HYDROLOGY PROJECT
Technical Assistance

World Bank & Government of The Netherlands funded

Training module # WQ - 35

Emission Spectroscopy and Nephelometry

New Delhi, February 2000

Table of contents

1. Module context

This module introduces the principles of emission spectroscopy and nephelometry, and the instruments which are used for these analyses. Some other related modules are listed below.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

No.	Module title	Code	Objectives
1.	Basic water quality concepts	**WQ - 01**	• water pollutants • ambient water quality standards • monitoring water quality
2.	How to measure pH	**WQ - 07**	• pH meter and electrodes • precautions
3.	Use of Ion selective probes	**WQ - 33**	• precautions required in use of ion selective probes.
4.	Absorption Spectroscopy	**WQ - 34**	• understand the principle of absorption spectroscopy • explain the use of absorption spectroscopy for chemical analyses

2. *Module profile*

Title	:	Emission Spectroscopy and Nephelometry
Target group	:	HIS function(s): Q2, Q3, Q5, Q6
Duration	:	One session of 60 min.
Objectives	:	After the training the participants will be able to*:*

- understand the principles of emission spectroscopy and nephelometry
- explain how emission spectroscopy and nephelometry are used for specific laboratory analyses

Key concepts	:	

- emission spectroscopy
- flame photometers
- nephelometry and turbidimetry
- turbidimeters
- applications

Training methods	:	Lecture, exercises, discussion, demonstration of equipment
Training tools required	:	Board, flipchart, OHS
Handouts	:	As provided in this module
Further reading and references	:	

- Chemistry for environmental engineers – C.N.Sawyer, P.L.McCarty & G.F.Parkin, McGraw – Hill, Inc, 1994
- Standard methods for the examination of water and wastewaters, AWWA, 19th edition, 1995

3. *Session plan*

No	Activities	Time	Tools
1	*Preparations*		
2	*Introduction*: • Ask participants to state different instruments for water quality analysis • Explain reasons to use emission spectroscopy and nephelometry	10 min	OHS
3	*Flame photometers, theoretical concepts and definitions:* • Basic instrument • Means of producing emission • Filter, photocell, galvanometer • Principle of sodium analysis	20 min	OHS
4	*Turbidimeter and nephelometer:* • Difference between analyses, and instruments • significance of turbidity • instrument components • Principle of sulphate analysis	20 min	OHS
5	*Maintenance*	5 min	
6	*Exercise*		
7	*Wrap up and evaluation*	5 min	

4. *Overhead/flipchart master*

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 24-26, maximum two levels
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/Equations	OHS-Equation	Use of a table will ease horizontal alignment over more lines (columns) Use equation editor for advanced formatting only

Emission spectroscopy and nephelometry

- Emission spectroscopy and Nephelometry are 2 common analytical methods

- Both methods rely on measurement of light

- In Emission spectroscopy, the light *Emitted* by heated metal atoms in vapourised water

- In Nephelometry, the light *Scattered* by particles in water is measured

- Nephelometry is related to 'Turbidimetry'

Emission spectroscopy

- Flame emission spectroscopy:

    - *Also known as 'Atomic Emission Spectroscopy'*

    - *Also known as 'Flame Photometry'*

- Primarily used in the determination of alkali metals: K^+, Na^+

- Other metals which can be measured: Ca^{++}, Mg^{++}, Sr^{++}

Emission spectroscopy: Principle (1)

- Many metallic elements will emit a characteristic radiation, when subjected to suitable excitation (e.g. flame)

