetraacetate in 900 ml of distilled water

5.22 Adjust the pH to 8.5 with conc. ammonium hydroxide and dilute to 1 liter

5.3 Dilute ammonium chloride EDTA solution

5.31 Dilute 300 ml of ammonium chloride EDTA solution to 500 ml with distilled water

5.4 Color reagent

5.41 Dissolve 10 g sulfanilamide and 1 g N (1-naphthyl) -ethylene-diamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to 1 liter with distilled water

5.5 Zinc sulphate solution

5.51 Dissolve 100 g $ZnSO_4.7H_2O$ in distilled water

5.52 Dilute to 1 liter

5.6 Sodium Hydroxide solution (6N)

5.61 Dissolve 240 g NaOH in 500 ml distilled water

5.62 Cool and dilute to 1 liter

5.7 Dilute hydrochloride acid (6N)

5.71 Dilute 50 ml of conc.HCl to 100 ml with distilled water

5.8 Copper sulfate solution (2%)

5.81 Dissolve 20 g of $CuSO_4.5H_2O$ in 500 ml of distilled water

5.82 Dilute to 1 liter

5.9 Stock nitrate solution

5.91 Dissolve 7.218 g KNO_3 in distilled water and dilute to 1000 ml

5.92 Preserve with 2 ml of chloroform per liter

5.10 Standard nitrate solution

5.10.1 Dilute 10.0 ml of nitrate stock solution (5.9) to 1000 ml with distilled water

5.11 Stock nitrite solution

5.11.1 Dissolve 6.072 g KNO_2 in 500 ml of distilled water

5.11.2 Dilute to 1000 ml

5.11.3 Preserve with 2 ml of chloroform and keep under refrigeration

5.12 Standard nitrite solution

5.12.1 Dilute 10.0 ml of stock nitrite solution (5.11) to 1000 ml with distilled water

5.13 Standard solutions

5.13.1 Using the standard nitrate solution prepare the following standards in 100 ml volumetric flasks

Conc. mg NO_3-N/l	**ml of standard solution/100 ml**
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

6. Procedure

6.1 Turbidity removal (use one of the following methods)

6.11 Filter sample through a glass fiber filter or a 0.45 u membrane filter

6.12 Add 1 ml $ZnSO_4$ solution (5.5) to 100 ml of sample and mix thoroughly. Add 0.4-0.5 ml sodium hydroxide solution (5.6) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand for few minutes to allow the heavy flocculent precipitate to settle.

6.2 Oil and grease removal

6.21 Adjust the pH of 100 ml of filtered sample to 2 by addition of con. HCl

6.22 Extract the oil and grease from the aqueous solution with two 25 ml portions of an organic solvent. (Freon, chloroform or equivalent)

6.3 Preparation of reduction column

6.31 Insert a glass wool plug to the bottom of the column and fill with distilled water

6.32 Add sufficient Cu-Cd granules to produce a column, 18.5 cm long (maintain the water level above the granules)

6.33 Wash the column with 200 ml dilute NH_4Cl-EDTA solution (5.3)

6.34 Activate the column by passing 100 ml of a solution mixture of 25 ml of 1.0 mg/l NO_3 standard and 75 ml of NH_4Cl-EDTA solution (5.2) through the column

6.4 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH

6.5 To 25 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride EDTA solution (5.2) and mix

6.6 Pour sample into column and collect sample at a rate of 7-10 ml per minute

6.7 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask. Reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent

6.8 Add 2 ml of color reagent to 50.0 ml of sample. Allow 10 min. for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank

6.9 Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard of the same concentration to verify the efficiency of the reduction column

7. Calculation

7.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against NO_3 concentrations

7.2 Compute concentration of samples from the standard curve

7.3 For less than 25 ml sample

$$\text{mg } (NO_2 + NO_3) - N/l = \frac{A \times 25}{\text{ml sample used}}$$

Where, A = concentration of nitrate from standard curve

Note: * Analysis should be made as soon as possible.

* If analysis is done within 24 hours, the sample should be preserved by refrigeration at 4^0c

* When required to store samples more than 24 hours, they should be preserved with sulfuric acid (2 ml H_2SO_4 per liter)

* Samples for reduction column must not be preserved with mercuric chloride

Reference

1. EPA/600/4-79/020 Method for Chemical analysis of water and wastes

NITRITE **Spectrophotometric**

NO_2 - N mg/l

Linear range	0.01 to 1.0 mg NO_2-N/l
Interferences	Strong oxidants or reductant will affect the nitrite concentrations High alkalinity (>600 mg/l) will give low results
Precision and Accuracy	In a single laboratory, using wastewater samples containing 0.04 and 0.24 mg/l NO^3 + NO^2, the precision was reported as 12.5% and 1.6% In a single laboratory,using wastewater samples at concentrations of 0.24 and 0.55 mg NO^3 + NO^2 N/l, the recoveries were reported as 100% and 102% respectively

1. Background

   1.1 The method is applicable to drinking, surface and saline waters, domestic and industrial wastes

2. Summary of Method

   2.1 The diazonium compound is formed by diozotisation of sulfanilamide with nitric in water under acid conditions

   2.2 Then it is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to produce a reddish-purple color which is read in a spectrophotometer at 540 nm

3. Apparatus

   3.1 Spectrophotometer equipped with 1 cm or larger cells for use at 540 nm

   3.2 Nessler tubes (50 ml) or volumetric flasks (50 ml)

4. Reagents

   4.1 Distilled water free of nitrite and nitrate

   4.2 Buffer color reagent

   4.3 Nitrite stock solution

   4.4 Nitrite standard solution

5. Preparation of standards

5.1 Buffer color reagent

5.11 To 250 ml of distilled water, add 105 ml conc. hydrochloric acid, 5 g sulfanilamide and 0.5g N-(1-naphthyl) ethylenediamine dihydrochloride

5.12 Stir until dissolved

5.13 Add 136 g of sodium acetate and again stir until dissolved

5.14 Dilute to 500 ml with distilled water

5.2 Nitrite sock solution

5.21 Dissolve 0.1493 g of dried (24 hours in desiccator) anhydrous sodium nitrite in distilled water

5.22 Dilute to 1000 ml

5.23 Preserve with 2 ml chloroform per liter

5.3 Nitrite standard solution

5.31 Dilute 10.0 ml of the stock solution to 1000 ml

6. Procedure

6.1 Adjust the pH of the sample to 6 with 1:3 HCl

6.2 If necessary, filter the sample through a 0.45 u pore size filter using the first portion

6.3 Place 50 ml of sample or an aliquot diluted to 50 ml in a 50 ml Nessler tube, hold until preparation of standards is completed

6.4 At the same time prepare a series of standards in 50 ml Nessler tubes as follows

ml of standard solution	conc. when diluted to 50 ml (mg/l)
0.0	blank
0.5	0.01
1.0	0.02
1.5	0.03
2.0	0.04
3.0	0.06
4.0	0.08
5.0	0.10
10.0	0.20

6.5 Add 2 ml of buffer-color reagent to each standard and sample, mix and allow color to develop for at least 15 min. The color reaction medium should be between pH 1.5 and 2.0

6.6 Read the absorption in the spectrophotometer at 540 nm against the blank and plot concentration of NO_2-N against absorbance

7. Calculation

7.1 Read the concentration of NO_2-N directly from the curve

7.2 For less than 50 ml of sample

$$NO_2\text{-N, mg/l} = \frac{\text{mg/l from std.curve} \times 50}{\text{ml sample used}}$$

Note: * Samples should be analyzed as soon as possible. They may be stored for 24 to 48 hours at 4^0c

