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PAPER 5

SAMPLING AND ANALYSIS OF WATER AND WASTEWATER

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SAMPLING AND ANALYSIS OF WATER AND WASTEWATER

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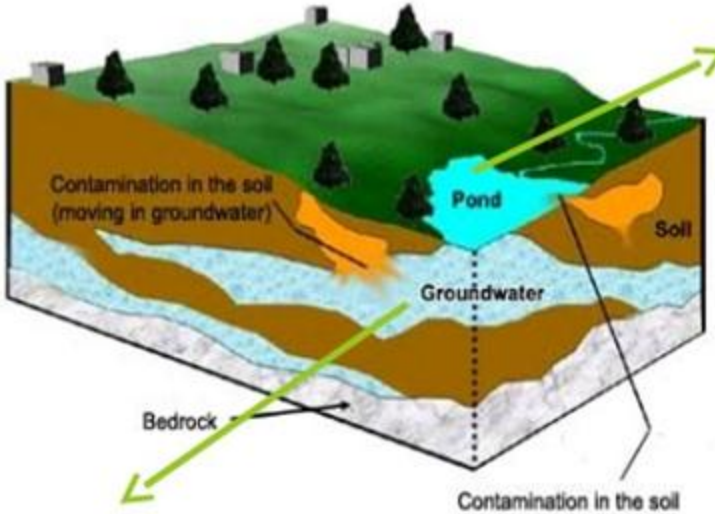
OUTLINE

1. Water and wastewater characteristics
2. Test methods
3. Instrumentation
4. Sample validity
5. Conclusion

WATER AND WASTEWATER

- Water
  - surface water
    - river, lake, marine
  - ground water
- Wastewater
  - industrial effluent
  - domestic effluent

SURFACE WATER & GROUND WATER



SURFACE WATER

- Usually rainwater that collects in surface water bodies, like oceans, lakes, or streams.
- Another source - groundwater that comes out of the ground from springs.
- Become polluted when contaminants come into direct contact and either dissolve or physically mix with the water.

GROUNDWATER

- Water underneath the ground.
- Comes from rain water or water from surface water like lakes or streams that soaks into the soil.
- The water is stored underground in the tiny spaces between rocks and soil grains and can move around within the soil.
- Groundwater contamination occurs when the water comes into contact with contaminants.

SURFACE WATER & GROUND WATER

General characteristics of surface water and ground water

Surface water	Ground water
Varying composition	Constant composition
Low mineralization	High mineralization
High turbidity	Little turbidity
Colour	Low or no colour
Presence of microorganism	Bacteriologically safe
Dissolved oxygen	No dissolved oxygen
Low hardness	High hardness
Taste and colour	H_2S, Fe, Mn
Possible chemical toxicity	

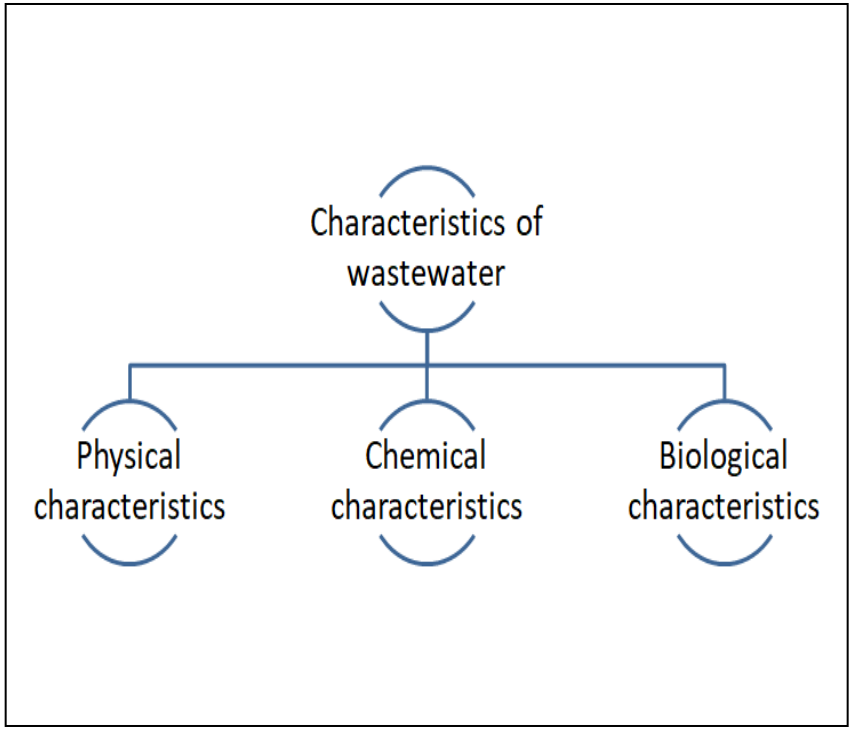
WASTEWATER

- Wastewater
  - any water Negatively Affected in quality by Human
  - used water from:
    - domestic
    - commercial
    - industry
  - has physical, chemical and biological impurities
  - can be polluted
  - can be toxic

