

Hydrochemistry

Lecture 1

Fundamentals of Aquatic Chemistry

- Importance of water for humans
- Water withdrawal
- Important properties of water
- Anomalies of water
- Molecule of water
- Hydrogen bonds
- The hydrologic cycle
- Aquatic life
- Main aquatic chemical processes

Hydrochemistry

Lecture 2

Chemical composition of natural waters

- Dissolved gases
- Metals in water
- Biogenic elements
- Cycle of biogenic elements in hydrosphere
- Types of natural waters
- Surface water
- Water from precipitations

Hydrochemistry

Lecture 3

Groundwater and seawater

- Groundwater
- Mineral water, its classification
- Artesian water
- Connate water
- Geothermal water
- Seawater

Hydrochemistry

Lecture 4

Water pollutions and wastewater

- Sources of water pollution
- Wastewater
- Content and properties of waste water
- Chemical pollutant limitations
- Wastewater treatment

Hydrochemistry

Lecture 5

Basic stages of water analysis

- Choice of analytical method
- Sampling
- Methods of sample preservation
- Determination of physical properties of water
- Content of soluble and insoluble compounds
- Redox potential
- Electrical conductivity

Hydrochemistry

Lecture 6

Methods of investigation of integral water characteristics

- Chemical, physico-chemical, physical, biological methods of analysis
- Portable laboratories
- Total Kjeldahl nitrogen (TKN)
- Organic nitrogen
- Total phosphorus.
- Organic carbon
- Biochemical oxygen demand (BOD)
- Chemical oxygen demand (COD)

Hydrochemistry

Lecture 7

Individual indexes for determination of chemical content of water (Part I)

- pH and pOH
- Dissolved oxygen
- Hydrogen sulfide and sulfides
- Acidity and alkalinity
- Components of carbonate system
- Chlorides and sulphates
- Hardness of water
- Potassium and sodium
- Calcium and magnesium

Hydrochemistry

Lecture 8

Individual indexes for determination of chemical content of water (Part II)

- Ammonia and ammonia salts
- Nitrates and nitrites
- Phosphates and polyphosphates
- Silicium
- Iron
- Microelements (Mn, Cu, Zn, Co, Mo)

Hydrochemistry

Lecture 9

Toxic inorganic substances determination

- Al, As, Be, V, Bi, Cd, Ni, Hg, Pb, Se, Ti, Cr determination
- Radionuclides

Hydrochemistry

Lecture 10

Organic compounds in water

- Dissolved organic carbon (DOC)
- Amines
- Aminoacids
- Aromatic carbohydrates
- Proteins
- Humic and fulvic acids
- Lignosulfonic acids and tannin
- Oil products
- Organic acids
- Surfactants
- Saccharides and starch
- Phenols

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Lecture 11

Pesticides in water

- The pesticide cycle
- The impact of pesticides on water quality
- Factors affecting pesticide toxicity in aquatic systems
- Organochlorine insecticides
- Organophosphate insecticides
- Chlorophenoxy herbicides
- Carbamates

Hydrochemistry

Lecture 12

Modern problems of water analysis

- Test-methods in water analysis
- Chemical sensors
- Optic chemical sensors
- Biosensors
- Maximum permissible concentrations (MPC)
- Requirements for water quality in Europe
- Statistical treatment of results
- Characterizing experimental errors

Bibliography

- Principles of Water Quality Control, Ed. by Thy Tebbutt, BUTTERWORTH HEINEMANN, 288 p. 1997.
- Manahan Stanley E. Environmental science, technology and chemistry, CRC, 744 p. 2000.
- Nabivanec B.J., Suchan V.V., Kalabina L.V. Environmental analytical chemistry, Lybid, 304 p. 1996.
- Nabivanec B.J., Osadchyj V.I., Osadcha N.M., Nabivanec J.B. Analitychna chimija poverchnevych vod, Naukova dumka, 455 p. 2007.
- NALCO Water Handbook (2nd Edition), Ed. by Kemmer F.N., MCGRAW-HILL, 924 p. 1988.

- **Fieldwork**
 - the subject has theoretical specification
- **Practice**
 - elaboration of oral presentation to the selected topic (assignment, tutorial)
- **Requirements to oral examination**
 - active participation in seminars
 - elaboration of oral presentation to the selected topic
 - test examination to the basic terms
 - knowledge of the text materials provided

Hydrochemistry

Lecture 1

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WATER

- Three-quarters of the Earth surface is covered with water.
- Life came into being in this water. As living things became more complex and specialized, they left the sea for the land, taking water with them as the major part of their bodies. On the planet Earth, water is life.

HUMAN USE FRESHWATER FOR:

- drinking
- cooking
- washing
- carrying wastes
- cooling machines
- irrigating crops
- recreation
- industrial purposes
- etc.

WATER WITHDRAWAL

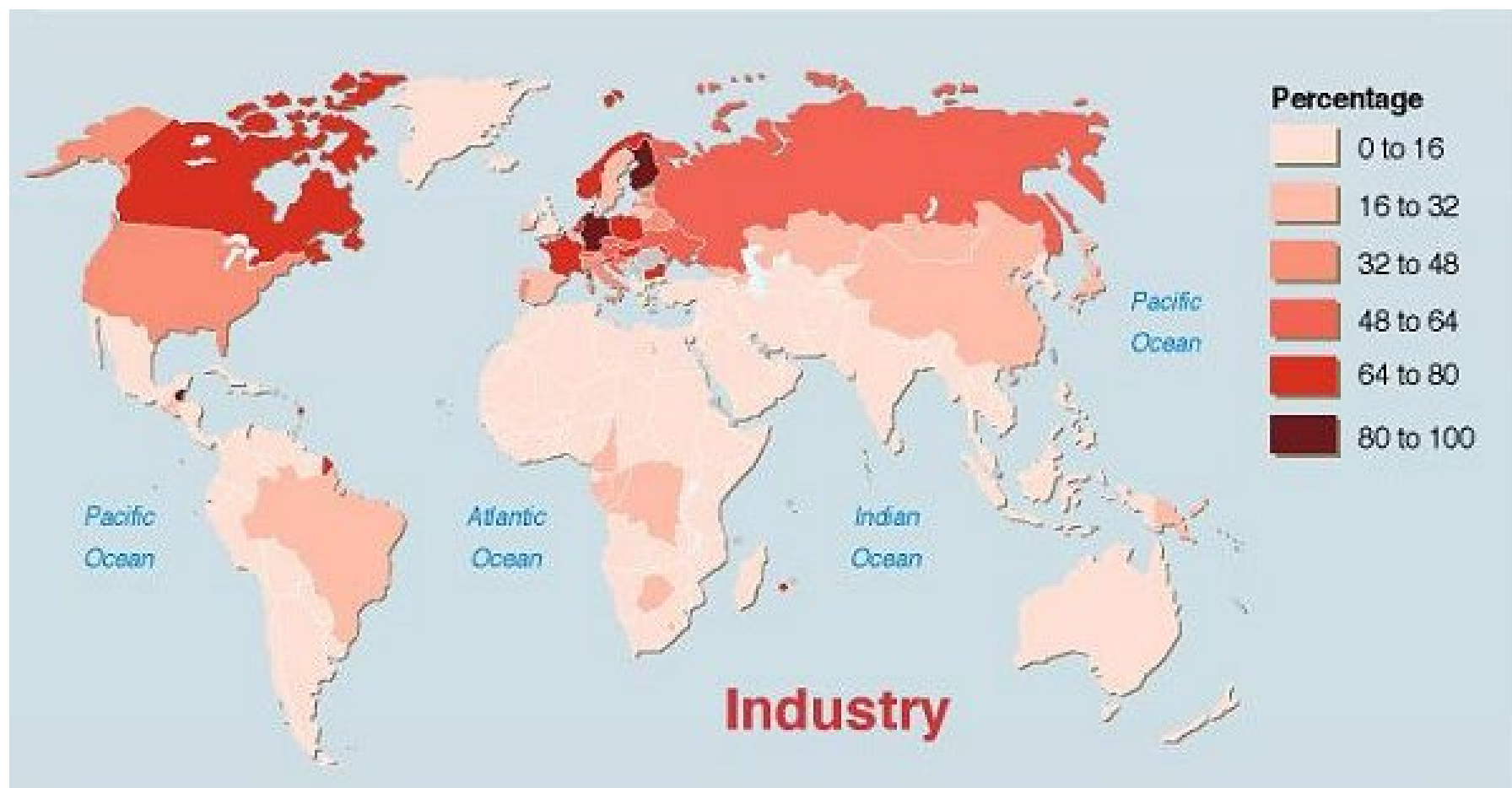
The average annual water withdrawal for use by humans is currently about 8% ($0.032 \times 10^6 \text{km}^3$) of renewable freshwater resources on a global basis. Of this:

69% - agriculture

23% - industry/power

8% - domestic purposes

WATER WITHDRAWAL BY SECTOR



Source: *World Resources 2000-2001, People and Ecosystems: The Fraying Web of Life*, World Resources Institute (WRI), Washington DC, 2000.

Freshwater Withdrawal by Sector in 2000



Source: *World Resources 2000-2001, People and Ecosystems: The Fraying Web of Life*, World Resources Institute (WRI) Washington DC, 2000.

WATER WITHDRAWAL BY SECTOR

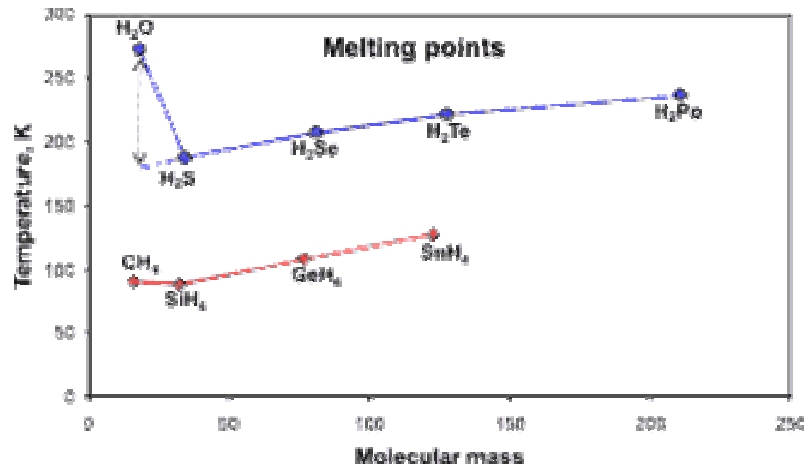


Source: *World Resources 2000-2001, People and Ecosystems: The Fraying Web of Life*, World Resources Institute (WRI), Washington DC, 2000.

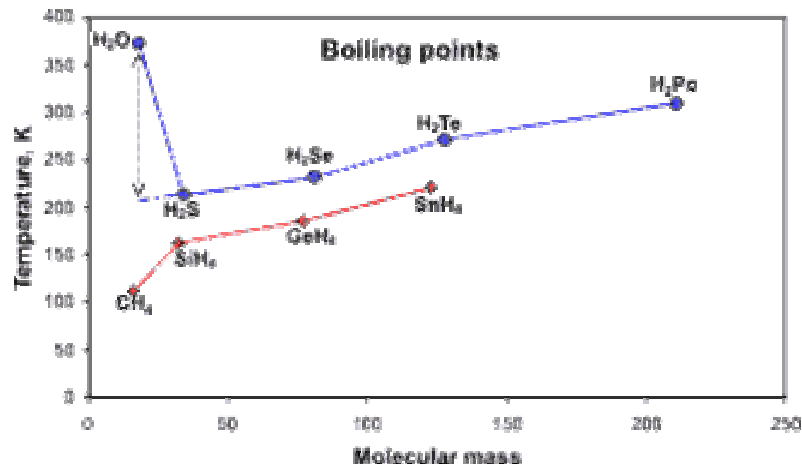
IMPORTANT PROPERTIES OF WATER

- Excellent solvent
- Highest dielectric constant of any common liquid
- Higher surface tension than any other liquid
- Transparent to visible and longer-wavelength fraction of ultraviolet light
- Maximum density as a liquid at 4°C
- Higher heat of evaporation than any other material
- Higher latent heat of fusion than any other liquid except ammonia
- Higher heat capacity than any other liquid except graphical regions ammonia

ANOMALIES OF WATER

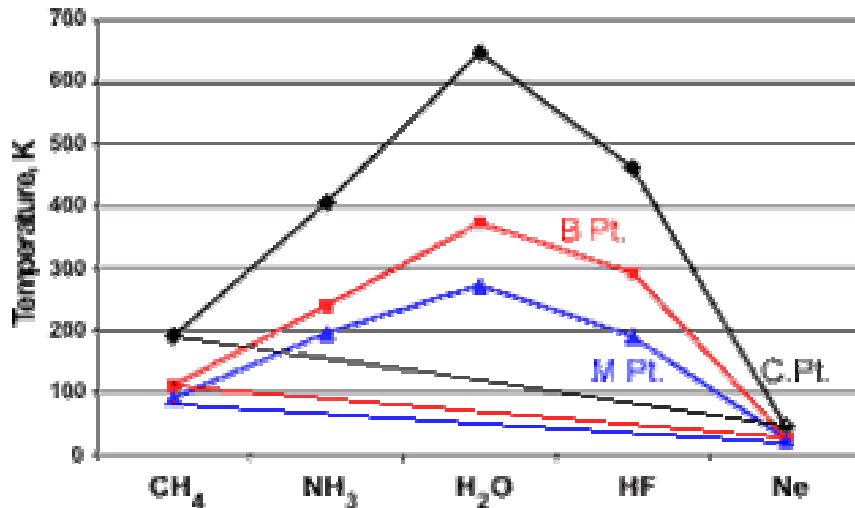
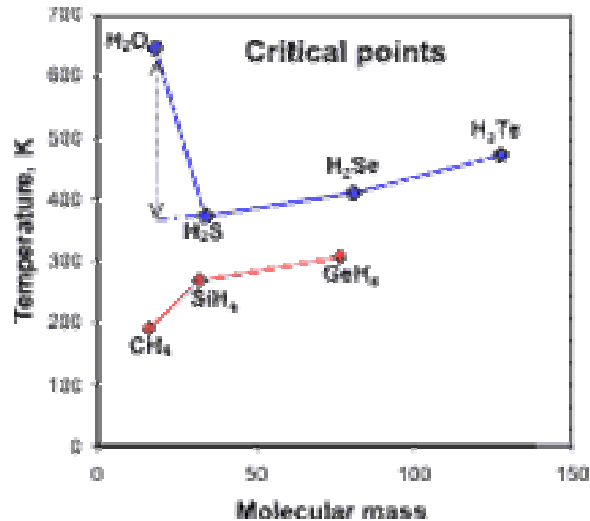


- Water has unusually high melting point.



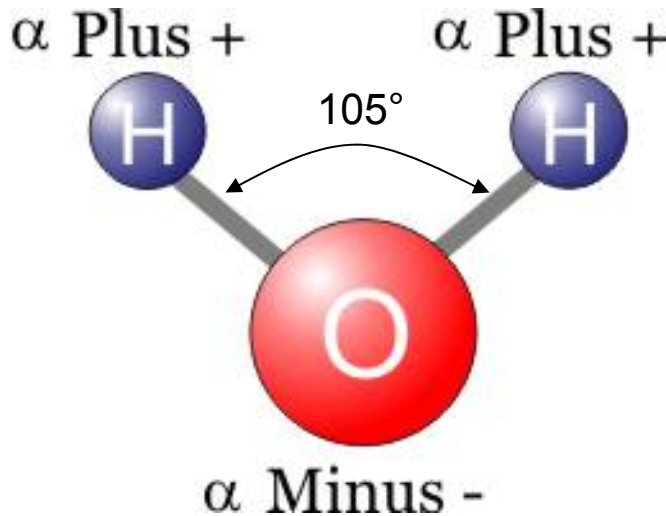
- Water has unusually high boiling point.

ANOMALIES OF WATER



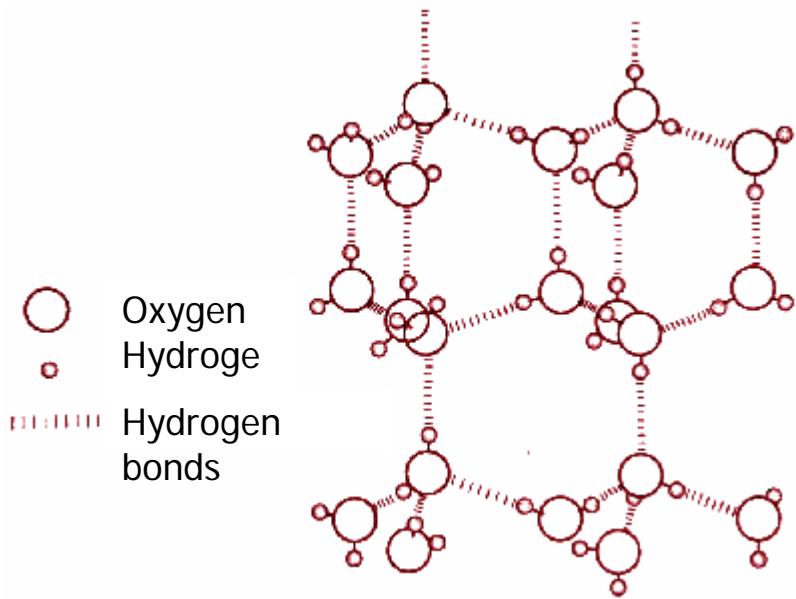
- Water has unusually high critical point.
- Solid water exists in a wider variety of stable (and metastable) crystal and amorphous structures than other materials.
- The structure of liquid water changes at high pressure.
- Water has unusually high viscosity.

MOLECULE OF WATER



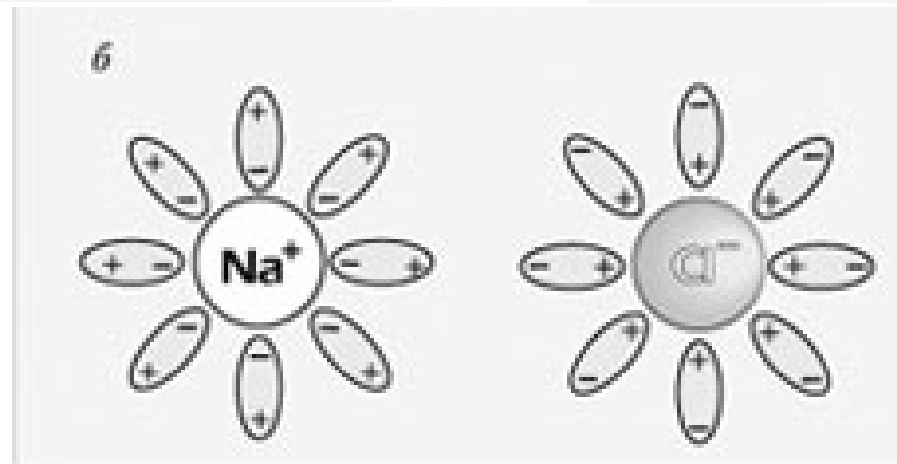
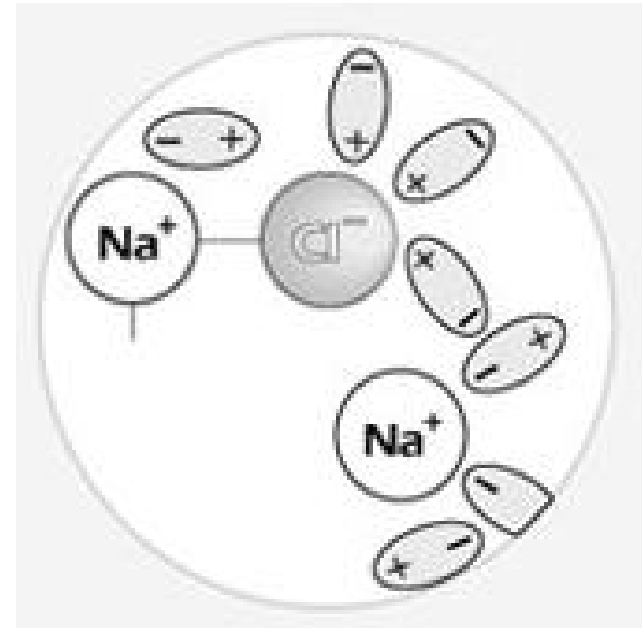
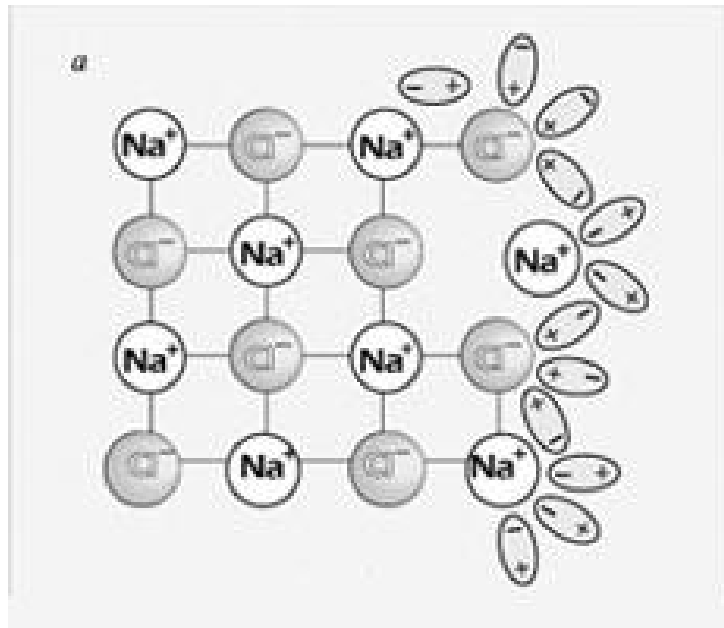
- is made up of two hydrogen atoms bonded to an oxygen atom.
- these atoms form an angle of 105°
- behaves like a dipole
- can form hydrogen bonds

HYDROGEN BONDS

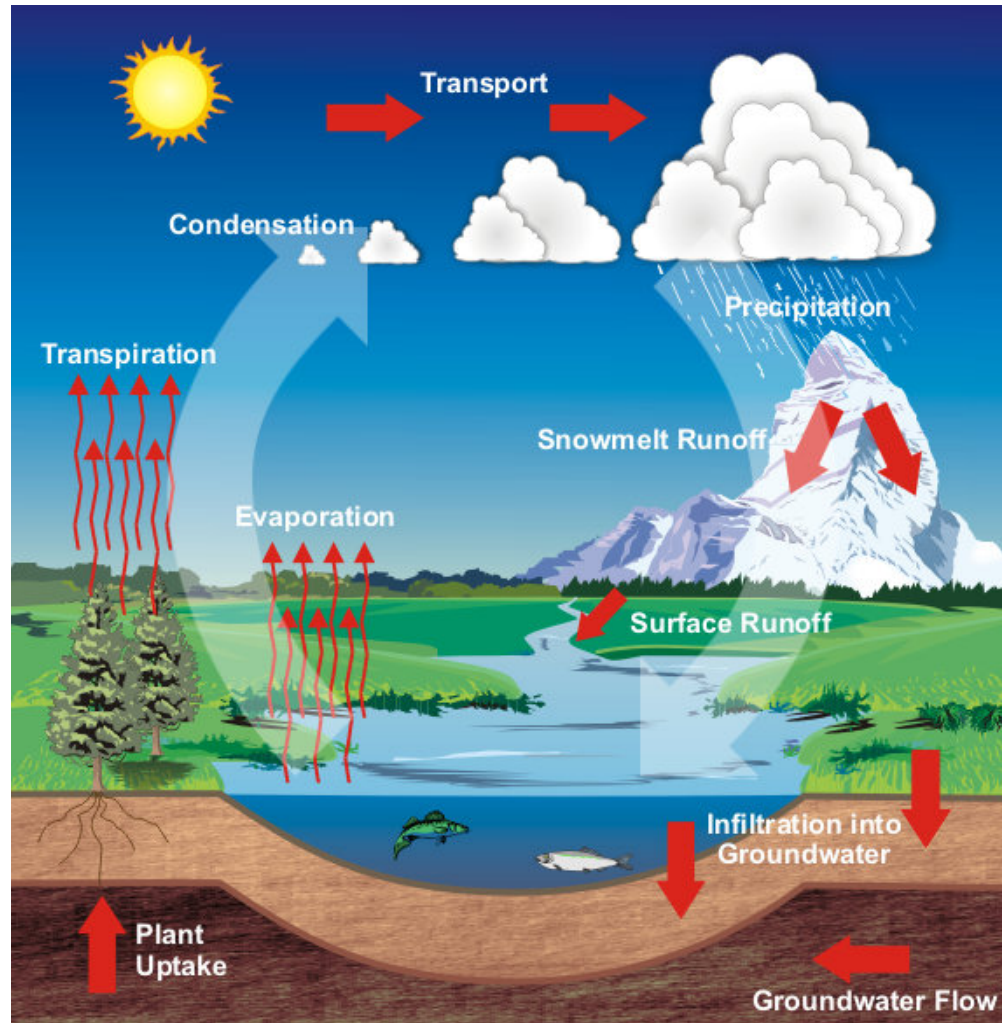


- each molecule being linked to others by up to four hydrogen bonds
- each oxygen atom tending to surround itself with four hydrogen atoms in a tetrahedral arrangement
- hexagonal rings of oxygen atoms are formed to create a kinked three-dimensional structure

DISSOLVING OF IONIC COMPOUNDS



THE HYDROLOGIC CYCLE



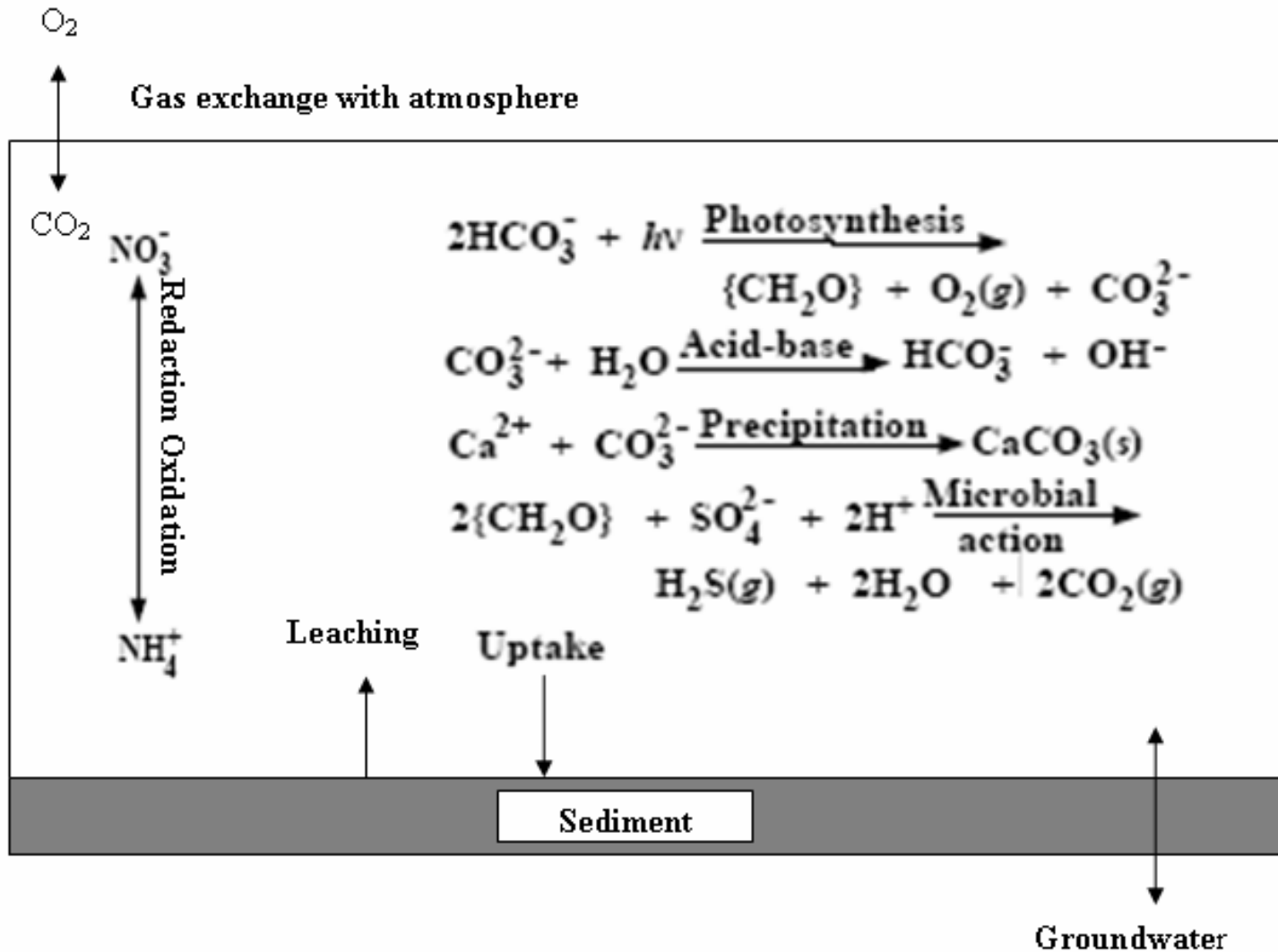
AQUATIC LIFE

- **Autotrophic** organisms:
utilize solar or chemical energy to fix elements
- **Heterotrophic** organisms
utilize the organic substances produced by autotrophic organisms
- **Decomposers**
break down material of biological origin to simple compounds

AQUATIC LIFE IS STRONGLY INFLUENCED BY

- Temperature
- Transparency
- Turbulence
- Dissolved oxygen
- Biochemical oxygen demand
- Carbon dioxide concentration
- Salinity of water

MAJOR AQUATIC CHEMICAL PROCESSES



Hydrochemistry

Lecture 2

Chemical composition of natural waters

- Dissolved gases
- Metals in water
- Biogenic elements
- Cycle of biogenic elements in hydrosphere
- Types of natural waters
- Surface water
- Water from precipitations

CHEMICAL COMPOSITION OF NATURAL WATERS

- **Dissolved gases** – O_2 , CO_2 , H_2S , CH_4 , etc
- **Main ions** – HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+} .
- **Biogenic elements** – N, P, Si, Fe
- **Microelements** – Mn, Cu, Zn, Co, Mo (biometals), Ni, Cr, Cd, Pb, Hg, F⁻ and others (inorganical industrial pollutants)
- **Organical compounds** - Organic carbon, amines, aminoacids, proteins, humic and fulvoacids, oils, carbonyl compounds, organic acids, pesticides, synthetic detergents, etc

OXYGEN IN WATER

Oxygen:

- comes from the atmosphere
- is produced by photosynthetic action of algae

Oxygen is consumed:

- at night when the algae consume oxygen as part of their metabolic processes
- metabolic processes of other organisms
- degradation of biomass
- biodegradation of pollutants

CARBON DIOXIDE IN WATER

- Carbon dioxide (CO₂) is the most important weak acid in water.
- Algae in water utilize dissolved CO₂ in the synthesis of biomass.
- High concentrations of free carbon dioxide in water may adversely affect respiration and gas exchange of aquatic animals. It may even cause death and should not exceed levels of 25 mg/L in water.

