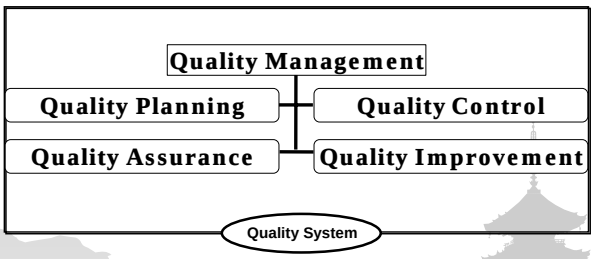
Annex 2-3 : Lecture Materials for Training

2.3.3 Chemical and Biological Water Quality

MATERIALS
FOR
LECTURE TRAINING
ON
CHEMICAL AND BIOLOGICAL
WATER QUALITY ANALYSIS
IN DAMASCUS DFEA

JICA EXPERT TEAM

Quality System And Elements of Quality Management



- Objectives of QA

To have clear and concise records of all procedures related to data quality

Achieved by: Establishing protocols and quality criteria for all aspects of laboratory works

➢ How to Ensure Accuracy and Reliability?

Implementation of QA/QC

Securement of Accuracy and Reliability of Analyzed Data

➢ What is the Goal of QA/QC?

►Implement correct or standardized methodologies in every monitoring processes :

- **Sampling process,**
- **Analysis process,**
- **Data handling process,**
- **Reporting process**

►Minimize or avoid the introduction of error in every monitoring processes

Components of Q/A

Lab. Works	Actions Taken
• Operation of standard procedure	– Preparation of SOP – Examination of new method
• Maintenance of analytical equipment	– Regular calibration – Supply of consumables
• Securing of validity of analysis	– Securing of quality of reagent – Technical training
• Evaluation of analyzed data	– Recording of analytical condition – Examination of deviation
• Review of management system	– Reporting – Necessary revising

Definition of Quality Control

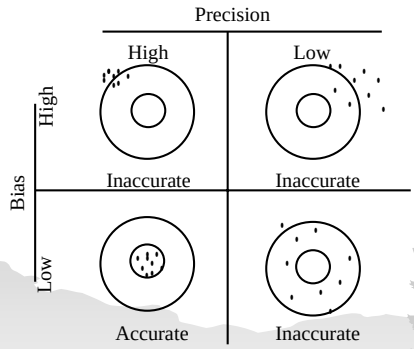
- Part of quality management focused on **fulfilling quality requirements** [ISO9000].
- Operational techniques and activities to fulfill requirements for quality.
- "Internal quality control"

⇨ Conducted within a laboratory to monitor performance

- "External quality control"

⇨ Leading to comparison with other reference laboratories or consensus results amongst several laboratories

Data Quality (Definition of accuracy)



Quality Indicators (1)

- Bias

A measure of systematic error.

1.Due to the method,

2.A laboratory's use of method

⇨ Method bias: measured by a laboratory intercomparison study. The difference between the grand average and the known (or true) value.

Lab. bias: Difference between the laboratory average recovery and the true value

Quality Indicators (2)

- Precision

A measure of the closeness with which multiple analyses of a given sample agree with each other.

Can be assessed by:

⇨
- ✓Replicate analyses,
- ✓Repeated analyses of a stable standard, or
- ✓Analysis of known additions to samples.

Specified by the standard deviation of the results.

➢ **How to Ensure Accuracy and Reliability?**

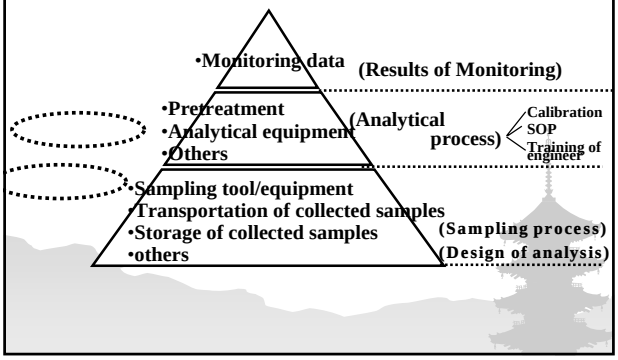
How to Ensure Accuracy and Reliability?

Implementation of QA/QC

⇧

Securement of Accuracy and Reliability of Analyzed Data

2. Reliability Pyramid of Monitored Data



Lecture Training
For
Chemical and Biological Water Quality Analysis

Lecture
Analysis Using Ion Selective Electrode

2007 January

Shinsuke SATO
The JICA Expert Team

1

Activity of Ion

- Hydrogen ion activity
  Ion activity ⇨ $[a^+]$, $[b^-]$, $[X]$ ・・・

$$a = \gamma C$$

a: Ionic activity, γ : Coefficient of activity (< 1),
C: Concentration of Ion

In low concentration
$\gamma \approx 1$ ⇨ $a \approx C$

2

Concept of pH

- Hydrogen ion activity

$$K_w = [H^+][OH^-] / [H_2O] = \text{Constant}$$
$$= 1.8 \times 10^{-16}$$

$$pH = -\log_{10}[H^+]$$
$$= \log_{10} 1/[H^+]$$

pH can be measured by pH meter.
⇨ pH meter measures the hydrogen activity.
⇨ pH meter is the kind of Ion Selective Electrode.

3

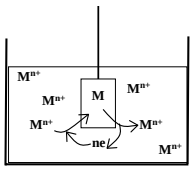
Electrode Potential

E → Potential difference

$$M^{n+} + ne \rightleftarrows M$$

Reduction / Oxidation

- When the oxidation-reduction reaction reaches equilibrium, the metal plate shows the constant electric potential (E) to the solution.



Concept of Half-Cell

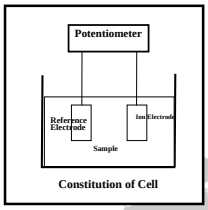
4

Nernst Equation

- Potential difference (E) is described by the Nernst Equation:

$$E = E_0 + RT/nF \times \ln [M^+]$$

E_0: Formal electrode potential,
R: Gas constant (8.31 [J/mol K])
T: Temperature in Kelvins,
n: Number of electrons transferred,
F: Faraday's constant (9.64853×10^4 [K/mol]),
$[M^+]$: Activity of ion ($\gamma \times C_M$)



Constitution of Cell

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Ion Selective Electrode (ISE)

- The electrode that responses the specific ion dissolved in a solution,
- Frequently used in laboratory analysis, in industry, process control, physiological measurements, and environmental monitoring,
- Kind of transducer (sensor) which converts the activity of a specific ion dissolved in a solution into an electricalpotential,
- The electricalpotential (voltage) is theoretically dependent on the logarithm of the ionic activity,
- The sensing part of the electrode is usually made as an ion-specific membrane.

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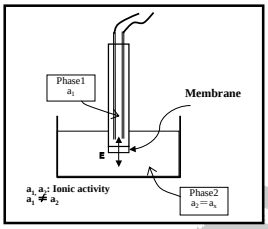
Ion Selective Membrane

- Boundary between two phases,
- Specific ion can penetrate between two phases,
- Electrochemical equilibrium is to be reached,
- Potential difference (E) across the membrane is to generate,
- Potential difference (E) generated can be given by Nernst Equation.



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Potential Difference (E) Across the Membrane

$E = RT/nF \cdot \ln (a_2/a_1)$ ⟸ Nernst Equation

- If the activity of the target ion in phase 1 is kept constant, the unknown activity in phase 2 ($a_2 = a_x$) is related to (E) by:

$E = RT/n_xF \cdot \ln (a_x/a_1)$

$= RT/n_xF \cdot (2.303\log(a_x) - 2.303\log(a_1))$

$= \text{const} + S \cdot \log (a_x)$

- Nernst equation above shows that a plot of measured potential versus log(*a*) will therefore give a straight line. ⟹ Calibration Curve

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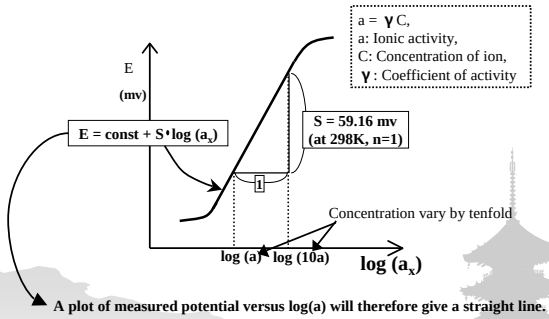
Calibration Curve of an Ion Selective Electrode



A plot of measured potential versus log(a) will therefore give a straight line.

9

Calibration and Ionic Strength

- Using a series of calibrating solutions the response curve or calibration curve of an ion-selective electrode can be measured and plotted as the signal (electromotive force) versus the activity of the target ion.
- The linear range of the calibration curve is usually applied to determine the activity of the target ion in any unknown solution.
- It should be pointed out that only at constant ionic strength, a linear relationship between the signal measured and the concentration of the target ion is maintained.
- In order to keep a ionic strength in constant, the ion that does not react with the target ion, and does not affect the electrode potential is added to the sample and the standard solutions generally.
- The solution that contains the ions mentioned above are so called "Ionic Strength Adjuster (ISA)".

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Some Example of Ionic Strength Adjuster (ISA)

Ion Analyzed	ISA Used
NO_3^-	2M $(NH_4)_2SO_4$
Cl^-	5M $NaNO_3$
CN^-	10M NaOH
F^-	CH_3COOH, NaCl, CDTA

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Lecture Training
For
Chemical and Biological Water Quality Analysis

Lecture
Oil and Grease in Water

2007 January

Shinsuke SATO
The JICA Expert Team

1

What is Oil and Grease in Water

- General
  - Petroleum oil
    - Crude oil, and,
    - Oil products
  - Plant/animal oil

Not a specific single substance

Measurement

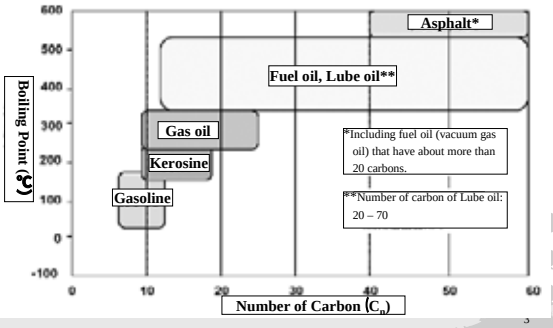
Mixture of variety of liquid hydrocarbons of which boiling points are different respectively.

Measurement

Total hydrocarbons (TH)

2

What is Petroleum?
(Range of Boiling Point and Number of Carbon of Oil Product)



3

What Items are to be Monitored?

1. **Concentration of Total Hydrocarbon**
2. **Qualitative/Quantitative Analysis of Oil Component**
3. **Others (PAHs, Oil membrane, Tar ball, etc.)**

4

How will Oil be detected in the water?

Major Method for Measuring Oil in Water

- Observation under microscope,
- Measurement of particle size distribution,
- Extraction-Nephelometer method,
- Determination of oil content,
  - Measurement of Content of Total Hydrocarbon (TH)
  - Analysis of Oil Component (Qualitative/Quantitative)

5

What is TH?
From Analytical Standpoint

- **Definition of measurement of TH**
  - ☑Measurement of substance extracted by solvent
- **Definition of TH**
  - ☑Any material recovered as a substance soluble in the solvent, and not volatilized during the test
  - ☑Group of substances with similar physical characteristics that are determined quantitatively on the basis of their common solubility in an organic extracting solvent

⇨ Extractable materials that may be determined are relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, grease and related materials.

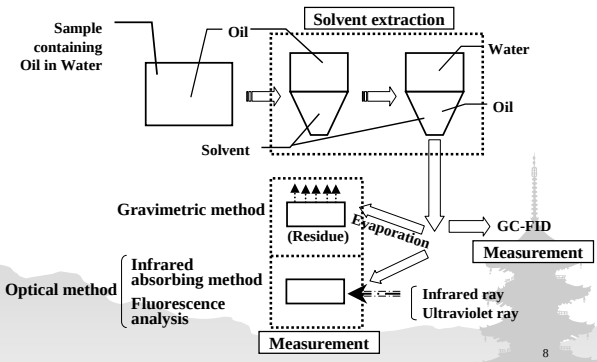
6

How to measure TH

- **Partition-Gravimetric method**
- **Partition-Infrared method**
- **Partition-Fluorescence method**
- **Partition GC-FID method**

7

Determination of Concentration of Oil in Water (Concept of Measurement of TH)



8

How to measure TH

- **Solvent for Extraction**
  - Petroleum ether,
  - n-hexane (C_6H_{14}) ⇨ JIS, USEPA recommended
  - Trichlorotrifluoroethane ($C_2Cl_3F_3$) ⇨ Dropped due to the environmental problem associated with chlorofluorocarbons
  - 80% n-hexane and 20% methyl-*tert*-butyl ether
  - Tetrachloromethane (CCl_4) ⇨ Dropped due to the environmental problem associated with chlorofluorocarbons
  - Chlorotrifluororhylene (S-316) ⇦ Adopted for HORIBA Oil Content Meter

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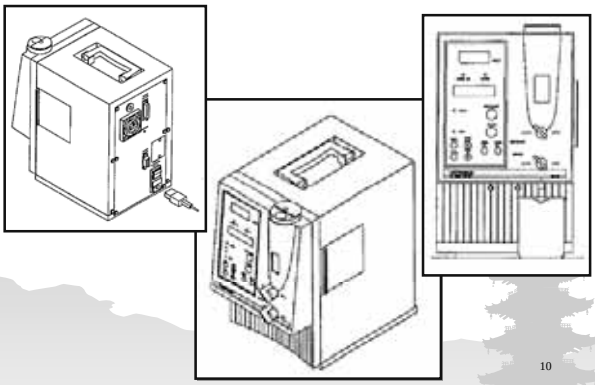
HORIBA OIL CONTENT ANALYZER (OCMA-310)



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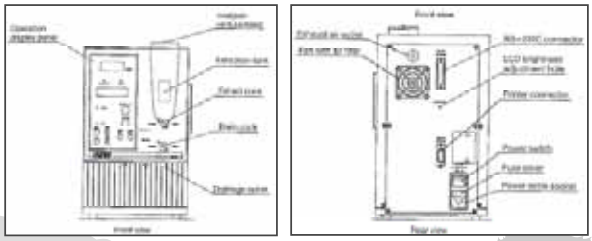
HORIBA OIL CONTENT ANALYZER (OCMA-310)



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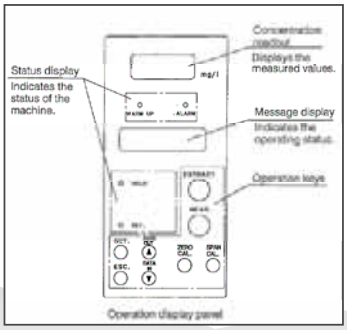
HORIBA OIL CONTENT ANALYZER (OCMA-310)



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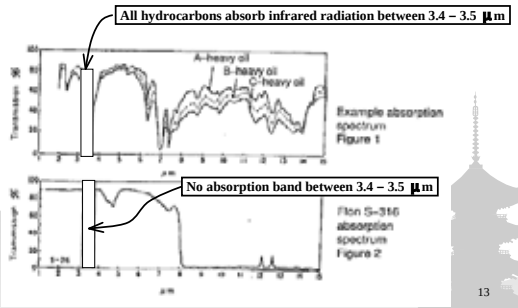
Measurement Principle

- Infrared absorption method
  - Measure absorption in the 3.4 – 3.5 μm wavelengths



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Extraction Solvent

- S-316
- Double chlorotrifluorothylene
  $Cl(CF_2\text{-}CFCl)_2Cl$
  - Molecular weight: 304
  - Boiling point: +134℃
  - Freezing point: -143℃
  - Specific gravity: 1.75 (at 25℃)
  - Low toxicity to people
  - No-combustible

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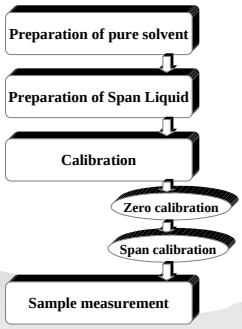
Measurement Sequence



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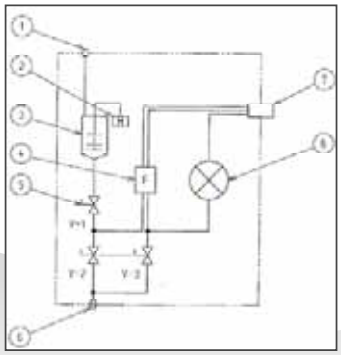
Flow Diagram of
HORIBA OIL CONTENT ANALYZER (OCMA-310)



No.	Parts name
1	Sample inlet
2	Stirrer
3	Extracting chamber
4	Filter
5	Ball valve
6	Drain
7	Air Vent
8	Analyzer unit

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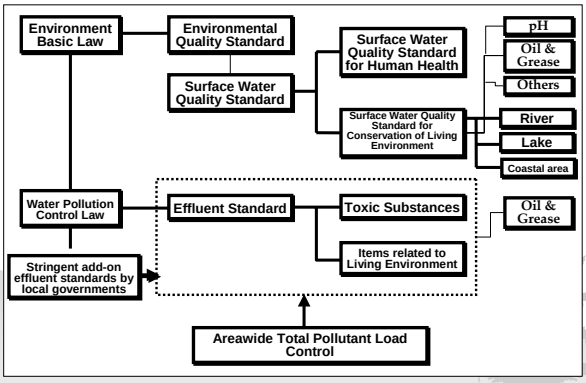
Regulation and Control System of Water Pollution in Japan



Regulation of Oil & Grease in Water (Case of Japan and Kazakhstan)

Regulated substance	*Determination method*	*Regulation value*	*Country*
Total Petroleum Hydrocarbon (TPH)	*•Partition-Fluorescence method, •Partition-Gravimetric method*	*Less than 0.05 mg/L (MPC for fishery purpose)*	*Kazakhstan*
Total Petroleum Hydrocarbon (TPH)	*•Partition-Gravimetric method, •Partition-Infrared method, •Others*	*·Not detected (Environmental water quality standard), ·Less than 5 mg/L (Effluent standard) ·Less than 2 mg/L, 1 mg/L, etc. (Stringent add-on effluent standards by local governments)*	*Japan*

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Thank You
for Your
Attention

Lecture Training
For
Chemical and Biological Water Quality Analysis

Lecture
Solids

2007 January

Shinsuke SATO
The JICA Expert Team

1

Solids in Water

What is the Solids in Water?

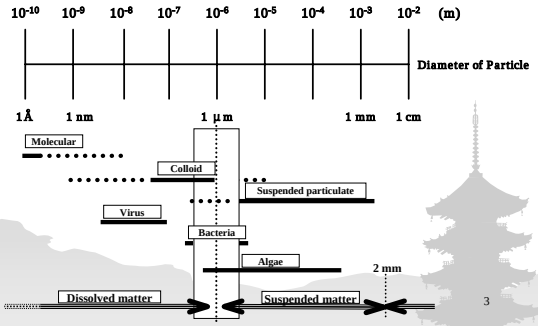
- Suspended matter and/or Dissolved matter in water,
- There are no clear distinction between suspended solids and dissolved matter.

Significance of Solids in Water

- Affect water or effluent quality adversely,
- High dissolved solids causes inferior palatability and may induce an unfavorable physiological reaction,
- Highly mineralized water is cause of trouble of industrial applications,
- High in suspended solids is esthetically unsatisfactory such purpose as bathing.

2

Size of Variety of Particles in Water



3

What is Total Solids?

- **<u>Total Solids</u>**:

Term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature.

4

Categories of Solids in Water

- Total Solids
  = Total Suspended Solids + Total Dissolved Solids
  (Measured by gravimetric method: Unit; mg/L)
  = Total Settleable Solids + Total Nonsettleable Solids
  (Measured by volumetric method: Unit; mL/L), and
  (Measured by gravimetric method: Unit; mg/L)

  ✓ Total Suspended Solids: the dry-weight of particles trapped by a filter, typically of a specified size,
  ✓ Total Dissolved Solids: the portion of solids that passes through the filter of a specified pore size.

  ✓ Total Settleable Solids: the material settling out of suspension within a defined period,

5

Measurement of Total Suspended Solids
(Gravimetric method)

- Apparatus

  Size compatible with the filter holder

  ✓Filter holder,
  ✓Glass-fiber filter (Whatman GF/C or equivalent),
  ✓Suction flask,
  ✓Drying oven,
  ✓Desiccator,
  ✓Analytical balance, capacity 200g (or more), accuracy 0.1 mg
  ✓Vacuum pump or aspirator

6

Procedure of Measurement
(Gravimetric method)

Measurement of suspended solids means to measure an actual weighing of particulate material present in the sample, and consists of following two series of procedures:

1. Filtering by glass-fiber filter, and
2. Drying at a temperature of 103 – 105℃ for fixed period (at least 1 h) to a constant weight

- The result of a measurement cannot include materials that are volatile under the condition of the procedure
- The results should be reported as: total suspended solids at ….℃, type of filter and pore size or number

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Procedure of Measurement (2)
(Gravimetric method)

1. Prior to a measurement, remove large floating material or submerged agglomerates of nonhomogeneous materials using a sieve,
2. A well-mixed sample is filtered through a weighted standard glass-fiber filter,
3. Residue retained on the filter is dried to a constant weight at 103 – 105℃,
4. The increase in weight of the filter represents the total suspended solids

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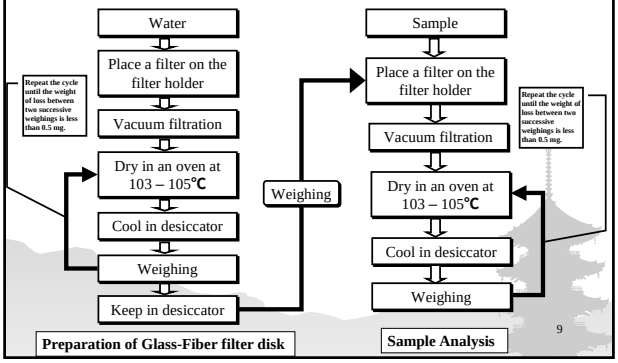
Procedure of Determination of SS
(Gravimetric method)



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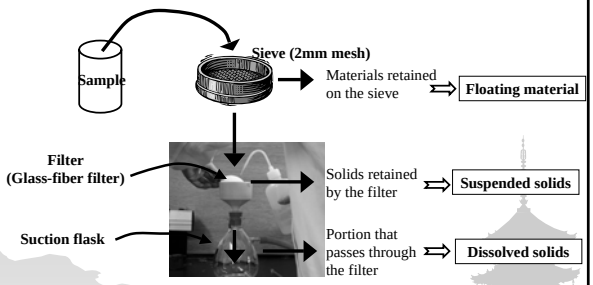
Measurement of Suspended Solids and Dissolved Solids
(Gravimetric Method)



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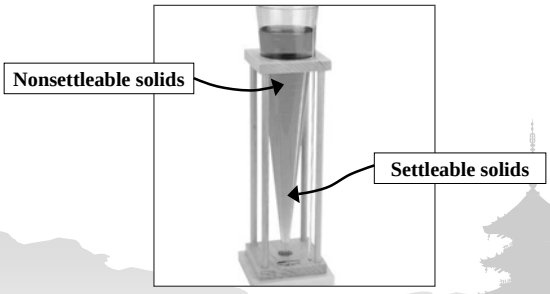
Measurement of Settleable Solids and Nonsettleable Solids
(Volumetric Method)



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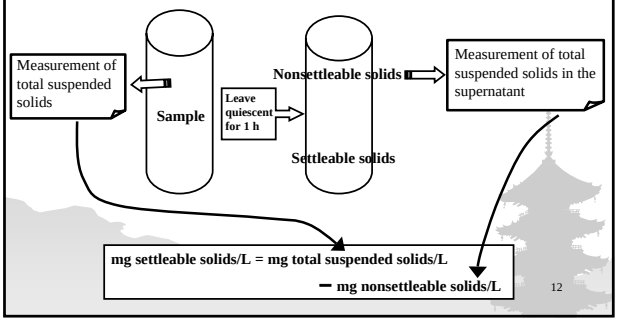
Measurement of Settleable Solids and Nonsettleable Solids
(Gravimetric Method)



12

Type and Feature of Glass-fiber filter

Type	Thickness (mm)	Pore size (μm)
GF/A	0.26	1.6
GF/B	0.68	1.0
GF/C	**0.26**	**1.2**
GF/D	0.68	2.7
GF/F	0.42	0.7

(Source: Whatman catalog)

13

Notes for Sample Handling and Preservation

- Use resistant-glass or plastic bottles, provide that the material in suspension does not adhere to container walls.
- Begin analysis as soon as possible.
- Refrigerate sample at 4℃ up to the time of analysis to minimize microbiological decomposition of solids.
- Preferably do not hold samples more than 24 h.

14

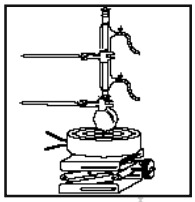
Lecture Training
For
Chemical and Biological Water Quality Analysis

Lecture
Measurement of COD_{Cr}
by Open Reflux Method

2007 June

Shinsuke SATO
The JICA Expert Team

Measurement of COD_{Cr} by Open Reflux Method



Contents

Review of Concept of COD (1)

- COD ⇨ **C**hemical **O**xygen **D**emand
- Definition ⇨ **the amount of a specified oxidant** that reacts with a sample under controlled conditions
- Expressed in mg/L
- Oxidant: Potassium permanganate [$KMnO_4$]
  Potassium dichromate [$K_2Cr_2O_7$]

Review of Concept of COD (2)

- Oxidant
  - **$KMnO_4$**
    - Oxidation ratio: Medium
    - Easy to use
    - Good reproducibility
    - Adopted in Japan
  - **$K_2Cr_2O_7$**
    - Oxidation ratio: Strong
    - Generate hazardous waste (Hg)
    - Commonly used in many countries
    - Adopted in Open Reflux Method

Review of Concept of COD (2) History ($KMnO_4$)

- For many years, the strong oxidizing agent of potassium permanganate ($KMnO_4$) was used for measuring COD,
- Measurements by Permanganate were called *oxygen consumed from permanganate*, rather than the oxygen demand of organic substances,
- Effectiveness of $KMnO_4$at oxidizing organic compounds varied widely, and in many cases BOD measurements were often much greater than results from COD measurements.
- This indicated that $KMnO_4$ was not able to effectively oxidize all organic compounds in water, rendering it a relatively poor oxidizing agent for determining COD.

Review of Concept of COD (2) History ($K_2Cr_2O_7$)

- Other oxidizing agents such as ceric sulfate, potassium iodate, and potassium dichromate have been used to determine COD,
- Of these, potassium dichromate (K2Cr2O7) has been shown to be the most effective:
  - It is relatively cheep,
  - Easy to purify, and
  - Is able to nearly completely oxidize almost all organic compounds

Review of Concept of COD (2) Using $K_2Cr_2O_7$

- $K_2Cr_2O_7$ is a strong oxidizing agent under acid conditions. (Acidity is usually achieved by the addition of Sulfuric acid.)

The reaction of $K_2Cr_2O_7$ with organic compounds is given by:

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d + c)H^+ \Rightarrow nCO_2 + (a + 8d - 3c)/2 \cdot H_2O + cNH^{4+} + 2dCr^{3+}$$

Where: $d = 2n/3 + a/6 - b/3 - c/2$

- **Most commonly, a 0.25 N (0.04167 M) solution of $K_2Cr_2O_7$ is used for COD determination, although for samples with COD below 50 mgt/L, a lower concentration of $K_2Cr_2O_7$ is preferred.**

Oxidation by Dichromate

Oxidation – Reduction Reaction by Chromate

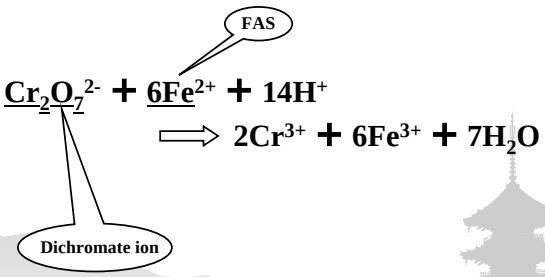
$$\underline{Cr_2O_7^{2-}} + 14H^+ + \underline{6e^-} \rightarrow 2Cr^{3+} + 7H_2O$$

$$\underline{O_2} + 4H^+ + \underline{4e^-} \rightarrow 2H_2O$$

Oxidation by Oxygen

1 mol of potassium dichromate is equivalent to $(6/4)O_2 = 32 \times 6/4 = 48$ g (O_2)

Titration with FAS



Concept of Open Reflux Method (1)

- Principle

The sample is boiled under reflux with potassium dichromate and silver sulfate catalyst in strong sulfuric acid.

Part of the dichromate is reduced by organic matter and the remainder is titrated with ferrous ammonium sulfate.

Concept of Open Reflux Method (2)

- **Principle**
  - Most types of organic matter are oxidized by **a boiling mixture of chromic and sulfuric acids**,
  - Sample is refluxed in strongly acid solution (digestion) with **a known excess of potassium dichromate ($K_2Cr_2O_7$)**,
  - After digestion, **the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate** to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent.

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H2O$$

Concept of Open Reflux Method Equipment Required

1. **500-milliliter (ml) Erlenmeyer flask with standard (24/40) tapered glass joints,**
2. **Riebig reflux condensers (12-inch) with standard tapered glass joints,**
3. **Electric hot plate with magnetic stirrer,**
4. **Volumetric pipets (10, 25, and 50-ml capacity),**
5. **Buret, 50 ml or 25 ml - 0.1 ml accuracy,**
6. **Buret stand and clamp,**
7. **Analytical balance, accuracy 0.001 gram (g),**
8. **Spatula,**
9. **Volumetric flasks (1,000 ml capacity),**
10. **Boiling beads, glass,**
11. **Magnetic stirrer and stirring bars**

Concept of Open Reflux Method
Chemicals Required

1. Potassium dichromate ($K_2Cr_2O_7$) 0.25 N (0.04167 M),
2. Sulfuric acid (H_2SO_4, d = 1.84)) silver sulfate (Ag_2SO_4) solution,
3. Mercuric sulfate ($HgSO_4$) crystals,
4. Ferrous ammonium sulfate (FAS) $[Fe(NH_4)_2(SO_4)_2]\cdot 6H_2O$ 0.25 N (0.25 M)
5. Ferroin indicator (1, 10-phenanthroline and ferrous ammonium sulfate) ,
6. Potassium hydrogen phthalate (KHP),
7. Conc. Sulfuric acid (H_2SO_4) (d = 1.84)
8. Distilled water

Chemical Preparation (1)

- ***Standard potassium dichromate***

1. Dry potassium dichromate ($K_2Cr_2O_7$) in Oven at 103℃ for 24hrs.
2. Dissolve 12.259g of $K_2Cr_2O_7$ in distilled water to 1-liter volume in a volumetric flask.