WASTEWATER

- Types of wastewater
  - domestic wastewater (sewage)
    - wastewater coming from home, commercial areas
    - containing human excrete
  - industrial wastewater
    - coming from varies process from industries

CHARACTERISTICS OF WASTEWATER



- Physical
  - colour, odor, solids, turbidity, temperature
- Chemical
  - metals
  - anions
  - pesticides etc
- Biological
  - oil & grease
  - microbes

CHARACTERISTICS WASTEWATER

Typical range of concentrations of untreated domestic wastewater

Parameter	Range, mg/L
Total solids	350-1200
Dissolved solids	250-850
Suspended solids	100-350
BOD	100-300
COD	250-1000

CHARACTERISTICS WASTEWATER

Typical range of concentration for some untreated industrial wastewater

Industry	pH	BOD5, mg/L	Suspended solids, mg/L	COD, mg/L	Oil and grease, mg/L
Dairy	4	14,000	12,150	21,100	320
Textile	6.5	840	1,800	1,500	155
Pulp & paper	8	360	1,640	2,300	-
Beverage	9	760	620	1,150	-
Tannery	10	2,370	2,600	4,950	115
Food canning	5.5	800	2,200	1,400	94

WHY WE NEED TO TREAT WASTEWATER?

- To comply to regulation
- To protect land, water resources, aquatic life
- Safe guard public health
- Reuse of water

REGULATORY REQUIREMENTS

Sewage discharge

SECOND SCHEDULE
(Regulation 7)
ACCEPTABLE CONDITIONS OF SEWAGE DISCHARGE OF STANDARDS A AND B

(i) New sewage treatment system

	Parameter	Unit	Standard A	Standard B
	(1)	(2)	(3)	(4)
(a)	Temperature	°C	40	40
(b)	pH Value	-	6.0-9.0	5.5-9.0
(c)	BOD5 at 20°C	mg/L	20	50
(d)	COD	mg/L	120	200
(e)	Suspended Solids	mg/L	50	100
(f)	Oil and Grease	mg/L	5.0	10.0
(g)	Ammonical Nitrogen (enclosed water body)	mg/L	5.0	5.0
(h)	Ammonical Nitrogen (river)	mg/L	10.0	20.0
(i)	Nitrate – Nitrogen (river)	mg/L	20.0	50.0
(j)	Nitrate – Nitrogen (enclosed water body)	mg/L	10.0	10.0
(k)	Phosphorous (enclosed water body)	mg/L	5.0	10.0

Note : Standard A is applicable to discharges into any inland waters within catchment areas listed in the Third Schedule, while Standard B is applicable to any other inland waters or Malaysian waters.

REGULATORY REQUIREMENTS

Sewage discharge

(ii) Existing sewage treatment system (approved before January 1999)

This category refers to all sewerage treatment systems which were approved before the Guidelines for Developers: Sewerage Treatment Vol. IV, 2nd edition and were enforced by the Department of Sewerage Service, Ministry of Housing and Local Government, beginning January 1999. Below are the acceptable conditions for sewerage discharge according to type of sewage treatment systems:

			Type of Sewage Treatment System									
		Communal Septic Tank	Imhoff Tank		Aerated Lagoon				Oxidation Pond		Mechanical System	
	Parameter	Unit	A	B	A	B	A	B	A	B	A	B
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
(a)	BOD_5 at 20°C	mg/L	200	200	175	175	100	100	120	120	60	60
(b)	COD	mg/L	-	-	-	-	300	300	360	360	180	240
(c)	Suspended Solids	mg/L	180	180	150	150	120	120	150	150	100	120
(d)	Oil and Grease	mg/L	-	-	-	-	-	-	-	-	20	20
(e)	Ammoniacal Nitrogen	mg/L	-	-	100	100	80	80	70	70	60	60

REGULATORY REQUIREMENTS

Sewage discharge

(iii) Existing sewage treatment system (approved after January 1999)

All sewerage treatment systems which were approved after the Guidelines for Developers: Sewerage Treatment Vol. IV, 2nd edition and were enforced by the Department of Sewerage Service, Ministry of Housing and Local Government, beginning January 1999 and up to date of coming into operation of these Regulations.