Carbon Dioxide comes to water:

- from the atmosphere



- from solid carbonate minerals



- as a product of metabolic processes
- when water seeps through layers of decaying organic matter
- when water infiltrates the ground, it may dissolve a great deal of CO₂ produced by the respiration of organisms in the soil

METALS IN WATER

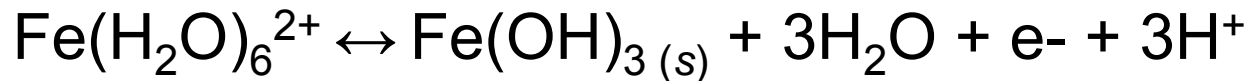
- Metal ions in water solution are present in forms such as the hydrated metal cation $M(H_2O)_x^{n+}$.
- Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions including acid-base:



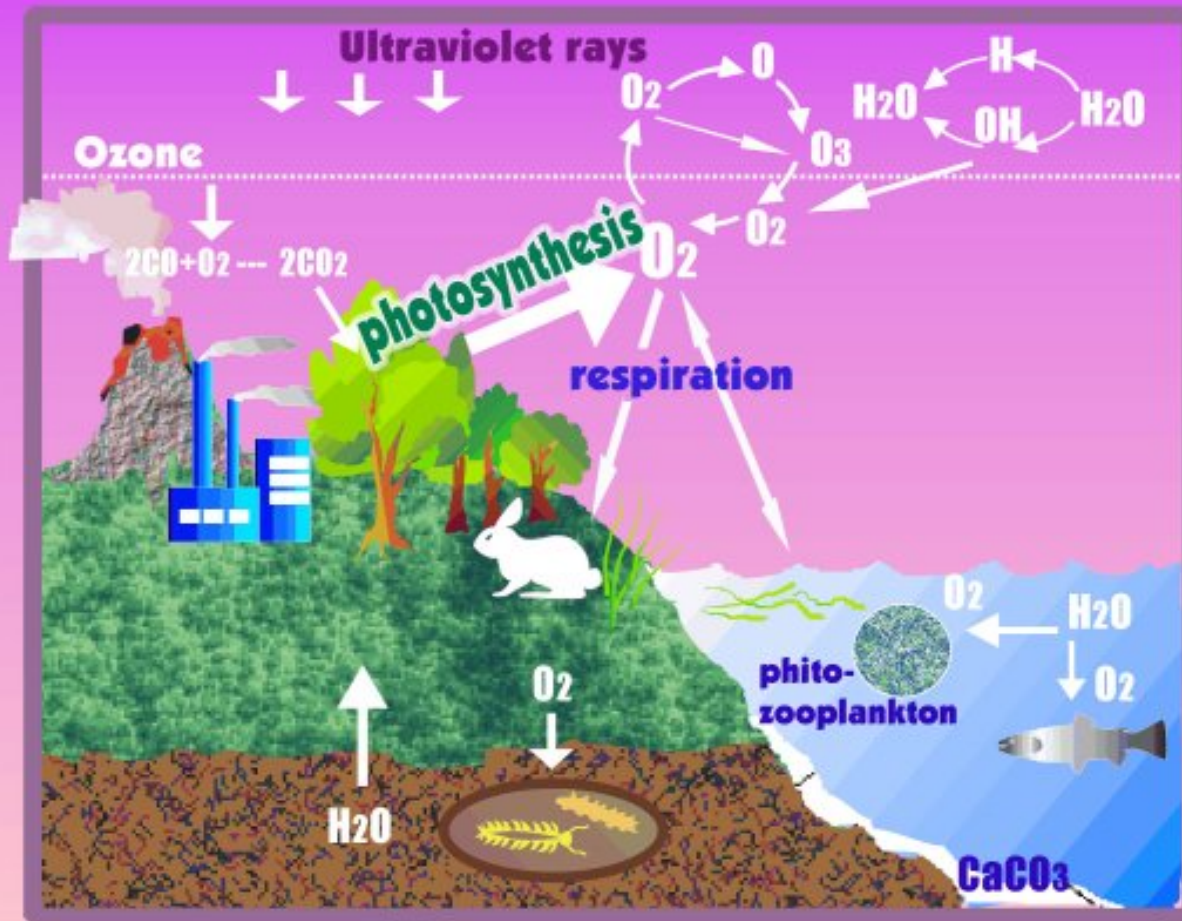
precipitation:



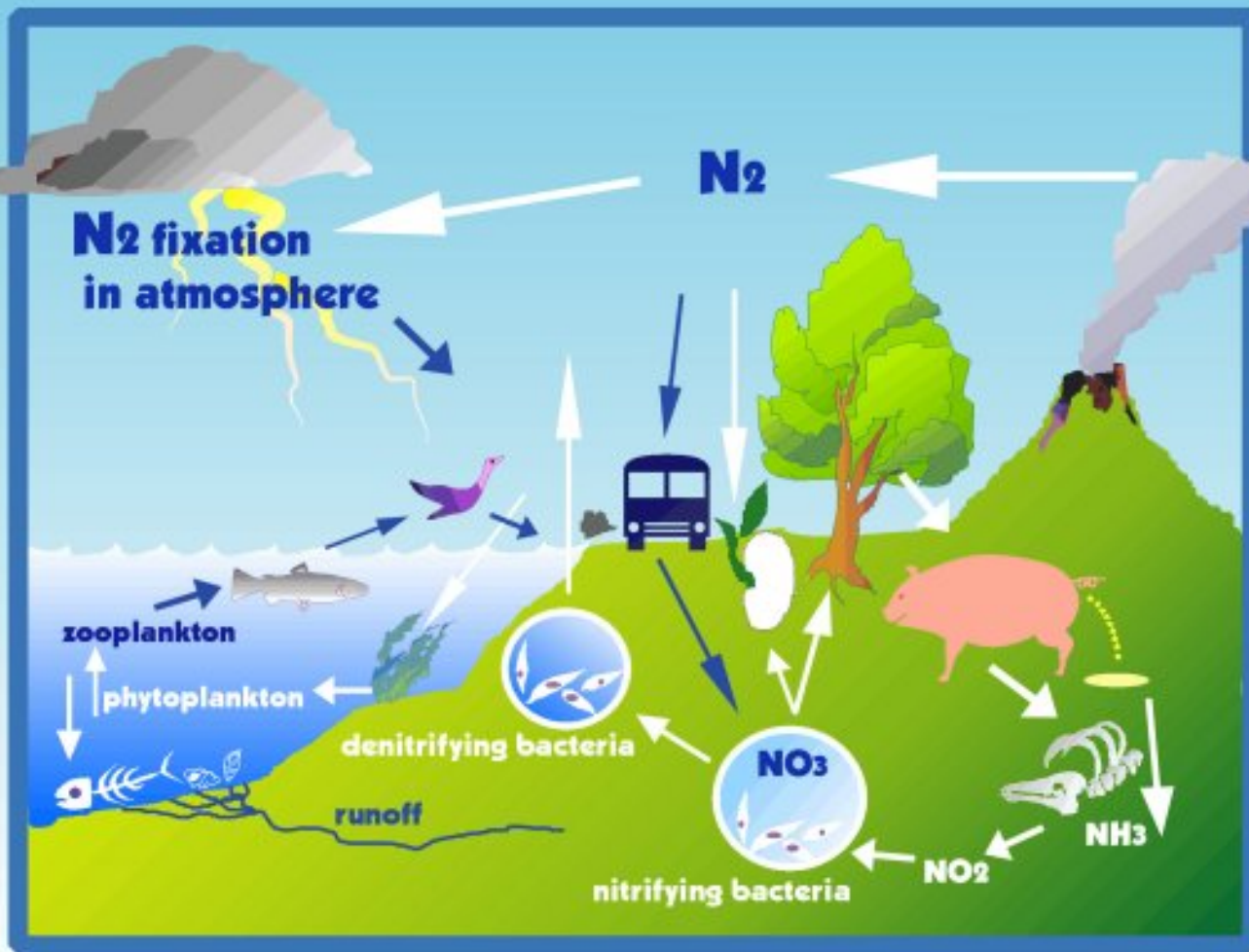
and oxidation-reduction reactions:



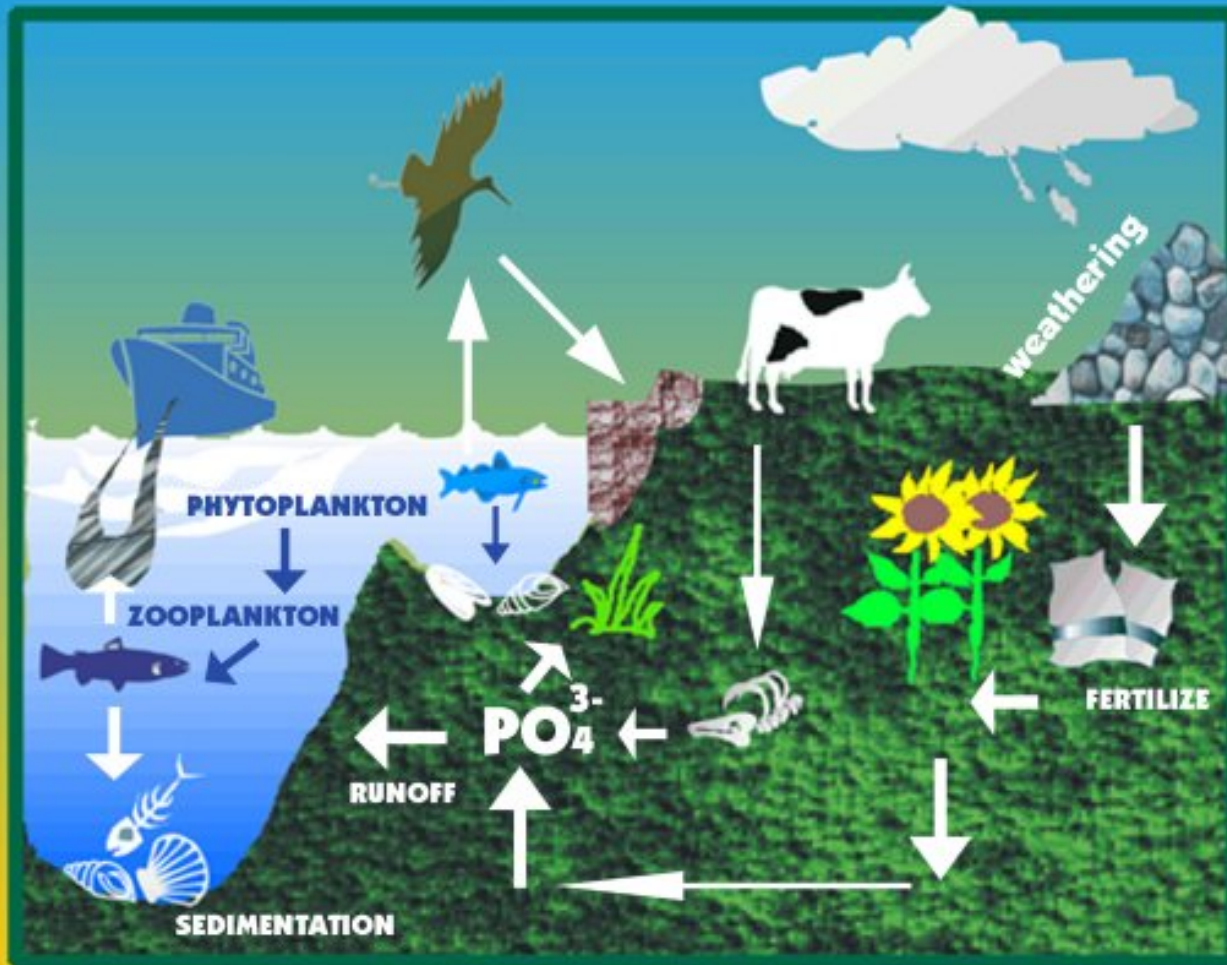
OXYGEN CYCLE



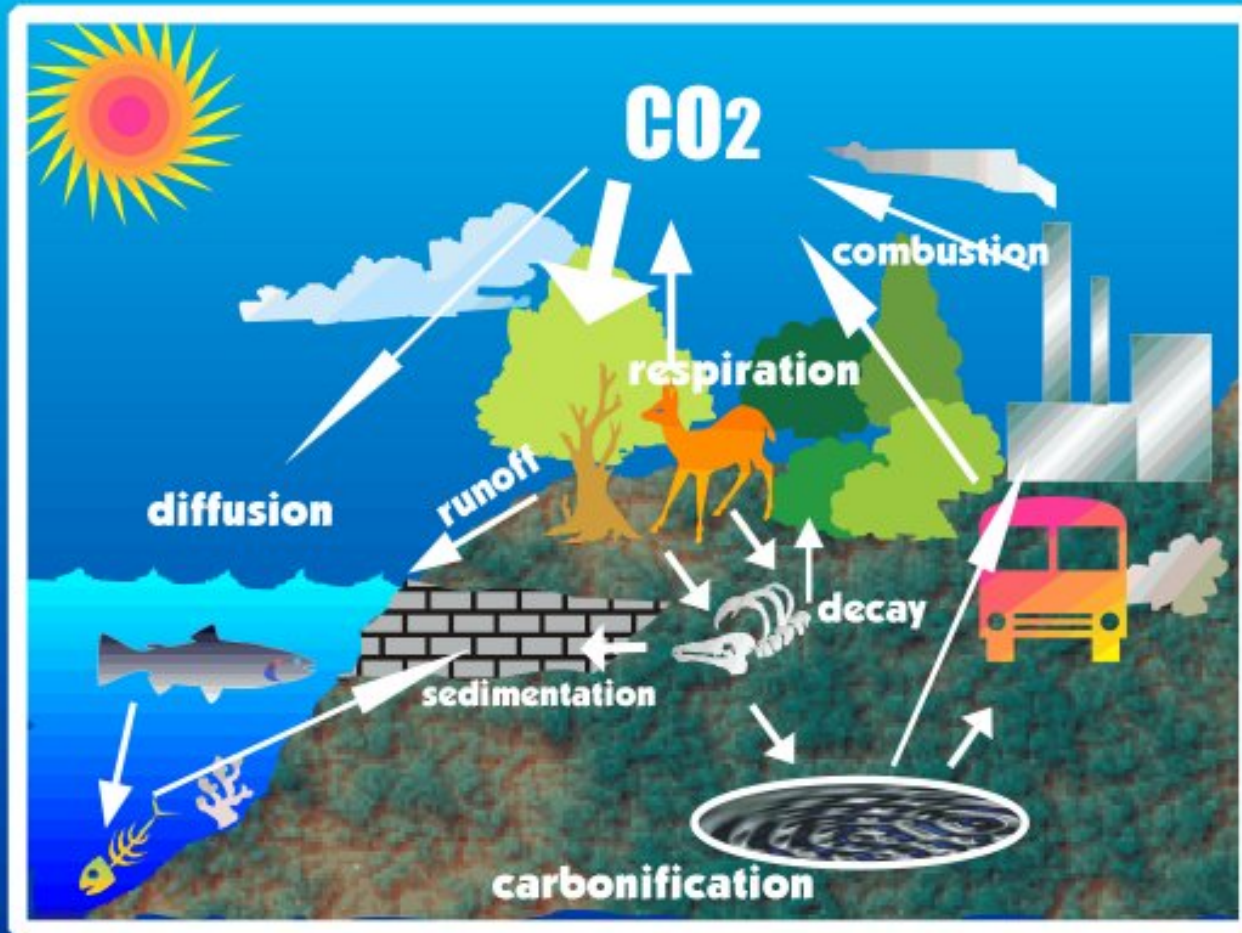
NITROGEN CYCLE



PHOSPHORUS CYCLE



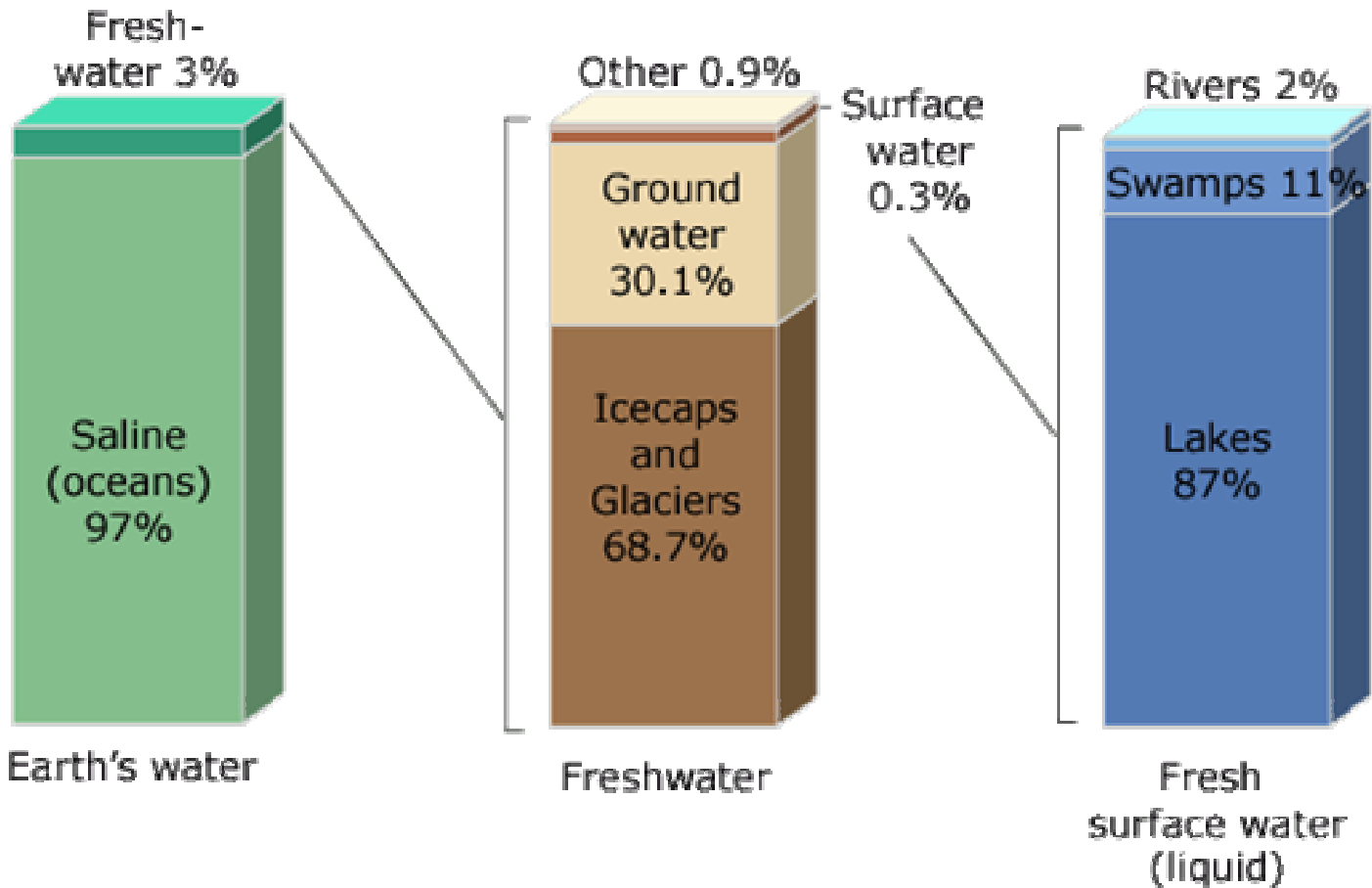
CARBON CYCLE



TYPES OF NATURAL WATERS

- Surface water (rivers, lakes, swamps, reservoirs, ponds etc.)
- Ground water (artesian and mineral waters)
- Sea and ocean water
- Precipitation

Distribution of Earth's Water



SURFACE WATER

- the streams (of all sizes, from large rivers to small creeks),
- ponds,
- lakes,
- reservoirs (man-made lakes),
- freshwater wetlands.

The World's Surface Water

Precipitation, Evaporation and Runoff by Region



Source: Peter H. Gleick, *Water in Crisis*, New York Oxford University Press, 1993.

THE QUALITY OF SURFACE WATERS

- The quality of surface waters is a result of the interaction between abiotic and biotic factors.

Biotic factors:

- diversity of species
- the water biocenoses

THE QUALITY OF SURFACE WATERS

Abiotic factors:

- the climate
- the conditions in the watershed for transformation of rainfall into a flow
 - ❖ geomorphological - indentation of the relief, slope of the basin;
 - ❖ geological - structure of the rocks;
 - ❖ soil - type of soils;
 - ❖ vegetation - type, age and density of the forest vegetation, afforestation
- the morphometric index of the river (width, depth, curve)
- hydrodynamic characteristics (speed of the river flow),
- temperature of water

THE QUALITY OF SURFACE WATERS

The **abiotic factors** directly and indirectly affect:

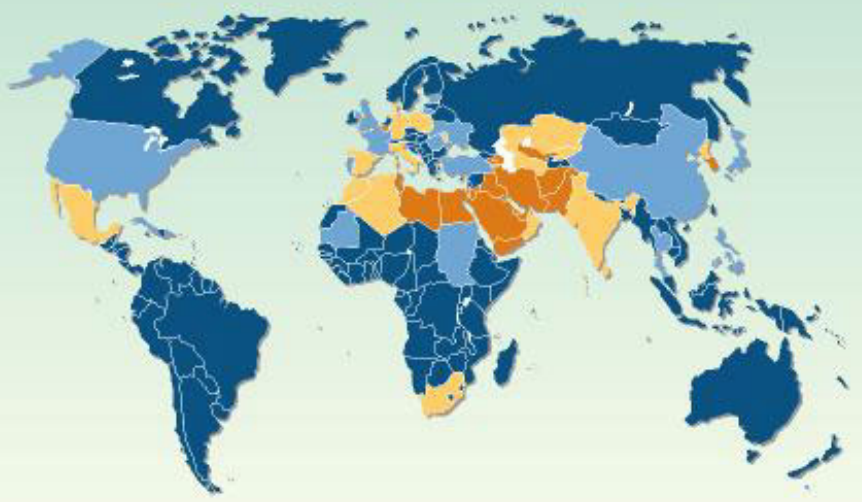
- the ionic composition,
- mineralization,
- the function of the water ecosystems,
- etc

The **biotic factors** to a great extent affect:

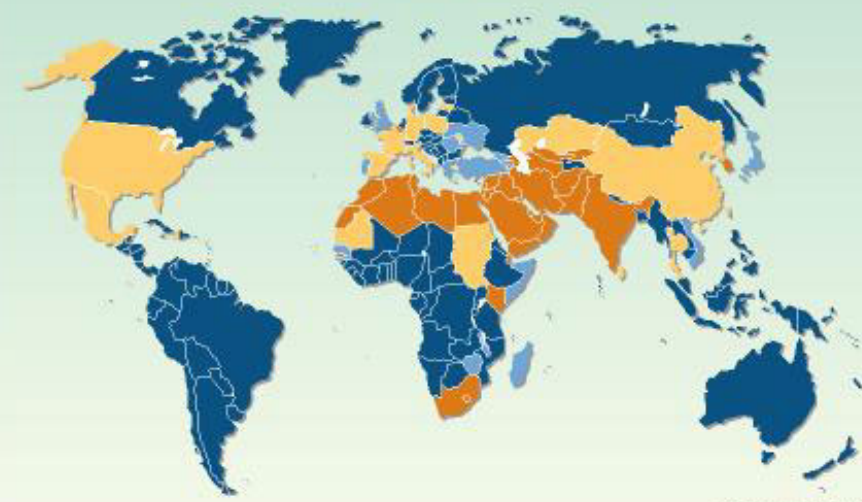
- the interrelations between the organisms
- their relations with the surrounding water environment

Freshwater Stress

1995



2025



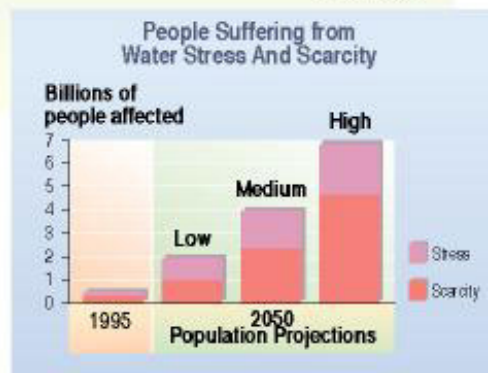
Water withdrawal as percentage of total available

- Over 40%
- 40% - 20%
- 20% - 10%
- Less than 10%

PHILIPPE PEKACEWICZ
FEBRUARY 2002



Source: World Meteorological Organisation (WMO), Geneva, 1996; Global Environment Outlook 2000 (GEO), UNEP, Earthscan, London, 1999.



CHEMICAL CONTENT OF SURFACE WATERS

Ingredient	Content
Dissolved Oxygen	0 – 15 mg/l
H ₂ S	-
pH	6.8 – 8.5
pH (swamps)	4.5 – 5
Main ions	
Mg ²⁺	0.5 – 50 mg/l
Na ⁺ + K ⁺	1 – 75 mg/l
Ca ²⁺	10 – 120 mg/l
Cl ⁻	5 – 80 mg/l
SO ₄ ²⁻	2 – 120 mg/l
HCO ₃ ⁻	10 – 250 mg/l

CHEMICAL CONTENT OF SURFACE WATERS

Ingredient	Content, mg/l
Biogenic elements	
Total Fe	0.01 – 2
Total Si	1 – 10
Organic phosphorus	0.01 – 0.2
Inorganic phosphorus	0.01 – 0.5
Organic nitrogen	0.2 – 2
NO ₃ ⁻	0 – 2
NO ₂ ⁻	0 – 0.5
NH ₄ ⁺ +NH ₃	0.02 – 1.5

CHEMICAL CONTENT OF SURFACE WATERS

Ingredient	Content, mg/l
Microelements – industrial pollutants	
Cd	≤ 0.0001
Pb	0.0001 – 0.005
Cr	0.0001 – 0.005
Ni	0.0005 – 0.01
Microelements - biometals	
Co	0.0001 – 0.005
Mo	0.0005 – 0.01
Cu	0.002 – 0.05
Zn	0.003 – 0.10
Mn	0.002 - 1

CHEMICAL CONTENT OF SURFACE WATERS

Ingredient	Content, mg/l
Organic compounds	
Carbonyl compounds	0.02 – 2
Esters	0.05 – 8
Organic acids	0.5 – 15
Carbohydrates	0.01 – 2
Saccharides	0.05 – 2
Amines	0.03 – 3
Aminoacids	0.004 – 5
Proteins	0.02 – 5
Fulvic acids	0.5 – 10
Humic acids	0.02 - 2

MAXIMUM PERMISSIBLE CONCENTRATIONS (MPC) FOR SURFACE WATER, LOW 296/2005 SK

Element	Concentration, mg/ml
Ca	200
Mg	100
Fe	2
Al	0.2
Mn	0.3
Zn	0.1
Cu	20
Pb	20
Co	50
Ni	20
	10
Cd	5
As	30

WATER FROM PRECIPITATION

- In the composition of the precipitation in natural conditions the hydrocarbonic ions predominate and the interrelation between the basic ions is:
 $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$
- Precipitation that falls through forest vegetation changes their chemical composition and pH, and then directly affects river water.
- On the other hand a great amount of precipitation forms high waters, which reduce the total number of the contained hydrochemical elements.

Hydrochemistry

Lecture 3

Groundwater and seawater

- Groundwater
- Mineral water, its classification
- Artesian water
- Connate water
- Geothermal water
- Seawater

GROUNDWATER

- **Groundwater** is the water found in the spaces between soil particles and cracks in rocks underground.
- Ground water is an important part of the water cycle.
- Ground water is the part of precipitation that seeps down through the soil until it reaches rock material that is saturated with water.
- Groundwater represents the largest single source of freshwater in the hydrological cycle (about 95% globally)

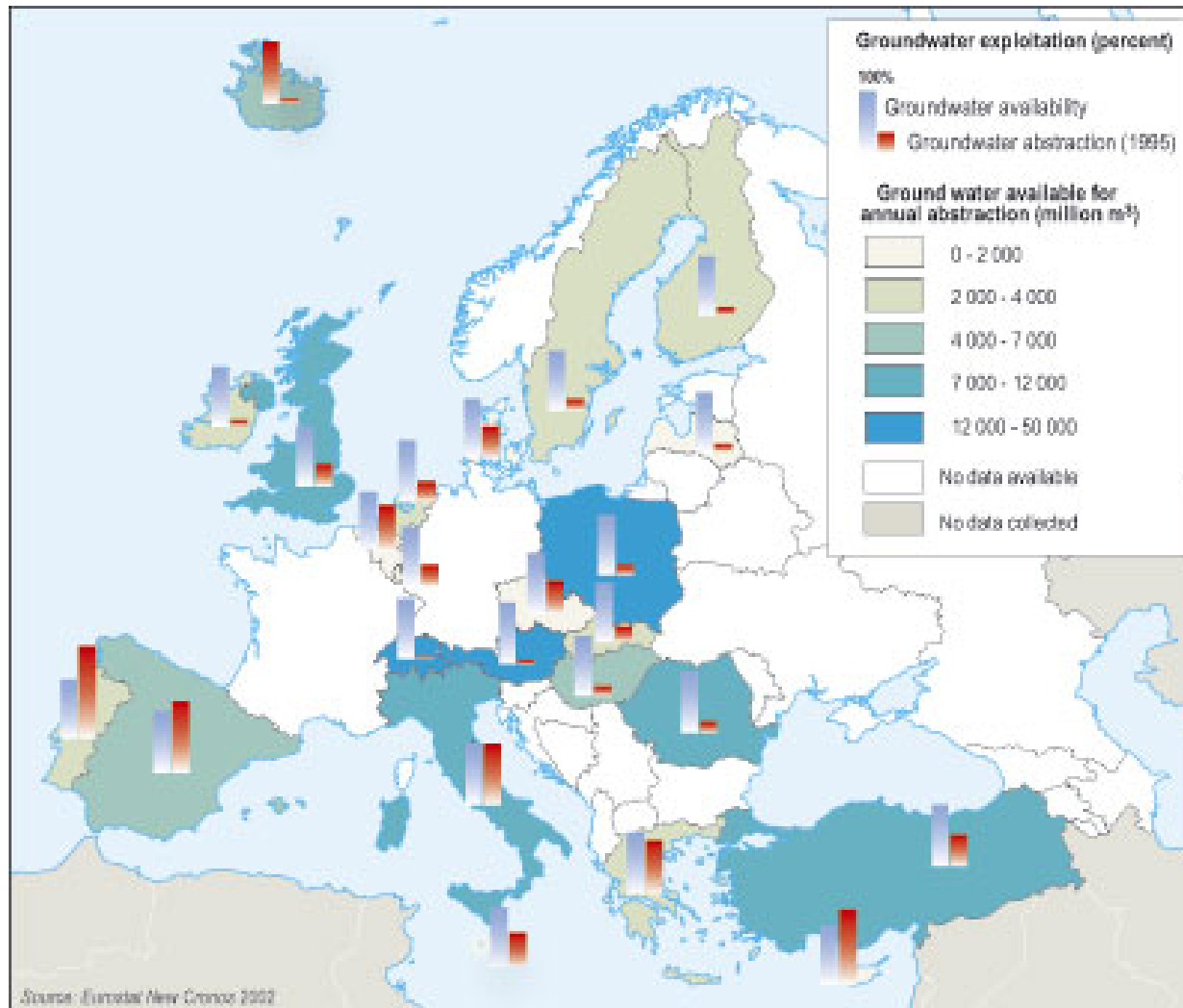
GROUNDWATER

The majority of groundwater is used for

- irrigation
- drinking
- industrial processes
- at an accelerating rate.
- agriculture

Of all of the earth's water that's useable by humans, 98% is groundwater.

