# Environmental Chemistry

# Chemical Oxygen Demand

## A Conventional Perspective

Lecture 8

**COD**

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# Presentation Menu

- General consideration
- History
- COD by potassium dichromate
- COD using potassium permanganate
- Examples on calculations

# General considerations

COD measures organic strength of both domestic and industrial wastewater

Total quantity of oxygen required for oxidation to $CO_2$ and $H_2O$:

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right)O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right)H_2O + cNH_3$$

# … General considerations

**Basis**: All organic compounds, except few, can be oxidized by the action of strong oxidizing agents under acid conditions, regardless of the biological assimilability of the substances, including glucose and lignin.

Amino nitrogen with an oxidation number of (–3) will be converted to ammonia nitrogen.

Organic nitrogen in higher oxidation states will be converted to nitrates.

Value of COD is higher than BOD.

# Main limitation of COD

**(Based on conventional understanding)**:

Inability to differentiate between biologically oxidizable and biologically inert organic matter

Does not provide any evidence of the rate at which the biologically active material would be stabilized under conditions that exist in nature.

# Main advantages of COD
**(Based on conventional understanding)**:

Short time required for evaluation (about 3 hours, BOD will consume 5 days)

COD data can be interpreted in terms of BOD values after sufficient trends has been accumulated to establish reliable correlation factors.

# Pollution load related to persons

| Parameters | Denmark | USA | Malaysia |
|---|---|---|---|
| BOD, kg/cap.yr | 20-25 | 30-35 | **15-35** |
| COD, kg/cap.yr | 30-35 | 30-35 | **30-35** |
| N-total, kg/cap.yr | 5-7 | 3-5 | **5-7** |
| P-total, kg/cap.yr | 1.5-2 | 1.5-2 | **1.5-2.5** |
| Phenols, g/cap.yr | 10-20 | - | - |
| Hg, kg/cap.yr | 0.1-0.2 | - | - |
| Pb, kg/cap.yr | 5-10 | - | - |
| Cd, kg/cap.yr | 0.2-0.4 | - | - |

# Ratio of parameters in sewage

| Ratio | Low | Typical | High |
|---|---|---|---|
| COD/BOD | 1.5-2.0 | 2.0-2.5 | 2.5-3.5 |
| COD/TN | 6-8 | 8-12 | 12-16 |
| COD/TP | 20-35 | 35-45 | 45-60 |
| BOD/TN | 3-4 | 4-6 | 6-8 |
| BOD/TP | 10-15 | 15-20 | 20-30 |
| COD/VSS | 1.2-1.4 | 1.4-1.6 | 1.6-2.0 |
| VSS/SS | 0.4-0.6 | 0.6-0.8 | 0.8-0.9 |
| COD/TOC | 2.0-2.5 | 2.5-3.0 | 3.0-3.5 |

# Analysis for organics in sewage

| Parameters | Names | Raw sewage | Biotreatment without nitrification |
|---|---|---|---|
| $COD_p$ | COD (potassium permanganate alkaline) | 180 | 30 |
| $BOD_5$ | 5-day BOD | 280 | 25 |
| $BOD_7$ | 7-day BOD | 320 | 30 |
| $BOD_\infty$ | Total BOD | 400 | 35 |
| COD | COD (potassium dichromate) | 600 | 100 |
| $S_s$ | Easily biodegradable matters | 60 | 5 |
| $X_s$ | Slowly biodegradable matters | 200 | 10 |
| TOC | Total organic carbon ($800^oC$) | 200 | 35 |

Note: All units are mg/l

# History, a bit …

- Potassium permanganate was originally used for COD test: COD>BOD values
- Potassium permanganate is not able complete the oxidation process to end point.
- Other oxidizing agents were used:
  - Ceric sulfate
  - Potassium iodate
  - Potassium dichormate
- Potassium dichromate is the most reliable, and suitable able to oxidize a wide variety of organics almost completely to $CO_2$ and $H_2O$