Parameter	*Unit*	*Standard* A	B
(a) BOD_5 at 20°C	mg/L	20	50
(b) COD	mg/L	120	200
(c) Suspended Solids	mg/L	50	100
(d) Oil and Grease	mg/L	20	20
(e) Ammoniacal Nitrogen	mg/L	50	50

REGULATORY REQUIREMENTS

Industrial discharge

FIFTH SCHEDULE
[Paragraph 11(1) (a)]

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT FOR MIXED EFFLUENT OF STANDARDS A AND B

	Parameter	Unit	Standard	
			A	B
	(1)	(2)	(3)	(4)
(i)	Temperature	°C	40	40
(ii)	pH Value	-	6.0-9.0	5.5-9.0
(iii)	BOD_5 at 20°C	mg/L	20	40
(iv)	Suspended Solids	mg/L	50	100
(v)	Mercury	mg/L	0.005	0.05
(vi)	Cadmium	mg/L	0.01	0.02
(vii)	Chromium, Hexavalent	mg/L	0.05	0.05
(viii)	Chromium, Trivalent	mg/L	0.20	1.0
(ix)	Arsenic	mg/L	0.05	0.10
(x)	Cyanide	mg/L	0.05	0.10
(xi)	Lead	mg/L	0.10	0.5
(xii)	Copper	mg/L	0.20	1.0
(xiii)	Manganese	mg/L	0.20	1.0
(xiv)	Nickel	mg/L	0.20	1.0
(xv)	Tin	mg/L	0.20	1.0
(xvi)	Zinc	mg/L	2.0	2.0
(xvii)	Boron	mg/L	1.0	4.0
(xviii)	Iron (Fe)	mg/L	1.0	5.0
(xix)	Silver	mg/L	0.1	1.0
(xx)	Aluminium	mg/L	10	15
(xxi)	Selenium	mg/L	0.02	0.5
(xxii)	Barium	mg/L	1.0	2.0
(xxiii)	Fluoride	mg/L	2.0	5.0
(xxiv)	Formaldehyde	mg/L	1.0	2.0
(xxv)	Phenol	mg/L	0.001	1.0
(xxvi)	Free Chlorine	mg/L	1.0	2.0
(xxvii)	Sulphide	mg/L	0.50	0.50
(xxviii)	Oil and Grease	mg/L	1.0	10
(xxix)	Ammoniacal Nitrogen	mg/L	10	20
(xxx)	Colour	ADMI*	100	200

ADMI- American Dye Manufactures Institute

REGULATORY REQUIREMENTS

Industrial discharge

(Regulation 12)

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT CONTAINING CHEMICAL OXYGEN DEMAND (COD) FOR SPECIFIC TRADE OR INDUSTRY SECTOR

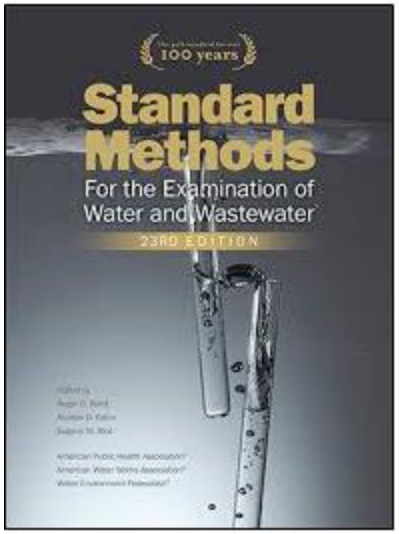
(1) Trade/Industry	(2) Unit	(3) Standard	(4) Standard
(a) Pulp and paper industry			
(i) Pulp mill	mg/L	80	350
(ii) Paper mill (recycled)	mg/L	80	250
(iii) Pulp and paper mill	mg/L	80	300
(b) Textile industry	mg/L	80	250
(c) Fermentation and distillery industry	mg/L	400	400
(d) Other Industries	mg/L	80	200

TEST METHODS

WHAT IS METHOD?

A body of procedures and techniques for performing an activity (such as sampling, chemical analysis and quantification), systematically presented, in order which they are to be executed

TEST METHODS



ASTM INTERNATIONAL
Standards Worldwide

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ISO International Organization for Standardization

TEST METHODS

Regulatory Methods

Approved methods mandatory under law or certain program

- American Public Health Association (APHA)

Consensus Methods

Methods published by professional organizations

- American Society for testing materials (ASTM)
- Association of official analytical chemist (AOAC)

TEST METHODS

Standard methods typically has the following components:

- Scope and application: overview and potential problems/variations
- Summary of method: overview of analysis
- Interferences: contamination of sample during handling
- Safety: protection of analyst
- Apparatus and materials: details of laboratory hardware
- Reagents: details of chemicals, preparation of standards
- Calibration: responses, calibration curves, and quantitation
- Quality control: proof that laboratory can meet specifications of method
- Sample collection, preservation, handling: details of sampling
- Extraction procedure: details of method to extract organics from matrix
- Instrumentation: type of instrumentation and operating procedures
- Qualitative identification
- Calculations: quantitative analysis
- Method performance: MDLs