GROUNDWATER RESOURCES AND ABSTRACTIONS



GROUNDWATER

The term groundwater includes:

- Mineral Water
- Artesian Water
- Connate Water
- Geothermal Water

MINERAL WATER

- Must contain no less than 250 parts per million (ppm) total dissolved solids (TDS) with the solids being the minerals in the water
- Must come from a geologically and physically protected underground water source Is distinguished from other types of water by the regular mineral and trace elements present
- No minerals may be added to this water

MINERAL WATER CLASSIFICATIONS

- CO₂ concentration – 0.5 – 1.4 g/l – low-carbon water
1.4 – 2.5 g/l – carbonated water
> 2.5 g/l – high-carbon water
- H₂S concentration – 10 – 50 mg/l – low sulphide
50 – 100 mg/l – Moderately sulphide
100 – 250 mg/l – high sulphide
> 250 mg/l very high sulphide

MINERAL WATER CLASSIFICATIONS

- pH – 3 – 3.5 – high acid water
 - 3.5 – 5.5 – acid water
 - 5.5 – 6.8 – low acid water
 - 6.8 – 7.2 – neutral water
 - 7.2 – 8.5 – low alkaline water
 - > 8.5 – alkaline water
- Temperature – ≤ 20 °C – cold
 - 20 – 35°C – warm
 - 35 – 42°C – hot, thermal
 - > 42°C very hot

CHEMICAL CONTENT OF TRANSCARPATHIAN MINERAL WATERS

Microelement	Concentration, mg/l
Li	0.1 – 20
Mn	0.04 – 4
Fe	0.05 – 40
Co	$2 \cdot 10^{-4}$ - $2 \cdot 10^{-2}$
Ni	0 – 0.3
Cu	$5 \cdot 10^{-3}$ – 5.0
Zn	0 – 5
B	0.02 – 600
Al	0.01 – 7.0
F	0.01 – 5.0
Br	0 – 50
I	0 - 3

ARTESIAN WATER

- **Artesian water** is groundwater that flows freely upwards out of an artesian bore or well.
- From a well in a confined aquifer. Water level in well must be at a higher elevation than the top of the aquifer. May also be known as "artesian well water"
- Artesian water may also be relatively highly mineralized, owing to the long travel time, and contain gases and dissolved iron, which may precipitate on the surface.

CONNATE WATER

- Because of its long contact with rock material, connate water can change chemical composition throughout the history of the rock and become highly mineralized.
- Connate water can be more dense and saline compared with seawater; connate water salinities can range from 20 to more than 300 grams per liter.

GEOCHEMICAL COMPOSITION OF CONNATE WATER

Chemical Component	Concentration, mg/l
Na ⁺	65,000
K ⁺	500
Mg ²⁺	28,000
Ca ²⁺	165,000
Ba ²⁺	0.1
Sr ²⁺	1,300
Fe ²⁺	0.1
Cl ⁻	138,360
Br ⁻	10
SO ₄ ²⁻	260
HCO ₃ ⁻	100
Organics	55
pH	5.8

GEOHERMAL WATER

- **Geothermal water** has a temperature appreciably higher than that of the local average annual air temperature.
- In general, a spring is considered hot when its temperature is about 12.2 °C higher than mean annual ambient temperature.
- The relative terms geothermal water, warm springs, and hot springs are common.

GEO THERMAL ENERGY

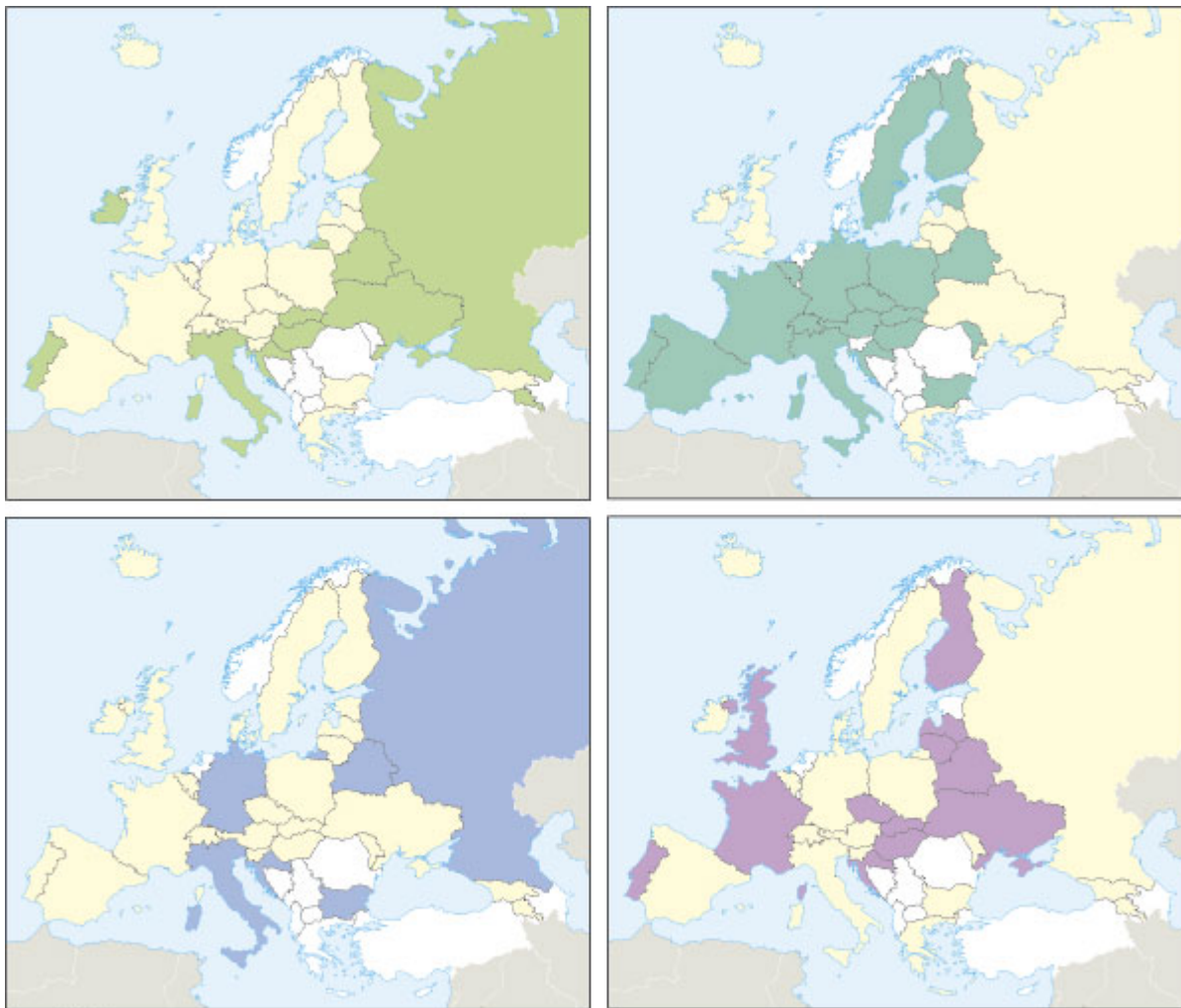
Worldwide, there are about 12,000 thermal megawatts of installed direct uses of geothermal fluids in nearly 30 countries, replacing the combustion of fossil fuels equivalent to burning 830 million gallons of oil or 4.4 million tons of coal per year.

ESTIMATED PERCENTAGE OF DRINKING WATER SUPPLY OBTAINED FROM GROUNDWATER

Region	Percent	Population served (millions)
Asia–Pacific	32	1 000 – 2 000
Europe	75	200 – 500
Central and South America	29	150
USA	51	135
Australia	15	3
Africa	NA	NA
World	-	1 500 – 2 750

Source: UNEP 2003

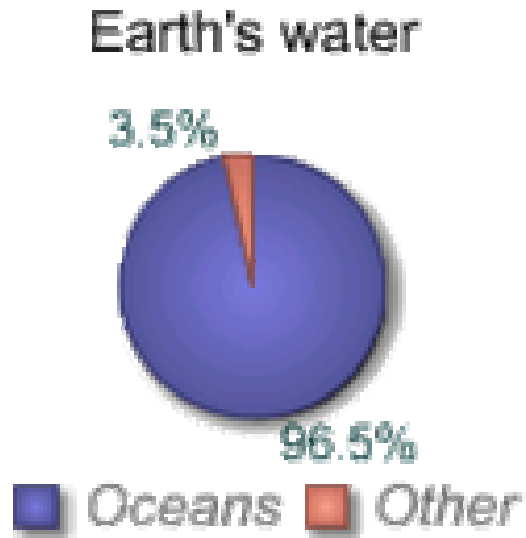
DRINKING WATER QUALITY



Source: EEA, 2002

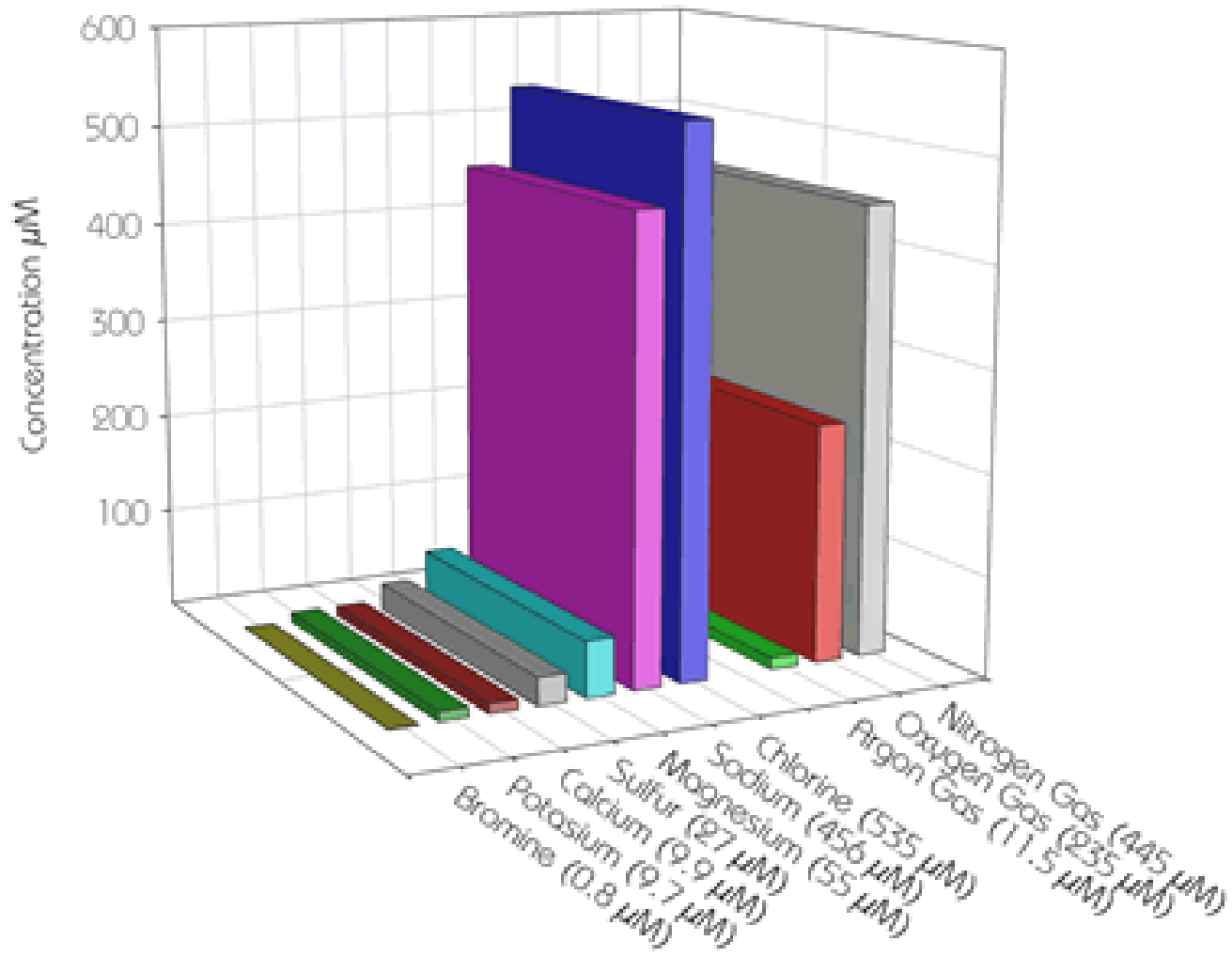


OCEAN AND SEAWATER



- The ocean holds 98% of the 1.4 billion cubic kilometers of water on the planet
- Seawater ranges in salinity, but a useful approximation is 35 g/kg; or 35 parts per thousand or 3.5%

Seawater Composition



CHEMICAL CONTENT OF SEAWATER

Ingredient	Content, gr/kg
Main ions	
Cl ⁻	19.353
SO ₄ ²⁻	2.712
HCO ₃ ⁻	0.142
Br ⁻	0.067
Mg ²⁺	1.294
Ca ²⁺	0.413
K ⁺	0.387
Na ⁺	10.76
Sr ²⁺	0.008

MICROELEMENTS IN SEAWATER

Element	Concentration, μg/l	Element	Concentration, μg/l
Li	200	Co, Sb, Cs	0.5
Rb	120	La, Y	0.3
I	60	Bi	0.2
Ba	30	Cd, Pb, W	0.1
In	20	Cr	0.05
Al, Fe, Zn, Mo	10	Hg	0.033
Cu, Ag, Sn, U	3	Te	0.01
V, Mn, Ni	2	Au	0.004
Ti	1	Ra	1·10 ⁻⁷

Hydrochemistry

Lecture 4

Water pollutions and wastewater

- Sources of water pollution
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- Content and properties of waste water
- Chemical pollutant limitations
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SOURCES OF WATER POLLUTION

- Industrial
- Municipal
- Agricultural
- Natural (animal, vegetable, soil)
- Stormwater (garbage, soil runoff, spills)
- Landfill
- Underground storage tank

WASTEWATER

- The wastewater can contain physical, chemical and biological pollutants in any form or quantity and cannot adequately be estimated without actual measuring and testing.
- The wastewater will either be discharged directly into a receiving body of water or into the sewerage system of a municipality, or it will be reused or recycled.

CHEMICAL POLLUTANT LIMITATIONS

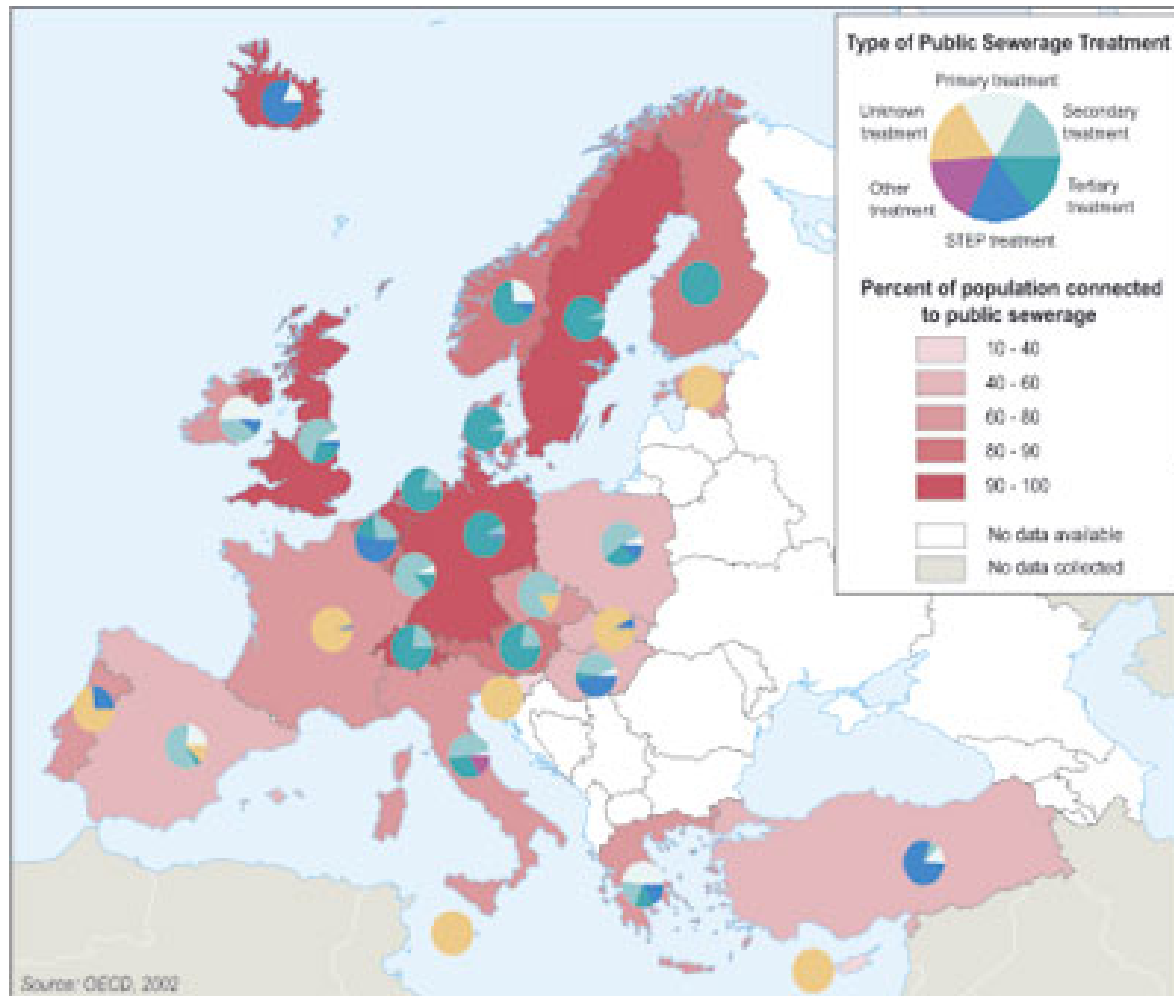
(WATER QUALITY CONTROL HANDBOOK)

Chemical	Drinking water protection	Fish & Wildlife protection
Ammonia	-	0.02mg/l
Arsenic	50g/l	-
Barium	1mg/l	-
Beryllium	-	11 μ g/l in soft water 1100 μ g/l in hard water
Cadmium	10g/l	4 μ g/l in soft water 12 μ g/l in hard water
Chromium	50g/l	100 μ g/l
Copper	1mg/l	0,1x 96 hr LC ₅₀
Cyanide	-	5 μ g/l

TYPICAL COMPOSITION OF MUNICIPAL WASTEWATER AND THE DESIRED LEVEL OF TREATMENT

Contaminant	Concentration in wastewater	Desired concentration after treatment
Total solids (TS)	average 720 mg/L	
Total dissolved solids (TDS)	200 – 1000 mg/L	
Total suspended solids (TSS)	100 – 350 mg/L	30 – 45 mg/L
Volatile suspended solids (VSS)	165 mg/L	
BOD (5-day, 20°C)	100 – 300 mg/L	25 mg/L
Nitrogen	20 – 80 mg/L	10 mg/L
Phosphorus	5 – 20 mg/L	2 mg/L
Chlorides	50 mg/L	
Sulfates	30 mg/L	
Alkalinity	2 meq/L	
Grease	100 mg/L	
Coliform bacteria	10^7 – 10^8 per 100 mL	zero
Volatile organic compounds (VOCs)	0.1 – 0.4	minimal

PUBLIC SEWERAGE TREATMENT IN EUROPE



WASTEWATER TREATMENT

Wastewater treatment can be made up of roughly three (consecutive) steps and a preliminary process called pre-treatment.

- **Pre-treatment** is the removal of stones, sand and fat/grease using mechanical processes such as screening, settlement or flotation.



(www.norfolk.gov/Utilities/produce/process.asp)



(www.coffeyville.com/Water.htm)

- **Primary treatment** is the removal of suspended solids by passing waste water through settlement or flotation tanks.

WASTEWATER TREATMENT

- **Secondary treatment** is biological treatment: waste water passes through tanks where bacteria breakdown pollutants and transform them into sludge.
- **Tertiary**, more advanced, treatment involves nutrient removal or disinfection by means of chlorination, ultraviolet (UV) radiation or ozone treatment.



(www.huntingburg.org/waste_water_photos.htm)

BIOLOGICAL WASTEWATER TREATMENT TECHNOLOGIES

Activated sludge

Applications

- Low concentration organics
- Some inorganics

Advantages

- Removal of dissolved constituents
- Low maintenance
- Breakdown process
- Relatively safe
- Low capital costs
- Relatively easy to operate

Disadvantages

- Volatile emissions
- Waste sludge disposal
- High energy costs
- Susceptible to shock loadings and toxins
- Susceptible to seasonal changes

BIOLOGICAL WASTEWATER TREATMENT TECHNOLOGIES

Trickling filters, Fixed-film reactors

Applications

- Low concentration organics
- Some inorganics

Advantages

- Removal of dissolved constituents
- Low maintenance
- Breakdown process
- Relatively safe
- Reduced sludge generation

Disadvantages

- Volatile emissions
- Susceptible to shocks loadings and toxins
- Susceptible to seasonal changes
- Relatively high capital costs
- Relatively high operating costs

BIOLOGICAL WASTEWATER TREATMENT TECHNOLOGIES

Aerated lagoons, Stabilization ponds

Applications

- Low concentration organics
- Some inorganics

Advantages

- Removal of dissolved constituents
- Low maintenance
- Breakdown process
- Relatively safe
- Low capital costs
- Low energy costs
- Easy to operate
- Infrequent waste sludge

Disadvantages

- Volatile emissions
- Susceptible to shocks and toxins
- Susceptible to seasonal changes
- High land requirement
- No operational control

BIOLOGICAL WASTEWATER TREATMENT TECHNOLOGIES

Anaerobic degradation

Applications

- Low concentration organics
- Chlorinated organics
- Inorganics

Advantages

- Removal of dissolved constituents
- Breakdown process
- Treatment of chlorinated wastes
- Methane generation (= fuel)
- Reduced sludge generation

Disadvantages

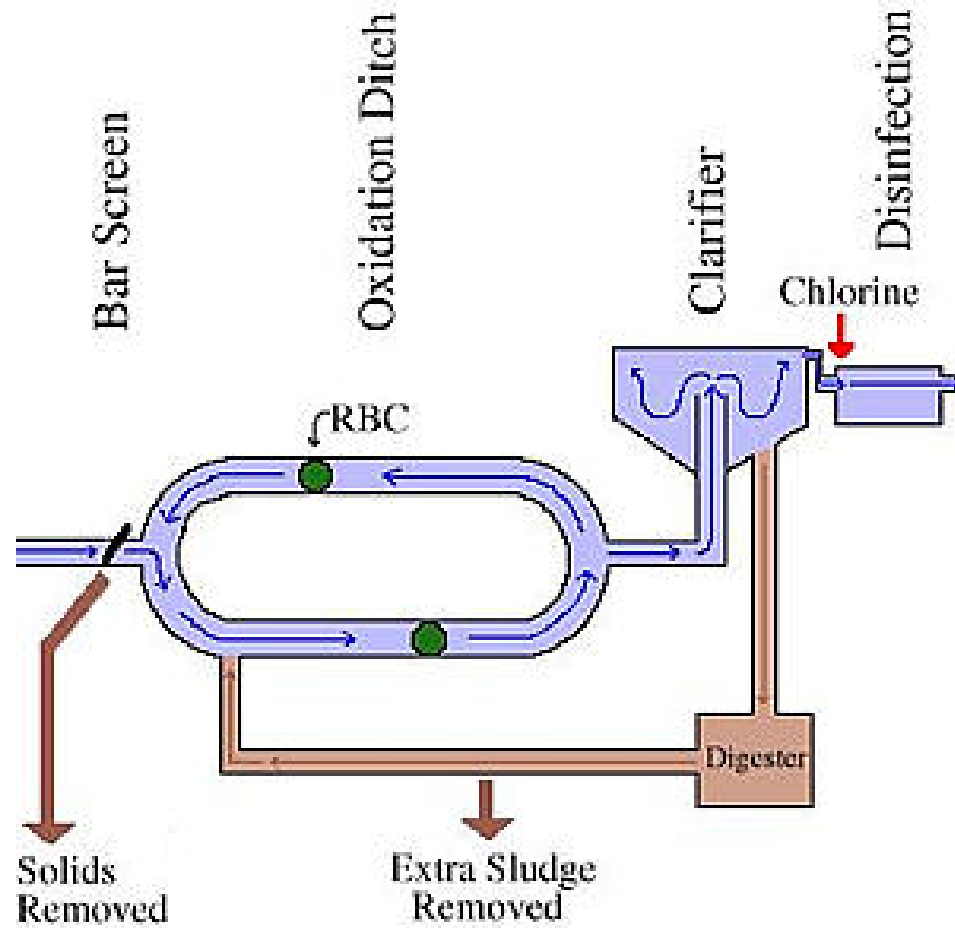
- Susceptible to shocks loadings and toxins
- Susceptible to seasonal changes
- Relatively high capital costs
- Relatively high operating costs

THE OXIDATION DITCH PROCESS

- The **oxidation ditch** is a circular basin through which the wastewater flows.
- After pretreatment, water flows through the oxidation ditches, where RBC's and microorganisms in returned activated sludge break down the B.O.D. Then the sludge is removed in a clarifier and the remaining water is disinfected. This process differs from that of a packaged plant by a longer retention time and by more types of microorganisms digesting the B.O.D.
- Greater ammonia removal can be achieved by having two oxidation ditches, each at a different pH. Diversion basins can be used to prevent washouts during periods of heavy rainfall.
- Oxidation ditches have the advantage of much more efficient sludge removal. But they are costly, not only in monetary terms, but also in terms of pollution to the environment.

.

THE OXIDATION DITCH PROCESS



PHYSICAL-CHEMICAL TREATMENT OF MUNICIPAL WASTEWATER

- The capital costs of physical-chemical facilities can be less than those of biological treatment facilities, and they usually require less land. They are able to cope with toxic materials and overloads better. However, they require careful operator control and consume relatively large amounts of energy.

Basically, a physical-chemical treatment process involves:

- Removal of scum and solid objects
- Clarification, generally with addition of a coagulant, and frequently with the addition of other chemicals (such as lime for phosphorus removal)
- Filtration to remove filterable solids
- Activated carbon adsorption
- Disinfection

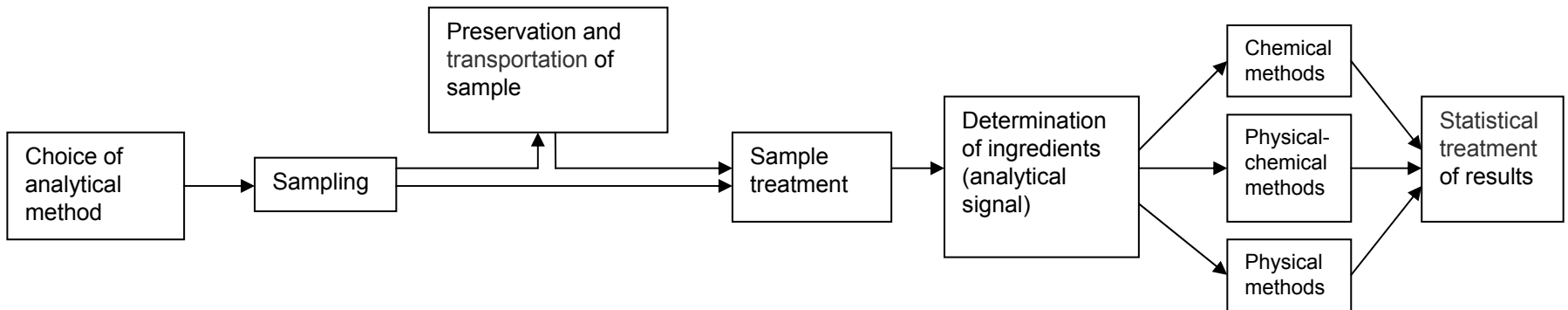
Hydrochemistry

Lecture 5

Basic stages of water analysis

- Choice of analytical method
- Sampling
- Methods of sample preservation
- Determination of physical properties of water
- Content of soluble and insoluble compounds
- Redox potential
- Electrical conductivity

COMMON SCHEMA OF ANALYSIS OF NATURAL OBJECTS



CHOICE OF ANALYTICAL METHOD

To choose analytical method following conditions of determination should be considered:

- Sample size
- Selectivity
- Possibility of analysis on the place of sampling
- Detection limit and adequacy of analysis

SAMPLING

These procedures may be quite different for various species in water. In general, separate samples must be collected for chemical and biological analysis because the sampling and preservation techniques differ significantly. Usually, the shorter the time interval between sample collection and analysis, the more accurate the analysis will be.

RULES OF SAMPLING

- The sampling method will yield a representative sample;
- The sample location is in appropriate area;
- The sample comes from appropriate depth;
- Methods of sampling, transport of sample, storage and further treatment should not change concentration of compounds that will be determined;
- The amount of samples should be enough for analysis.

CATEGORIES OF SAMPLES

- **Grab samples** are taken at a single time and in a single place. Therefore, they are very specific with respect to time and location.
- **Composite samples** are collected over an extended time and may encompass different locations as well. (A composite sample has the advantage of providing an overall picture from only one analysis)

In principle, the average results from a large number of grab samples give the same information as a composite sample.

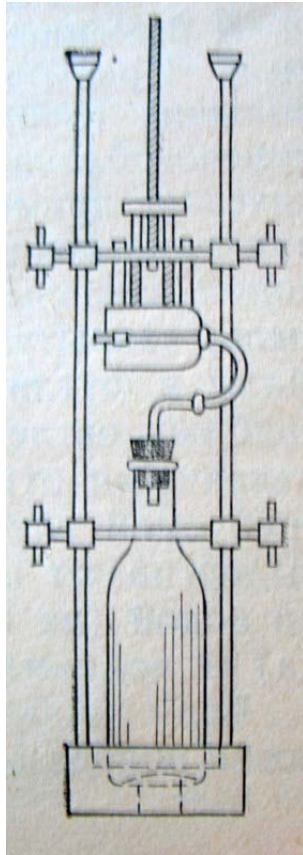
METHODS OF SAMPLING

- Non-permanent – for analysis of deep underground waters or for periodical quality control of natural water
- Multiple:
 - ❖ Zonal – sampling of different depth and different places of water object
 - ❖ Periodical sampling after definite time (seasons, decades, days, hours)

SAMPLERS

- Samplers for surface waters can obtain samples from whatever depth may be desired. A complete program for surface waters would include sampling at a number of elevations from surface to bottom.
- Wastewater samplers have special characteristics depending on the nature of the waste. Some of these devices are designed for placement in a calibrated flume.
- Other samplers operate on a timed sequence, and the identification of each sample must then be referred to a flowmeter chart so that a flow-proportional composite can be prepared from the individual samples.