$K_2Cr_2O_7 = 39.1\times2+52.0\times2+16\times7=$ **294.2**

$12.259/294.2 = 0.04167$ M

⇨ This reagent undergoes a six-electron reduction reaction; the equivalent concentration is $6 \times 0.04167 \times 6 = 0.25$ N (1 mL solution is equivalent to 2 mg O)

Chemical Preparation (2)

- ***Sulfuric acid solution (reagent)***

1. Add reagent grade silver sulfate (Ag_2SO_4) to a conc. Sulfuric acid (H_2SO_4) at the rate of 5.5 g Ag_2SO_4 per kg H_2SO_4 and mix until the silver sulfate goes into solution.
2. Let stand 1 to 2 days to dissolve.

Chemical Preparation (3)

- ***Standard ferrous ammonium sulfate (FAS) titrant***

1. Dissolve 98.0 g of ferrous ammonium sulfate hexahydrate (FAS) $[Fe(NH_4)_2(SO_4)_2]\cdot 6H_2O$ in distilled water. (0.25N FAS Solution)
2. Add 20 mL conc. H_2SO_4 (d = 1.84), cool, and dilute to exactly 1,000 mL in volumetric flask.
3. Standardize this solution daily against standard $K_2Cr_2O_7$ solution.

Chemical Preparation (4)

A) Standardization of FAS

1. **Dilute 10.0 mL** of standard potassium dichromate (0.04167 M: $K_2Cr_2O_7$) solution **to 100 mL** with distilled water in Erlenmeyer flask.
2. Slowly **add 30 mL of conc. Sulfuric acid** (H_2SO_4) and cool to room temperature.
3. **Titrate with FAS titrant**, using 2 to 3 drops (0.10 to 0.15 mL) of ferroin indicator till the **color changes from greenishblue to wine red**.

◆ The molarity (normality) of FAS solution is given by the following formula:

$$\text{Molarity of FAS solution} = \frac{\text{(Volume of 0.04167 M } K_2Cr_2O_7\text{ solution titrated, mL)}}{\text{(Volume of FAS used in titration, mL)}} \times 0.25$$

Chemical Preparation (5)

- ***Ferroin indicator solution***

- Dissolve 1.485 g 1,10-phenanthroline monohydrate and 695 mg $FeSO_4\cdot 7H_2O$ in distilled water and dilute to 100 mL.

- ***Potassium hydrogen phthalate (KHP) standard***

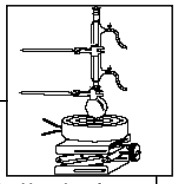
1. Lightly crush and then dry potassium hydrogen phthalate ($HOOCC_6H_4COOK$) to constant weight at 120℃.
2. Dissolve 425 mg of KHP in distilled water and dilute to 1,000 mL.

KHP has a theoretical COD of 1.176 mg O2/mg

This solution has a theoretical COD of 500 μg O_2/mL.

This solution is stable when refrigerated for up to 3 months.

Setting Up Reflux



1. Step 1
   - Place the heater on a desk
   - Clamp the **flask** above the heater
2. Step 2
   - Insert **reflux conderser**, clamp it in place, and attach rubber tubing for cooling water
3. Step 3
   - Turn on and adjust the **water flow**
4. Step 4
   - Remove condenser, then **add reactants, solvent and stirrer/boiling stones**
5. Step 5
   - **Commence heating**; adjust heating until a gentle boiling is obtained. Readjust water flow or heating rate if necessary
6. Step 6
   - After reflux, remove heater and allow flask to cool. Transfer contents to appropriate flask and disassemble the apparatus

Basic Concept of Open Reflux Method Principle

(A)		COD substances in Sample
(B)		COD substances consume a known excess of $K_2Cr_2O_7$
(C)	B	Remaining unreduced $K_2Cr_2O_7$ is titrated with FAS
(D)	A	A known excess of $K_2Cr_2O_7$ added to blank is titrated with FAS
(E)	A - B	Difference of (D) and (C) corresponds to the amount of the COD substances

Procedure of Measurement by Open Reflux Method (1)

B) Treatment of samples with COD of >50 mg O2/L:

1. Blend samples if necessary and pipet **50.00 mL into a 500-mL refluxing flask**. For samples with a COD of >900 mg O2/L, use a smaller portion dilute to 50.00 mL.
2. **Add 1 g $HgSO_4$** and very slowly **add 5.0 mL sulfuric acid reagent**, with mixing to dissolve $HgSO_4$. Cool while mixing to avoid possible loss of volatile materials.
3. **Add 25.00 mL 0.04167M $K_2Cr_2O_7$ solution** and mix. Attach flask to condenser and turn on cooling water.
4. **Add remaining sulfuric acid reagent (70 mL)** through open end of condenser. Continue swirling and mixing while adding sulfuric acid reagent.

✓ **CAUTION:** ***Mix reflux mixture thoroughly before applying heat to prevent local heating of flask bottom and a possible blowout of flask contents.***

Procedure of Measurement by Open Reflux Method (2)

5. Cover open end of condenser with a small beaker to prevent foreign material from entering refluxing mixture and **reflux for 2 hrs**. Cool and wash down condenser with distilled water.
6. Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water.
7. Cool to room temperature and **titrate excess $K_2Cr_2O_7$ with FAS, using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator**. Although the quantity of ferroin indicator is not critical, use the same volume for all titrations.

Procedure of Measurement by Open Reflux Method (3)

8. Take as **the end point** of the titration the first sharp **color change from greenishblue to wine red** that persists for 1 min or longer.
9. Duplicate determinations should agree within 5% of their average.
10. Samples with suspended solid or components that are slow to oxidize may require additional determinations.
11. Reflux in the same manner, preferably simultaneously with sample, a blank consisting of 50 mL of distilled water together with the reagents and titrate as mentioned above.

Procedure of Measurement by Open Reflux Method (4)

- **Calculation**

Concentration of COD_{Cr} can be given by the formula below:

COD as mg O_2/L = ((A- B) × M × 8000)／(mL sample)

where :

A = mL FAS used for blank,
B = mL FAS used for sample,
M = molarity of FAS
8000 = milliequivalent weight of oxygen × 1000ml/L

Derivation of Calculation Formula

① A – B = Difference of amount of FAS (M 0.25N) used for titration (mL) against $K_2Cr_2O_7$

② (A – B) × M ⇨ Equivalent of $K_2Cr_2O_7$ reacted with FAS (milli-mole of FAS)

③ 1 mole of FAS is equivalent to 1/6 mole of $K_2Cr_2O_7$

④ (A – B) × M × 1/6 ⇨ Correspond amount of $K_2Cr_2O_7$ with FAS (milli-mole of $K_2Cr_2O_7$)

⑤ 1 milli-mole of K_2Cr_2O7 is equivalent to 48mg Oxygen (O_2)

⑥ (A – B) × M × 1/6 × 48 ÷ V ⇨ Corresponding COD substances contained in sample (mg O_2/mL)

⑦ (A – B) × M × 1/6 × 48 ÷ V × 1,000
= **(A – B) × M × 8,000/V** ⇨ COD as mg O_2/L

Precautions of Measuring Procedure (1)

1. The strength of sulfuric acid in the final solution should be at least 18 N.
2. The order of making the analytical mixture should be i) sample, ii) $HgSO_4$ (i) and ii) are sometimes reversible) , iii) $K_2Cr_2O_7$, and conc. H_2SO_4 (slowly with swirling).
3. When $HgSO_4$ is added, mix well so that the chlorides are converted into poorly ionized mercuric chloride.
4. After refluxing, allow to cool, use the required amount of distilled water for washing the condenser, allow to cool and then titrate.
5. As far as possible. Reflux blank and samples should be analyzed simultaneously.

Precautions of Measuring Procedure (2)

6. The interference caused by chloride can be eliminated by the addition of mercuric sulfate (HgSO4) to the sample prior to addition of other reagents; about 480 mg of HgSO4 is adequate to complex 40 mg Cl^- ions in the form of poorly ionized $HgCl_2$.
7. Silver sulfate is added to conc. H_2SO_4 (5.5 g/kg acid) as a catalyst. This accelerates the oxidation of straight chain aliphatic and aromatic compounds.

Sample Handling (1)

- Samples should be taken with bottles that do not release organic substances into water; glass-stoppered glass bottles are satisfactory. Unstable samples should be tested without delay, especially wastewater and polluted water samples. Natural, not heavily polluted, water should be analyzed on the same day or at least within 24 hours and the sample should be kept cold before analysis.
- If there is to be a delay before analysis, the sample may **be preserved** by **adding sulfuric acid** (H_2SO_4, d = 1.84), about 2 mL diluted 1 + 2 to each 100 mL of sample. If samples are to be stored for longer than 24 hours, deep freezing is recommended.

Sample Handling (2)

- Depending on the aim of the analysis, COD can **be determined on unfiltered and/or filtered samples**.
- When both determinations are carried out, the **difference gives the COD of the particular matter**.
- Samples containing settleable solids should be homogenised sufficiently by means of a blender to permit representative sampling for the COD determination in unfiltered samples.
- For the analysis of filtrate, the original (not homogenised) sample is used.
- Filtration through glass-fiber filter is recommended, but hard paper filters may be used if the sample has a high COD. The filters should be pre-rinsed with distilled water.

Procedure of Measurement by Open Reflux Method (5)

- ***Determination of standard solution***
  - ✓ Evaluate the technique and quality of reagents by conducting the test on a standard potassium hydrogen phthalate (KHP) solution. [$HOOCC_6H_4COOK$]
  - ✓ KHP has a theoretical COD of 1.176 mg O_2/mg-KHP.
  - ✓ Dissolve 425 mg of KHP in distilled water and dilute to 1,000 mL for a 500 mg/L COD solution.
  - ✓ A recovery of 98 – 100 % of the theoretical COD can be expected.
  - ✓ This solution is stable when refrigerated, but not indefinitely. Weekly preparation usually is satisfactory.

Procedure
For
Measurement of Low Concentration COD (< 50 mg O_2/L)

- Follow the normal procedure aforementioned in [**Procedure of Measurement by Open Reflux Method (1)] with two exceptions:**
  - ① **Use standard $K_2Cr_2O_7$ solution of 0.025N (0.004167M),**
  - ② **Titrate with standardized 0.025N FAS.**

✓ Even a trace of organic matter on the glassware or from the atmosphere may cause gross error

⟹ **Exercise extreme care**

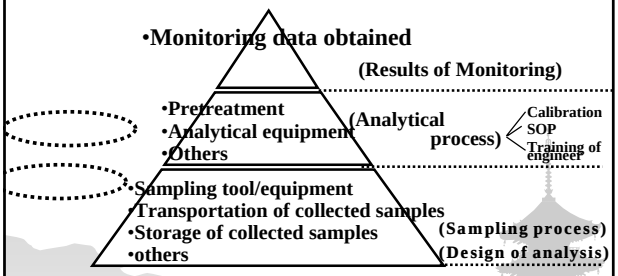
Lecture Training
For
Chemical and Biological Water Quality Analysis

Lecture
(Lecture at DAM, HOM, ALP and DAMC)
Sampling Guide

2007 July, August

Shinsuke SATO
The JICA Expert Team

Reliability Pyramid of Monitoring Data



Importance of Sampling

- Element of QA/QC
- How to secure the reliability of Sampling

Sampling Factor
- – Parameter,
- – Analytical method adopted,
- – Container
- – Preservation method,
- – Holding time

Sampling Guide (1)
(Parameters for Chemical & Biological Water Quality)

Parameter	Oil & Grease	PO_4^{3-}
Analytical method	Solvent extraction/ Infrared absorptiometry	Spectral photometric
Container	G, Wide-mouth	P or G, Wash with HCl, Don't use commercial detergents
Preservation	pH below 2 with H_2SO_4 or HCl	If prompt analysis is not possible, preserve samples by filtering immediately and storing at 4℃.
Minimum sample volume	1,000 mL	100 mL
Holding time	28 days	48 hrs

Sampling Guide (2)
(Parameters for Chemical & Biological Water Quality)

Parameter	NH_3-N	Surfactants
Analytical method	Spectral photometric	Spectral photometric
Container	P or G	P or G
Preservation	Refrigerate at 4℃ or less for samples to analyzed within 24 hrs. pH below 2 with H_2SO_4 Neutralize with 5.0N NaOH before analysis	Refrigerate at 4℃ or less
Minimum sample volume	500 mL	(500 mL)
Holding time	7 days (28 days stored sample)	24 hrs

Sampling Guide (3)
(Parameters for Chemical & Biological Water Quality)

Parameter	Cr-T	Cr(Ⅵ)
Analytical method	Spectral photometric	Spectral photometric
Container	P or G (Acid-washed container)	P or G (Acid-washed container)
Preservation	pH below 2 with HNO_3 Adjust the pH to about 4 with 5.0N NaOH before analysis	Store at 4℃ or less up to 24 hrs. Must be analyzed within 24 hrs
Minimum sample volume	300 mL	300 mL
Holding time	6 months	24 hrs

Sampling Guide (4)
(Parameters for Chemical & Biological Water Quality)

Parameter	S^{2-}	NO_3^-
Analytical method	Ion Selective electrode (ISE)	Spectral photometric or ISE
Container	P or G	P or G
Preservation	Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Add 4 drops of 2N $Zn(CH_3COO)_2 2H_2O$))solution in the sample bottle per 100 mL sample before sampling. And then adjust pH to above 9 by adding NaOH, Refrigerate	pH below 2 with H_2SO_4, Refrigerate
Minimum sample volume	100 mL	200 mL
Holding time	7 days	48 hrs

Sampling Guide (5)
(Parameters for Chemical & Biological Water Quality)

Parameter	Cl^-	F^-	CN^-
Analytical method	ISE	ISE	ISE
Container	P or G	P	P (Amber) or G (Amber)
Preservation	No special Preservation	No special Preservation	pH above 12 with NaOH, Refrigerate
Minimum sample volume	100 mL	300 mL	500 mL
Holding time	28 days	28 days	28 days

Sampling Guide (6)
(Parameters for Chemical & Biological Water Quality)

Parameter	Suspended solid and Settleable solid
Analytical method	Filtrate weight, Still standing
Container	P or G (Be provided that the material in suspended suspension does not adhere to container walls))
Preservation	Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4℃ up to the time of analysis to minimize microbiological decomposition of solids. Transportation and short-term storage of sample will not normally affect the results of the test. Bring samples to room temperature before analysis.
Minimum sample volume	(1,000 mL)
Holding time	Preferably do not hold samples more than 24hrs. In no case hold sample more than 7 days.

Sampling Guide (7)
(Parameters for Chemical & Biological Water Quality)

Parameter	COD_{Cr}
Analytical method	Open reflux method
Container	P or G (Preferably collect samples in glass bottles.)
Preservation	pH below 2 with H_2SO_4, Analyze unstable samples without delay. If delay before analysis is unavoidable, preserve sample by acidification to pH≤2 with H_2SO_4. Preferably acidify any sample that cannot be analyzed the same day it is collected. Blend samples containing Settleable solids with a homogenizer to permit representative sampling. Make preliminary dilutions for wastes containing a high COD to reduce the error inherent in measuring small sample volume. Refrigerate
Minimum sample volume	100 mL
Holding time	7 days

Sampling Guide (8)
(Parameters for Chemical & Biological Water Quality)

Parameter	Total Coliform
Analytical method	Membrane filter technique
Container	P or G (Should be properly sterilized, either with alcohol, or using an autoclave, etc.)
Preservation	pH below 2 with HCl
Minimum sample volume	100 mL
Holding time	6 hrs

Environmental Monitoring Plan should be revised and/or modified taking into account the new parameters such as chromium, surfactants, oil & grease, etc. !


Thank You
for Your
Attention

Lecture Training
For
Environmental Management and Monitoring

Lecture
Basis of Water Quality Analysis

2006 Jan. – Feb.

The JICA Expert Team

1

➢ CONTENTS

2

Classification of Determination Method

Determination method		Analytical Item
Chemical analysis	Volumetric analysis	Hardness(Ca^{2+}, Mg^{2+}), Alkalinity, Acidity, DO, BOD, COD, etc.
	Gravimetric analysis	SS, VSS, CCE, Freon/N-Hexane extracts, etc.
Instrumental analysis	Absorption spectrophotometry (Colorimetric method) (Visible, UV, IR)	Turbidity, Cl, SO_4^{2-}, NH_4^+-N, NO_2-N, NO_3-N, PO_4^{3-}, Color, etc
	Gas chromatography (GC), (GC-MS) Liquid chromatography (LC) Ion chromatography	Volatile organic substances Soluble organic substances Inorganic anion, Alkali metal
	Atomic absorption method ICP Emission spectrometer	Metal Metal element, etc.
	Others	Temp., DO, EC, etc.

3

Method and Instrument for Basic Water Analysis

NO.	Parameter	Method	Instrument
1	pH	Electrode method	sensION1 Portable pH meter
2	Water temp.		Thermometer
3	Color	APHA Platinum-Cobalt method	Colorimeter (DR/890)
4	TDS	Electrode method	sensION5 Portable EC & TDS meter
5	DO	Membrane Electrode method	sensION 6 Portable DO meter
6	SS	Photometric method	Colorimeter (DR/890)
7	COD_{Cr}	Reactor Digestion method	Reactor (DRB 200-1) & Colorimeter (DR/890)
8	NO_3-N	Cadmium Reduction method	Colorimeter (DR/890)
9	NH_3-N	Salicylate method	Colorimeter (DR/890)
10	PO_4^{3+}	Amino Acid method	Colorimeter (DR/890)
11	Cl^-	Silver Nitrate Method	Digital Titrator (Model 16900)
12	BOD_5	Manometric (Pressure sensor) method	OxiTop
13	EC	Electrode method	sensION5 Portable EC & TDS meter
14	Turbidity	Nephelometric method	2100P Portable Turbidity

4

Determination of Nitrate (NO_3-N) in water (1)

Feature of NO_3

- ✓ The most highly oxidized form of nitrogen compounds
- ✓ Commonly present in surface and ground waters, because it is the end product of the aerobic decomposition of organic nitrogenous matter
- ✓ Significant sources of nitrate are chemical fertilizers from cultivated land and drainage from livestock feedlots, as well as domestic and some industrial waters.
- ✓ Nutrient taken up by plants and assimilated into cell protein
- ✓ Cause water quality problems associated with eutrophication

5

Determination of Nitrate (NO_3-N) in water (2)

Determination

- ✓ Helps the assessment of the character and degree of oxidation in surface waters, in groundwater penetrating through soil layers, in biological processes and in the advanced treatment of wastewater
- ✓ Generally difficult because of interferences,
- ✓ And much more difficult in wastewaters because of higher concentrations of numerous interfering substances

6

Determination of Nitrate (NO_3-N) in water (3)

Determination method (**Cadmium reduction method**)

✓Principle

Nitrate is reduced to nitrite by cadmium. Nitrite, that originally present plus that reduced from nitrate, is then determined

✓Interferences

Low results may be obtained for samples that contain high concentrations of iron, copper or other metals. Addition of EDTA to the samples will eliminate this interference.

Presence of strong oxidants or reductants will readily affect the nitrite concentrations. High alkalinity will give low results

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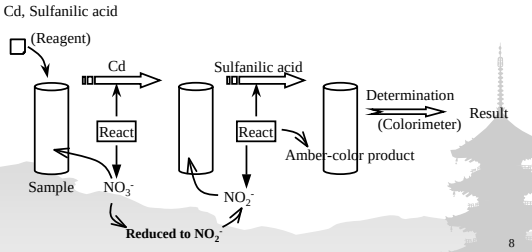
Summary of Determination Method (2)

- Nitrate (NO_3^--N)
- Method: Cadmium Reduction Method



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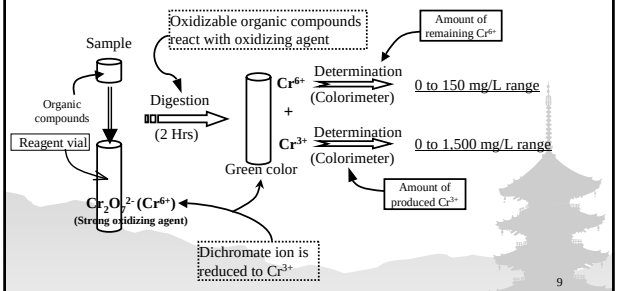
Summary of Determination Method (1)

- COD
- Method: Reactor Digestion Method



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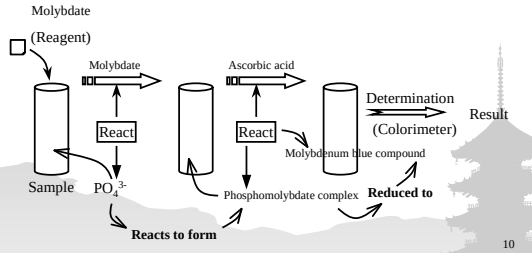
Summary of Determination Method (4)

- Phosphorus (PO_4^{3-}), Low range (0 to 2.50 mg/L)
- Method: Ascorbic Acid Method



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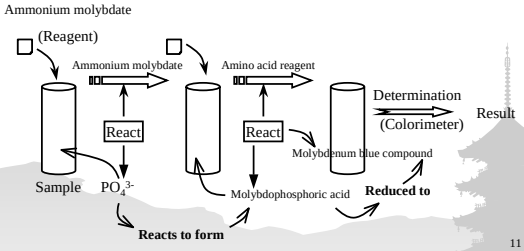
Summary of Determination Method (3)

- Phosphorus (PO_4^{3-}), High range (0 to 30.00 mg/L)
- Method: Amino Acid Method



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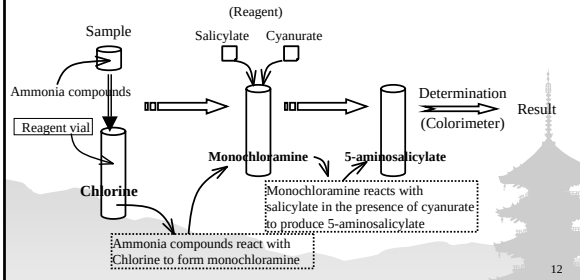
Summary of Determination Method (5)

- Nitrogen, Ammonia (NH_3-N)
- Method: Salicylate Method



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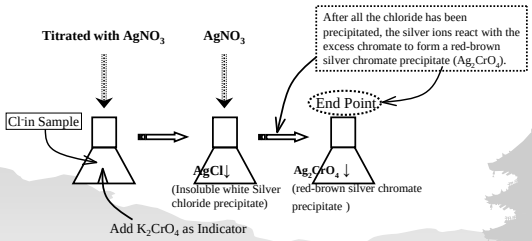
Summary of Determination Method (6)

- Chloride (Cl^-)
- Method: Silver Nitrate Method



Absorption Spectrophotometry (Colorimeter)

- Photometoric method to determine the concentration of substance in the solution.
- Apparatus that allows the absorbance of a solution at a particular frequency (color) of visual light to be determined.
- Make it possible to ascertain the concentration of a known solute, since it is proportional to the absorbance.
- Based on the Lambert-Beer law

Principle of Colorimeter (1)

- Lambert-Beer Law

  Correlation between:
  - Absorbance: A, (Dimensionless)
  - Path length traveled: L (cm)
  - Concentration of absorbent substance: c (mol/l)

⇨ **Absorbance of a substance is proportional to its concentration and length of path traveled**

Principle of Colorimeter (2)

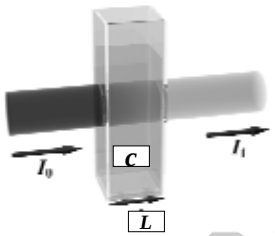
Lambert-Beer Law

$T = I_l/I_0$ (Absorptivity)

$A = \log_{10}(I_0/I_l) = \log_{10}(1/T)$

A = Absorbance of solution

$A = \varepsilon \times C \times L$



Where:

I_0 = intensity of the incident light

I_l = intensity after passing through the solution

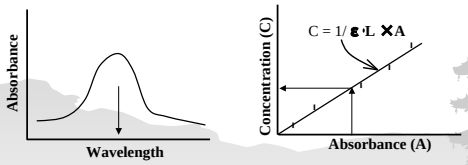
C = concentration of absorbing species in the material

L = distance that the light travels through the material (the path length)

ε = absorption coefficient

Principle of Colorimeter (3)

- **The equation shows that absorbance depends on the total quantity of the absorbent in the light path through the cell**
- **Plotting absorbance against concentration, straight line passing through the origin (0,0) can be obtained.**
- **Concentration of a substance dissolved in liquids can be determined by measuring the absorbance A.**



Interference Control

- Many analytical procedures are subject to interferences from substances present in the sample
- Interference may cause analytical results to be either too high or too low

⇩

- Necessity of interference control

Type of Interference

- React as though it were the objective substance to be analyses ⇨ Produce high result
- React with the objective substance ⇨ Produce low result
- Combine with analytical reagent ⇨ Prevent it from reacting with objective substance

Example:

In photometric method, turbidity may be considered as a "substance" that acts like the one being determined ⇨ Reduce light transmission

19

Counteracting for Interference (1)

The best way to minimize interference is to remove the interfering substance or to make it innocuous

1. Remove either the objective substance or the interfering substance physically
   ⇨ Distill off substance (fluoride, ammonia, etc.) leaving interferences behind,
   Absorption on an ion-exchange resin

20

Counteracting for Interference (2)

2. Adjust the pH so that only objective substance will react
   ⇨ Example:
   Adjust the pH to 2 so that volatile acids will distill from a solution
3. Oxidize (digest) or reduce the sample to convert the interfering substance to a harmless form ⇨ Example: Reduce chlorine to chloride by adding thiosulfate

21

Counteracting for Interference (3)

4. Add a suitable agent to complex the interfering substance so that it is innocuous although still present
5. A combination of the above four techniques
6. Color and turbidity ⇨ Use of activated carbon, flocculating agent, filtration.

22

Compensation of Interference for Photometric Determination

If none of above techniques is practical
⇨ Compensation can be used

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Photometric Compensation for Interference by Color or Turbidity

1. Measure sample without addition of reagents (sample blank)
2. The instrument response is due to sample absorbance or turbidity other than caused by the objective substance
3. Make calibration curve and the sample blank absorbance is subtracted from the sample absorbance

24

Interferences of NO_3 Analysis by Cadmium Reduction Method

Interfering Substance	Interference Levels and Treatment
Chloride (Cl^-)	**Above 100 mg/L-Cl^- will cause low results. The test may be used at high chloride concentrations but a calibration must be done using standards spiked to the same chloride concentration.**
Ferric ion	**All levels**
Nitrite (NO_2^-)	**All levels** **Compensate using Bromine Water and Phenol sln.**
pH	**Strong buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.**
Strong oxidizing and reducing substances	**Interference at all levels**

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Interferences of PO_4 Analysis by Amino Acid Method (1)

Interfering Substance	Interference Levels and Treatment
Calcium	Greater than 10,000 mg/L as $CaCO_3$
Chloride (Cl^-)	Greater than 150,000 mg/L as Cl^-
Colored samples	Add Sulfuric Acid Standard sln. to sample. Use this instead of untreated sample as the blank.
High salt levels	May cause low results. To eliminate, dilute the sample until two successive dilutions yield about the same result.
Magnesium	Greater than 40,000 mg/L as $CaCO_3$
Nitrites (NO_2^-)	Bleach the blue color. Remove nitrite interference by adding sulfuric acid to the sample.
Phosphates, high levels (PO_4^{3-})	As the concentration of phosphate increases, the color changes from blue to green, then to yellow and finally to brown. The brown color may suggest a concentration as high as 100,000 mg/L PO_4^{3-}. If a color other than blue is formed, dilute the sample and reset.

26

Interferences of PO_4 Analysis by Amino Acid Method (2)

Interfering Substance	Interference Levels and Treatment
Sulfide (S^{2-})	For samples with sulfide concentration less than 5 mg/L, sulfide interference may be removed by oxidation by Bromine Water.
Temperature	For best results, sample temperature should be 21±3℃
Turbidity	May give inconsistent results for two reasons. Some suspended particles may dissolve because of the acid used in the test. Also, desorption of orthophosphate from particles may occur. For highly turbid samples, add H_2SO_4 Standard Sln. to sample.
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment.

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Interferences of PO_4 Analysis by Ascorbic Acid Method (1)

Interfering Substance	Interference Levels and Treatment
Aluminium	Greater than 200 mg/L
Arsenate	All levels
Chromium	Greater than 100 mg/L
Copper	Greater than 10 mg/L
Hydrogen sulfide	All levels
Iron	Greater than 100 mg/L
Nickel	Greater than 300 mg/L
Silica	Greater than 50 mg/L

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Interferences of PO_4 Analysis by Ascorbic Acid Method (2)

Interfering Substance	Interference Levels and Treatment
Turbidity or color	Large amounts may cause inconsistent results in the test because the acid present in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles. For highly turbid or colored samples, add Phosphate Pretreatment Pillow to sample.
Zinc	Greater than 80 mg/L
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment. pH 2 to 10 is recommended.

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Interferences of NH_3-N Analysis by Salicylate Method (1)

Interfering Substance	Interference Levels and Treatment
Acidic or basic samples	Adjust to approximately pH7. Use NaOH Standard Sln. for acidic samples and HCl Standard Sln. for basic samples.
Calcium	50,000 mg/L as $CaCO_3$
Glycine, hydrazine	Will cause intensified colors in the prepared sample.
Magnesium	300,000 mg/L as $CaCO_3$
Iron	Iron interference will be eliminated by adding the same concentration of iron to the deionized water in Step 4.
Nitrite	600 mg/L as NO_2^--N
Nitrate	5,000 mg/L as NO_3^--N

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Interferences of NH_3-N Analysis by Salicylate Method (2)

Interfering Substance	Interference Levels and Treatment
Orthophosphate	5,000 mg/L as PO_4^{3-}-P
Sulfate (SO_4^{2-})	6,000 mg/L as SO_4^{2-}
Sulfide (S^{2-})	Sulfide will intensify the color. Sulfide interference will be eliminated by using the pretreated sample (Sulfide inhibitor Reagent Powder Pillow added and filtered) in Step 4.
Turbidity and Color	Give erroneous high values. Samples with severe interferences require distillation.

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Interferences of COD Determination by Reactor Digestion Method

- Primary interference
  ⟹ Chloride
- Countermeasure:
  - Each COD vial contains mercuric sulfate ($HgSO_4$) to eliminate chloride interference up to 2,000 mg/L
  - Samples with higher chloride concentration should be diluted
  - If sample dilution cause the COD concentration to be too low for accurate determination, add $HgSO_4$ to each vial before sample is added

32

Interferences of Cl^- Analysis by Silver Nitrate Method (1)

Interfering Substance	Interference Levels and Treatment
Iron	Iron in excess of 10 mg/L masks the end point
Orthophosphate	Orthophosphate in excess of 25 mg/L will precipitate the silver.
Sulfite (SO_3^{2-})	Sulfite in excess of 10 mg/L interferes. Eliminate sulfite interference by adding hydrogen peroxide in step 4.
Sulfide (S^{2-})	Remove sulfide interference by adding the contents of one Sulfide Inhibitor Reagent Powder Pillow to sample, and filtering through a folded filter paper.
Cyanide, iodide, and bromide	Cyanide, iodide, and bromide interfere directly and titrate as chloride.
Strongly alkaline or acid samples	Neutralize strongly alkaline or acid samples to pH of 2 to 7 with H_2SO_4 or NaOH.