TEST METHODS

Standard method for the examination of water and waste water

- First published 1905
- Current edition: 24th
- Published by American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF)
- Referred to as “mother” of all method
- Commonly referred to as standard method (SM)

TEST METHODS

The structure of the method:

Part	Description
1000	Introduction
2000	Physical and aggregate properties
3000	Metals
4000	Inorganic nonmetallic constituents
5000	Aggregate organic constituents
6000	Individual organic compounds
7000	Radioactivity
8000	Toxicity
9000	Microbiological examination
10000	Biological examination

TEST METHODS

Aggregate properties

- Turbidity
- Colour
- Odor
- Taste
- Acidity
- Alkalinity
- Hardness
- Conductivity
- Salinity
- Solids
- Temperature

Aggregate organic properties

- BOD
- COD
- TOC
- Oil and grease
- Phenol
- Surfactants

TEST METHODS

- Wet chemistry and common techniques
  - Gravimetric
    - solids, moisture, sulfate and oil and grease.
  - Volumetric/titrimetric
    - electrochemically based instrument
    - acid-base reaction, oxidation-reduction (redox) reaction, complexation/chelation reaction and precipitation reaction

TEST METHODS

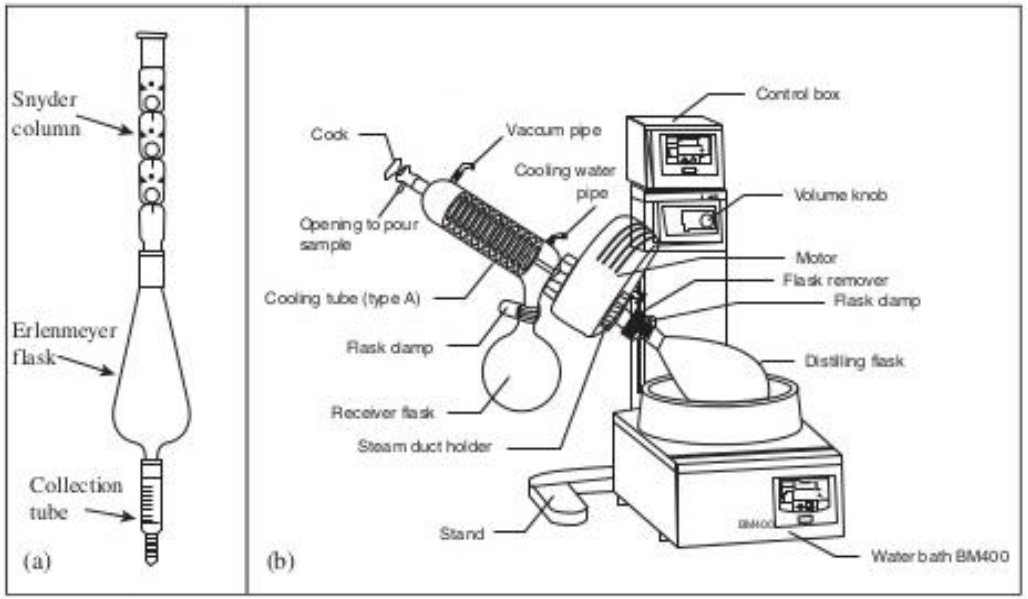
Parameters	Method/Operation*	EPA	APHA (SM_{20})
Moisture	G/Oven Drying	-	-
Solids	G/Filtration	160.1 to 160.4	2540A to G
Acidity	T (acid-base)	350.1	2310 B
Alkalinity	T (acid-base)	310.1 & 310.2	2320 B
Hardness	T (complexation)	130.1 & 130.2	2340 C
DO	T (redox)	360.2	4500 O B to F
BOD	T (redox)	405.1	5210 B
COD	T (redox)/Reflux	410.1 to 410.3	5220 C
Oil and Grease	G/Extraction/Distillation	413.1	5520 B
Residual Chlorine	T (redox)	330.2 to 330.4	4500 D
Chloride	T (precipitation)	325.3	4500-Cl^- B
Ammonia	T (acid-base)/Distillation	350.2	4500-NH_3 C
Cyanide	T (complexation)/Distillation	335.1	4500-CN^- D
Sulfide	T (redox)/Distillation	376.1 & 9030 A	4500-S^{2-} F

* G: Gravimetric; T: Titrimetric; SM_{20}: Standard Method, 20th Edition.