SAMPLERS



- Electrical
- Mechanical
- Pneumatic

Simple equipment for sampling
(Mayer bottle)

SAMPLERS



Multi water sampler



Water Sampler Used to remove a small quantity of water from a stream or other body of water for use in testing its quality

PRESERVATIVES AND PRESERVATION METHODS USED WITH WATER SAMPLES

Preservative or technique used	Effect on sample	Type of samples for which the method is used
Nitric acid	Keeps metals in solution	Metal-containing samples
Sulfuric acid	Bactericide Formation of sulfates with volatile bases	Biodegradable samples containing organic carbon, oil, or grease Samples containing amines or ammonia
Sodium hydroxide	Formation of sodium salts from volatile acids	Samples containing volatile organic acids or cyanides
Chemical reaction	Fix a particular constituent	Samples to be analyzed for dissolved oxygen using the Winkler method

THE COMMONLY DETERMINED PHYSICAL PROPERTIES OF WATER

- Colour
- Residue (solids)
- Temperature
- Turbidity
- Density
- Transparency
- Taste
- Odour
- Specific conductance
- Redox potential

DETERMINATION OF PHYSICAL PROPERTIES OF WATER

- **Temperature** is measured during sampling because solubility of different substances, especially gases, depends on it. For measurement accurate thermometer is used.
- **Density** depends on concentration of dissolved compounds and dredges as well as temperature. Density is determined by gravimetric method using densimeter (g/cm^3) at $20.0 \pm 0.5^\circ\text{C}$
- **Transparency** depends on colour and turbidity. For determination visual method is used.
- Natural waters are usually colourless. **Colour** of water is caused by colourful humic compounds and iron (III) compounds. For determination visual method or comparison with standard are used.

DETERMINATION OF PHYSICAL PROPERTIES OF WATER

- **Turbidity** in water is measured by the effect of the fine suspended particles on a light beam. Light-interference analytical methods are classified as nephelometric, and one system of turbidity measurement uses *nephelometric turbidity units*.
- **Taste** depends on presence of natural substances or pollutants in water. Taste is determined only in drinking waters.
- **Odour** of water is caused by volatile organic matters. Drinking and industrial waters should have no smell. Firstly character of smell is determined and then intensity of smell. Method for determination is organoleptic.

CONTENT OF SOLUBLE AND INSOLUBLE COMPOUNDS

- **Solid matter occurs in most waters as suspended solids and colloidal matter.**
- The concentration of **suspended solids** is determined by filtration, the collected solids on the filter membrane being dried and weighed.
- Those suspended solids which are large and heavy are called **settleable solids**, and these may be determined volumetrically in a settling cone as a simple control test or weighed.
- The solids remaining with supernatant water above the settled matter are fine and called **turbidity**.
- For the removal of **colloidal materials** from water when they exceed acceptable concentration limits adsorbents are used. Many of the heavy metals are present in colloidal form and are removed from water by coagulation, filtration, adsorption, or a combination of these methods.

REDOX POTENTIAL

- **Eh** a measure of the number of electrons in solution is the redox potential of an aqueous solution
- Redox potential of natural waters depends on dissolved gases and should be determined on the place of sampling
- For measurement platinum and silver chloride electrodes are used
- Calculated with the Nernst equation

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{C_{\text{Ox}}}{C_{\text{Red}}}$$

ELECTRICAL CONDUCTIVITY

- The concentration of total dissolved solids (TDS) is related to electrical conductivity (EC; mhos/cm) or specific conductance.
- The conductivity shows the capacity of water to transmit electrical current.
- TDS and conductivity affect the water sample and the solubility of slightly soluble compounds and gases in water (e.g. CaCO_3 , and O_2).

ELECTRICAL CONDUCTIVITY



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Hydrochemistry

Lecture 6

Methods of investigation of integral water characteristics

- Chemical, physico-chemical, physical, biological methods of analysis
- Portable laboratories
- Total Kjeldahl nitrogen (TKN)
- Organic nitrogen
- Total phosphorus.
- Organic carbon
- Biochemical oxygen demand (BOD)
- Chemical oxygen demand (COD)

IMPORTANT METHODS OF ANALYSIS OF WATER CHEMICAL CONTENT

- Chemical
- Physico-chemical
- Physical
- Biological

CHEMICAL METHODS

- **Volumetric analysis**, in which volumes of reagents are measured
- **Gravimetric analysis**, in which masses are measured.

PHYSICO-CHEMICAL AND PHYSICAL METHODS

- Spectrophotometric methods
 - Absorption spectrophotometry
 - Atomic absorption analyse
 - Emission analyse
 - Electrochemical methods of analysis
 - Potentiometry
 - Polarography
 - Voltamperometry
- Chromatography
 - High-performance liquid chromatography
 - Ion chromatography
- Mass spectrometry
- Radiometry

PORTABLE LABORATORIES



SMART 2[®] Water Analysis Laboratory This portable lab measures 24 water quality parameters

<http://www.lamotte.com>

The “TINY LAB” portable laboratory

<http://www.riochem.com>



PORTABLE SPECTROPHOTOMETERS

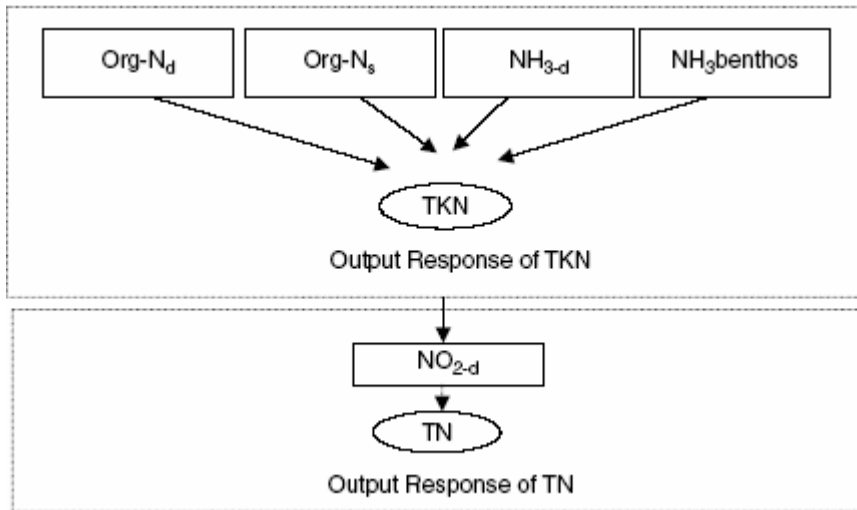


SPECTRO Portable Spectrophotometer
www.globalw.com/products/spectro



T100 Portable Spectrophotometer
www.pginstruments.com

TOTAL KJELDAHL NITROGEN (TKN)



- **Preservation** of sample for determination of TKN:
10mL 10% H₂SO₄ per liter
- **Determination:**
Kjeldahl digestion —
distillation — Nesslerization or
titration with standard acid
- Kjeldahl digestion:
sample + conc. H₂SO₄ +
K₂SO₄ (t = 315 – 370 °C),
kat.– Cu²⁺, Hg²⁺ or Se

ORGANIC NITROGEN

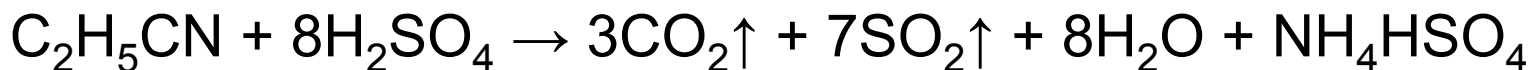
- Organic nitrogen is total combined ammonia nitrogen
- **Preservation** of sample for determination of organic nitrogen:
10mL 10% H₂SO₄ per liter
- **Determination:**
Evolution of free ammonia (pH 7.4)— Kjeldahl digestion
— distillation — Nesslerization or titration with standard acid

DIGESTION OF ORGANIC NITROGEN CONTAINING COMPOUNDS

- Amides



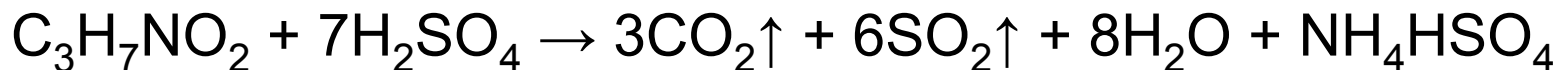
- Nitriles



- Aminoacids



- Nitro compounds



TOTAL PHOSPHORUS

- Total phosphorus is total of soluble and insoluble phosphorus
- Soluble phosphorus compounds are orthophosphoric acid (H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}), meta-, pyro- and polyphosphates, organic compounds – phospholipids, nucleic acids, etc.
- Insoluble phosphorus compounds are natural minerals, organic compounds.
- **Preservation** of sample for determination of total phosphorus:
10mL 0.4% HgCl_2 per liter
- **Determination:**
Oxidation with persulfate — reversion — photometric (molybdenum blue method)

ORGANIC CARBON

- **Preservation** of sample for determination of organic carbon:
10mL 10% H₂SO₄ per liter
- **Determination:**
Total organic carbon analyzer — IR detector:
 - ❖ Combustion / NDIR Method
 - ❖ Persulfate oxidation / NDIR Method

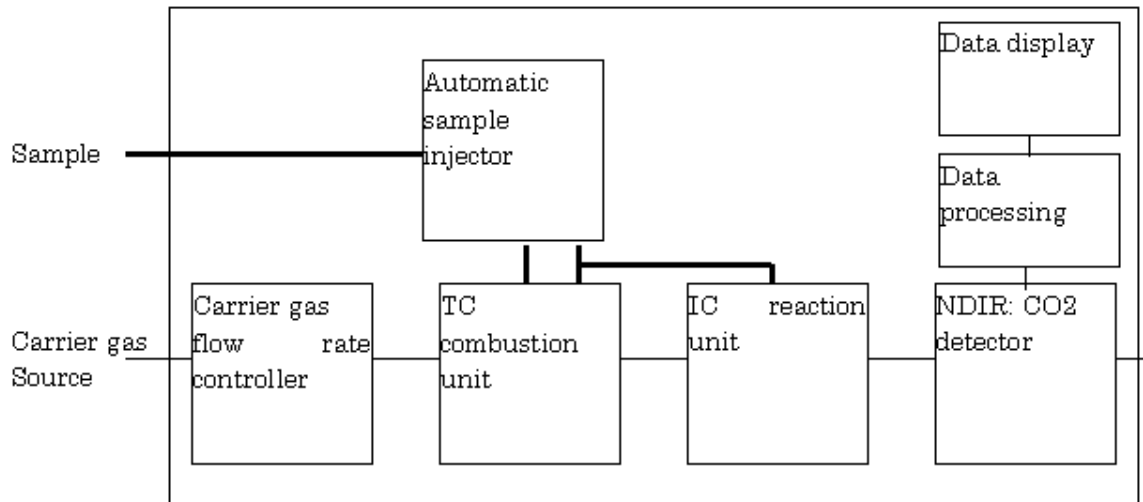
TOC ANALYZERS



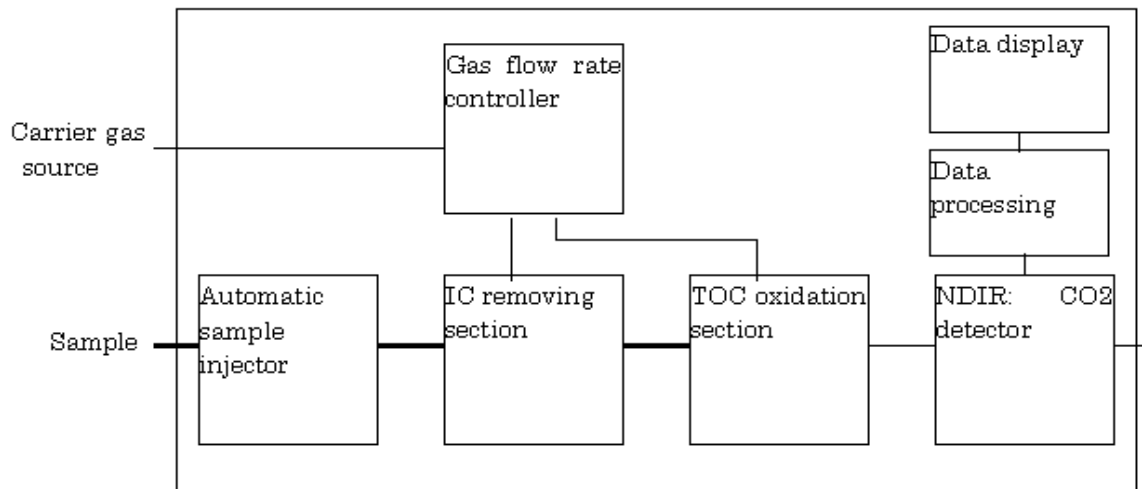
Zellweger Analytics 383760
2100 Lab TOC Analyzer
<http://lab.biostad.com>



5310 C Laboratory TOC
Analyzer
www.geinstruments.com



An example of combustion / NDIR method TOC analyzer

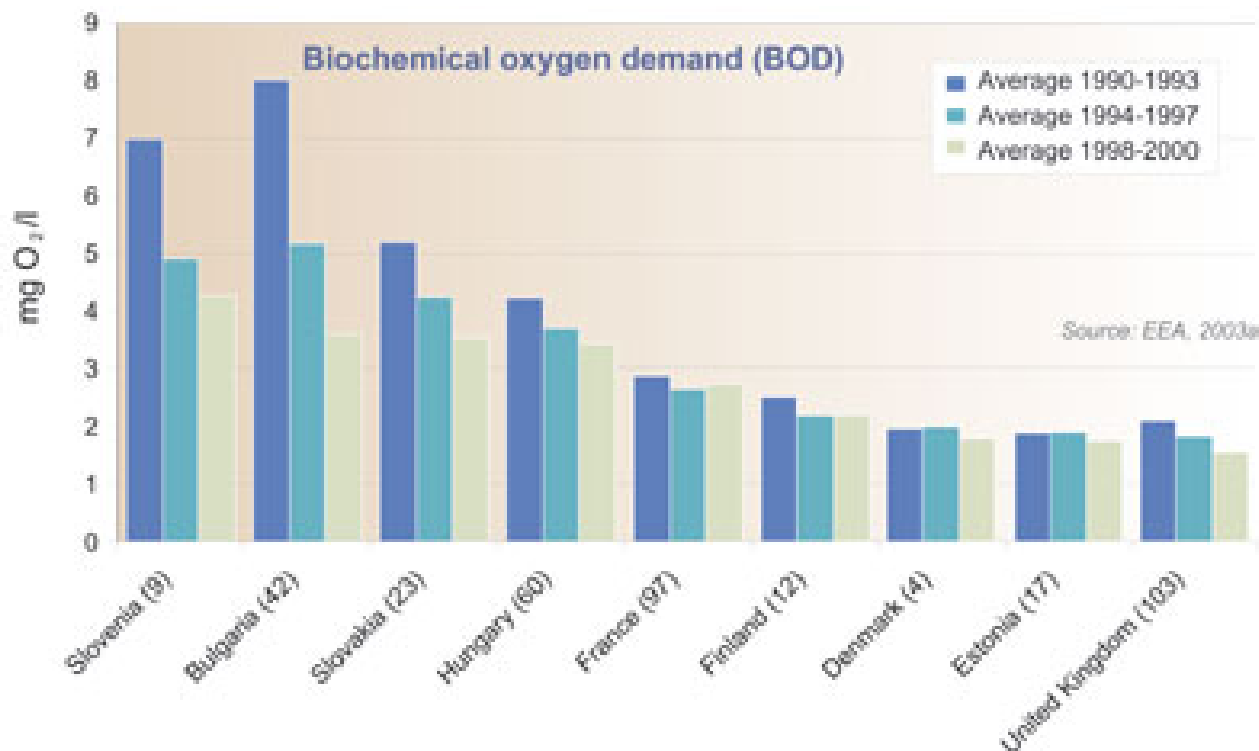


An example of persulfate oxidation / NDIR method TOC analyzer

BIOCHEMICAL OXYGEN DEMAND (BOD)

- Biochemical (Biological) Oxygen Demand (BOD) is the rate of oxygen consumption from water or wastewater by microorganisms, which are converting the waste materials to simpler compounds.
- BOD is an index of the degree of organic pollution in water. It is the amount of oxygen in a unit volume of water at a given temperature and for a given time.

AVERAGE BOD CONCENTRATIONS BY COUNTRY



Note: Figures in brackets indicate the number of stations.
Data are for BOD₅ for all stations except for Finland and Estonia which are for BOD₇

BIOCHEMICAL OXYGEN DEMAND (BOD)

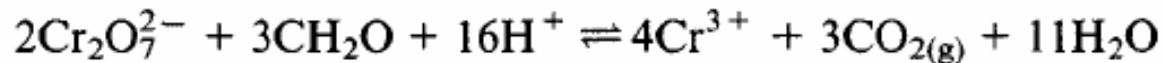


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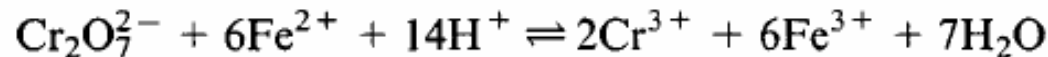
- **Preservation** of sample for determination of BOD:
10mL 10% H_2SO_4 per liter or refrigeration
- **Determination:**
Dilution — 5 day incubation — dissolved oxygen determination using probe method

CHEMICAL OXYGEN DEMAND (COD)

The Chemical Oxygen Demand (COD) is determined by using powerful oxidizing agent, dichromate ($\text{Cr}_2\text{O}_7^{2-}$), to oxidize organic matter,



followed by back-titration of excess added dichromate with Fe^{2+}



As $\text{Cr}_2\text{O}_7^{2-}$ oxidizes substances not oxidized by O_2 , the COD is usually greater than the BOD and to some extent overestimates the threat posed to oxygen content.

CHEMICAL OXYGEN DEMAND (COD)



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Hydrochemistry

Lecture 7

Individual indexes for determination of chemical content of water (Part I)

- pH and pOH
- Dissolved oxygen
- Hydrogen sulfide and sulfides
- Acidity and alkalinity
- Components of carbonate system
- Chlorides and sulphates
- Hardness of water
- Potassium and sodium
- Calcium and magnesium

INDIVIDUAL INDEXES FOR DETERMINATION OF CHEMICAL CONTENT OF WATER

- pH and pOH
- dissolved oxygen
- hydrogen sulfide and sulfides
- acidity
- alkalinity
- components of carbonate system
- chlorides
- sulphates
- hardness of water
- potassium, sodium, calcium and magnesium
- ammonia and ammonia salts
- nitrates and nitrites
- phosphates and polyphosphates
- silicium
- ferum
- biometals (Mn, Cu, Zn, Co, Mo)
- toxic inorganic substances (Al, As, Be, V, Bi, Cd, Ni, Hg, Pb, Se, Ti, Cr)
- organic substances

pH and pOH



- Determination of pH is measurement of hydrogen ion activity in aqueous solution:

$$\text{pH} = -\log[\text{H}^+]$$

- The hydrogen ion concentration can be measured with a pH meter with glass electrode.
- It can also be titrated when the concentration becomes high enough to be detectable by chemical analysis. Since pH is a logarithmic function, the hydrogen ion concentration increases by a factor of 10 for each unit of pH reduction.
- Determination is performed right after sampling without preservation.

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pOH} = -\log[\text{OH}^-]$$

pH and pOH

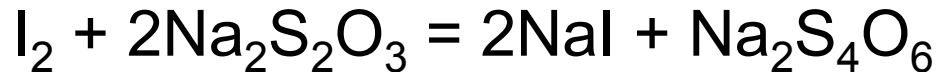
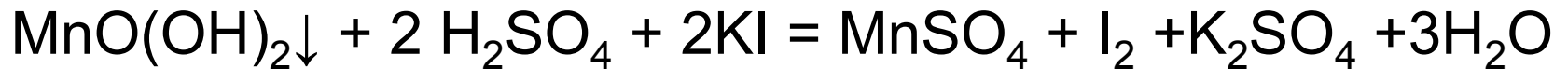
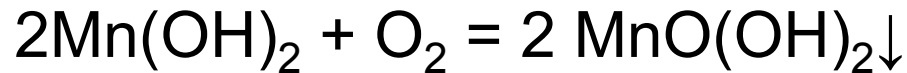


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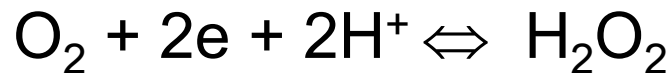
DISSOLVED OXYGEN

Determination:

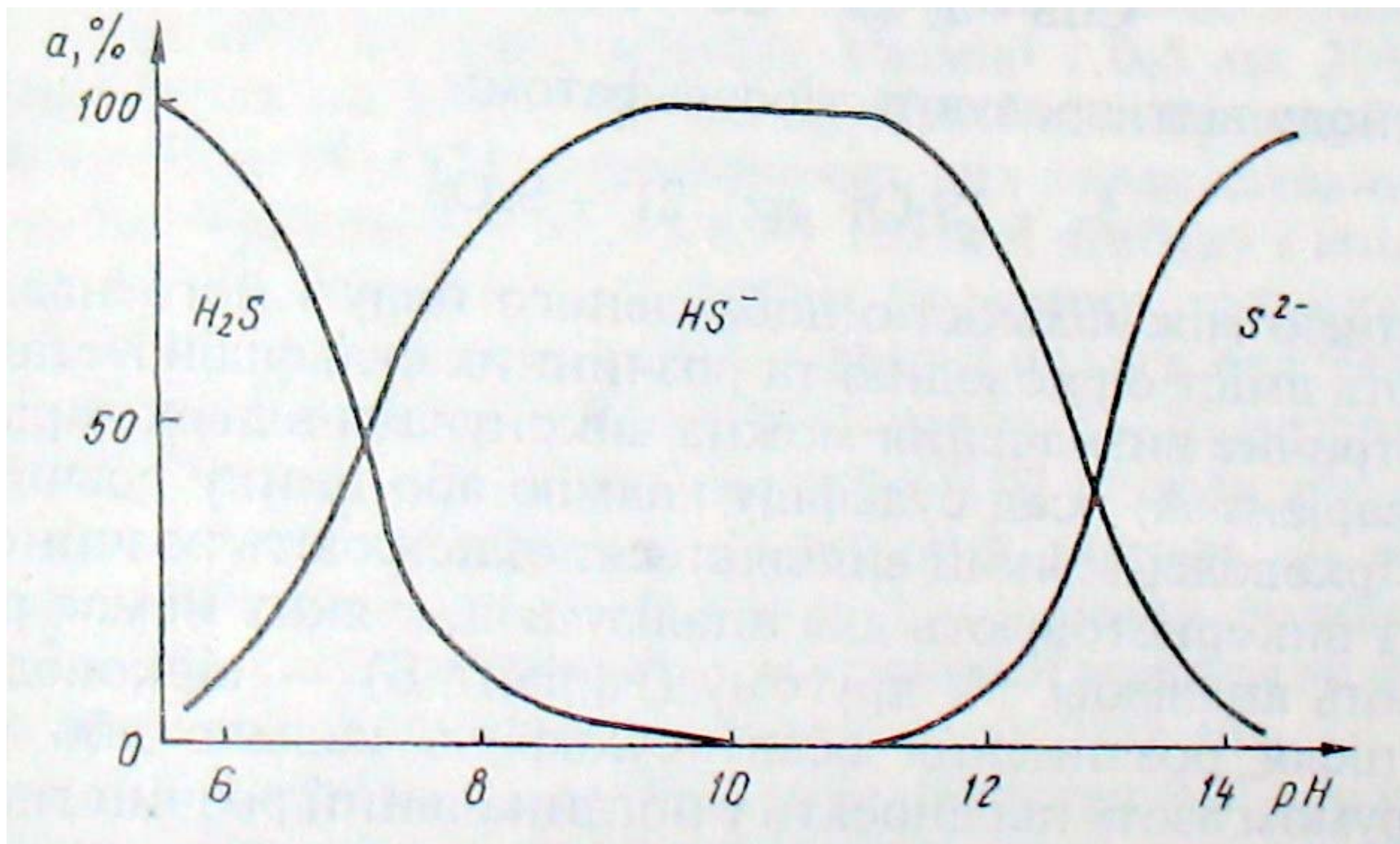
- Iodometric titration (detection limit is 0.05 mg/l)



- Polarographic method



DISTRIBUTION OF SPECIES DIAGRAM FOR THE H_2S - HS^- - S^{2-} SYSTEM IN WATER



HYDROGEN SULFIDE AND SULFIDES

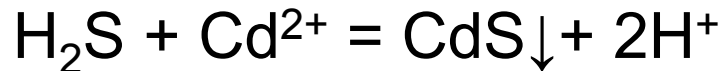
- Hydrogen sulfide exists in water in following forms: H_2S , HS^- , S^{2-} .

- **Preservation:**

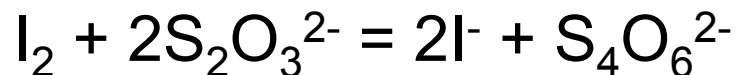
5 mL 24% $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ per liter

- **Determination:**

1. Iodometric titration (detection limit is 0.05 mg/l)



Titration of excess of I_2 :

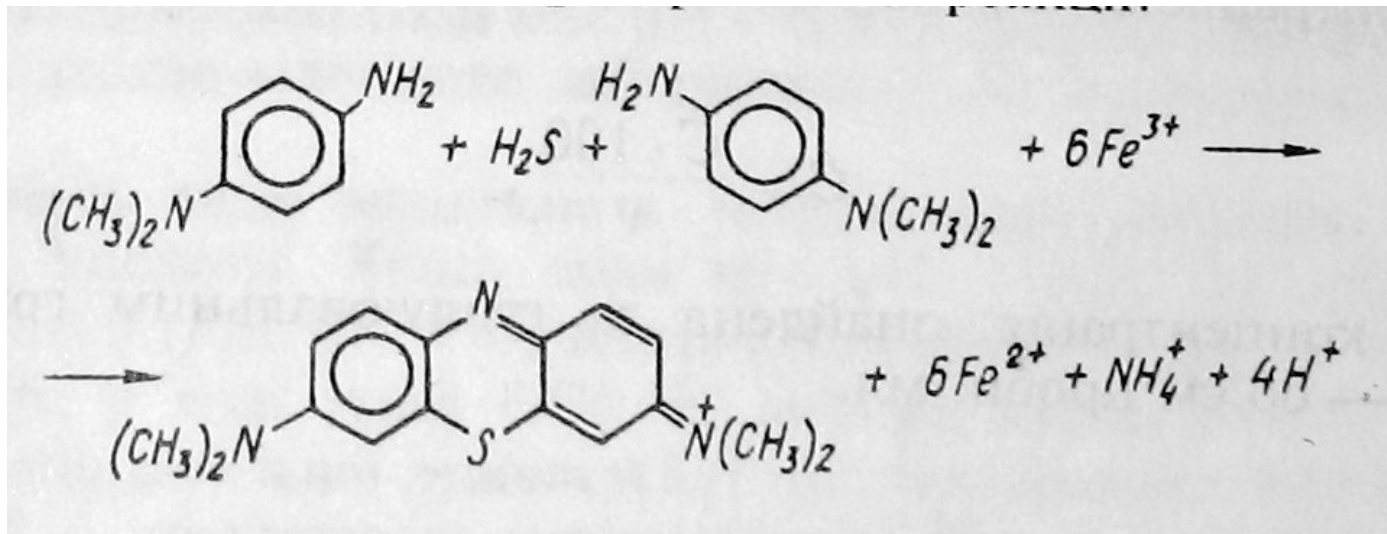


2. Photometric method (detection limit is 0.1 mg/l)



HYDROGEN SULFIDE AND SULFIDES

- 3. Photometric determination with dimethylparaphenylenediamine, pH 0.5, $\lambda=667\text{nm}$ (detection limit is 0.05 mg/l)



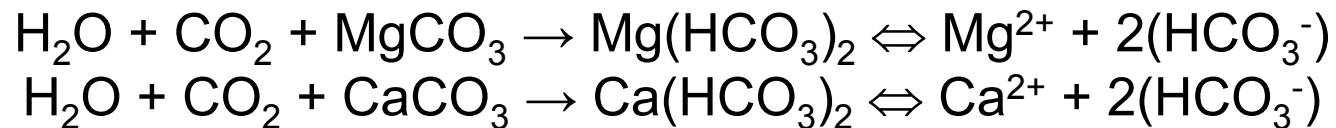
WATER ALKALINITY

- The capacity of water to accept H⁺ ions (protons) is called **alkalinity**.
- Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Frequently, the alkalinity of water must be known to calculate the quantities of chemicals to be added in treating the water.
- Highly alkaline water often has a high pH and generally contains elevated levels of dissolved solids.
- It is important to distinguish between high *basicity*, manifested by an elevated pH, and high *alkalinity*, the capacity to accept H⁺. Whereas pH is an *intensity* factor, alkalinity is a *capacity* factor
- In engineering terms, alkalinity frequently is expressed in units of mg/L of CaCO₃, based upon the following acid-neutralizing reaction:

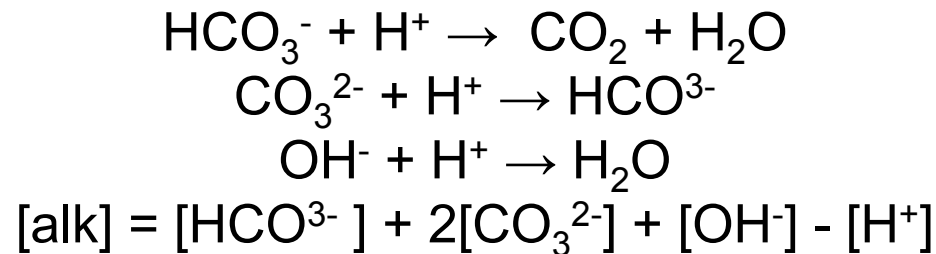


THE SOURCE OF ALKALINITY

Water containing CO_2 from the atmosphere and from respiration of soil organisms dissolves magnesium and calcium from a common mineral dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) produce alkalinity in ground water:

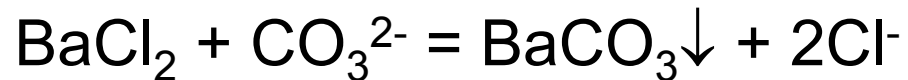


Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonate ion, and hydroxide ion:



DETERMINATION OF ALKALINITY

- *Phenolphthalein alkalinity* - titration with acid to the pH at which HCO_3^- is the predominant carbonate species (pH 8.3)
- *Total alkalinity* - titration with acid to the methyl orange endpoint (pH 4.3), where both bicarbonate and carbonate species have been converted to CO_2 .
- *Hydroxide alkalinity* - precipitation of carbonate with BaCl_2 , titration with standard acid to phenolphthalein endpoint.



- **Preservation** for determination of all kinds of alkalinity is keeping sample cool

WATER ACIDITY

- **Acidity** as applied to natural water and wastewater is the capacity of the water to neutralize OH^- .