Reference

1. EPA/600/4-79/020 Method for Chemical analysis of water and wastes

2. Standard method for the examination of water and wastewater, 17th edition, 1989

DISSOLVED OXYGEN **Titrimetric**
mg/l

Interferences	Oxidizing and reducing agents, nitrate ions, ferrous ions and organic matter will interfere
Precision and accuracy	Exact data are unavailable on the precision and accuracy; however, the reproducibility is reported approximately as 0.2 mg/l of DO at the 7.5 mg/l level

1. Background

   1.1 The method is applicable for use with most wastewaters and streams that contain nitrate, nitrogen and not more than 1 mg/l of ferrous ions

   1.2 Other oxidizing and reducing materials should be absent

   1.3 The dissolved oxygen probe technique gives comparable results on all sample types

2. Summary of method

   2.1 The precipitate with manganous sulfate combines with the dissolved oxygen in the sample to form a brown precipitate (manganic hydroxide)

   2.2 Upon acidification with sulfuric acid, the manganic hydroxide forms manganic sulfate which acts as an oxidizing agent to release free iodine from the potassium iodide

   2.3 The iodine is then titrated with sodium thiosulfate

3. Apparatus

   3.1 Sample bottles - 300 ml ± 3 ml capacity BOD incubation bottles with tapered ground glass pointed stoppers and flared mouths

   3.2 Pipets with elongated tips capable of delivering 2.0 ml ± 0.10 ml of reagent

4. Reagents

   4.1 Manganous sulfate solution

   4.2 Alkaline iodide - azide solution

   4.3 Sulfuric acid

4.4 Starch solution

4.5 Potassium Fluoride solution

4.6 Sodium thiosulfate stock solution

4.7 Sodium thiosulfate standard titrant

4.8 Potassium bioiodate standard

5. Preparation of standards

5.1 Manganous sulfate solution

5.11 Dissolve 480 g Manganous sulfate ($MNSO_4.4H_2O$) in distilled water and dilute to one liter

5.2 Alkaline iodide-azide solution

5.21 Dissolve 500 g of Sodium hydroxide or 700 g of Potassium hydroxide and 135 g of Sodium iodide or 150 g of Potassium iodide in distilled water and dilute to one liter

5.22 Add 10 g of azide (NaN_3) dissolved in 40 ml of distilled water

5.3 Starch solution

5.31 Prepare an emulsion of 10g soluble starch in a motar or beaker with a small quantity of distilled water

5.32 Pour this emulsion into one liter of boiling water, allow to boil for few minutes

5.33 Let settle overnight

5.34 Use the clear supernate

5.4 Potassium fluoride solution

5.41 Dissolve 40 g potassium fluoride ($KF.2H_2O$) in distilled water

5.42 Dilute to 100 ml

5.5 Sodium thiosulfate stock solution (0.75 N)

5.51 Dissolve 186.15 g $Na_2S_2O_3.5H_2O$ in boiled and cooled distilled water

5.52 Dilute to 1 liter

5.53 Preserve by adding 5 ml chloroform

5.6 Sodium thiosulfate standard titrant (0.0375 N)

5.61 Dilute 50.0 ml of stock solution to 1 liter

5.62 Preserve by adding 5 ml of chloroform

5.7 Potassium bioiodate standard (0.0375 N)

5.71 Dissolve 4.873 g of Potassium bioiodate previously dried for 2 hours at 103^{0}C in 1000 ml distilled water

5.72 To prepare working standard dilute 250 ml to 1000 ml for 0.0375 N bioiodate solution

6. Procedure

6.1 To the sample collected in the BOD incubation bottle (300 ml), add 2 ml of the manganous sulfate solution

6.2 Add 2 ml of the alkaline iodide-azide solution

6.3 Stopper with care to exclude air bubbles and mix well by inverting the bottles several times

6.4 When the precipitate is settled, shake again

6.5 When settling has produced at least 200 ml of clear supernatant, carefully remove the stopper and immediately add 2 ml of conc. H_2SO_4 by allowing the acid to run down the neck of the bottle

6.6 Re-stopper and mix by gentle inversion until the iodine is uniformly distributed throughout the bottle

6.7 Transfer the entire bottle contents by inversion into a 500 ml wide mouth flask

6.8 Titrate with 0.0375 N thiosulfate solution to pale straw color (if the end point is overrun back titrate with 0.0021 M bi-iodate solution added dropwise)

6.9 Add 1-2 ml of starch solution and continue to titrate to the first disappearance of the blue color. If ferric ion is present (100 to 200 mg/l) add 1.0 ml of KF solution before acidification

7. Calculation

7.1 Each ml of 0.0375 N sodium thiosulfate titrant is equivalent to 1 mg DO when the entire bottle contents are titrated

7.2 The solubility of DO in distilled water,

$$\text{ml/L DO} = \frac{(P - \mu) \times 0.678}{35 + T} \quad \text{at } 0^0 - 30^0\ C$$

$$\text{ml/L DO} = \frac{(P - \mu) \times 0.827}{49 + T} \quad \text{at } 30^0 - 50^0\ C$$

Where, P (mmHg) - barometric pressure

T (^{0}C) - temperature

μ (mmHg) - Saturated vapor pressure

Note: * Various modifications for dissolved oxygen have been developed to compensate or eliminate interferences.

* The azide modification removes interference caused by nitrite, permanganate modification for the presence of ferrous ion, alum flocculation modification for the presence of suspended solids and the copper sulfate sulfamic acid flocculation modification on activated-sludge mixed liquor.

References

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

2. Standard methods for the examination of water and wastewater, 17th edition, 1989

AVAILABLE PHOSPHORUS
mg/l

COLORIMETRIC

Linear range	0.01 to 0.5 mg/l
Interferences	High concentrations of silica may cause positive interference. Salt concentrations higher than 20%, nitrite and sulfide may also interfere.
Precision and accuracy	For natural water samples containing increments of orthophosphate of 0.029 and 0.383 mg P/l, the precision was reported as 34% and 6% respectively Accuracy was reported as -4.95% and -1.76% respectively for above two samples

1. Background

   1.1 The method covers the determination of orthophosphates in drinking, surface and saline waters and domestic and industrial wastes

2. Summary of method

   2.1 Ammonium molybdate and antimony potassium tartrate react with orthophosphate to form an antimony phosphate molybdate complex

   2.2 The complex is reduced with ascorbic acid to form a deep colored blue molybdenum complex

   2.3 The color intensity is proportional to the phosphorous concentration

3. Apparatus

   3.1 A spectrophotometer suitable for measurement at 880 nm with path length of 20 mm or more

   3.2 Acid-washed glassware (wash with 1:3 Hcl and distilled water)

4. Reagents

   4.1 Phenolphthalein indicator solution

   4.2 Sulfuric acid (31+69)

   4.3 Combined reagent

4.4 Standard phosphorus solution

5. Preparation of standards

5.1 Phenolphthalein indicator solution (5 g/l)

5.11 Dissolve 0.5 g of phenolphthalein in a mixture of 50 ml ethyl or isopropyl alcohol and 50 ml water

5.2 Sulfuric acid (31+69)

5.21 Add 310 ml of concentrated sulfuric acid to about 600 ml of water

5.22 Cool the solution and dilute to 1 liter with water

5.3 Combined reagent

5.31 Dissolve 0.5 g of ascorbic acid in 100 ml of solution mixture (5.4)

5.4 Solution mixture

5.41 Dissolve 0.13 g of antimony potassium tartrate [$K(SbO)C_4H_4O_6.1/2\ H_2O$] in a 1 liter volumetric flask containing about 700 ml water

5.42 Add 5.6 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] and shake the flask until dissolved

5.43 Cautiously add 70 ml of concentrated sulfuric acid while stirring

5.44 Cool the solution and dilute to 1 liter

5.5 Standard phosphorus solution (1.00 ml = 0.0025 mg P)

5.51 Prepare a stock solution by dissolving 0.2197 g of potassium dihydrogen phosphate (dried at 105°C for 1 hour) in water and diluting to 1 liter with water