- The *Intensity* of emitted radiation, at some particular wavelength, can be correlated to the amount of element present
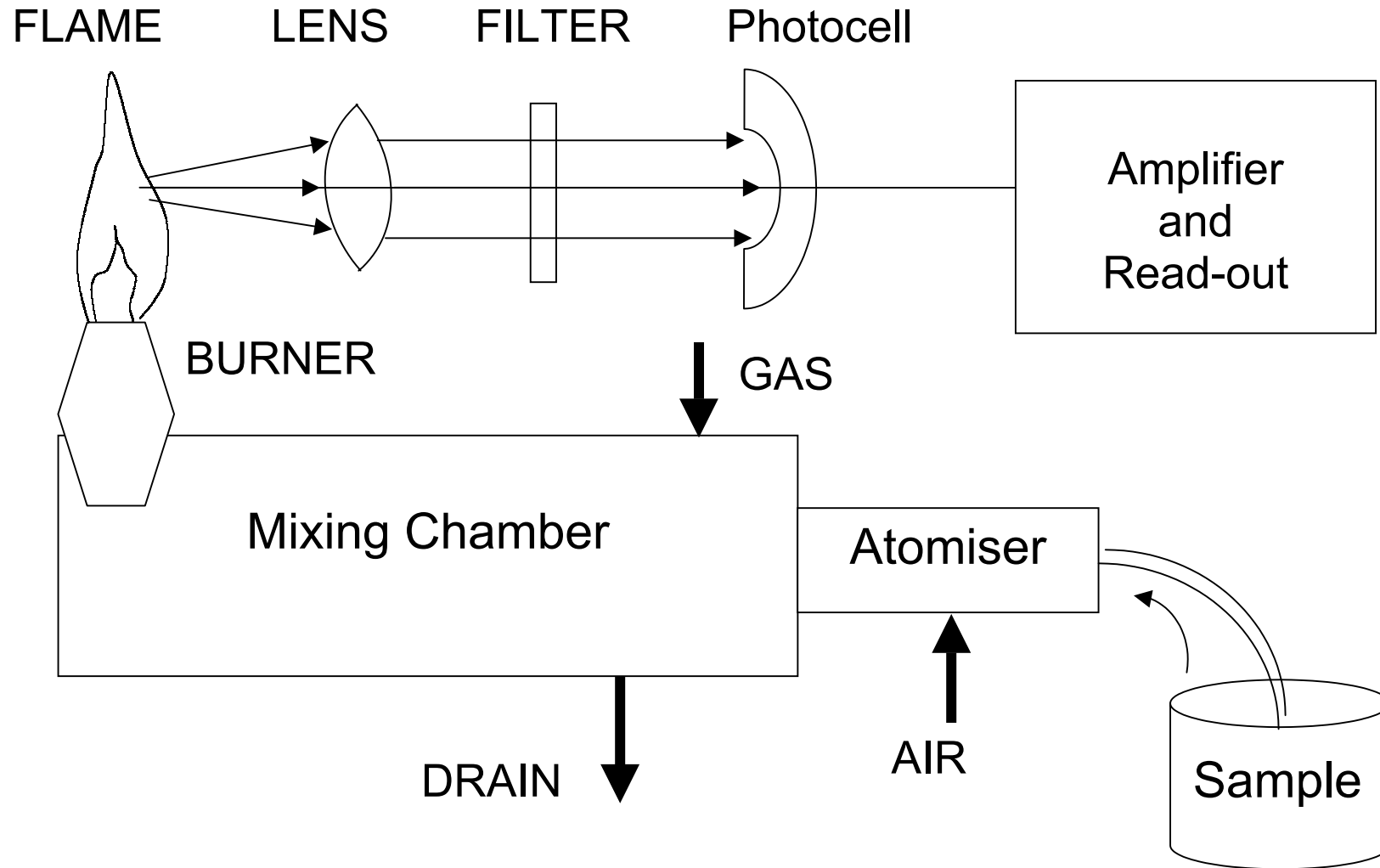
Emission spectroscopy: Principle (2)

- *Liquid sample is sucked into instrument*

- *Metal salts get vaporised ('atomized')*

- *Metals atoms are excited by energy of the flame*

- *Excited atoms emit radiation characteristic of the metal*

- *Intensity of radiation increases with concentration of element*

- *Linear relation between intensity & concentration*

Emission spectroscopy: Principle (3)

- Emitted radiation is measured:

    - *Emitted radiation passes through lens and optical filter*

    - *Photocell reads the characteristic radiation*

    - *Amplifier & digital read-out of radiation intensity*

Emission spectroscopy: Instrument (1)

FLAME   LENS   FILTER   Photocell

Amplifier and Read-out

BURNER

GAS

Mixing Chamber

Atomiser

DRAIN

AIR

Sample

Emission spectroscopy: Instrument (2)

- The Atomiser:

  - *stream of air is blown across the opening to the sample inlet jet, creates suction in central tube*

  - *sample is drawn to the air stream and a fine mist is formed*

- The Flame:

  - *Typically acetylene gas together with air*

- Sensor:

  - *Lens, slit, filter, photocell, amplifier and read-out*
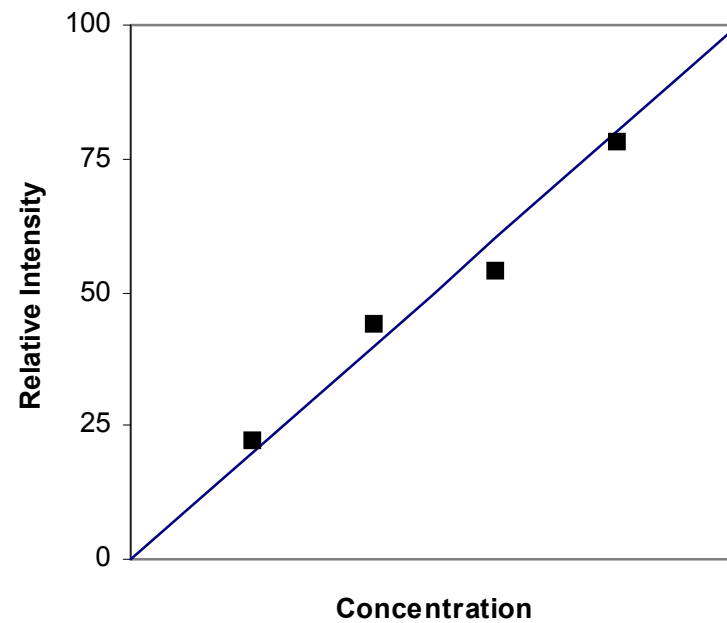
Emission spectroscopy: Measurement (1)