33

Items to be checked when a problem is detected with an analytical method

1. **Calculations and records**
2. **Standard solutions**
3. **Reagents**
4. **Equipment**
5. **Quality control materials**

34

Necessary checks to be carried out when a problem is detected with an analytical method (1)

1. **<u>Calculations and records</u>**
   - **Check calculations for a transposition of digits or arithmetic errors.**
   - **Confirm that results have been recorded in the proper units and that any transfer of data from one record to another has been made correctly.**

35

Necessary checks to be carried out when a problem is detected with an analytical method (2)

2. **<u>Standard solutions</u>**
   - **Check the standard solutions that are used for calibrating equipment.**
   - **Old solutions may have deteriorated and errors may have occurred in the preparation of new ones.**
   - **Check on storage conditions, the age of solutions and their expected shelf-life.**

36

Necessary checks to be carried out when a problem is detected with an analytical method (3)

3. Reagents

- **Check whether old reagents have deteriorated.**
- **Check fresh reagents to ensure that they have been properly prepared.**
- **Check the storage conditions of reagents, especially those that must be stored away from the light or at a controlled temperature.**
- **Check the shelf-life of reagents, discarding any that are outdated or have been improperly stored.**

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Necessary checks to be carried out when a problem is detected with an analytical method (4)

4. Equipment

- **Check calibration records and maintenance records for all reagent dispensers and measuring equipment used for the analysis of the variable where the method is out of control.**
- **Items such as automatic pipettes, balances etc. should be checked and recalibrated if appropriate.**
- **Ascertain that equipment is being properly used.**

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Necessary checks to be carried out when a problem is detected with an analytical method (5)

5. Quality control materials

- **Check on the storage conditions of quality control materials, ensuring that bottles are tightly sealed and that they are not being subjected to extremes of temperature.**
- **Run analyses on several aliquots to determine whether the concentration of the variable remains within two standard deviations of the target value and close to the mean of the last 20 determinations.**

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➢ **How to Ensure Accuracy and Reliability?**

Implementation of QA/QC

⇧

Securement of Accuracy and Reliability of Analyzed Data

40

- Objectives of QA

To have clear and concise records of all procedures related to data quality

⇧

Achieved by: Establishing protocols/rules and quality criteria for all aspects of laboratory works

41

➢ **What is the Goal of QA/QC?**

► **Implement correct or standardized methodologies in every monitoring processes :**

- **Sampling process,**
- **Analysis process,**
- **Data handling process,**
- **Reporting process**

⇨

► **Minimize or avoid the introduction of error in every monitoring processes**

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Components of Q/A

Lab. Works	Actions Taken
• Operation of standard procedure	– Preparation of SOP – Examination of new method
• Maintenance of analytical equipment	– Regular calibration – Supply of consumables
• Securing of validity of analysis	– Securing of quality of reagent – Technical training
• Evaluation of analyzed data	– Recording of analytical condition – Examination of deviation
• Review of management system	– Reporting – Necessary revising

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Quality Indicators (1)

- Bias

A measure of systematic error.

1.Due to the method,

2.A laboratory's use of method

} Two Components

⇨ Method bias: measured by a laboratory intercomparison study. The difference between the grand average and the known (or true) value.

Lab. bias: Difference between the laboratory average recovery and the true value

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Quality Indicators (2)

- Precision

A measure of the closeness with which multiple analyses of a given sample agree with each other.

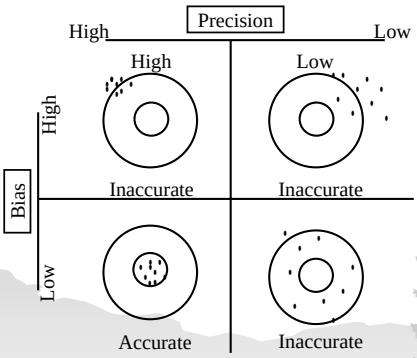
Can be assessed by:

⇨
- ✓Replicate analyses,
- ✓Repeated analyses of a stable standard, or
- ✓Analysis of known additions to samples.

Specified by the standard deviation of the results.

45

Data Quality (Definition of accuracy)



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Estimated Detection Limit (EDL)

No.	Parameter	Method	Measuring Range	EDL
1	NO_3^--N	Cadmium reduction method	0 to 30.0 mg/L	**0.8 mg/L NO_3^--N**
2			0 to 5.0 mg/L	**0.2 mg/L NO_3^--N**
3	PO_4^{3-}	Amino acid method	0 to 30.00 mg/L	**0.14 mg/L PO_4^{3-}**
4		Ascorbic acid method	0 to 2.50 mg/L	**0.05 mg/L PO_4^{3-}**
5	NH_3-N	Salicylate method	0 to 50 mg/L	**1 mg/L NH_3-N**
6			0 to 2.50 mg/L	**0.08 mg/L NH_3-N**
7	COD	Reactor digestion method	0 to 150 mg/L	**4 mg/L COD**
8			0 to 1,500 mg/L	**30 mg/L COD**

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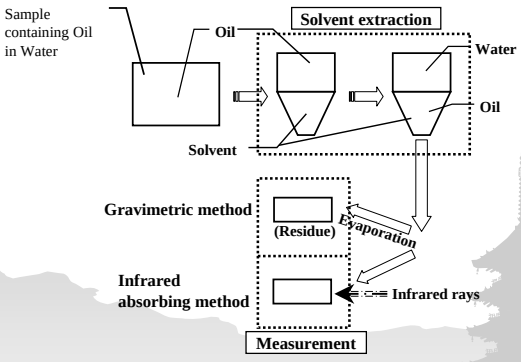
Determination of Concentration of Oil & Grease in Water



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49

Lecture Training
For
Chemical and Biological Water Quality Analysis

Lecture
Analysis Using Ion Selective Electrode-2

2006 August, 2007 November

Shinsuke SATO
The JICA Expert Team

1

Activity of Ion

- Hydrogen ion activity
  Ion activity ⇨ $[a^+]$, $[b^-]$, $[X]$ ・・・

$$a = \gamma C$$

a: Ionic activity, γ : Coefficient of activity (< 1),
C: Concentration of Ion

In low concentration
$\gamma \approx 1$ ⇨ $a \approx C$

2

Concept of pH

- Hydrogen ion activity

$$K_w = [H^+][OH^-] / [H2O] = \text{Constant}$$
$$= 1.8 \times 10^{-16}$$

$$pH = -\log_{10}[H^+]$$
$$= \log_{10} 1/[H^+]$$

pH can be measured by pH meter.
⇨ pH meter measures the hydrogen activity.
⇨ pH meter is the kind of Ion Selective Electrode.

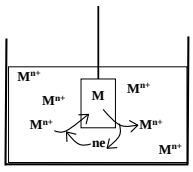
3

Electrode Potential

E → Potential difference

Reduction
$M^{n+} + ne \rightleftharpoons M$
Oxidation

- When the oxidation-reduction reaction reaches equilibrium, the metal plate shows the constant electric potential (E) to the solution.



Concept of Half-Cell

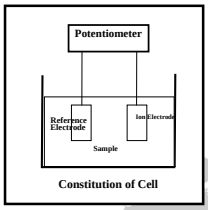
4

Nernst Equation

- Potential difference (E) is described by the Nernst Equation:

$$E = E_0 + RT/nF \times \ln [M^+]$$

E_0: Formal electrode potential,
R: Gas constant (8.31 [J/mol K])
T: Temperature in Kelvins,
n: Number of electrons transferred,
F: Faraday's constant (9.64853×10^4 [K/mol]),
$[M^+]$: Activity of ion ($\gamma \times C_M$)



Constitution of Cell

5

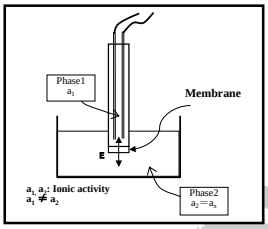
Ion Selective Electrode (ISE)

- The electrode that responses the specific ion dissolved in a solution,
- Frequently used in laboratory analysis, in industry, process control, physiological measurements, and environmental monitoring,
- Kind of transducer (sensor) which converts the activity of a specific ion dissolved in a solution into an electricalpotential,
- The electricalpotential (voltage) is theoretically dependent on the logarithm of the ionic activity,
- The sensing part of the electrode is usually made as an ion-specific membrane.

6

Ion Selective Membrane

- Boundary between two phases,
- Specific ion can penetrate between two phases,
- Electrochemical equilibrium is to be reached,
- Potential difference (E) across the membrane is to generate,
- Potential difference (E) generated can be given by Nernst Equation.



Potential Difference (E) Across the Membrane

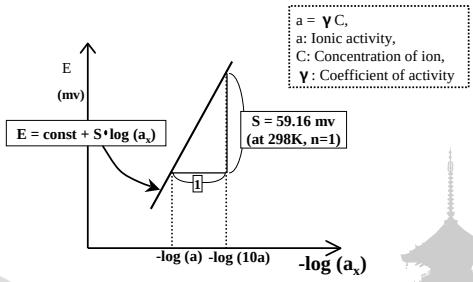
$$E = RT/nF \cdot \ln (a_2/a_1)$$

- If the activity of the target ion in phase 1 is kept constant, the unknown activity in phase 2 ($a_2 = a_x$) is related to (E) by:

$$E = RT/n_xF \cdot \ln (a_x/a_1)$$
$$= RT/n_xF \cdot (2.303\log(a_x) - 2.303\log(a_1))$$
$$= \text{const} + S \cdot \log (a_x)$$

- Nernst equation above shows that a plot of measured potential versus log(*a*) will therefore give a straight line.

Calibration Curve of an Ion Selective Electrode



Calibration and Ionic Strength

- Using a series of calibrating solutions the response curve or calibration curve of an ion-selective electrode can be measured and plotted as the signal (electromotive force) versus the activity of the target ion.
- The linear range of the calibration curve is usually applied to determine the activity of the target ion in any unknown solution.
- it should be pointed out that only at constant ionic strength, a linear relationship between the signal measured and the concentration of the target ion is maintained.
- In order to keep a ionic strength in constant, the ion that does not react with the target ion, and does not affect the electrode potential is added to the sample and the standard solutions generally.
- The solution that contains the ions mentioned above are so called "Ionic Strength Adjuster (ISA)".

Some Example of Ionic Strength Adjuster (ISA)

Ion Analyzed	ISA Used
NO_3^-	2M $(NH_4)_2SO_4$
Cl^-	5M $NaNO_3$
CN^-	10M NaOH
F^-	CH_3COOH, NaCl, CDTA

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Lecture Training
For
Chemical and Biological Water Quality Analysis

Lecture
Total Coliform

2007 July, August

Shinsuke SATO
The JICA Expert Team

What is Total Coliform? (1)

- The term coliform bacteria represents a vaguely defined group of organisms which have a long history in water quality assessment.

What is Total Coliform? (2)

- Pathogenic organism ≠ Coliform bacteria
- Number in water
  - Pathogenic organism: Small
  - Coliform bacteria: Large
- Coliform bacteria mostly includes pathogenic organism
- Test (Measurement)
  - Pathogenic organism: Difficult
  - Coliform bacteria: Relatively easy

What is Total Coliform? (3)

- The term "total coliform" refers to **a large group** of:
  - Gram-negative,
  - Rod-shaped bacteria

  that **share several characteristics**.

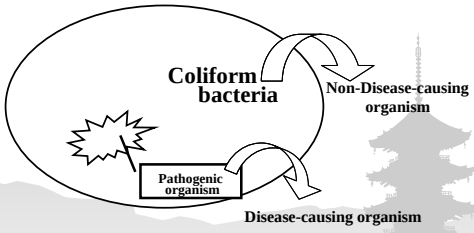
Pathogens: bacteria, protozoa, and viruses that make people sick

What is Total Coliform? (4)

- Non-disease-causing organisms found in soil or vegetation and in the intestinal tract of warm-blooded animals (fecal coli.).
- Present in much larger numbers than the more dangerous pathogens, and react to the natural environment and treatment processes in a manner and degree similar to pathogens.

What is Total Coliform? (5)

- One of the general sanitary water quality indicator that suggests the possibility of presence of pathogenic organism.



Why test for coliform bacteria? (1)

1. Most coliforms are not pathogens
2. The presence of very few coliforms in water
   ⇨ Water probably contains no pathogenic organisms
3. Presence of large number of coliforms
   ⇨ Very high probability of contamination by pathogenic organism
4. Number of pathogenic organism ⇨ Relatively small
   ⇨ Very difficult to isolate and identify specific pathogenic organism

Why test for coliform bacteria (2)

5. Observing/Testing of coliform bacteria
   ⇨ Increase or decrease of many pathogenic organism can be estimated
   ⇨ Total coliforms are indicators and are more common and easy to test

Total coliforms are mostly natural residents of soil and water. Coliform bacterias are those that are usually found in the fecal material of animals. Their presence usually means that the water may be contaminated by sewage effluent. Finding the source of the problem and correcting it is very important.

Where they are found? (1)

- There are many pollution sources.
- Domestic animals contribute heavily to the population of coliform
- Including runoff from:
  - **Woodland**
  - **Pastures**
  - **Feedlots**
  - **Septic tank**
  - **Sewage plants**
  - **Animals and wild fowl**
  - **Others**

How to measure/test coliforms?

- In the laboratory, tests are to conduct using following principles
  - **Grown in or on a medium containing lactose, at a temperature 35 or 37℃**
  - **Provisionally identified by the production of acid and gas from the fermentation of lactose**

Selection of Analytical Method

- Commonly used two techniques

1. "Multiple fermentation tube" technique or "Most probable number" technique

   Measured portion of water sample are placed in test-tubes containing a culture-medium. The tubes are then incubated for a standard time at a standard temperature

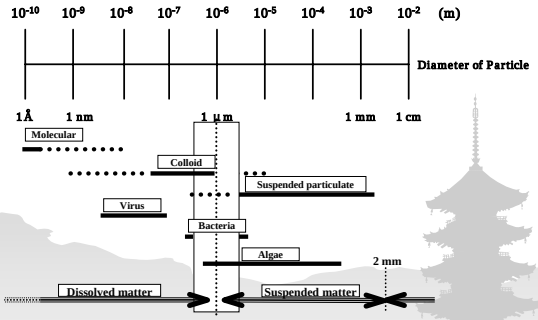
2. "**Membrane filter**" technique ⇦ **To be adopted**

   Measured volume of sample is passed through a fine filter that retains bacteria. The filter is then placed on culture medium and incubated.

Comparison of Method

Multiple fermentation tube technique	Membrane Filter technique
Slower: Requires 48 hrs for a positive	More rapid: Requires 24 hrs
More labor- intensive	Less labor-intensive
Requires more culture medium	Requires less culture medium
More sensitive	Less sensitive
Result obtained indirectly by statistical approximation (low precision)	Results obtained directly by colony count (high precision)
Not readily adaptable for use in the field	Readily adapted for use in the field
Applicable to all types of water	Not applicable to turbid water

Size of Variety of Particles in Water



Membrane Filter Technique

- Introduced in the late 1950s as an alternative to the "Multiple fermentation tube" technique.
- Offers the advantage of <u>isolating discrete</u> colonies of bacteria.

⇕

- Whereas the multiple fermentation tube technique only indicate <u>the presence or absence of an approximate number or organism</u>.

Procedure of Membrane Filter Technique (Outline)

- A definite volume of sample; in the case of drinking water normally 100 mL, is passed through a 47 mm membrane of uniform pore diameter, usually 0.45 μ, using a filter funnel and vacuum system.
- Any organism in the sample are trapped/retained on the surface of the membrane. The filter is then placed in a petri dish with nutrient medium and incubate at an appropriate temperature.
- The passage of nutrients through the filter facilitates the growth of organisms on the upper surface of the membrane.
- The discrete colonies that form on the surface of the membrane is transferred to a colony counter and number of colonies is to be counted.

Outline Procedure

① Measured volume of water is filtered through a cellulose acetate membrane of uniform pore diameter

⇩

② Bacteria are retained on the surface of the membrane

⇩

③ The membrane is placed on a suitable selective medium (culture media) in a sterilized container, and incubated at an appropriate temperature

⇩

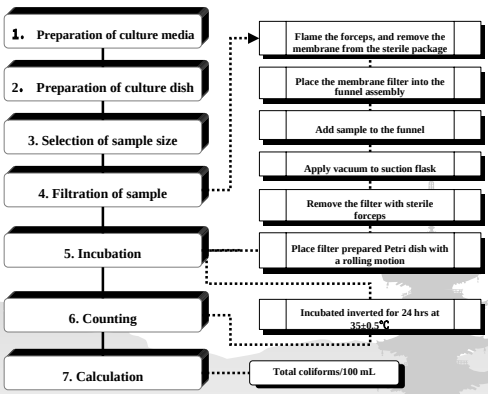
④ If coliforms and/or faecal coliforms are present in the water sample, characteristic colonies form that can be counted directly

(Note: All materials and equipment must be sterilized prior to use)

Apparatus and Materials

① Dilution bottles or tubes,
② Pipets and graduated cylinders,
③ Containers for culture media,
④ Culture dishes (Petri-type dishes),
⑤ Filtration units,
⑥ Filter membrane,
⑦ Forceps,
⑧ Colony counter,
⑨ Sterilizing device (autoclave, oven, etc.)

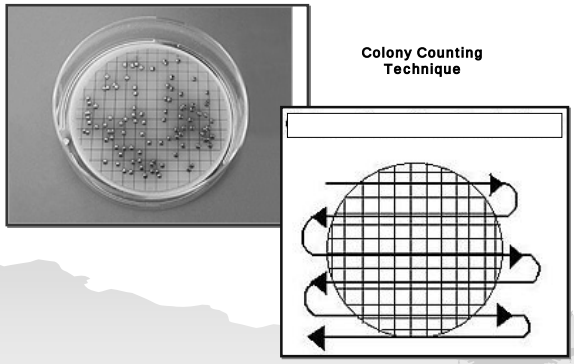
Procedure of Membrane Filter Technique



Colony Counting (1)

- When counting the colonies the entire surface of the filter should be scanned using a 10x -- 15x binocular, wide-field dissecting microscope, etc.
- Number of colonies yield
  - Ideally ····· About 50/membrance
  - Not more than ····· 200/membrance
  - Preferably ····· 20 to 80/membrance
- Counts for each filter should be recorded on the laboratory data sheet.

Colony Counting (2)



Culture Media (1)

- A substance or material used for the growth of coliform bacteria
- To be selected in accordance with kind of coliform bacteria detected
- Can be obtained in the form of dehydrated (Granular culture media)
- M-Endo is a representative culture media for the enumeration of Escherichia coil (e-coli) in the Standard Total Coliform Membrane Filter Method

Culture Media (2)

- Heat-sensitive
- Don't heat any longer than necessary
- Storage of dehydrated culture media
  - To be stored in a dry, dark place at a temperature of about +15 to 25℃
  - Containers should be well sealed and tightly closed
  - Absorption of water leads to pH shifts and eventually clumping

Selection of Sample Size

- To be governed by expected bacteria density
- Ideal sample volume
  - About 50 coliform colonies per membrane,
  - Not more than 200 colonies,
  - Preferably 20 – 80 colonies per membrane
- To be selected in accordance with sample type

Suggested volume to be filtered (1)

Sample type	Sample volume (mL)					
	100	10	1 [1]	0.1 [1,2]	0.01 [1,2]	0.001 [1,2]
Treated drinking water	★					
Partially treated drinking water	★	★				
Recreational water			★	★		
Protected source water		★	★			
Surface water			★	★		
Wastewater			★	★	★	
Discharge from sewage treatment plant		★	★	★	★	
Ponds, rivers, stormwater runoff			★	★	★	★
Raw sewage				★	★	★
Feedlot runoff				★	★	★
Well, spring	★	★				

Suggested volume to be filtered (2)

[1] Small volume should be added to the filtration apparatus together with a minimum of 9 mL of sterile diluent to ensure adequate dispersal across the surface of the filter membrane.

[2] 1.0, 0.1, 0.01 and 0.001 mL volumes are filtered after first preparing serial dilutions of the sample.

To filter:
- 1.0 mL of sample, use 10 mL of 1/10 dilution
- 0.1 mL of sample, use 10 mL of 1/100 dilution
- 0.01 mL of sample, use 10 mL of 1/1,000 dilution
- 0.001 mL of sample, use 10 mL of 1/10,000 dilution

Sample Collection, Preservation, and Handling

- Clean all glassware thoroughly with a suitable detergent and hot water, rinse with hot water to remove all traces of residual washing compound, and finally, rinse with distilled water.
- Sterilize glassware for not less than 2 hr at a temperature of 170℃.
- Sterilize sample bottles not made of plastic, as above, or in an autoclave at 121℃ for 15 min.

Lecture Training
For
Chemical and Biological Water Quality Analysis

Lecture
Sulfide

2007 January

Shinsuke SATO
The JICA Expert Team

1

What is Sulfide ?

- Formally, "Sulfide" is the dianion, S^{2-}
- Chemical compounds containing sulfur in its lowest oxidation number of -2 within sulfur compound cycle.
- Exist in water as a form of **H_2S** (Hydrogen sulfide), **HS^-** (Hydrogen sulfide ion), **S^{2-}** (Sulfide ion), as well as acid-soluble **metallic sulfides** present in suspended matter.
- Ratio of the above substances depends on pH of water

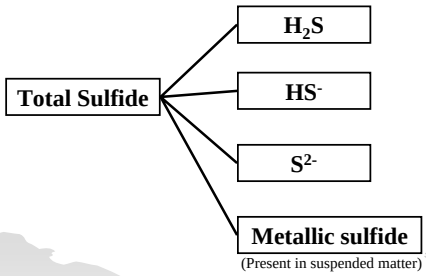
2

Categories of Sulfide

- Total Sulfide
  ⇨ **Dissolved Sulfide** + **Suspended Sulfide**
  - Dissolved Sulfide
    ⇨ H_2S (un-ionized), HS^-, S^{2-}
  - Suspended Sulfide (Un-dissolved)
    ⇨ Metallic Sulfide such as Li_2S, Na_2S

3

Total Sulfide



4

Occurrence and Significance of Sulfide

- Present normally in anaerobic condition
- Often present in groundwater, especially in hot springs
- Produced mostly from the bacterial reduction of sulfate ⇨ Decomposition of organic matter
- Escape into the air from sulfide-containing wastewater ⇨ Causes odor nuisances
- Gaseous H_2S is very toxic
- Oxidized to H_2SO_4 ⇨ Cause of corrosion

5

Determination Method

- ✓ Ion-Selective Electrode Method
- ✓ Methylene Blue Method using Spectrophotometer

⇨ Determination of total sulfide

Sulfide + **Ferric chloride** + **Dimethyl-*p*-phenylenediamine**

⟹ **Methylene blue**

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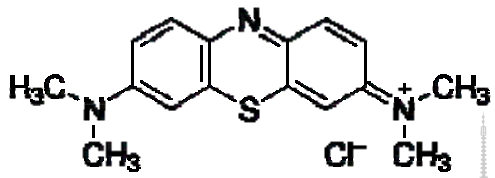
Chemical Structure of Methylene Blue



Chemical Name:

3,7-bis(Dimethylamino)-phenazathionium chloride Tetramethylthionine chloride

7

Sampling and Storage

- Unstable
- Easily oxidized
- Disperse into air making H_2S

⇨ Carry out the test immediately after sampling

8

Sampling and Storage

- Collect samples in clean plastic or glass bottles
- Fill completely and cap tightly
- Take samples with minimum aeration
- Preservation of samples taken
  - ✓ Put zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) solution into the bottles
  - ✓ Add NaOH if necessary (pH should be at least 9)

9

Preparation of Sulfide Standards (1)

- Prepare sulfide standards from sodium nonahydrate ($Na_2S \cdot 9H_2O$) crystals
- Quickly rinse in dissolved-oxygen-free water to remove surface contamination
- Blot crystal dry with a tissue, then rapidly transfer to a tared, stoppered weighing bottle containing 5 to 10 mL dissolved-oxygen-free water
- Determine amount of $Na_2S \cdot 9H_2O$ in weighing bottle by difference, then multiply the weight by 0.133 to determine the amount of S^{2-}

10

Preparation of Sulfide Standards (2)

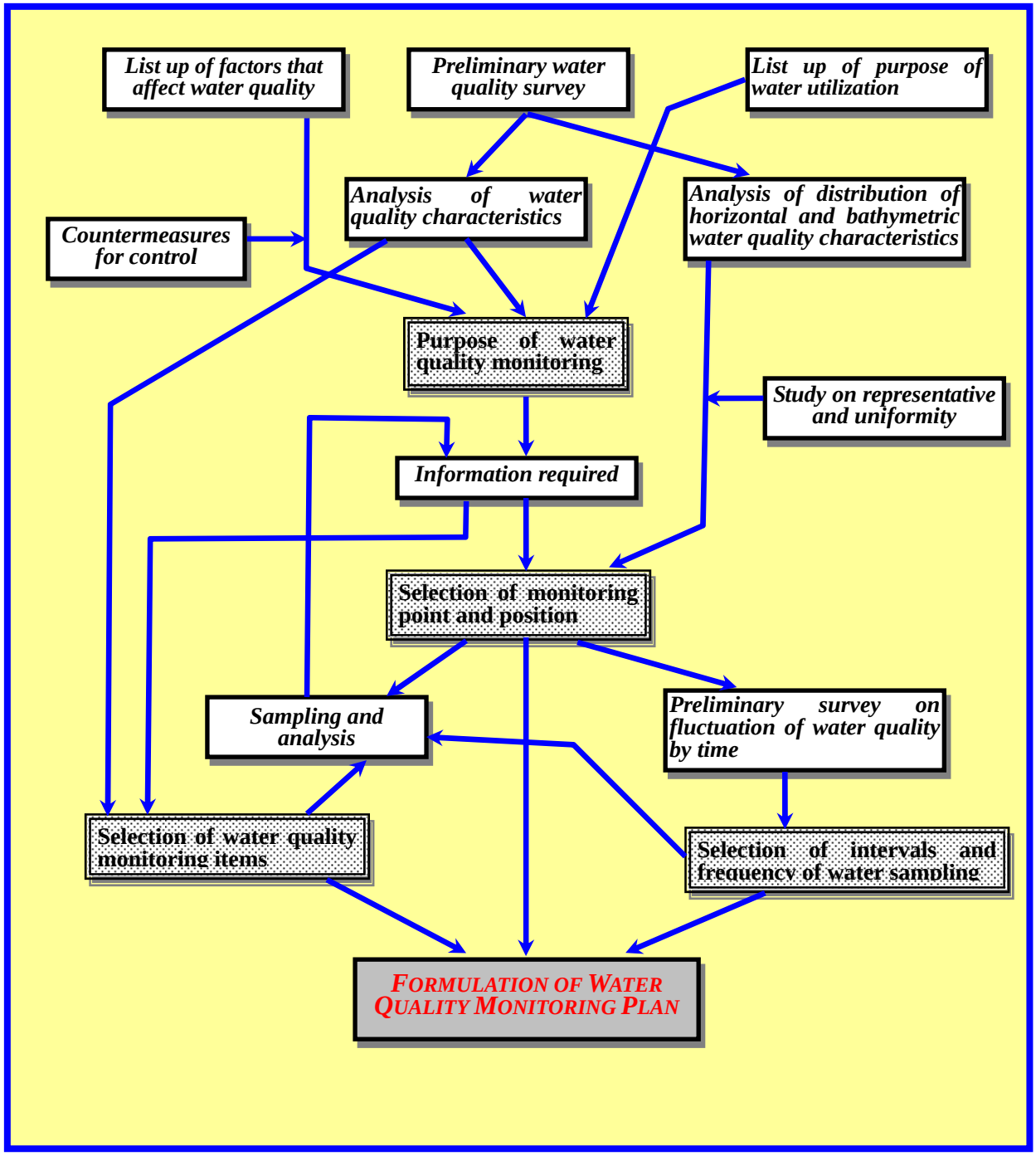
- Avoid excess agitation and mixing of the solution with atmospheric oxygen
- Quantitatively transfer and dilute entire contents of weighing bottle to an appropriate size volumetric flask with dissolved-oxygen-free water to prepare a known concentration sulfide stock solution
- Store stock solution with minimum headspace for no more than 1 week

11

Thank You for Your Kind Attention

12

FORMULATION OF WATER QUALITY MONITORING PLAN



Analysis Using UV/VIS Spectrophotometer

Ⅰ. GENERAL INFORMATION ON UV/VIS SPECTROPHOTOMETER

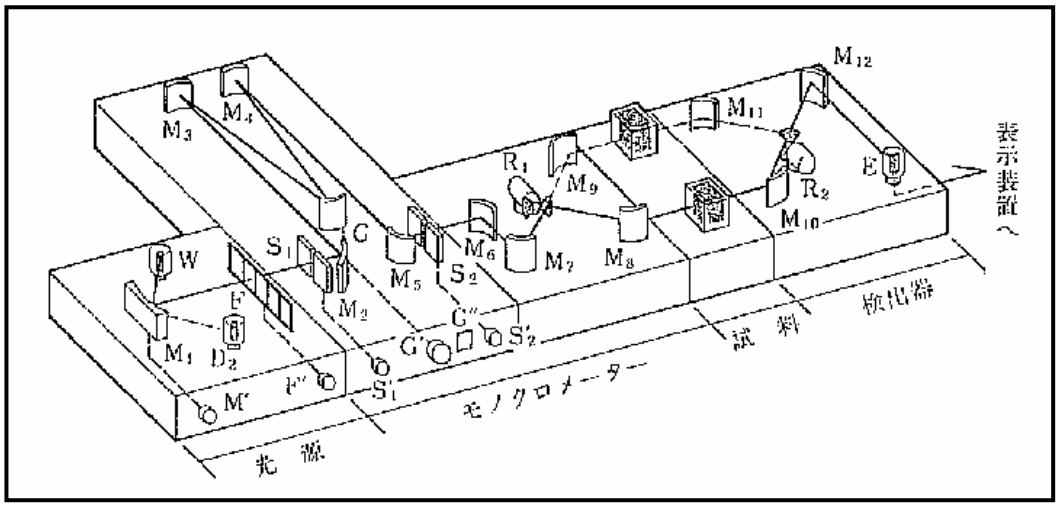
1. UV/VIS Spectrophotometer

Many compounds absorb ultraviolet (UV) or visible (VIS) light. A Spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the color, or more specifically, the wavelength of light. In other word, the spectrophotometer measures how much of the light is absorbed by the sample. The most common application of spectrophotometer is the measurement of light absorption, but they can be designed to measure diffuse or specular reflectance.