5.52 To prepare the standard solution, dilute 50 ml of the stock solution to 1 liter with water

6. Calibration

6.1 Pipet out 0,1,2,4,7 and 10 ml of standard phosphorus solutions into 125 ml Erlenmeyer flasks and dilute each to 50 ml with water (Gives 0, 0.05, 0.1, 0.2, 0.35 and 0.5 mg/l of phosphorus)

6.2 Add 10 ml of combined reagent (5.3) to each standard and swirl each flask

6.3 After a minimum of 10 min. but no longer than 30 min., measure the color absorbance of each solution at 880 nm (use the zero standard as the reference)

6.4 Plot ppm (milligram per liter) of phosphorus versus the absorbance (a straight line passing through the origin should be obtained)

7. Procedure

7.1 Pipet a volume of sample no greater than 50 ml (contain less than 0.25 mg of orthophosphate) into a 125 ml Erlenmeyer flask

7.2 Dilute the sample to 50 ml with water if necessary

7.3 Add a drop of phenolphthalein indicator solution

7.4 If a red color develops add sulfuric acid (5.2) dropwise to just discharge the color

7.5 Add 10 ml of combined reagent to the sample and mix well

7.6 After a minimum of 10 min., measure the absorbance of the blue color at 880 nm (use 50 ml of water treated similarly to the sample as the reference)

7.7 Determine the ppm of phosphorus from the calibration curve

8. Calculation

Orthophosphate, mg/l = (A*50)/B

where, A = phosphorus indicated by the calibration curve, mg/l

B = volume of sample analyzed in ml

Note: * Interference from nitrite or sulfide can be eliminated by adding an excess of bromide water or a saturated potassium permanganate solution to the sample

* If the temperature of the test solution is less than 20°C, the color may develop slowly and incompletely

References

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

2. Standard methods for the examination of water and wastewater, 17th edition, 1989

3. Annual book of ASTM standards volu.11.01 water(1), 1993

TOTAL PHOSPHOROUS **COLORIMETRIC**
mg/l

Linear range	0.01 to 1.2 mg P/l
Interference	Arsenate and high concentrations of iron may interfere
Precision and accuracy	For natural water samples containing increments of total phosphorus of 0.110 and 0.882 mg P/l, the precision was reported as 30% and 15% respectively Accuracy was reported as +3.09% and -0.92% respectively for the two samples

1. Background

   1.1 The method covers the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.

2. Summary of method

   2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

3. Apparatus

   3.1 Spectrophotometer suitable for measurements at 660 or 880 nm with a path length of 1 cm.

   3.2 Acid washed glassware (wash with 1.1 HCl and distilled water).

   3.3 Water bath, 95^0 c.

4. Reagents

   4.1 Ammonium molybdate-antimony potassium tartrate solution.

   4.2 Ascorbic acid solution.

   4.3 Sulfuric acid (11 N).

   4.4 Sodium bisulfite solution.

   4.5 Ammonium persulfate.

4.6 Phosphorus solution stock.

4.7 Phosphorus solution standard.

5. Preparation of standards

5.1 Ammonium molybdate-antimony potassium tartrate solution.

5.11 Dissolve 8 g of ammonium molybdate and 0.2 g antimony potassium tartrate in 800 ml of distilled water and dilute to 1 liter.

5.2 Ascorbic acid solution

5.21 Dissolve 60 g of ascorbic acid in 800 ml of distilled water and dilute to 1 liter.

5.22 Add 2 ml of acetone.

5.3 Sulfuric acid, 11 N

5.31 Slowly add 310 ml of conc. H_2SO_4 to approximately 600 ml distilled water.

5.32 Cool and dilute to 1000 ml.

5.4 Sodium bisulfite solution

5.41 Dissolve 5.2 g of $NaHSO_3$ in 100 ml of 1.0 N H_2SO_4.

5.5 Phosphorus solution stock

5.51 Dissolve 0.4393 g of pre dried (105^{0}C for one hour) KH_2PO_4 in distilled water and dilute to 1 liter.

5.6 Phosphorus solution standard

5.61 Dilute 100 ml of stock phosphorus solution to 1 liter with distilled water.

5.62 Prepare an approximate series of standards by diluting suitable volumes of standard or stock solutions to 100 ml with distilled water.

6. Procedure

6.1 Transfer 50 ml of sample or an aliquot diluted to 50 ml into a 125 ml Erlenmeyer flask.

6.2 Add 1 ml of 11 N sulfuric acid.

6.3 Add 0.4 g ammonium persulfate, mix and boil gently for approximately 30-40 min. or until a final volume of about 10 ml is reached.

6.4 Alternatively heat for 30 min. in an autoclave at 121^0 c (15-20 psi).

6.5 Cool, dilute to approximately 40 ml and filter.

6.6 For samples containing arsenic or high levels of iron, add 5 ml of sodium bisulfite, mix and place in a 95° c water bath for 30 min. Cool and dilute to 50 ml.

6.7 To 50 ml of sample or standard add 4 ml of ammonium molybdate-antimony potassium tartrate and mix.

6.8 Add 2 ml of ascorbic acid solution and mix.

6.9 After 5 min. measure the absorbance at 650 nm with a spectrophotometer.

6.10 Determine the phosphorus concentration from the standard curve. The color is stable for at least 1 hour.

7. Calculation

7.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phosphorus concentrations.

7.2 Obtain concentration value of sample directly from standard curve.

7.3 Report results as P, mg/l.

Note: * If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

* Sample containers may be of plastic material or of Pyrex glass.

* The sample should be preserved by the addition of 2 ml conc. H_2SO_4 per liter and refrigeration at 4° c.

* The interferences may be eliminated by the bisulfite treatment.

References

1. EPA/600/4-79/020 Methods for Chemical Analysis of Water and Wastes.

2. Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

SULFATE **Turbidimetric**
mg/l

Linear range	All concentration ranges of sulfate
Detection limit	1 mg/l sulfate
Interference	Suspended matter in the sample and color may interfere
Precision and Accuracy	For a synthetic, unknown sample containing 259 mg/l sulfate, a relative standard deviation of 4.7% and a relative error of 1.9% were reported

1. Background

   1.1 The method is suitable for drinking and surface waters, domestic and industrial wastes

2. Summary of method

   2.1 Sulfate ion is converted to a barium sulphate suspension. The resulting turbidity is then determined

3. Apparatus

   3.1 Magnetic stirrer

   3.2 Photometer

   3.3 Stop watch

   3.4 Measuring spoon (capacity 0.2 to 0.3 ml)

4. Reagents

   4.1 Conditioning reagent

   4.2 Barium chloride crystals

   4.3 Sodium carbonate solution

   4.4 Standard sulfate solution

5. Preparation of standards

   5.1 Conditioning reagent

      5.11 Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g NaCl in solution in a container

5.12 Add 50 ml glycerol and mix

5.2 Standard sulfate solution

5.21 Dissolve 142.0 mg anhydrous Na_2SO_4 in distilled water in a 1 liter volumetric flask

5.22 Dilute to the mark with distilled water

6. Calibration

6.1 Prepare a calibration curve using standard sulfate solution (follow 7.1 and 7.2)

6.2 Space standards at 5 mg/l increments in the 0-40 mg/l sulfate range

6.3 Check reliability of calibration curve by running a standard with every 3 or 4 samples

7. Procedure

7.1 Formation of barium sulfate turbidity

7.11 Place 100 ml sample, or a suitable portion diluted to 100 ml into a 250 Erlenmeyer flask

7.12 Add exactly 5.0 ml conditioning reagent

7.13 Mix in the stirring apparatus

7.14 While the solution is being stirred, add a measuring spoonful of $BaCl_2$ crystals and begin timing immediately

7.15 Stir exactly for 1.0 minute at constant speed

7.2 Measurement of barium sulfate turbidity

7.21 Immediately after the stirring period has ended, pour solution into absorbance cell

7.22 Measure turbidity at 30 second intervals for 4 minutes (at 420 nm)

7.23 Record the maximum reading obtained in the 4 minute period

7.3 Correction for sample color and turbidity

7.31 Run a sample blank using the procedure 7.1 and 7.2 without the addition of barium chloride

8. Calculation

Read mg- SO_4 from calibration curve

$$mg\text{-}SO_4/l = \frac{mg\text{-}SO_4 \times 1000}{ml\ sample}$$

Note: * Silica in concentrations over 500 mg/l will interfere

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes
2. Standard methods for the examination of water and wastewater, 17th Edition, 1989.
3. Annual Book of ASTM standards,vol.11.02,1986

