- Dr Salah Hassouna
- Dr HeshamZaki
- Dr Moustafa Abbasy

Why water analysis?

1. Detect changes in water quality.
2. Comply with laws and regulations.
3. Design a treatment system for wastewater.
4. Monitor water quality in an area.

WATER ANALYSIS FOR ENVIRONMENTAL STUDIES

By

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NO FACEBOOK Please

How to identify an unknown substance?

- Humidity (water content)
- Organic/inorganic contents
  - Inorganics such as:
    - Salts
    - Inert
    - Metals
    - etc.
  - could be identified by specific scheme
  - Organics could be identified by:
    - Solvents solubility
    - Fractionation by partitioning
    - Mass determination
    - Molecular configuration

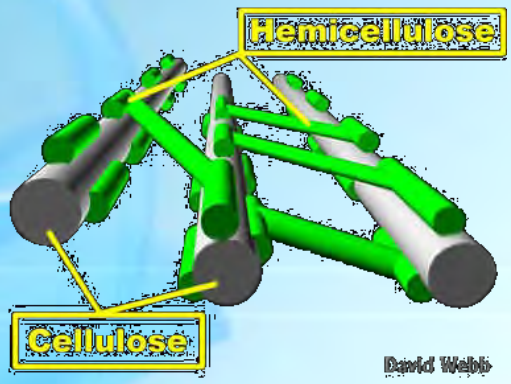
Inorganic materials

- Colourimetric
- Titration methods
- Spectrophotometry
- Potentiometric
- Instrumental analysis

Organics

- Synthetic Compounds
- Natural Compounds

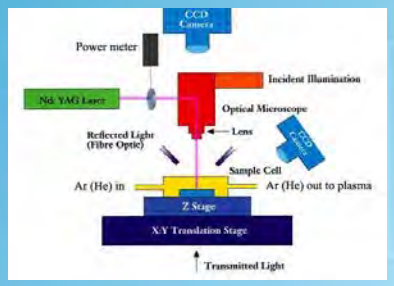
- **Solvent extraction**
- **Selective dyes**
- **Instrumental analysis**



- Carbohydrates
- Proteins
- Lipids

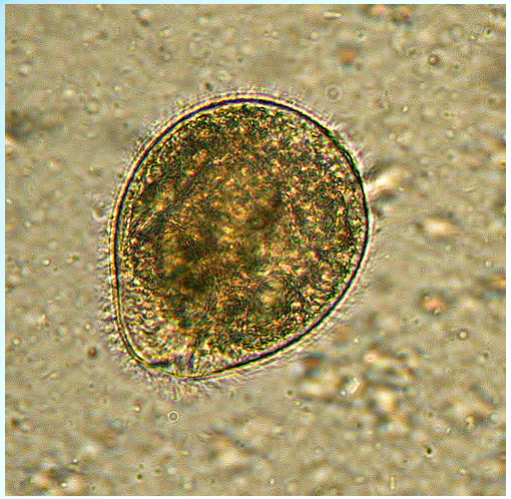
Instruments for detailed analysis

- Infra-red (IR)
- GC & GC/Mass
- Spectrophotometer (UV/Vis)
- NMR (Nuclear Magnetic Resonance)
- ICP (Inductively Coupled Plasma) & ICP/MS
- Atomic Absorption (AA)



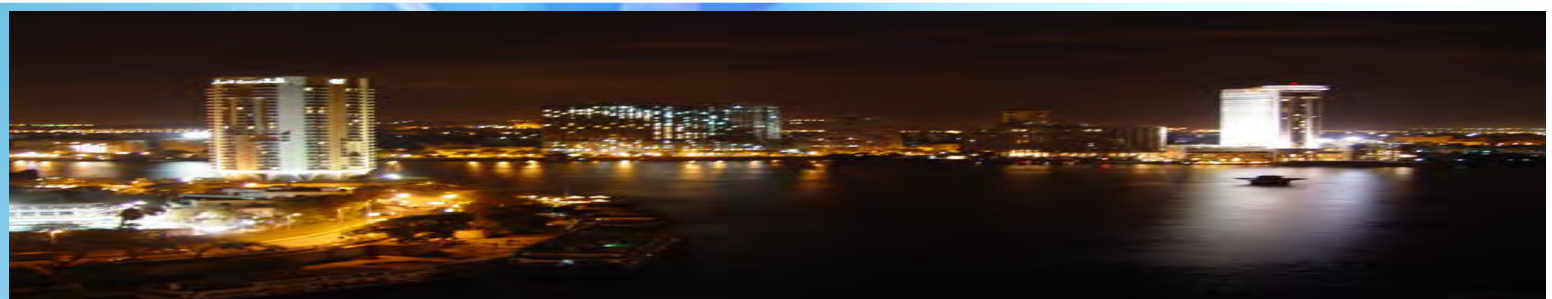
Water Quality Indices

- Organic load
- Nutrients
- Toxic & hazardous substances
- Pathogenic & parasitic agents



River Nile Water Quality (average)

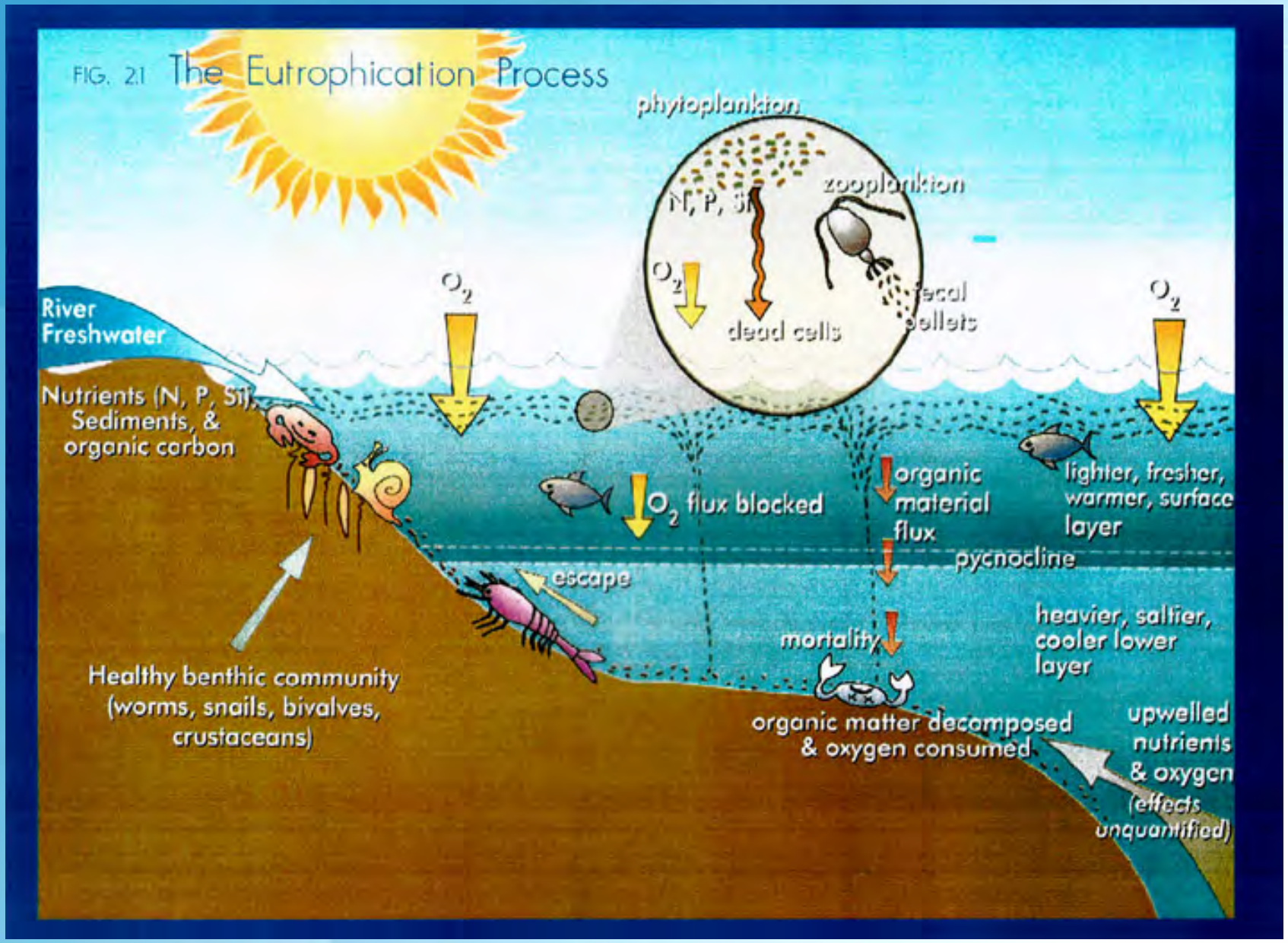
Parameter	Value	units	Parameter	value	units
pH	7.5	units	COD	24	mg/L
TOC	10	mg/L	BOD	9	mg/L
Turbidity	6	NTU	TDS	250	mg/L
DO	6.1	mg/L	TSS	6.2	mg/L
EC	300	μmhos/cm	Nitrate	1.8	mg/L
Tot Alkalinity	160	mg/L	Nitrite	0.01	mg/L
Tot Hardness	150	mg/L	Ammonia - NH_3	0.06	mg/L
Mg Hardness	110	mg/L	Sulfate	45	mg/L
Ca Hardness	50	mg/L	Phosphate	0.1	mg/L
Chloride	35	mg/L	Silica	3.5	mg/L
Iron	0.4	mg/L	Potassium	7	mg/L



Seawater Analysis

Parameter	Value	Units	Parameter	Value	Units
pH	7.99	units	***Chl-a***	1.20	mg/m
Salinity	38,900	ppm	**Cl**	19,500	mg/L
TSS	28,600	mg/L	**Na**	10,770	mg/L
DO	5.65	mg/L	**Ca**	412	mg/L
COD	4.20	mg/L	**Mg**	1,290	mg/L
BOD	2.41	mg/L	**K**	380	mg/L
NH_4	0.65	mg/L	**Ni**	0.15	µg/L
NO_2	0.12	mg/L	**Pb**	4.03	µg/L
NO_3	4.38	mg/L	**Cu**	5.70	mg/L
TN	6.00	mg/L	**Fe**	34.07	mg/L
Silicate	1.75	mg/L	**Zn**	32.75	µg/L
Sulfate	2,700	mg/L	**Bromide**	66	mg/L
Bicarbonate	145	mg/L	**Fluoride**	1.0	mg/L

Water Pollution



Laws & Regulations in control of water quality

Law	Title	Executive Decrees/ remarks
93/1962	Discharges	Decree **44/2000** MCH
48/1982	Protection of River Nile	Amendments 2010
4/1994	Environmental law	"
9/2009	Environmental law	Modified from 4/1994
27/1978	Drinking water Guidelines	Decree **458/2007** MOHP

Law 48/82							Law 4/94	Ministerial Decree 44/2000
	Fresh water bodies must not exeed	*to River Nile south*	*to Nile branches + Underground water*	*Drains to Fresh water courses*	*to Brakish water bodies*		*Sea*	*Sewarage systems*
					Sewarage systems	*Industrial effluents*		
Temp C*	5 above	35	35	5 above	35	35	10 above	
pH*	7-8.5	6-8	6-9	7-8.5	6-9	6-9	6-9	6-9.5
Colour*	<100	0	0	100	-		-	no limits
BOD	6	30	20	10	60	60	60	600
COD**	10	15-40	10-30	6-15	40-80	50-100	100	1100
DO	>5			>5				
Total Solids	500	1,200	800	500	2,000	2,000	2,000	
Suspended Solids		30	30		50	60	60	800
Ash		1100	700				1800	
Oil & Grease	0.1	5		1	10	10	15	100
Nitrate		30	30	45	50	40	40	25
P(i) [inorganic]		1	1	1	0	10	15	
Ammonia	0.5			0.5			3	25
Organic N	<1							
Total Alkalinity	20-150			50-200				
Sluphites	<200							
Sulphides		1	1		1	1	1	
Phenol		0.002	0.001	0.02	0	0.005	1	0.5
Flourides		0.5	0.5	0.5	0	0.5	1	
Residual Chlorine		1	1					
Turbidity*							50 NTU	
Coliform MPN*				5,000	5,000	5,000	5,000	
all in mg/L except*								
**if two values then first for Dichromate, second for Permenganate								

Water Quality Measurements

1. Physical Parameters
2. Chemical Parameters
3. Biological Parameters

Methods of Water Analysis

- Standard method
- Proposed method
- Obsolete method

A Standard Method

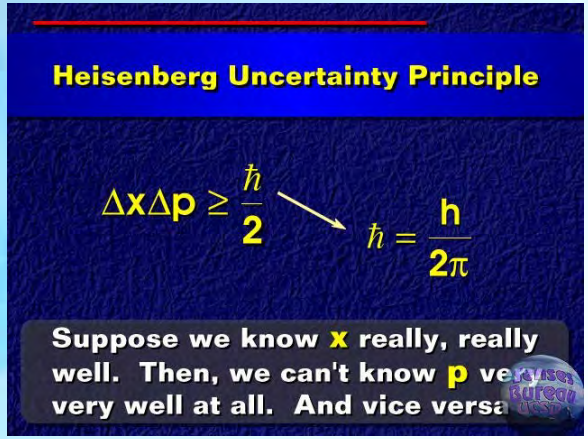
- Sampling
- Limit of detection
- Precision and Bias
- Interferences

Standard Methods

- **Method applications**
- **Method validation**

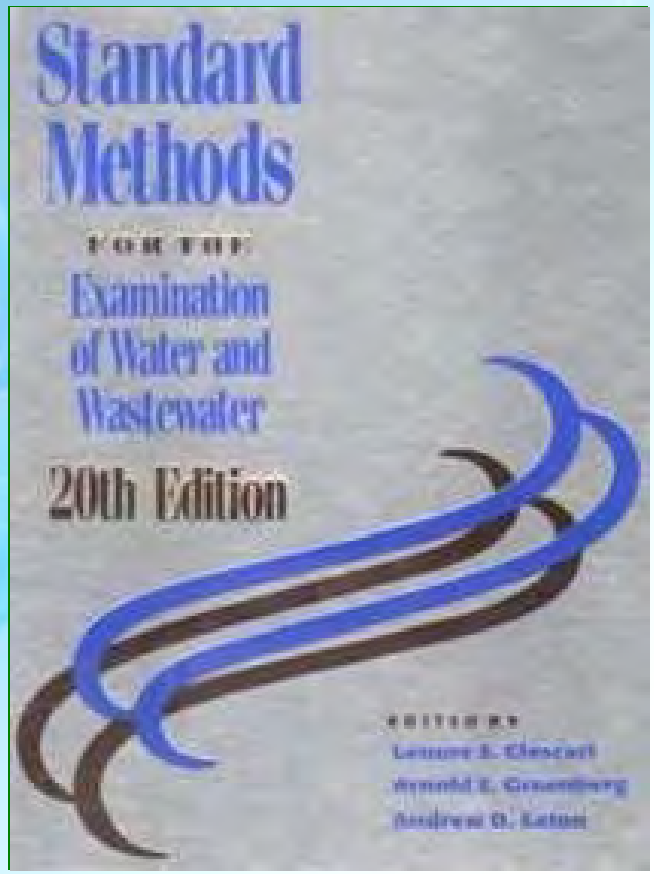
Trueness of Measurements [uncertainty]

1. Selectivity
2. Specificity
3. Precision
4. Repeatability
5. Reproducibility
6. Linearity
7. Minimum Detection Limit
8. Standard Error & Standard Deviation



Standard Methods for Water Analyses

- **SMEWWW** [APHA& AWWA & WEF]
- **ASTM** [American Society for Testing and Materials]
- **BSA** [British Standards Institution]
- **DIN** [Deutsches Institut für Normung]



General Considerations in Lab Analysis

[The 10 commandments]

1. You should follow all safety precautions for lab work.
2. Remember that all glassware are calibrated at certain temp (25°C).
3. You should know how to get ultrapure water (free of ions, i.e. 18ΩOHM).
4. You should know how to prepare standard solutions [e.g. NaOH/HCl].
5. You should know what concentrations you should use for standard curve construction for any assay.