# History, again …

## Why COD with potassium dichromate?

- Potassium dichromate is the most reliable, and suitable able to oxidize a wide variety of organics almost completely to $CO_2$ and $H_2O$
- Potassium dichromate can easily measured in case of any excess

# History, again …

## Procedure for COD with potassium dichromate?

- Potassium dichromate requires strong acidic and high temperature conditions to be able to oxidize a wide variety of organics almost completely to $CO_2$ and $H_2O$
- Result: volatile matters originally present and formed during the digestion period are lost (unless provision is made to prevent their escape – normally using reflux condensers to allow sample to be boiled without significant loss of volatile organic compounds)

# History, again …

## Procedure for COD with potassium dichromate?

- Certain low-molecular-weight fatty acids are not oxidized by dichromate unless a catalyst is present.
- Normal catalyst: silver ion
- However, aromatic hydrocarbons and pyridine are not oxidized under any circumstances using dichromate!!!

# COD with Potassium Dichromate

- Potassium dichromate is relatively cheap
- Dichromate ion is a very potent oxidizing agents in solutions that are strongly acidic.
- The reaction, where organic nitrogen is all in a reduced state (oxidation number on –3):

$$H_2O + cNH_4^+ + 2dCr_3^{+} \xrightarrow{\frac{a+8d-3c}{2}\ \Delta}$$

$$d = \frac{2n}{3} + \frac{2}{6} - \frac{b}{3} - \frac{c}{2}$$

# Concept for COD test

- Use various chemical oxidants, particularly:
  - Potassium permanganate
  - Potassium dichromate
- COD by potassium permanganate is incomplete, and the values are used to estimate the necessary dilution for BOD test
- Potassium dichromate will increase the oxidation of organics, and various inorganics e.g. $NO_2^{-1}$, $S^{-2}$, $Fe^{2+}$ and $SO_3^{2-}$.
- COD with permanganate gives a good picture of the total content of organics

# Measurement of excess oxidizing agents

- Excess of oxidizing agent must be present to ensure that all organics are oxidized completely
- Measuring the excess is important to ensure the actual amount reduced can be determined.
- All solutions of reducing agents are gradually oxidized by oxygen dissolved from the air unless special care is taken to protect them from oxygen
- Ferrous ion is used as reducing agent for dichromate
- Normally use ferrous ammonium sulfate:

$$6Fe^{2+} + CrO_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 7H_2O$$

# ORP indicator for COD test

- Oxidation-reduction potential (ORP) obviously changed at the end of the oxidation-reduction reactions.

- How to detect the changes?

  Electrometrics is used to detect the changes.

  Chemical indicators such as Ferroin (ferrous 1,10-phenanthroline sulfate) that change the color to brown

# Calculations for COD test

- No direct measurement is available for COD test because a solution of a reducing agent must be used to determine how much the oxidizing agent was used.
- How to determine COD values?

$$COD(mg/l) = \frac{8000(blank*titr.-sample*titr.)[norm.Fe(NH_4)_2(SO_4)_2]}{mlsample}$$

# Inorganic Interferences in COD test

- Certain reduced inorganic ions can be oxidized under the conditions of the COD test
- Cause errors in COD measurement
- Example: Chlorides cause the most serious problem because of their normally high concentration in most wastewater:

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$$

- Interference can be eliminated using mercuric sulfate to the sample prior to the addition of other reagents:

$$Hg^{2+} + 2Cl^- \Leftrightarrow HgCl_2$$

# Comparison between COD and BOD

| Items | BOD | COD |
|---|---|---|
| Oxidation process | By microorganisms | By chemical oxidants |
| Oxidation rate | Slow, days | Fast, hours |
| Testing rate | 5 days | 3 hours |
| Values | Organics | Organics, partly inorganics |
| Mass balance | No | Yes |
| Procedures | Manual | Automatics |
| Design of WWTP | Yes | Yes, growing |

# COD-fractionation
## (Activated Sludge Model No. 1)

$$COD_{total} = S_S + S_I + X_S + X_I$$

Ss = dissolved, easily biodegradable organics
SI = dissolved biologically inert organics
Xs = suspended, slowly biodegradable organics
XI = suspended, biological inert organics

# COD-fractionation

- Massive analysis and calculation involved
- Very instrumental for plant design, control and automation
- Inert matters ($X_i$ and $S_i$) include substances which are biodegraded so slowly
- Characterization of biodegradable into $S_s$ and $X_s$ is not accurate, but the dissolved solids are dominated by easily degradable organics whereas the suspended solids are dominated by slowly degradable substances.