- For Na^+ and K^+ the spectra are simple, consisting of a few wavelengths

- Na^+ produce a characteristic yellow emission at 589 nm,

- Concentrations can be measured to $\pm$ 1 mg/l

- K^+ produce a characteristic emission at 766.5 nm

- Concentrations can be measured to $\pm$ 0.1 mg/l

Emission Spectroscopy: Measurement (2)

- Make series of standard solutions, known concentrations

- Set flame photometer to correct λ

- Measure emission intensity of standards

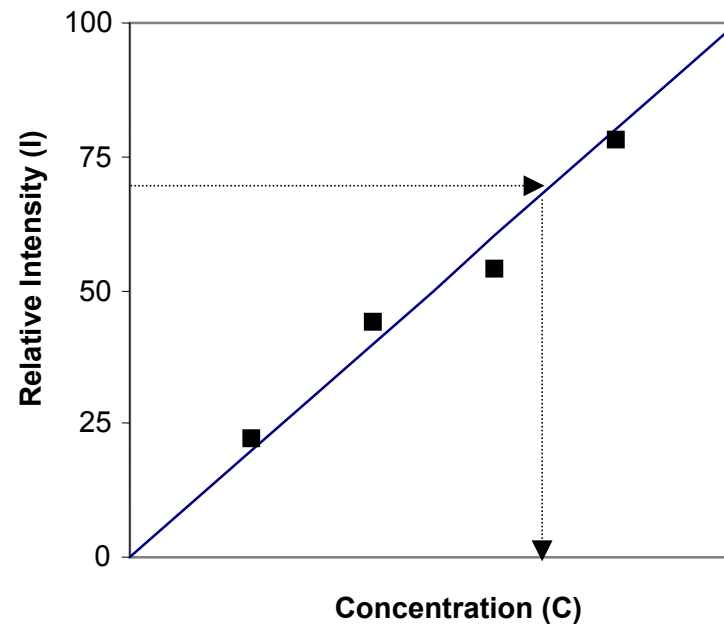- Plot calibration curve: Intensity vs. Concentration

Emission spectroscopy: Measurement (3)

● Calibration curve: Linear relation between Intensity & Concentration

Emission spectroscopy: Measurement (4)

● Measure Intensity (I) of unknown, read Concentration (C)

Nephelometry & Turbidity (1)

- Turbidity is one of the basic measurements of water quality

- Turbid water looks dark or 'dirty'

- Turbidity is an important consideration for many uses of water:

    - *potability of water*

    - *use in industry*

    - *ecology*

Nephelometry & Turbidity (2)

- Turbidity caused by suspended and colloidal particles in water

- Particles can be inorganic and organic:

    - *clay, silt, mud, silica, rust, calcium carbonate, algae, bacteria, organic material*

- Particles absorb and scatter light

- Turbidimetry and Nephelometry are two (similar) methods to measure turbidity
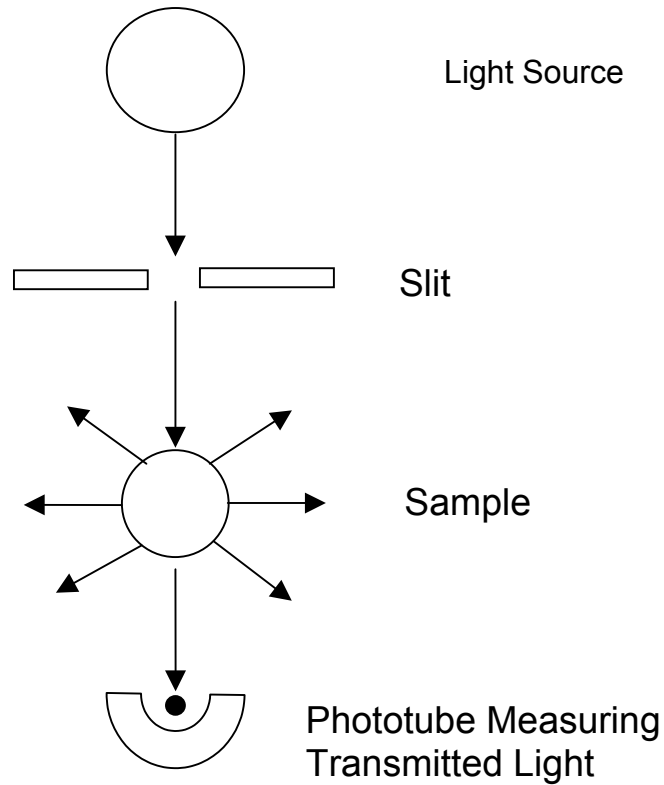
Nephelometry & Turbidity (3)