General Considerations in Lab Analysis

[The 10 commandments]

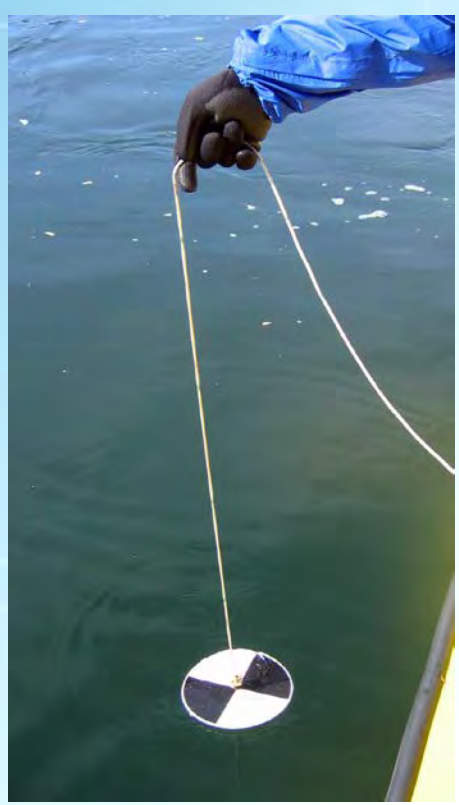
6. You should know how to calibrate basic lab essentials [pH meter, balances, micropipettes].
7. You should know storage time and temp of solutions, reagents, etc.]
8. You should follow the calibration timetable of all equipment in the lab.
9. You should know the uncertainty items of the method you are using fir analysis.
10. Repeat any one to make them 10!!

Water Analysis for:

1. Fresh & brackish water bodies
2. Seawater
3. Underground water
4. Potable water
5. Wastewater
6. Industrial water [Production + Cooling + Utilities]
7. Agricultural drainage water

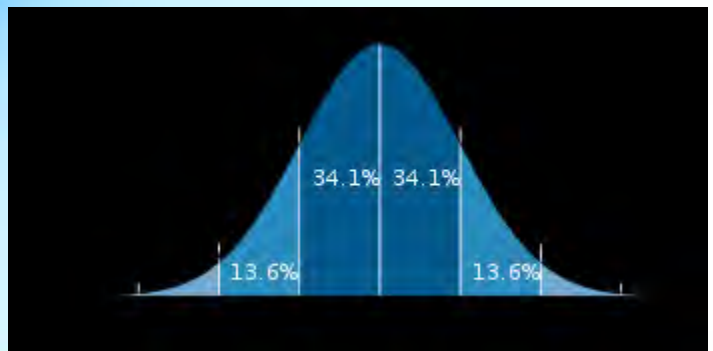
On-site measurements

1. Water clarity
   (Secchi disk)
2. Temperature
3. DO
4. pH
5. Salinity



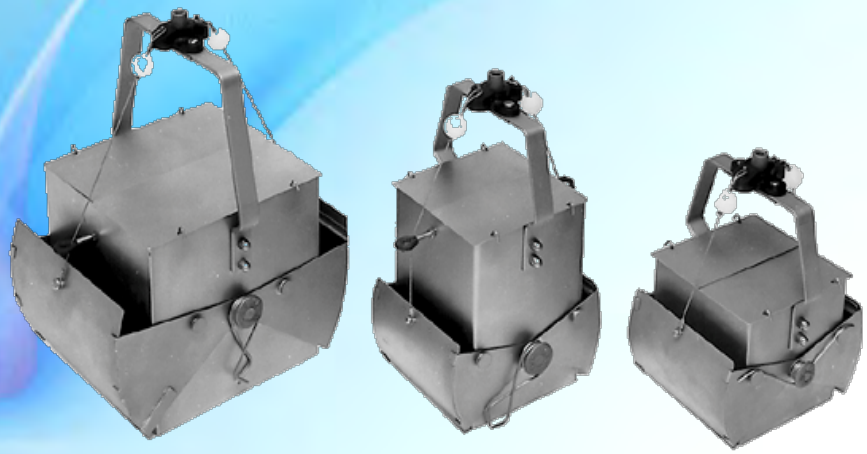
Water Analyses

1. On-site measurements.
2. Sampling procedure.
3. Samples' selection and collection.
4. Samples preservation and handling.
5. Lab analyses.
6. Instruments used in water quality testing.
7. Results uncertainty.



Sampling of water bodies

- Grab-sampler
  - (sediments)
- Inverted Bottles
  - (water @ different depths)

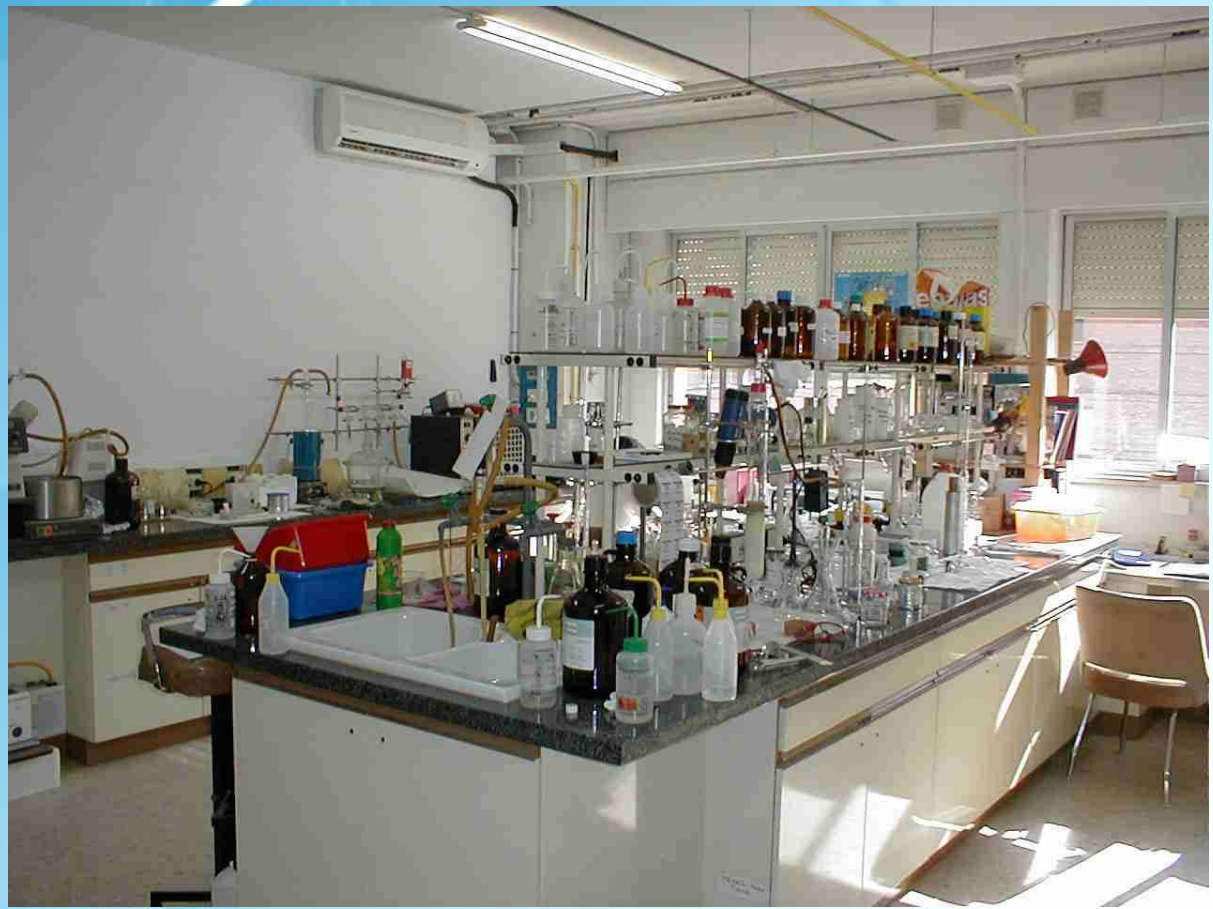


Sample's Preservation

- **DO**= Manganous sulfate ($MnSO_4$)
- **Ammonia**= acidification below pH2
- **Phenol** = acidification below pH2

- Cool storage (Ice Box)

Laboratory Water Testing



Organic load

- BOD_5
- COD
- Nutrients
  - P compounds
  - N
    - Org
    - Nitrate
    - Nitrite
    - Ammonia

- **Solids:**
  1. Total Solids
  2. Dissolved Solids
  3. Suspended Solids
  4. Volatile Solids
  5. Settleable solids (Imhoff Cone)
- **Turbidity**
- **Oil & Grease**

Water Quality Parameters

- Total Alkalinity
- Total Hardness
- Heavy metals
- Phenol
- Pesticides
- Detergents
- Residual chlorine

Gas chromatograph

Atomic Absorption

Oil & Grease

- **Gravimetric**

Turbidity

- **NTU** (Nephelometer Turbidity Units)
- **What is the difference between a spectrophotometer and a Turbidimeter?**
- **PEG Standards**

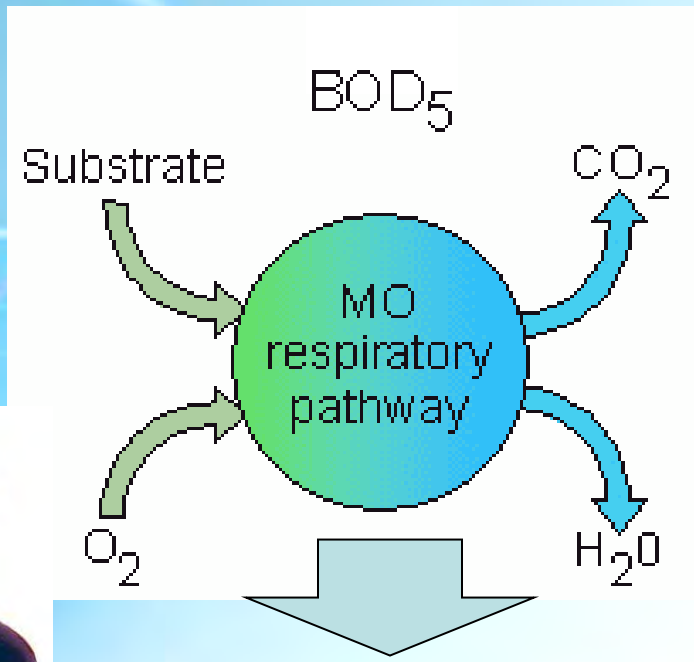
- Nephel in Greek = cloud

TOC [Total Organic Carbon]

- is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality.
    1. Acidification
    2. Oxidation
    3. Detection and Quantification
- samples are combusted at 1,350 °C in an oxygen-rich atmosphere. All carbon present converts to carbon dioxide which is measured by an Infrared Detector. Alternatively ultra-violet light alone oxidizes the carbon within the sample to produce CO2.
- The UV oxidation method offers the most reliable, low maintenance method of analyzing TOC in ultra-pure waters

BOD

- BOD_5
- BOD ultimate
- BOD seeded

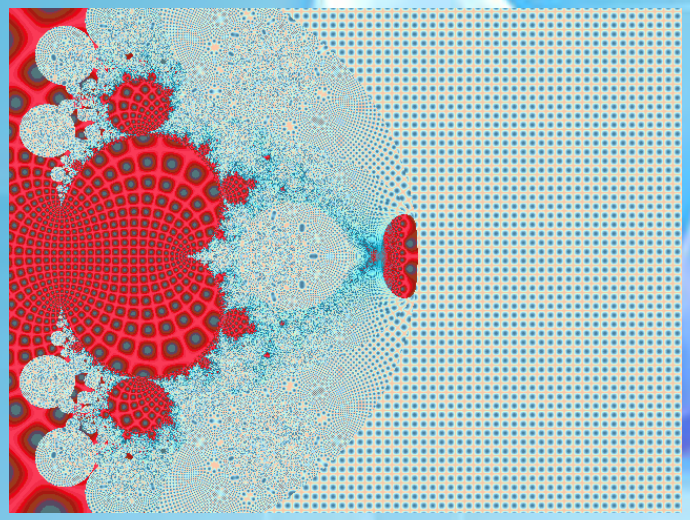


BOD attention!!