# COD-fractionation:
## Analysis of samples

Analytical procedures of $X_s$ and $S_s$:

- Filtration to segregate dissolved and particulate components
- Biological degradation rate estimation

# COD-fractionation:
## Respirometric technique

# Why OUR and NUR?

Enables mass balance calculations to be carried out when designing sewer, WWTPs.

Can be carried out automatically.

Relatively fast compared to the 5 day BOD tests.

OUR and NUR fractions give a better picture of the transformation of organic matter.

# How to Measure OUR and NUR?

**RESPIROMETERS**

Technique is called RESPIROMETRY

# Water & Wastewater Characterization using Respirometric Analysis

Use respirometer

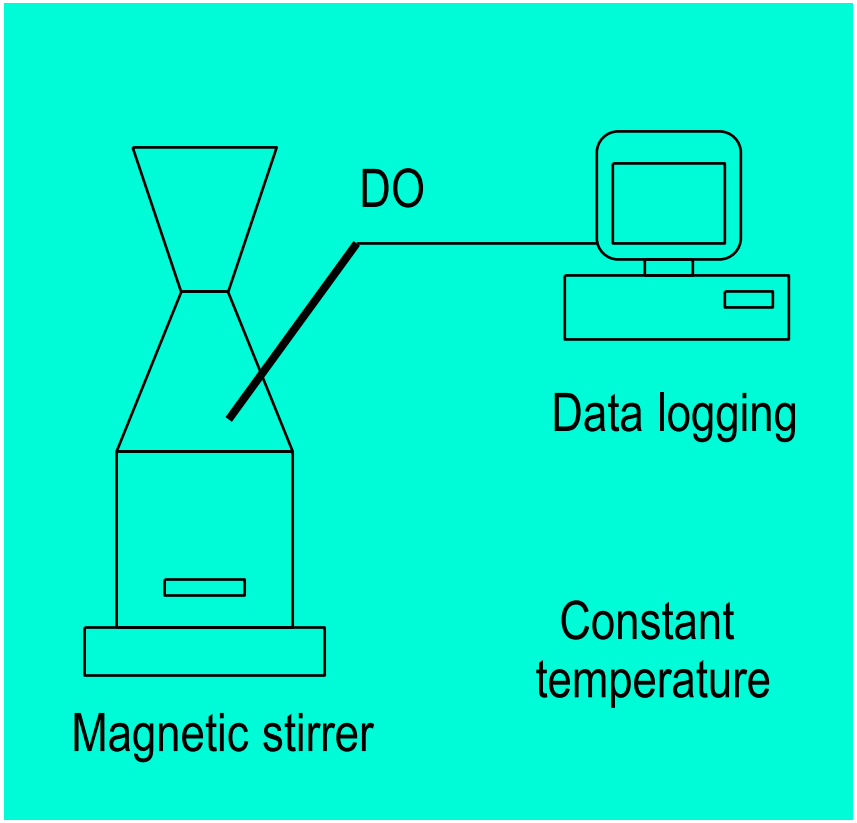
Based on respiration rate

Principle: Utilized DO is directly associated to:

biomass growth
substrate removal

Gives detailed information on the composition of wastewater

Use COD fractionation

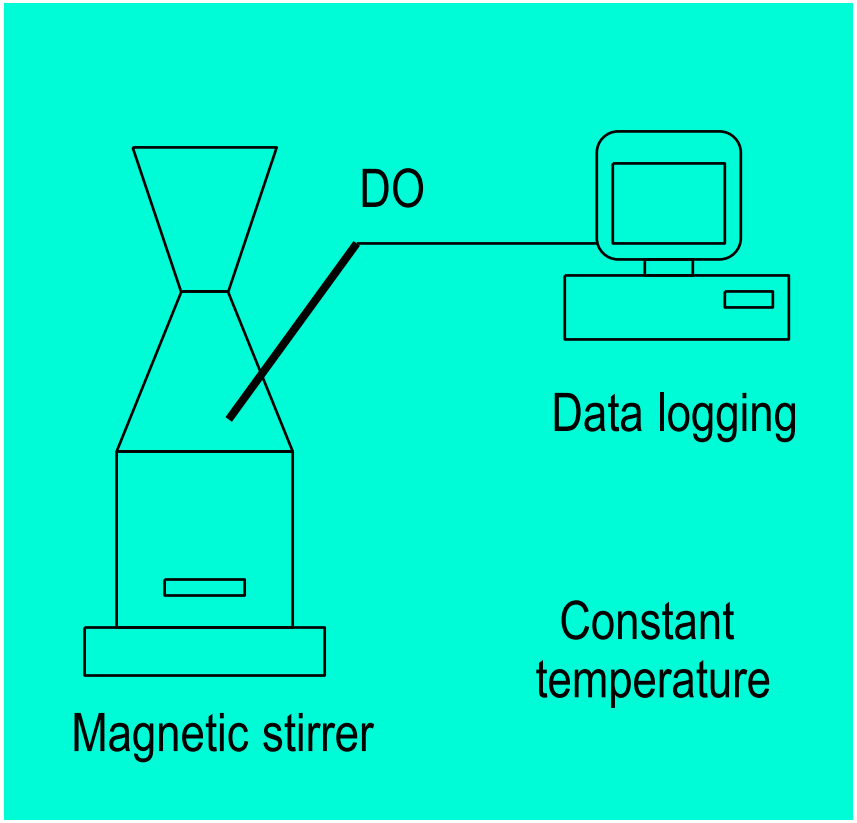


# Water & Wastewater Characterization using Respirometric Analysis

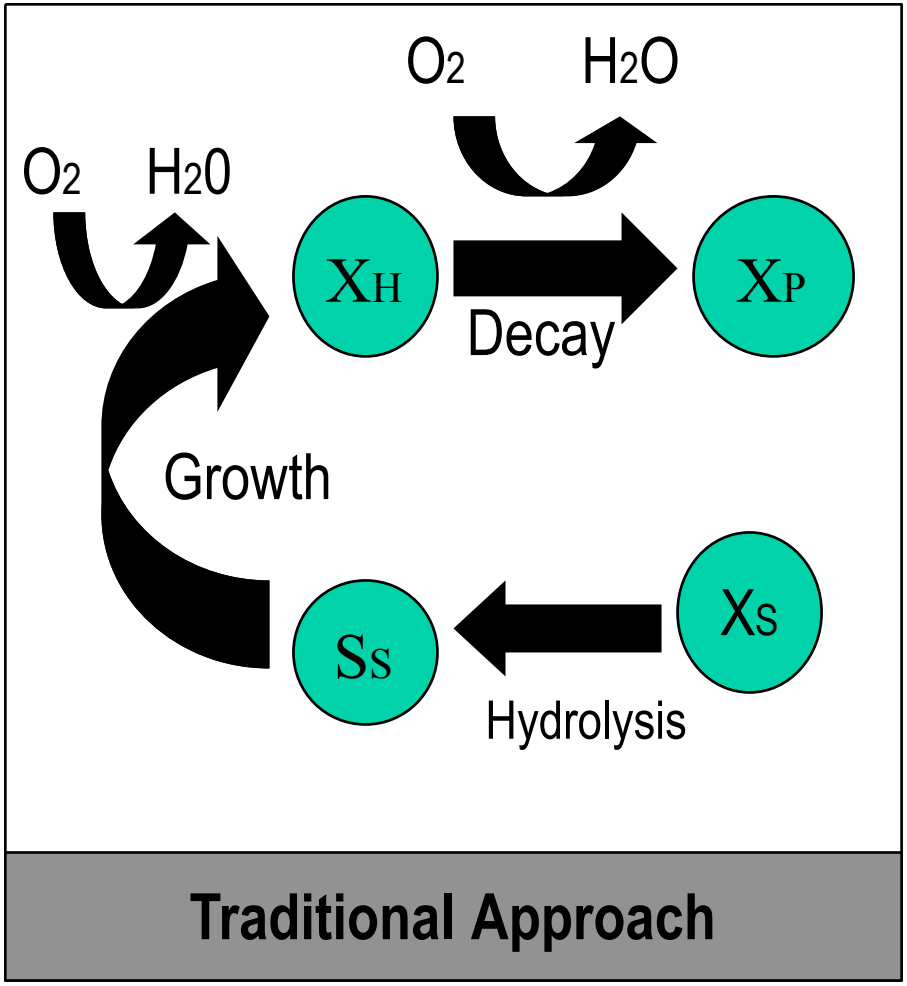
Respiration rate is an important indicator of process condition