TEST METHODS

Common laboratory techniques

- The basic laboratory techniques all phases of water and wastewater analysis
  - Filtration
  - Centrifugation
  - Distillation
  - Reflux
  - Concentration
  - Digestion
  - Extraction



INSTRUMENTATION

- Electrochemical/potentiometric
  - Measurement of pH
  - Measurement of ions by ion selective electrodes (ISEs)
  - Potentiometric titration
- Voltametric/titration
  - Measurement of dissolve oxygen (DO)
  - Measurement of anions
  - Measurement of metals by aniodic stripping voltametric

INSTRUMENTATION

- Trace metals
  - Spectroscopic
    - Flame Atomic Absorption (FAA)
    - Inductively coupled plasma – optical emission spectrometer (ICP-OES)
    - Graphite flame atomic absorption (GFAA)
    - Inductively coupled plasma-mass spectrometer (ICP-MS)
    - Hydride generation system

INSTRUMENTATION

- Gases, volatiles and semivolatiles
  - Gas chromatography (GC)
  - Detectors:
    - Thermal conductivity detector (TCD)
    - Flame ionization detector (FID)
    - Electron captured detector (ECD)

INSTRUMENTATION

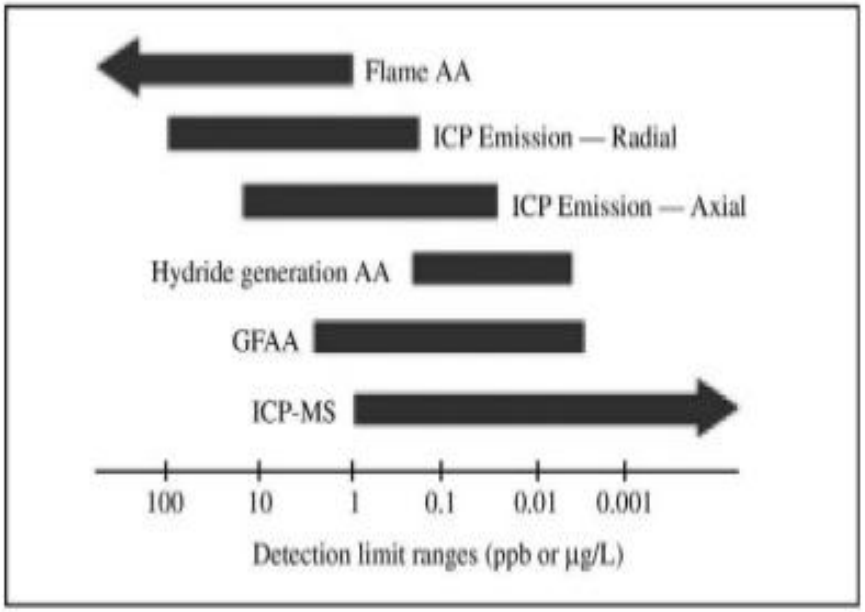
- Semivolatiles and non-volatiles
  - Liquid chromatography (LC)
  - Detectors:
    - UV detector
    - Fluorescence detector
    - Refractive index detector

INSTRUMENTATION

- Selection of Instruments
  - Detection limit
  - Analytical working range
  - Sample through put
  - Cost
  - Interferences
  - Ease of use
  - Method availability

INSTRUMENTATION

- Detection limit/sensitivity
  - Low detection limit required for trace analysis
  - For trace metals analysis various instrumental techniques with different DL available
  - DL decreases: FAA > ICP-OES > Hydride > GFAA > ICP-MS



INSTRUMENTATION

- Trace organic analysis

Detector	Principles	Applications	Sensitivity range	Linearity
TCD	Conduct away heat	Universal	Fair	Good
FID	Burn in H_2—O_2 flame and ionize	Universal for hydrocarbons	Very good	Excellent
ECD	Electronegative compounds capture electron (e^-) from ^{63}Ni	Selective for halogens; No response to hydrocarbons	Excellent	Poor
PID	Analyte ionized by UV light	Selective for aromatics	Excellent	Excellent
NPD	Ionization at the alkali metal anode	Selective for N, P containing compounds	Excellent	Excellent
FPD	Flame and then chemiluminescene measurement	Selective for S, P containing compounds	Very good	Excellent
Hall	Catalytic conversion to ions, then measured by conductivity	Selective for halogens, S, N containing compounds	Excellent	Excellent
MS	Electron impact or chemical ionization	Universal; Provide structural information	Excellent	Excellent

INSTRUMENTATION

- Trace organic analysis
  - Gas chromatography (GC)

	TCD	FID	ECD	PID	NPD	Hall	MS
Benzene	X	X	N	X	N	N	X
DDT	X	X	X	X	N	X	X
α-BHC	X	Poor	X	N	N	X	X
Chlordane	X	Poor	X	X	N	X	X
TCE	X	Poor	X	N	N	X	X

X: Applicable; N: Not applicable

INSTRUMENTATION

- Trace organic analysis
  - Liquid chromatography (LC)