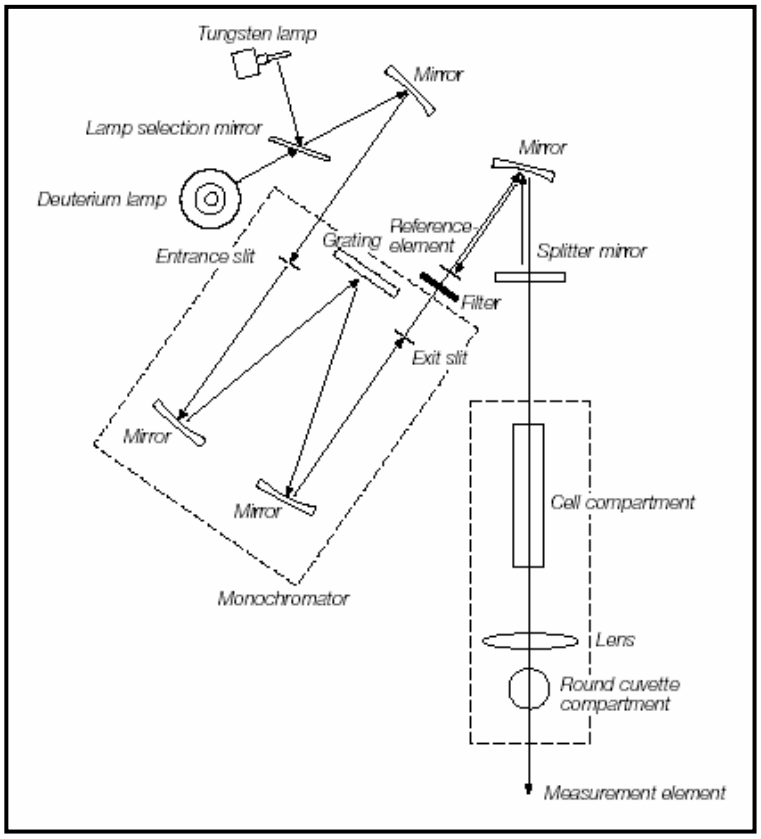
The instrument used in UV/VIS spectroscopy is called a UV/VIS spectrophotometer. To obtain absorption information, a sample is placed on the spectrophotometer and ultraviolet and/or visible light at a certain wavelength (or range of wavelengths) is transmitted through the sample.

UV/VIS spectrophotometer is routinely used in the quantitative determination of solutions of transition metals and highly conjected organic compounds.

There are two major classes of spectrophotometers; single beam and double beam spectrophotometer. In a single-beam ultraviolet-visible spectrophotometer, the light only passes through the sample. In a double-beam ultraviolet-visible spectrophotometer, the light passes through a *beam chopper* which alternately directs the beam through the sample or a reference cell several times per second. A double spectrophotometer measures the ratio of the light intensity on two different paths, and a single beam spectrophotometer measures the absolute light intensity. Although ratio measurements are easier, and generally stabler, single beam instruments have advantages, for instance they can have a large dynamic range.



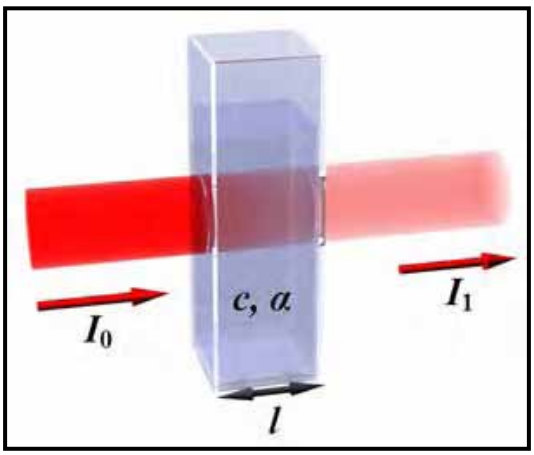
Double Beam Spectrophotometer



Single Beam Spectrophotometer (DR 5000)

2. Beer-Lambert Law

In optics, the **Beer-Lambert law**, also known as **Beer's law** or the **Lambert-Beer law** or the **Beer-Lambert-Bouguer law** is an emprical relationship that relates the absorption of light to the properties of the material through which the light is travelling and is applied to determine concentrations of an absorbing species in solution.



– Transmittance, $T = I_l / I_0$

– % Transmittance, $\%T = 100\ T$

– Absorbance : A

$A = \log_{10} I_0 / I_l = \log_{10} 1/T = -\log_{10} I_l / I_0$

$A = \log_{10} 100/\%T = 2 - \log_{10} \%T$

Here:

A is absorbance,

I_0 is the intensity of the light before it enters the sample,

I_l is the intensity of light at a specified wavelength λ that has passed through a sample (transmitted light intensity),

λ is the wavelength of the light,

c is the concentration of absorbing species in the material (mol/L),

l is the distance that the light travels through the material (the pass length: cm)

There are several ways in which the law can be expressed. Among these, Beer-Lambert law is normally expressed as :

$$\mathbf{A = -\log_{10} I_l / I_0 = \alpha \cdot c \cdot l}$$

Here:

α is a constant known as the molar absorptivity or molar absorptivity (L/mol・cm)

Formula above mentioned shows that the absorbance of a sample is proportional to the thickness of the sample and the concentration of the absorbing species in the sample, in contrast to the transmittance $T = I_l / I_0$ of a sample, which varies exponentially with thickness and concentration. If monochromatic light is used in the appropriate concentration range, the Beer-Lambert law is reliable with great accuracy. Consequently, the concentration of a substance dissolved in liquids can be determined by measuring the absorbance A.

Note that the term absorption refers to the physical process of absorbing light, while absorbance refers to the mathematical quantity. Also, absorbance does not always measure absorption: if a given sample is, for example, a dispersion, part of the incident light will be in fact scattered by the dispersed particles, and not really absorbed. The linear relationship between concentration and absorbance is both simple and straightforward, which is why we prefer to express the Beer-Lambert law using absorbance as a measure of the absorption rather than %T.

3. Application

UV/VIS spectrophotometer is routinely used in the quantitative determination of solutions of transition metals and highly conjugated organic compounds. It is possible to do so because transition metals are often colored because of the possibility of d-d electronic transitions within the metal atoms. Organic molecules, especially those with a high degree of conjugation also absorb light in the UV or visible regions of the electromagnetic spectrum.

The solvents for these determinations are often water for water soluble compounds, or ethanol

for organic-soluble compounds due to the low UV-cutoff.

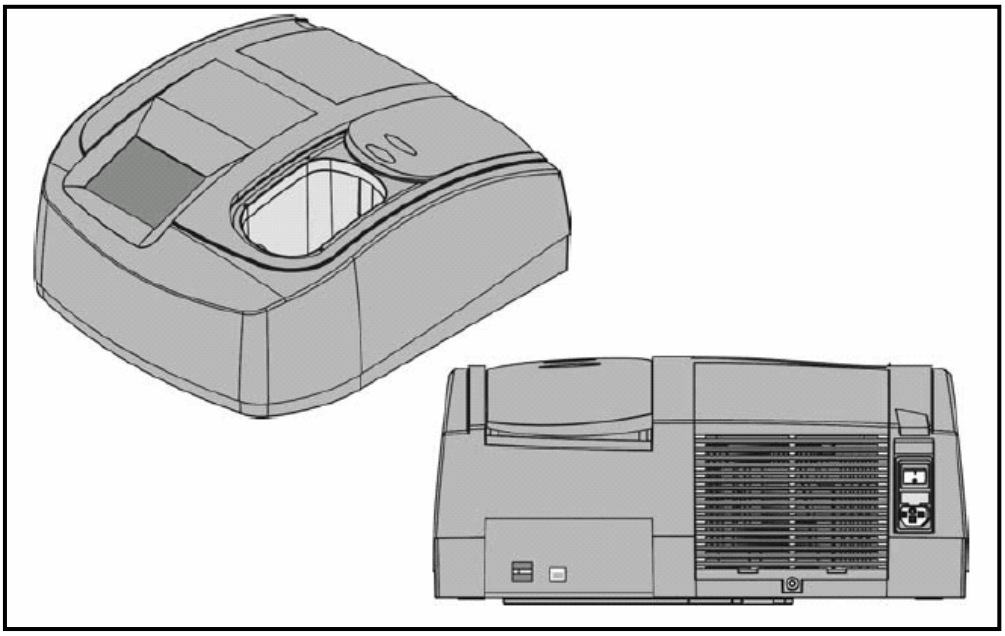
The Beer-Lambert law states that within small ranges, the concentration of the desired compound varies linearly with the absorbance. Thus UV/VIS spectrophotometer can determine the concentration of unknown solution, based on reference molar absorptivity or more accurately, using a calibration curve.

Ⅱ. DR 5000

1. Specifications

Wavelength Range: 190 – 1100 nm
Wavelength Accuracy: ± 1 nm in Wavelength Range 200 - 900 nm
Wavelength Resolution: 0.1 nm
Source Lamp: Gas-filled Tungsten (visible) and Deuterium (UV)

2. Front and Back View



3. Lamp

– The tungsten lamp produces light in the visible spectrum 320 to 1100 nm.
– The deuterium lamp (UV-lamp) available produces light in the ultraviolet spectrum 190 to 360 nm.
– In the overlap zone from 320 to 360 nm, either the deuterium lamp (UV-lamp) or the tungsten lamp can be used for measurements.

The lifetime of the lamps is influenced
– by on-off operation and the length of time in use.
– Typical use is to turn the instrument on for the entire 8-10 hour shift, and then off until the next day.

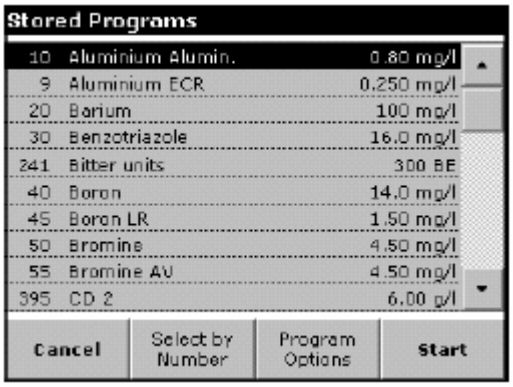
Lamp Component

Material No.
Chem. & Bio. 060717-1

The Lamp compartment is on the left side behind the display and is provided with ventilation on the back side. The tungsten and deuterium (UV) lamp are installed in the lamp compartment. On the back side a fan is installed for cooling of electric components. The ventilation system operates automatically.

4. Determination of Parameters using Stored Programs

1) Selecting a saved test/method



1. Touch **Stored Programs** in the ”Mainenu“ to see an alphabetical list of stored programs with program numbers. The Stored Programs list will appear.
2. Highlight your selection by touching it or **Select by Number** to search for the program by number.

Note: *Use the scroll bar to scroll through the list quickly.*
Note: *If you already know the number of the test or method, touch* ***Select by Number****. Use the alphanumeric keypad to enter the test number and confirm your input by touching* ***OK****.*

3. Touch **Start** to run the program.

Note: *After a program is selected, the screen for that parameter will appear. You do not need to select the wavelength.*
Note: *Follow the chemical procedures described in the corresponding SOP*

4. Touch **Options** for Parameter Setup.
• **More...:** for further Options
• **Store Off/On:** with the **Store On** setting, all measurement data are stored automatically. With the **Store Off** setting, no measurement data are stored.
• **% Trans/Conc/Abs:** to switch to % transmittance, concentration or absorbance readings
• **Send Data icon:** to send Data to a printer, computer or USB memory stick

• **Timer icon:** this functions as a stopwatch. It helps to ensure that the steps of an analysis are correctly timed (e.g. reaction times, wait times, etc., can be exactly specified). When the specified time has elapsed, an acoustic signal is emitted. The use of the timer has no influence on the measurement program.

2) Analysis of Sample

1. Touch **Stored Programs** and select a program.
2. Insert the blank vial into the cell holder and close the cell compartment.
3. Touch **Zero**.

4. Insert the sample vial into the cell holder and close the cell compartment.
5. The result will be displayed.
Note: *If the Reading Mode is set to Single, touch* ***Read*** *to obtain the result.*
Note: *During the warm-up phase of the UV lamp, the message "Warming up" is displayed and the "UV lamp" symbol flashes. As soon as the UV lamp is ready, the blank reading is carried out.*
Note: **Zero** *and* **Read** *are disabled until the cell compartment is closed.*

Water Quality Standards in Japan

Environmental Quality Standards for Water Pollution

Under the Basic Environment Law, Environmental Quality Standards (EQS) for water pollutants are target levels for water quality that are to be achieved and maintained in public waters. These standards are established to achieve two major goals: 1) protection of human health and 2) conservation of the living environment. The former health items are stipulated uniformly for all public water areas as national standard. As regards the latter living environmental items, types of water areas are set up in accordance with the purpose of water use for rivers, lake and reservoirs, and coastal areas, with standard established for each, and environmental quality standards are established specifically by each water use category.

In March 1993, the Environment Agency broadened and strengthened the EQS for protecting human health. As a result, EQS for a total of twenty-three substances including cadmium and total cyanide are now stipulated. These EQS were established with due consideration of potential health hazards associated with the intake of these substances through drinking water and/or fish and shellfish. In addition, twenty-five other items were also selected for precautionary monitoring in water environments. In March 1997, EQS for groundwater pollution were also established.

EQS values for the living environment have been established for biochemical oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), and other variables. To prevent eutrophication, EQS for nitrogen and phosphorus were established for lakes and reservoirs. Provisional guideline values have also been set for sediments contaminated by mercury and polychlorinated biphenyl compounds (PCBs). Removal of the zsediments is required if the guideline values are exceeded.

✧ Environmental Quality Standards for Water Pollutants

Environmental Quality Standards for Human Health

Item	Standard Values
cadmium	0.01 mg/liter or less
total cyanide	0.01 mg/liter or less
lead	0.01 mg/liter or less
chromium (VI)	0.05 mg/liter or less
arsenic	0.01 mg/liter or less
total mercury	0.0005 mg/liter or less
alkyl mercury	not detectable
PCBs	not detectable
dichloromethane	0.02 mg/liter or less
carbon tetrachloride	0.002 mg/liter or less
1, 2-dichloroethane	0.004 mg/liter or less
1, 1-dichloroethylene	0.02 mg/liter or less
cis-1, 2-dichloroethylene	0.04 mg/liter or less
1, 1, 1-trichloroethane	1.0 mg/liter or less
1, 1, 2-trichloroethane	0.006 mg/liter or less
trichloroethylene	0.03 mg/liter or less
tetrachloroethylene	0.01 mg/liter or less
1, 3-dichloropropene	0.002 mg/liter or less
thiuram	0.006 mg/liter or less
simazine	0.003 mg/liter or less
thiobencarb	0.02 mg/liter or less
benzene	0.01 mg/liter or less
selenium	0.01 mg/liter or less

Standard values are the annual mean. However, the value for total CN is the maximum value.
(Source: Environment Agency)

Monitored Substances and Guideline Values

Categories	Guideline Values
chloroform	0.06 mg/liter or less
trans-1, 2-dichloroethylene	0.04 mg/liter or less
1, 2-dichlorpropane	0.06 mg/liter or less
p-dichlorobenzene	0.3 mg/liter or less
isoxathion	0.008 mg/liter or less
diazinon	0.005 mg/liter or less
fenitrothion	0.003 mg/liter or less
isoprothiolane	0.04 mg/liter or less
oxine copper	0.04 mg/liter or less
chlorothaloni	0.008 mg/liter or less
propyzamide	0.006 mg/liter or less
EPN	0.01 mg/liter or less
dichlorvos	0.02 mg/liter or less
fenobucarb	0.008 mg/liter or less
IBP	-
CNP	0.6 mg/liter or less
toluene	0.4 mg/liter or less
xylene di (2-ethylhexyl) phtalate	0.06 mg/liter or less
boron	0.2 mg/liter or less
fluoride	0.8 mg/liter or less
nickel	0.01 mg/liter or less
molybdenum	0.07 mg/liter or less
antimony	0.002 mg/liter or less
nitrate-N and nitrite-N	10 mg/liter or less

(Source : Environment Agency)

✧ Environmental Quality Standards for Conservation of the Living Environment

(a) Rivers

class	Item	Standard value				
	Water use	pH	BOD	SS	DO	Total coliform
AA	Water supply class 1, conservation of natural environment, and uses listed in A-E	6.5-8.5	1 mg/l or less	25 mg/l or less	7.5 mg/l or more	50 MPN/100ml or less
A	Water supply class 2, fishery class 1, bathing and uses listed in B-E	6.5-8.5	2 mg/l or less	25 mg/l or less	7.5 mg/l or more	1000 MPN/100ml or less
B	Water supply class 3, fishery class 2, and uses listed in C-E	6.5-8.5	3 mg/l or less	25 mg/l or less	5 mg/l or more	5000 MPN/100ml or less
C	Fishery class 3, industrial water class 1, and uses listed in D-E	6.5-8.5	5 mg/l or less	50 mg/l or less	5 mg/l or more	-
D	Industrial water class 2, agricultural water, and uses listed in E	6.0-8.5	8 mg/l or less	100 mg/l or less	2 mg/l or more	-
E	Industry water class 3 and conservation of environment	6.0-8.5	10 mg/l or less	Floating Matter such as garbage should not be observed	2 mg/l or more	-

(BOD : Biochemical Oxygen Demand, SS : Suspended Solids, DO : Dissolved Oxygen)

Notes :

1. Standard values are based on daily average values. The same applies to the standard values of lakes and coastal waters.
2. At intake for agriculture, pH shall be between 6.0 and 7.5 and DO shall be more than 5mg/l. The same applies to the standard values of lakes.

(b) Lakes (natural lakes and reservoirs that have 10 million cubic meters of water or more)

class	Item	Standard value				
	Water use	pH	COD	SS	DO	Total coliform
AA	Water supply class 1, fishery class 1, conservation of natural environment,	6.5-8.5	1 mg/l or less	1 mg/l or less	7.5 mg/l or more	50 MPN/100ml or less

class	Item	Standard value				
	Water use	pH	COD	SS	DO	Total coliform
	and uses listed in A-C					
A	Water supply classes 2 and 3, fishery class 2, bathing, and uses listed in B-C	6.5-8.5	3 mg/l or less	5 mg/l or less	7.5 mg/l or more	1000 MPN/100ml or less
B	Fishery class 3, industrial water class 1, agricultural water, and uses listed in C	6.5-8.5	5 mg/l or less	15 mg/l or less	5 mg/l or more	-
C	Industrial water class 2 and conservation of the environment	6.5-8.5	8 mg/l or less	Floating matter such as garbage shall not be observed	2 mg/l or more	-

(COD: Chemical Oxygen Demand, SS: Suspended Solids, DO: Dissolved Oxygen)

class	Item	Standard value	
	Water use	Total nitrogen	Total phosphorus
I	Conservation of natural environment and uses listed in II-V	0.1 mg/l or less	0.005 mg/l or less
II	Water supply classes 1, 2, and 3 (except special types), fishery class 1, bathing, and uses listed in III-V	0.2 mg/l or less	0.01 mg/l or less
III	Water supply class 3 (special types) and uses listed in IV-V	0.4 mg/l or less	0.03 mg/l or less
IV	Fishery class 2 and uses listed in V	0.6 mg/l or less	0.05 mg/l or less
V	Fishery class 3, industrial water, agricultural water, and conservation of the environment	1 mg/l or less	0.1 mg/l or less

Notes:

1. Standard values are set in terms of annual averages.
2. Standard values are applicable only to the lakes and reservoirs where phytoplankton bloom may occur, and standard values for total nitrogen are applicable to lakes and reservoirs where nitrogen limits phytoplankton growth.

3. Standard values for total phosphorus are not applicable to agricultural water uses.

(c) Coastal Waters

class	Item	Standard value				
	Water use	**pH**	**COD**	**DO**	**Total coliform**	**N-hexane Extracts (oil, etc.)**
A	Fishery class 1, bathing, conservation of the natural environment, and uses listed in B-C	7.8-8.3	2 mg/l or less	7.5 mg/l or less	1000 MPN/100ml or less	Not detectable
B	Fishery class 2, industrial water and the uses listed in C	7.8-8.3	3 mg/l or less	5 mg/l or less	-	Not detectable
C	Conservation of the environment	7.8-8.3	8 mg/l or less	2 mg/l or less	-	-

(COD: Chemical Oxygen Demand, DO: Dissolved Oxygen)

Note:Total coliform should be 70MPN/100ml or less for the fishery class 1 to cultivate oyster to be eaten raw.

class	Item	Standard value	
	Water use	Total nitrogen	Total phosphorus
I	Conservation of the natural environment and uses listed in II-IV (except fishery classes 2 and 3)	0.2 mg/l or less	0.02 mg/l or less
II	Fishery class 1, bathing, and the uses listed in III-IV (except fishery classes 2 and 3)	0.3 mg/l or less	0.03 mg/l or less
III	Fishery class 2 and the uses listed in IV (except fishery class 3)	0.6 mg/l or less	0.05 mg/l or less
IV	Fishery class 3, industrial water, and conservation of habitable environments for marine biota	1 mg/l or less	0.09 mg/l or less

Note:

1. Standard values are set in terms of annual averages.
2. Standard values are applicable only to marine areas where marine phytoplankton blooms may occur.

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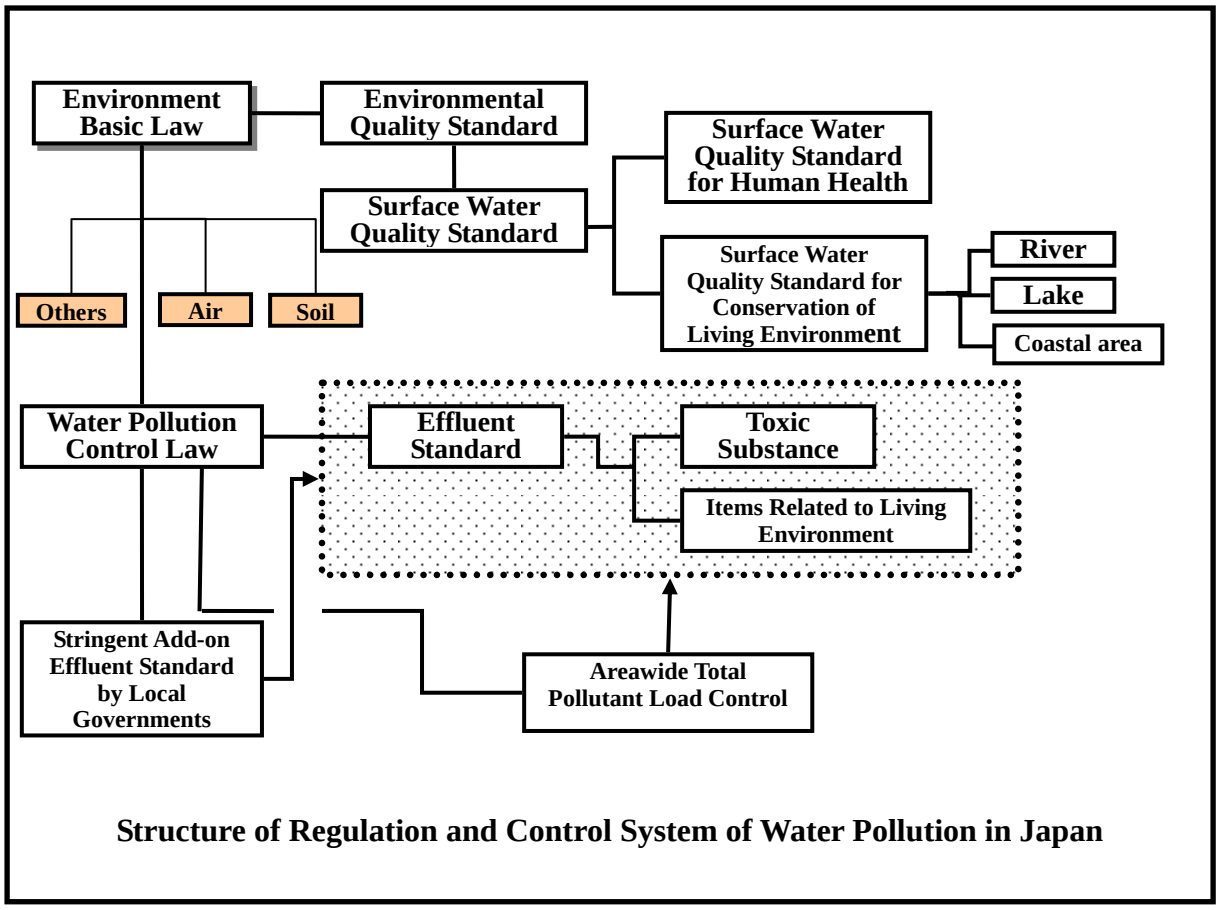
✧ Effluent Standard (Toxic Substances)

Kind of Toxic Substance	Maximum Allowable Concentration	Kind of Toxic Substance	Maximum Allowable Concentration
Cadmium compounds	0.1 mg/l	Carbontetrachloride	0.02 mg/l
Cyanide	1 mg/l	1,2-Dichloroethane	0.04 mg/l
Organophosphorus compounds (limited to parathion, methyl parathion, methyl dimethon and EPN)	1 mg/l	1,1-Dichloroethylene	0.2 mg/l
Lead and its compounds	0.1 mg/l	Cis-1,2-Dichloroethylene	0.4 mg/l
Chromium (VI) compounds	0.5 mg/l	1,1,1-Trichloroethane	3 mg/l
Arsenic and its compounds	0.1 mg/l	1,1,2-Trichloroethane	0.06 mg/l
Total mercury	0.005 mg/l	1,3-dichloropropene	0.02 mg/l
Alkyl mercury	Not detected	Thiram	0.06 mg/l
PCB	0.003 mg/l	Simazine	0.03 mg/l
Tri-chloroethylene	0.3 mg/l	Thiobencarb	0.2 mg/l
Tetra-chloroethylene	0.1 mg/l	Benzene	0.1 mg/l
Di-chloromethane	0.2 mg/l	Selenium and its compounds	0.1 mg/l

✧ Effluent Standard (Items Related to Living Environment)

Item	Maximum Allowable Concentration	Item	Maximum Allowable Concentration
pH	5.8 – 8.6(excluding coastal area) 5.0 – 9.0(Coastal area)	Zinc (Zn)	5 mg/l
BOD	160 mg/l(Daily average 120)	Soluble iron (Fe)	10 mg/l
COD	160 mg/l(Daily average 120)	Soluble manganese (Mn)	10 mg/l
SS	200 mg/l(Daily average 150)	Chromium (Cr)	2 mg/l
N-Hexane extracts (mineral oil)	5 mg/l	Fluorine (F)	15 mg/l
N-Hexane extracts(vegetable and animal oil)	30 mg/l	Number of coliform group	Daily average 3,000/cm3
Phenols	5 mg/l	Total Nitrogen (N)	120 mg/l(Daily average 60)
Copper (Cu)	3 mg/l	Total Phosphorous	16 mg/l(Daily average 8)



Structure of Regulation and Control System of Water Pollution in Japan

Electric Conductivity of Natural Water

Kind of Natural Water	EC (μ S/cm)
Rainwater	10 – 30
River water	
Upstream	50 – 100
Downstream	200 - 400

Concentration of Nitrate in Natural Water

Kind of Natural Water	Nitrate NO3-N (mg/L)
Rainwater	0.2 – 0.4
River water	
Upstream	0.2 – 1
Downstream	2 – 6
Spring water, Groundwater (Tokyo)	2 - 10

Concentration of Ammonia in Natural Water

Kind of Natural Water	Ammonia NH3-N (mg/L)
Rainwater	0.1 – 0.4
River water	
Upstream	Less than 0.05
Downstream	0.5 – 5
Spring water	Less than 0.05

Concentration of Phosphorous in Natural Water

Kind of Natural Water	Phosphorus PO4-P (mg/L)
Rainwater	0.5
River water	
Upstream	Less than 0.05
Downstream	0.1 – 1.0

1. Review of Concept of pH

pH is a measure of the activity of hydrogen ions (H^+) in a solution and, therefore, its acidity. For dilute solutions, however, it is convenient to substitute the activity of the hydrogen ions with the molarity (mol/L) of the hydrogen ions.

In aqueous systems, the hydrogen ion activity is dictated by the dissociation constant of water given below:

$Kw = [H^+][OH^-]/[H_2O] = 1.8 \times 10^{-16}$

Here, $[H_2O] = 1{,}000/18$ (mol/L)

$[H^+][OH^-] = 1{,}000/18 \times 1.8 \times 10^{-16}$

$= 1.0 \times 10^{-14}$

pH is generally expressed without units, the number arises from a definition based on the activity of hydrogen ions in the solution. The pH scale is a reverse logarithmic representation of relative hydrogen proton (H+) concentration.

Due to this dissociation constant, a neutral solution (hydrogen ion activity equals hydroxide ion activity) has a pH of approximately 7. Aqueous solutions with pH values lower than 7 are considered acidic, while pH values higher than 7 are considered basic.

The precise formula for calculating pH is:

$$\mathrm{pH} = -\log_{10}(a_{H+})$$

a_{H^+} denotes the activity of H^+ ions, and is unitless.

Some common pH values

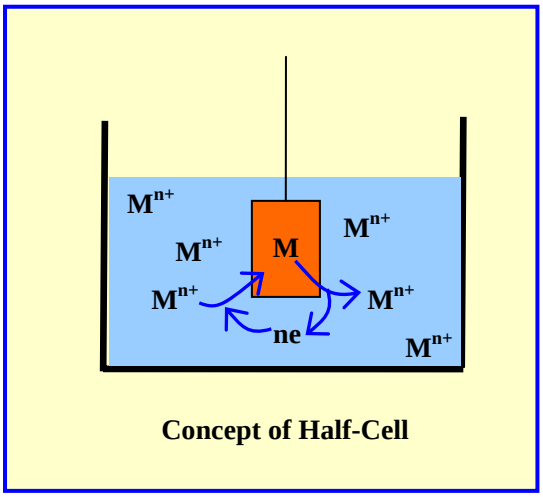
Substance	pH
Acid mine runoff	-3.6 – 1.0
Battery acid	-0.5
Gastric acid	1.5 – 2.0
Lemon juice	2.4
Cola	2.5
Vinegar	2.9
Orange or apple juice	3.5
Beer	4.5
Acid Rain	<5.0
Coffee	5.0
Tea or healthy skin	5.5
Milk	6.5
Pure water	7.0
Healthy human saliva	6.5 – 7.4
Blood	7.34 – 7.45
Sea water	8.0
Hand soap	9.0 – 10.0
Household ammonia	11.5
Bleach	12.5
Household lye	13.5

The pH can be measured by using pH meter together with pH-selective electrodes. A pH meter is the kind of ion selective electrode that measure the activity of hydrogen ions in the solution.

2. Concept of Electrode Potential

Basis of Potentiometric Analysis

Suppose that metal plate M is immersed into the solution of metal ion M^{n+}.
The metal M that is composed of the metal atom has a tendency to dissolve into the solution to become metal ion M^{n+}. In other word, the metal M is oxidized to metal ion M^{n+}, and release electron on the metal plate.
On the other hand, ion M^{n+} in the solution has a tendency to deposit on the plate as a metal. In other word, the metal ion M^{n+} is reduced to the metal receiving electron.