- **pH & nutrients requirements.**
- **Dilution water precautions.**
- **Dark storage importance.**
- **Avoidance of complete depletion of oxygen.**
- **DENITRIFICATION inhibitor addition:**
  - **TCMP”** *2-chloro-6-(trichloromethyl) pyridine*

BOD Dilutions

Direct pipetting into 300mL bottles	
Range of BOD	mL sample
1,200 - 4,200	0.5
600 - 2,100	1.0
300 - 1,050	2.0
120 - 420	5.0
60 - 210	10.0
30 - 105	20.0
12 - 42	50.0
6 - 21	100.0
0 – 7	300.0



Using separate container	
Range of BOD	% mixture
1,000 - 3,500	0.2
400 - 1,400	0.5
200 - 700	1.0
100 - 350	2.0
40 - 140	5.0
20 - 70	10.0
10 - 35	20.0
4 - 14	50.0
0 - 7	100.00

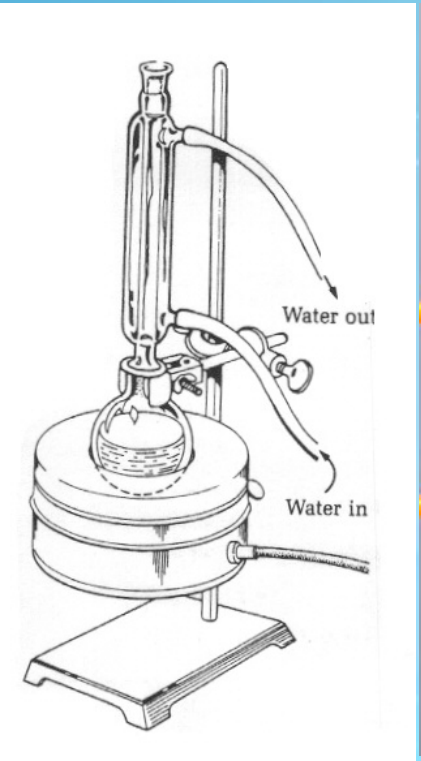
BOD Bottle-cap Sensor

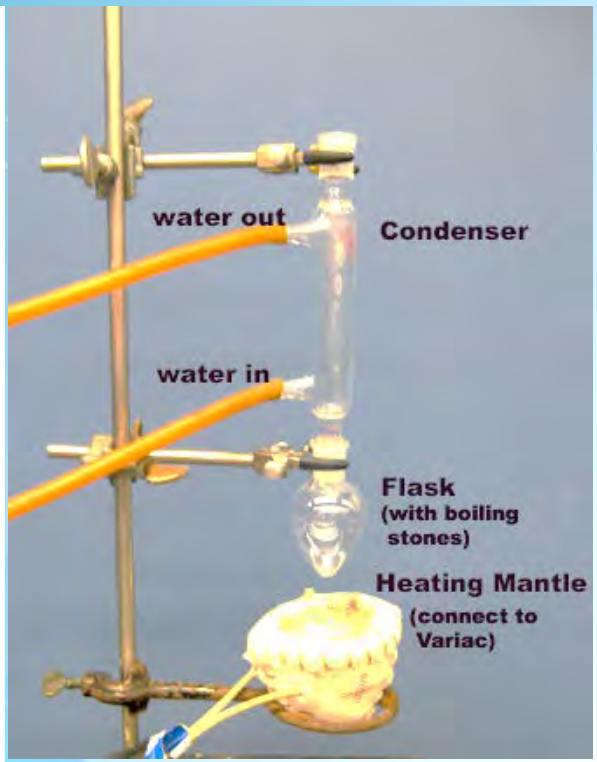
COD

- **Oxidizers:**
  - **Dichromate**
  - **Permanganate**
  - **Manganese III**
- **Interferences with chlorides**

COD

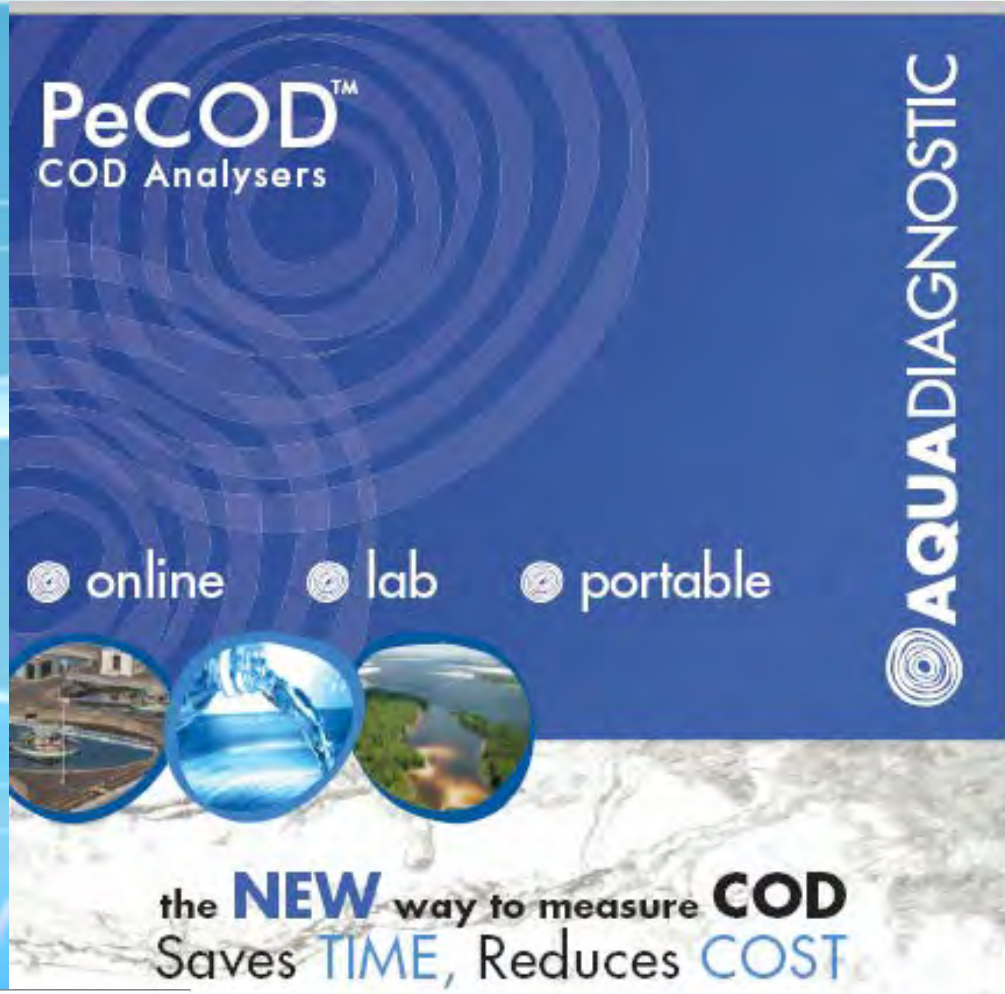
- **Open reflux**
- **Closed reflux**

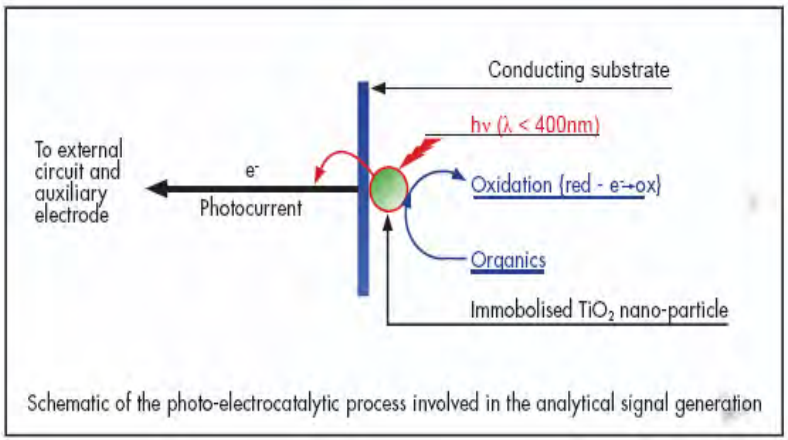




New COD

- **Photoelectrocatalytic**
- **The powerful oxidation potential of UV-illuminated TiO2 ensures that almost all species will be fully oxidized giving a true measure of COD.**



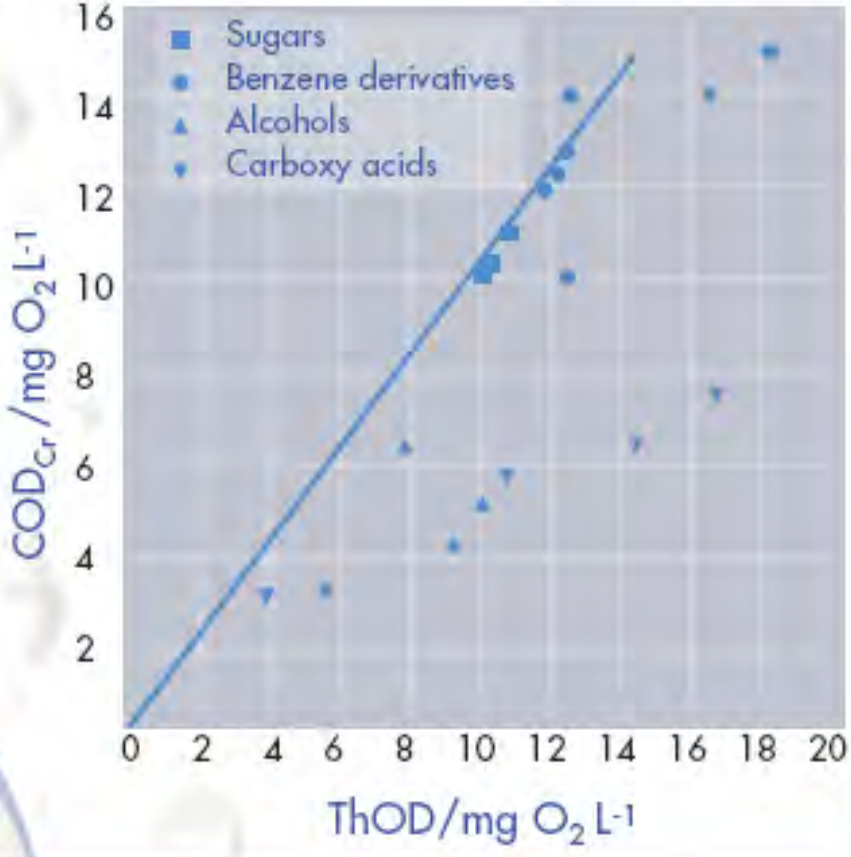


Schematic of the photo-electrocatalytic process involved in the analytical signal generation

Comparison between the two methods

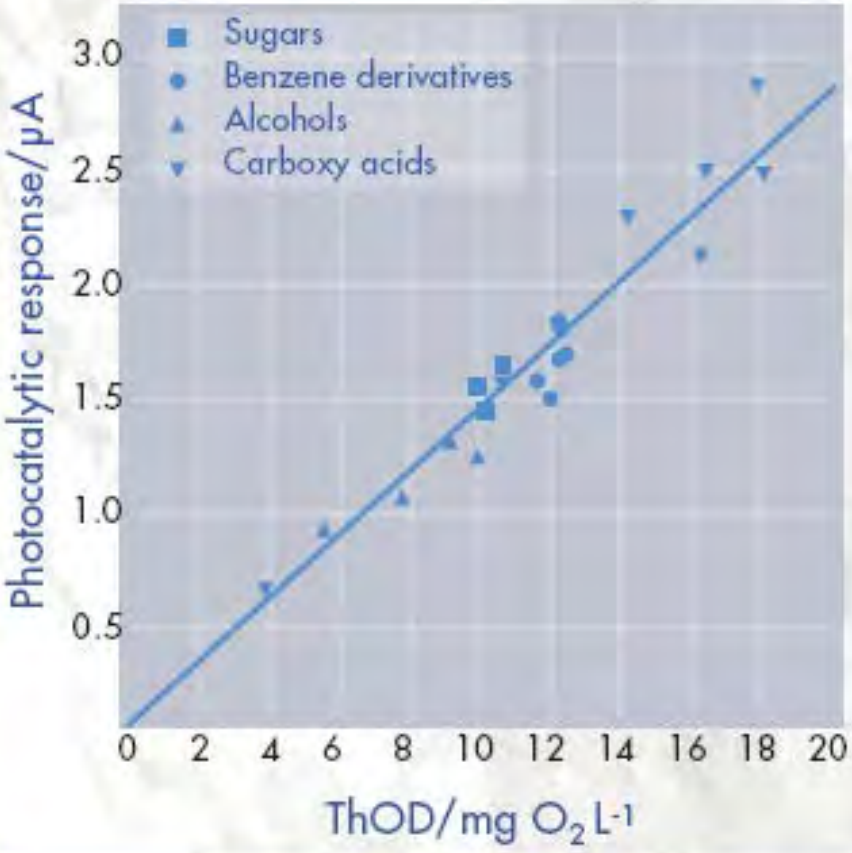
Dichromate method

Relationship between ThOD and COD_{Cr}



Photocatalytic

Relationship between ThOD and the response of the photocatalytic oxidation method.

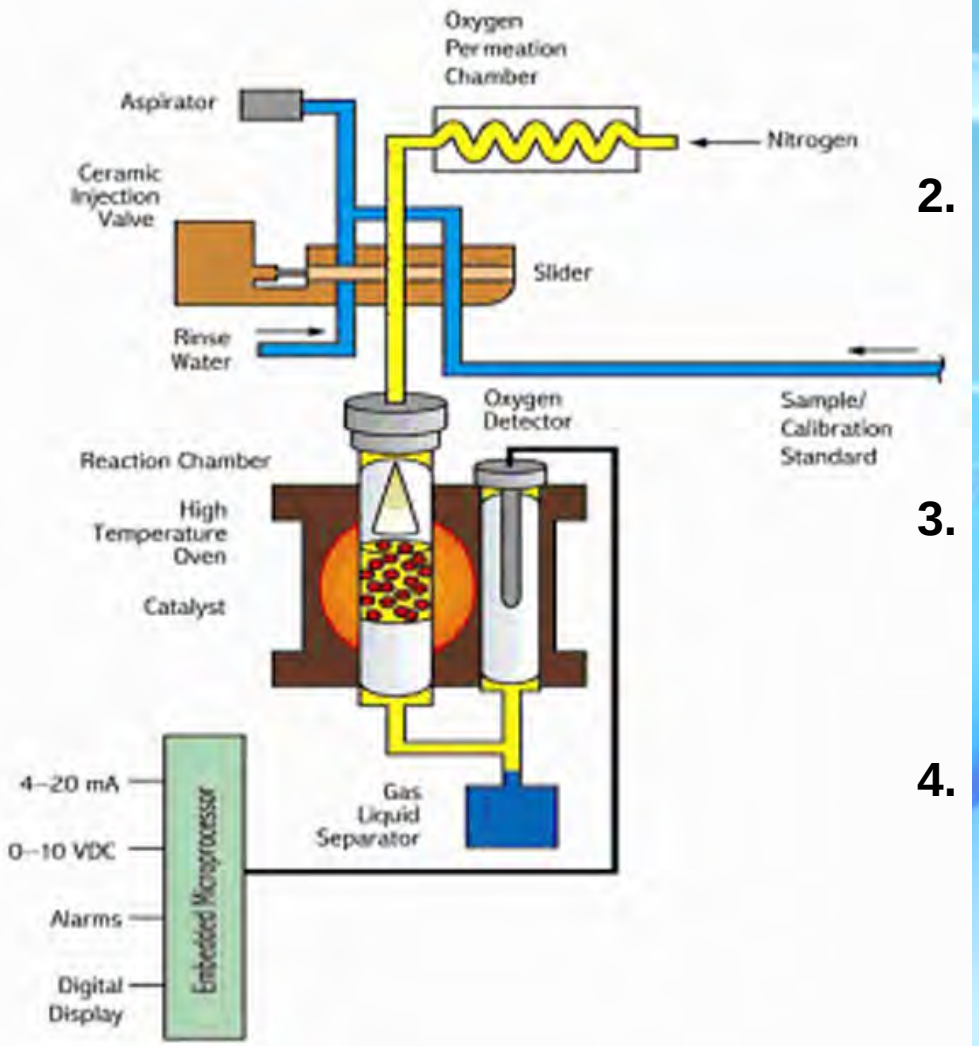


Total Oxygen Demand (ASTM)

Friday 27 January, 2012

the analysis is based on the change in oxygen reading of the carrier gas compared to that when a sample is introduced.