- In Turbidimetry, light p*assing through* a sample is measured

    - *Instrument used is a 'Turbidimeter'*

    - *A spectrophotometer or photometer can be used as a turbidimeter to measure light transmission/absorbance at $\lambda = 420$ nm*

Nephelometry & Turbidity (4)

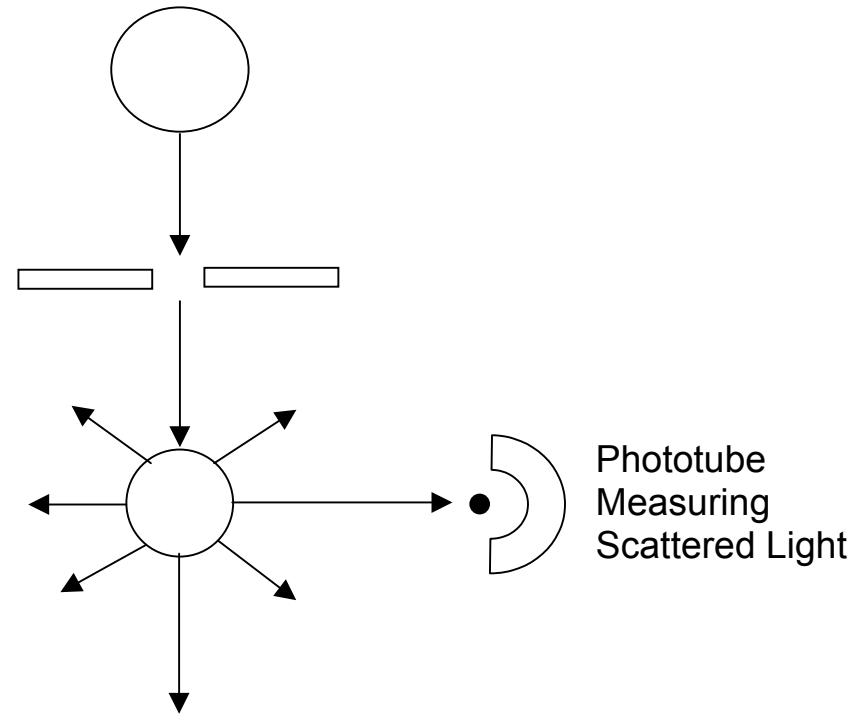● In Nephelometry, the light S*cattered* by the suspended particles in a sample is measured

- *Instrument used is a 'Nephelometer' or 'Nephelometric Turbidimeter'*

- *Nephelometry is more sensitive for very dilute suspentions*

Nephelometry & Turbidity (5)

Light Source

Slit

Sample

Phototube Measuring
Transmitted Light

Turbidimeter

Phototube
Measuring
Scattered Light

Nephelometer

Nephelometry & Turbidity: Units

- Basic unit of turbidity is Nephelometric Turbidity Unit (NTU)

- NTU has replaced previous unit of 'Jackson candle turbidity units' (JTU)

- Formazin suspensions are used as a standard for calibration

- Formazin particles have uniform size and shape

Nephelometry & Turbidity: Typical Values

Water Type	NTU
Surface Water (Rainy season)	1000 and above
Treated tap water	1 to 2
De-mineralised water	0.1 to 0.5
Water filtered through membrane filter	0.05 or less

Nephelometry: Interferences

- All dust, dirt, scratches or finger marks on the instrument will interfere with the measurements

- Instrument components and sample tubes must be kept dry and clean

5. Evaluation sheets

6. *Handout*

Emission spectroscopy and nephelometry

- Emission spectroscopy and Nephelometry are 2 common analytical methods
- Both methods rely on measurement of light
- In Emission spectroscopy, the light *Emitted* by heated metal atoms in vapourised water
- In Nephelometry, the light *Scattered* by particles in water is measured
- Nephelometry is related to 'Turbidimetry'

Emission spectroscopy

- Flame emission spectroscopy:
    - *Also known as 'Atomic Emission Spectroscopy'*
    - *Also known as 'Flame Photometry'*
- Primarily used in the determination of alkali metals: K^+, Na^+
- Other metals which can be measured: Ca^{++}, Mg^{++}, Sr^{++}

Emission spectroscopy: Principle (1)

- Many metallic elements will emit a characteristic radiation, when subjected to suitable excitation (e.g. flame)
- The *Intensity* of emitted radiation, at some particular wavelength, can be correlated to the amount of element present

Emission spectroscopy: Principle (2)