Concept of Half-Cell

$$M^{n+} + ne \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} M$$

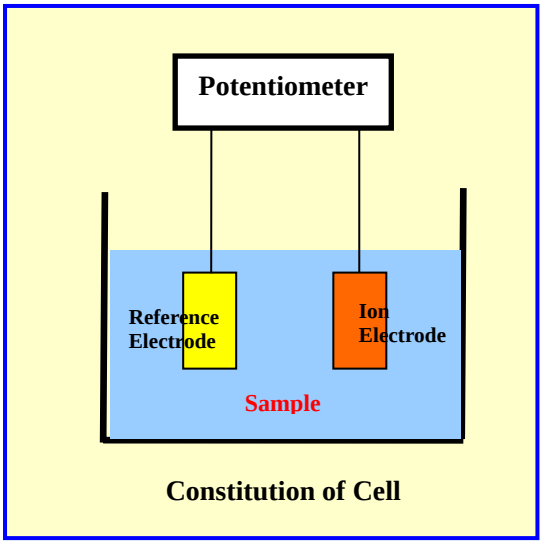
E

Electrode Potential

When the oxidation-reduction reaction above mentioned reaches equilibrium, the metal plate (electrode) shows the constant electric potential to the solution. Equilibrium means that the transfer of ions from the metal plate into solution is equal to the transfer from the solution to the metal plate. The potential difference (E) is described by the **Nernst equation**:

$$E = E_0 + RT/nF \cdot \ln a$$

where E_0 is the formal electrode potential, R is the gas constant, T is temperature in Kelvins, n is the number of electrons transferred, F is Faraday's constant, and *a* is the activity of the analyte ion.



Constitution of Cell

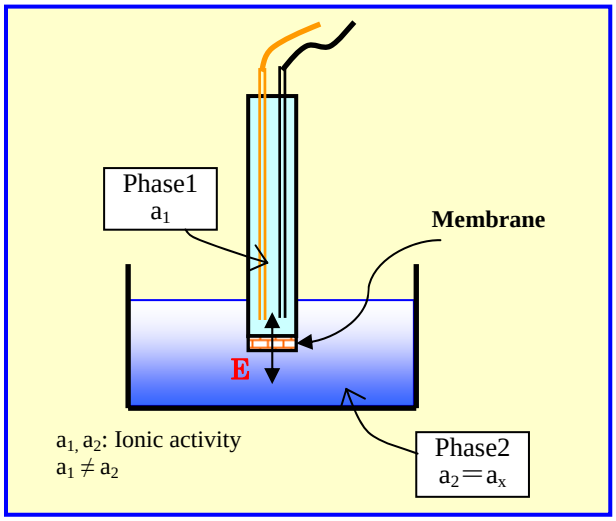
Due to the reason that the electrode potential of the half-cell can not be measured individually, the electromotive force of a cell that is constituted combining two half-cells is measured. This is the basis of the potentiometric analysis.

3. Ion Selective Electrode

2-1 General

Chemical sensors are miniaturized analytical devices, which can deliver real-time and on-line information on the presence of specific compounds or ions in complex samples. Ion selective electrode is the electrode that responses the specific ion dissolved in a solution, and generally called as an **Ion-selective electrode (ISE).** Among various classes of chemical sensors, ion-selective electrodes (ISE) are one of the most frequently used potentiometric sensors during laboratory analysis as well as in industry, process control, physiological measurements, and environmental monitoring.

An ISE is a transducer (sensor) which converts the activity of a specific ion dissolved in a solution into an electrical potential which can be measured by a voltmeter. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. The sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode.



An ion-selective membrane is the key component of all potentiometric ion sensors. It establishes the preference with which the sensor responds to the specific ion in the presence of various interfering ions from the sample. If ions can penetrate the boundary between two phases, then an electrochemical equilibrium will be reached. When the membrane separates two solutions of different ionic activities (a_1 and a_2) and provided the membrane is only permeable to this single type of ion, the potential difference (E) across the membrane is described by the Nernst equation:

$$\mathbf{E = RT/nF \cdot ln\ (a_2/a_1)}$$

If the activity of the target ion in phase 1 is kept constant, the unknown activity in phase 2 ($a_2 = a_x$) is related to (E) by:

$$\mathbf{E = RT/n_xF \cdot ln\ (a_x/a_1)}$$

$$= RT/n_xF \cdot (2.303\log(a_x) - 2.303\log(a_1))$$

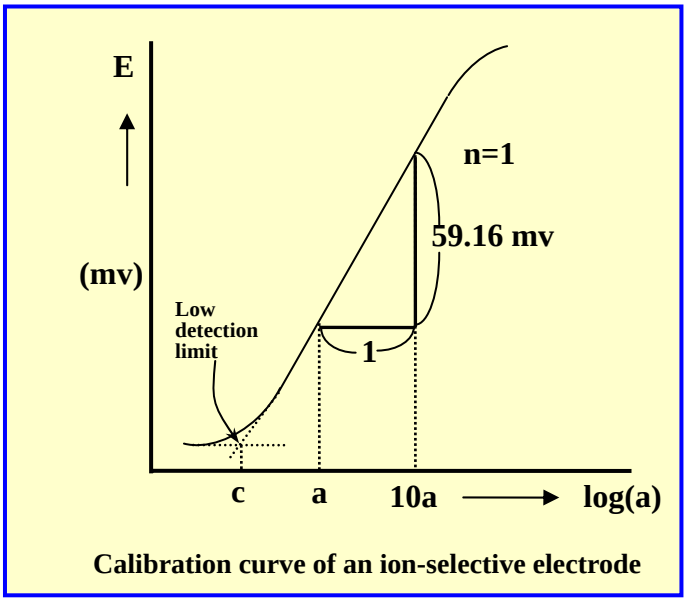
$$= const + S \cdot \log(a_x)$$

where,

a: ionic activity ($a = \gamma C$), γ: coefficient of activity, C: concentration of ion, $\gamma < 1$, S=59.16/n [mV] at 298 K and n_x - the charge of the target ion.

Nernst equation above mentioned shows that a plot of measured potential versus log(*a*) will therefore give a straight line. In practice the potential difference i.e. the electromotive force is measured between an ion selective electrode and a reference electrode, placed in the sample solution.

Using a series of calibrating solutions the response curve or calibration curve of an ion-selective electrode can be measured and plotted as the signal (electromotive force) versus the activity of the target ion. The linear range of the calibration curve is usually applied to determine the activity of the target ion in any unknown solution. However, it should be pointed out that only at constant ionic strength, a linear relationship between the signal measured and the concentration of the target ion is maintained. In order to keep a ionic strength in constant, the ion that does not react with the target ion, and does not affect the electrode potential is added to the sample and the standard solutions generally. The solution that contains the ions mentioned above are so called “Ionic Strength Adjuster (ISA)”.



Calibration curve of an ion-selective electrode

2-2 Membrane

As mentioned before, the sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode.

Types of ion-selective membrane

There are four main types of ion-selective membrane used in ion-selective electrodes:

1) Glass membranes

Glass membranes are made from an ion-exchange type of glass (silicate of chalcogenide). This type of ISE has good selectivity, but only for several single-charged cations; mainly H^+, Na^+, and Ag^+. Chalcogenide glass also has selectivity for double-charged metal ions, such as Pb^{2+}, and Cd^{2+}. The glass membrane has excellent chemical durability and can work in very aggressive media. A very common example of this type of electrode is the pH glass electrode.

2) Crystalline membranes

Crystalline membranes are made from mono- or polycrystallites of a single substance. They have good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response. Selectivity of crystalline membranes can be for both cation and anion of the membrane-forming substance. An example is the fluoride selective electrode based on LaF_3 crystals. The electrodes of chloride, cyanide, sulfide are also equipped with this type of membrance.

3) Ion exchange resin membranes

Ion-exchange resins are based on special organic polymer membranes which contain a specific ion-exchange substance (resin). This is the most widespread type of ion-specific electrode. Usage of specific resins allows preparation of selective electrodes for tens of different ions, both single-atom or multi-atom. They are also the most widespread electrodes with anionic selectivity. However, such electrodes have low chemical and physical durability as well as "survival time". An example is the potassium selective electrode, based on valinomycin as an ion-exchange agent.

4) Enzyme electrodes

Enzyme electrodes definitely are not true ion-selective electrodes but usually are considered within the ion-specific electrode topic. Such an electrode has a "double reaction" mechanism - an enzyme reacts with a specific substance, and the product of this reaction (usually H^+ or OH^-) is detected by a true ion-selective electrode, such as a pH-selective electrodes. All these reactions occur inside a special membrane which covers the true ion-selective electrode, which is why enzyme electrodes sometimes are

considered as ion-selective. An example is glucose selective electrodes.

2-3 Properties of Ion Selective Electrode

The properties of an ion-selective electrode are characterized by parameters like:

Selectivity

The selectivity is one of the most important characteristics of an electrode, as it often determines whether a reliable measurement in the sample is possible or not.

Slope

Slope of the linear part of the measured calibration curve of the electrode. The theoretical value according to the Nernst equation is: 59.16 [mV/log(a_x)]at 298 K for a single charged ion or 59.16/2 = 29.58 [mV per decade] for a double charged ion. A useful slope can be regarded as 50-60 [mV per decade] (25-30 [mV per decade] for double charged ion respectively). However, in certain applications the value of the electrode slope is not critical and worse value does not exclude its usefulness.

Range of linear response

At high and very low target ion activities there are deviations from linearity. Typically, the electrode calibration curve exhibits linear response range between 10^{-1}M and 10^{-5}M.

Detection limit

According the IUPAC recommendation the detection limit is defined by the cross-sectionof the two extrapolated linear parts od the ion-selective calibration curve. In practice, detection limit on the order of 10^{-5}-10^{-6}M is measured for most of ion-selective electrodes. The observed detection limit is often governed by the presence of other interfering ions or impurities. If for example metal buffers are used to eliminate the effects which lead to the contamination of very dilute solutions, it is possible to enhance the detection limit down to 10^{-10}M.

Response time

In earlier IUPAC recommendations, it was defined as the time between the instant at which the ion-selective electrode and a reference electrode are dipped in the sample solution (or the time at which the ion concentration in a solution is changed on contact with ISE and a reference electrode) and the first instant at which the potential of the cell

becomes equal to its steady-state value within 1 [mV] or has reached 90% of the final value (in certain cases also 63% or 95%).This definition can be extended to consider the drift of the system. In this case, the second time instant is defined as the one at which the EMF/time slope becomes equal to a limiting value. However, it should be pointed out that a single time constant does not describe the form of the electrode response function. Moreover, in many investigations the response time of the overall measuring system is determined, which influences on the response time of the ISE.

2-4 Interferences

The most serious problem limiting use of ion-selective electrodes is interference from other, undesired, ions. No ion-selective electrodes are completely ion-specific; all are sensitive to other ions having similar physical properties, to an extent which depends on the degree of similarity. Most of these interferences are weak enough to be ignored, but in some cases the electrode may actually be much more sensitive to the interfering ion than to the desired ion, requiring that the interfering ion be present only in relatively very low concentrations, or entirely absent. In practice, the relative sensitivities of each type of ion-specific electrode to various interfering ions is generally known and should be checked for each case; however the precise degree of interference depends on many factors, preventing precise correction of readings. Instead, the calculation of relative degree of interference from the concentration of interfering ions can only be used as a guide to determine whether the approximate extent of the interference will allow reliable measurements, or whether the experiment will need to be redesigned so as to reduce the effect of interfering ions.

Summary of Analysis using UV/VIS Spectrophotometer/DR-5000/HACH

Parameter		Phosphorus, Reactive (Orthophosphate)			Chromium, Total		
Method	No.	8048			8024		
	Method	Ascorbic Acid method			Alkaline Hypobromite Oxidation Method		
	Scope and Application	1.For water, wastewater, and seawater 2.Equivalent to USEPA method 365.2 and Standard Method 4500-P-E for wastewater			1.For water and wastewater 2.Equivalent to Standard Method 3500-CRD for wastewater		
	Principle	Orthophosphate react with molybdate in an acid medium to produce a mixed phosphate/molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. Test results are measured at 880 nm.			Trivalent chromium in the sample is oxidized to the hexavalent form by hypobromite ion under alkaline conditions. The sample is acidified. The total chromium content is determined by the **1,5-Diphenylcarbohydrazide method.** Determine trivalent chromium by subtracting the results of a separate hexavalent chromium test from the results of the total chromium test. Test results are measured at 540 nm.		
Program No.		490			100		
Range		0.02 to 2.50 mg/L PO_4^{3-}			0.01 to 0.70 mg/L		
Required Reagents		**Name**	**Q'ty/Test**	**Cat. No.**	**Name**	**Q'ty/Test**	**Cat. No.**
		1.PhosVer®3 Phosphate Reagent Powder Pillows, 10-mL	1	21060-69	1.Acid Reagent Powder Pillows	1	2126-99
					2.ChromaVer®3 Chromium Reagent Powder Pillows	1	12066-99
					3.Chromium 1 Reagent Powder Pillows	1	2043-99
					4. Chromium 2 Reagent Powder Pillows	1	2044-99
Required Apparatus		**Name**		**Q'ty/Test**	**Name**		**Q'ty/Test**
		1.Sample Cells, 1-inch square, 10 mL, matched pair		2	1.Sample Cells, 1-inch square, 10 mL, matched pair		2
		2.Stopper for 18mm Tube		1	2.Sample Cell, 10-20-25 mL, with cap		1
					3. Hot plate, Water bath and Rack		1
Sample Collection, Storage, and Preservation		Collect sample in plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in phosphate analysis. Analyze samples immediately for best results. If prompt analysis is not possible, preserve samples by filtering immediately and storing at 4℃ for up to 48 hours. The sample should be at room temperature before analysis.			Collect sample in acid-washed glass or plastic containers. To preserve samples, adjust the pH to 2 or less with nitric acid. This requires approximately 2 mL per liter of the acid. Store preserved samples at room temperature up to six months. Adjust the pH to about 4 with 5.0 N Sodium Hydroxide before analysis. Correct the test result for volume additions.		

Parameter		Chromium, Hxavalent			Nitrogen, Ammonia		
Method	No.	8023			8038		
	Method	1,5-Diphenylcarbohydrazide Method			Nessler Method		
	Scope and Application	1.For water and wastewater 2.Adapted from Standard Methods for the Examination of Water and Wastewater			1.For water, wastewater, and seawater 2.USEPA accepted		
	Principle	Hexavalent chromium is determined by the 1,5-Diphenylcarbohydrazide method using a single a single dry powder formulation called ChromaVer 3 Chromium Reagent. This reagent contains an acidic buffer combined with 1,5-Diphenylcarbohydrazide, which reacts to give a purple color when hexavalent chromium is present. Test results are measured at 540 nm.			The Mineral Stabilizer complexes hardness in the sample. The Polyvinyl Alchol Dispersing Agent aids the color formation in the reaction of Nessler Reagent with ammonium ions. A yellow color is formed proportional to the ammonia concentration. Test results are measured at 425 nm.		
Program No.		90			380		
Range		0.010 to 0.700 mg/L Cr(VI)			0.02 to 2.50 mg/L NH_3-N		
Required Reagents		Name	Q'ty/Test	Cat. No.	Name	Q'ty/Test	Cat. No.
		1.ChromaVer®3 Chromium Reagent Powder Pillows	1	12710-99	1.Nessler Reagent	2 mL	21194-49
					2.Mineral Stabilizer	6 drops	23766-26
					3.Polyvinyl Alcohol Dispersing Agent	6 drops	23765-26
					4.Deionized water	25 mL	
Required Apparatus		Name		Q'ty/Test	Name		Q'ty/Test
		1.Sample Cells, 1-inch square, 10mL, matched pair		2	1.Cylinder, graduated, mixing, 25-mL		2
					2.Paazipet, 1-mL		2
					3.Pipet filler, safety bulb		1
					4.Sample Cells, 1-inch square, 10-mL, matched pair		2
Sample Collection, Storage, and Preservation		Collect samples in a cleaned glass or plastic container. Store at 4℃(39F) up to 24 hours. Samples must be analyzed within 24 hours.			Collect sample in clean glass or plastic bottles. If chlorine is present, add one drop of 0.1 N Sodium Thiosulfate for each 0.3 mg/L Cl_2 in a 1-liter sample. Preserve the sample by reducing the pH to 2 or less with sulfuric acid (at least 2 mL). Store at 4℃(39F) 尾rえss。Preserved sample may be stored up to 28 days. Warm samples to room temperature and neutralize with 5 N Sodium Hydroxide before analysis. Correct the test result for volume additions.		

Parameter		Surfactants, Anionic (Detergents)					
Method	No.	8028					
	Method	Crystal Violet Method					
	Scope and Application	For water , wastewater, and seawater					
	Principle	Detergents, ABS (alkyl benzene sulfonate), or LAS (linear alkklate sulfonate) are determined by association with crystal violet dye and extraction of the ion-pair complex into benzene. Test results are measured at 605 nm.					
Program No.		710					
Range		0.002 to 0.275 mg/L as LAS					
Required Reagents		Name	Q'ty/Test	Cat. No.	Name	Q'ty/Test	Cat. No.
		1.Benzene, ACS	55 mL				
		2.Buffer Solution, sulfate-type	10 mL	452-49			
		3.Detergent Reagent Powder Pillows	1 pillow	1008-68			
Required Apparatus		Name		Q'ty/Test	Name		Q'ty/Test
		1.Clippers, for opening powder pillow		1			
		2.Cylinder, graduated, 25 mL		1			
		3.Cylinder, graduated, 50 mL		1			
		4.Cylinder, graduated 500 mL		1			
		4.Funnel, separatory, 500 mL		1			
		5.Sample cells, 10, 25 mL stoppered		2			
		6.Support ring, and stand		1			
Sample Collection, Storage, and Preservation		Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible, but they may be stored at least 24 hours by cooling to 4 °C (39F). Warm to room temperature before testing.					

1. Oil & Grease in Water

How to measure/determine?

1) Determination of Oil content,

2) Observation under microscope,

3) Measurement of particle size distribution (Coulter Counter Method)

4) Analysis of composition (Analysis using GC, GC/MS, etc.)

2. Principle of Determination of Oil & Grease in Water

1) Definition

Group of substances with similar physical characteristics that are determined quantitatively on the basis of their common solubility in an organic extracting solvent

⇒ **Any material recovered as a substance soluble in the solvent, and not volatilized during the test**

2) Method

① Partition-Gravimetric Method,

② Partition-Infrared Method,

③ Partition-Fluorescence Method

④ Soxhlet method ⇒ Designed for samples that might contain volatile hydrocarbons

3) Solvent

① Petroleum ether,

② n-hexane, ⇒ JIS, US EPA recommend

③ Trichlorotrifluoroethane,

⇒ Dropped due to the environmental problem associated with chlorofluorocarbons

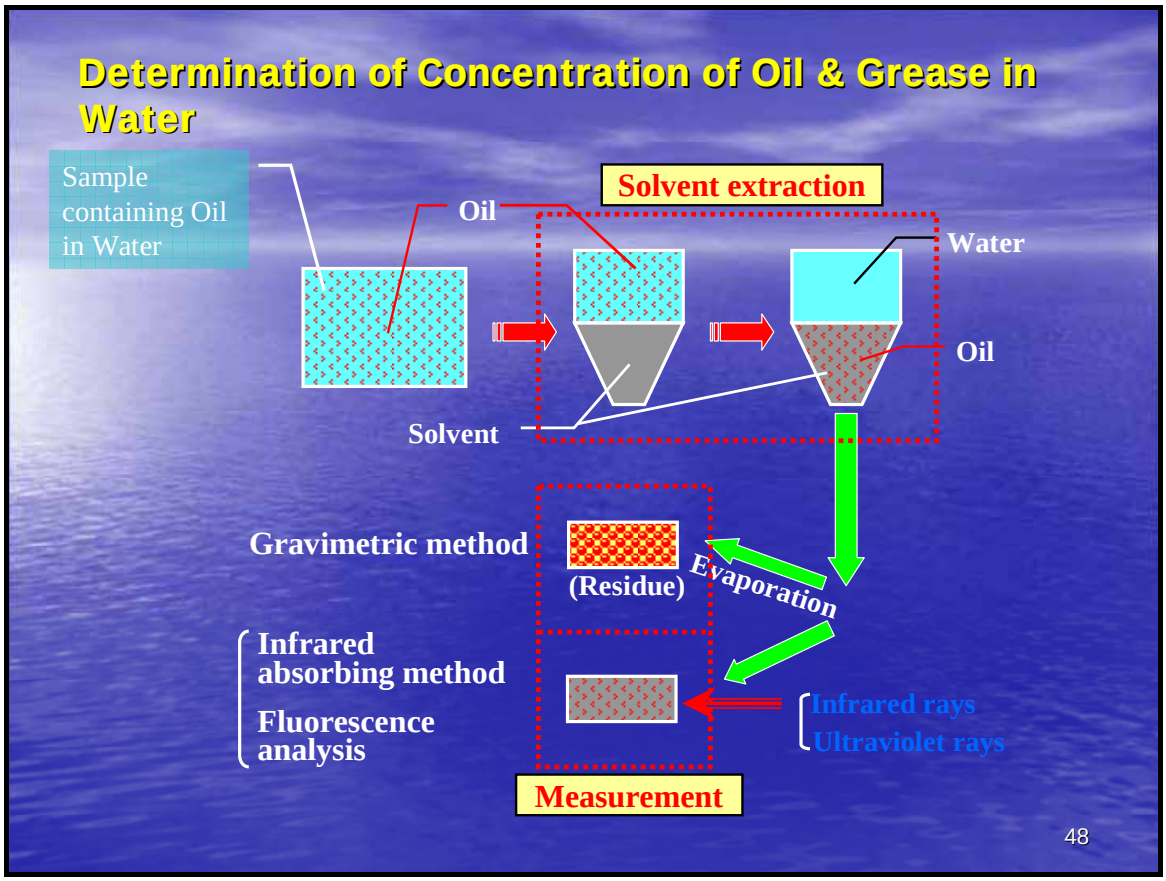
④ 80% n-hexane and 20% methyl-*tert*-butyl ether),

⑤ Tetrachloromethane,

➡ Dropped due to the environmental problem associated with chlorofluorocarbons

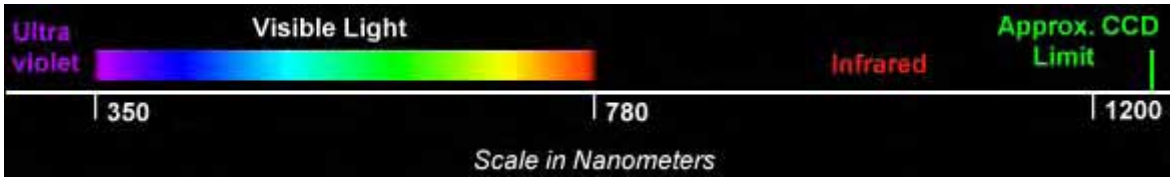
⑥ **Chlorotrifluororhylene (S-316)**

Solvent recycling is strongly recommended

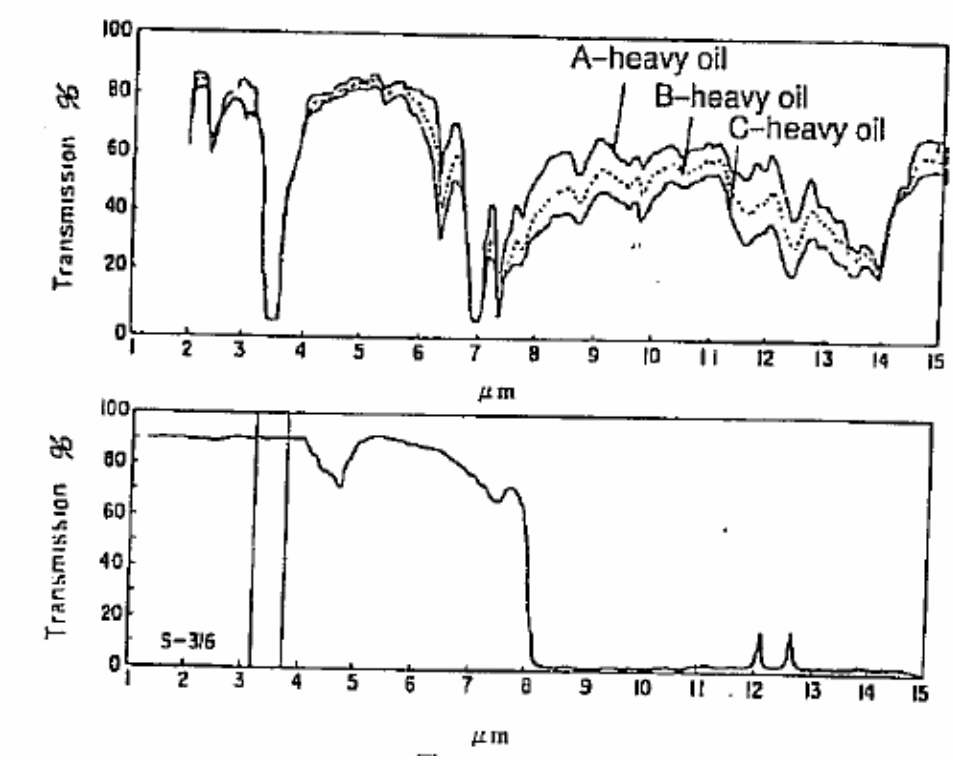


What is Infrared Light?

Infrared light is light which has a wavelength longer than that which the human eye can see. If infrared light were visible you'd see it above the red in a rainbow. The graph below shows where infrared lies on the electromagnetic scale:



You can see here that visible light lies between 350nm and 780nm from violet to red. Similarly, ultra-violet light is also invisible to the eye but lies above the range of visibility. Infrared is often used for surveillance where it is necessary to monitor dark places without people being aware of the filming. The cameras can see the infrared light clearly lighting the scene up, but to the human eye it is totally dark.



Material No.
Chem. & Bio. 060703-1

The HORIBA oil content meter (OCMA-310) measures absorption in the 3.4 – 3.5 micrometer range. The two graph above show the absorption spectra of petroleum and (2) S-316 solvent. All hydrocarbons, including oils, absorb infrared radiation between 3.4 – 3.5 micrometers. As a result, the unit measures any hydrocarbons un the extraction solvent without distortion of values due to the presence of the solvent.

3. Regulation in Japan

Effluent Standard (Items related to Living Environment)

Item	Maximum Allowable Concentration	Item	Maximum Allowable Concentration
pH	5.8 – 8.6(excluding coastal area) 5.0 – 9.0(Coastal area)	Zinc (Zn)	5 mg/l
BOD	160 mg/l(Daily average 120)	Soluble iron (Fe)	10 mg/l
COD	160 mg/l(Daily average 120)	Soluble manganese (Mn)	10 mg/l
SS	200 mg/l(Daily average 150)	Chromium (Cr)	2 mg/l
N-Hexane extracts (mineral oil)	5 mg/l	Fluorine (F)	15 mg/l
N-Hexane extracts(vegetable and animal oil)	30 mg/l	Number of coliform group	Daily average 3,000/cm3
Phenols	5 mg/l	Total Nitrogen (N)	120 mg/l(Daily average 60)
Copper (Cu)	3 mg/l	Total Phosphorous	16 mg/l(Daily average 8)

Environmental Water Quality Standards for the Conservation of Living Environment for Coastal Area

Category	Adaptation of Water Use	Standard Value				
		pH	COD	DO	Total coliform	N-Hexane extracts
A	· Water supply: class-1 · Bathing · Natural environment preservation, and · Other uses listed in B and C columns	7.8 – 8.3	2 mg/L or less	7.5 mg/L or more	1,000 MPN/100ml or less	Not detected
B	· Water supply: class-2, · Industrial water, and · Other uses listed in C column	7.8 – 8.3	3 mg/L or less	5 mg/L or more		Not detected
C	· Industrial water	7.0 – 8.3	8 mg/L or less	2 mg/L or more		

Sulfide

1. Occurrence and Significance

- The term sulfide refers to several types of chemical compounds containing sulfur in its lowest oxidation number of -2.
- Formally, “sulfide” is the dianion, S^{2-}, which exists in strongly alkaline aqueous solutions formed from H_2S or alkali metal such as Li_2S, Na_2S, and K_2S.
- Sulfide is exceptionally basic and, with a pH > 14, it does not exist in appreciable concentrations even in highly alkaline water.
- Instead, sulfide combines with protons to form HS^-, which is variously called **hydrogen sulfide** ion, **hydrosulfide** ion, **sulfhydryl** ion, or **bisulfide** ion.
- At still lower pH's (<7), HS^- converts to H_2S, hydrogen sulfide.
- Thus, the exact sulfur species obtained upon dissolving sulfide salts depends on the pH of the final solution.
- Sulfide often is present in groundwater, especially in hot springs.
- Its common presence in wastewaters comes partly from the decomposition of organic matter, sometimes from industrial waters, but mostly from the bacterial reduction of sulfate.
- Hydrogen sulfide escaping into the air from sulfide-containing wastewater causes odor nuisances.
- Gaseous H_2S is very toxic and has claimed the lives of numerous workers in sewers.
- It attacks metals directly and indirectly has caused serious corrosion of concrete sewers because it is oxidized biologically to H_2SO_4 on the pipe wall.

2. Categories of Sulfides

From an analytical standpoint, three categories of sulfide in water and wastewater are distinguished.

a. ***Total sulfide*** includes dissolved H2S and HS-, as well as acid-soluble metallic sulfides present in suspended matter.

b. ***Dissolved sulfide*** is that remaining after suspended solids have been removed by flocculation and settling.

c. ***Un-ionized hydrogen sulfide*** may be calculated from the concentration of dissolved sulfide, the sample pH, and the practical ionization constant of H_2S.

3. Determination method

– Ion-selective electrode method

– Methylene blue method

This method can determine the total sulfide, namely hydrogen sulfide and acid-soluble metal sulfide in water. The method is based on the reaction of sulfide, ferric chloride, and dimethyl-*p*-phenylenediamine to produce methylene blue. The intensity of the blue color is proportional to the sulfide concentration. Test results are measured at 665nm.

Determination of Soluble Sulfide

Determine soluble sulfide by centrifuging the sample in completely filled, capped tubes and analyzing the supernatant. Insoluble sulfides are then estimated by subtracting the soluble sulfide concentration from the total sulfide result.

4. Sampling and Storage

Sulfide ion is unstable because of being easily oxidized or dispersing into air making hydrogen sulfide, therefore, carry out the test immediately after sampling.

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Take samples with minimum aeration (Avoid excessive agitation or prolonged exposure to air.) Either analyze samples immediately after collection or preserve for later analysis with zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$)solution. To preserve a sample for a total sulfide determination put zinc acetate and sodium hydroxide solutions into bottle before filling it with sample. Use 4 drops of 2*N* zinc acetate solution per 100mL sample. Increase volume of zinc acetate solution if the sulfide concentration is expected to be greater than 64 mg/L. The final pH should be at least 9. Add NaOH if necessary.

5. Preparation of Sulfide Standards

Take care in preparing reliable stock solutions of sulfide for calibration and quality control. Prepare sulfide standards from sodium nonahydrate ($Na_2S \cdot 9H_2O$) crystals.