5.5 Organics

BIOCHEMICAL OXYGEN DEMAND **Titrimetric**
BOD_5 mg/l

Linear range	The working range is equal to the difference between the maximum initial DO and minimum DO residual of 1 mg/l multiplied by the dilution factor
Detection limit	2 mg/l DO
Interferences	Long storage between collection and analysis may degrade the samples, resulting low BOD values
Precision and Accuracy	For natural water samples having mean values of 2.1 and 175 mg/l BOD, the precision was reported as 33% and 15% respectively

1. Background

   1.1 The test is used for determination of the relative oxygen requirements of municipal and industrial wastewaters

2. Summary of Method

   2.1 The sample of waste or an appropriate dilution is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yield a measure of the biochemical oxygen demand

3. Apparatus

   3.1 Incubation bottles, 250-300 ml capacity

      3.11 Clean bottles with a detergent, rinse thoroughly and drain before use

      3.12 To avoid drawing air into the dilution bottle during incubation, use a waterseal

   3.2 Air incubator or water bath
   (Thermostatically controlled at 20 ± 1°C)

4. Reagents

4.1 Phosphate buffer solution

4.2 Magnesium sulfate solution

4.3 Calcium chloride solution

4.4 Ferric chloride solution

4.5 Acid and alkali solution

4.6 Sodium sulfite solution

4.7 Nitrification inhibitor- 2-chloro-6-(trichloromethyl)pyridine

4.8 Ammonium chloride solution

5. Preparation of standards

5.1 Phosphate buffer solution

5.11 Dissolve 8.5 g KH_2PO_4, 21.75g K_2HPO_4, 33.4 g $Na_2HPO_4.7H_2O$ and 1.7 g NH_4Cl in about 500 ml distilled water and dilute to 1 liter (The pH should be 7.2 without further adjustment)

5.2 Magnesium sulfate solution

5.21 Dissolve 22.5 g $MgSO_4.7H_2O$ in distilled water

5.22 Dilute to 1 liter

5.3 Calcium chloride solution

5.31 Dissolve 27.5 g $CaCl_2$ in distilled water

5.32 Dilute to 1 liter

5.4 Ferric chloride solution

5.41 Dissolve 0.25 g $FeCl_3.6H_2O$ in distilled water

5.42 Dilute to 1 liter

5.5 Acid and alkali solution

5.51 Acid- slowly add 28 ml conc. sulfuric acid to distilled water and dilute to 1 liter

5.52 Alkali- Dissolve 40 g sodium hydroxide in distilled water and dilute to 1 liter

5.6 Sodium sulfite solution

5.61 Dissolve 1.575 of Na_2SO_3 in 1000 ml distilled water. (this solution is not

stable)

5.7 Ammonium chloride solution

5.71 Dissolve 1.15 g NH_4Cl in about 500 ml distilled water, adjust pH to 7.2 with NaOH solution

5.72 Dilute to 1 liter

6. Procedure

6.1 Preparation of dilution water

6.11 Place desired volume of water in a suitable bottle and add 1 ml each of phosphate buffer, $MgSO_4$, $CaCl_2$ and $FeCl_3$ solutions per liter of water (seed dilution water if desired)

6.12 Before use, bring temperature of dilution water to 20°C

6.13 Saturate with DO by shaking in a partially filled bottle or by aerating with organic free filtered air

6.14 Store in cotton-plugged bottles long enough for water to become saturated with DO

6.2 Sample pretreatment

6.21 Neutralize samples to pH 6.5 to 7.5 with a solution of sulfuric acid or sodium hydroxide of such strength that the quantity of reagent does not dilute the sample by more than 5%

6.22 If residual chlorine is present in the sample dechlorinate the sample and seed the dilution water

6.23 Special study and treatment is needed for the samples containing toxic substances such as industrial wastes

6.24 For samples containing more than 9 mg DO/l at 20°C to prevent loss of oxygen during incubation, reduce DO to saturation at 20°C.

6.25 This can be done by bringing the sample to about 20°C in a partially filled bottle, while agitating by vigorous shaking or by aerating with clean, filtered compressed air

6.26 Bring samples to 20 ± 1°C before making dilution

6.27 If nitrification inhibition is desired add 3 mg 2-chloro-6(trichloro methyl)

pyridene to each 300 ml bottle before capping or add sufficient amounts to the dilution water to make a final concentration of 10 mg/l

6.3 Dilution technique

6.31 Dilution that results in a range of 1 to 2 mg/l of residual DO after 5 days of incubation, produces the most reliable results

6.32 Make several dilutions of prepared sample to obtain DO uptake in this range

6.33 Prepare dilution directly in BOD bottles. The number of bottles to be prepared for each dilution depends on the DO technique and the number of replicates desired

6.34 When seeding is necessary, add seed directly to dilution water or directly to the BOD bottles

6.35 Fill bottles with enough dilution water, so that insertion of stopper will displace all air, leaving no bubbles

6.36 For dilutions greater than 1:100 make a primary dilution in a graduated cylinder before making final dilution in the bottle

6.4 Determination of initial DO

6.41 Refer the procedure given in the test method for dissolved oxygen to determine DO

6.42 If the sample contains materials those react rapidly with DO, determine initial DO immediately after filling BOD bottle with diluted sample

6.43 Use the azide modification of the iodometric method to determine initial DO on all sample dilutions, dilution water blanks, and where appropriate seed controls

6.5 Dilution water blank

6.51 Use a dilution water blank as a rough check on quality of unseeded dilution bottles

6.52 Determine initial and final DO as above (6.4) The DO uptake should not be more than 0.2 mg/l

6.6 Incubation

6.61 Incubate BOD bottles containing desired dilutions at 20°C ± 1°C and waterseal

6.7 Determination of final DO

6.71 After 5 day incubation determine DO in sample dilutions and blanks as in 6.4

7. Calculation

when dilution water is not seeded

$$BOD_5 \text{ mg/l} = \frac{D_1 - D_2}{P}$$

When dilution water is seeded

$$BOD_5 \text{ mg/l} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

Where, D_1 = DO of diluted sample immediately after preparation mg/l

D_2 = DO of diluted sample after 5 day incubation at 20°C mg/l

P = decimal volumetric fraction of sample used

B_2 = DO of seed control after incubation mg/l

f = ratio of seed in diluted sample to seed in seed control, ie. (% seed in diluted sample)/(% seed in seed control)

B_1 = DO of seed control before incubation mg/l

Note: * It is necessary to have micro-organisms capable of oxidizing the biodegradable organic matter in the sample for samples do not contain a sufficient microbial population.

* In such situations seed the dilution water by adding a population of microorganisms .