Applications:

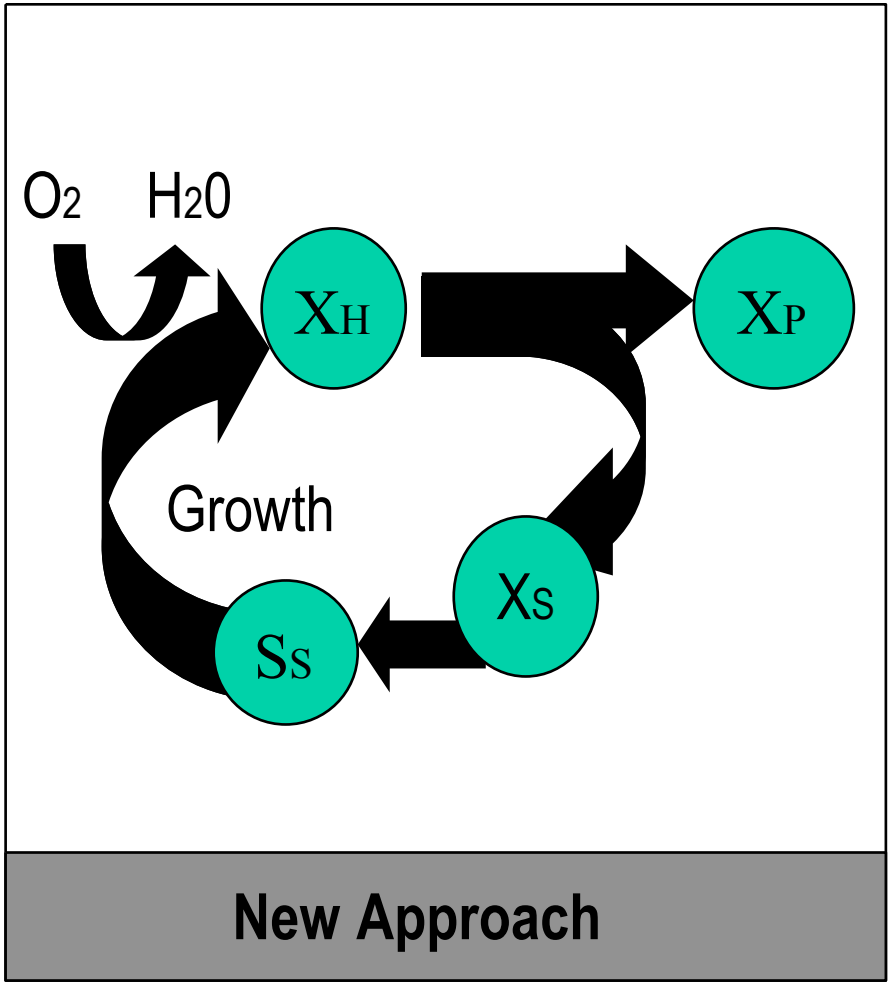
- biokinetic parameters
- biodegradation rate modeling
- process control