Preferably remove single crystals of $Na_2S \cdot 9H_2O$ from reagent bottle with nonmetallic tweezers; quickly rinse in degassed reagent water to remove surface contamination. Blot crystal dry with a tissue, then rapidly transfer to a tared, stoppered weighing bottle containing 5 to 10 mL degassed reagent water. Repeat procedure until desired amount of sodium sulfide is in weighing bottle. Determine amount of $Na_2S \cdot 9H_2O$ in weighing bottle by difference, then multiply the weight by 0.133 to determine the amount of S^{2-}. Avoid excess agitation and mixing of the solution with atmospheric oxygen. Quantitatively transfer and dilute entire contents of weighing bottle to an appropriate size volumetric flask with degassed reagent water to prepare a known concentration sulfide stock solution (3.750 g $Na_2S \cdot 9H_2O$ diluted to a final volume of 500 mL will give a stock solution of which 1.00 mL = 1.00 mg S^{2-}) Store stock solution with minimum headspace for no more than 1 week.

Solids

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solid analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations. Solids in water/wastewater generally can be divided into a few categories as mentioned below according to the forms in water/wastewater.

1. Definitions

"**Total solids**" is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes "**total suspended solids**", the portion of total solids retained by a filter, and "**total dissolved solids**", the portion that passes through the filter.

The type of filter holder, the pore size, porosity, area, and thickness of the filter and physical nature, particle size, and amount of material deposited on the filter are the principal factors affecting separation of suspended solids from dissolved solids. "**Dissolved solids**" is the portion of solids that passes through a filter of 0.45 to 1 μm nominal pore size under specified conditions. At the same time "suspended solids" can be defined as the portion of solids retained on the filter. In this meaning, "suspended solids" was at one time called non-filterable residue (NFR).

"Suspended solids" refers to the dry-weight of particles trapped by a filter, typically of a specified pore size. Generally the diameter of the particulates are not exceeding 2mm. It is used as one indicator of water quality. From an analytical standpoint, "suspended solids" is the portion retained on the filter. The term "**total suspended solids**" (TSS) applies to the dry weight of the material that is removed from a measured volume of water sample by filtration through a standard filter. The test is basically empirical and is not subject to the usual criteria of accuracy.

"**Settleable solids**" is the term applied to the material settling out of suspension within a

defined period. The settling time depends on the purpose of test, however, 30 to 60 minutes are normally applied.

2. Sample Handling and Preservation

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4℃ up to the time of analysis to minimize microbiological decomposition of solids. Transportation and short-term storage of sample will not normally affect the results of the test. Preferably do not hold samples more than 24 h. In no case hold sample more than 7 d. Bring samples to room temperature before analysis.

3. Apparatus

- ✓ Filter holder,
- ✓ Glass-fiber filter paper, Whatman GF/C or equivalent, of a size compatible with the filter holder,
- ✓ Suction flask,
- ✓ Drying oven,
- ✓ Desiccator,
- ✓ Analytical balance, capacity 200 g (or more), accuracy 0.1 mg,
- ✓ Vacuum pump or aspirator.

4. Procedure of Determination

1) General

To achieve reproducibility and comparability of results requires close attention to procedure details, especially filter characteristics and time and temperature of drying. The method described is based on the following conditions:

a. Filtering by glass-fiber filter (Whatman GF/C grade or equivalent), and

b. Drying at a temperature of 103 – 105℃ for two hours to a constant weight, i.e. a variability of not more than 0.5 mg.

If other filters (paper, membrane, etc.) or other temperatures are used, it is necessary to report the specifications followed (e.g. total suspended solids at …. ℃, type of filter and pore size or number).

It is obvious that the result of a test cannot include materials that are volatile under the condition of the procedure.

2) Total Suspended Solids Dried at 103 – 105℃

Prior to an analysis, exclude large floating particle or submerged agglomerates of nonhomogeneous materials from the sample using a sieve (2 mm mesh). Then, a well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105℃. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume.

a. Preparation of glass-fiber filter disk

① Place a filter disk on the filter holder. Assemble filter holder in suction flask apparatus, connect to vacuum source and apply vacuum.

② Wash the filter disk with three successive 20-mL portions of distilled water. Continue to apply vacuum for 2-3 minutes after the water has passed through the filter. Discard the filtrate.

③ Remove the filter from filtration apparatus and transfer to an inert aluminum weighing dish. Dry in an oven at 103 – 105℃ for at least 1 h.

④ Cool in desiccator to balance temperature and weigh on an analytical balance.

⑤ Repeat the cycle of drying, desiccating and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less.

⑥ Store in desiccator until needed.

b. Sample analysis

① Remove the filter disk from the desiccator, weigh it and record its weight.

② Place the filter in filter holder and assemble the filter holder in the suction flask

apparatus. Connect to the vacuum source and apply vacuum.

③ Wet the filter with a few drops of distilled water to seat the filter.

④ Shake the sample vigorously and measure out 100 mL in a 100-mL graduated cylinder or volumetric flask. Pour this portion of the sample into the filter funnel, being careful not to disturb the seating of the filter disk.

⑤ Rinse out the measuring flask or cylinder with small quantity of distilled water. If the sample is very low in suspended material, a larger volume of sample may be used.

⑥ When filtration is complete, carefully remove the filter disk from the filter holder with tweezers and place it in the drying oven. Dry for at least 1 hour at 103 – 105℃. Cool in a desiccator and weigh.

⑦ Repeat the drying, desiccating and weighing cycle until the weight loss between two successive weighings is less than 0.5 mg.

⑧ Record the final weight obtained.

c. Calculation

$$\text{Total suspended solids} = \frac{A - B}{C} \quad \text{mg/L}$$

where

A = weight of filter + solids (mg)

B = weight of filter (mg)

C = volume of sample filtered (mL)

Report the results as:

Total suspended solids dried a ….. ℃, …… mg/L

3) Settleable solids

Settleable solids in surface and saline waters as well as domestic and industrial waters may be determined and reported on either a volume (mL/L) or a weight (mg/L) basis.

a. Volumetric method:

The volumetric method requires an Imhoff cone.

Fill an Imhoff cone to the 1-L mark with a well-mixed sample. Settle for 45 min, gently agitate sample near the sides of the cone with a rod or by spinning, settle 15 min longer, and record volume of Settleable solids in the cone as milliliters per liter (mL/L). If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settled solids. The practical lower limit of measurement depends on sample concentration and generally is in the range of 0.1 to 1.0 mL/L. Where a separation of Settleable and floating materials occurs, do not estimate the floating material as Settleable matter. Replicates usually are not required.

b. Gravimetric method:

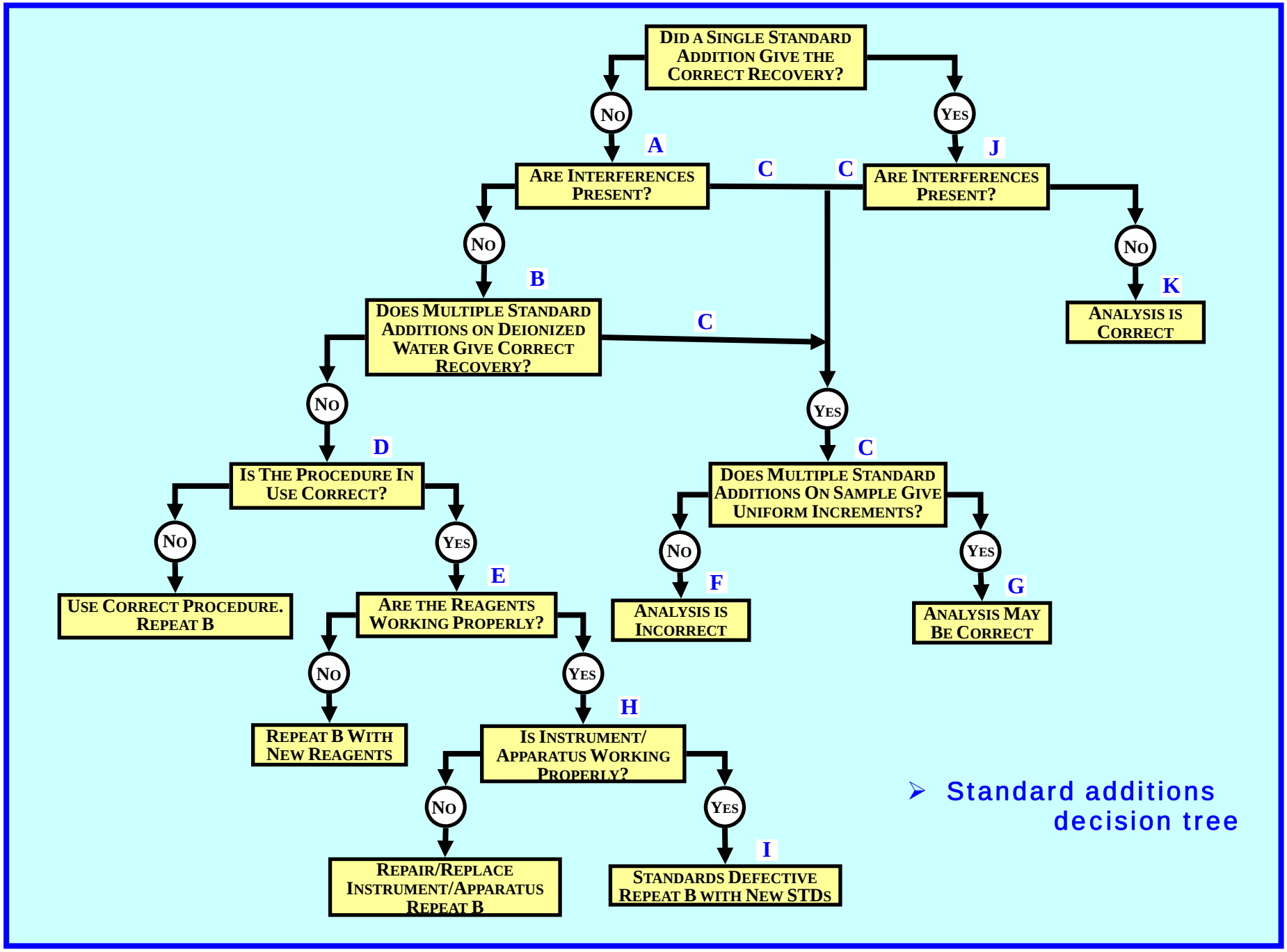
① Determine total suspended solids as mentioned above.

② Pour a well-mixed sample into a glass vessel of not less than 9 cm diameter using not less than 1 L and sufficient sample to give a depth of 20 cm. Alternatively use a glass vessel of greater diameter and a large volume of sample. Let stand quiescent for 1 h and, without disturbing the settled or floating materials, siphon 250 mL from center of container at a point halfway between the surface of the settled material and the liquid surface. Determine total suspended solids (milligram per liter) of this supernatant liquor. These are the nonsettleable solids.

<u>Calculation</u>

mg settleable solids/L

= mg total suspended solids/L － mg nonsettleable solids/L


Did a Single Standard Addition Give the Correct Recovery?
No
A
Yes
J
Are Interferences Present?
C
C
Are Interferences Present?
No
B
No
K
Does Multiple Standard Additions on Deionized Water Give Correct Recovery?
C
Analysis is Correct
No
D
Yes
C
Is The Procedure In Use Correct?
Does Multiple Standard Additions On Sample Give Uniform Increments?
No
Yes
No
F
Yes
G
E
Use Correct Procedure. Repeat B
Are the Reagents Working Properly?
Analysis is Incorrect
Analysis May Be Correct
No
Yes
H
Repeat B With New Reagents
Is Instrument/ Apparatus Working Properly?
No
Yes
I
Repair/Replace Instrument/Apparatus Repeat B
Standards Defective Repeat B with New STDs
Standard additions decision tree

Procedure for Low Level Chloride Determination by ISE

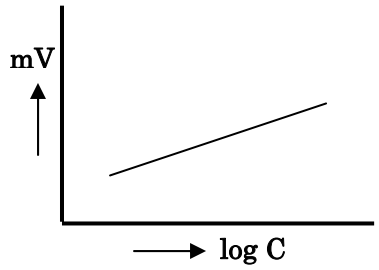
◆ Low level chloride measurement : In the non-linear portion of the calibration curve

1. Dilute 20 ml of standard ISA (5M $NaNO_3$) to 100 ml with distilled water.
2. This low level ISA (1 M $NaNO_3$) is added at the rate of 1 ml to each 100 ml of sample.
3. Use the 1,000 mg/L standard solution for low level calibration. Standards should be prepared fresh daily.
4. Add 1 ml of the low level ISA to a 100 ml volumetric flask and fill to the mark with distilled water. Pour this solution into a 150 ml beaker and place the beaker on the magnetic stirrer. Begin stirring at a constant rate.
5. Place the electrode tips in the solution. Assure that the meter is in the mV mode.
6. Add increments of 1,000 mg/L standard as given in Table below.
7. After the reading has stabilized, record the mV reading after each addition.

Step	Added Volume (ml)	Concentration (mgt/L)	mV
1	0.1	1.0	
2	0.1	2.0	
3	0.2	4.0	
4	0.2	6.0	
5	0.4	9.9	
6	2.0	29.0	
7	2.0	48.0	

Solutions: addition of 1,000 mg/L

8. On a semi-logarithmic graph paper, plot the millivolt reading (linear axis) against the concentration (log axis)



9. Rinse the electrodes in distilled water and blot dry.
10. Measure out 100 ml of the sample into a 150 ml beaker, add 1 ml of low level ISA, and place the beaker on the magnetic stirrer. Begin stirring. Lower the electrode tips into the solution. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.
11. Prepare a new low level calibration curve daily. Check the calibration curve every two hours by repeating Steps 1-8

Arabic

محاضرة تدريبية حول
الإدارة والمراقبة البيئية

المحاضرة -- 2:
التحليل الأساسي لجودة المياه

كانون الثاني -- شباط
2006

فريق خبراء جايكا

تصنيف طرق التحديد

بند التحليل	طريقة التحديد	
القساوة(Ca^{2+}, Mg^{2+}), القلوية, الحموضة, DO, BOD, COD, etc.	التحليل بالقياس الحجمي	التحليل الكيميائي
SS, VSS, CCE, مستقلصات الفرين/الهيكسان	التحليل بالقياس الوزني	
الكلور, Cl, SO_4^{2-}, NH_4-N, NO_2-N, NO_3-N, PO_4^{3-}, الفلور, etc	قياس امتصاصية الطيف الضوئي (طريقة القياس اللوني) (تحت الحمراء, أو حتى البنفسجي, مرئي)	التحليل بالأجهزة
المواد العضوية الطيارة المواد العضوية المذابة المبيدات الفلورية, الهيدروكربونات العطرية المتعددة الحلقات	الكروماتوغرافيا الغازية (GC), (GC-MS) الكروماتوغرافيا السائلة (LC) الكروماتوغرافيا الشاردية	
المعادن العناصر المعدنية الخ.	طريقة الامتصاص الذري القياس الضوئي للانبعاثات	
الحرارة, DO, EC, etc.	أخرى	

تحديد النترات (NO3-N) في المياه (1)

مسمة الـ NO_3

- ✓ مركبات النتروجين ذات الأكسدة العالية
- ✓ يوجد بشكل شائع في المياه السطحية ومياه الآبار حيث أنه الناتج الأخير لتحلل المواد النتروجينية العضوية
- ✓ تعتبر الأسمدة الكيميائية من الأراضي الزراعية، ومياه الصرف من الأعلاف الحيوانية ومياه الصرف الصحي والصناعي من أهم مصادر النترات.
- ✓ المغذيات التي تعطى للنباتات والتي يتم تحولها إلى البروتين بالتمثيل الغذائي
- ✓ مشاكل جودة المياه المصاحبة للتشبع الغذائي

طرق وأجهزة التحليل الأساسي للمياه

الرقم	المعيار	الطريقة	الجهاز
1	pH	طريقة الالكترود	sensION1 Portable pH meter
2	حرارة المياه		Thermometer
3	اللون	طريقة البلاتينيوم-كوبالت APHA	Colorimeter (DR/890)
4	TDS	طريقة الالكترود	sensIONS Portable EC & TDS meter
5	DO	طريقة غشاء الالكترود	sensION 6 Portable DO meter
6	SS	طريقة القياس الضوئي	Colorimeter (DR/890)
7	COD_{Cr}	طريقة مفاعل الهضم	Reactor (DRB 200-1) & Colorimeter (DR/890)
8	NO_3-N	طريقة حمض الكادميوم	Colorimeter (DR/890)
9	NH_3-N	طريقة السالسيلات	Colorimeter (DR/890)
10	PO_4^{3-}	طريقة الحمض الأميني	Colorimeter (DR/890)
11	Cl	طريقة نترات الفضة	Digital Titrater (Model 16900)
12	BOD_5	طريقة القياس المانومتري (حساس الضغط)	OxiTop
13	EC	طريقة الالكترود	sensIONS Portable EC & TDS meter
14	العكارة	طريقة القياس التيربيدومتري	2100P Portable Turbidity

تحديد النترات (NO3-N) في المياه (2)

التحديد

- ✓ تساعد في تقدير صفة ودرجة الأكسدة في المياه السطحية، ومياه الآبار المتسربة عبر التربة، وفي العمليات البيولوجية و في المعالجة المتقدمة لمياه الصرف.
- ✓ يكون تحديدها صعباً بشكل عام بسبب التدخلات.
- ✓ وأصعب ما تكون في مياه الصرف الصحي بسبب التركيز العالي للمواد المتدخلة العديدة.

تحديد النترات (NO3-N) في المياه (3)

التحديد بطريقة خفض الكادميوم

✓المبدأ

يتم تخفيض النترات إلى النتريت بواسطة الكادميوم. ثم يتم تحديد النتريت الموجود أصلاً بالإضافة إلى النترات المخفضة إلى النتريت.

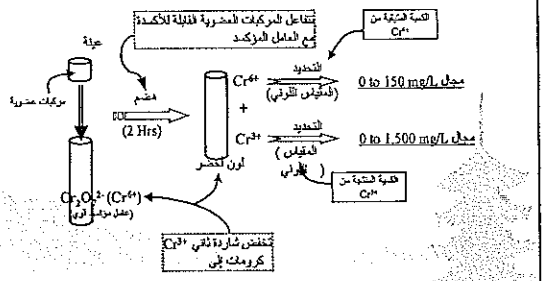
✓التدخلات

قد يتم الحصول على نتائج منخفضة في العينات التي تحوي تركيز عالي من الحديد والنحاس أو المعادن الأخرى. إن إضافة الكاشف EDTA إلى العينة يمكن أن يزيل هذا التدخل

إن وجود المؤكسدات القوية يؤثر على تراكيز النتريت. القلوية العالية تعطي نتائج منخفضة.

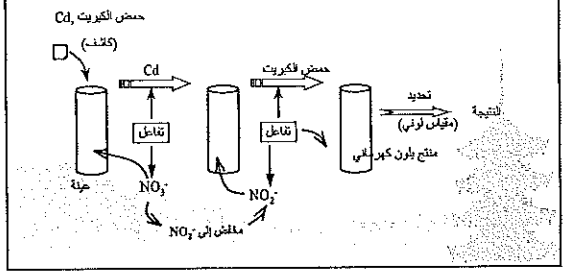
ملخص طريقة التحديد (1)

- COD
- الطريقة: مفاعل الهضم



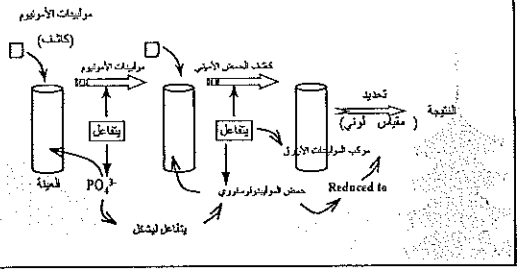
ملخص طريقة التحديد (2)

- النترات (NO_3^--N)
- الطريقة: خفض الكادميوم



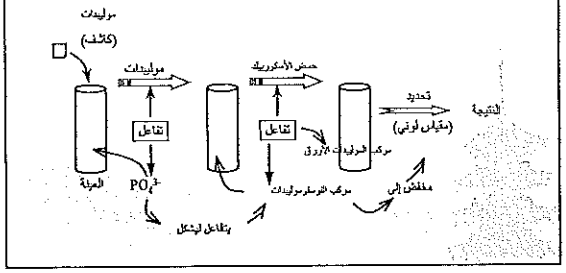
ملخص طريقة التحديد (4)

- الفوسفور (PO_4^{3-}) ، مجال منخفض (0 إلى 30،00 ملغ/ل)
- طريقة الحمض الأميني



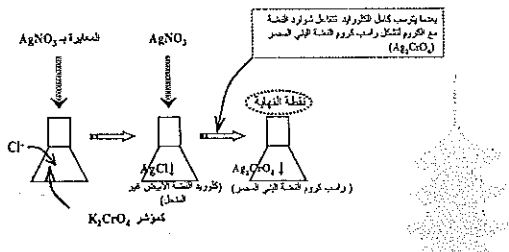
ملخص طريقة التحديد (4)

- الفوسفور (PO_4^{3-}) ، مجال منخفض (0 إلى 2.50 ملغ/ل)
- طريقة حمض الأسكوربيك



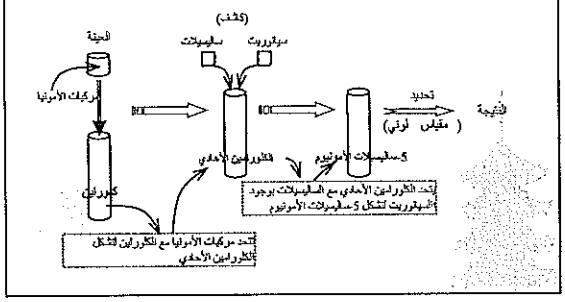
ملخص طريقة التحديد (6)

- الكلورايد (Cl^-)
- طريقة نترات الفضة



ملخص طريقة التحديد (5)

- نتروجين، أمونيا (NH_3-N)
- طريقة الساليسيلات



مبدأ مقياس اللون (1)

- قانون لامبرت-بير

علاقة متبادلة بين:

– الامتصاص: أ، بدون أبعاد

– طول الطريق المقطوع: ل (سم)

– تركيز المواد الممتصة c (mol/l)

⇨ **إن امتصاص مادة ما يتناسب مع تركيزها وطول الطريق الذي تقطعه**

الامتصاص السبيكتروفوتومتري (مقياس اللون)

- طريقة القياس الضوئي لتحديد تركيز المادة في المحلول.
- جهاز يسمح بتحديد امتصاص المحلول في تواتر معين (اللون) للضوء
- يسمح بالتأكد من تركيز محلول معروف حيث أنه تناسبي بالنسبة للامتصاص
- يستند على قانون لامبرت-بير

مبدأ مقياس اللون (2)

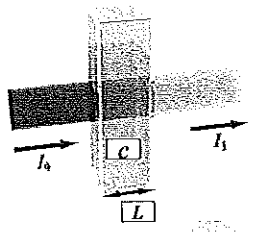
قانون لامبرت-بير

$T = I_i/I_0$ (الامتصاص)

$A = \log_{10}(I_0/I_i) = \log_{10}(1/T)$

A = امتصاص المحلول

$$A = \varepsilon \times C \times L$$



حيث:

I_0 = كثافة الضوء الحالي

I_i = كثافته بعد مروره بالمحلول

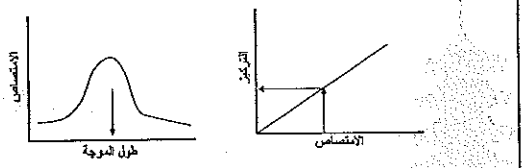
C = تركيز العناصر الماصة في المادة

L = المسافة التي يقطعها الضوء من خلال المادة

ε = معامل الامتصاص

مبدأ مقياس اللون (3)

- توضح المعادلة بأن الامتصاص يعتمد على الكمية الإجمالية الممتصة في مسار الضوء عبر الخلية
- يمكن الحصول على الخط المستقيم الذي يمر عبر الأصل (0.0) وذلك بتحديد الامتصاص مقابل التركيز على الخط البياني
- يمكن تحديد تركيز المادة المنحلة في السائل بقياس الامتصاص أ



أنماط التدخلات

- تتفاعل كما لو أنها المادة المستهدفة في التحليل ⇦ تعطي نتيجة عالية
- تتفاعل مع المادة المستهدفة ⇦ تعطي نتيجة منخفضة
- ضمها مع الكاشف التحليلي ⇦ يمنعها من التفاعل مع المادة المستهدفة

مثال:

في طريقة القياس الضوئي يمكن اعتبار العكارة "كمادة" تعمل كالمادة التي تم تحديدها ⇦ يخفض انتقال الضوء

ضبط التدخلات

- تخضع العديد من إجراءات التحليل إلى العديد من تدخلات من المواد الموجودة في العينة
- تسبب التدخلات إلى نتيجة إما عالية جداً أو منخفضة جداً

⇩

- ضرورة ضبط التدخلات

الإجراء المضاد للتدخلات (1)

أن أفضل طريقة لتقليل التدخلات هي إزالة المادة المتدخلة أو جعلها غير ضارة

1. إزالة إما المادة المستهدفة أو المتدخلة فيزيائياً
   ⟸ ترشيح المادة أو تقطيرها (الفلورايد، الأمونيا..الخ) بزيل التدخل
   الامتصاص في راتنج تبادل الأيونات

الإجراء المضاد للتدخلات (2)

2. تعديل الـ pH وبذلك تقوم المادة المستهدفة فقط بالتفاعل
   ⟸ مثال:
   تعديل الـ pH إلى 2 وبذلك يتم ترشيح الحمض الطيار من المحلول
3. أكسدة (هضم) أو إنقاص العينة لتحويل المادة المتدخلة إلى شكل غير ضار ⟸ مثال: خفض الكلوراين إلى الكلورايد بإضافة الثيوسولفات

تعويض التدخل للقياس الضوئي

إذا كانت التقنيات المذكورة غير ممكنة التطبيق

⟸ يمكن استخدام التعويض

الإجراء المضاد للتدخلات (3)

4. أضف عامل مناسب ليشكل مركباً مع المادة المتدخلة وبذلك تصبح غير ضارة بالرغم من وجودها
5. جمع التقنيات الأربع المذكورة
6. اللون والعكارة ⟸ استخدم الكربون المفعل العامل المسبب لتلبد المعلقات، الفلترة.

التدخلات في تحليل الـ NO_3 بطريقة تخفيض الكادميوم

مستويات التدخل والمعالجة	المادة المتدخلة
فوق 100 ملغ/ل بسبب الـ Cl نتيجة منخفضة. يمكن استخدام الاختبار بتراكيز الكلورايد العالية ولكن يجب إجراء المعايرة باستخدام ستاندرات من نفس تراكيز الكلورايد	الكلورايد
جميع المستويات	شوارد الحديد
جميع المستويات التعويض باستخدام ماء البيرومين والفينول	النتريت
العينات ذات المنتج القوي أو ذات الـ pH الأقصى تتجاوز قدرة ممتصة الكواشف وتحتاج إلى معالجة مسبقة	pH
تدخل في جميع المستويات	مواد مؤكسدة قوية ومختزلة

تعويض القياس الضوئي للتدخل من اللون أو العكارة

1. قم بقياس العينة بدون إضافة الكواشف (عينة البلانك)
2. يكون تجاوب الجهاز نتيجة امتصاص العينة أو العكارة وليس بسبب المادة المستهدفة.
3. إعمل منحنى المعايرة واطرح امتصاص البلانك من امتصاص العينة

التدخلات في تحليل الـ PO_4
بطريقة الحمض الأميني (1)

مستويات التدخل والمعالجة	المادة المتدخلة
أكبر من 10,000 ملغ/ل كـ $CaCO_3$	الكالسيوم
أكبر من 150,000 ملغ/ل كـ Cl^-	الكلورايد
أضف متقدرد حمض للوسفات إلى العينة واستخدمها كبلانك بدلاً عن العينة غير المعالجة.	العينات الملونة
قد تعطي نتيجة منخفضة. للتخلص منها قم بالتمديد حتى يعطي التمديد نتيجتين متقاربتين نفس النتيجة تقريبا.	مستويات عالية من الملح
أكبر من 40,000 ملغ/ل كـ $CaCO_3$	مغنيزيوم
قم بتبييض اللون الأزرق. ثم بإزالة تدخل النتريت بإضافة حمض الكبريت إلى العينة	النتريت (NO_2^-)
بدلما يزداد تركيز الفوسفات يتغير اللون من الأزرق إلى الأخضر ثم الأصفر وفي النهاية إلى البني. وبما اللون البني على وجود تركيز عالي يصل إلى 100,000 ملغ/ل من الـ PO_4^{3-}. إذا تشكل لون غير الأزرق قم بالتمديد ثم أعد التجربة.	الفوسفات، مستويات عالية (PO_4^{3-})

التدخلات في تحليل الـ PO_4
بطريقة الحمض الأميني (2)

مستويات التدخل والمعالجة	المادة المتدخلة
العينات التي يكون تركيز السلفيد أقل من 5 ملغ/ل، يمكن إزالة تدخل السلفيد بواسطة الأكسدة بماء البرومين	السلفيد (S^{2-})
للأفضل النتائج يجب أن تكون درجة حرارة العينة $21\pm3°C$	درجة الحرارة
يمكن أن تعطي نتائج غير ثابتة لسببين. قد تكون بعض المواد المعلقة قد انحلت بسبب الحمض المستخدم وقد تعطي المعلقات الأورثوفوسفات. للعينات ذات العكارة الشديدة أضف متقدرد الـ H_2SO_4 إلى العينة	العكارة
قد تتجاوز قدرة معالجة الكواشف وتحتاج إلى معالجة مسبقة	عينات ذات معالجة عالية أو ذات pH أقصى

التدخلات في تحليل الـ PO_4
بطريقة الحمض الأسكوربي (1)

مستويات التدخل والمعالجة	المادة المتدخلة
أكبر من 200 ملغ/ل	الألمنيوم
جميع المستويات	الأرسنيت
أكبر من 100 ملغ/ل	الكروم
أكبر من 10 ملغ/ل	النحاس
جميع المستويات	كبريت الهيدروجين
أكبر من 100 ملغ/ل	الحديد
أكبر من 300 ملغ/ل	النيكل
أكبر من 50 ملغ/ل	السيليكا

التدخلات في تحليل الـ PO_4
بطريقة الحمض الأسكوربي (2)

مستويات التدخل والمعالجة	المادة المتدخلة
الكميات الكبيرة قد تعطي نتائج غير ثابتة لأن الحمض الموجود في مسحوق الوسادة قد يحل بعض المواد العالقة وبسبب انتاج الأورثوفوسفات من العوالق. للعينات شديدة التعكير أو اللون أضف وسادة من الفوسفات إلى العينة للمعالجة المسبقة	العكارة أو اللون
أكبر من 80 ملغ/ل	الزئبق
قد تتجاوز قدرة معالجة الكواشف وتحتاج إلى معالجة مسبقة	عينات ذات معالجة عالية أو ذات pH أقصى