- *Liquid sample is sucked into instrument*
- *Metal salts get vaporised ('atomized')*
- *Metals atoms are excited by energy of the flame*
- *Excited atoms emit radiation characteristic of the metal*
- *Intensity of radiation increases with concentration of element*
- *Linear relation between intensity & concentration*

Emission spectroscopy: Principle (3)

- Emitted radiation is measured:
    - *Emitted radiation passes through lens and optical filter*
    - *Photocell reads the characteristic radiation*
    - *Amplifier & digital read-out of radiation intensity*

Emission spectroscopy: Instrument (2)

- The Atomiser:
    - *stream of air is blown across the opening to the sample inlet jet, creates suction in central tube*
    - *sample is drawn to the air stream and a fine mist is formed*
- The Flame:
    - *Typically acetylene gas together with air*
- Sensor:
    - *Lens, slit, filter, photocell, amplifier and read-out*

Emission spectroscopy: Measurement (1)

- For Na^+ and K^+ the spectra are simple, consisting of a few wavelengths
- Na^+ produce a characteristic yellow emission at 589 nm,
- Concentrations can be measured to $\pm$ 1 mg/l
- K^+ produce a characteristic emission at 766.5 nm
- Concentrations can be measured to $\pm$ 0.1 mg/l

Emission Spectroscopy: Measurement (2)

- Make series of standard solutions, known concentrations
- Set flame photometer to correct λ
- Measure emission intensity of standards
- Plot calibration curve: Intensity vs. Concentration

Emission spectroscopy: Measurement (3)

- Calibration curve: Linear relation between Intensity & Concentration

Emission spectroscopy: Measurement (4)

- Measure Intensity (I) of unknown, read Concentration (C)

Nephelometry & Turbidity (1)

- Turbidity is one of the basic measurements of water quality
- Turbid water looks dark or 'dirty'
- Turbidity is an important consideration for many uses of water:
    - *potability of water*
    - *use in industry*
    - *ecology*

Nephelometry & Turbidity (2)

- Turbidity caused by suspended and colloidal particles in water
- Particles can be inorganic and organic:
    - *clay, silt, mud, silica, rust, calcium carbonate, algae, bacteria, organic material*
- Particles absorb and scatter light
- Turbidimetry and Nephelometry are two (similar) methods to measure turbidity

Nephelometry & Turbidity (3)

- In Turbidimetry, light p*assing through* a sample is measured
    - *Instrument used is a 'Turbidimeter'*
    - *A spectrophotometer or photometer can be used as a turbidimeter to measure light transmission/absorbance at*
      $\lambda = 420\ nm$

Nephelometry & Turbidity (4)

- In Nephelometry, the light S*cattered* by the suspended particles in a sample is measured
    - *Instrument used is a 'Nephelometer' or 'Nephelometric Turbidimeter'*
    - *Nephelometry is more sensitive for very dilute suspensions*

Nephelometry & Turbidity: Units

- Basic unit of turbidity is Nephelometric Turbidity Unit (NTU)
- NTU has replaced previous unit of 'Jackson candle turbidity units' (JTU)
- Formazin suspensions are used as a standard for calibration
- Formazin particles have uniform size and shape

Nephelometry & Turbidity: Typical Values

Water Type	NTU
Surface Water (Rainy season)	1000 and above
Treated tap water	1 to 2
De-mineralised water	0.1 to 0.5
Water filtered through membrane filter	0.05 or less

Nephelometry: Interferences

- All dust, dirt, scratches or finger marks on the instrument will interfere with the measurements
- Instrument components and sample tubes must be kept dry and clean

Add copy of Main text in chapter 8, for all participants.

7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

8. Main text

Contents

Emission Spectroscopy and Nephelometry

1. Introduction

Atomic emission spectroscopy and nephelometry are two different methods which can be used to measure chemical substances in water samples. Both methods rely on the measurement of light.

Atomic emission spectroscopy

In emission spectroscopy, the light radiation *emitted* by metal atoms when heated in a flame is measured. If a solution containing a metallic salt (or some other metallic compound) is aspirated into a flame (e.g. of acetylene burning in air), a vapour which contains atoms of the metal may be formed. Some of these gaseous metal atoms may be raised to an energy level which is sufficiently high to permit the emission of radiation characteristic of the metal, e.g. the characteristic yellow colour imparted to flames by compounds of sodium. This is the basis of atomic flame emission spectroscopy, which is also referred to as flame emission spectroscopy (FES) or flame photometry.

Atomic emission spectroscopy is used in the determination of alkali metals as they are excited by the relatively low excitation energy of the flame. Sodium and Potassium are more frequently determined because of their importance in aquatic and biological systems.