* The preferred seed is effluent from biological treatment systems processing the waste

Reference

1. EPA/600/4-79/020 Method for Chemical analysis of water and wastes

2. Standard method for the examination of water and wastewater, 17th edition, 1989

CHEMICAL OXYGEN DEMAND **Titrimetric**
COD mg/l (low level)

Linear range	5-50 mg/l COD
Interferences	Traces of organic materials either from glassware or atmosphere may cause a positive error. Chlorides are oxidized by dichromate and represent a positive interference
Precision and accuracy	For a sample of distilled water containing 12.3 mg/l COD, the precision was reported as 34% with an accuracy of 0.3% relative error

1. Background

   1.1 The method can be applied to the analysis of surface waters, domestic and industrial wastes with low demand characteristics

2. Summary of Method

   2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid

   2.2 The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator

3. Apparatus

   3.1 Reflux apparatus

   Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint

4. Reagents

   4.1 Distilled water (should be very low in organic matter)

   4.2 Standard potassium dichromate solution

   4.3 Sulfuric acid reagent

   4.4 Standard ferrous ammonium sulfate solution

   4.5 Mercuric sulfate powder

4.6 Phenanthroline ferrous sulfate indicator solution

4.7 Silver sulfate powder

4.8 Sulfuric acid conc.

5. Preparation of standards

5.1 Standard potassium dichromate solution (0.025N)

5.11 Dissolve 12.259 g $K_2Cr_2O_7$, (primary standard grade, previously dried at 103^0C for two hours) in distilled water

5.12 Dilute to 1000 ml

5.13 Mix the solution thoroughly then dilute 100.0 ml to 1000 ml with distilled water

5.2 Sulfuric acid reagent

5.21 Dissolve (with continuous stirring) 23.5 g silver sulfate, in 4.09 kg bottle of sulfuric acid

5.3 Standard ferrous ammonium sulfate (0.025N)

5.31 Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water

5.32 Add 20 ml conc. H_2SO_4 (4.8), cool and dilute to 1 liter

5.33 This solution must be standardized daily against $K_2Cr_2O_7$ solution

5.4 Phenanthroline ferrous sulfate indicator solution

5.41 Dissolve 1.48 g of 1-10 (ortho) phenanthroline monohydrate, together with 0.70 g of $FeSO_4.7H_2O$ in 100 ml of water

6. Procedure

6.1 Standardization of ferrous ammonium sulfate solution

6.11 To 200 ml of distilled water add 25.0 ml of 0.025 N $K_2Cr_2O_7$ (4.2) solution

6.12 Add 20 ml of H_2SO_4 (4.8) and cool

6.13 Titrate with ferrous ammonium sulfate (4.4) using 3 drops of ferroin indicator (4.6)

6.14 The color change is sharp, going from blue-green to reddish-brown

$$\text{Normality} \quad \frac{(\text{ml } K_2Cr_2O_7)(0.025)}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

6.2 Place several boiling stones in the reflux flask, followed by 50.0 ml of sample or an aliquot dilute to 50.0. ml and 1 g of $HgSO_4$

6.3 Add 5.0 ml conc. H_2SO_4 (4.8), swirl until the mercuric sulfate has dissolved

6.4 Place reflux flask in an ice bath and slowly add (with swirling) 25.0 ml of 0.025 N $K_2Cr_2O_7$ (4.2) -

6.5 Now add 70 ml of sulfuric acid silver sulfate solution (4.3) to the cooled reflux flask, again using slow addition with swirling motion

6.51 If volatile organics are present in the sample, use an Allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization

6.6 Apply heat to the flask and reflux for 2 hours

6.7 Allow the flask to cool and wash down the condenser with about 25 ml of distilled water (if a round bottom flask has been used, transfer the mixture to a 500 ml Erlenmeyer flask washing out the reflux flask 3 or 4 times with distilled water)

6.8 Dilute the acid solution to about 300 ml with distilled water and allow the solution to cool to about room temperature

6.9 Add 8 to 10 drops of ferroin indicator (4.6) to the solution and titrate excess dichromate with 0.025 N ferrous ammonium sulfate (4.4) solution to the end point. The color changing from a blue-green to a reddish hue .

6.10 Simultaneously run a blank determination using a low COD water in place of the sample

7. Calculation

$$\text{COD, mg/l} = \frac{(A-B)N \times 8000}{S}$$

Where, A = volume of $Fe(NH_4)_2(SO_4)_2$ solute required for titration of the blank in ml

B = volume of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample in ml

N = normality of the $Fe(NH_4)_2(SO_4)_2$ solution

S = volume of sample used for the test in ml

Note: * For organic carbon concentrations greater than 50 mg/l the titrimetric method mid level should be used

* When the chloride level exceeds 1000 mg/l in the sample the titrimetric method high level should be used

* Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby eliminating the interference

* Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition

Reference

1. EPA/600/4-79/020 Method for Chemical analysis of water and wastes

2. Standard method for the examination of water and wastewater, 17th edition, 1989

TOTAL ORGANIC CARBON **UV promoted oxidation**
μg/l

Linear range	50 μg/l to 10 mg/l
Interference	Homogenizing of the sample may cause loss of organic carbon yielding low results
Precision and accuracy	For water samples containing 3.11 and 0.07 mg/l total organic carbon, the precision was reported as 4% and 29% respectively The accuracy was reported as 80% and 91% of recoveries for samples containing 5.0 and 1.0 mg/l total organic carbon respectively

1. Background

1.1 The method is applicable for drinking water and other waters containing carbonaceous matter which is soluble or has a particle size of 0.2 mm or less

2. Summary of method

2.1 A sample combined with acidified persulfate reagent is purged with helium to transfer inorganic CO_2 and purgeable organics to a CO_2 scrubber.

2.2 CO_2 is removed by helium purge

2.3 The purgeable organic carbon is then converted to methane by a reduction system

2.4 The methane is detected by a flame ionization detector

2.5 Nonpurgeable organics are subjected to intense ultraviolet illumination in the presence of the acidified persulfate reagent

2.6 Then nonpurgeables are converted to CO_2

2.7 In a second sparger by a helium purge CO_2 is transferred to the reduction system and into the detector for methane measurement

3. Apparatus

3.1 A blender

3.2 Carbon analyzer

3.3 Sampling device (a 50 ml glass syringe)

4. Reagents

4.1 Reagent distilled water

4.2 Potassium hydrogen phthalate stock solution

4.3 potassium hydrogen phthalate (2 mg/l)

4.4 potassium hydrogen phthalate (5 mg/l)

4.5 Potassium hydrogen phthalate (10 mg/l)

4.6 Acidified persulfate reagent

4.7 Carbonate-bicarbonate stock solution (1000 mg carbon/l)

4.8 Carbonate-bicarbonate standard solution (50 mg/l)

5. Preparation of standards

5.1 Potassium hydrogen phthalate stock solution

5.11 Dissolve 1.063 g of potassium hydrogen phthalate in reagent distilled water

5.12 Dilute to 1 liter

5.2 Potassium hydrogen phthalate solution (2 mg/l)

5.21 Pipet 4 ml of potassium hydrogen phthalate stock solution into a 1 liter volumetric flask

5.22 Dilute to the mark with reagent distilled water

5.3 Potassium hydrogen phthalate solution (5 mg/l)

5.31 Pipet 1 ml of potassium hydrogen phthalate stock solution into a 100 ml volumetric flask

5.32 Dilute to the mark with reagent distilled water

5.4 Potassium hydrogen phthalate solution (10 mg/l)

5.41 Pipet 2 ml of potassium hydrogen phthalate stock solution into a 100 ml volumetric flask

5.42 Dilute to the mark with reagent distilled water

5.5 Acidified persulfate reagent

5.51 Place 100 ml of reagent distilled water in a container

5.52 Add 5 g of potassium persulfate

5.53 Add 3 ml of concentrated (85%) phosphoric acid

5.6 Carbonate-bicarbonate stock solution (1000 mg C/l)

5.61 Place 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate in a 100 ml volumetric flask

5.62 Dissolve with reagent distilled water and dilute to the mark

5.7 Carbonate-bicarbonate standard solution (50 mg C/l)

5.71 Place 5 ml of the stock solution (5.6) in a 100 ml volumetric flask

5.72 Dilute to the mark with reagent distilled water

6. Calibration

6.1 Calibration of the analyzer

6.11 Run the reagent distilled water and potassium hydrogen phthalate solution (5.0 mg/l)

6.12 Transfer 10 ml of the solution with reagent to the first sparger and start analyzer cycle

6.13 Ignore the meter reading for the first cycle

6.14 Transfer a second 10 ml of the solution with reagent and start the cycle

6.15 Record the meter reading of the final carbon value for the reagent distilled water and the standard (5.3)

6.16 If the meter reading is more than 25% above or below the calculated value of standard (5.3) reanalyze and set the calibration within 25%