# Modeling Approach

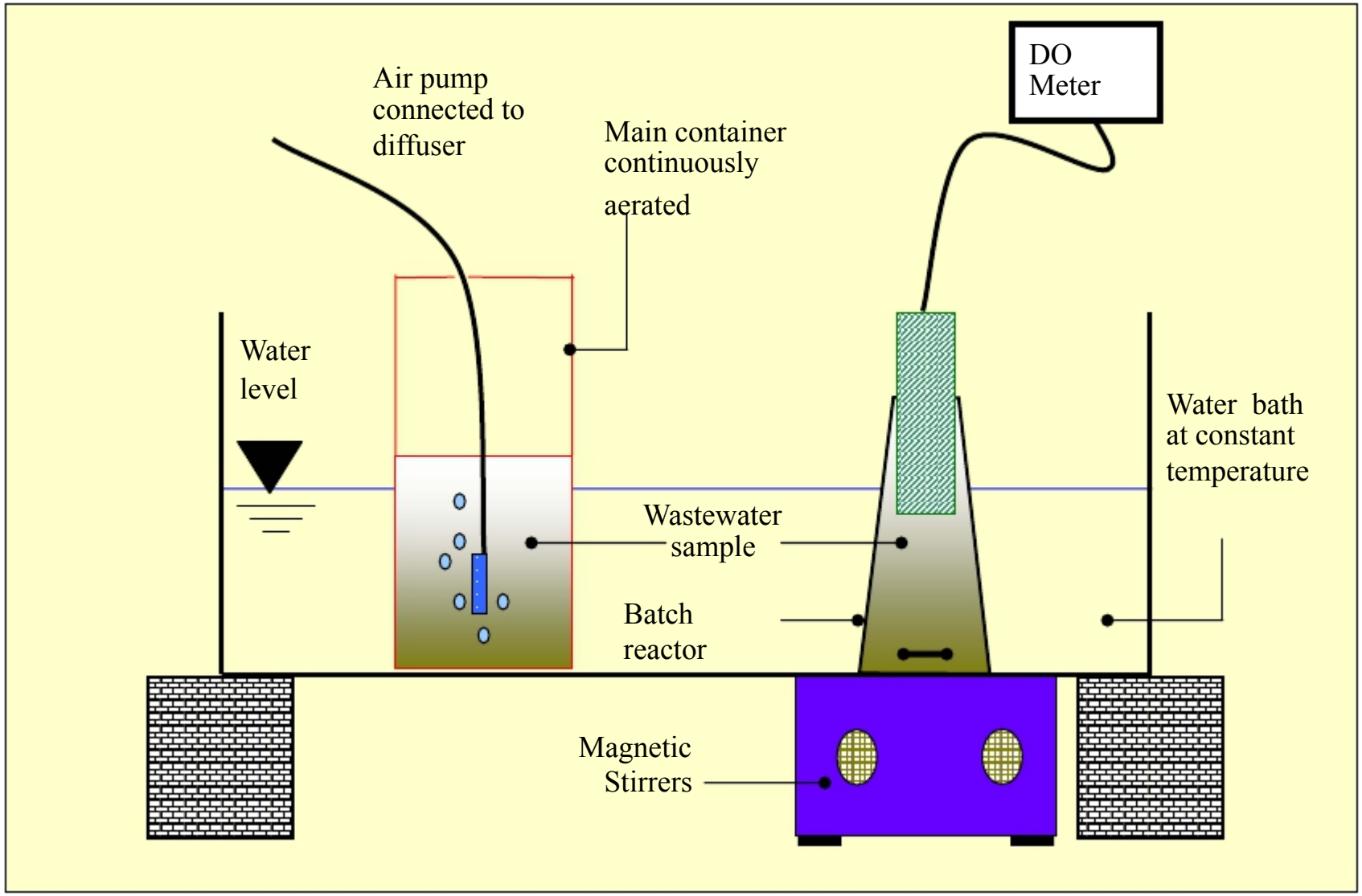



Traditional Approach




New Approach

# Respirometric Analysis