Detector	Applications	Mass LOD (State of the art)[a]	Approximate linear range[b]
UV-VIS absorption	Specific for UV-VIS light-absorbing compounds	1 pg	10^4
Fluorescence	Specific for compounds able to fluoresce	10 fg	10^5
Refractive index	Universal detector; No gradient flow can be used	10 ng	10^3
Conductivity	Specific for ionic species	500 pg	10^5
Mass spectrometry	Universal detector	1 pg	10^5

INSTRUMENTATION

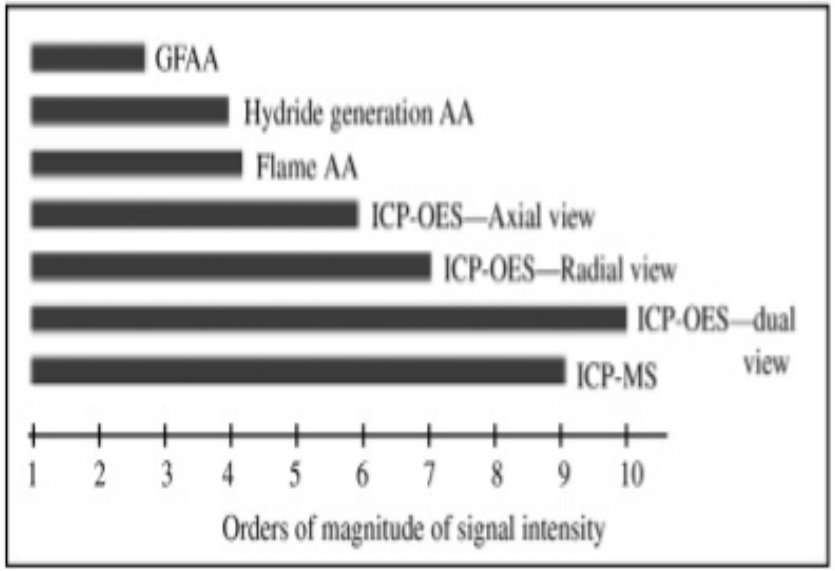
- Ion chromatography (IC)

Membrane	Analyte ions
Glass	$H^{+(1,2)}$, Ag^{+}, K^{+}, Li^{+}, Na^{+}, NH_4^{+}
Solid phase	$Br^{-(1)}$, $Cl^{-(1,2)}$, $CN^{-(1,2)}$, $F^{-(1,2)}$, I^{-}, SCN^{-}, $S^{2-(1,2)}$, Ag^{+}, Cd^{2+}, Cu^{2+}, Pb^{2+}
Liquid phase	BF_4^{-}, ClO_4^{-}, $NO_3^{-(1,2)}$, Ca^{2+}, $K^{+(2)}$, hardness ($Ca^{2+} + Mg^{2+}$)

[a]Standard methods are available from (1) U.S. EPA and (2) APHA (1998).

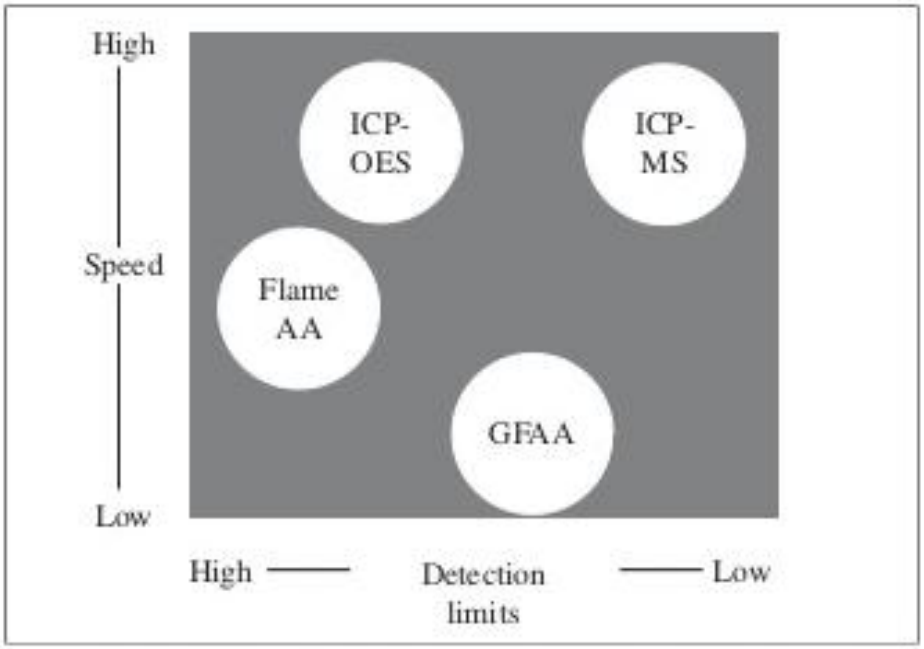
INSTRUMENTATION

- Analytical working range
  - Quantitative results obtained without recalibrate the system
  - Working range increase: GFAA < FAA < ICP-OES < ICP-MS