TOD



1. A percent of oxygen is admitted to nitrogen carrier gas (whose pressure and flow rate is controlled) via a dosing cell. The quantity of oxygen is controlled by a range selector.
2. The mixture of gases flows through the injection valve, reaction chamber, to the oxygen detector. The detector monitors the oxygen concentration in the carrier gas.
3. Sample is vacuum aspirated through the injection valve and a precise volume is injected to a catalyst maintained at 900°C .
4. The sample is quantitatively oxidized, which consumes part of the oxygen in the carrier gas. The oxygen depletion correlates directly to the oxygen in the sample.

TOC, TC, TOD, BOD & COD !!

Parameter	TOC	TC	TOD	BOD	COD
Analysis time	5–10 minutes	3–10 minutes	2–10 minutes	5–6 days	2–3 hours
Initial cost	highest	high	high	lowest	moderate
Precision	±2%	±2%	±2%	±15%	±8%
Solids recovery	excellent	excellent	excellent	poor	variable
Effects of toxics	none	none	none	high	none
Measurement units	mg C/l	mg C/l	mg C/l	mg O2/l	mg O2/l
Results include:					
SO_3^{2-}, S^{2-}, and organic S	no	no	yes	yes	yes
organic nitrogen	no	no	yes	yes	yes
chloride	no	no	no	no	yes

TOD

- Reading within 3 minutes
- TOD is unaffected by the presence of inorganic carbon
- TOD analysis will also indicate noncarbonaceous materials that consume or contribute oxygen, i.e. the oxygen demand of ammonia, sulfite and sulfides will be reflected in the TOD measurement.
- TOD reflects the oxidation state of the chemical compound (that is, urea and formic acid have the same number of carbon atoms, yet urea has five times the oxygen demand of formic acid).

Qs ???????

1. What does the ratio between BOD and COD mean?
2. Could you calculate COD from BOD values or *vise-versa*?
3. Could BOD value be more than the COD value?
4. Is there a relation between TSS, TS, TDS, TOC, NTU and BOD or COD?

Alkalinity

- Mainly carbonates
- 150-160(mg/L) x 0.6= carbonates

Hardness

- Presence of multivalent cations (valence more than one +)
- Mainly Ca^{2+} & Mg^{2+} , but Fe, Al, Zn and Mn
  - Soft 0-60 mg/l
  - Moderate hard 61-120 mg/l
  - Hard 121-180 mg/l
  - Very hard >180 mg/l
- Importance to industrial water use; no proven health effects on humans, only on soaping.
- Mainly ground water problem in Egypt (dolomite, sand stone, etc.....)

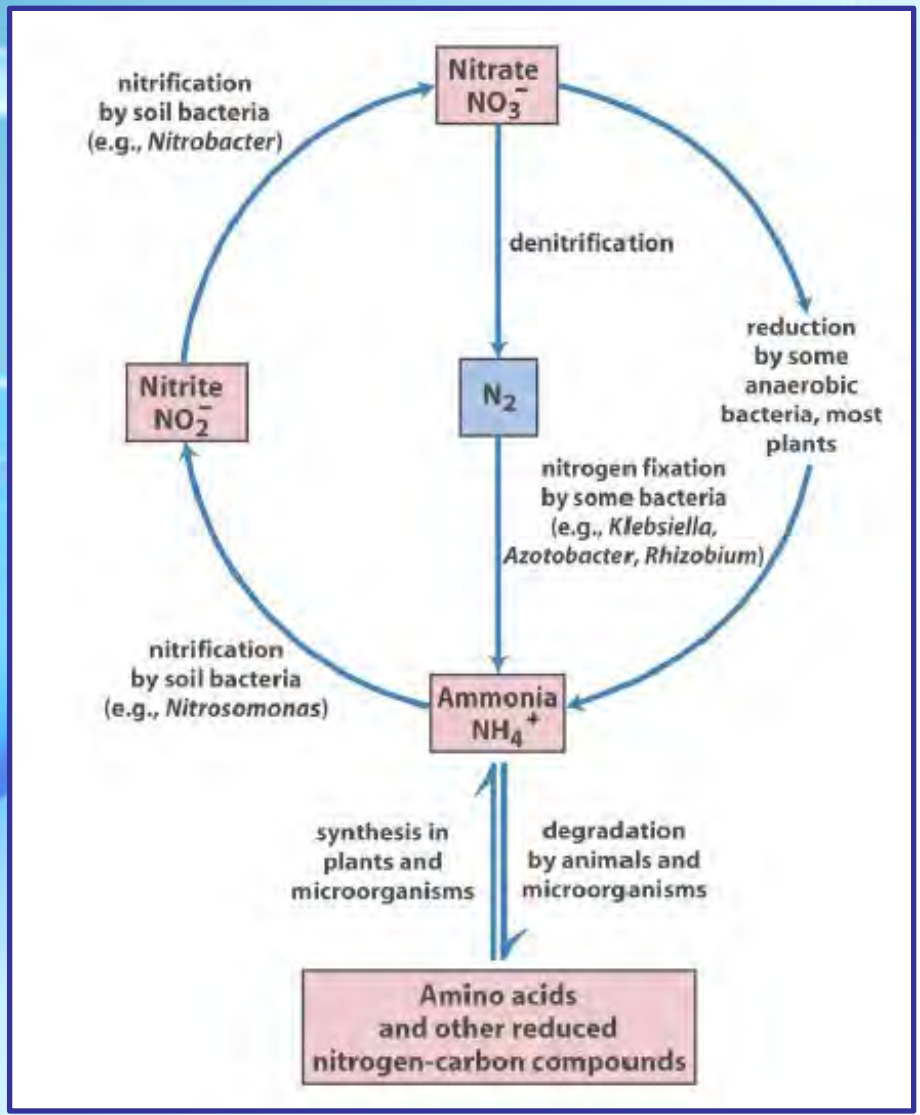
Measurements of Hardness

- Titration against Na_2EDTA +indicator
- Sodium cyanide is used to overcome interferences (very toxic).

- Ion exchange resins are used to soften the water, as well as RO.