Turbidimetery and Nephelometry

In Nephelometry, the light *scattered* by particles in water is measured. Suspension of particles in water interfering with passage of light is called turbidity. The turbidity of a sample may be measured either by its effect on the scattering of light, which is termed 'Nephelometery', or by its effect on transmission of light, which is termed 'Turbidimetery'. These methods use common electric photometers to measure light intensity. Nephelometric measurement is more sensitive for very dilute solutions, but for moderately heavy turbidity, either this or turbidimetric measurements can be made.

In turbidimetry, the amount of light passing through a solution is measured. The higher the turbidity, the smaller the quantity of light transmitted.

In nephelometry, on the other hand, the detecting cell is placed at right angles to the light source to measure light scattered by the turbidity particles.

2. Atomic emission spectroscopy

Atomic emission spectroscopy is also known as 'Flame Emission Spectroscopy' or 'Flame Photometry'. The instrument used for analysis is commonly known as the 'Flame Photometer'. The method is used primarily for analysis of alkali metals (K^+ and Na^+). Other metals can be measured with emission spectroscopy, such as Ca^{+2}, Mg^{+2}, Sr^{+2} , though alternative methods may be better.

Although flame spectroscopy was first studied by in 1860, it was established in 1930 as an important analytical method for the determination of alkali metals.

It is known that many elements under suitable excitation emit radiations of characteristic wavelength. This fact is utilised in the familiar qualitative flame test for the alkali and alkaline earth elements. For these elements, such as sodium and potassium, the spectra are simple, consisting of only a few wavelengths.

General Principle

The general principle of the analysis is that many metallic elements will emit a characteristic radiation when subjected to a suitable excitation (e.g. flame).

Quantitative analysis with the spectrograph is based on an empirical relation between the intensity (power) of the emitted radiation of some particular wavelength and the quantity of the corresponding elements in the sample.

General Method of Analysis

The basic diagram of a flame photometer is shown in Figure1. In this method of analysis, first an emission radiation is created:

- the solution being tested is first sucked into the instrument
- In the **atomiser**, air at a certain pressure is blown in. Two types of atomisers are available: Right angle type, and Concentric type. In both atomisers, a stream of air is blown across the opening of the sample inlet jet, creating a suction. The sample is drawn into the air stream, where it forms a fine mist. The sample is broken into fine particles and the metal salts get vaporised (atomised)
- Particles get carried with the compressed air towards to the **mixing chamber**. Here the compressed air carrying metal particles is mixed with the fuel gas. Fuel gas is typically acetylene. Ordinary cooking gas may also be used.
- The fuel gas mixture is fed into the **burner** for producing the flame.
- In the **flame** the metal particles emit radiation, producing a colour whose wavelength is characteristic of the element present in the sample. The intensity of the radiation varies with the concentration of the metallic ions in the solution.

After the radiation is emitted, it must then be measured:

- Radiation from the flame passes through a lens, a slit, a optical filter and falls on the photocell. The lens and filter isolate the particular wavelength characteristic of the metal ions being measured.
- The photocell measures the characteristic radiation.
- Amplifier and digital read-out give the radiation intensity

Specific Analysis: Na$^+$ and K$^+$

Sodium and Potassium are routinely analysed with Emission Spectroscopy. For these elements, the emission spectra are simple, consisting of a few wavelengths:

- Na is determined at λ = 589 nm; concentrations can be measured to $\pm$ 1 mg/l.
- K is determined at λ =766.5 nm; concentrations can be measured to $\pm$ 0.1 mg/l.