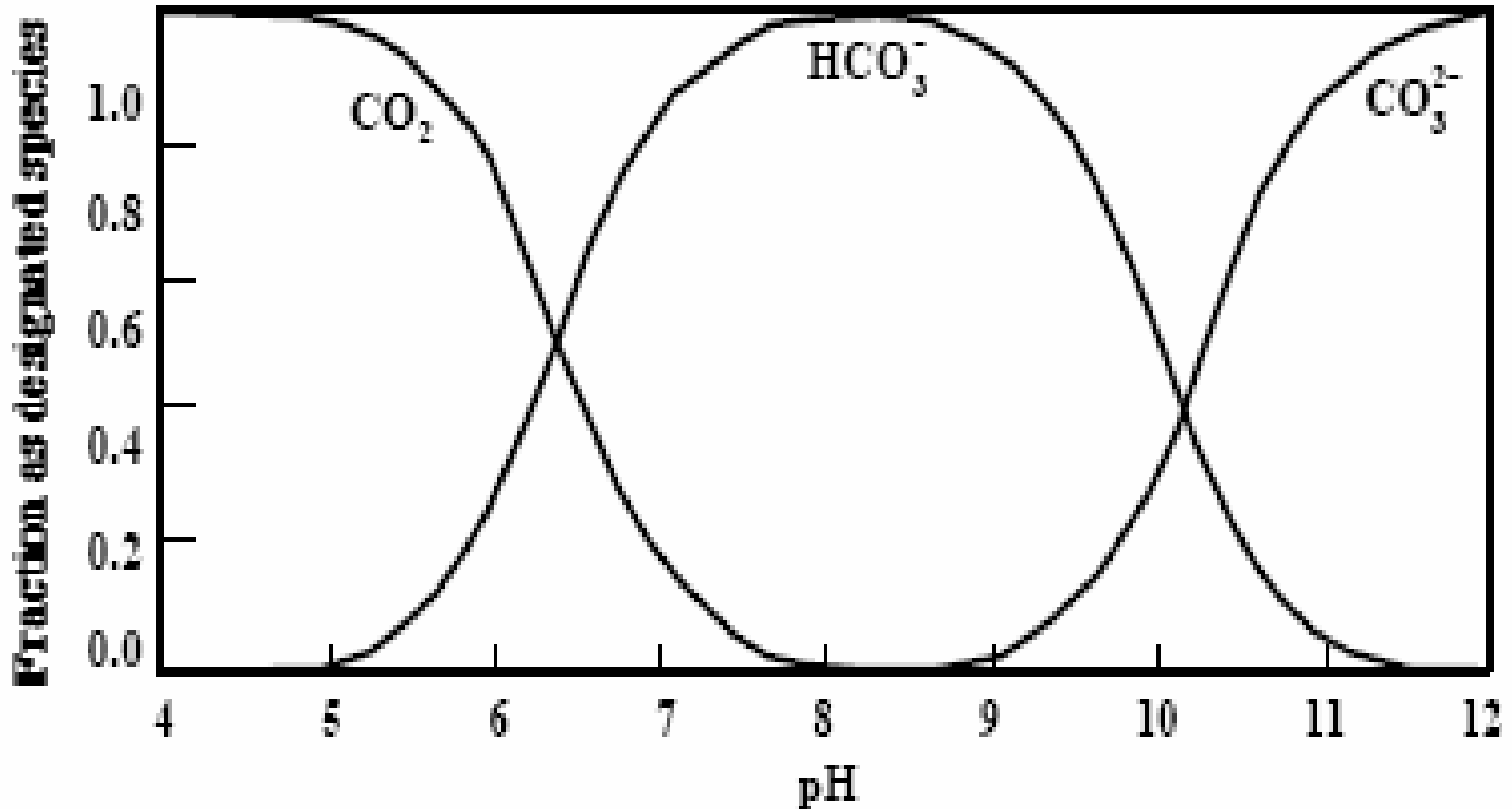
Acidity results from the presence of:

- weak acids, particularly CO_2
- sometimes H_2PO_4^- , H_2S , proteins, and fatty acids
- acidic metal ions, particularly Fe^{3+}

DETERMINATION OF ACIDITY

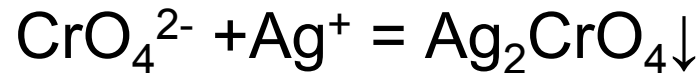
- *Total acidity* - titration with standard base to phenolphthalein endpoint
- *Free mineral acidity* - Titration with standard base to methyl orange endpoint, or potentiometric to pH 4.5
- **Preservation** for determination of all kinds of acidity is keeping sample cool

DISTRIBUTION OF SPECIES DIAGRAM FOR THE $\text{CO}_2\text{-HCO}_3^-\text{-CO}_3^{2-}$ SYSTEM IN WATER



CHLORIDES DETERMINATION

- Titration with silver nitrate — chromate indicator – detection limit is 2 mg/l



- Indirect titration with potassium thiocyanate – Fe(III) indicator (Folgard's method) – detection limit is 2 mg/l



Titration of excess of Ag^+ :

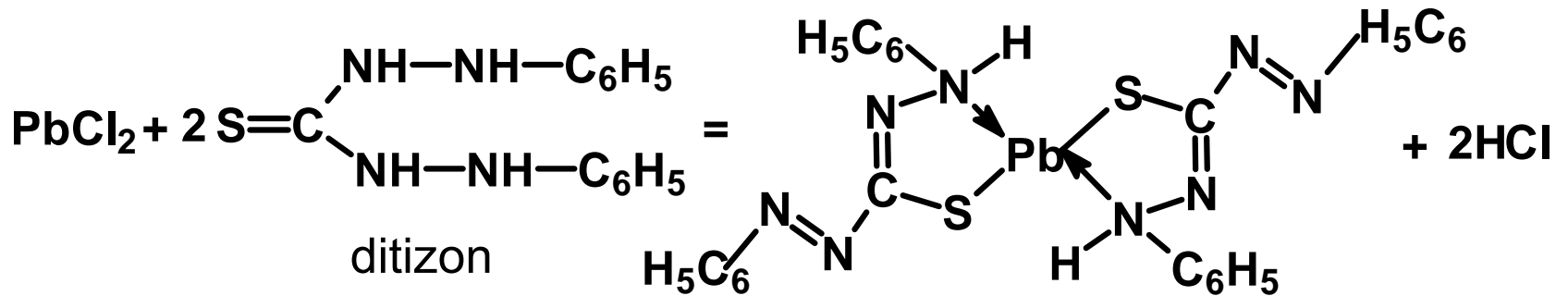
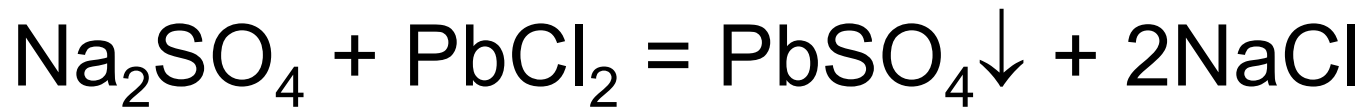


- Mercurimetry – diphenylcarbazone indicator.

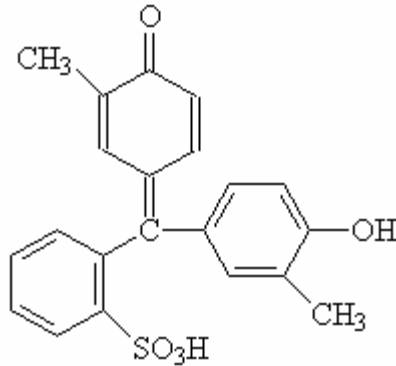


SULPHATES DETERMINATION

- Titration with plumbum nitrate — ditizon indicator



SULPHATES DETERMINATION



Cresol Red

- Chelatometric back titration
– Cresol Red - (o-Cresolsulfonphthalein)
indicator

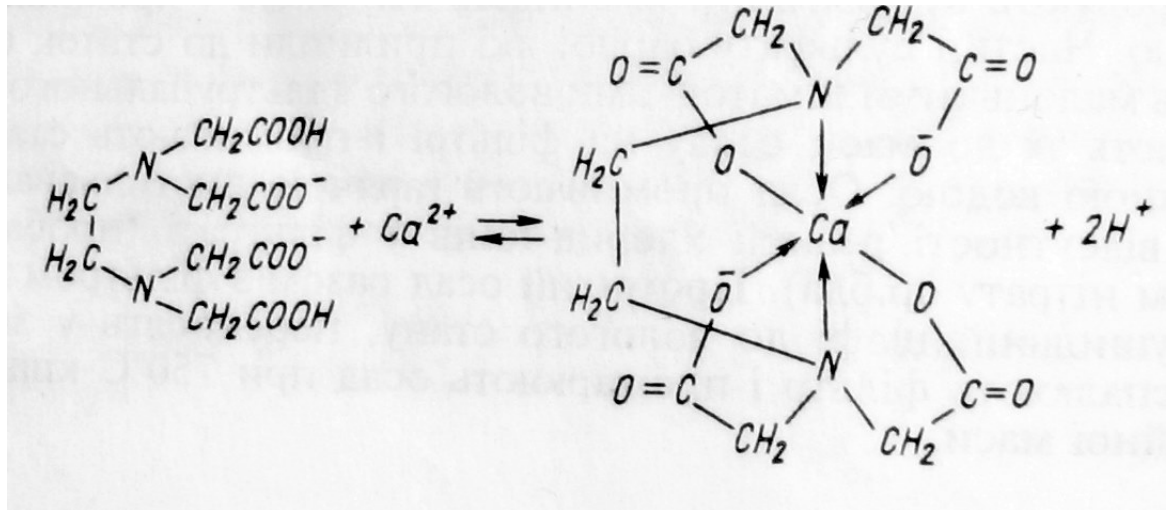
- Gravimetric determination as BaSO₄
$$\text{Na}_2\text{SO}_4 + \text{BaCl}_2 = \text{BaSO}_4\downarrow + 2\text{NaCl}$$
- Turbidometric determination

HARDNESS OF WATER

- Hardness is correlated with TDS (Total dissolved solids). It represents total concentration of Ca^{2+} and Mg^{2+} ions, and is reported in equivalent CaCO_3 .

Determination:

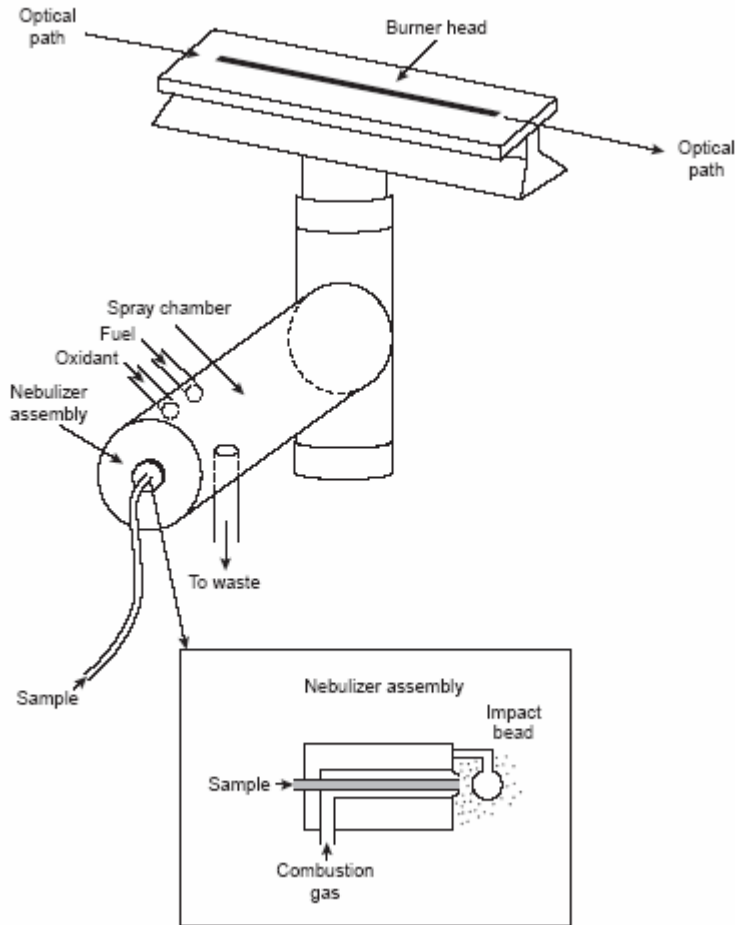
- calculated from the results of separate calcium and magnesium tests
- titration with ethylenediaminetetracetic acid (EDTA)



RELATION BETWEEN HARDNESS CONCENTRATION AND CLASSIFICATION OF NATURAL WATER

Hardness as mg/L CaCO₃	Classification
0 – 60	Soft
61 – 120	Moderately hard
121 – 180	Hard
>180	Very hard

POTASSIUM DETERMINATION



- Atomic absorption spectroscopy (concentration range is 0.1 – 2 mg/l)
- Flame photometry, propane – butane flame, $\lambda=768.2$ nm (concentration range is > 0.1 mg/l)

Determination is performed without **preservation** in no more than one day after sampling.

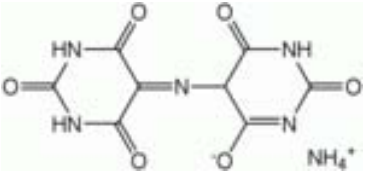
Flame atomization assembly equipped with spray chamber and slot burner. The inset shows the nebulizer assembly.

SODIUM DETERMINATION

- Atomic absorption spectroscopy (concentration range is 0.003 – 1 mg/l)
 - ❖ Flame Atomization – detection limit is 0.2 ppb
 - ❖ Electrothermal Atomization - detection limit is 0.004 ppb
- Flame photometry, propane – butane flame, $\lambda=589.3$ nm

Determination is performed without **preservation** in no more than one day after sampling.

CALCIUM DETERMINATION

Analysis	Method	Preservation
Total calcium (Ca)	<ul style="list-style-type: none"> •Atomic absorption spectroscopy (concentration range is 0.2 – 7 mg/l) •Chelatometric titration – murexide indicator <div style="text-align: center; margin-top: 10px;">  <p>murexide</p> </div>	5 mL 10% HNO ₃ per liter
Soluble calcium (Ca)	Filtration — atomic absorption (concentration range is 0.2 – 7 mg/l)	None or filter sample thru 0.45 μm millipore and add 5 mL 10% HNO ₃ per liter

MAGNESIUM DETERMINATION

Analysis	Method	Preservation
Total magnesium (Mg)	<ul style="list-style-type: none">•Atomic absorption spectroscopy (concentration range is 0.02 – 0.5 mg/l)•Difference between hardness of water and total calcium	5 mL 10% HNO ₃ per liter
Soluble magnesium (Mg)	Filtration — atomic absorption spectroscopy (concentration range is 0.02 – 0.5 mg/l)	None or filter sample thru 0.45 μm millipore and add 5 mL 10% HNO ₃ per liter

Hydrochemistry

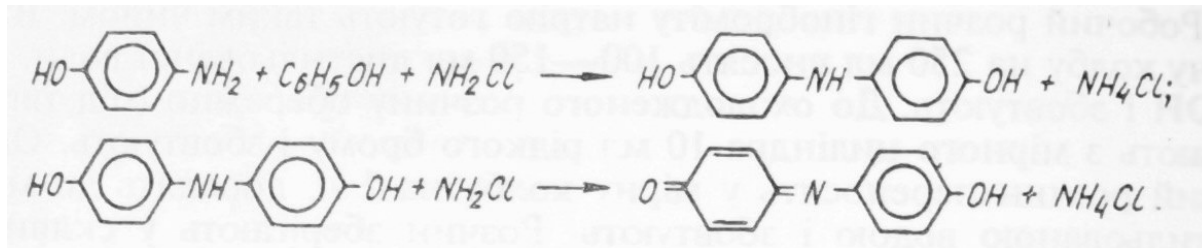
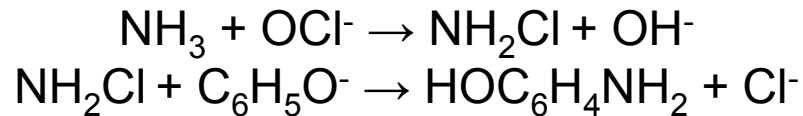
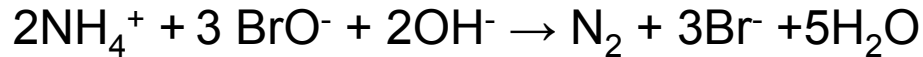
Lecture 8

Individual indexes for determination of chemical content of water (Part II)

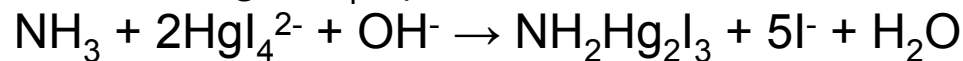
- Ammonia and ammonia salts
- Nitrates and nitrites
- Phosphates and polyphosphates
- Silicium
- Iron
- Microelements (Mn, Cu, Zn, Co, Mo)

AMMONIA AND AMMONIA SALTS DETERMINATION

- Distillation at pH 9.5 followed by Amperometric titration
- Photometric phenol-hypochlorite method, pH 13, $\lambda=625$ nm



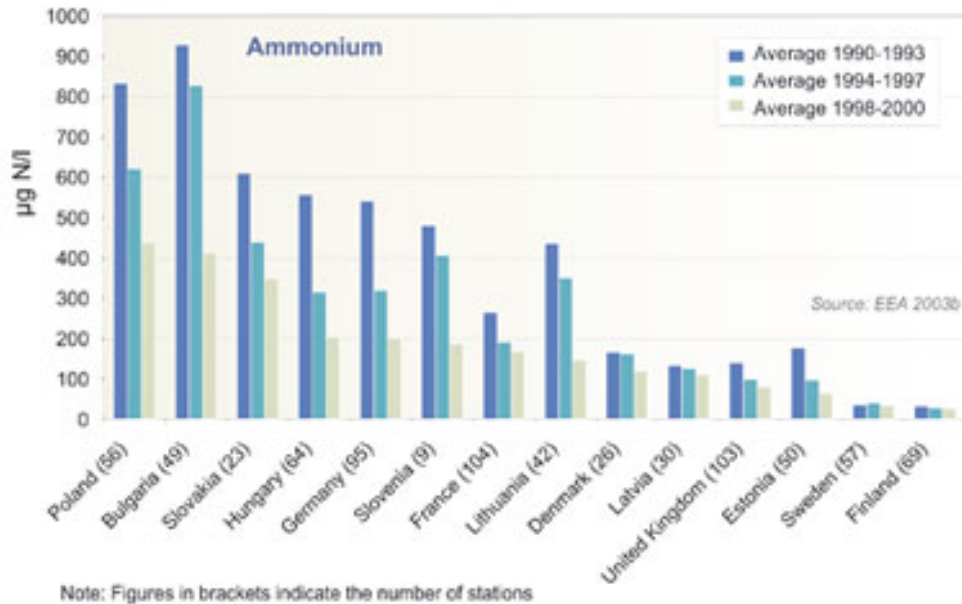
- Distillation at pH 9.5 followed by Nesslerization photometry, $\lambda=425$ nm (detection limit is 0.05 mg NH_4^+/l)



Preservation:

10 mL 10% H_2SO_4 per liter

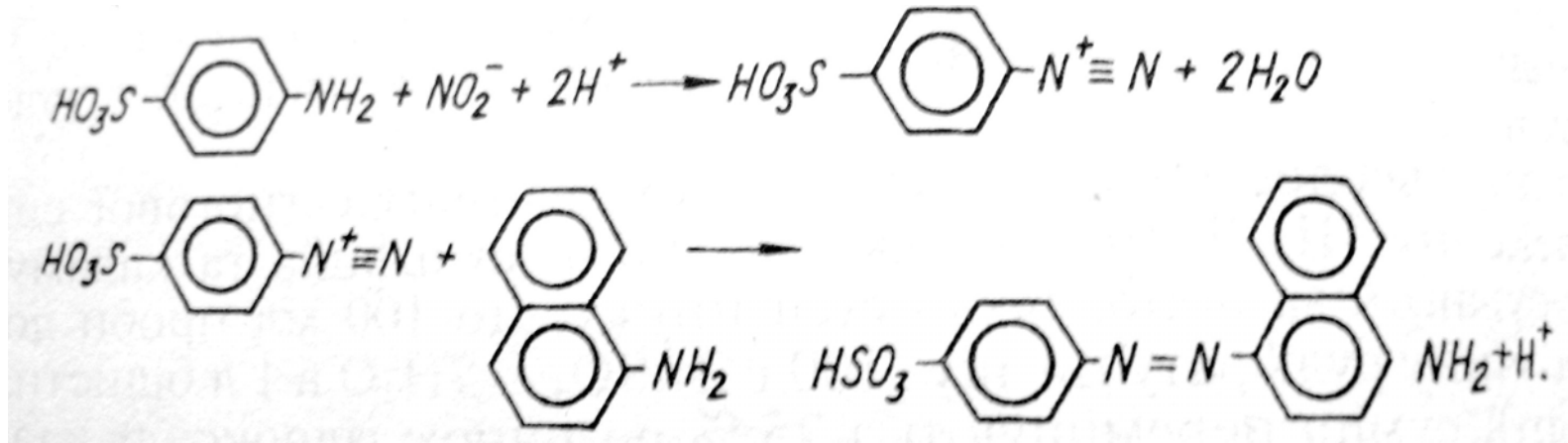
AVERAGE AMMONIUM CONCENTRATION BY COUNTRY



Ammonium concentrations are normally raised as a result of organic pollution, caused by discharges from wastewater treatment plants, industrial effluents and agricultural runoff.

NITRITES DETERMINATION

Photometric (diazotization), $\lambda=520$ nm –
detection limit is 0.002 mg NO_2^-/l

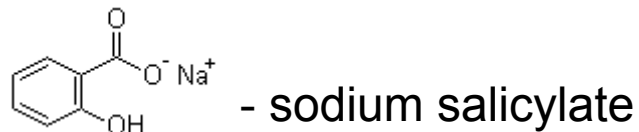


Preservation:

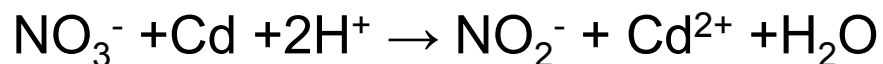
10mL 0.4% HgCl_2 per liter

NITRATES DETERMINATION

- Photometric with phenoldisulfonic acid, $\lambda=410$ nm (detection limit is 0.5 mg NO_3^-/l)
- Photometric with sodium salicylate, $\lambda=410$ nm (detection limit is 0.1 mg NO_3^-/l)



- Cadmium reduction — photometric (diazotization) - detection limit is 0.005 mg/l



- Potentiometric with nitrate ion-selective electrode in presents of 1% solution aluminium alum (detection limit is 6 mg/l)

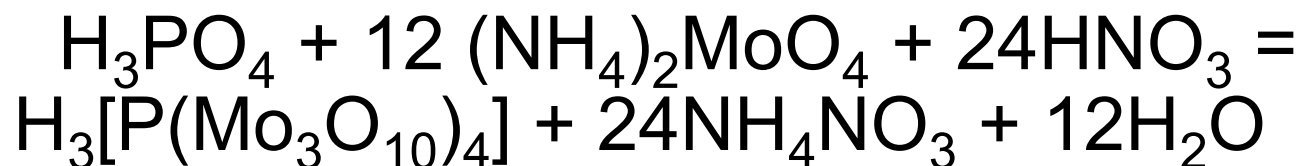
Preservation:

- 10mL 10% H_2SO_4 per liter

PHOSPHATES AND POLYPHOSPHATES DETERMINATION

Analysis	Code	Definition	Method	Preservation
Phosphorus (P)- total	D4	Total organic and inorganic phosphorus	Oxidation with persulfate — reversion — photometric	10mL 0.4% HgCl ₂ per liter
Phosphorus (P)- total inorganic	D2	Soluble and insoluble ortho and polyphosphate	Reversion in acid — photometric	
Phosphorus (P)- soluble inorganic	D2S	Soluble ortho- and polyphosphate	Filtration — reversion — photometric	
Phosphorus (P)- ortho	D	Soluble ortho phosphate	Photometric	
Phosphorus (P)- organic	D3	Total organic phosphorus	D4-D2	

PHOTOMETRIC MOLYBDENUM BLUE METHOD FOR DETERMINATION OF PHOSPHATES

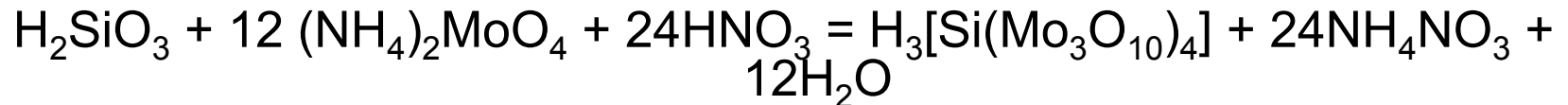


- After reduction the solution has intensive blue colour, $\lambda=720$ nm
- In presence of Sb reaction becomes rapid and heating is not necessary, $\lambda = 670 - 690$ nm
- Detection limit is $0.02 \text{ mg PO}_4^{3-}/\text{l}$

SILICIUM DETERMINATION

Monomer silicium forms:

- Photometric as yellow polyoxometalate (detection limit is 1 mg SiO₂/l)

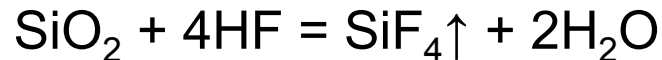


H₃[Si(Mo₃O₁₀)₄] has intensive yellow colour

- Photometric (ammonium molybdate with 1- amino — 2-naphthol 4-sulfonic acid reduction)

Total silicium:

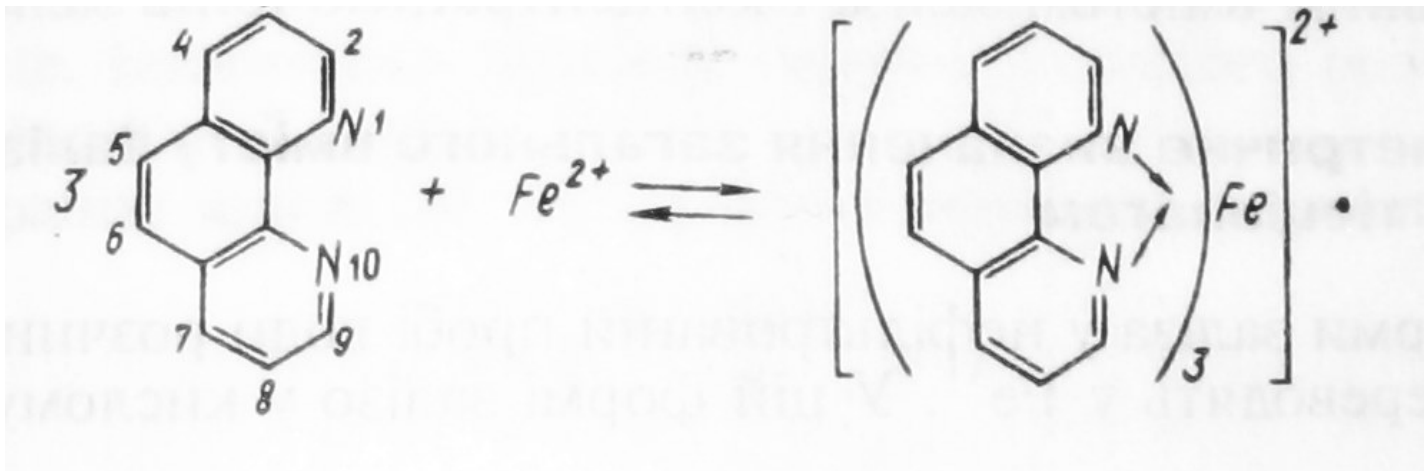
- Photometry as monomer forms after basic hydrolysis
- Photometry as blue reduced silicium - molybdenum complex, λ=815 nm (detection limit is 0.1 mg SiO₂/l)
- Gravimetric (detection limit is 5 mg Si)



IRON DETERMINATION

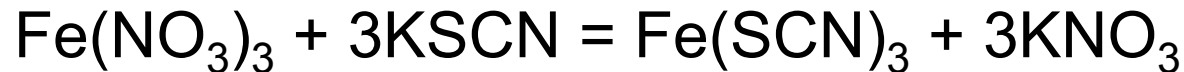
Usually total iron (soluble and insoluble) is determined.