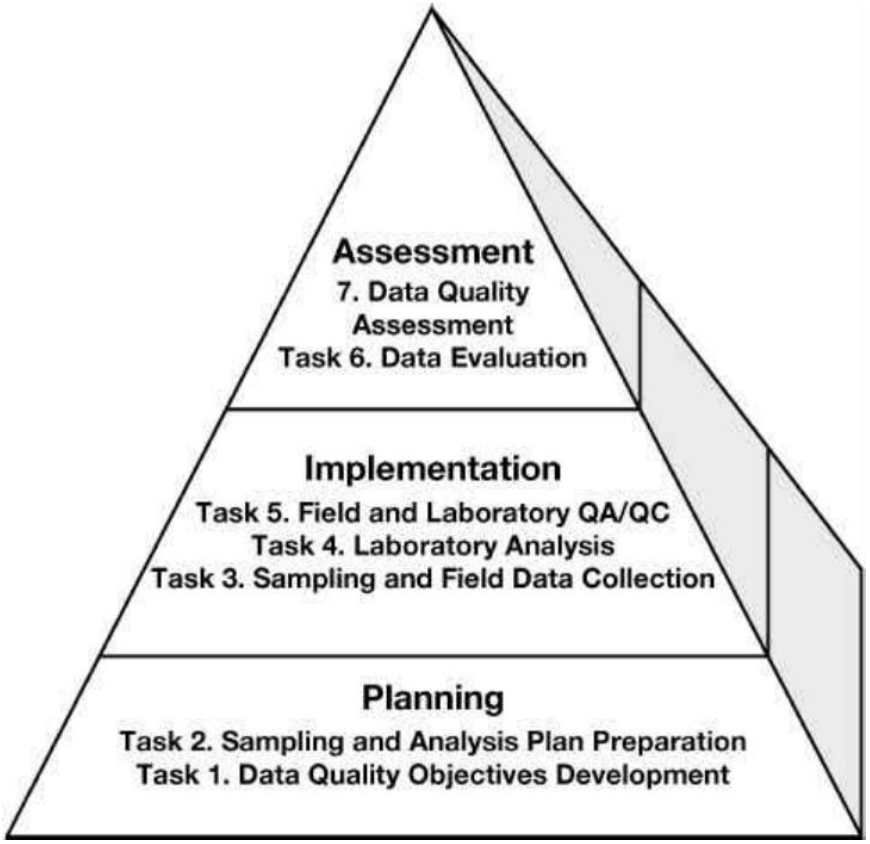


INSTRUMENTATION

- Other consideration
  - Interferences, cost, through put, method availability



SAMPLE VALIDITY



USEPA outlined 3 phases of data collection process to get quality valid data

SAMPLE VALIDITY

1. Planning

   systematic planning demands foresight and experience, and its goal is to produce a set of sufficiently detailed planning

   1a. Data quality objectives

   1b. Sampling and analysis preparation

SAMPLE VALIDITY

1a. Data quality objectives

- Qualitative and quantitative statements:
  - clarify study objectives
  - determining the type, quality, and quantity of data that would be sufficient for valid decision making.

SAMPLE VALIDITY

1b. Sampling and analysis preparation

- The most important stage
- If a sample not collected properly , not representative, then all careful lab work useless
- Errors can occurs during sampling and analysis
- Sampling errors:
  - Sampling
  - Sample preservation
  - Sample transportation

SAMPLE VALIDITY

- Analytical errors:
  - Sample preparation
  - Sample analysis
  - Data analysis
- Two types of error
  - Systematic error – errors can be traced to their sources
    - Improper sampling, analytical error, instrument problem etc
  - Random error – source cannot be traced/identified

SAMPLE VALIDITY

2. Implementation

   2a. Sampling and field data collection

   2b. Laboratory analysis

   2c. Field and laboratory QA/QC

SAMPLE VALIDITY

2a. Sampling and field data collection

- Main tasks including:
  - Sampling procedures
  - Sample custody and tracking
  - Preservation techniques
  - Equipment decontamination
  - Field screening
  - Record keeping

SAMPLE VALIDITY

- Validity of the sample
  - Validity of sampling sites
  - Validity of sampling frequency and timing
- Representativeness of sample
  - Sample size
  - Sample collection
  - Sample storage and transportation

SAMPLE VALIDITY

- Sampling techniques
  - Grab, composting, random, systematic, cluster and many more
  - Compound specific/sample type (river water, groundwater)
- Collected sample must be identified
- Stored in a secured location for preservation of sample integrity
- Transferred to laboratory with ID and requested analysis