6.17 Reanalyze the system blank and begin 6.11 again, until the meter reading is within 25%

6.18 Calculate the factor for the deviation of the instrument reading for the standard from the calculated value

$$\frac{\text{standard reading-calculated value}}{\text{calculated value}} = \text{FACTOR}$$

Where, the calculated value is obtained by using the weight of potassium hydrogen phthalate and does not include the carbon contributed by the reagent distilled water

6.19 Calculate the adjusted reading by,

calculated value + (RDW - (FACTOR*RDW)) = mean reagent distilled value

6.20 Push in CALIBRATE button after READY light comes on and adjust the SPAN control to the ADJUSTED READING calculated in 6.19

7. Procedure

7.1 Analyze the standards 5.2 and 5.4 in order to check the linearity of the instrument (follow 6.11 to 6.14)

7.2 Record the meter reading of the final carbon value for each of the standards 5.2 and 5.4

7.3 Analyze the samples (follow 6.11 to 6.14)

7.4 Record the meter reading of the final carbon value for each sample

8. Calculation

8.1 The values are read off the final digital readout in μg/l

8.2 The system blank reading obtained must be subtracted from all reagent distilled water, standard and sample readings

Note: * Total organic carbon measured by this method is the sum of the purgeable organic carbon and nonpurgeable organic carbon

* Purgeable organic carbon is the organic carbon matter that is transferred to the gas phase when the sample is purged with helium and which passes through the CO_2 scrubber

* Nonpurgeable organic carbon is the remainder after removal of purgeable organic carbon and which is converted to CO_2

Reference

1. EPA/600/4-79/020 Methods for chemical analysis of water and wastes

5.6 Microbial Parameters

5.6.1 Introduction

Clean water is not a suitable substrate for the growth of microorganisms. The microbial growth in the water can be aggravated when water is contaminated with organic matter which provide food for microbes. For example, waste water usually contains a high level of germs specially pathogens which can then find their way in to surface and groundwater. Therefore, care should be taken that drinking water should be free from pathogenic microbes.

Microbiological analysis of water is used to monitor the ... diversity and density of microbes available in natural waters. In general such analysis includes determining the total number of germs capable of multiply..... colony counts) as well as the detecting special type of germs which are considered as to the presence of hygienically unacceptable contamination including pathogenic microbes.

Microbes in Water

Type	Shape	Status
Bacteria	unicellular	common
Viruses	unicellular > 1μm	rare
Yeasts	unicellular/cdn > < 2 μ	rare
Moulds	< 2μ de...unicellular	rare
Algae	unicellular/column	common
Protozoa	unicellular	common

Bacteria are the most important micro-organisms in water microbiology. Considerably smaller than bacteria are viruses which are significance for waste water and ..... is more or less numerous extract. However, analysis of water for viruses is time consuming and often troublesome and complicated. Yeast and moulds are not very common in surface

water and they only play a subordinate role in surface water microbiology. They are frequently detected together with bacteria when analysis are being carried out with culture. Algae can also be considered as a group of microbes living in water. However, their diversity and density can easily be detected under light microscopes. The same applies to the unicellular animals known as protozoa.

Bacteria are just visible under an optical microscope with thousand fold magnification especially when the cells have been .... by a suitable method.

5.6.2 *General requirement for microbiological work*

1. Analysis of pathogenic germs must be carried out only by experts with the appropriate special knowledge, observing the necessary precautions
2. Analysis of non-pathogenic germs also requires trained personnel and facilities which are suitably equipped for microbiological work
3. Glassware and equipment must be carefully cleaned and sterilized each time before they are used
4. All apparatus must be mechanically cleaned using cleaning agents, rinse first with clean tap water and then with 1% hydrochloric acid and finally with distilled or demineralized water. Glassware and equipment must be autoclaved at 120 °C for 30 min. before the cleaning process to avoid infection in the process of washing and rinsing
5. After cleaning the apparatus and glassware must be first dried then sterilized for 2 h at 180 °C to 200 °C in a hot air sterilizer
6. Culture media and culture solution must be sterilized with superheated steam in an autoclave at 121 °C for 20-30 min. at 1psi

7. Secondary infection or technical errors in sampling can falsify the accuracy of the extra microbiological investigation; therefore it is important that sampling must be carried out precisely

5.6.3 *The total colony counts - Pour plate method*

In order to determine the colony count, 1 ml of water in each case is pipetted into a sterile Petri culture dish and mixed with sterile nutrient gelatine or sterile nutrient agar. Nutrient gelatine is liquefied in a water bath at 35 °C and cooled to about 30 °C before pouring into the culture dish. Nutrient agar is liquefied in boiling water and cooled to 46 ° ± 2 °C before use. Before liquefying, a visual inspection should be carried out to check whether the nutrient medium contained in the tube is free of secondary infection, i.e. there are no indications of stored colonies of bacteria. 10 ml of the liquefied nutrient medium are added free of air bubbles to the pipetted water in the culture dish. Secondary infection from pumping or from water droplets on the outside of the nutrient medium glass should be avoided when filling the nutrient medium into the culture dish. Before pouring the nutrient medium, the tube edge should be flamed. Immediately after pouring, the nutrient medium and the water are mixed well by carefully swirling the culture dish sealed with a lid, using a motion in the shape of a "figure 8". The prepared culture must then be allowed to solidify in a horizontal position.

Nutrient gelatine solidifies at temperature below 25 °C and cooling is therefore necessary in certain circumstances.

If high counts are expected in the water to be examined, it is advisable to prepare a series of dilutions with sterile water and then to test the dilution stages 1:100, 1:1000, etc.

The culture with the solidified layer of nutrient medium is incubated at the prescribed temperature in the incubator or incubating chamber, whereby a maximum of 4 to 6 plates should be stacked one above the other. Plates and nutrient agar medium should be turned over after solidification and incubated with the layer of nutrient medium upwards in order to avoid precipitation of condensed water, particularly at higher incubation temperatures.

After the prescribed incubation period has elapsed, the visible colonies are counted with

the aid of a magnifying glass with 6x to 8x magnification. In order to facilitate counting, any suitable counting device can be used. Only cultures with a count not exceeding 300/ml should be used to determine the count. If dilution series were prepared of contaminated waters, those plates on which between 30 and 300 colonies have grown should be counted. If more than 1/4 of the surface of the nutrient medium is overgrown with spreading colonies, the plate should be discarded.

Gelatine cultures can only be incubated at 20 ^{0} ± 2 ^{0}C, as they liquefy at higher temperatures. Liquefication of gelatine is also possible as a result of microorganisms with proteolytic enzymes. It is therefore, recommended that an agar culture be prepared in addition to gelatine cultures, in which the germ yield, is as a rule higher than in agar cultures, so that figures for the numbers of germs can still be given even when gelatine liquefiers are present. Gelatine liquefiers frequently occur in surface water. The figures obtained from dilution series should be multiplied according to the stage of dilution

1. **If the colony count determined lies above 100, the figures are rounded down to complete tens, in the case of values over 1000 to complete hundreds, etc.**

2. **It is usual to indicate the nutrient media used and the length and temperature of incubation in the analysis report.**

5.6.4 The membrane filter method

In the membrane filter process, larger quantities of water can be pressed or sucked through a sterile membrane filter inserted in the sterile filtering device. The filter is then stretched free of bubbles on the surface of the solidified nutrient medium in a Petri culture dish and the culture thus prepared is then incubated. The nutrient substances in the medium migrate through the layer of the membrane filter to the germs on its upper surface so that they can form colonies there. It is important in this context that the surface of the filter does not remain excessively damp, because the germs float away in the residual water and no countable individual colonies are formed. In general, fewer

germs are recorded by the membrane filter method than by the pour-plate method which is officially prescribed in many cases.