- Photometric with 1,10-phenanthroline, pH 2 – 9, $\lambda=510$ nm, $\epsilon=11000$ (detection limit is 0.05 mg/l)

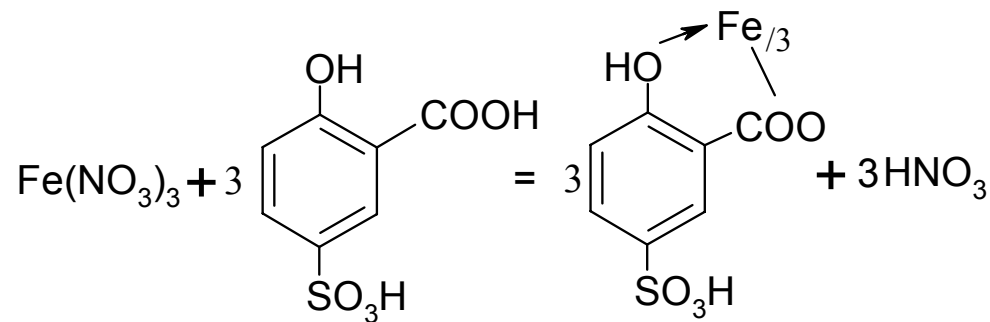


IRON DETERMINATION

- Photometric with thiocyanate, $\lambda=500$ nm (detection limit is 0.05 mg Fe/l)



- Photometric with sulfosalicylic acid (detection limit is 0.1 mg Fe/l)



- Atomic absorption spectroscopy
 - ❖ Flame Atomization (concentration range is 0.3 – 5 mg/l)
 - ❖ Electrothermal Atomization (concentration range is 0.005 – 0.1 mg/l)

BIOMETALS

- Water contains 10 biometals:

Main ions { Ca
Mg
Na
K

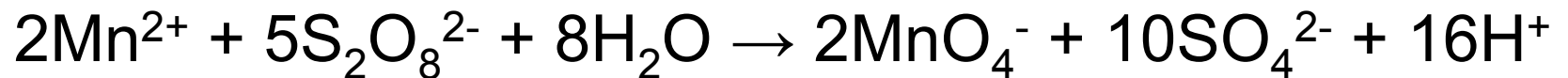
Fe - Biogenic element

Mn }
Cu }
Zn }
Co }
Mo } Microelements

MICROELEMENTS DETERMINATION

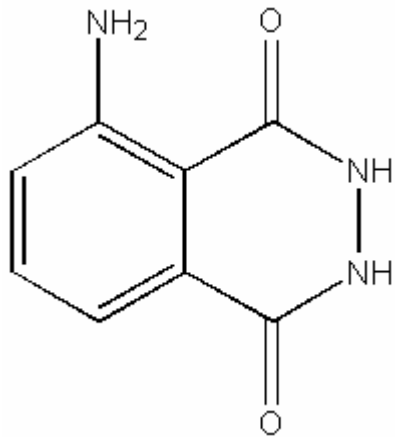
- **Manganese (Mn):**

- ❖ Atomic absorption spectroscopy, $\lambda=279.5$ nm
 - ❖ Flame Atomization (concentration range is 0.1 – 3 mg/l)
 - ❖ Electrothermal Atomization (concentration range is 0.01 – 0.03 mg/l)
- ❖ Photometric determination after oxidation with persulphate, $\lambda=540$ nm (detection limit is 50 μg Mn/l)



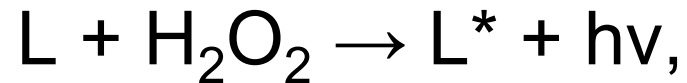
MICROELEMENTS DETERMINATION

- **Manganese (Mn):**



luminol

- ❖ Chemiluminescent method, luminol (5-Amino-2,3-dihydro-1,4-phthalazinedione), pH 9.6



L – luminol molecule

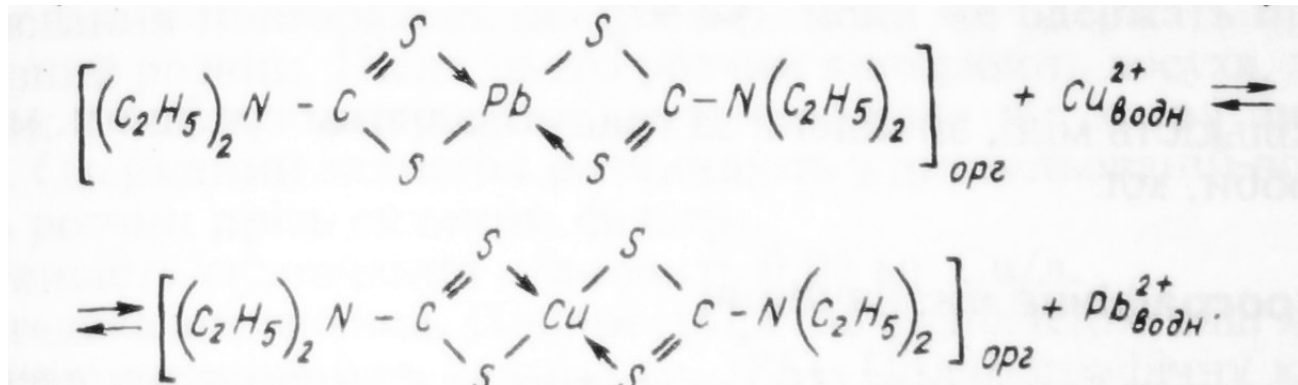
MICROELEMENTS DETERMINATION

- **Copper (Cu):**
 - ❖ Atomic absorption spectroscopy, air–acetylene flame, $\lambda = 324.8$ nm with a slit width of 0.5 nm (concentration range is 0.01 – 0.7 mg/l)
 - ❖ Polarography, $E_{1/2} = -0.54$ V (1 mol/l NH_4OH , 1 mol/l NH_4Cl) - detection limit is 0.05 mg Cu/l
 - ❖ Chemiluminiscent method, luminol, pH 11 – 12 (detection limit is $5 \cdot 10^{-4}$ μg Cu)

MICROELEMENTS DETERMINATION

- **Copper (Cu):**

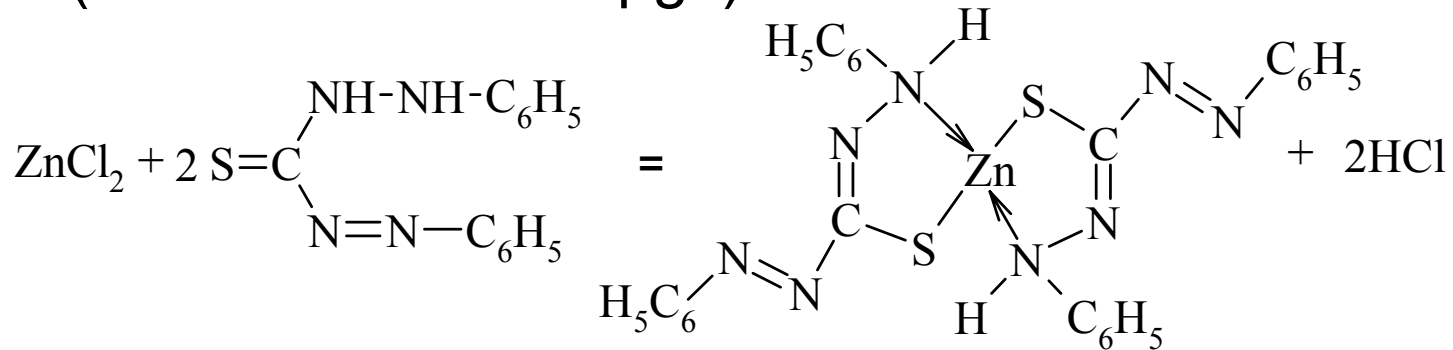
- ❖ Extraction – photometric determination with plumbum diethyldithiocarbamate, $\lambda = 430 \text{ nm}$ (detection limit is $2 \mu\text{g Cu}$)



MICROELEMENTS DETERMINATION

- **Zinc (Zn):**

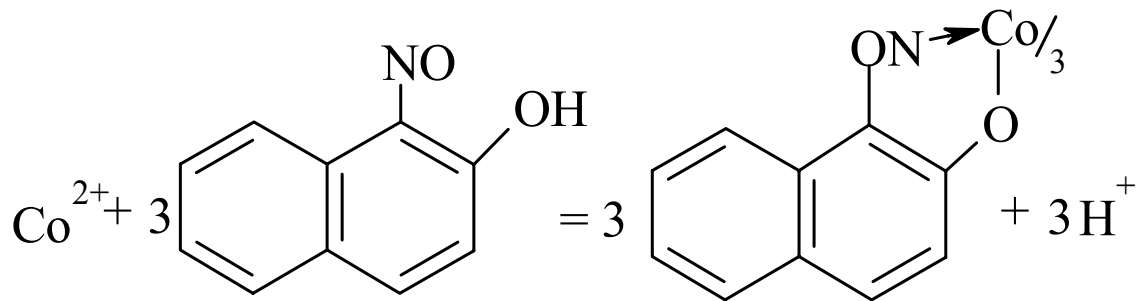
- ❖ Atomic absorption spectroscopy, air–acetylene flame, $\lambda=213.9$ nm with a slit width of 1.0 nm (concentration range is 0.0025 – 0.05 mg/l)
- ❖ Extraction – photometric determination with ditizon, pH 4 – 7 (detection limit is 2 $\mu\text{g/l}$)



- ❖ Inversion voltamperometry, $E = -0.12$ V (detection limit is $1.5 \cdot 10^{-3}$ $\mu\text{g Zn/l}$)

MICROELEMENTS DETERMINATION

- **Cobalt (Co):**
 - ❖ Atomic absorption spectroscopy
 - ❖ Flame Atomization (concentration range is 0.5 – 5 mg/l)
 - ❖ Electrothermal Atomization (concentration range is 0.05 – 0.1 mg/l)
 - ❖ Photometric determination with nitroso-R-salt, pH ~ 5.5, $\lambda = 520$ nm (detection limit is 1 $\mu\text{g Co/l}$)



MICROELEMENTS DETERMINATION

- **Molybdenum (Mo):**
 - ❖ Atomic absorption spectroscopy
 - ❖ Flame Atomization (concentration range is 1 – 40 mg/l)
 - ❖ Electrothermal Atomization (concentration range is 0.003 – 0.06 mg/l)
 - ❖ Photometric determination with thiocyanate, $\lambda = 470$ nm (detection limit is 10 $\mu\text{g Mo/l}$)

PRESERVATION OF SAMPLES FOR MICROELEMENTS DETERMINATION

- For determination of total microelement concentration:
5 mL 10% HNO₃ per liter
- For determination of soluble form of microelement concentration:
Filter sample through 0.45 μm millipore and add 5 mL 10% HNO₃ per liter

Hydrochemistry

Lecture 9

Toxic inorganic substances determination

- Al, As, Be, V, Bi, Cd, Ni, Hg, Pb, Se, Ti, Cr determination
- Radionuclides

TOXIC INORGANIC SUBSTANCES DETERMINATION

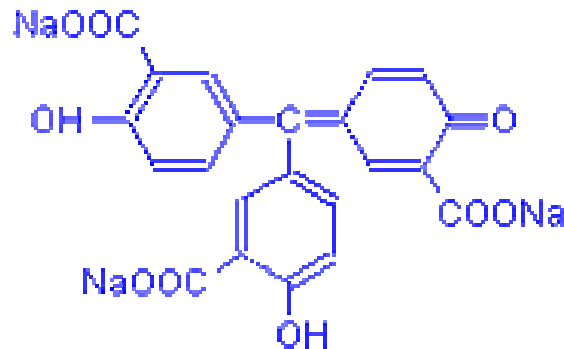
- **Aluminum (Al):**

- ❖ Atomic absorption spectroscopy

- ❖ Flame Atomization – detection limit is 20 ppb

- ❖ Electrothermal Atomization - detection limit is 0.01 ppb

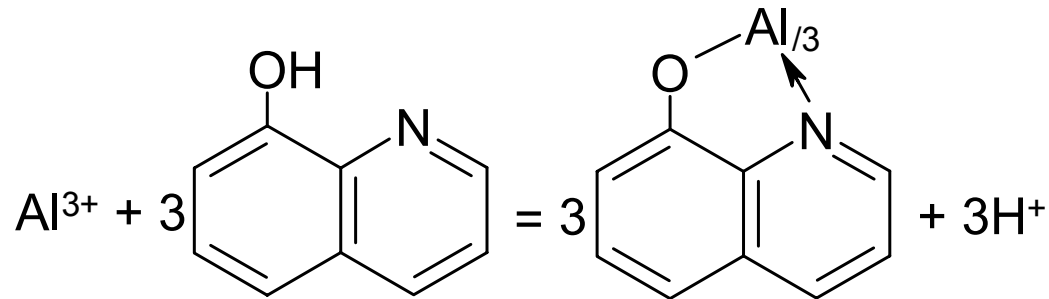
- ❖ Photometric determination with aluminon, $\lambda=525$ nm
(detection limit is 0.05 mg Al/l)



aluminon

TOXIC INORGANIC SUBSTANCES DETERMINATION

- **Aluminum (Al):**
 - ❖ Extraction – photometric determination with 8-oxichinolin, pH 4.3 – 4.5 (detection limit is 0.01 mg Al/l)



TOXIC INORGANIC SUBSTANCES DETERMINATION

- **Arsenic (As):**
 - ❖ Atomic absorption spectroscopy — flameless (graphite furnace) - detection limit is 0.08 ppb
 - ❖ Atomic absorption spectroscopy - flame (hydride generation) - detection limit is 0.02 ppb
 - ❖ Photometric determination (reaction of arsine, AsH_3 , with silver diethylthiocarbamate in pyridine, forming a red complex), $\lambda=540$ nm (detection limit is 10 $\mu\text{g As/l}$)

TOXIC INORGANIC SUBSTANCES DETERMINATION

- **Beryllium (Be):**
 - ❖ Atomic absorption spectroscopy (concentration range is 0.003 – 2 mg/l)
 - ❖ Flame Atomization – detection limit is 1 ppb
 - ❖ Electrothermal Atomization - detection limit is 0.003 ppb
 - ❖ Photometric determination with berilon III, pH 13, $\lambda=530$ nm (detection limit is 40 $\mu\text{g Be/l}$)
 - ❖ Photometric determination with aluminon, $\lambda=515$ nm (detection limit is 50 $\mu\text{g Be/l}$)

TOXIC INORGANIC SUBSTANCES DETERMINATION

- **Vanadium (V):**
 - ❖ Atomic absorption spectroscopy
 - ❖ Flame Atomization – detection limit is 20 ppb
 - ❖ Electrothermal Atomization - detection limit is 0.1 ppb
 - ❖ Extraction – photometric determination with N-benzene-N-phenylhydroxylamine, $\lambda=546$ nm (detection limit is 0.05 mg V/l)
 $V_2O_3[C_6H_5CO(C_6H_5)NO]_4$ - violet colour

TOXIC INORGANIC SUBSTANCES DETERMINATION

- **Bismuth (Bi):**

- ❖ Atomic absorption spectroscopy

- ❖ Flame Atomization – detection limit is 20 ppb
- ❖ Electrothermal Atomization - detection limit is 0.1 ppb
- ❖ hydride vaporization method - detection limit is 0.02 ppb

- ❖ Photometric determination with thiocarbamide, $\lambda=470$ nm or 322 nm (detection limit is 0.05 mg Bi/l)

$[\text{Bi}(\text{CSN}_2\text{H}_4)_9]^{3+}$ - yellow colour

TOXIC INORGANIC SUBSTANCES DETERMINATION

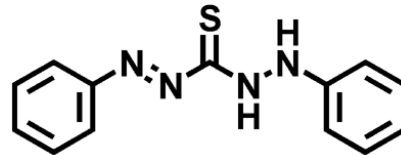
- **Cadmium (Cd):**

- ❖ Atomic absorption spectroscopy, $\lambda=226$ nm

 - ❖ Flame Atomization – detection limit is 0.5 ppb

 - ❖ Electrothermal Atomization - detection limit is 0.0002 ppb

- ❖ Extraction – photometric determination with ditizon, $\lambda=540$ nm (detection limit is 0.05 mg Cd/l)



ditizon

- ❖ Polarography, $E_{1/2} = -0.81$ V (1 mol/l NH_4OH , 1 mol/l NH_4Cl) - detection limit is 0.05 mg Cd/l

TOXIC INORGANIC SUBSTANCES DETERMINATION

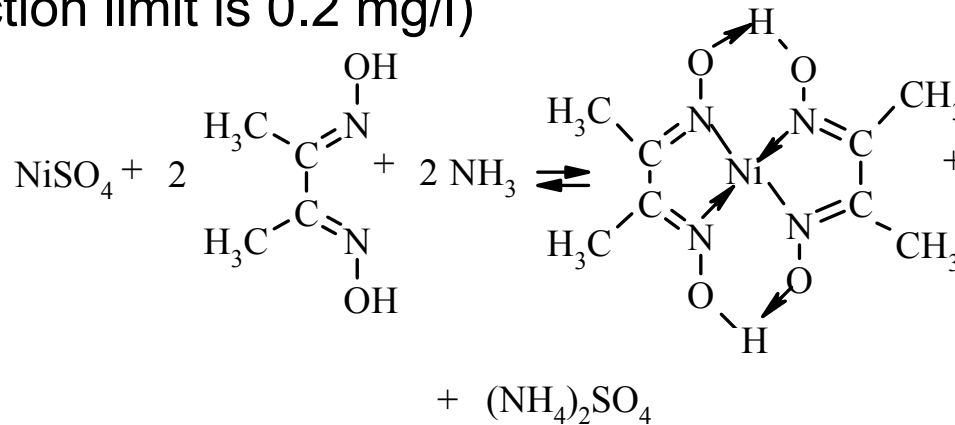
- **Nickel (Ni):**

- ❖ Atomic absorption spectroscopy

- ❖ Flame Atomization (concentration range is 0.3 – 5 mg/l)

- ❖ Electrothermal Atomization (concentration range is 0.005 – 0.1 mg/l)

- ❖ Photometric determination with dimethylglyoxime, $\lambda=540$ nm (detection limit is 0.2 mg/l)



- ❖ Polarography, $E_{1/2} = -1.09$ V (1 mol/l NH_4OH , 1 mol/l NH_4Cl) - detection limit is 0.01 mg Ni/l

TOXIC INORGANIC SUBSTANCES DETERMINATION

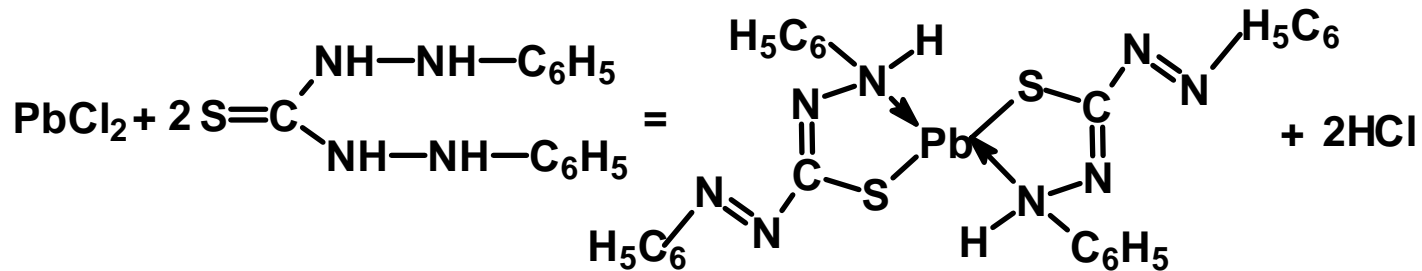
- **Mercury (Hg):**
 - ❖ Flameless atomic absorption spectroscopy (cold vapor technique), $\lambda=253.7$ nm - detection limit is 0.001 ppb
 - ❖ Extraction – photometric determination with ditizon, pH 1.5 – 2, $\lambda=490$ nm (detection limit is 0.5 $\mu\text{g Hg/l}$)

TOXIC INORGANIC SUBSTANCES DETERMINATION

- **Lead (Pb):**
 - ❖ Atomic absorption spectroscopy, $\lambda=217$ nm
 - ❖ Flame Atomization (concentration range is 1 – 20 mg/l)
 - ❖ Electrothermal Atomization (concentration range is 0.005 – 0.1 mg/l)
 - ❖ Inversion Voltammetry

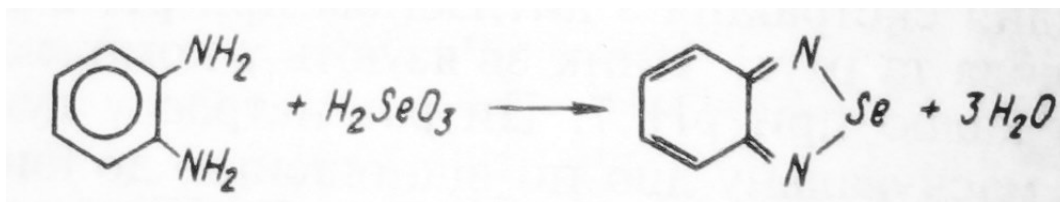
TOXIC INORGANIC SUBSTANCES DETERMINATION

- **Lead (Pb):**
 - ❖ Extraction – photometric determination with ditizon, pH 8 – 9, $\lambda=520$ nm (detection limit is 2 $\mu\text{g Pb/l}$)



TOXIC INORGANIC SUBSTANCES DETERMINATION

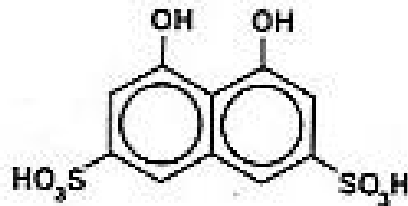
- **Selenium (Se):**
 - ❖ Atomic absorption spectroscopy — flameless (graphite furnace) - detection limit is 0.05 ppb
 - ❖ Atomic absorption spectroscopy – flame (hydride generation) - detection limit is 0.02 ppb
 - ❖ Extraction – photometric determination with diaminobenzidine, pH 0 – 2.5, $\lambda=335$ nm



TOXIC INORGANIC SUBSTANCES DETERMINATION

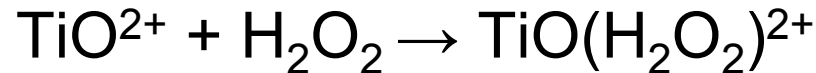
- **Titanium (Ti):**

- ❖ Atomic absorption spectroscopy (concentration range is 0.1 – 0.5 mg/l)
- ❖ Photometric determination with chromotropic acid, pH 2 – 5, $\lambda=465$ nm (detection limit is 1 mg Ti/l)



Chromotropic Acid

- ❖ Photometric determination with hydrogen peroxide, $\lambda=400$ – 450 nm (detection limit is 2 mg Ti/l)



TOXIC INORGANIC SUBSTANCES DETERMINATION

- **Chromium (Cr) - total:**

- ❖ Atomic absorption spectroscopy

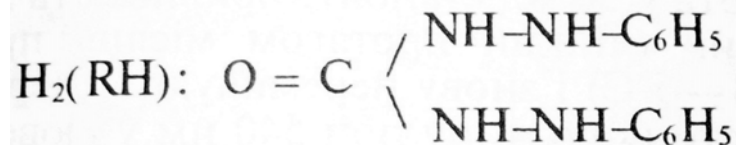
- ❖ Flame Atomization – detection limit is 2 ppb

- ❖ Electrothermal Atomization - detection limit is 0.004 ppb

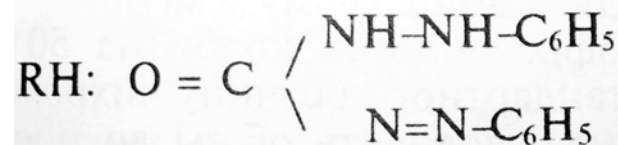
- ❖ Photometric determination with diphenylcarbazide, pH 3, $\lambda=540$ nm, $\epsilon=41350$ (detection limit is 10 $\mu\text{g Cr/l}$)



where



carbazide



carbazone

CHROMIUM DETERMINATION

Analysis	Methods	Preservation
Chromium (VI)	<ul style="list-style-type: none">•Photometric determination with diphenylcarbazide•Titration with thiosulfate	None
Chromium (III)	<ul style="list-style-type: none">•Atomic absorption spectroscopy after separation from Chromium (VI)•Photometric determination with diphenylcarbazide after sedimentation with MgO (pH 10.5 – 11.0)	

PRESERVATION OF SAMPLES FOR TOXIC INORGANIC SUBSTANCES DETERMINATION

- 5 mL 10% HNO_3 per liter
- For aluminum and arsenic determination:
5 mL conc. HCL per liter
- For beryllium determination:
1.5 mL conc. H_2SO_4 per liter

PRODUCTION OF RADIONUCLIDES

- weapons and nuclear reactors
- fission products of heavy nuclei of such elements as uranium or plutonium.
- reaction of neutrons with stable nuclei.
- natural sources
- nuclear power plants
- by-products of metallurgical processing of radioactive materials.

DETERMINATION OF RADIONUCLIDES

- Radioactive contamination of water is normally detected by measurements of gross beta and gross alpha activity, a procedure that is simpler than detecting individual isotopes. The measurement is carried out from a sample formed by evaporating water to a very thin layer on a small pan, which is then inserted inside an internal proportional counter.
- More detailed information can be obtained for radionuclides that emit gamma rays by the use of gamma spectrum analysis. This technique employs solid state detectors to resolve rather closely spaced gamma peaks in the sample's spectra.
- In conjunction with multichannel spectrometric data analysis, it is possible to determine a number of radionuclides in the same sample without chemical separation.

Hydrochemistry

Lecture 10

Organic compounds in water

- Dissolved organic carbon (DOC)
- Amines
- Aminoacids
- Aromatic carbohydrates
- Proteins
- Humic and fulvic acids
- Lignosulfonic acids and tannin
- Oil products
- Organic acids
- Surfactants
- Saccharides and starch
- Phenols

ORGANIC COMPOUNDS IN WATER

Organic compounds are derived from:

- living organism
- domestic use
- agricultural applications
- industrial sources:
 - ❖ chemical industrie
 - ❖ petrochemical industrie

Organic compounds in water also affect the water quality:

- cause disagreeable tastes and odours in drinking water.
- carcinogenic agents (Vinyl chloride, benzene and other)
cancer-suspect agent (chloroform)

NATURAL ORGANIC MATTER

Naturally occurring organic compounds in terrestrial water include:

- carbohydrates (sugars and cellulose)
- lipids (neutral fats)
- proteins (the building blocks of proteins are amino acids)
- enzymes
- complexes of proteins with other organic compounds (for example, tannins)

MAN-MADE ORGANICS

- Synthetic organic compounds include a broad variety of aliphatic and aromatic compounds.
- Many manufactured organic compounds may be found at very low concentrations in natural water.
- Isolation, identification and evaluation of health effects of these synthetic organics at low concentrations are lacking.

MAN-MADE ORGANICS

- chlorinated solvents
- majority of pesticides,
- petroleum components,
- synthetic chemicals
- petroleum products (including solvents, pharmaceuticals, plastics, dyes, and detergents)

DISSOLVED ORGANIC CARBON (DOC)

- The parameter, dissolved organic carbon (DOC), is a commonly used measure for the concentration of organic compounds in aqueous solution.
- DOC is the fraction of total organic carbon (TOC is all carbon atoms covalently bonded in organic molecules) in water that passes through a 0.45 micron pore-diameter filter.
- Determination:
 - (1) initial removal of inorganic carbon species,
 - (2) oxidation of the organic material into carbon dioxide (micro dichromate oxidation procedure),
 - (3) quantification of the carbon dioxide produced.

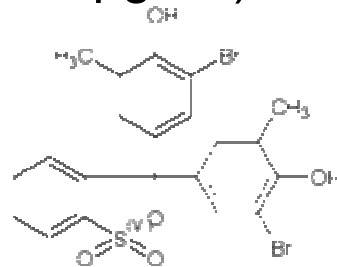
DISSOLVED ORGANIC CARBON (DOC)

- Typical DOC concentrations for groundwater range from a few micrograms to several 10 mg per liter and more.
- DOC concentrations depend on:
 - ❖ climate,
 - ❖ soil and vegetation coverage,
 - ❖ land use.

AMINES

Determination:

- Total amines – photometric determination with Bromocresol purple (4,4'-(1,1-Dioxido-3H-2,1-benzoxathiole-3,3-diyl)- bis(2-bromo-6-methylphenol)) and with previous separation by diffusion method, $\lambda=410$ nm (detection limit is 1 $\mu\text{g N/l}$)



Bromocresol purple

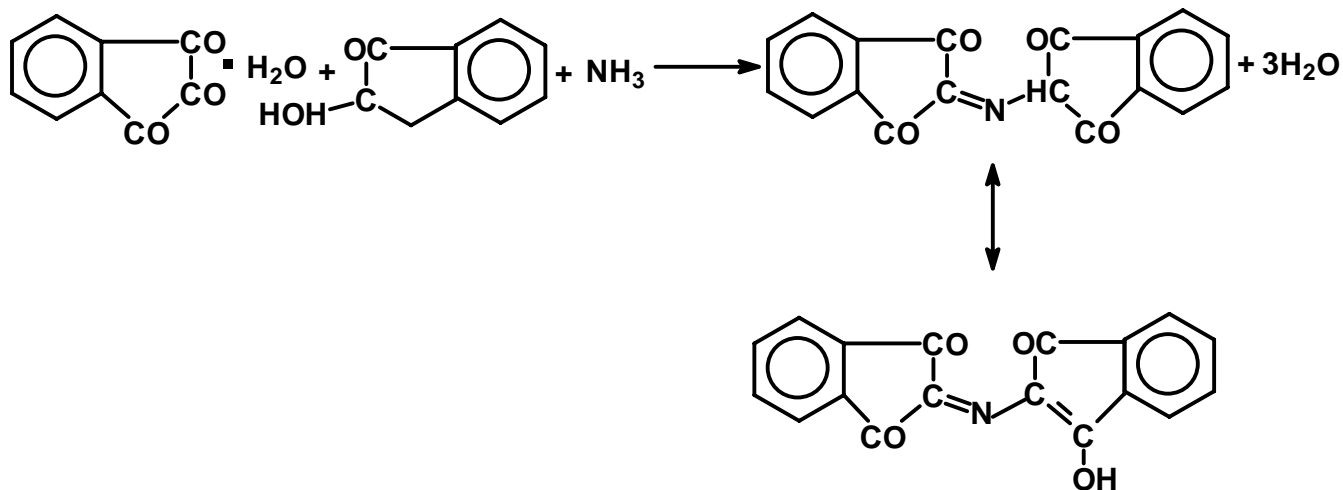
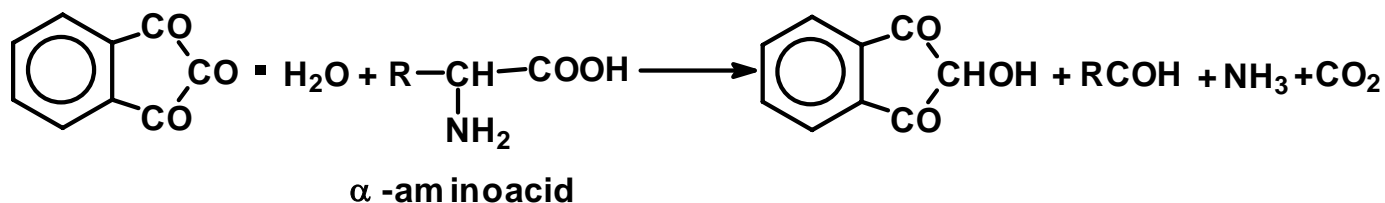
- Gas chromatography (detection limit is 0.1 μg)

Preservation:

Right after sampling adding HCl (pH of sample 4 – 5). In lab – filtration through a 0.45 micron pore-diameter filter and adding HCl (pH of sample 1 – 2).

AMINOACIDS DETERMINATION

Photometric, $\lambda=625 - 750$ nm (detection limit is $2.0 - 2.5 \mu\text{g}$)



red – violet coloured

AROMATIC CARBOHYDRATES

Determination:

Photometric method - aromatic carbohydrates form brown products with mixture of formaldehyde with H_2SO_4 , $\lambda=413$ nm (detection limit is 0.025 mg C_6H_6)

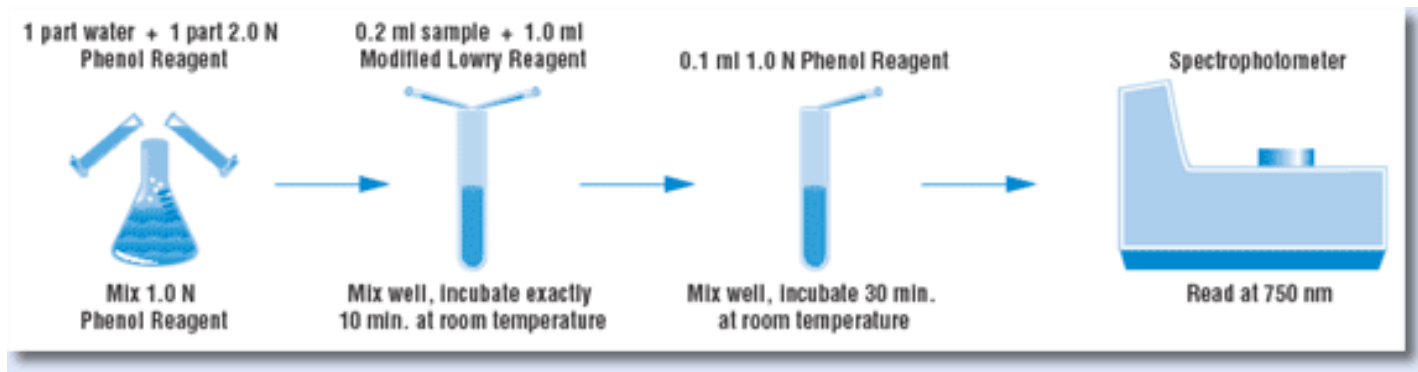
Preservation:

Keep sample cool (determination in no more than one day)

PROTEINS

Determination:

- Photometric method – proteins reduce Folin reagent (mixture of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ with $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), $\lambda=597$ nm (detection limit is 50 μg)
- Photometric method - Lowry reagent (1-1,500 $\mu\text{g}/\text{ml}$)



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Preconcentration:

freezing

HUMIC AND FULVIC ACIDS

- Humic acid is the fraction of humic substances that is not soluble in water under acidic conditions ($\text{pH} < 2$) but is soluble at higher pH values, whereas fulvic acid is the fraction of humic substances that is soluble in water under all pH conditions.
- Humic substances are biopolymers that vary in color from light yellowbrown (fulvic acid) to dark brown (humic acid) and black (humin).

HUMIC AND FULVIC ACIDS

Determination:

- Titration (if concentration of humic and fulvic acids is higher than concentration of other organic compounds)
- As humic and fulvic acids have different solubility in different pH range they can be separated by filtration. Then they can be determined separately as COD.