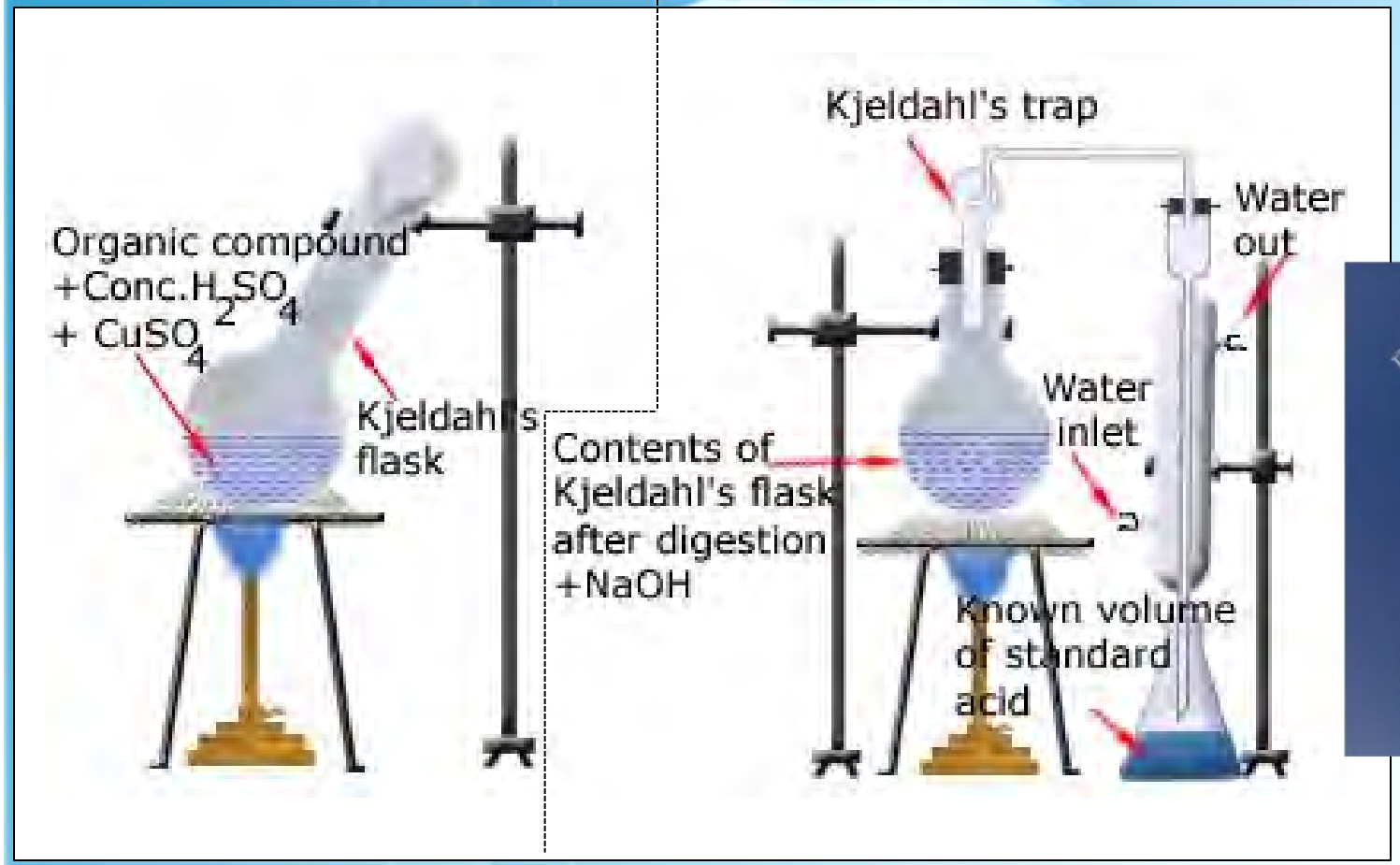
Nitrogen in samples

- Total Nitrogen
- $Nitrogen_{org}$ (Kejldahl N)
- Ammonia
- Nitrate
- Nitrite



Total Nitrogen

- **Kjeldahl nitrogen distilling apparatus**



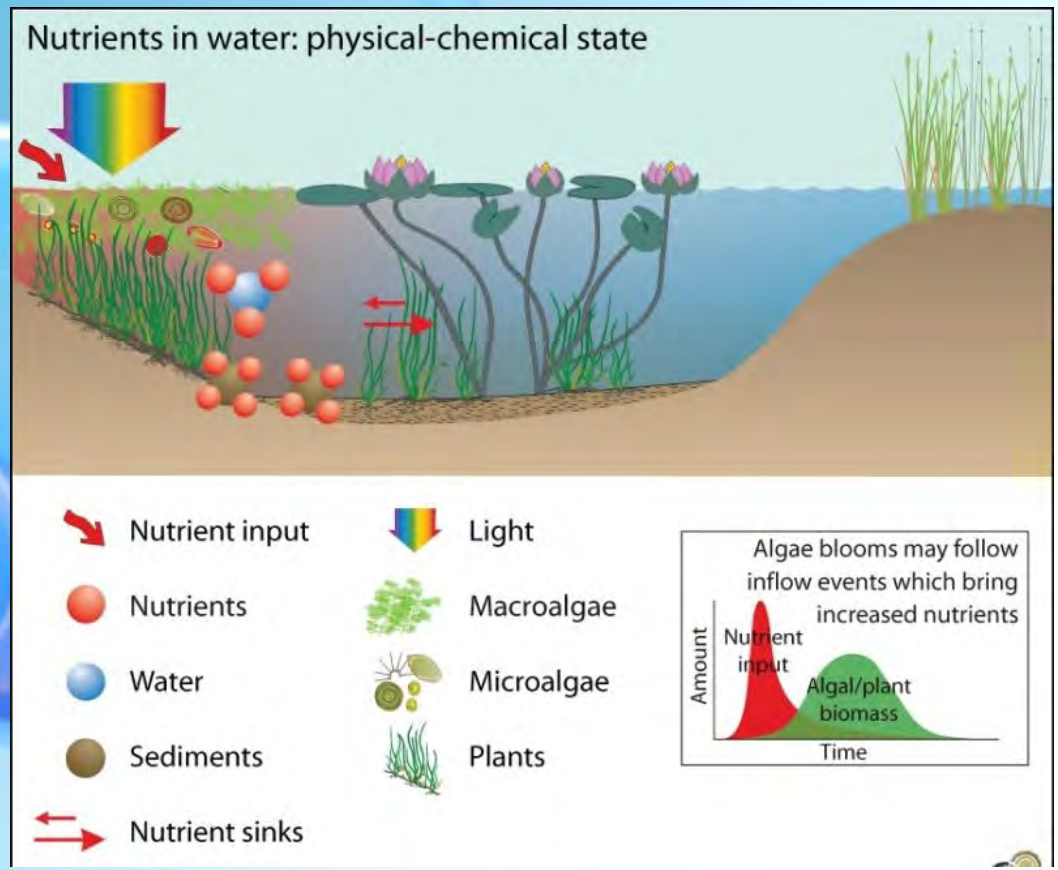
Automated Kjeldahl

Nitrate

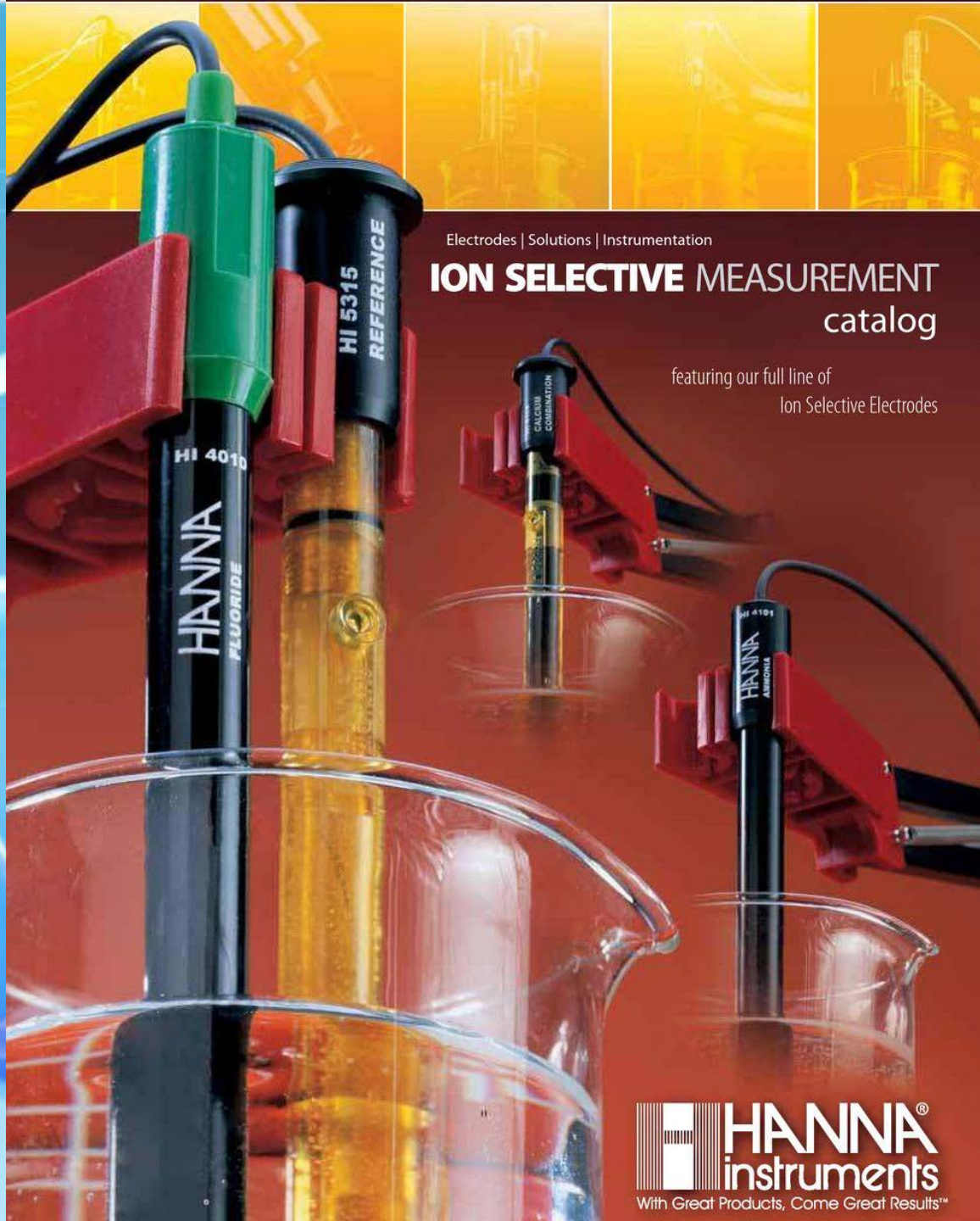
- Nitrate (NO3-) ***is very difficult*** to measure directly, whereas nitrite (NO2-) is easier to measure.
- Nitrate (NO3-) in the water sample is converted to nitrite (NO2–) by cadmium to the water sample.
- A second chemical is then added to the water sample and reacts with the nitrite (NO2-) to cause a color change proportional to the amount of nitrite in the sample.
- The measurement in the nitrate gives the combined concentration of nitrite (if present) and nitrate.
- The chemical reaction that causes nitrate (NO3-) to change to nitrite (NO2-) is an oxidation–reduction reaction, which involves the exchange of electrons from one molecule to another molecule. i.e. Cadmium removes electrons from nitrate (NO3-) to form nitrite (NO2-).

Other nutrients

- Phosphorous
  - Total
  - Dissolved
- Sulfur
  - Sulfate
  - Sulfide
- Silica
  -

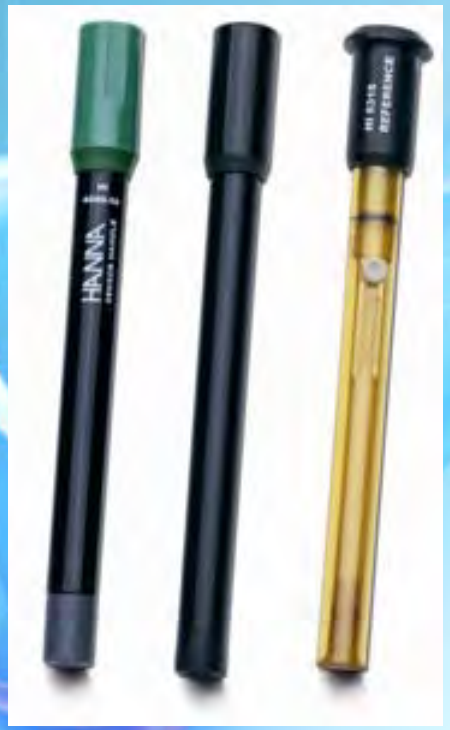


ISE
measurements



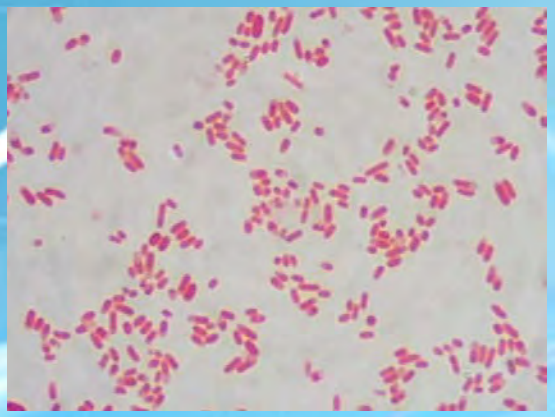
Potentiometric Tools
Ion selective electrodes

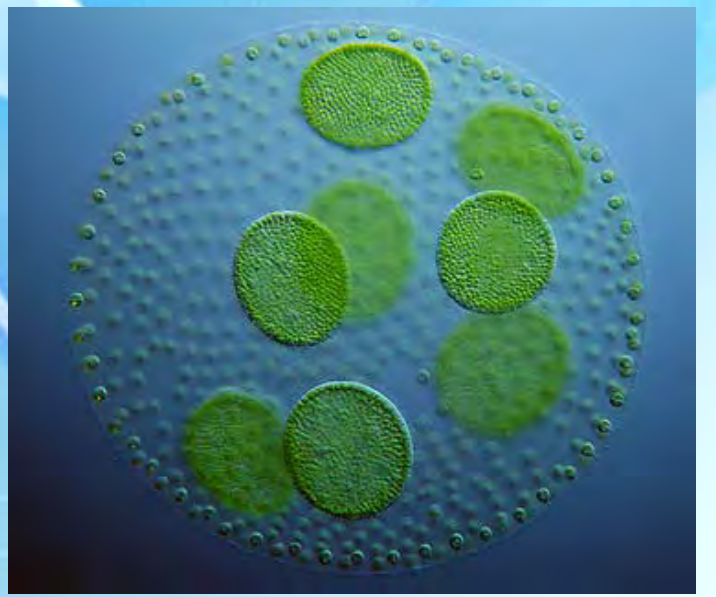
- Chloride
- Ammonia
- Nitrate
- Fluoride
- Potassium
- Calcium
- Sodium
- sulfide



- Bromide
- Iodide
- Copper
- Lead
- Perchlorate
- Cyanide
- Hardness
- Surfactants

BIOLOGICAL EXAMINATIONS





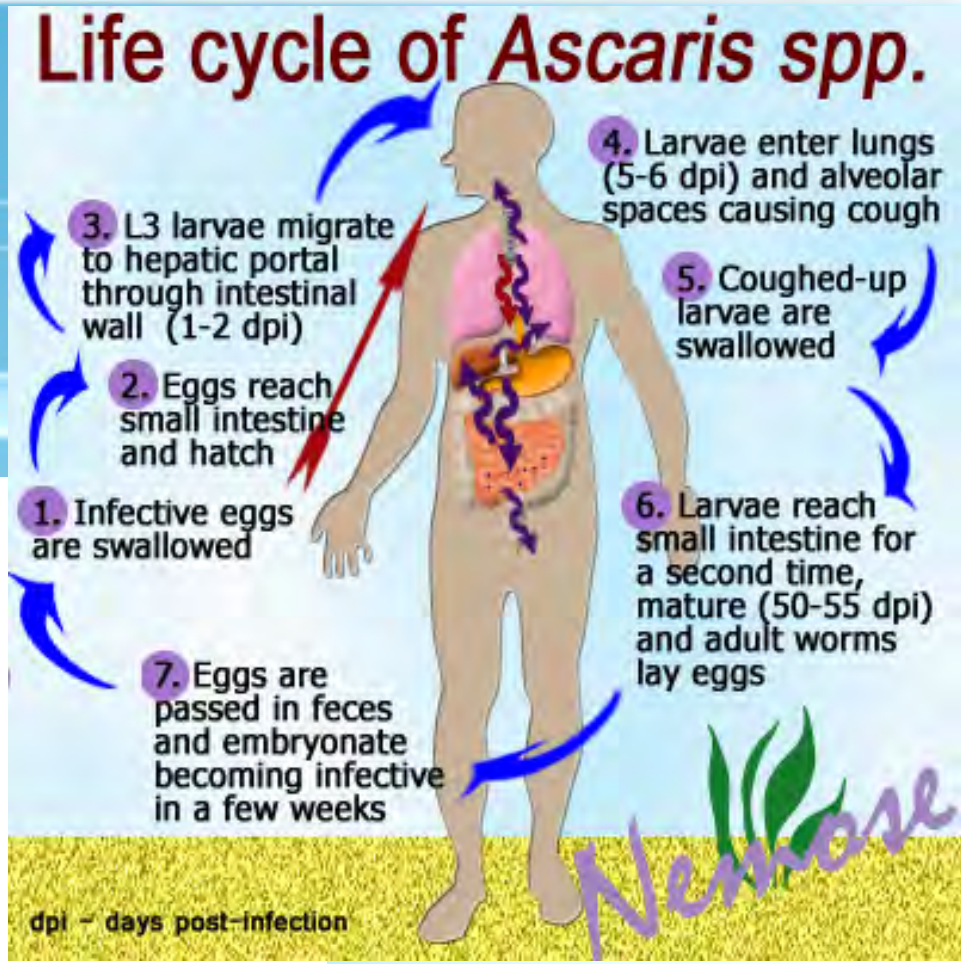
Pathogens & Parasites

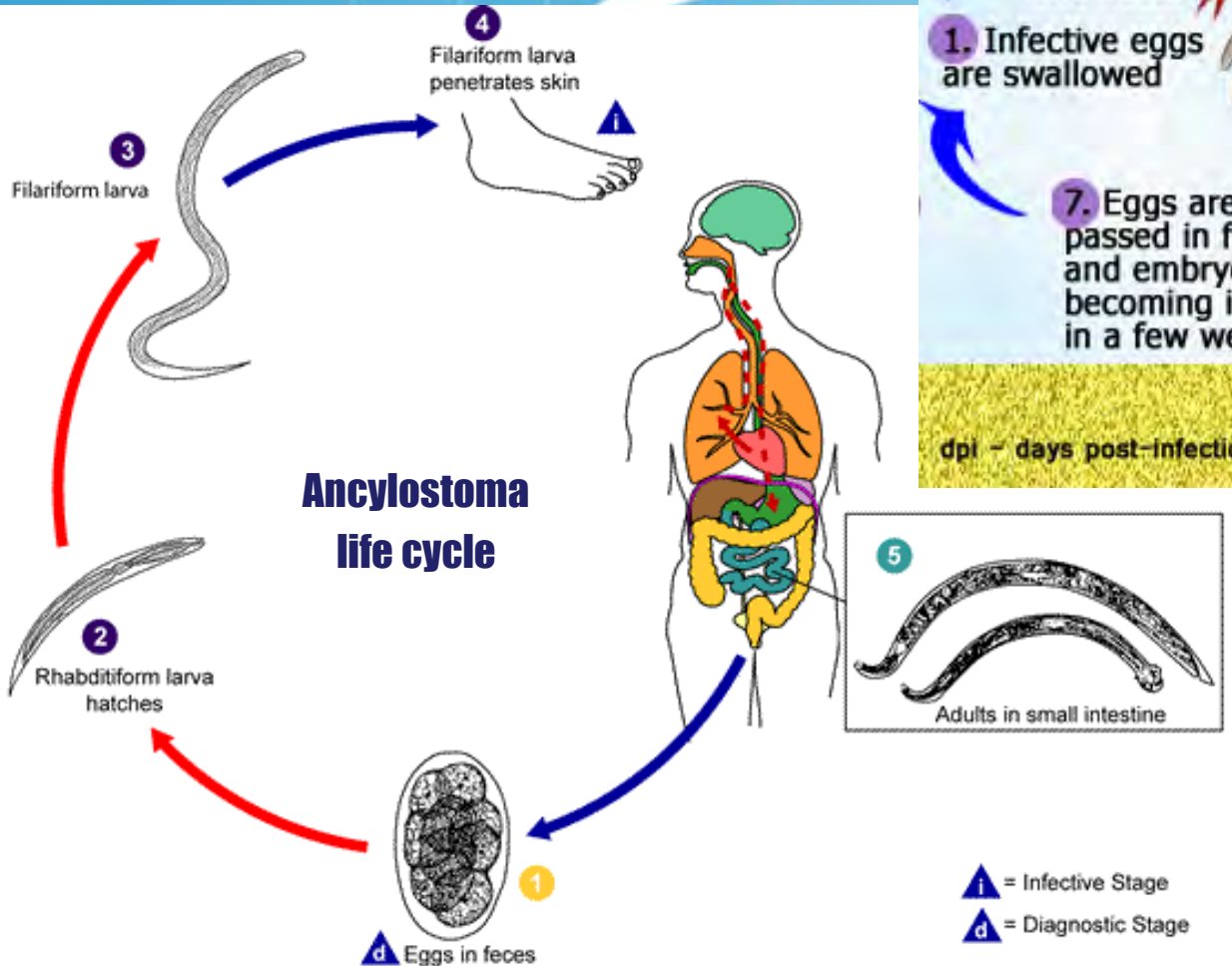
- *Shigella* spp
- Pathogenic *Escherichia coli*
- *Vibrio cholerae*
- *Campylobacter jejuni*
- *Salmonella typhi*
- Adenoviruses
- Enteroviruses
- Hepatitis A & E
- Norwalk virus
- Rota virus
- Small round viruses
- *Giardia intestinalis*
- *Cryptosporidium parvum*
- *Entamoeba histolytica*