Instead of the nutrient agar in Petri culture dishes, cardboard culture discs may also be used. The manufacturers of cardboard culture discs have incorporated soluble nutrient substances into the cardboard disc and sterilized them. The analyst must moisten the cardboard culture disc with sterile water according to the manufacturer's instructions and then place the filter disc on the cardboard, also making sure that there are no air bubbles.

Colony counts can also be made using the surface method. In this 0.1 to 0.3 ml water is spread out on the surface of the solidified, sterile agar culture medium in the petri dish with the aid of a sterile spatula (Drigalski spatula). However, this method also results in certain differences from the pour-plate method.

Detection of Escherichia coli and coliform bacteria

The cultivation of these microbes is carried out in one process. Two methods can be employed:

1. Liquid enrichment with lactose-peptone solution
2. Membrane-filter method using endoagar or endo-nutrient cardboard disks

5.6.5 Liquid enrichment method

Where the only question to be decided is whether Escherichia coli and/or coliform bacteria are present in 100 ml water or not, it is sufficient to mix 100 ml of the water being analyzed with 100 ml lactose-peptone solution of double concentration. After an incubation period of 20 ± 4 hours at 37 °C, an examination is done to see whether acid and gas are being formed or not. If they are not being formed, the composition of the water in terms of its levels of Escherichia coli and coliform bacteria meets the drinking water requirements and the analysis can be stopped. If, however, it is established that the lactose is fermenting with the formation of gas and acid, one has to establish whether the germs causing this are Escherichia coli or coliform bacteria, or whether the germs

do not belong to the group of coliforms. For this, a small quantity of the lactose-peptone solution, which has become turbid as a result of the growth of germs, is removed with a sterile platinum loop and fractionated on the endoagar (fractionated means that the spreading is not carried out with the loop over the entire endo plate but that instead just one single strip of germs is applied to the surface of the culture medium at the edge of the Petri dish).

With the second loop, part of the material is now spread out on a third of the culture medium surface at right angles to the first. Then the dish is turned through a further 20^0 and part of the material is applied with a third sterile loop to the part of the culture medium surface which has not yet been coated. It is possible in this way to obtain individual colonies, which can then be identified in the so-called "colour series".

Moist, dark red colonies with a gold, iridescent metallic sheen can be suspected of being Escherichia coli. Coliform bacteria grow as moist, red colonies with a continuous or discontinuous metallic sheen, with or without the formation of slime.

Generally speaking, colour series work today is carried out using the prepared systems or kits which are commercially available, such as API, Entero-tube, Titertek, etc. These consist of prepared culture medium systems which are inoculated with the cell material from one single colony and then incubated. Handling and incubation must be carried out in accordance with the manufacturer's instructions. Evaluation is frequently carried out by determining a number code on the basis of positive or negative metabolic reactions which take place with the individual culture mediums used. After determining the number code, one can read off the type of germ the suspect colony consists of in the catalogue supplied.

When such prepared or ready-to-use systems are not available, the identification culture mediums must be prepared in accordance with the recipes given in the section on culture media. These are then inoculated and evaluated in accordance with the characteristics

obtained.

Incubation : at 35 °C for 48 hrs

Membrane filter method

1. Preparation of plate

Dispense 1 ml portion of sterile medium into 50 x 9 mm Petri dishes. Let them solidify at room temperature. Solidified plates may be stored inverted in a plastic bag in a refrigerator preferably no longer than 1 week.

Filter appropriate volume of sample (i.e. to give 20 to 200 colony forming units per filter) through 0.45 μ grided membrane filter pare. (47 mm in diameter) under partial vacuum pressor. Rinse the filter with sterile water and place it an agar in Petri dish. Incubate at 35 °C for 48 h if using m-HPC agar.

Counts of bacteria of fecal origin in surface water which suffer little human impact vary from <1 to 3000 organisms per 100 ml. However, surface water in areas of high population density can have counts up to 10 million organisms per 100 ml.

Media	Use for	Remarks
Tryptone glucose yeast agar	pour plate, spread plate	gives lower counts
m-HPC agar	membrane filter	high nutrient media
R2A agar	pour plate, spread plate	gives high counts

Spread plate method

* Prepare sample dilution as required, pipept 0.1 or 0.5 ml sample on to surface of pre-dried agar plate.

* Distribute inoculum evenly over the surface using a sterile bent glass-rod while rotating the dish by hand.
* Let inoculum be absorbed completely into the media before incubating.

Determination of Total coliform groups

The coliform group comprises all aerobic and facultative anaerobic g... negative non-spore forming rod-shaped bacteria that ferment lactose with gas and acid formation within 48 h at 35 ^{0}C.

Method for determination of coliform groups

1. Multiple tube fermentation Technique
2. Membrane filter Technique

Multiple-Tube fermentation Technique

In this method results of the examination of replicate tubes and dilutions are reported in terms of the Most Probable Number (MPN) of organisms present which indicates the mean density of coliform present in the sample. Bacterial density can be estimated by the formulae given or from the table using the number of positive tubes in the multiple dilutions.

Media: Various media have been proposed for the study of anaerobic bacteria. There is no single medium that we can recommend unequivocally.

CHAPTER 6 LABORATORY ORGANIZATION, DATA PROCESSING, QUALITY CONTROL AND DISSEMINATION

6.1 Laboratory Organization

Laboratories must be organized or set up to meet the objectives of each assessment programme. Attention should be paid mainly to the choice of analytical methods. In many countries monitoring laboratories are organized on two tires. Regional laboratories (lower level) to conduct basic determination not requiring very complex equipment and central laboratories (higher level) to conduct more complex analysis requiring elaborate equipment and well trained personnel. In addition central laboratories often provide the regional laboratories with methodology. Compatibility of water quality data from different laboratories can only be ensured if identical or at least similar methods are used.

Progress in analytical chemistry has stimulated the appearance of new, more elaborate and more efficient methods. However, replacement of existing methods often results in data compatibility with older methods which can cause problems in the statistical analysis of data time series. Studies of the compatibility of new with old methods must be undertaken. If new method is accepted into a monitoring programme an overlap period is required where samples are analyzed by both the new and old methods.

6.2 Data Processing

Analytical data collected by laboratories, together with the information on sampling and hydrological parameters are usually sent to data treatment center which is not practicable in our country. However, it is reasonable to have a common information centre which can summarise the data from the entire country. The main objective of a data processing centre is the development, replenishment and management of data bank. At the initial stage of data bank development, attention should be focused principally on the accuracy of the stored information because the forms of output may be improved in the process of data bank exploitation.

6.3 Quality Control Program

Quality Control [QC] is the process of monitoring laboratory analyses to ensure results of known and defensible quality. A QC programme monitors test performance, and helps to identify problems with a specific analysis, and helps scientists in assessing the reliability of results. **Quality Control Programme** is generally confined to a particular laboratory.

Basic QC programme involves the analysis of control sample at the same time water samples are analyzed for the constituent of interest. The quality control materials are drawn from a pool that allows the same sample to be analyzed at frequent intervals over a long period (these controls will be supplied by the central laboratory). This process provides data on the same sample over an extended period.

It is common for a specific control sample to be analyzed several times a day for a period of a year or more. Data obtained from these analyses are processed statistically, and trends in the values are monitored to asses the testing reliability.