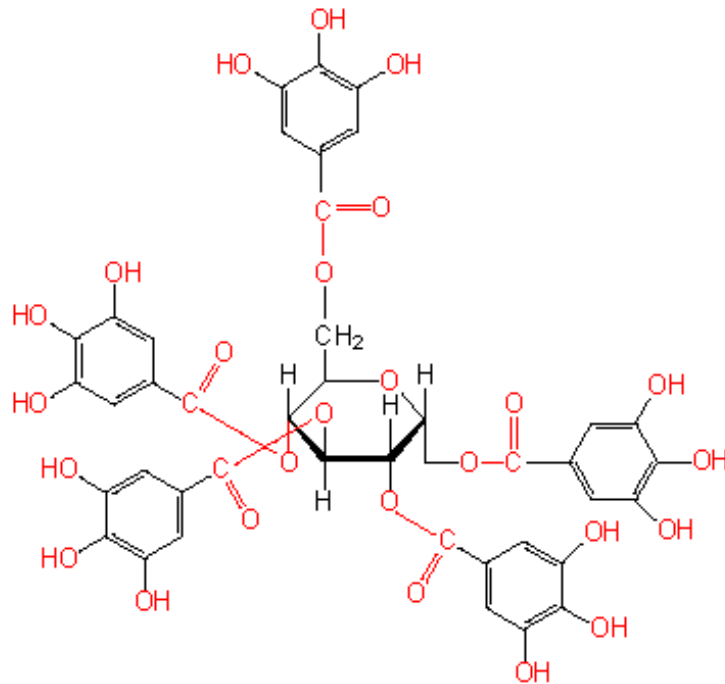
Preservation:

Keep sample cool

LIGNOSULFONIC ACIDS AND TANNIN

- Lignosulfonic acids are dark brown products of sulfonated lignin.
- The presence of elevated tannin or lignosulfonic acids levels in water results in a yellowish-brown discoloration.

LIGNOSULFONIC ACIDS AND TANNIN



tannin

Determination:

- Photometric - blue colour from tungstophosphoric and molybdophosphoric acids, $\lambda=700$ nm (detection limit is 0.1 mg/l for tannin and 0.3 mg/l for lignin)
- Photometric determination with nitrite (for 5-100 mg/l and more) $\lambda=430$ nm

Determination is performed without **preservation** in no more than three days after sampling.

OIL PRODUCTS

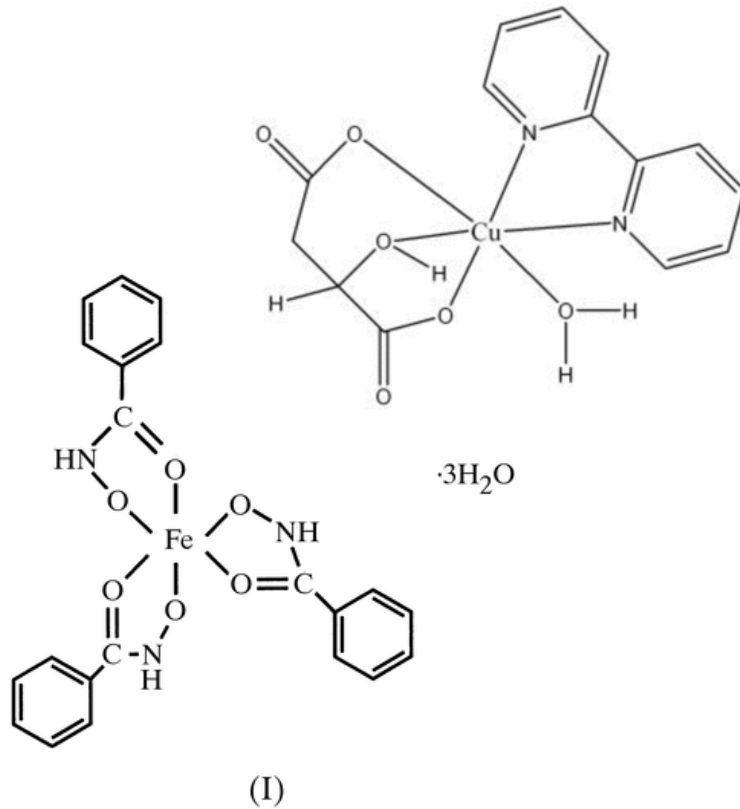
Determination:

- liquid - liquid extraction with CCl_4 - column chromatographic determination using IR detector, $\lambda=2700 - 3100 \text{ cm}^{-1}$ (detection limit is 0.05 – 0.1 mg/l)
- liquid - liquid extraction with CCl_4 - thin-layer chromatographic determination using IR (2700 – 3100 cm^{-1}), UV ($\lambda=270\text{nm}$) or luminescent detector – detection limit is 0.02 mg/l

Preservation:

2 ml CCl_4 per liter

ORGANIC ACIDS



Examples of coloured compound of Cu^{2+} and Fe^{3+} with different organic acids

Determination:

- Gravimetric
 1. Precipitation with Ba^{2+} or Ag^+
 2. Extraction with diethyl ether and drying
- Titration
- Photometric (coloured compounds with Cu^{2+} and Fe^{3+})
- Gas chromatography

Preservation:

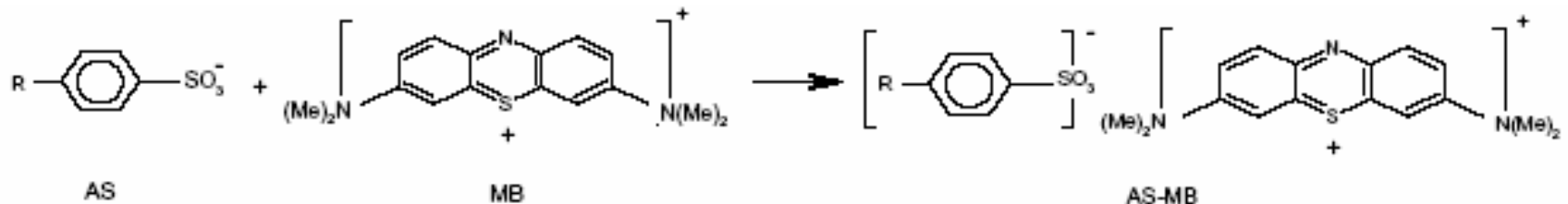
Keep sample cool (2 - 4 °C)

ANIONIC SURFACTANTS

Anionic surfactants	Formula
Sodium alkansulfonat	$(C_nH_{2n+1}C_mH_{2m+1})CHSO_3Na$
Sodium alkylsulphate	$C_nH_{2n+1}OSO_3Na$ where $n = 6-16$
Sodium dodecyl sulphate	$C_{12}H_{25}OSO_3Na$
Sodium alkylbenzolsulfonat	$C_nH_{2n+1}C_6H_4SO_3Na$ where $n = 12-18$

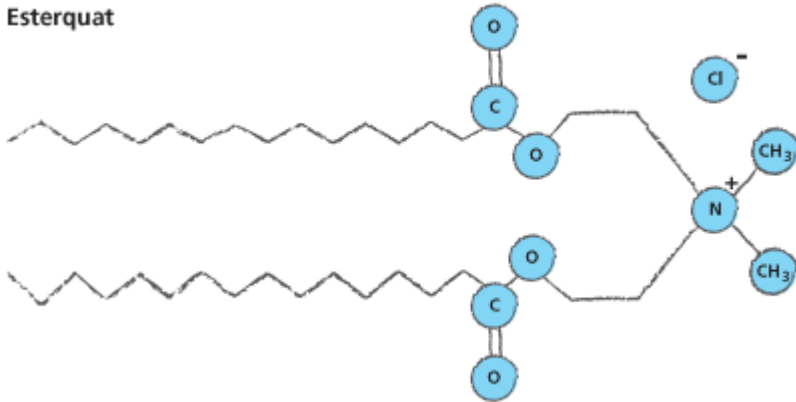
SURFACTANTS DETERMINATION

- **Anionic surfactants** – Photometric (reaction with methylene blue dye to form blue salt and chloroform extraction), $\lambda=650$ nm, $\epsilon=2.3 \cdot 10^4$

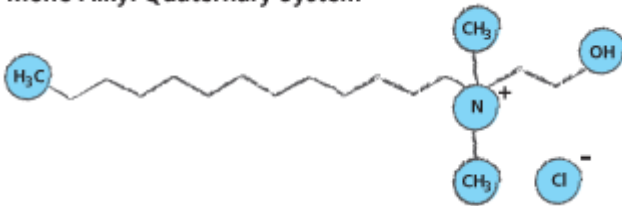


SURFACTANTS DETERMINATION

Esterquat

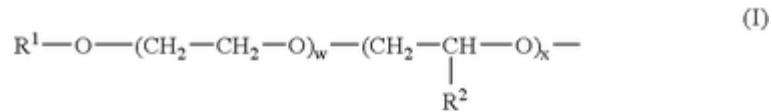


Mono Alkyl Quaternary System

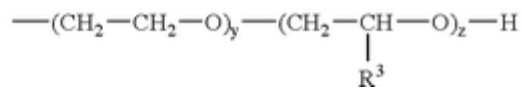


- **Cationic surfactants**
 - Photometric (reaction with bromphenyl blue dye to form blue salt and chloroform extraction), pH 2, $\lambda=416$ nm

SURFACTANTS DETERMINATION



(I)

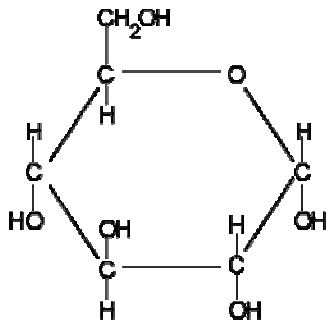


R¹ is a straight-chain or branched, saturated or mono- or polyunsaturated C6-24-alkyl or alkenyl radical; each group R² and R³, independently of one another, is chosen from —CH₃, —CH₂CH₃, —CH₂CH₂—CH₃, CH(CH₃)₂ and the indices w, x, y, z, independently of one another, are integers from 1 to 6.

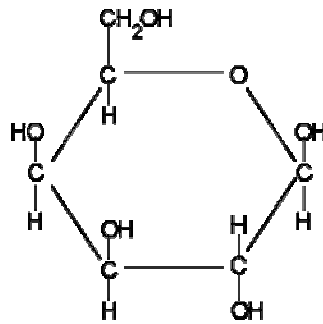
- **Nonionic surfactants** - Photometric (reaction with cobalt tetrathiocyanate to form blue salt and chloroform extraction), λ=600 nm

SACCHARIDES AND STARCH DETERMINATION

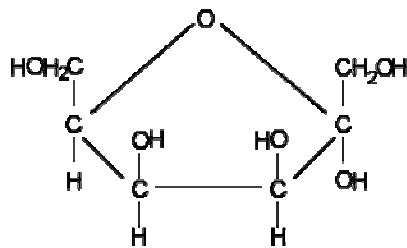
Structures of Common Monosaccharides



Glucose



Galactose

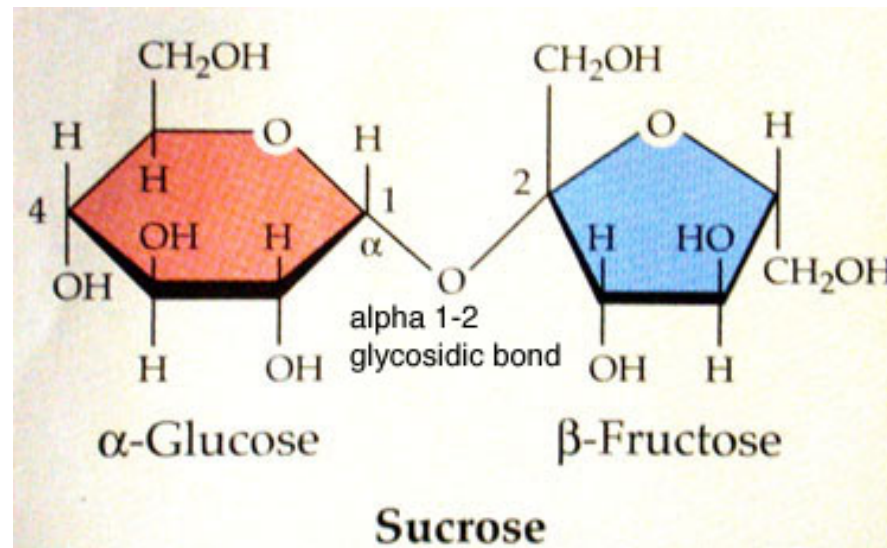


Fructose

- Monosaccharides - titration using Fehling reagent
($\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KNaC}_4\text{O}_6\text{H}_4 \cdot 4\text{H}_2\text{O} + \text{KOH}$)

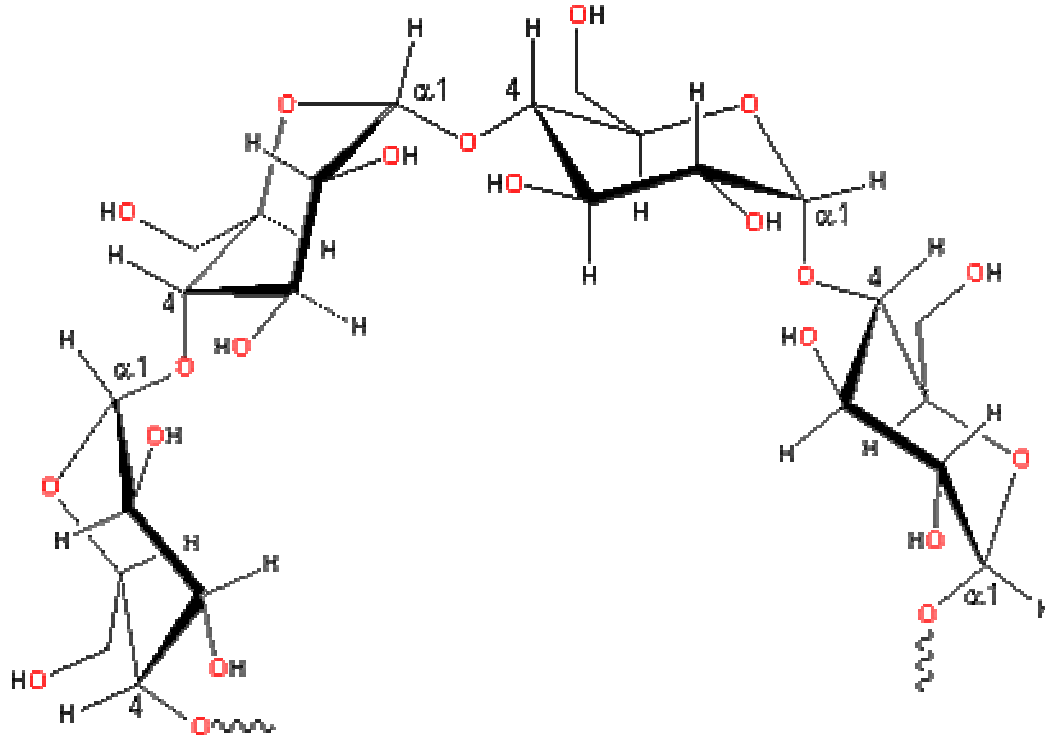
SACCHARIDES AND STARCH DETERMINATION

- Disaccharides – acid hydrolysis - titration using Fehling reagent



SACCHARIDES AND STARCH DETERMINATION

- Starch – filtration – hydrolytic splitting – titration using Fehling reagent

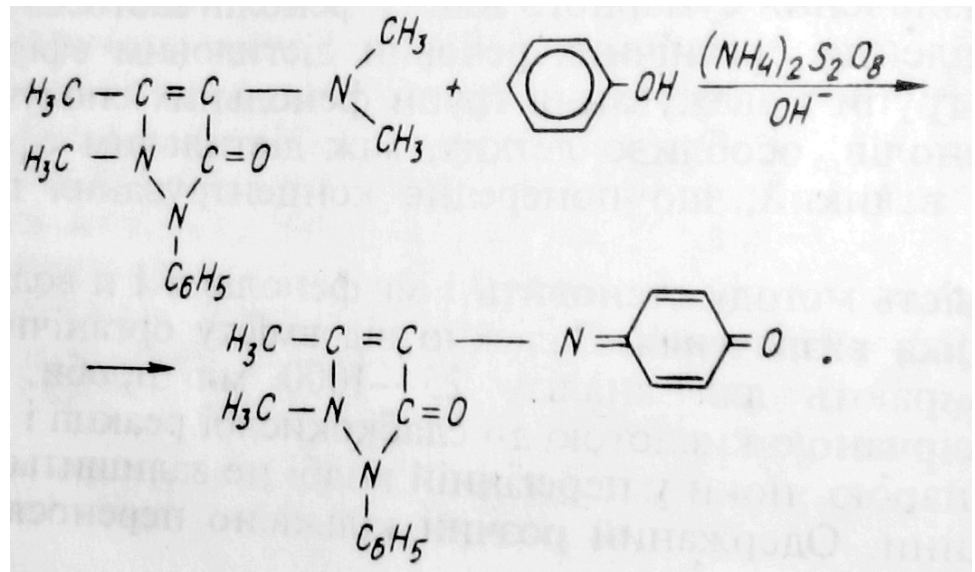


PHENOLS DETERMINATION

- Total phenols – Distillation – extraction with diethyl ether – gravimetric determination (detection limit is 1 mg/l)
- Volatile phenols – Distillation – photometric (reaction with 4-aminoantipyrine at pH 10 in the presence of potassium ferricyanide, forming an antipyrine dye which is extracted into pyridine), $\lambda=460$ nm (detection limit is 1 $\mu\text{g/l}$)

Preservation:

- 5 mL 20% CuSO_4
- Lower pH to less than 4 with 10% H_3PO_4 .
- Keep sample cool.
- Ship immediately.



Hydrochemistry

Lecture 11

Pesticides in water

- The pesticide cycle
- The impact of pesticides on water quality
- Factors affecting pesticide toxicity in aquatic systems
- Organochlorine insecticides
- Organophosphate insecticides
- Chlorophenoxy herbicides
- Carbamates

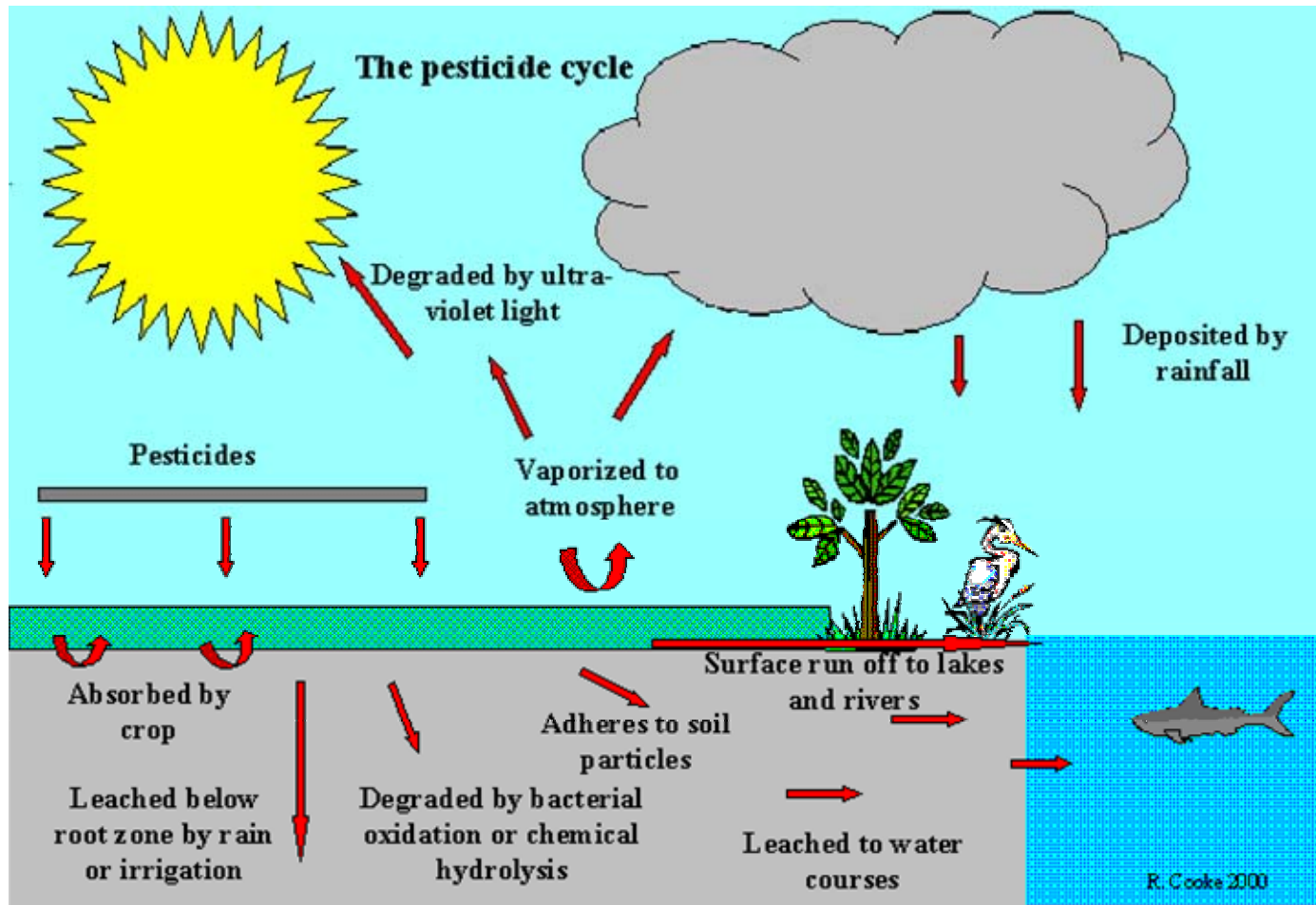
PESTICIDES

The term "**pesticide**" is a composite term that includes all chemicals that are used to kill or control pests.

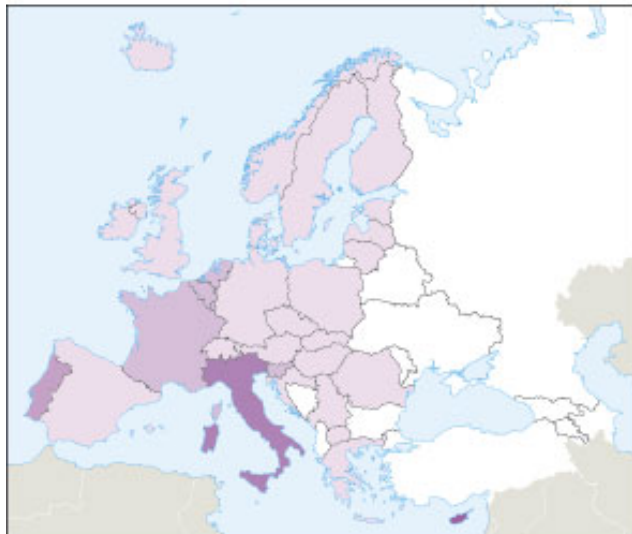
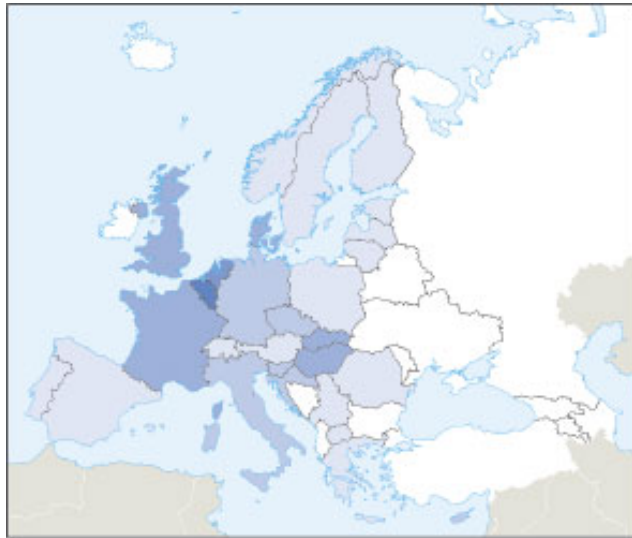
Classification:

- herbicides (weeds, plants),
- insecticides (insects),
- fungicides (fungi),
- nematocides (nematodes),
- rodenticides (rodents).
- molluscicides (snails and slugs),
- avicides (repel birds),
- piscicides (fish control),
- bactericides (bacteria),
- slimicides (slime-causing organisms in water),
- algicides (algae).

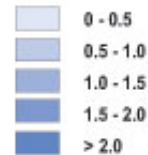
THE PESTICIDE CYCLE



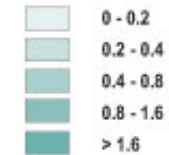
PESTICIDES IN EUROPE



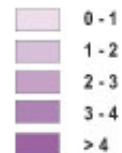
Herbicide consumption per agricultural land area unit (Kg/ha)



Insecticide consumption per agricultural land area unit (Kg/ha)



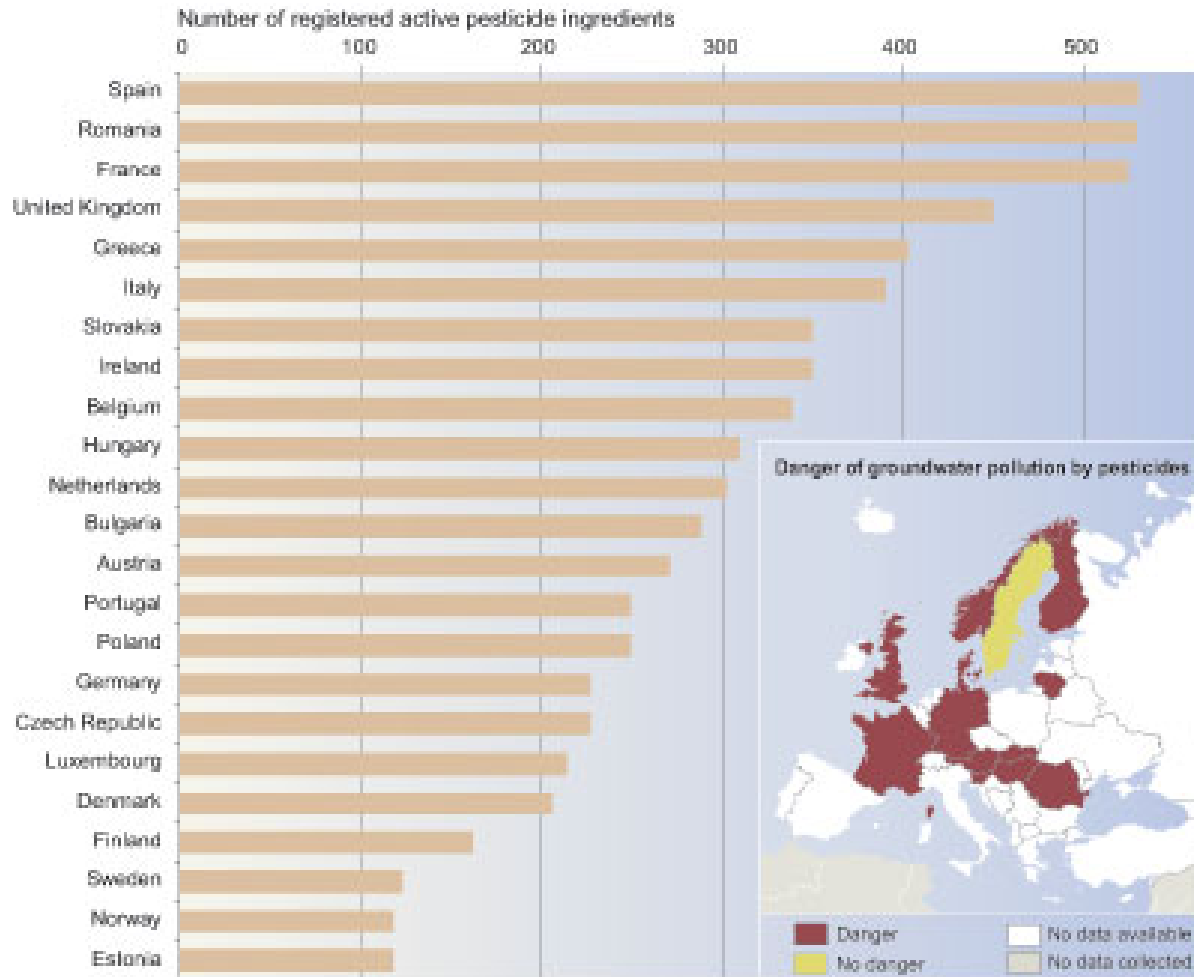
Fungicide consumption per agricultural land area unit (Kg/ha)



White box: No data available
Brown box: No data collected

Source: EEA, 2003r

NUMBER OF REGISTERED ACTIVE PESTICIDE INGREDIENTS



Source: EEA 2003

THE IMPACT OF PESTICIDES ON WATER QUALITY

The impact of pesticides on water quality is associated with the following factors:

- Active ingredient in the pesticide formulation. ·
Contaminants that exist as impurities in the active ingredient.
- Additives that are mixed with the active ingredient (wetting agents, diluents or solvents, extenders, adhesives, buffers, preservatives and emulsifiers).
- Degradates that is formed during chemical, microbial or photochemical degradation of the active ingredient.

HOW DO PESTICIDES GET INTO WATER SUPPLIES?

Pesticides that are not taken up by plants, adsorbed by soils or broken down by sunlight, soil organisms or chemical reactions may ultimately reach groundwater sources of drinking water.

This will depend upon

- the nature of the soil,
- depth to groundwater,
- chemical properties of the pesticide,
- the amount and timing of precipitation or irrigation in the area.

FACTORS AFFECTING PESTICIDES TOXICITY IN AQUATIC SYSTEMS

The ecological impacts of pesticides in water are determined by the following criteria:

- toxicity
- persistence
- degradates
- environmental fate

TOXICITY

- Mammalian and non-mammalian toxicity usually expressed as LD₅₀ ("Lethal Dose": concentration of the pesticide which will kill half the test organisms over a specified test period). The lower the LD₅₀, the greater the toxicity; **values of 0-10 are extremely toxic** (OMAF, 1991).
- Drinking water and food guidelines are determined using a risk-based assessment. Generally, Risk = Exposure (amount and/or duration) × Toxicity.
- Toxic response (effect) can be **acute** (death) or **chronic** (an effect that does not cause death over the test period but which causes observable effects in the test organism such as cancers and tumours, reproductive failure, growth inhibition, teratogenic effects, etc.).

PERSISTENCE

- Measured as half-life (time required for the ambient concentration to decrease by 50%).
- Persistence is determined by biotic and abiotic degradational processes. Biotic processes are biodegradation and metabolism; abiotic processes are mainly hydrolysis, photolysis, and oxidation.
- Modern pesticides tend to have short half lives that reflect the period over which the pest needs to be controlled.

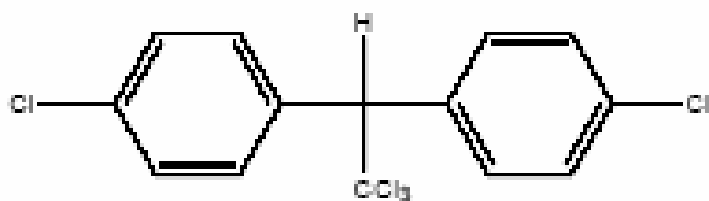
DEGRADATES

The degradational process may lead to formation of "degradates" which may have greater, equal or lesser toxicity than the parent compound.

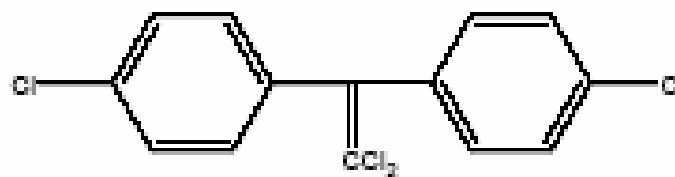
As an example, DDT degrades to DDD and DDE.