for OUR Measurements



# Experiment OUR

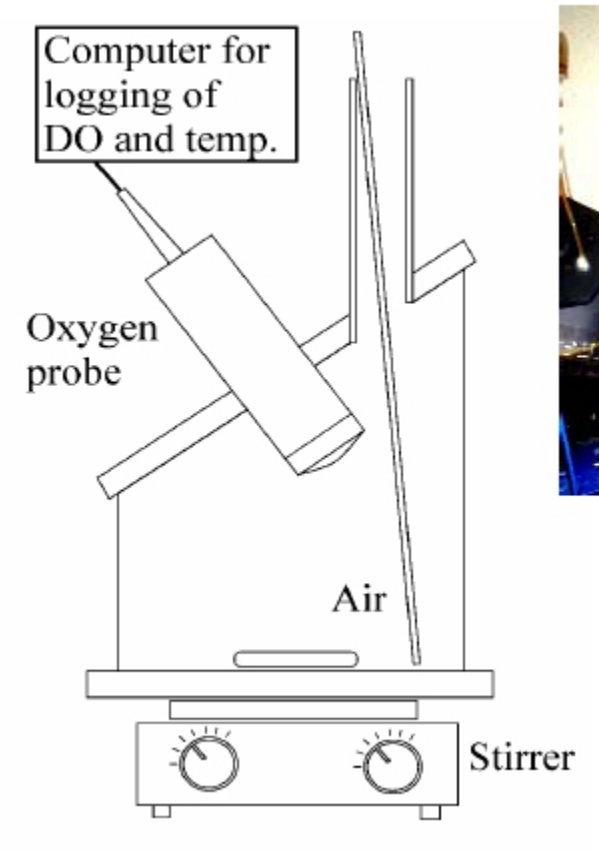
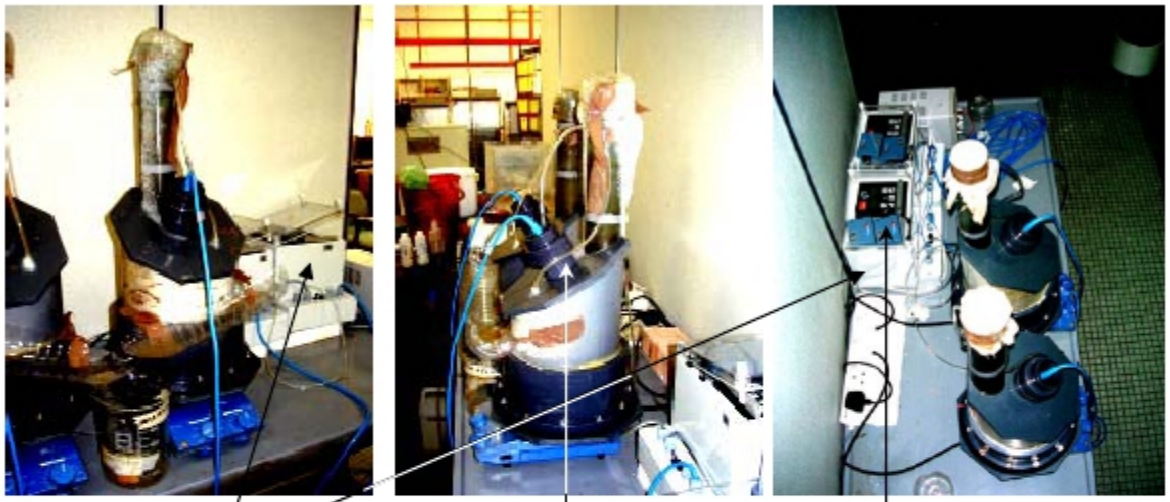