Procedure:
1. Make a series of standard solutions, of known concentrations.
2. Set Flame Photometer to correct λ
3. Measure the emission intensity of the standards
4. Plot a standard curve: Intensity vs. Concentration
5. Measure intensity of unknowns, then read concentration from standard curve (Figure 2)
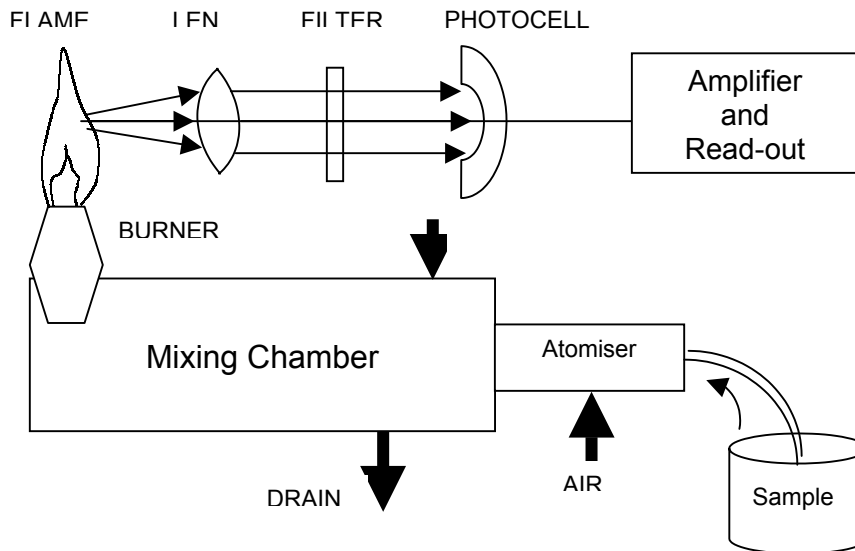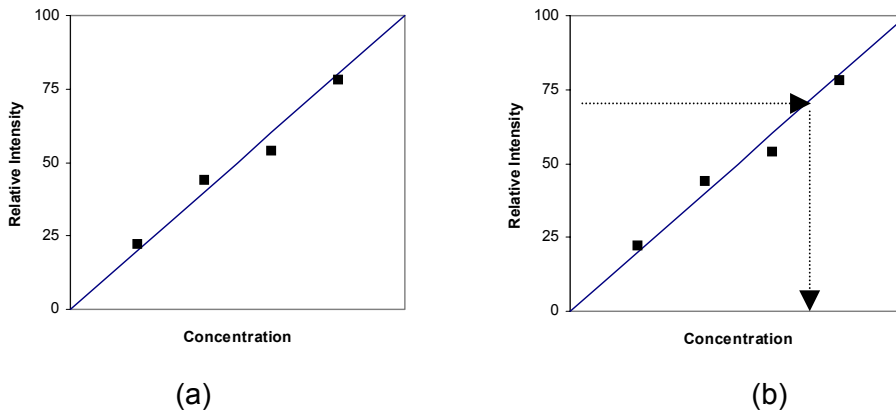
FI AMF   **I FN**   **FII TFR**   **PHOTOCELL**

Amplifier and Read-out

BURNER

Mixing Chamber

Atomiser

DRAIN

AIR

Sample

Figure 1: The main components of the Flame Photometer

(a)   (b)

Figure 2: (a): a standard curve showing linear relation of emitted light intensity (I) with sample concentration (C)
(b): Reading the concentrations of an unknown using the standard curve after measuring the intensity

Interferences

At high concentrations of solutes, the analysis can be influenced by the composition of sample solutions. The concomitant elements may act upon the intensity of emission of test elements. It is seen that the emission intensity of any alkali metal increases in the presence of other alkali metals. Specifically, high concentrations of calcium and potassium can interfere with sodium analyses. High concentrations of calcium, magnesium and sodium can interfere with potassium analyses. Normally such interferences are not a problem. If such high concentrations of interfering ions are present, special analytical procedures can be followed, such as adding a "Radiation Buffer".

3. Nephelometry & Turbidimetry

Turbidity is one of the basic measurements of water quality, such as colour, odour, and temperature. Turbid water looks dark, and 'dirty'. This is caused by the presence of suspended and colloidal substances of various origin like clay, silt, mud, silica, rust, calcium carbonate as well as microscopic aquatic organisms like algae, and bacteria.

Analysis of Turbidity

Turbidity is caused by suspension of particles in water, interfering with passage of light. The turbidity of a sample may be measured either by its effect on the transmission of light, which is termed turbidimetery, or by its effect on the scattering of light, which is termed Nephelometery.

The analytical methods employ common electric photometers that can measure light intensity (Figure 3). The turbidimeter or nephelometer mainly consists of four parts – light source, optical components (e.g. slit), sample compartment and a photocell for the measurement of light either transmitted through the sample or scattered from the suspended particles in the sample. The photocell detects light and an electronic amplifier measures the light intensities.

In Turbidimetry, the amount of light *passing through* a solution is measured. The higher the turbidity, the smaller the quantity of light transmitted (i.e. more light is absorbed). Any spectrophotometer or photometer can be used as a turbidimeter, without modification. Since property concerns visible light the measurement is commonly carried out at 420 nm.

In nephelometry, on the other hand, the detecting cell is placed at right angles to the light source, to measure light *scattered* by particles. The intensity of the scattered light serves as a measure of the turbidity. The instrument is called a 'Nephelometer' or a 'Nephelometric Turbidimeter'. A spectrophotometer can be used, however, a special attachment is required for nephelometry.