من الأفضل أن يكون الـ pH من 2 إلى 10

تدخل الـ NH_3-N
بطريقة الساليسيلات (1)

مستويات التدخل والمعالجة	المادة المتدخلة
قم بتعديل الـ pH إلى 7 تقريبا. استخدم متقدرد الـ NaOH للعينات الحمضية والـ HCL للعينات الأساسية	عينة حمضية أو أساسية
50,000 mg/L as $CaCO_3$	كالسيوم
بسبب كثافة الألوان في العينات المحضرة	غليسين، فيرازين
300,000 mg/L as $CaCO_3$	مغنيزيوم
يمكن إزالة تدخل الحديد بإضافة نفس تركيز الحديد إلى الماء منزوع الشوارد في الخطوة 4	حديد
600 mg/L as NO_2-N	نتريت
5,000 mg/L as NO_3-N	نترات

تدخل الـ NH_3-N
بطريقة الساليسيلات (2)

مستويات التدخل والمعالجة	المادة المتدخلة
5,000 mg/L as PO_4^{3-}-P	أورثوفوسفات
6,000 mg/L as SO_4^{2-}	مسلفات
سوف يكشف السلفيد اللون يمكن إزالة تدخل السلفيد باستخدام العينة المعالجة مسبقاً (إضافة كاشف مانع السلفيد والفترة)	سلفيد
تعطي قيم عالية خاطئة. تحتاج العينات ذات التدخلات الحادة إلى الترشيح	العكارة واللون

التدخلات في تحليل الـ Cl
بطريقة نترات الفضة

مستويات التدخل والمعالجة	المادة المتدخلة
الحديد أكثر من 10 ملغ/ل يؤدي إلى نقطة النهاية غير الحقيقية	الحديد
الأورثوفوسفات أكثر من 25 ملغ/ل يؤدي إلى ترسيب الفضة	الأورثوفوسفات
السولفات أكثر من 10 ملغ/ل يسبب التدخل. لإزالة تدخل السولفات أضف بيروكسيد الهيدروجين في الخطوة 4	السولفات
لإزالة التدخل من السيانيد أضف محتويات وسادة واحدة من كاشف مانع السيانيد إلى العينة وقم بالفلترة بواسطة ورق الفلترة	السيانيد
تتم إزالة تدخلات السيانيد، اليود، البروميد بالمعايرة الثانية مثل الكلور	السيانيد، اليود، البروميد
قم بتعديل الـ pH للعينات ذات القلوية أو الحموضة العالية من 2 إلى 7 مع H_2SO_4 or NaOH	عينات ذات قلوية أو حموضة عالية

التدخلات في تحديد الـ COD
طريقة هضم المفاعل

- التدخل الأولي
  ⟸ الكلورايد
- الاجراءات المضادة:
  - تحتوي كل قارورة COD السلفات الزئبقية ($HgSO_4$) لإزالة تدخل الكلورايد حتى 2,000 ملغ/ل
  - يجب تمديد العينات ذات التركيز العالي من الكلورايد
  - إذا كان التمديد سبباً في أن يكون تركيز الـ COD منخفضاً جداً وغير دقيق، أضف $HgSO_4$ قبل إضافة العينة

الكشف اللازم إجراءه عند حدوث مشكلة
في أي طريقة تحليل (1)

1. <u>الحسابات والتسجيل</u>
   - تحقق من الحسابات وتحويل الأرقام أو الأخطاء الرياضية
   - تأكد من تسجيل البيانات في الوحدات المناسبة ومن أن تحويل البيانات من سجل لآخر قد تم بشكل صحيح

البنود التي يجب التحقق منها عند حدوث مشكلة في طريقة التحليل

1. الحسابات والتسجيل
2. محاليل الستاندرد
3. الكواشف
4. الجهاز
5. مواد ضبط الجودة

الكشف اللازم إجراءه عند حدوث مشكلة
في أي طريقة تحليل (3)

3. <u>الكواشف</u>
   - تحقق فيما إذا كانت الكواشف قد فسدت.
   - تحقق من أنه تم إعداد الكواشف الجديدة بشكل صحيح
   - تحقق من ظروف تخزين الكواشف، لاسيما تلك التي تحتاج إلى التخزين بعيداً عن الضوء وفي درجة حرارة معينة
   - تحقق من تاريخ انتهاء مفعول الكواشف وتخلص من الكواشف التي انتهى مفعولها أو التي لم تخزن بشكل مناسب

الكشف اللازم إجراءه عند حدوث مشكلة
في أي طريقة تحليل (2)

2. <u>المحاليل القياسية</u>
   - تحقق من المحاليل القياسية المستخدمة في معايرة الجهاز
   - قد تكون المحاليل القديمة قد فسدت وأنه تم حدوث أخطاء أثناء تحضير المحاليل الجديدة
   - تحقق من شروط التخزين، عمر المحاليل وتاريخ انتهاء المفعول

الكشف اللازم إجراءه عند حدوث مشكلة
في أي طريقة تحليل (4)

4. الجهاز
- تحقق من سجلات المعايرة والصيانة والحفظ للكواشف وأجهزة القياس المستخدمة في التحليل عندما تفقد ضبط طريقة التحليل
- يجب إعادة معايرة الماصات الأوتوماتيكية والميزان..الخ عند اللزوم
- تأكد من استخدام الجهاز بشكل صحيح

➢ How to Ensure Accuracy and Reliability?

تنفيذ ضمان الجودة/ضبط الجودة

تأمين الدقة والوثوقية لبيانات التحليل

• الهدف من ضمان الجودة

الحصول على سجلات واضحة ومختصرة للإجراءات المتعلقة بجودة البيانات

يمكن الحصول عليها بـ:

انشاء بروتوكول ومعايير الجودة لجميع أعمال المخبر

الكشف اللازم إجراءه عند حدوث مشكلة
في أي طريقة تحليل (5)

5. مواد ضبط الجودة
- تحقق من شروط تخزين مواد ضبط الجودة وتأكد من أن القوارير قد أغلقت بإحكام وأنها ليست عرضة للحرارة الزائدة
- قم بالتحليل على قواسم عديدة لتحديد بقاء التركيز ضمن انحرافين قياسيين للقيمة المستهدفة وأنها قريبة من آخر 20 تحديد

مكونات ضمان الجودة

أعمال المخبر:	الإجراءات المطبقة:
• تشغيل الإجراء القياسي	ـ إعداد الـ SOP ـ اختبار طرق جديدة
• صيانة أجهزة التحليل	ـ معايرة منتظمة ـ تأمين المواد المستهلكة
• تأمين صحة التحليل	ـ تأمين كواشف ذات جودة ـ التدريب الفني
• تقييم بيانات التحليل	ـ تسجيل شروط التحليل ـ اختبار الانحراف
• مراجعة نظام الإدارة	ـ كتابة التقرير ـ مراجعة ضرورية

➢ما هو الهدف من ضمان الجودة/ضبط الجودة ؟

➢ تنفيذ منهجية صحيحة أو قياسية في كل عمليات المراقبة:
- عملية الاعتيان
- عملية التحليل
- عملية معالجة البيانات
- عملية كتابة التقرير

الهدف

➢ التقليل من أو تجنب الخطأ في كل عمليات المراقبة

مؤشرات الجودة (1)

- الانحياز

هو قياس الأخطاء الرتيبة

1. ناتجة عن الطريقة
2. استخدام المخبر للطريقة

مكونين اثنين

انحياز الطريقة: يتم قياسها عن طريق المقارنة الداخلية في المختبر . الفرق بين المعدل الأقصى والقيمة الحقيقية أو المعروفة

انحياز المختبر: الفرق بين معدل المختبر والقيمة الحقيقية

مؤشرات الجودة (2)

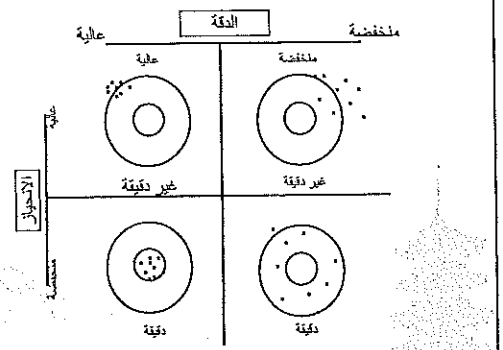
- الدقة

قياس التقارب عند القيام بعدة تحاليل للعينة نفسها وتكون النتائج متوافقة مع بعضها

يمكن الحصول بـ:

- ✓إعادة التحليل في أحوال مطابقة
- ✓تحليل متكرر لستاندرد ثابت ، او
- ✓تحليل إضافات معروفة إلى العينات. محددة بالانحراف القياسي للنتائج

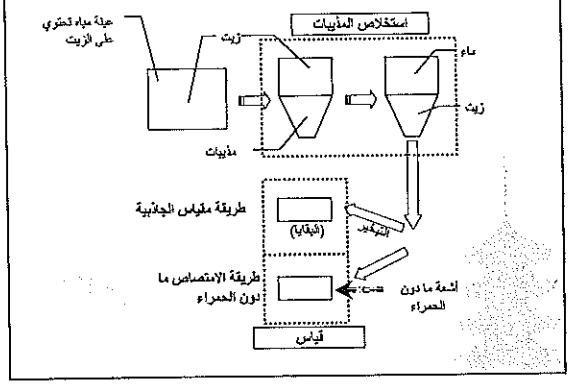
جودة البيانات (تعريف الدقة)



تقدير حدود الكشف

No.	المعيار	الطريقة	مجال القياس	حدود الكشف
1	NO_3-N	طريقة تخفيض الكادميوم	0 to 30.0 mg/L	0.8 mg/L NO_3-N
2			0 to 5.0 mg/L	0.2 mg/L NO_3-N
3	PO_4^{3-}	طريقة الحمض الأميني	0 to 30.00 mg/L	0.14 mg/L PO_4^{3-}
4		طريقة الحمض الأسكوربي	0 to 2.50 mg/L	0.05 mg/L PO_4^{3-}
5	NH_3-N	طريقة السالسيلات	0 to 50 mg/L	1 mg/L NH_3-N
6			0 to 2.50 mg/L	0.08 mg/L NH_3-N
7	COD	طريقة هضم المفاعل	0 to 150 mg/L	4 mg/L COD
8			0 to 1,500 mg/L	30 mg/L COD

تحديد تركيز الزيوت والشحوم في المياه



شكرا لاهتمامكم

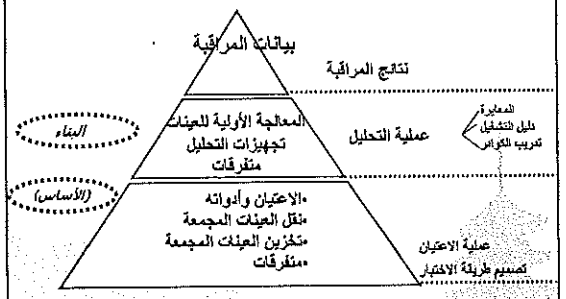
التدريب النظري على
تحليل جودة المياه الكيميائية والبيولوجية

المحاضرة 12
دليل الاعتيان

تموز 2007

شينسوكي ساتو
فريق خبراء جايكا

2. Reliability Pyramid of Monitored Data



أهمية الاعتيان

- عنصر هام في تحليل الجودة وتضبط الجودة
- كيف نضمن موثوقية الاعتيان

عوامل الاعتيان

- القرينة
- طريقة التحليل المتبعة
- الوعاء
- طريقة الحفظ
- زمن الحفظ

دليل الاعتيان (1)
قرائن الجودة الكيميائية والبيولوجية للمياه

القرينة	الزيوت والشحوم	رباعي الفوسفات-PO_4
طريقة التحليل المتبعة	استخلاص المذيب / قياس امتصاص الأشعة تحت الحمراء	القياس الطيفي (السبكترو)
الحاوية	حاوية من نوع G عريضة الفوهة	حاوية من نوع P أو G يجب غسل الحاوية بـ HCl 1:1 ومن ثم تغسل بالماء متزوع الشوارد. لا تستخدم المنظفات التجارية الحاوية على الفوسفات من اجل غسيل الزجاجيات
الحفظ	H_2SO_4 (1:1) أو HCl (1:1) بحيث ينخفض الـ pH إلى أقل من 2	وإذا لم يكن بالإمكان القيام بالتحليل على الفور، قم بحفظ العينات بعد ترشيحها وتبريدها حتى حرارة 4 مئوية
أصغر حجم للعينة	1,000 mL	100 mL
مدة الحفظ	28 يوم	48 ساعة

دليل الاعتيان (2)
قرائن الجودة الكيميائية والبيولوجية للمياه

القرينة	الآزوت، الأمونيا (NH3-N)	المواد الملمعة منظفها (المنظفات) (Surfactants)
طريقة التحليل المتبعة	القياس الطيفي (السبكترو)	القياس الطيفي (السبكترو)
الحاوية	P أو G	P أو G
الحفظ	برد بدرجة حرارة 4 مئوية من أجل تحليلها خلال 24 ساعة ويجب تخفيض قيمة pH إلى أقل من 2 باستخدام H_2SO_4 (1:1) قم بتعديلها باستخدام ماءات الصوديوم 5 نظامي قبل الاختبار	خزن بدرجة حرارة 4م أو أقل (تبريد)، قم بتسخين العينة لتصبح مساوية لحرارة الغرفة قبل الاختبار
أصغر حجم للعينة	500 mL	500 mL
مدة الحفظ	7 أيام (جيدة محفوظة لمدة 28 يوم)	24 ساعة

دليل الاعتيان (3)
قرائن الجودة الكيميائية والبيولوجية للمياه

القرينة	الكروم الكلي (Cr-T)	الكروم السداسي (VI)
طريقة التحليل المتبعة	القياس الطيفي (السبكترو)	القياس الطيفي (السبكترو)
الحاوية	P أو G (حاوية مغسولة بالحمض)	G أو P (تغسل بمحلول HNO3 1:1، وتبرد)
الحفظ	قم بتخفيض الـ pH لتصبح أقل من 2 باستخدام حمض الأزوت ثم قم بتعديل الـ pH لتصبح حوالي 4 باستخدام 5N من هيدروكسيد الصوديوم NaOH قبيل التحليل	تخزن لمدة لا تتجاوز 24 ساعة ضمن حرارة 4م . حيث يجب أن تحلل خلال 24 ساعة من الاعتيان.
أصغر حجم للعينة	300 mL	300 mL
مدة الحفظ	6 أشهر	24 ساعة

دليل الاعتيان (4)
قرائن الجودة الكيميائية والبيولوجية للمياه

القرينة	الكبريت (S2-)	النترات (NO3-)
طريقة التحليل المتبعة	الكترود الشوارد النوعي او السبكترو	الكترود الشوارد النوعي
الحاوية	P أو G	P أو G
الحفظ	املأ كامل العبوة، وأغلق بإحكام وتجنب الاهتزازات القوية أو التعرض لمديد الهواء. أضف 4 نقط من 2N لستات الزنك لكل 100 ملل من العينة قبل الاعتيان. ومن ثم قم برفع قيمة الـ pH كي تصبح أكبر من 9 باستخدام هيدروكسيد الصوديوم، ثم قم بتبريدها	أضف (1:1) H2SO4 إلى العينة لتخفيض قيمة pH لتصبح أقل من 2. ثم بتبريدها.
أصغر حجم للعينة	100 mL	200 mL
مدة الحفظ	7 أيام	48 ساعة

دليل الاعتيان (5)
قرائن الجودة الكيميائية والبيولوجية للمياه

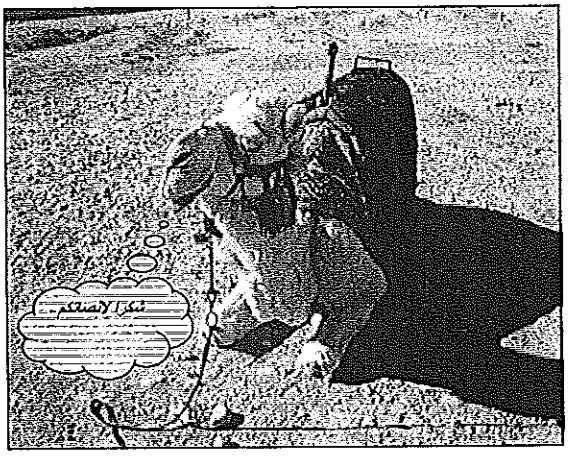
القرينة	الكلور (Cl-)	الفلور (F-)	(CN-)
طريقة التحليل المتبعة	الكترود الشوارد النوعي	الكترود الشوارد النوعي	الكترود الشوارد النوعي
الحاوية	P أو G	P	P
الحفظ	لا توجد طريقة خاصة	لا توجد طريقة خاصة	NaOH pH 12
أصغر حجم للعينة	100 mL	300 mL	500 mL
مدة الحفظ	28 أيام	28 أيام	28 أيام

دليل العتيان (6)
قرائن الجودة الكيميائية والبيولوجية للمياه

القرينة	COD_{Cr}
طريقة التحليل المتبعة	التكثيف المفتوح (Open Reflux)
الحاوية	P أو G (الزجاجية مفضلة)
الحفظ	أضف (1:1) H2SO4 إلى العينة لتخفيض قيمة pH لتصبح أقل من 2. وتفضل وضع العبوات التي لا يمكن تحليلها أي نفس اليوم في ظروف حامضية. يمكن تطبيق الفرامب أي عينة محتوية على جزيئات متروية باستخدام الشلاط وذلك لكي يصبح الجزء المأخوذ من العينة ممثلاً للعينة الطبيعية. ويجب تمديد العينات التي يعتقد بأن قيمة الـ COD فيها كبيرة تمديدا أوليا وذلك من أجل التقليل من الأخطاء الناجمة عن تحليل الحجوم الصغيرة. ثم تبريد العينة
أصغر حجم للعينة	100 mL
مدة الحفظ	7 أيام

دليل العتيان (6)
قرائن الجودة الكيميائية والبيولوجية للمياه

القرينة	الكروم الكلي
طريقة التحليل المتبعة	طريقة المرشحات
الحاوية	P أو G (يجب تعقيمها بشكل جيد، إما بالكحول، أو بالأوتوكلاف)
الحفظ	أضف (1:1) HCl إلى العينة لتخفيض قيمة pH لتصبح أقل من 2
أصغر حجم للعينة	100 mL
مدة الحفظ	6 ساعات



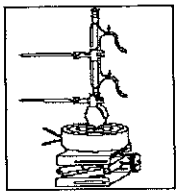
التدريب النظري على
تحليل جودة المياه الكيميائية والبيولوجية

المحاضرات 9- 10 و 11
قياس الاحتياج الكيميائي من الأوكسجين باستخدام الديكرومات COD_{Cr}
في طريقة التكثيف المفتوح (Open Reflux)

حزيران 2007

شينسوكي ساتو
فريق خبراء جايكا

قياس COD_{Cr} باستخدام طريقة التكثيف المفتوح



المحتوى

مراجعة لمبدأ الـ COD (1)

- الـ COD هو اختصار لـ Chemical Oxygen Demand
(الاحتياج الكيميائي للأوكسجين)
- تعريفه: كمية المادة المؤكسدة اللازمة للتفاعل مع العينة ضمن شروط محددة
- الواحدة: مغ/ل -mg/L
- المؤكسدات: برمنغنات البوتاسيوم $[KMnO_4]$

ديكرومات البوتاسيوم [K2Cr2O7]

مراجعة لمبدأ الـ COD (2)

- المؤكسدات:
  - برمنغنات البوتاسيوم $[KMnO_4]$
    - قوة الأكسدة: متوسطة
    - سهولة في الاستخدام
    - قابلية عالية للاستعادة
    - معتمدة في اليابان
  - ديكرومات البوتاسيوم $[K_2Cr_2O_7]$
    - قوة الأكسدة: قوية
    - تخلف موادا سامة (الزئبق...)
    - شائعة في الكثير من بلدان العالم
    - يتم استخدامها في طريقة التكثيف المفتوح

مراجعة لمبدأ الـ COD (2)
تاريخ استخدام $KMnO_4$

- لقد تم استخدام برمنغنات البوتاسيوم كمؤكسد قوي للعديد من السنوات لقياس الـ COD
- كانت تسمى نتيجة القياس باستخدام البرمنغنات "الأوكسجين المستهلك من البرمنغنات" بدلا من "احتياج المواد العضوية من الأوكسجين"
- تباينت فعالية $KMnO_4$ في أكسدة المواد العضوية، كما كانت قيم الـ BOD أكبر بكثير من قيم الـ COD في بعض الحالات
- دلت هذه الملاحظات أن مادة البرمنغنات لا تستطيع أن تؤكسد بعض المواد العضوية بشكل فعال، وبالتالي اعتبرت غير مناسبة إلى حد ما لقياس الـ COD

مراجعة لمبدأ الـ COD (2)
تاريخ استخدام $(K_2Cr_2O_7)$

- لقد تم استخدام مواد مؤكسدة أخرى كبديل عن البرمنغنات مثل كبريتات السيريوم $Ce(SO_4)_2$ ويودات البوتاسيوم KIO_3 وأخيرا ديكرومات البوتاسيوم
- وقد لوحظ بأن الديكرومات هي أكثرها فعالية وذلك للأسباب التالية
  - إنها رخيصة نسبيا
  - سهلة التنقية
  - قادرة على أكسدة معظم المواد العضوية

الأكسدة باستخدام الديكرومات

تفاعل الأكسدة- الإرجاع للديكرومات

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

$$\underline{O_2} + 4H^+ + \underline{4e^-} \rightarrow 2H_2O$$

الأكسدة باستخدام الأوكسجين

- مول واحد من الديكرومات يعادل

$(6/4)O_2 = 32 \times 6/4 = \underline{48\ g\ (O_2)}$

مراجعة لمبدأ الـ COD (2)

تاريخ استخدام ($K_2Cr_2O_7$)

- الديكرومات مؤكسد قوي ضمن الوسط الحامضي (يتم الحصول على الوسط الحامضي عادة بإضافة حمض الكبريت)
- العلاقة التالية تمثل تفاعل الديكرومات مع المواد العضوية

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d + c)H^+ \Rightarrow nCO_2 + (a + 8d - 3c)/2 \cdot H_2O + cNH^{4+} + 2dCr^{3+}$$

حيث: $d = 2n/3 + a/6 - b/3 - c/2$

- عادة يتم استخدام محلول ربع نظامي 0.25N من الديكرومات (مولينه 0.04167) من أجل تحديد قيمة الـ COD، ولكن يفضل استخدام تراكيز أخفض من الالديكرومات لتحديد قيمة الـ COD للعينات التي قيمة الـ COD فيها أقل من 50 ملغ/ل

نظرية التكثيف المفتوح (1)

- المبدأ

يتم غلي العينة وتكثيفها مع ديكرومات البوتاسيوم ووسيط من كبريتات الفضة في محلول حامضي قوي من حمض الكبريت

يتم استهلاك قسم من الديكرومات من قبل المادة العضوية ويتم معايرة الباقي باستخدام سلفات الأمونيوم الحديدية (FAS)

المعايرة باستخدام سلفات الأمونيوم الحديدية Ferrous Ammonium Sulphate (FAS)

$$\underline{Cr_2O_7^{2-}} + \underline{6Fe^{2+}} + 14H^+ \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

FAS

شاردة الديكرومات

نظرية التكثيف المفتوح

التجهيزات المطلوبة

1. دورق مخروطي 500 مل مع قوهة مصنفرة (40/24)
2. مكثف فريدريخ (12 بوصة) مل مع قوهة مصنفرة (40/24)
3. سخان كهربائي، أو فرن تسخين
4. ماصات حجمية (Volumetric pipets) قياسات مختلفة 10-25-50 مل
5. أنابيب معايرة سعة 50 مل بدقة 1 مل (Buret)
6. حوامل أنابيب المعايرة مع ملاقطها
7. ميزان حساس بدقة 0.001 غرام
8. ملعقة
9. دورق 1000 مل
10. خرزات للغلي
11. محرك مغناطيسي مع قضبان تحريك مغناطيسية

نظرية التكثيف المفتوح (2)

- المبادئ

– تؤكسد معظم أنواع المواد العضوية بغلي مزيج من حموض الكروم والكبريت

– يتم تكثيف العينة ضمن محلول حامضي قوي (عملية الهضم) مع كمية زائدة معلومة من كرومات البوتاسيوم ($\underline{K_2Cr_2O_7}$)

– بعد الهضم، يتم معاملة المتبقي من الديكرومات بالـ FAS من أجل تحديد كمية الديكرومات التي استهلكتها المواد العضوية القابلة للأكسدة، وذلك نسبة لكمية الأوكسجين اللازمة للأكسدة

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H2O$$

تحضير المواد الكيماوية (1)

- محلول ديكرومات البوتاسيوم النظامي

1. جفف مسحوق الديكرومات $K_2Cr_2O_7$ في الفرن بدرجة حرارة 103م لمدة 24 سا
2. أذب 12.259 من الديكرومات في الماء المقطر في دورق حجم 1 ل

$K_2Cr_2O_7 = 39.1 \times 2 + 52.0 \times 2 + 16 \times 7 = \underline{294.2}$

$12.259/294.2 = 0.04167$ M

⇦ سيخضع هذا الكاشف إلى تفاعل أكسدة-إرجاع من مرتبة 6 إلكترونات ، وبالتالي التركيز المكافئ هو 6 × أي

$0.04167 \times 6 = 0.25$ N

نظرية التكثيف المفتوح

المواد الكيماوية المطلوبة

1. ثاني كرومات البوتاسيوم (ديكرومات البوتاسيوم) $K_2Cr_2O_7$ 0.25 N ((0.04167 M)
2. محلول من حمض الكبريت (H_2SO_4, d = 1.84)) مع كبريتات الفضة (Ag_2SO_4) (كوسيط أو محرض)
3. بلورات كبريتات الزئبق ($HgSO_4$) لحجب شوارد الكلور في العينة.
4. سلفات الأمونيوم الحديدية $Fe[SO_4].[NH_4]2[SO_4].6H_2O$ Ferrous) (ammonium sulfate
5. محلول كاشف فرويون $[Fe(C_{12}H_8N_2)3]SO_4$ (10-1-فينونترولين وسلفات الأمونيوم الحديدية)
6. ((1, 10-phenanthroline and ferrous ammonium sulfate))
7. حمض إلكبريت المركز
8. ماء مقطر

تحضير المواد الكيماوية (2)

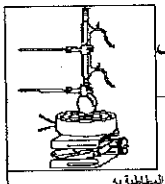
- محلول كاشف حمض الكبريت

1. أضف كبريتات الفضة Ag_2SO_4 إلى حمض الكبريت المركز وذلك نحو 5.5 غ لكل كغ من حمض الكبريت، واخلطها حتى تمام الامتزاج
2. ابقها ليوم أو يومين حتى تمام الذوبان

تحضير المواد الكيماوية (3)

1. محلول المعايرة من سلفات الأمونيوم الحديدية $Fe[SO_4].[NH_4]2[SO_4].6H_2O$ Ferrous ammonium) (sulfate
   1. أذب 98 غ من سلفات الأمونيوم الحديدية المائية في الماء المقطر
   2. أضف 20 مل من حمض الكبريت المركز (H_2SO_4 (d = 1.84)، بردها، ثم مددها لتصبح بحجم 1000 مل في دورق حجمي سعة 1000 مل
   3. قم بمعايرة المحلول بشكل يومي باستخدام المحلول النظامي من الديكرومات

تحضير تجهيزات التكثيف



- خطوة رقم 1:
  - ضع السخان على صحن الرافعة
  - ثبت الدورق فوق السخان
- خطوة رقم 2:
  - ضع المكثف في الدورق وثبته على الحامل، وقم بوصل الأنابيب المطاطية به
- خطوة رقم 3:
  - افتح الماء وقم بمعايرة التدفق
- خطوة رقم 4:
  - أبعد المكثف ثم أضف المواد المتفاعلة، المذيب، وخرزات الغلي (أو قضبان التحريك المغناطيسية)
- خطوة رقم 5:
  - إبدأ بالتسخين: قم بزيادة درجة الحرارة حتى تحصل على غليان بطيء، وقم بمعايرة تدفق الماء أو درجة الحرارة إن لزم الأمر
- خطوة رقم 6:
  - بعد التكثيف، أخفض الرافعة، ثم قم بإزالة السخان، ودع الدورق يتبرد. قم بنقل المحتويات إلى دورق مناسب، وقم بتفكيك التجهيزات.