Biological Examinations

Item	Standard
Total Bacterial Count	50 CFU/1ml/24hr
Total Coloiforms (MPN)	95% of samples free up to 100cm^3 for a year
Total Typical Colon Bacilli	Free
Colon Streptococci	Free
Algae	1 µg/L Microcystin in case of bluegreen outbreak
Protozoa	Free of living protozoa and all forms of parasites

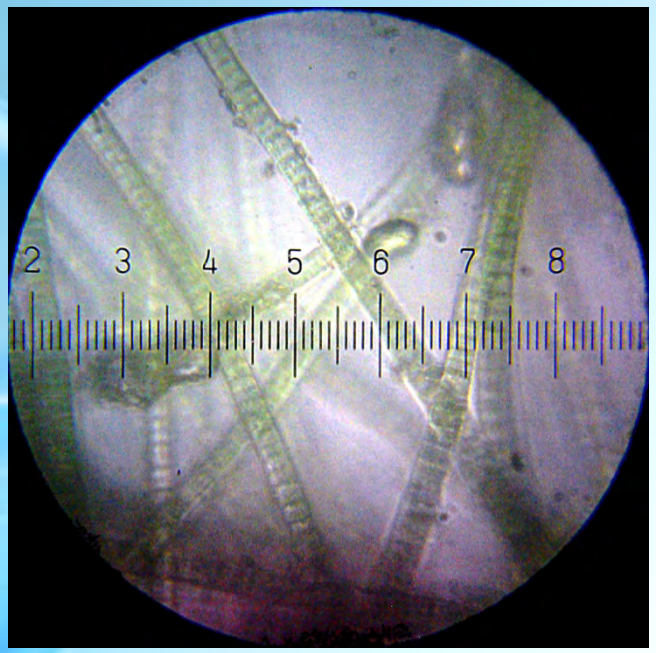
Parasites


Life cycle of Ascaris spp.
4. Larvae enter lungs (5-6 dpi) and alveolar spaces causing cough
3. L3 larvae migrate to hepatic portal through intestinal wall (1-2 dpi)
5. Coughed-up larvae are swallowed
2. Eggs reach small intestine and hatch
1. Infective eggs are swallowed
6. Larvae reach small intestine for a second time, mature (50-55 dpi) and adult worms lay eggs
7. Eggs are passed in feces and embryonate becoming infective in a few weeks
dpi – days post-infection
Newrose


4
Filariform larva penetrates skin
i
3
Filariform larva
Ancylostoma life cycle
5
Adults in small intestine
2
Rhabditiform larva hatches
1
d
Eggs in feces
i = Infective Stage
d = Diagnostic Stage

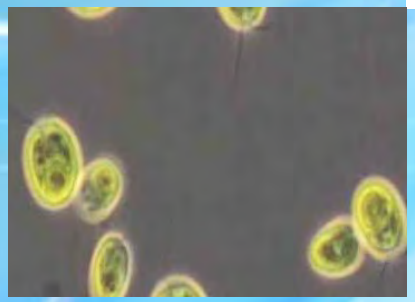
Biological Examinations

- Microscopic
- Growth
- Chlorophyll
- Serological
- Molecular (PCR)



Microbial Counts

- Bacteria
- Parasites
- Algae



- Direct counts : magnification if needed
- Indirect counts: Culture media

Membrane Filter (MF) Technique (Steps)

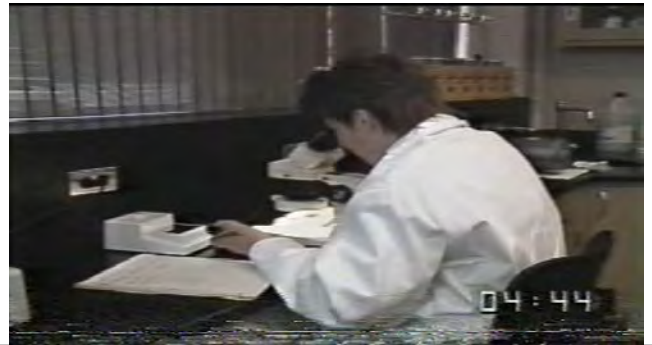
– **Sampling**

– **Culturing**

– **Examination**

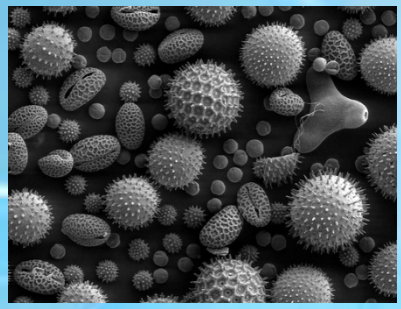
- **Filtration**

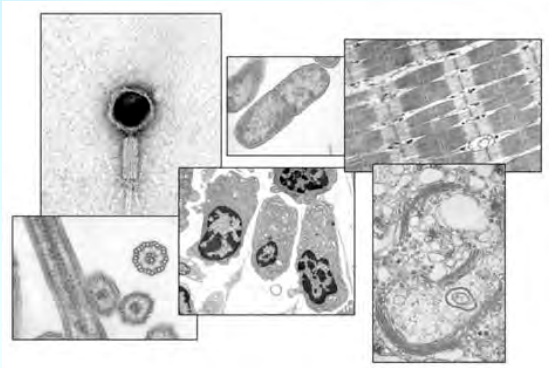
- **Incubation**



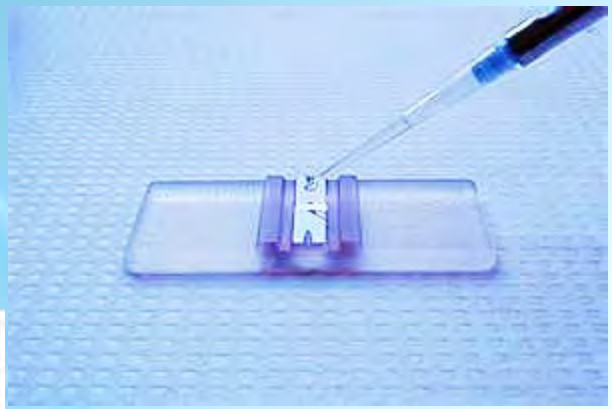
Microscopy

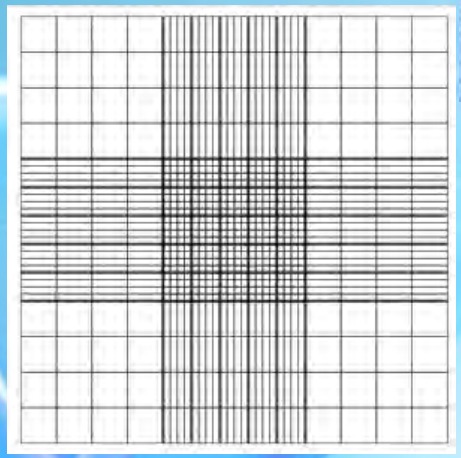
- Binocular
- Light
- Phase contrast
- Polarizing
- Dark Field
- SEM
- TEM

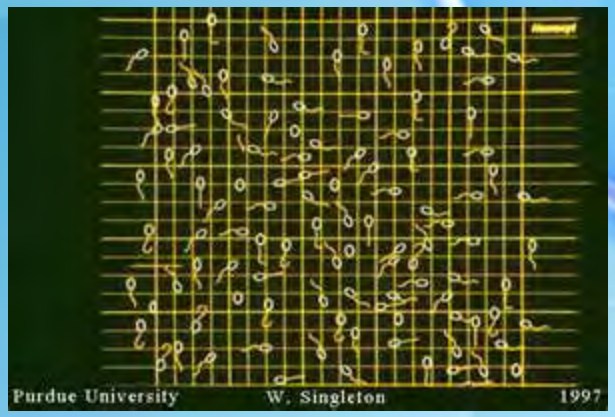




Hemocytometer



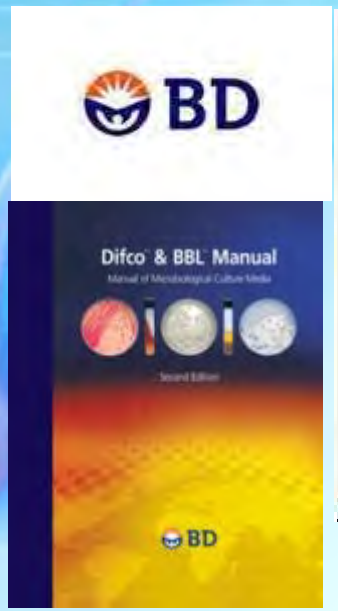


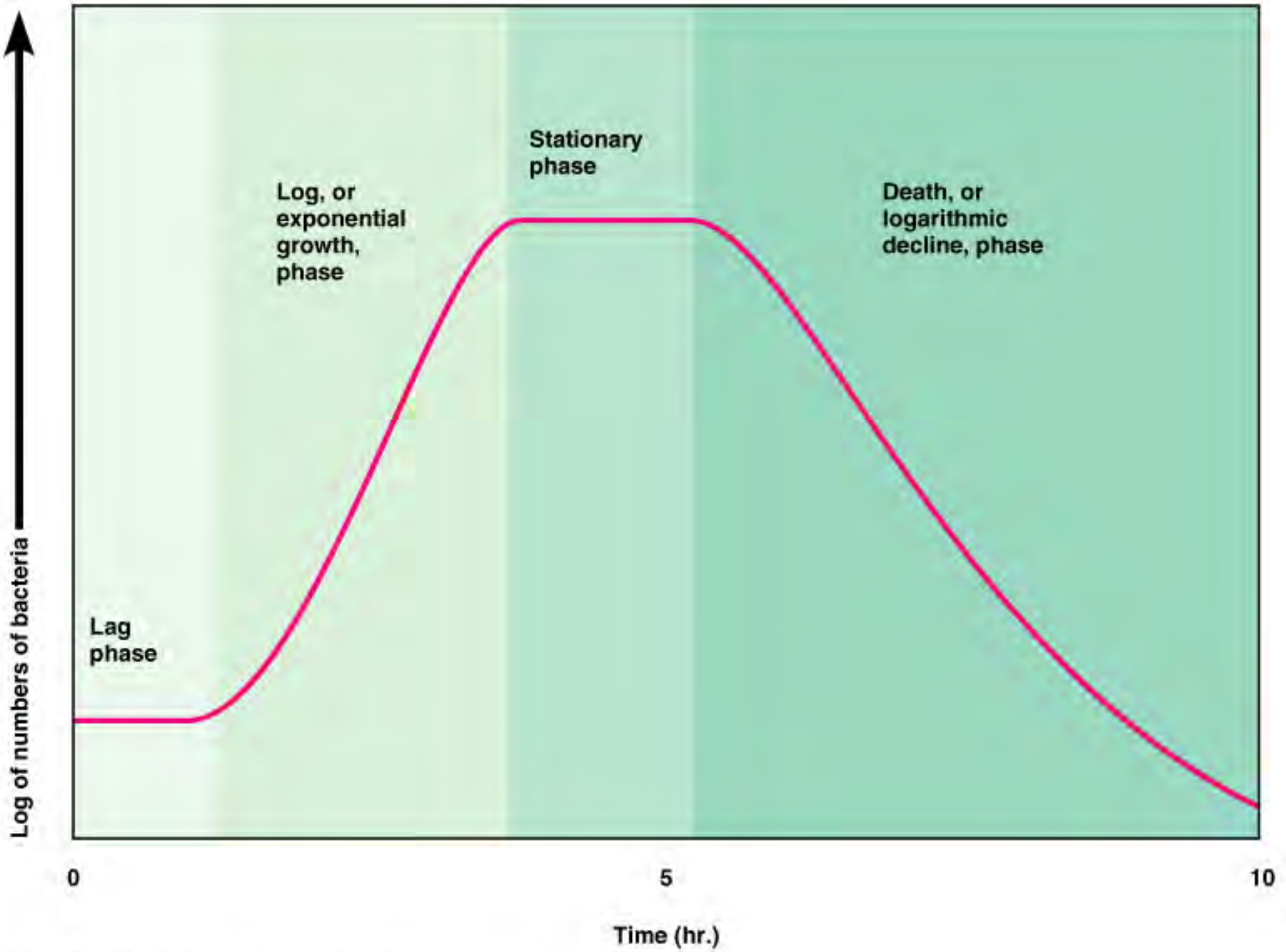


Microbial Counts

Specific Media

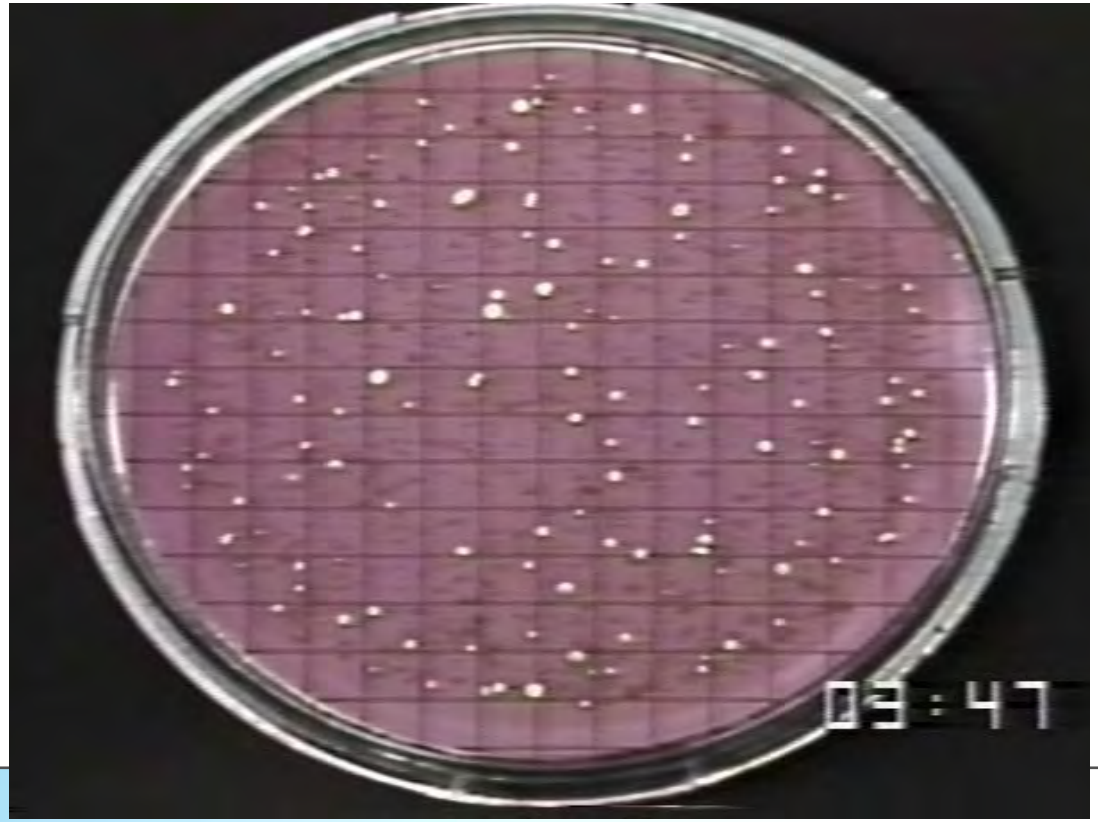
- For TPC
- For colon bacteria
- For *E. coli*
- For Streptococci