DDE (dichlorodiphenyldichloroethylene) and DDD (dichlorodiphenyldichloroethane) are chemicals similar to DDT that contaminate commercial DDT preparations. DDE has no commercial use. DDD was also used to kill pests, but its use has also been banned. One form of DDD has been used medically to treat cancer of the adrenal gland.

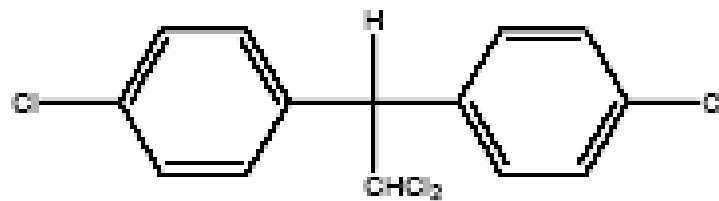
DDT DEGRADATION



p,p'-DDT

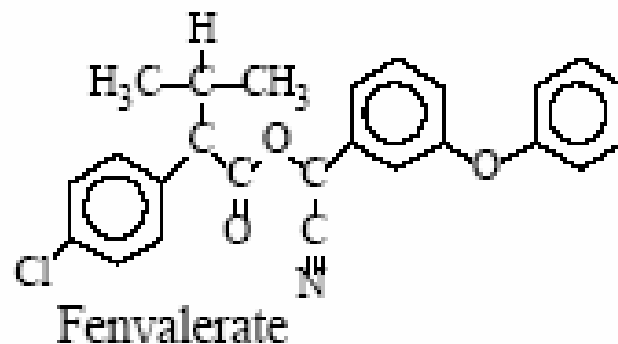
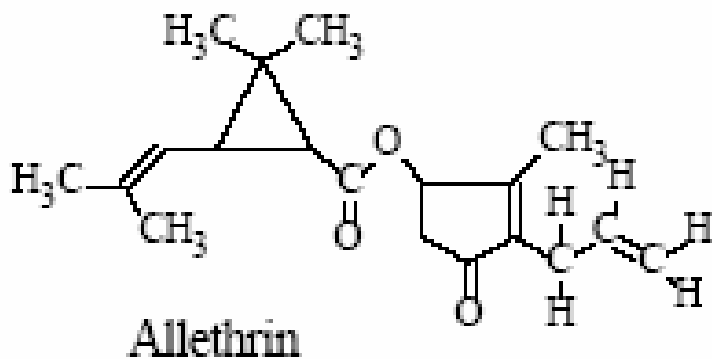
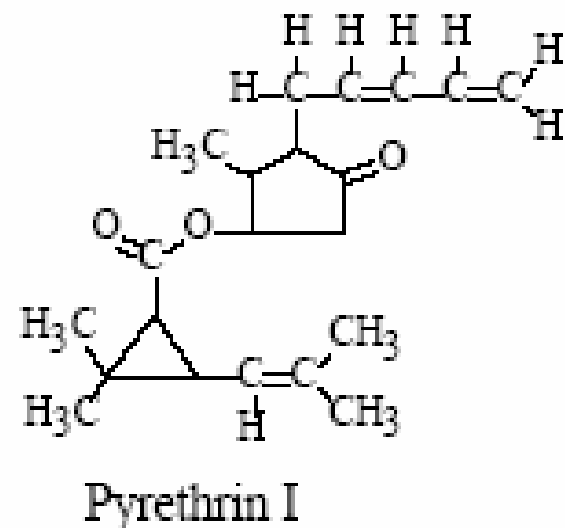
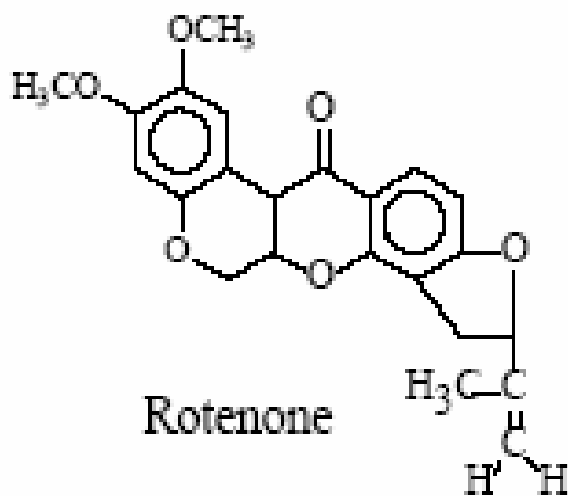
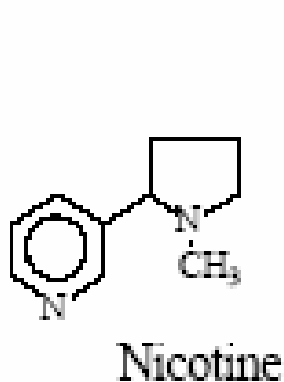


p,p'-DDE

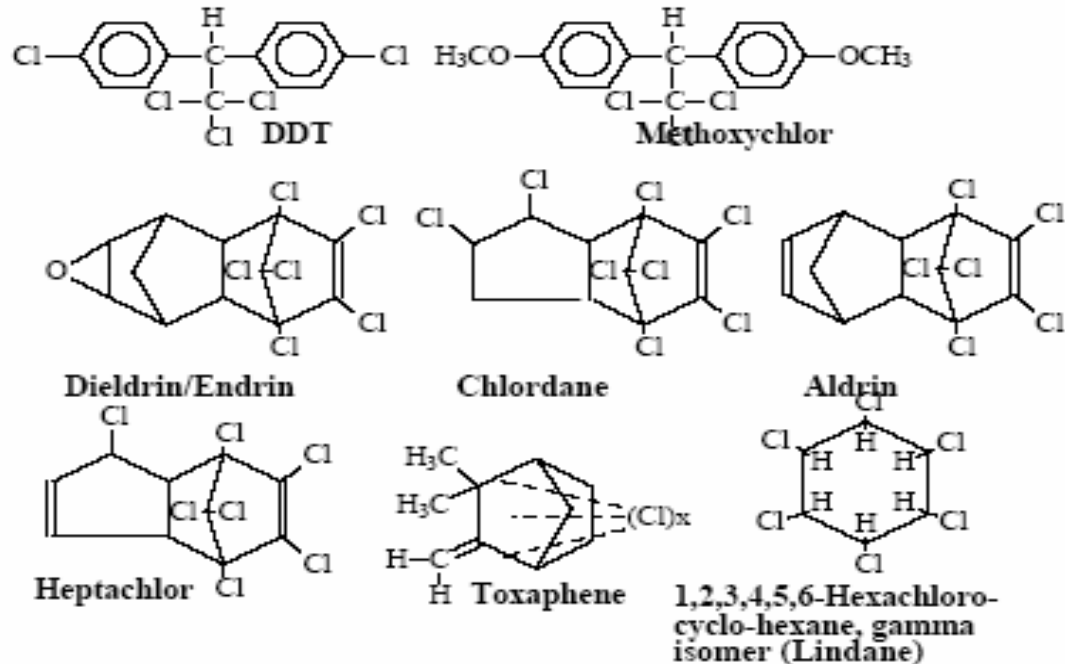


p,p'-DDD

COMMON BOTANICAL INSECTICIDES



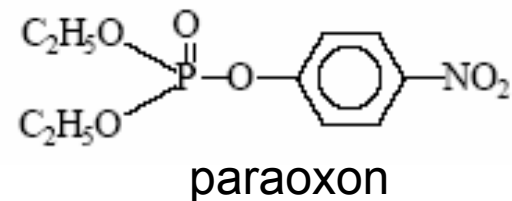
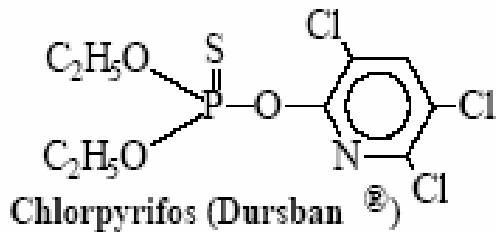
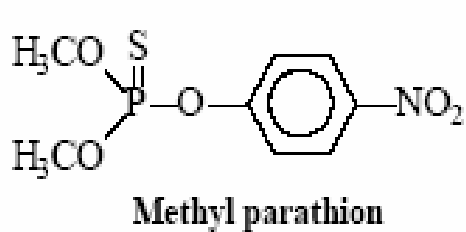
COMMON ORGANOCHLORINE INSECTICIDES



Determination:

- Chromatography-based EPA Methods
- Extraction with hexan - gas chromatography

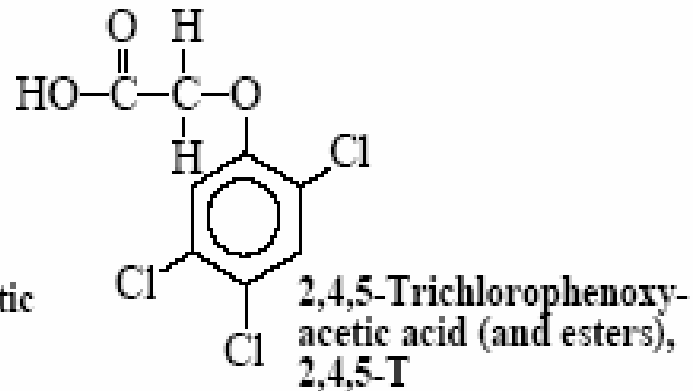
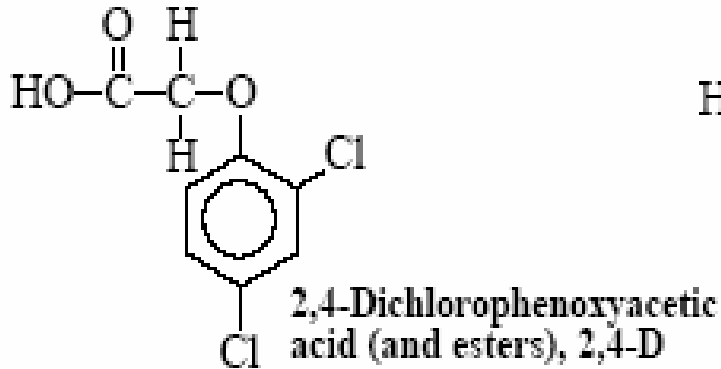
ORGANOPHOSPHATE INSECTICIDES



Determination:

- Chromatography-based EPA Methods
- Gas chromatography with a nitrogen-phosphorus detector
- Extraction with hexane or chloroform – thin-layer chromatography on silica gel (for detection bromphenol blue dye, silver nitrate are used)

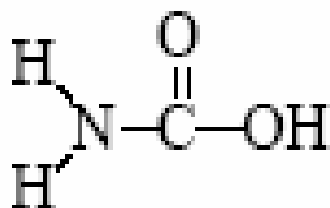
CHLOROPHENOXY HERBICIDES



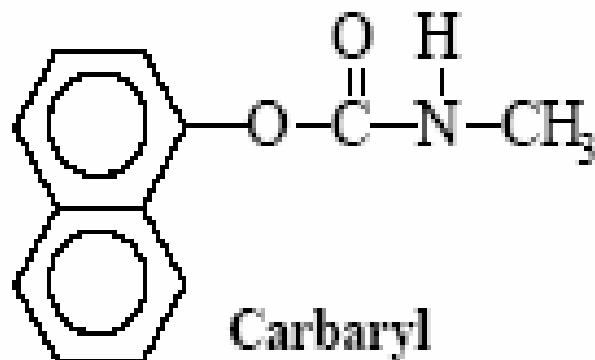
Determination:

- Gas chromatography
- Capillary liquid chromatography combined with solid phase extraction in a column packed with an anion exchanger based on MFE-Polymer

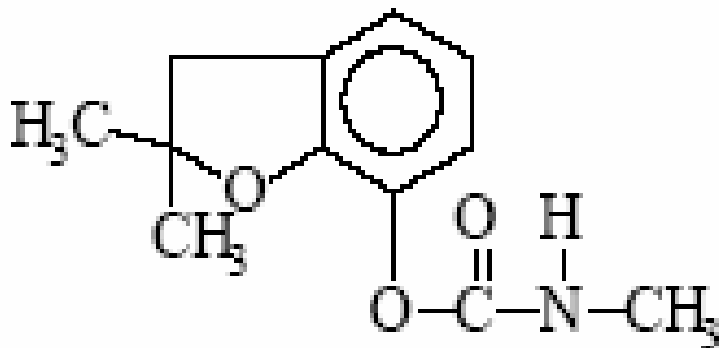
CARBAMIC ACID AND THREE INSECTICIDAL CARBAMATES



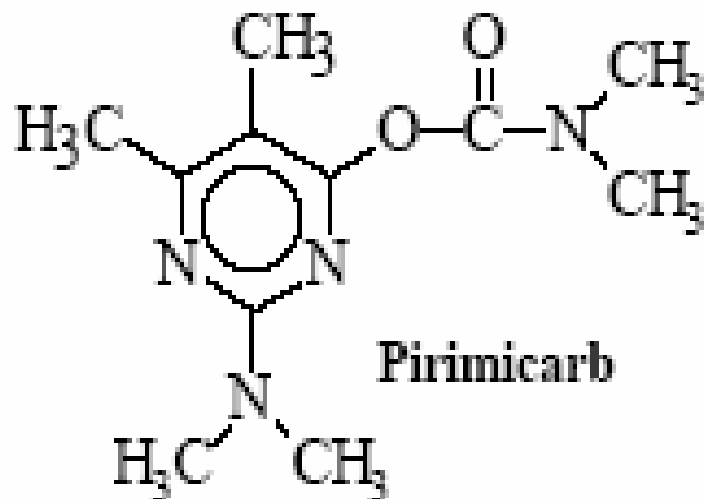
Carbamic acid



Carbaryl



Carbofuran



Pirimicarb

CARBAMATES DETERMINATION

- Gas chromatography with a nitrogen-phosphorus detector
- A normal-phase HPLC method
- A TLC method
- A method for dialkyldithiocarbamates by conversion to CS_2
- An extraction and colorimetric method

In recognition of pesticide abuse and of environmental and public health impacts the European countries have adopted a variety of measures that include the following (FAO/ECE, 1991):

- Reduction in use of pesticides (by up to 50% in some countries).
Bans on certain active ingredients.
- Revised pesticide registration criteria.
- Training and licensing of individuals that apply pesticides.
- Reduction of dose and improved scheduling of pesticide application to more effectively meet crop needs and to reduce preventative spraying.
- Testing and approval of spraying apparatus.
- Limitations on aerial spraying.
- Environmental tax on pesticides.
- Promote the use of mechanical and biological alternatives to pesticides.

Hydrochemistry

Lecture 12

Modern problems of water analysis

- Test-methods in water analysis
- Chemical sensors
- Optic chemical sensors
- Biosensors
- Maximum permissible concentrations (MPC)
- Requirements for water quality in Europe
- Statistical treatment of results
- Characterizing experimental errors

TEST-METHODS IN WATER ANALYSIS

- Test-methods are used for analysis of samples on place of sampling.
- They are effective for preliminary detection of elements on maximum permissible concentration (MPC) level.
- Test-methods don't need equipment and are used for visual control.

TEST-METHODS IN WATER ANALYSIS

Classification of test-methods:

- Test methods on filtration or chromatographic paper – drop method or dynamic method with preconcentration
- Test methods on silica gel – indicator powder or indicator tubes (less sensitive)
- Test methods on polyurethane foam – shaking with cube of polyurethane foam

CHEMICAL SENSORS

Chemical sensor is a portable miniaturized analytical device, which can deliver real-time and on-line information in presence of specific compounds or ions in complex samples

Chemical sensors can be categorized according to the types of transducer into

- electrochemical
- optical
- mass-sensitive
- heat-sensitive

AN OPTICAL SENSOR DEVICE CONSISTS OF THE FOLLOWING COMPONENTS

- the recognition element, where specific interaction and identification of the analyte takes place;
- the transducer element that converts the recognition process into a measurable optical signal;
- an optical device (process unit) which consists of at least a light source (in the simplest form a LED)
- a detector (in the simplest form a photodiode), which detects and converts the change of optical properties, after amplification of the primary signal, into a unit readout.

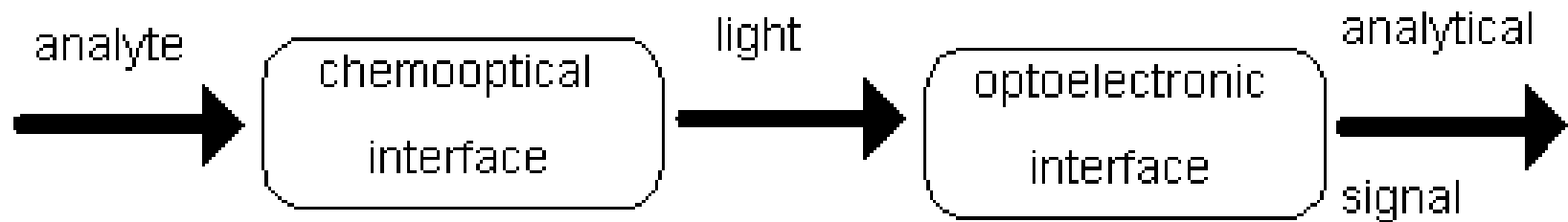
THE OPTICAL PROPERTIES MEASURED:

- absorbance,
- reflectance,
- luminescence,
- light polarization,
- Raman,
- other

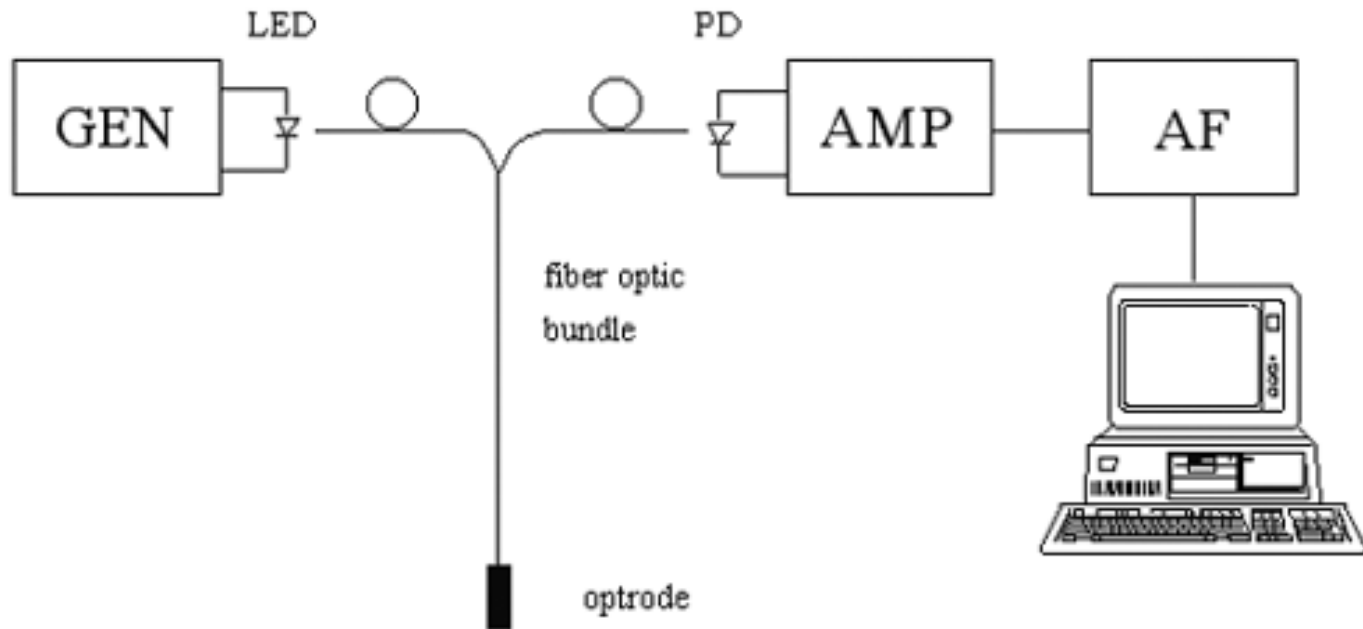
SENSING SCHEMES APPLIED IN OPTICAL ION SENSING

- Intrinsic Ion Sensing
- Biosensors
- Carrier Based Optical Sensors
- Sensors Based on Chromo- or Fluoroionophores
- Sensors Based on Dynamic Quenching of Luminescence

CONVERSION OF THE SIGNAL IN FIBER OPTIC CHEMICAL SENSOR



CONFIGURATION OF FIBER OPTIC pH SENSORS



GEN-square wave generator, LED-light emitting diode, PD-photodiode, AMP-transimpedance amplifier, AF-active filter

OXYGEN SENSORS



The FOXY (for Fiber Optic oXYgen sensor) unit operates by using a 470 nm light in pulsed or continuous transmission as a stimulation pulse.

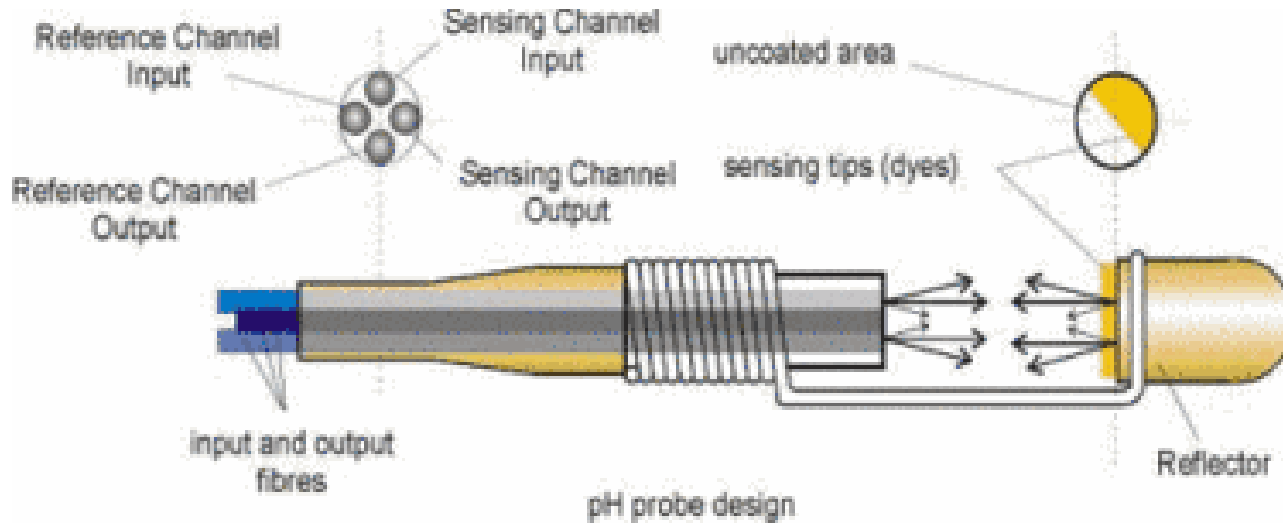
www.lternet.edu/technology/



Oxygen Optode/Temperature Sensor 3930 for measuring dissolved oxygen in fresh and salt water. The principle of measurement is based on the effect of dynamic luminescence quenching (lifetime based) by molecular oxygen.

www.aanderaa.com

pH SENSING



SOME COMMON BIOSENSOR MATERIALS

Analytes	Examples
Respiratory Gases	O ₂ , CO ₂
Anesthetic Gases	N ₂ O, Halothane
Toxic Gases	H ₂ S, Cl ₂ , CO, NH ₃
Flammable Gases	CH ₄
Ions	H ⁺ , Li ⁺ , K ⁺ , Na ⁺ , Ca ²⁺ , Phosphates, Heavy Metal Ions
Metabolites	Glucose, Urea
Trace Metabolites	Hormones, Steroids, Drugs
Toxic Vapors	Benzene, Toluene
Proteins and Nucleic Acids	DNA, RNA
Antigens and Antibodies	Human Ig, Anti-human Ig
Microorganisms	Viruses, Bacteria, Parasites

BIOSENSOR COMPONENTS

Transducer System	Measurement Mode	Typical Applications
Ion-Selective Electrode	Potentiometric	Ions in biological media, enzyme electrodes
Gas-Sensing Electrodes	Potentiometric	Gases, enzyme, organelle, cell or tissue electrodes
Field-Effect Transistors	Potentiometric	Ions, gases, enzyme substrates immunological analytes
Optoelectronic and Fiber-Optic Devices	Optical	pH; enzymes; immunological analytes
Thermistors	Calorimetric	Enzyme, organelle, gases, pollutants, antibiotics, vitamins
Enzyme Electrodes	Amperometric	Enzymes, immunological systems
Conductimeter	Conductance	Enzyme substrates

STANDARDS AND GUIDELINES FOR HEAVY METALS IN DRINKING WATER

Metal	European Water Quality Directive mg/l
Cd	0.005
Cu	2
Pb	0.01
Hg	0.001
Ni	0.02

MAXIMUM PERMISSIBLE CONCENTRATIONS (MPC)

Compound	MPC, mg/l
NH ₄	0.39
Cr	0.02
Cu	0.001
Oil products	0.05
Zn	0.01
BOD ₅	3
NO ₂	0.02
Synthetic surfactants	0.1
Phenols	0.001
NO ₃	9.1
Ni	0.01
Fe	0.5

STANDARD DEVIATION

Standard deviation is a statistical measure of the “average” deviation of data from the data’s mean value (s).

$$s = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n - 1}}$$

where X_i is one of n individual measurements, and \bar{X} is the mean.

Relative standard deviation

$$s_r = \frac{s}{\bar{X}}$$

The percent relative standard deviation is obtained by multiplying s_r by 100%.

CHARACTERIZING EXPERIMENTAL ERRORS

Accuracy

Accuracy is a measure of how close a measure of central tendency is to the true, or expected value, μ . Accuracy is usually expressed as either an absolute error

$$E = \bar{X} - \mu$$

or a percent relative error, E_r .

$$E_r = \frac{\bar{X} - \mu}{\mu} \times 100$$

CHARACTERIZING EXPERIMENTAL ERRORS

- **Sampling error** is an error introduced during the process of collecting a sample for analysis.
- **Method error** is an error due to limitations in the analytical method used to analyze a sample.
- **Measurement error** is an error due to limitations in the equipment and instruments used to do measurements.
- **Tolerance** is the maximum determinate measurement error for equipment or instrument as reported by the manufacturer.

CHARACTERIZING EXPERIMENTAL ERRORS

- **Personal error** is an error due to biases introduced by the analyst.
- **Constant determinate error** is a determinate error whose value is the same for all samples.
- **Proportional determinate error** is a determinate error whose value depends on the amount of sample analyzed.

PRECISION

- **Precision** is a measure of the spread of data about the central value and may be expressed as the range, the standard deviation, or the variance. Precision is commonly divided into two categories: repeatability and reproducibility.
- **Repeatability** is the precision for an analysis in which the only source of variability is the analysis of replicate samples.
- **Reproducibility** is the precision when comparing results of several samples, for several analysts or several methods.

THE DISTRIBUTION OF MEASUREMENTS AND RESULTS

The most commonly encountered continuous distribution is the Gaussian, or **normal distribution**, where the frequency of occurrence for a value, X , is given by

$$f(X) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{-(X - \mu)^2}{2\sigma^2}\right]$$

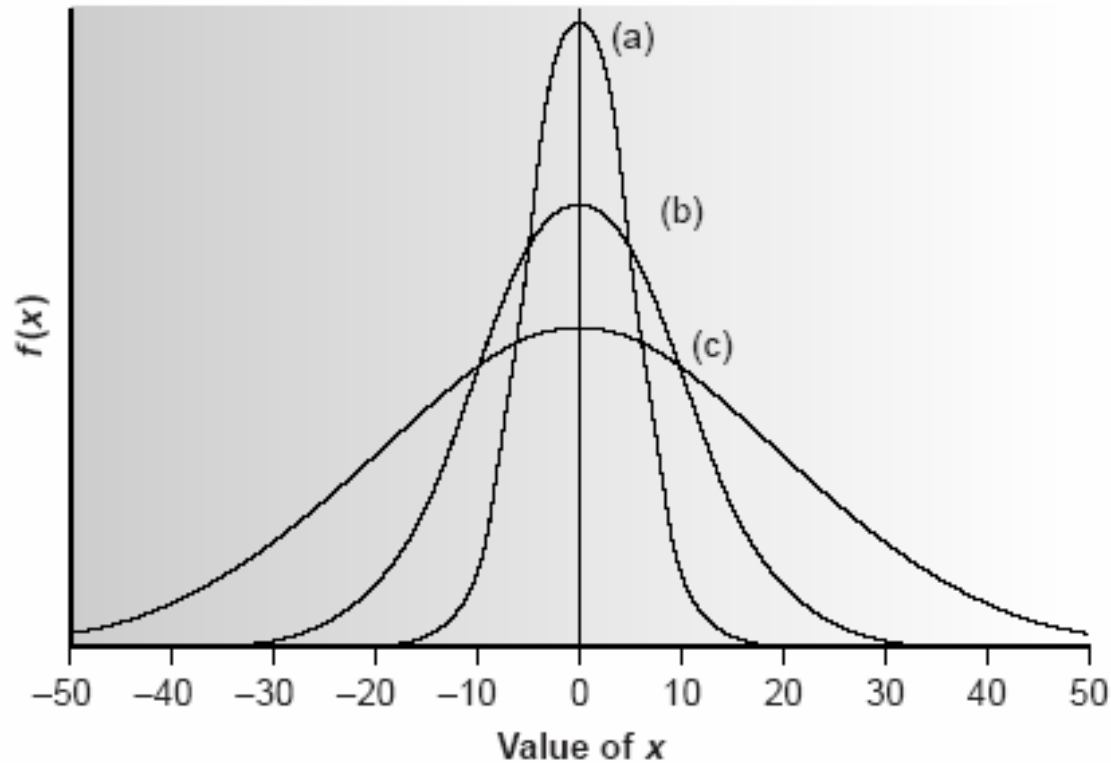
The shape of a normal distribution is determined by two parameters, the first of which is the population's central, or true mean value, μ , given as

$$\mu = \frac{\sum_{i=1}^N X_i}{n}$$

where n is the number of members in the population. The second parameter is the population's variance, σ^2 , which is calculated using the following equation

$$\sigma^2 = \frac{\sum_{i=1}^N (X_i - \mu)^2}{n}$$

NORMAL DISTRIBUTIONS



Normal distributions for (a) $\mu = 0$ and $\sigma^2 = 25$; (b) $\mu = 0$ and $\sigma^2 = 100$; and (c) $\mu = 0$ and $\sigma^2 = 400$.

CONFIDENCE INTERVALS

Confidence interval is range of results around a mean value that could be explained by random error.

$$X_i = \mu \pm z\sigma$$

where the factor z accounts for the desired level of confidence.

DETECTION LIMITS

Detection limit ($(S_A)_{DL}$) is the smallest concentration or absolute amount of analyte that can be reliably detected.

$$(S_A)_{DL} = S_{\text{reag}} + z\sigma_{\text{reag}}$$

where S_{reag} is the signal for a reagent blank, σ_{reag} is the known standard deviation for the reagent blank's signal, and z is a factor accounting for the desired confidence level.

Limit of quantitation ($(S_A)_{LOQ}$) is the smallest concentration or absolute amount of analyte that can be reliably determined (LOQ).

$$(S_A)_{LOQ} = S_{\text{reag}} + 10\sigma_{\text{reag}}$$