Control samples are provided with control values and +/- standard deviation range. This information allows an individual laboratory to compare its data. The data may help to identify a particular problem with an analysis or may indicate a better method for a procedure that is to be modified.

A good QC programme requires the following tests to be done regularly to ensure the reliability of data:

1. Assessment of Analyst competence
2. Reagent blank check
3. Calibration with standards
4. Duplicate analysis
5. Errors and Control charts

6.3.1 Assessment of Analyst Competence

It is very important to be conversant with a particular analytical method before proceeding with real-world analysis. Follow the procedure given below to self-check your ability.

Methodology

1. Select the water quality parameter that you intend to use in the assessment of analyst competence.
2. Prepare a standard sample having a concentration between 5 and 50 times of the detection limit.
3. Divide this standard into four portions of same concentration for replicate analysis.
4. Determine the concentration of replicates and record the results to calculate the precision of analysis.
5. Compare your results with the following chart. If the results do not give an acceptable value, get the confidence of the method before proceed further.

Analysis	Precision (%) Concentration < 20xD.L	Precision (%) Concentration > 20xD.L
Metals	75 - 125	90 - 110
Anions	75 - 125	90 - 110
Nutrients	75 - 125	90 - 110
TOC	75 - 125	90 - 110

[Source: Natrella, M.G., 1966. Experimental Statistics

6.3.2 Reagent Blank Check

The purity of reagents plays an important role in the overall results. Please follow the guidelines given in table x when selecting chemicals to prepare reagents for a particular analysis.

Rules of Thumb

Rule 1: Always analyse a minimum of 5% of the sample load as reagent blanks.

Rule 2: Analyse a reagent blank after any sample with a concentration than that of the highest standard to avoid carryover from one sample to another.

6.3.3 Calibration

Rules of Thumb

Rule 1: Always use four standards to plot calibration curve when an analysis is initiated.

Rule 2: Verify the validity of calibration curve by analyzing two standards within the linear range before using previous calibration curve again.

Rule 3: Do not report the values above the highest standard used in the calibration curve. Do a dilution to bring the concentration of the sample down to the linear range of calibration curve.

Rule 4: Remember! Lowest reportable value is the detection limit of the method, provided the result is less than 10 time detection limit.

Rule 5: If a blank is subtracted, report the result even if it is negative.

6.3.4 Duplicate Analysis

In order to assess the precision duplicate analyses is done. Always analyze 5% of the samples in duplicate. Check with table X for acceptable results of duplicate analysis.

6.3.5 Errors and Control Charts

Two types of errors may be encountered during analytical process: random and systematic.

Random Error

A random error is one with no trend or means of predicting it. Frequently occurring random errors include:

(a) Mislabeling a sample

(b) Pipeting errors

(c) Improper mixing of sample with reagents

(d) Voltage fluctuations not compensated by the instrument circuitry

(e) Temperature fluctuations.

Systematic Error

A systematic error will be seen as a trend in data. Control values gradually rise (or fall) from the previously established limits. This type of error include:

(a) Improper calibration

(b) Deterioration of reagents

(c) Sample instability

(d) Instrument drifts

Control Charts

Both random and systematic errors can be identified and corrected by plotting the control solution results in the form of **Control Charts.**

Construction of Control Charts

1. Obtain the mean and standard deviation of control solution. Usually the mean and standard deviation of the control solution is provided from the Central Monitoring Laboratory (Otherwise prepare the control solution as prescribed in note 1 to determine these parameters).
2. Plot the following lines as Y- co-ordinates:

Line 1	:	Mean (x)
Line 2	:	Warning limits (WL) |mean +/- 3s|
Line 3	:	Control limits (CL) |mean +/- 2s|

3. Plot the date analyzed as X- co-ordinates.
4. Prepare a separate control chart for each water quality parameter, and display it in the lab.

5. When conducting routine analyses, always include a sample of control solution in the batch.

6. Plot the results of control solution in the respective control chart. Before proceeding further analyses note the following:

Scatter of points	Precision
Average of points	Systematic change in calibration curve

Check Points

A. Control limit (CL)

If one measurement exceeds CL, repeat the analysis immediately. If the repeat within the CL, continue analysis. If it exceeds stop analysis and correct the problem.

B. Mean line (ML)

If six successive samples are above the ML, analyze another sample. If the next point is below the ML, continue analysis; if the next point is on the same side, discontinue analyses and correct the problem.

C. Warn limit (WL)

If two out of three successive points exceed a WL, analyze another sample. If the next point is less than WL, continue analysis; if the next point exceeds WL, discontinue analysis and correct the problem.

Note: * As a rule of thumb, always prepare a control solution of concentration near upper limit of the calibration curve.

6.4 Quality Assurance Programme

A good quality control programme is part of the overall goal of **Quality Assurance [QA]**, which encompasses every aspect of the laboratory operation from sample collection & preservation to the clear reporting of the final laboratory result. Therefore Quality Assurance is concerned with the total process, not simply control sample result validation.

Quality Assurance Check List

1. Quality assurance plan with authorization
2. Calibration graphs with recording facilities of occasional calibration points
3. Laboratory mean control charts
4. Quick guide of analytical methods
5. Quick guide of the operation/preventive maintenance of equipment
6. A laboratory copy of the operating manual and detection limit chart of all parameters analyzing in the lab
7. Status report of purity of reagents
8. Waste disposal procedures
9. Unified data coding sheets
10. Laboratory safety procedures
11. Laboratory book/ data recording

If these information are not in order, please make immediate arrangements to have the documents ready in the laboratory.

6.5 Interpretation and dissemination of data

Interpretation of data and dissemination of results are the final two steps in an assessment programme. Correctly, interpreted data will not be of much use if they are not disseminated to all relevant authorities. Scientists and public is a form which is readily understandable by and acceptable the largest audience. The form and level of data presentation is therefore crucial. Usually, the interpretation of data is undertaken by subject specialists. Interpretations should always refer to the objectives and should also propose improvements including simplifications in the monitoring activities as well as the need for further research and guidelines for environmental planning and economic development. Subsequently these findings should be discussed with the appropriate local, regional and national authorities and as required others such as the industrial development and or national planning b.... Beside these authorities results should be communicated to water resources management. The public, association for environmental protection, educational institution, other countries and to international organizations.

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APPENDIX UNITS

Equivalence of units

Quantity	Old style	SI system
Volume	l ml	dm^3 cm^3
Chemical amount	eq (substance from context)	mol (substance specified e.g. Na^+, $\frac{1}{2}Ca^{2+}$, $\frac{1}{5}KMNO_4$)
Mass concentration	$\mu g\ ml^{-1}$ = $mg\ l^{-1}$ = ppm = gm^{-3}	$\mu g\ cm^{-3}$ = $mg\ dm^{-3}$ = gm^{-3}
Chemical concentration	N = $eq\ l^{-1}$ (substance from context) meq l^{-1}	mol dm^{-3} (substance specified) mmol dm^{-3}

The non-standard symbol of chemical concentration 'M' applied to the SI 'mol dm^{-3}' is very useful:

for example Ca^{2+} 6.0 meq l^{-1}
$\frac{1}{2}Ca^{2+}$ 6.0 mmol l^{-1}
$\frac{1}{2}Ca^{2+}$ 6.0 mmol dm^{-3}
$\frac{1}{2}Ca^{2+}$ 6.0 mM

are interchangeable descriptions when used in an ionic balance calculation.

	%	specific gravity	concentration (mol l^{-1})
HCl	25	1.127	7.7
	36-38	1.18	12
HNO_3	65	1.40	14
	70	1.42	16
	96	1.50	23
	100	1.52	24
H_2SO_4	25	1.36	3
	96-98	1.84	18
H_3PO_4	88-90	1.75	16
	99	1.88	19
NH_4OH	25	0.91	13.4
	30	0.896	16
	35	0.88	19.5