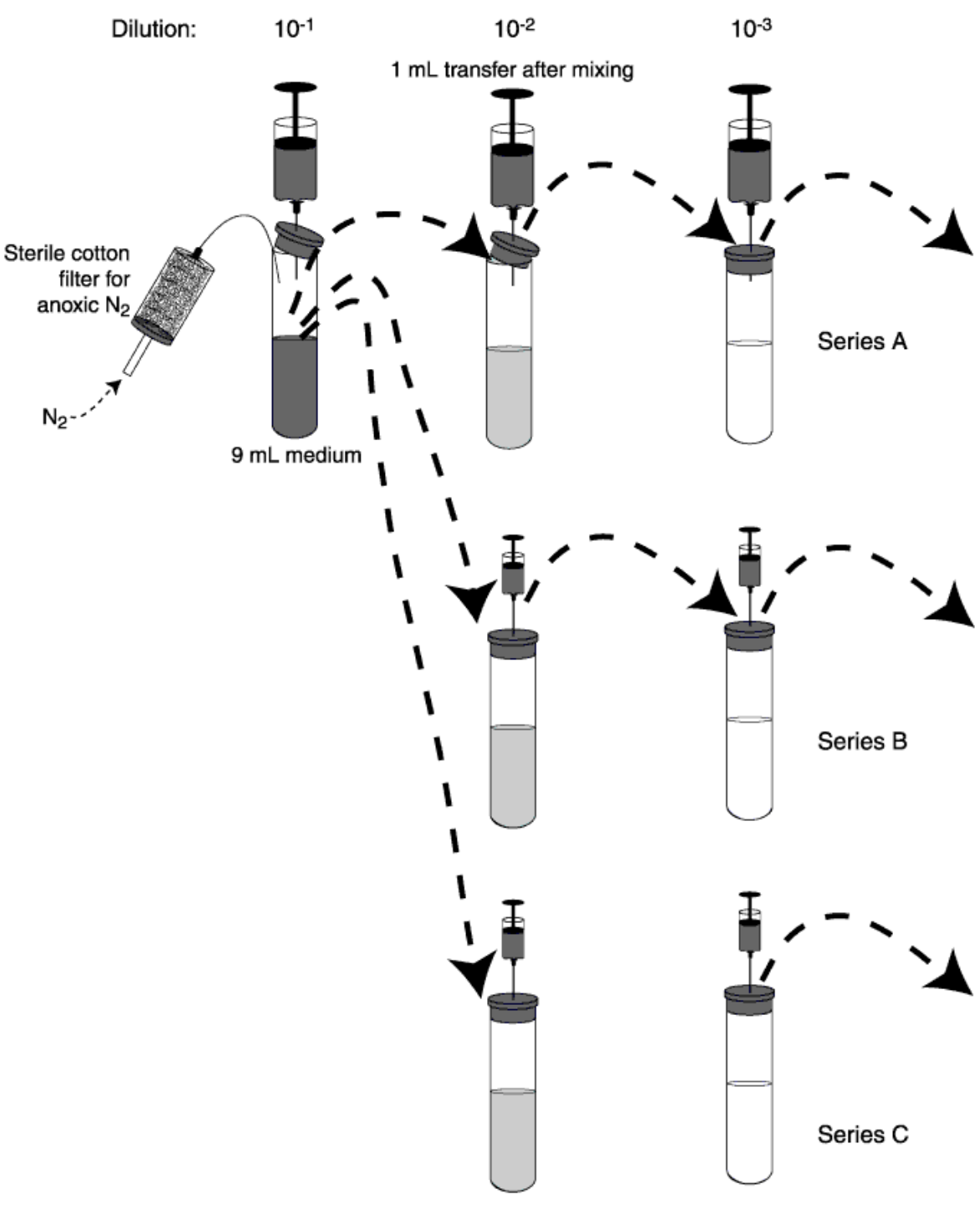


Total Coliform

- **Total Coliform bacteria are enumerated by the Membrane Filter (MF) procedure**



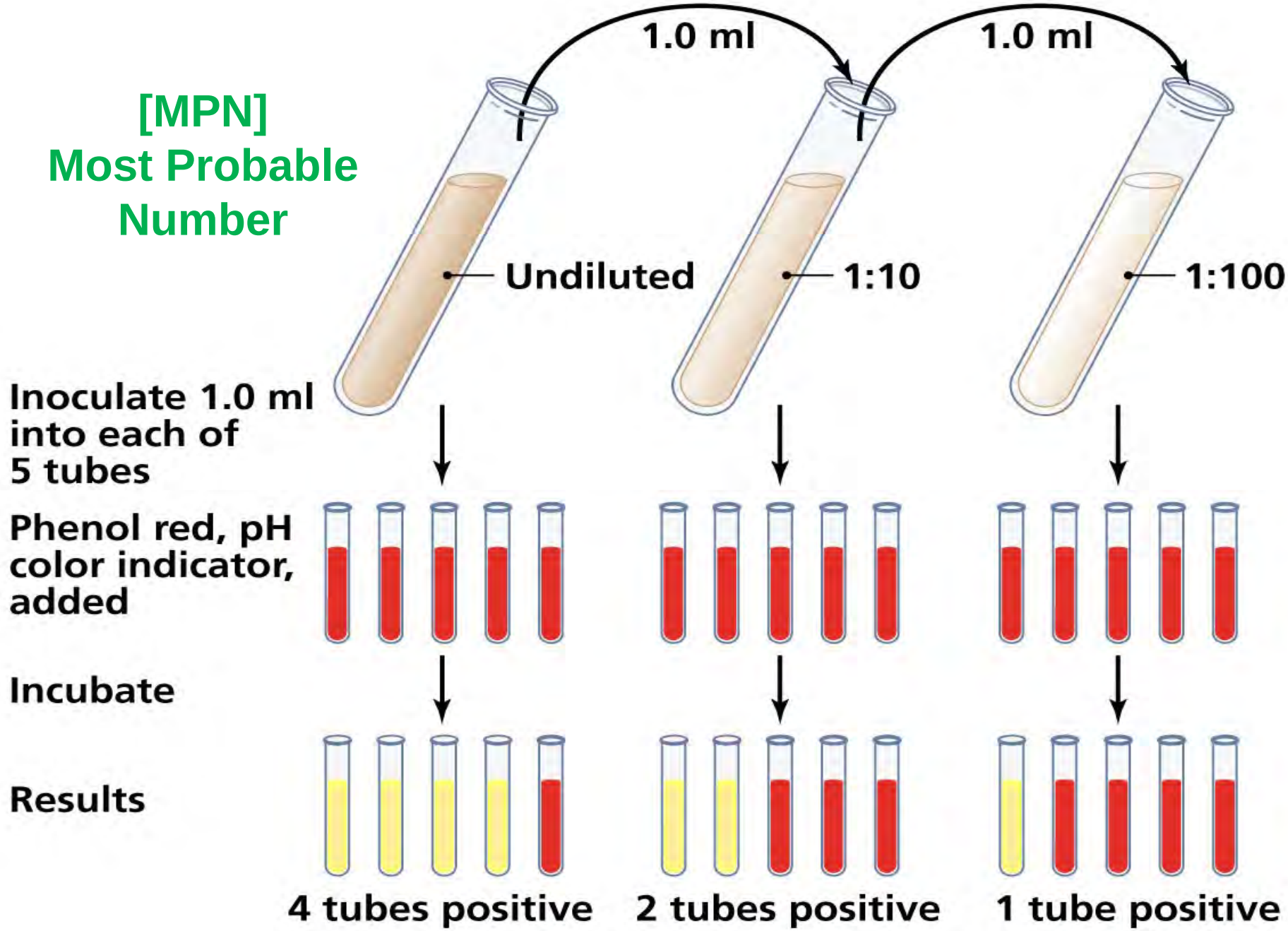
Serial dilutions



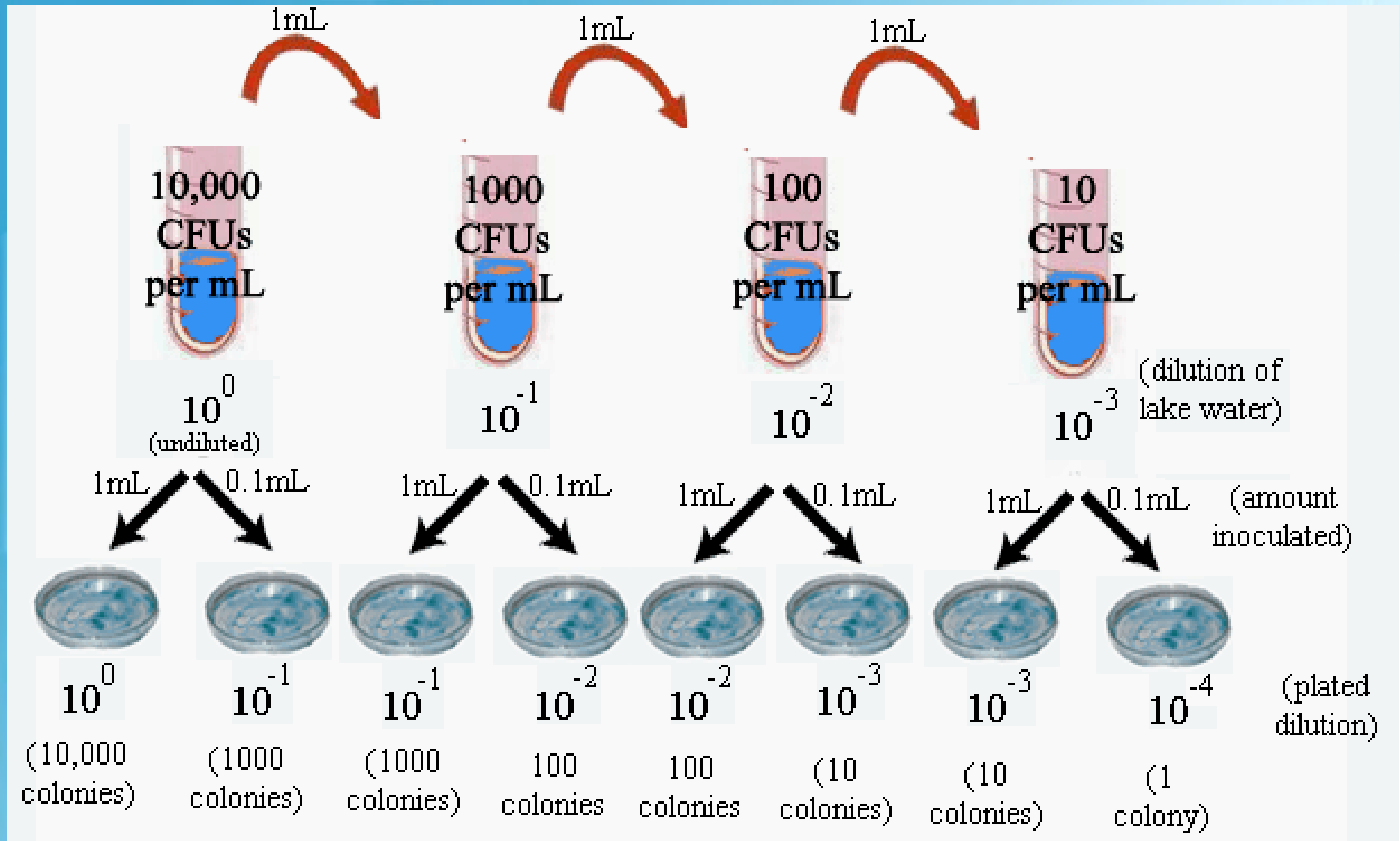
MPN bacterial count

- When using dilution if 10^{-3} show growth, while 10^{-4} does not; then it is possible to say that there are greater than $1X10^{3}$ cells/ml but less than $1X10^{4}$/ml.
- Bacteria are rarely, if ever, distribute evenly in a sample; e.g. if a 10 ml sample contains a total of 300 cells, not every ml will contain 30 cells. So MPN was envisaged.