SAMPLE VALIDITY

2b. Laboratory analysis

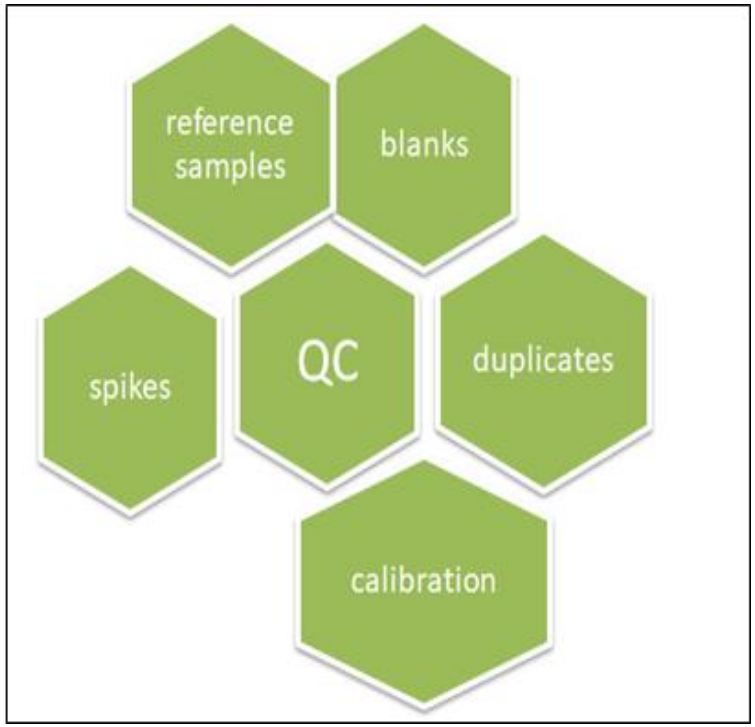
- Using various analytical techniques
- Identify and quantify hundreds of organic and inorganic analytes in an assortment of environmental matrices
- Environmental samples are transformed into data
- Various analytical methods
  - GC, FID, PID, MS, LC, UV-VIS ,IC

SAMPLE VALIDITY

2c. Field and laboratory QA/QC

- QA = integrated management system to ensure QC system in place and work as intended
- QC = A set of routine technical activities performed to control errors
- Actual validity of data depends on standard field and analytical laboratory QA/QC

SAMPLE VALIDITY



SAMPLE VALIDITY

2c. Field and laboratory QA/QC

- Actual validity of data depends on standard field and analytical laboratory QA/QC
- Field QA/QC
  - Equipment blank
    - Pre-cleaned equipment used to fill analyte-free matrices
  - Field blank
    - Prepared in the field
    - Go through the entire sampling procedure
    - Filled with clean matrixes
  - Travel blank
    - Only for VOCs
    - Prepared in laboratory

SAMPLE VALIDITY

- Laboratory QA/QC
- Basically 3 types:
  - Blanks – check contamination
  - Spikes – to check accuracy
  - Duplicates/replicates – to check precision

SAMPLE VALIDITY

- Below listed the required QC:
  - Reagent blanks - analyte free, to detect contamination
  - Reagent water spikes
    - Spike of small amount of analyte
    - monitor effectiveness of method
  - Laboratory control sample (LCS)
    - Contain known analyte with known concentration in clean matrix
  - Matrix spike & matrix spike duplicates
    - Field sample spiked in laboratory as described in LCS prior to sample preparation and analysis

SAMPLE VALIDITY

- Laboratory duplicates
  - Sample prepared and analysed at the same time
  - Check analytical performance precision and homogeneity
- Reference materials
  - Blind sample with known analyte and concentration
  - Validate analytical system and performance of analyst
- Calibration standards
  - Standard solution to plot calibration curve
- QC checks standards – to verify calibration curve
  - Standard solution to verify/conform calibration curve

SAMPLE VALIDITY

3. Assessment

3a. Data evaluation

- To check weather the collected data quality meet the acceptance criteria for precision, accuracy, representativeness, comparability and completeness
- Data validation/data reviewing – checking data against pre-established acceptance criteria

SAMPLE VALIDITY

3b. Data quality assessment

- A set of operating principles to produce defensible data of known accuracy and precision
- Involves a scientific and statistical process to ensure data collected are appropriate, quality and quantity to support the intended purpose

CONCLUSION

- Water and wastewater has distinguish characteristics
- There are various methods available to analyze to characterize them but also to assess the pollution or contamination levels
- From wet chemistry to high end instruments can be for identification and quantification
- Sample validity is a very important aspect to get a valid or defensible data

QUESTION & ANSWER

Thank You

mymecce