Nephelometric measurement is more sensitive for very dilute suspensions and low turbidity caused by fine particles (colloidal solutions). For moderately heavy turbidity, either this or turbidimetric measurements can be made.
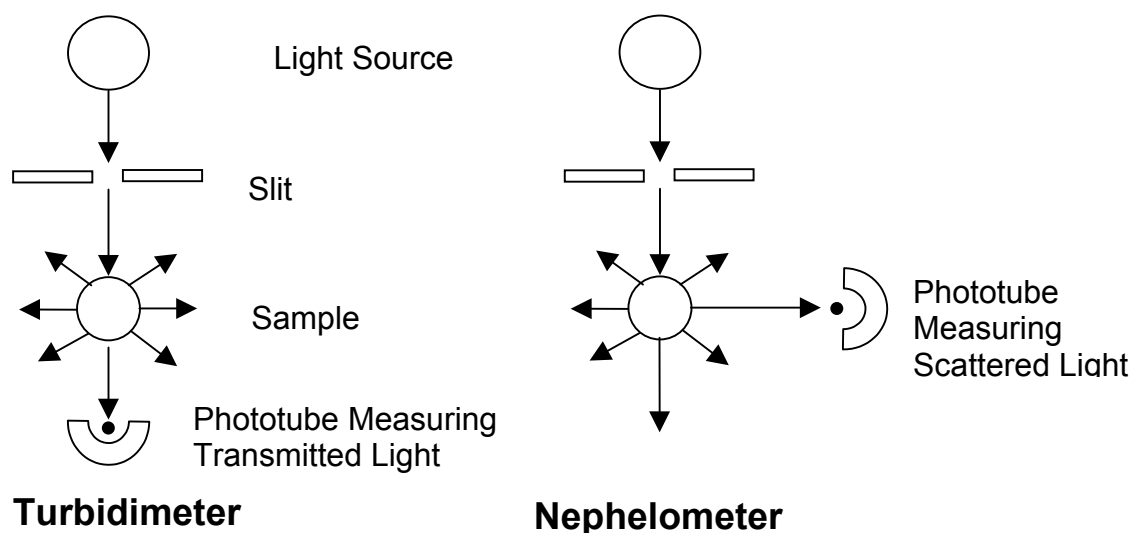

Light Source

Slit

Sample

Phototube Measuring
Transmitted Light

Phototube
Measuring
Scattered Light

Turbidimeter   **Nephelometer**

Figure 3 Diagram of Turbidity analysis by 'Turbidimetry' or 'Nephelometry'

Measurement of turbidity based on visual methods, such as Jackson's candle turbidimeter, although simple and cheaper, is not sensitive for low turbidities. The accuracy of visual instruments is also limited and depends upon the skill of the user's eye.

Significance of Turbidity Measurements

Turbidity is an important factor for many uses of water:

- **potability:** The turbidity is connected with potability of water directly, indirectly or aesthetically. High turbidity is generally associated with polluted water. Turbidity measurement is very important in deciding the quality of water samples. In fact, the turbidity is taken as an indicator for efficiency and performance of coagulation, flocculation, sedimentation and filtration processes of water treatment plants.
- **use in industry:** The turbidity of water being used in industry is also an important consideration in quality control for industries manufacturing chemicals, cosmetics, food products, beverages, etc.
- **ecology:** many aquatic animals and plants need clear water to survive. Turbidity is therefore damaging to ecology.

Turbidity Units

The standard Turbidity unit is called Nephelometric Turbidity Unit (NTU) because of the use of nephelometric method of measurement. The NTU has generally replaced the previous unit of 'Jackson candle turbidity units (JTU).

Typical turbidity values for different waters are given in Table 1

Table 1   Typical Turbidity Values for different waters

Type of water	NTU
Surface Water (Rainy season)	1000 and above
Treated tap water	1 to 2
De-mineralised water	0.1 to 0.5
Water filtered through membrane filter	0.05 or less

Calibration of Instrument and Measurement of Turbidity

Formazine is used as turbidity standard for calibration because it possesses the desired properties which other standards do not have. Formazin particles have uniform size and shape. Formazin can be synthesised and has reproducibility of one percent. Formazin stock solution has good stability (up to 1 year), thus making it an ideal turbidity standard. Calibration is made in NTU, the standard units of measurement.

Procedures for preparation of formazin stock standard, 4000 NTU, are in the Guidelines for Standard Analytical Procedures for Water Analysis. For each use, the dilute standards are prepared from stock solution, and the nephelometer must be calibrated according to manufacturer's operating instructions.

Interferences in Nephelometry:

Nephelometry is based on measuring light intensity. Several factors can interfere with the measurements:

- Dirty glassware
- Air bubbles in the sample
- Vibration that disturbs the surface visibility
- Colour of the sample

Maintenance :

Cleanliness is of utmost importance in all turbidity measurements. All the glass and optical parts must be protected from dust and scratches. Even the finger marks on the sample tube bottoms, mirror, source lamps and reflectors may disturb the measurement, accuracy and calibration. To prevent the polish bottoms of the sample tubes and plungers from scratching, it is advisable to keep these items on a soft cloth or tissue paper when not in use.

The sample tubes and condensing lenses etc may be washed with mild detergent and rinsed with distilled water. The filters and mirrors may be cleaned using a soft tissue paper or air syringe and may be wiped occasionally with a soft tissue soaked with distilled water or mild detergent. Never immerse these items in water or cleaning solutions. Also wipe the outside of the sample tube before placing into the housing; otherwise it may keep the mirror wet for long time and damage it permanently.