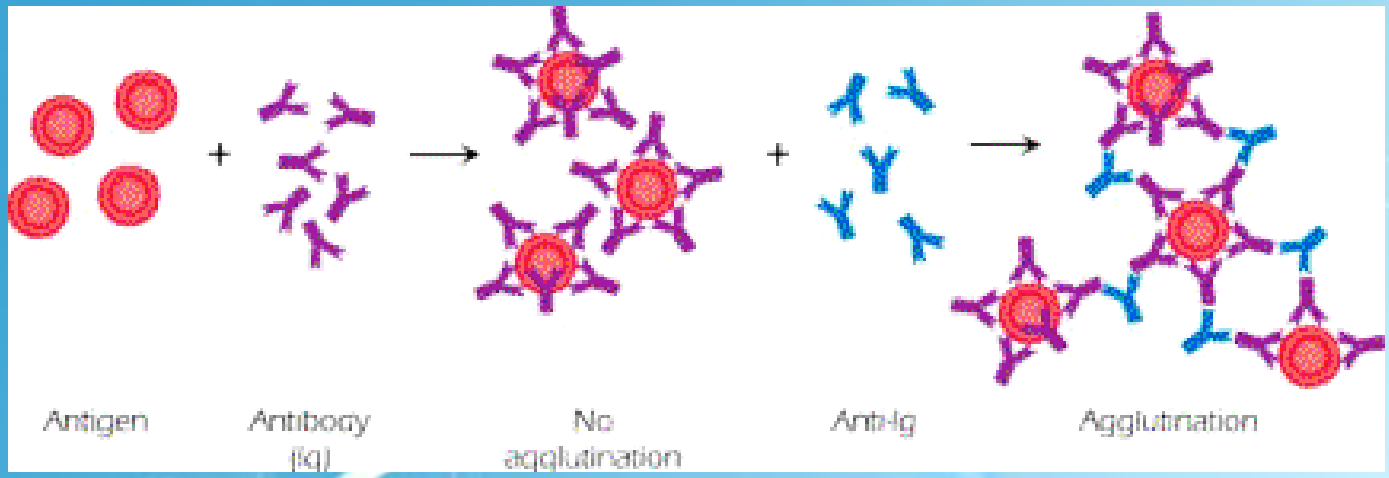
[MPN] Most Probable Number



MPN (3 dilutions + 3-10 tubes per dilution)



No. of Tubes Positive in:			MPN in the inoculum of the middle set of tubes
First Set	Middle Set	Last Set	
0	0	0	<0.03
0	0	1	0.030
0	0	2	0.060
0	0	3	0.090
0	1	0	0.030
0	1	1	0.061
0	1	2	0.092
0	1	3	0.120
0	2	0	0.062
0	2	1	0.093
0	2	2	0.120
0	2	3	0.160
0	3	0	0.094
0	3	1	0.130
0	3	2	0.160
0	3	3	0.190
1	0	0	0.036
1	0	1	0.072
1	0	2	0.110
1	0	3	0.150
1	1	0	0.073
1	1	1	0.110
1	1	2	0.150



Serological Methods

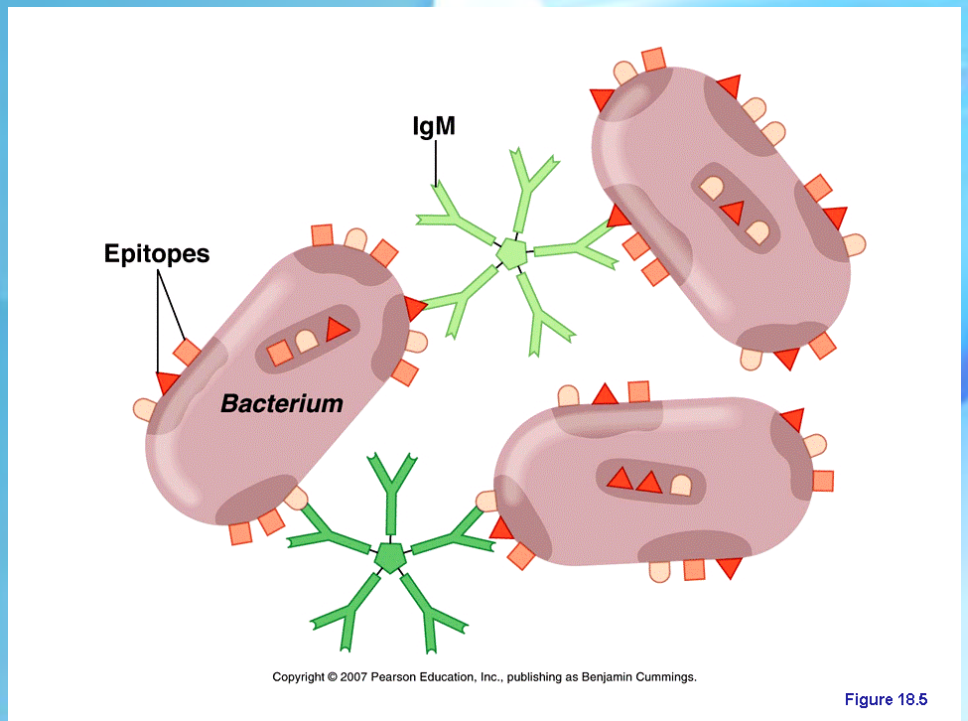
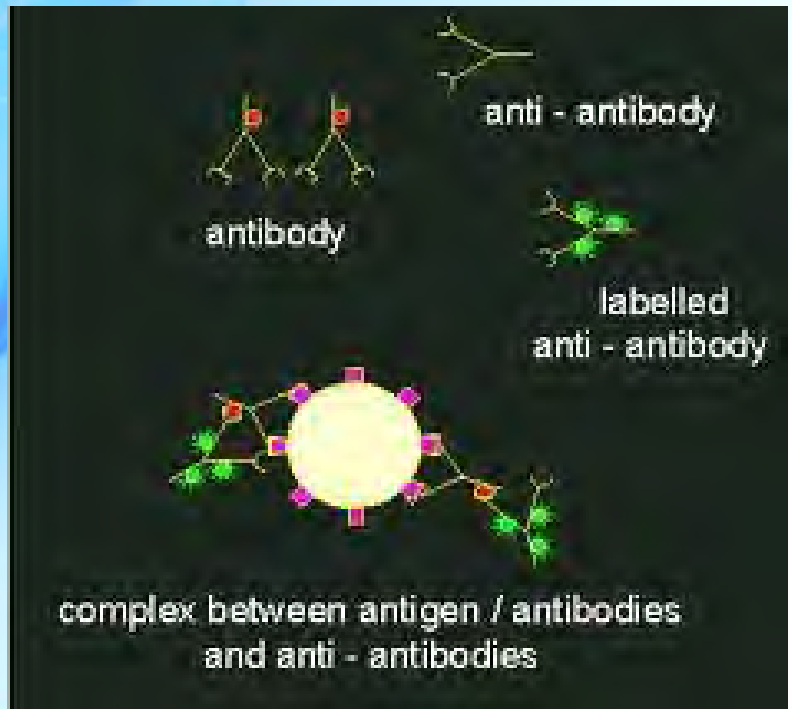
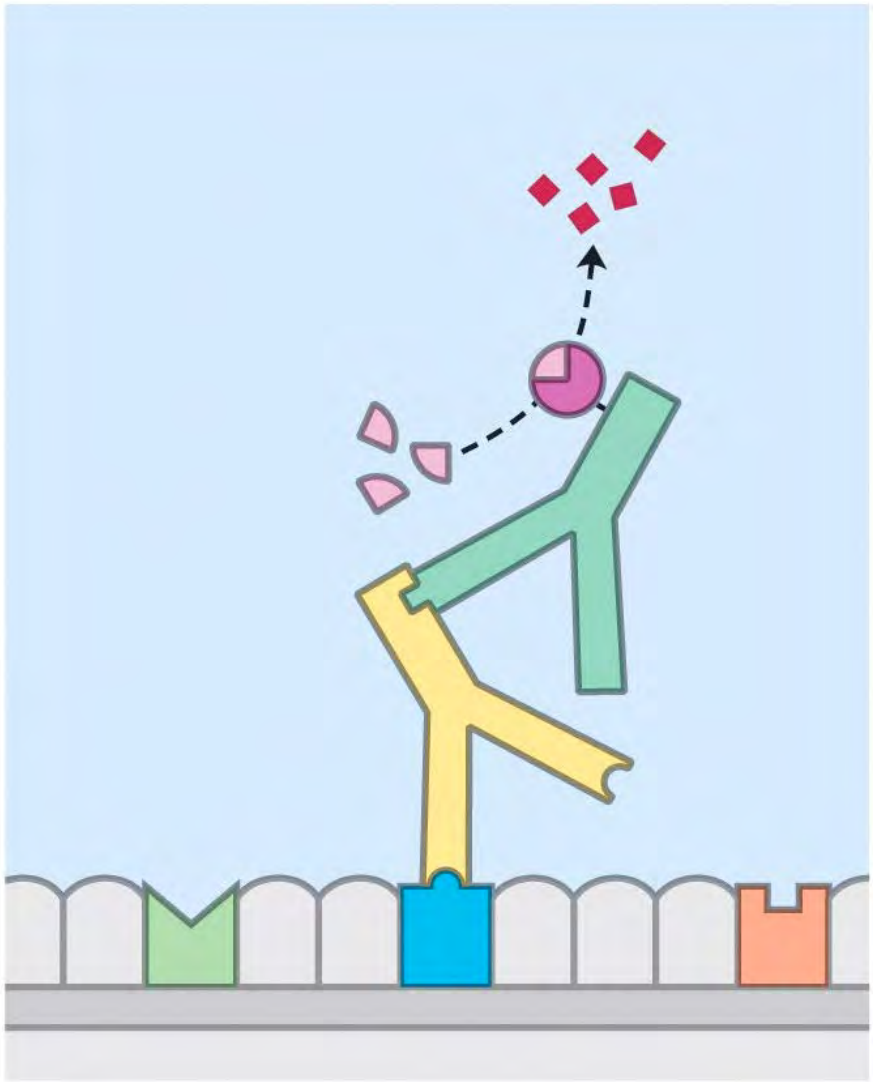


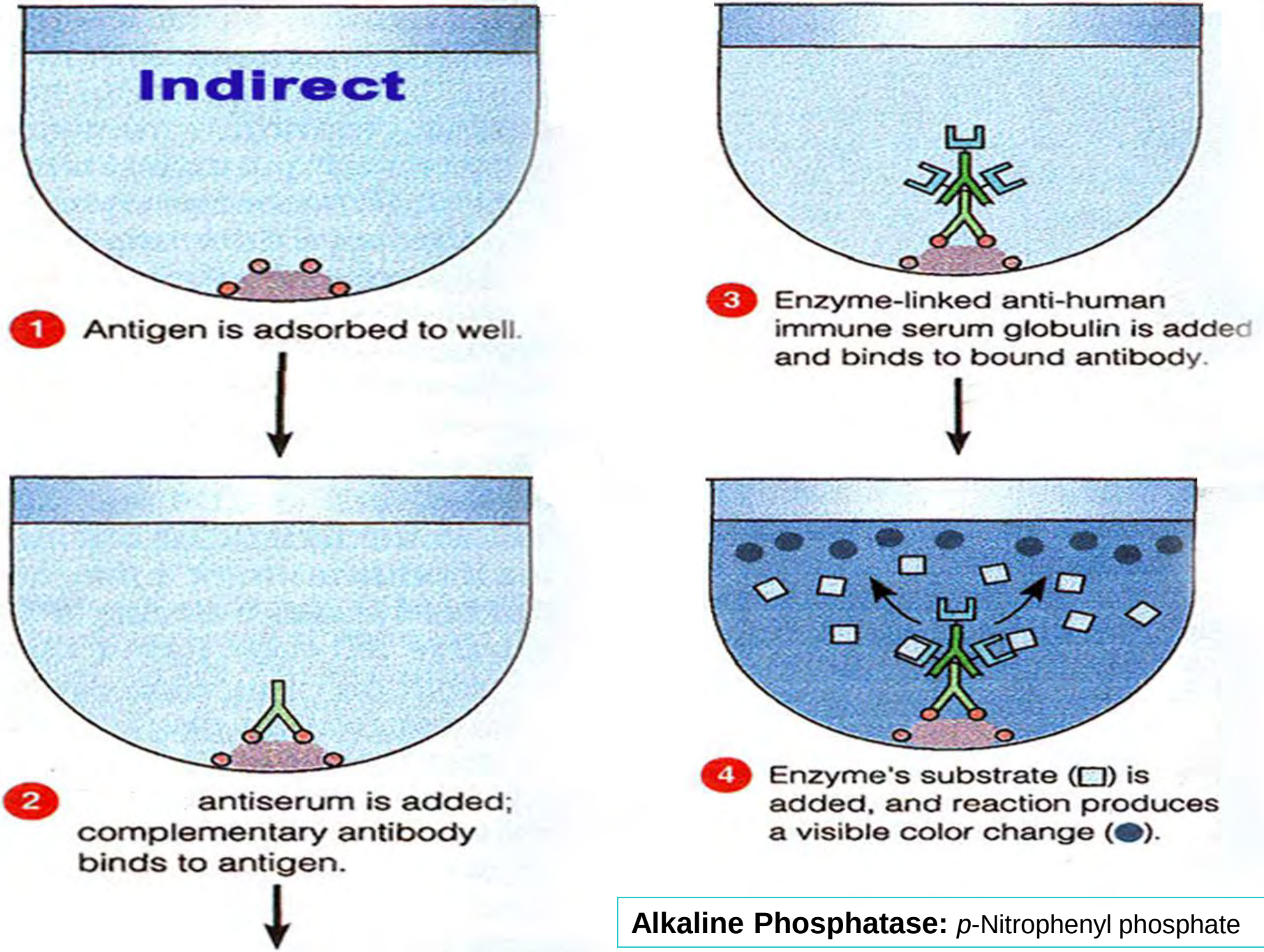
Figure 18.5



Serological Methods
ELISA (starting with AG)

1. Coat surface with sample (antigens).
2. Block unoccupied sites with nonspecific protein.
3. Incubate with primary antibody against specific antigen.
4. Incubate with antibody-enzyme complex that binds primary antibody.
5. Add substrate.
6. Formation of colored product indicates presence of specific antigen.





Alkaline Phosphatase: *p*-Nitrophenyl phosphate

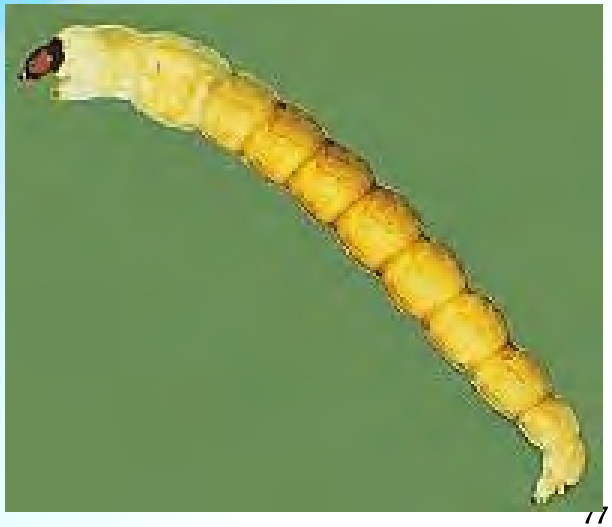
PCR for pathogens detection

- **Bacteria**
- **Viruses**

Principal of PCR detection

Toxicity Testing

1. *Daphnia magna*
2. *Chironomus riparius*
   [Diptera:Chironomidae]
3. *Artemia silana*



Conditions for toxicity bioassays

- Linearity and not “yes” or “no” response
- Dose response = Sensitivity

Water is a precious commodity

keep it safe.....