Figure 1



Danfoss USC Control Device

Computerboard IQ VmA data loggers

Danfoss EVITA Oxy 4100

# E.g. OUR Graph

Initially Present Ss

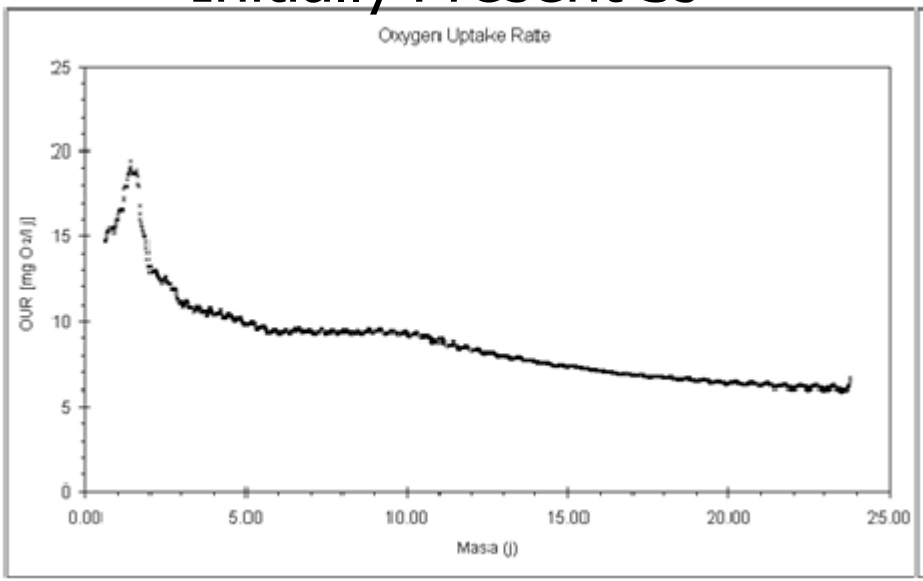



**Figure 2** Sample obtained 7.11.00, 7:15 Manhole 33

No Initially Present Ss

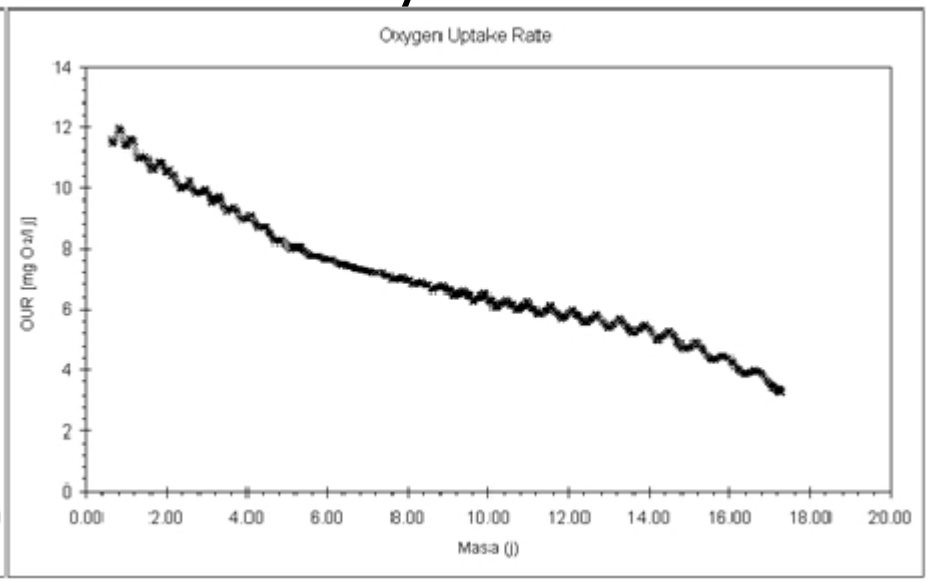



**Figure 3** Sample obtained 2.11.00, 14:50 Manhole 33