تحضير المواد الكيماوية (4)

A) تقييس محلول الـ FAS

1. قم بتمديد 10.0 مل من محلول ديكرومات البوتاسيوم ذو التركيز (0.04167 M: $K_2Cr_2O_7$) ليصبح حجمه 100 مل باستخدام الماء المقطر في دورق مخروطي
2. أضف ببطء 30 مل من حمض الكبريت المركز (H_2SO_4)، وقم بتبريدها حتى تصبح بحرارة الغرفة
3. عاملها بمحلول الـ FAS بعد إضافة 2-3 قطرات (0.1 – 0.15 مل) من محلول مشعر الفربون <u>حتى يتغير اللون من الأزرق المخضر إلى الأحمر الغامق</u>

- تعطى مولية (نظامية) محلول الـFAS بالعلاقة التالية

$$\text{مولية محلول الـ FAS} = 0.25 \times \frac{\text{حجم محلول البيكرومات (0.04167 M K2Cr2O7) بـ مل}}{\text{حجم محلول الـ FAS المستخدم بـ مل}}$$

خطوات طريقة التكثيف المفتوح (1)

B. معالجة العينات التي قيمة الـ COD فيها أكبر من 50 مع أوكسجين التر:

1- اخلط العينة إن دعت الحاجة، وخذ 50 ملل منها إلى دورق مسعة 500 ملل باستخدام ماصة. ومن أجل العينات التي قد تزيد فيها قيمة الـ COD عن 900 ملغ من الأوكسجين \ لتر خذ قسما أقل، وقم بتمديده حتى 50 ملل

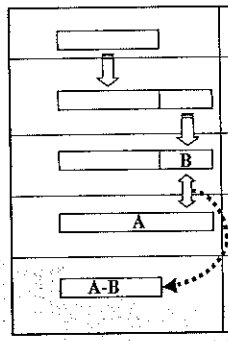
2- أضف 1 غرام من كبريتات الزئبق $HgSO_4$ وأضف ببطء 5 ملل من كاشف حمض الكبريت مع التحريك لإذابة حمض الكبريت. يجب القيام بتبريد المحلول أثناء التحريك من أجل ألا ترتفع درجة الحرارة إلى الحد الذي قد يؤدي إلى تطاير المواد الطيارة

3- أضف 25 ملل من محلول الديكرومات 0.04167M $K_2Cr_2O_7$ وحركها، قم بوصل الدورق إلى المكثف، وقم بفتح مياه التبريد

4- أضف كاشف حمض الكبريت المتبقي (70 ملل) من خلال فتحة المكثف، مع الإستمرار بالتحريك

تنبيه: قم بتحريك المزيج بشكل جيد قبل إشعال السخان من أجل تجنب حصول تسخين موضعي لأسفل الدورق وبالتالي انفجار محتوياته

المبدأ الأساسي لطريقة التكثيف المفتوح



(A)	محتوى العينة من المواد المتطلبة لـ COD
(B)	محتوى المادة من الـ COD يستهلك مقدارا ما من كمية الديكرومات التي يجب أن تكون كميتها أكبر من الحاجة
(C)	تعامل الكمية المتبقية من الديكرومات بمحلول الـ FAS
(D)	تضاف ذات الكمية من الديكرومات إلى عينة (شاهد) وتعامل بالـ FAS
(E)	الفارق بين القيمة في الخطة (D) والخطوة (C) يعبر عن محتوى العينة من المواد المتطلبة لـ COD

خطوات طريقة التكثيف المفتوح (2)

5. قم بتغطية الطرف المفتوح من المكثف ببيشر صغير من أجل منع المواد الأجنبية من الدخول من الأعلى، وقم بعملية التكثيف المفتوح لمدة 2 ساعة، بعد ذلك قم بتبريد المحتويات، وغسيل المكثف من الأعلى بالماء المقطر من أجل غسل المواد العالقة على سطوحه وإعادتها إلى العينة
6. قم بفصل المكثف، ثم قم بتمديد المحتويات إلى ضعف حجمها الأصلي بالماء المقطر (من أجل غسل جدران الدورق، وتسهيل عملية المعايرة)
7. قم بتبريد المزيج إلى حرارة الغرفة وعامل الزائد من الديكرومات بمحلول الـ FAS مع استخدام 0.1-0.15 ملغ (2-3 قطرة) من مشعر الفريون. ومع أن كمية المشعر غير هامة، ولكن يفضل استخدام ذات الكمية من أجل جميع العينات

خطوات طريقة التكثيف المفتوح (3)

8. خذ نقطة نهاية المعايرة على أنها النقطة التي يتحول فيها لون المزيج من الأزرق المخضر إلى الأحمر الغامق والذي يثبت لمدة 1 دقيقة على الأقل
9. يجب ألا تتباين القياسات في العينات المستنسخة عن 5% من الوسطي
10. قد تتطلب العينات ذات المحتوى الكبير من المواد المعلقة والبطيئة الأكسدة خطوات إضافية
11. قم بتكثيف شاهد من الماء المقطر (50 ملل) بذات الشروط ومع إضافة ذات الكمية من المواد الكيماوية ويفضل في نفس الوقت مع نسخ العينات، وقم بمعايرتها كما سبق وأسلفنا

خطوات طريقة التكثيف المفتوح (4)

- **الحسابات**

يعطى تركيز COD بالمعادلة التالية (ملغ أوكسجين \ لتر)

$$\text{COD as mg O2/L} = [(A-B) \times M \times 8000] / (\text{حجم العينة بالملل})$$

حيث

A: كمية الـ FAS بالملل المستخدم في الشاهد

B: كمية الـ FAS بالملل المستخدم في العينة

M: مولية الـ FAS

8000: الثابت الملليمتري المكافئ من الأوكسجين X 1000 ملل\ لتر

استخراج معادلة الحساب

① $A - B$: الفارق بين كميتي محلول FAS ($M \fallingdotseq 0.25N$) المستخدم في معايرة الديكرومات في الشاهد والعينة (ملل)

② $M \times (A - B)$: تكافئ كمية الديكرومات التي تفاعلت مع الـ FAS ⇨ (ميللي مول من الـ FAS)

③ 1 مول من FAS يعادل 1\6 مول من الديكرومات

④ $1/6 \times M \times (A - B)$: كمية الديكرومات التي تفاعلت مع الـ FAS (ميللي مول من الديكرومات) ⇨

⑤ 1 ميللي مول من الديكرومات يعادل 48 ملغ من الأوكسجين (O_2)

⑥ $48 \times 1/6 \times M \times (A - B) \div V$: الكمية المكافئة لمحتوى العينة من COD ⇨ ($mg\ O_2/mL$)

⑦ 1 ميللي مول من الديكرومات يعادل 48 ملغ من الأوكسجين، وبالتالي:

⑧ $48 \times 1/6 \times M \times (A - B) \div V \times 1,000$

أي كمية الـ COD بالملغ\لتر = $\underline{(A - B) \times M \times 8,000/V}$

ملاحظات على طريقة القياس (1)

1. يجب أن تكون قوة الحمض في المحلول النهائي 18 ن على الأقل
2. يجب أن يكون ترتيب تحضير الخليط كما يلي
   1. العينة
   2. كبريتات الزئبق (يمكننا أحيانا عكس الترتيب)
   3. الديكرومات
   4. حمض الكبريت المركز (ببطء ومع التحريك)
3. عند إضافة كبريتات الزئبق اخلط بشكل كاف بحيث يتم ترسيب شوارد الكلور بشكل كلورات الزئبق
4. بعد انتهاء عملية التكثيف انتظر حتى تتبرد العينة وثم استخدم كمية كافية من الماء المقطر لغسل جدران المكثف والدورق، ثم انتظر حتى يتبرد المزيج وبعدها تابع عملية المعايرة
5. يجب أن يتم تحليل العينة والشاهد في نفس الوقت إن أمكن

ملاحظات على طريقة القياس (2)

1. تضاف كبريتات الزئبق من أجل حجب تأثير الكلور وذلك قبل إضافة الكواشف الأخرى. وتكفي كمية 480 ملغ من كبريتات الزئبق من أجل ترسيب 40 ملغ/لتر من شوارد الكلور Cl^- بشكل كلورات الزئبق الضعيفة التشرد $HgCl_2$
2. تضاف كبريتات الفضة Ag_2SO_4 إلى حمض الكبريت المركز وذلك نحو 5.5 غ لكل كغ من حمض الكبريت وتعمل كوسيط أو محرض لأكسدة السلاسل الألفاتية والمركبات العطرية

معاملة العينات (1)

1. يجب أن تؤخذ العينات بأوعية لا تطلق مواد عضوية في الماء، وتعتبر الأوعية الزجاجية ذات الأغطية الزجاجية جيدة لهذا الغرض.
2. يجب تحليل العينات غير المستقرة وخاصة مياه الصرف الصحي والمياه شديدة التلوث، ولكن يمكن التساهل مع عينات مياه الشرب أو عينات المياه الطبيعية الغير ملوثة بشدة بحيث يتم تحليلها في نفس اليوم، ولكن قبل مرور 24 ساعة على الاعتيان مع حفظها مبردة
3. إذا كان من غير الممكن تحليل العينات على الفور فيجب حفظ العينات في ظروف حامضية وذلك باستخدام حمض كبريت كثافته 1.84 ممد بنسبة 1+2 (1 حجم من الحمض + 2 حجم من الماء المقطر) ووضع 2 مل منه لكل 100 مل من العينة. ويجب تحليل العينة على أية حال خلال 24 ساعة وينصح بتجميدها

معاملة العينات (2)

1. يمكن تنفيذ التجربة على عينات مفلترة أو غير مفلترة وذلك اعتمادا على الغاية من التجربة
2. وعندما يتم تنفيذ كلا التجربتين، فإن الفارق يعطينا محتوى المادة المعلقة من الـ COD
3. يمكن تطبيق الرواسب في عينة محتوية على جزيئات مترسبة باستخدام الخلاط وذلك لكي يصبح الجزء المأخوذ من العينة ممثلا للعينة الطبيعية
4. أما من أجل تنفيذ التجربة على العينة المفلترة، فعندئذ نكتفي بأخذ الكمية اللازمة من القسم الطبيعي (غير المختلط مع الرواسب)
5. ينصح بتفلترة العينة من خلال فلاتر الألياف الزجاجية، كما يمكن استخدام الفلاتر من الورق المقوى إذا كان محتوى المادة من الـ COD عاليا، ويجب أن تغسل الفلاتر أولا بالماء المقطر

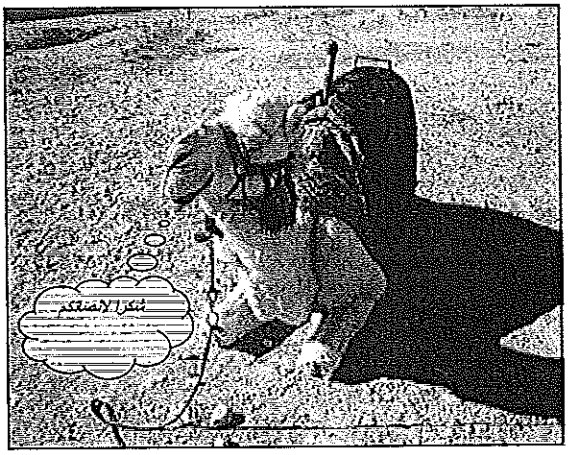
خطوات طريقة التكثيف المفتوح (4)

- *تحضير المحلول النظامي*
  - يمكن تثبيم نتيجة الطريقة وجودة الكواشف المستخدمة وذلك بتطبيق التجربة على المحلول النظامي من بوتاسيوم الهيدروجين فتالات (potassium hydrogen phthalate (KHP) ($HOOCC_6H_4COOK$)
  - لـ KHP قيمة نظرية من الـ COD تعادل 1.176 ملغ أوكسجين لكل ملغ من الـ KHP
  - اذب 425 ملغ من الـ KHP في الماء المقطر ومددها حتى 1000 مل للحصول على محلول محتوى الـ COD فيه 500 ملغ/لتر
  - يمكن الحصول على نتيجة تعادل 98-100% من قيمة الـ COD النظرية
  - إن هذا المحلول مستقر عن حفظه مبردا، ولكن ليس للأبد، ومن المفضل تحضيره بشكل أسبوعي.

اجراءات القياس للعينات التي محتواها من الـ COD أقل من 50 ملغ O_2 في اللتر

- اتبع الاجراءات التي تم ذكرها سابقا في القسم (طريقة القياس باستخدام التكثيف المفتوح (1) وما يليها ولكن مع استثناءين اثنين
  1- استخدم محلول ديكرومات نظاميته 0.025N (0.00416 مول)
  2- استخدم محلول الـ FAS الذي نظاميته 0.025N
- واتخذ كافة الاحتياطات اللازمة لكي لا تتداخل أية مواد عضوية من الجو المحيط في التجربة لأن أصغر الجسيمات العضوية سيؤدي إلى أخطاء كبيرة مع التراكيز القليلة.

⟸ توخ العناية والحذر


تذكر الاصدقاء

التدريب النظري على
تحليل جودة المياه الكيميائية والبيولوجية

المحاضرة 13
الكوليفورم الكلي (1)

تموز 2007

شينسوكي ساتو
فريق خبراء جايكا

ما هو الكوليفورم الكلي (1)

- يعبر مصطلح باكتيريا الكوليفورم عن مجموعة غير محددة من الأحياء التي لها تاريخ طويل من التأثير على تحديد جودة المياه

ما هو الكوليفورم الكلي (2)

- الأحياء المعدية ≠ بكتيريا الكوليفورم
- التعداد في الماء
  - الأحياء المعدية: صغير
  - بكتيريا الكوليفورم: كبير
- تتضمن بكتيريا الكوليفورم الأحياء المعدية
- القياس
  - الأحياء المعدية: صعب
  - بكتيريا الكوليفورم: سهل نسبيا

ما هو الكوليفورم الكلي (3)

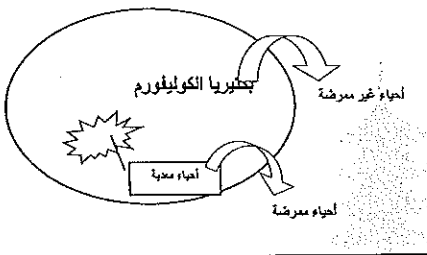
- يعبر مصطلح "الكوليفورم الكلي" عن **مجموعة كبيرة** من:
  - سلبية الغرام
  - العصيات
  - والتي تتشارك في مجموعة من الخواص

ما هو الكوليفورم الكلي (4)

- الباكتيريا غير الممرضة الموجودة في التربة أو الغطاء النباتي أو أمعاء الأحياء ذات الدم الحار (بكتيريا البراز)
- تتواجد بأعداد أكبر من الأحياء المعدية الأكثر خطورة، وتتفاعل مع البيئة المحيطة وعمليات المعالجة بشكل يشابه الأحياء المعدية

ما هو الكوليفورم الكلي (5)

- إنه مؤشر عام على جودة المياه من الناحية الصحية والذي يدل على وجود أحياء معدية.



لماذا نقوم باختبار بكتيريا الكوليفورم (1)

1. معظم الكوليفورم غير ممرضة
2. إن وجود بعض الكوليفورم في المياه يعني أن
   - ⟸ الماء قد يحتوي على بعض الأحياء الممرضة
3. وجود الكثير من الكوليفورم في الماء يعني أن
   - ⟸ إحتمال كبير للتلوث بالأحياء الممرضة
4. عدد الأحياء الممرضة قليل نسبيا أي
   - ⟸ من الصعب بمكان عزل وتحديد الأحياء المعدية

لماذا نقوم باختبار بكتيريا الكوليفورم (2)

5. مراقبة / قياس بكتيريا الكوليفورم
   - ⟸ يمكن تقدير زيادة أو نقصان العوامل الممرضة
   - ⟸ الكوليفورم الكلي هو مؤشر شائع وسهل القياس

...ن الكوليفورم كائنات تتواجد بشكل طبيعي في التربة والمياه، كما تتواجد بشكل طبيعي في المخلفات الحيوانية. ويبقى تواجدها عادة أن المصدر المائي قد اختلط مع مياه الصرف الصحي. وبالتالي فمن المهم تحديد مصدر ذلك التلوث

أين نجد الكوليفورم؟ (1)

- هنالك العديد من مصادر التلوث بالكوليفورم
- ينتج عن تربية الحيوانات تلوث شديد بالكوليفورم
- المنصرفات التالية تساهم بالتلوث بالكوليفورم
  - الغابات
  - المراعي
  - مزارع تربية الحيوان
  - أحواض تخمر الصرف الصحي
  - محطات معالجة الصرف الصحي
  - الحيوانات والطيور البرية
  - غيرها

كيف نقيس الكوليفورم

- يمكن قياس الكوليفورم في المختبر
- يتم القياس بإحدى الطريقتين التاليتين
  - استنبات الكوليفورم ضمن وسط يحتوي على اللاكتوز بدرجة حرارة 35-37 مئوية
  - يمكن التثبت من وجودها من خلال مراقبة تشكل الحموض أو الغاز جراء تخمر السكريات

المقارنة بين الطريقتين

	طريقة أنابيب التخمير المتعددة	طريقة الأغشية
السرعة	أبطأ: تحتاج 48 ساعة حضن	أسرع: تحتاج 24 ساعة حضن
الجهد	متطلبة	أقل تطلبا
كمية الوسط المغذي	أكثر	أقل
الحساسية	حساسة	أقل حساسية
الدقة	أقل دقة لأن النتائج تحسب بشكل غير مباشر (طرق إحصائية)	أدق، حيث يتم القياس بشكل مباشر (قياس عدد المستعمرات)
قابلية التطبيق في الحقل	لا يمكن تطبيقها في الحقل	يمكن استخدامها في الحقل
قابلية التطبيق	يمكن تطبيقها على جميع أشكال العينات	لا يمكن تطبيقها على عينات الماء العكر

اختيار طريقة الاختبار

- يتم استخدام طريقتين بشكل أساسي

1. طريقة "أنابيب الخمر المتعددة" كما و تسمى بطريقة "الرقم الأكثر احتمالا"

يتم وضع كمية من المياه قيد الاختبار في أنابيب اختبار ضمن وسط مناسب للاستنبات (يحتوي سكر اللاكتوز) ثم يتم حضن هذه الأنابيب لمدة معينة تحت درجة حرارة معينة

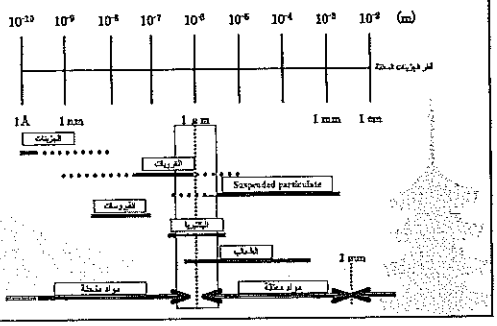
2. طريقة الأغشية (MF) (وهي الطريقة التي سنستخدمها)

يتم تمرير العينة من خلال غشاء قطر فتحاته معين، ثم وضعه على وسط مغذ (سكري) وحضنها بشروط معينة.

طريقة الترشيح من خلال الغشاء

- تم اقتراح هذه الطريقة في أواخر الخمسينات كطريقة بديلة عن طريقة الأنابيب المتعددة
- تقدم هذه الطريقة إمكانية عزل المستعمرات البكتيرية المشتتة
- بينما لا تقدم طريقة الأنابيب المتعددة سوى إمكانية تحديد وجود أو عدم وجود كمية تقريبية من البكتيريا

أحجام المواد الموجودة في المياه



ملخص الطريقة

① يتم ترشيح العينة من خلال غشاء من أسيتات السيليلوز ذي قطر فتحات نظامي

⇩

② يتم حجز الباكتيريا على سطح الغشاء

⇩

③ يتم وضع الغشاء على وسط مغذي منتقى بعناية في وعاء معقم، ويتم حضنه ضمن درجة حرارة مناسبة

⇩

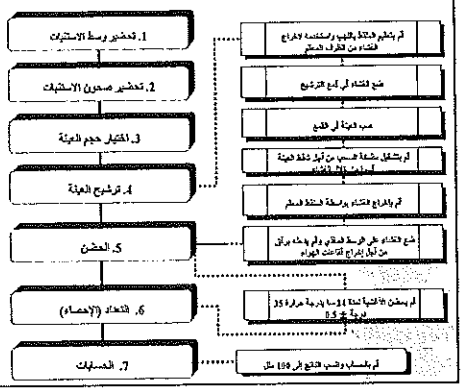
④ إذا وجدت أي آثار من الكوليفورم في عينة المياه، تظهر مستعمرات على سطح الغشاء يمكن إحصاؤها بسهولة

ملاحظة: يجب تعقيم جميع الأدوات المستخدمة قبيل الاستخدام.

إجراءات طريقة الترشيح الغشائي (خلاصة)

- يتم تمرير كمية معينة من العينة (100 مل في حالة الماء العذب) من خلال غشاء قطره 47 ملم وقطر فتحاته 0.45 ميكرون باستخدام قمع خاص ونظام تفريغ من الهواء
- يتم حجز معظم الكائنات الدقيقة مثل الباكتيريا على سطح الغشاء، ثم يوضع الغشاء على الوسط المغذي في صحون بيتري ويتم حضنها لزمن معلوم
- يمر الوسط المغذي من خلال ثقوب الغشاء لتتغذى عليه الكائنات الدقيقة
- يتم إحصاء المستعمرات المتشكلة باستخدام عداد المستعمرات

إجراءات طريقة الترشيح من خلال الغشاء (MF)



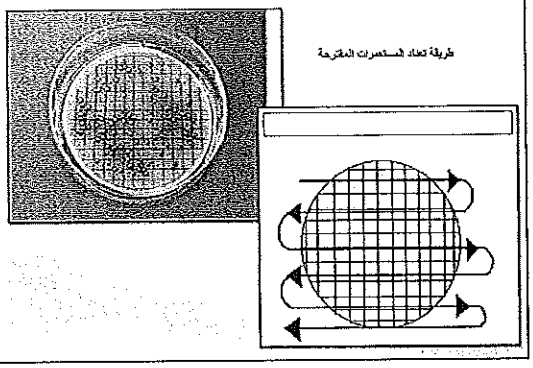
الأدوات والأجهزة اللازمة

① زجاجات أو أنابيب للتمديد
② ماصات، وأسطوانات مدرجة
③ صحون استنبات (صحون بيتري)
④ وحدة فلترة
⑤ أغشية (المميرين)
⑥ ملاقط
⑦ عداد المستعمرات
⑧ أجهزة تعقيم (أوتوكلاف، فرن... إلخ)

تعداد المستعمرات (الإحصاء) -1-

- من أجل تعداد المستعمرات يجب مسح سطح الغشاء باستخدام مكبرة تقوم بالتكبير 10-15 مرة أو ما يشابهها من أدوات تكبير
- يجب أن يكون الرقم منطقيا أي
  - الرقم الأمثل هو 50 مستعمرة في الغشاء
  - لا يجب أن يزيد عن 200 مستعمرة
  - يفضل أن يتراوح ما بين 20-80 مستعمرة
- يجب تسجيل جميع النتائج على السجل الخاص بالتجربة

تعداد المستعمرات (الإحصاء) -2-



الوسط المغذي -1-

- هو وسط لتغذية بكتيريا الكوليفورم
- يتم اختياره بحسب صنف بكتيريا الكوليفورم الذي نريد استنباته
- يمكن الحصول عليه من حبيبات مجففة
- يتم استخدام الوسط m-Endo من أجل استنبات الإشيرشيا كولي (e-coli) باستخدام طريقة الترشيح من خلال الأغشية النظامية

الوسط المغذي -2-

- الوسط المغذي حساس للحرارة
- لا تقم بتسخينها أكثر من اللازم
- من أجل تخزين حبيبات الوسط المغذي الجافة اتبع ما يلي:
  - تخزن في مكان جاف ومظلم بحرارة من 15 إلى 25 مئوية
  - يجب إحكام إغلاق الأوعية بعد الاستخدام
  - تؤدي عملية الحل بالماء إلى تغيير قيمة الـ pH وبالتالي التكثف

اختيار حجم العينة المناسب

- يحكمه كمية الباكتيريا المتوقعة في العينة
- إن الحجم الأمثل للعينة هو الذي سيعطينا عدد مستعمرات
  - الرقم الأمثل هو 50 مستعمرة في الغشاء
  - لا يجب أن يزيد عن 200 مستعمرة
  - يفضل أن يتراوح ما بين 20-80 مستعمرة
- وبالتالي هو متعلق بنوع العينة

حجم العينة المفضل لإجراء التجربة بطريقة MF

	100	10	1	0.1	0.01	0.001
	★					
	★	★				
			★	★		
		★	★			
				★	★	
			★	★		
		★	★	★	★	
			★	★	★	★
			★	★	★	★
				★	★	★
	★	★				

قطف العينات، نقلها، وحفظها

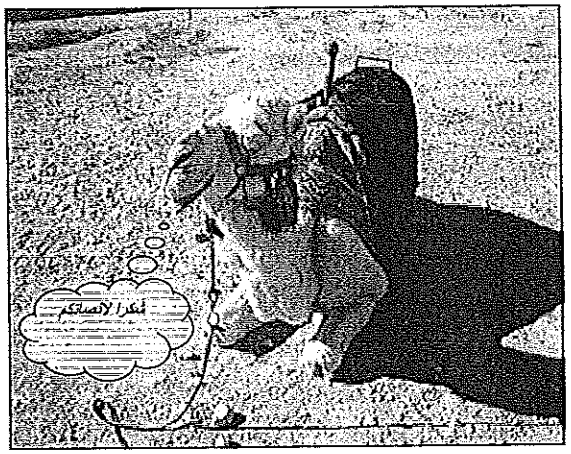
- قم بغسل الأوعية بشكل جيد باستخدام منظف مناسب والماء الحار، وقم بشطفها بالماء الحار من أجل إزالة أية آثار عالقة بها، ثم اغسها بالماء المقطر
- قم بتعقيم الزجاجيات لمدة ساعتين على الأقل بدرجة حرارة 170 في الفرن الجاف
- قم بتعقيم أواني الاعتيان المصنوعة من البلاستيك كما ورد سابقا، أو باستخدام الأوتوكلاف بدرجة حرارة 121 لمدة 15 دقيقة.

حجم العينة المفضل لإجراء التجربة بطريقة MF -2-

a. يجب وضع كمية قليلة من العينة في قمع الترشيح مع 9 ملل على الأقل من محلول التمديد من أجل ضمان التوزع المتجانس على سطح الغشاء

b. الأحجام الصغيرة من رتبة 1 و 0.1 و 0.01 و 0.001 ملل يتم تحضير العينات منها بعد سلسلة من التمديدات. فمن أجل ترشيح

-	1 ملل	من العينة استخدم 10 ملل ممددة 1:10
-	0.1 ملل	من العينة استخدم 10 ملل ممددة 1:100
-	0.01 ملل	من العينة استخدم 10 ملل ممددة 1:1000
-	0.001 ملل	من العينة استخدم 10 ملل ممددة 1:10000



محاضرة تدريبية
حول
التحاليل الكيميائية والبيولوجية لجودة المياه

المحاضرة 4-
التحليل باستخدام ناخب الشوارد النوعي

آب 2006؛ تشرين لثاني 2007

شينسوكي ساتو
فريق خبراء جايكا

1

نشاط الشوارد

- نشاط شاردة الهيدروجين

نشاط الشاردة: $\Rightarrow [a^+], [b^-], [X] \cdots$

$a = \gamma C$

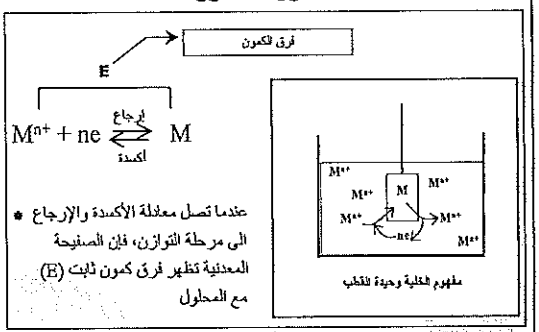
a: نشاط الشاردة, γ : معامل الفعالية (< 1),
C: التركيز الشاردي

في حال التراكيز المنخفضة:

$\gamma \approx 1 \Rightarrow a \approx C$

2

كمون الالكترود



- عندما تصل معادلة الأكسدة والإرجاع الى مرحلة التوازن، فإن الصفيحة المعدنية تظهر فرق كمون ثابت (E) مع المحلول

4

مفهوم الـ PH

- نشاط شاردة الهيدروجين

$K_w = [H^+][OH^-]/[H2O]$ = ثابت
$= 1.8 \times 10^{-16}$

$pH = -\log_{10} [H^+]$
$= \log_{10} 1/[H^+]$

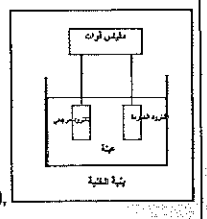
يمكن قياس الـ PH بواسطة مقياس الـ PH
$\Rightarrow$ مقياس الـ PH يقيس نشاط الهيدروجين
$\Rightarrow$ مقياس الـ PH هو أحد أنواع الكترود الشوارد النوعي

5

معادلة نيرنست

- يعبر عن فرق الكمون (E) بواسطة معادلة نيرست

$E = E_0 + RT/nF \times \ln [M^+]$



E_0: كمون الالكترود الأساسي
R: ثابت الغاز (8.31 [J/mol K])
T: درجة الحرارة (كيلفن)
n: عدد الالكترونات المنتقلة
F: ثابت فاراداي (9.64853 × 10^4 [K/mol]),
$[M^+]$: نشاط الشاردة ($\gamma \times C_M$)

3

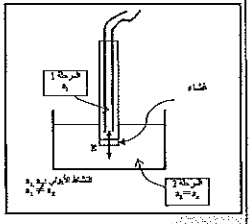
إلكترود الشوارد النوعي (ISE)

- هو الالكترود الذي يتحسس لوجود شاردة معينة ضمن محلول
- يستخدم بشكل متكرر في المخابر و الصناعة وعمليات المراقبة وفي القياسات الفيزيولوجية وفي مجال المراقبة البيئية
- هو نوع من المحول حيث يحول نشاط شاردة معينة منحلة ضمن محلول الى كمون كهربائي
- الكمون الكهربائي (الفولت) مرتبط بالنشاط الشاردي لوغاريتمياً
- يصنع القسم الحساس من الالكترود عادة من غشاء يتحسس لنوع معين من الشوارد

6

غشاء الشوارد النوعي

- هو الحد الفاصل بين مرحلتين.
- شاردة معينة تستطيع اختراقه والعبور بين المرحلتين.
- حتى الوصول الى توازن كهروكيميائي
- يتولد فرق في الكمون(E)عبر الغشاء.
- يتم حساب فرق الكمون المتولد باستخدام معادلة نيرست .



فرق الكمون (E) عبر الغشاء

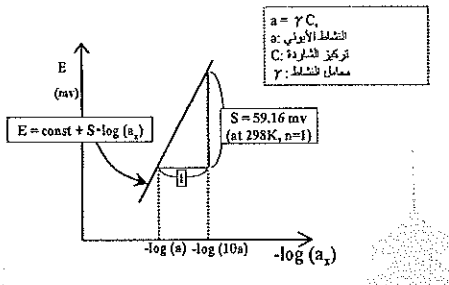
$$E = RT/nF \cdot \ln (a_2/a_1)$$

- إذا بقي نشاط الشاردة المدروسة في المرحلة الأولى ثابتاً فإن نشاطها غير المعروف في المرحلة 2 ($a_2=a_x$) مرتبط بقيمة (H) حسب العلاقة:

$$E = RT/n_xF \cdot \ln (a_x/a_1)$$
$$= RT/n_xF \cdot (2.303\log(a_x)-2.303\log(a_1))$$
$$= \text{const} + S \cdot \log (a_x)$$

- إن معادلة نيرست أعلاه تُظهر أن الخط البياني للكمون والمقاس مقابل log(a) هو خط مستقيم

منحنى المعايرة لإلكترود الشوارد النوعي



المعايرة والقوة الشاردية

- باستخدام سلسلة من محاليل المعايرة فإن منحنى الاستجابة أو منحنى المعايرة لإلكترود الشوارد النوعي يمكن قياسه ورسمه كعلاقة بين إشارة القوة المحركة الكهربائية وبين نشاط الشاردة المدروسة
- ان المجال الخطي لمنحنى المعايرة يستخدم عادة لتحديد نشاط الشاردة المدروسة الموجودة في أي محلول غير معروف
- تجدر الإشارة إلى أنه من أجل قوة شاردية ثابتة، فإن العلاقة الخطية بين الإشارة المقاسة وبين تركيز الشاردة المدروسة تبقى ثابتة
- من أجل الحفاظ على قوة أيونية ثابتة، تضاف عادة شاردة معينة أخرى إلى العينة والمحاليل العيارية بحيث لا تتفاعل مع الشاردة المدروسة ولا تؤثر على كمون الألكترود
- إن المحلول الذي يحتوي على الشوارد المذكورة أعلاه يسمى: ضابط القوة الشاردية (ISA)

بعض الأمثلة حول ضابط القوة الشاردية (ISA)

الشاردة المحللة	ضابط القوة الشاردية المستخدم
NO_3^-	2M $(NH_4)_2SO_4$
Cl^-	5M $NaNO_3$
CN^-	10M NaOH
F^-	CH_3COOH, NaCl, CDTA

شكراً لإصغائكم

Lecture Training for
Basic Water Quality Monitoring (1st)

Lecture-3: Basis of Water Quality Monitoring (WQM)

June 2005

By Matsue Ryunan

(The JICA Expert Team)

1

1. Parameters to be Covered by the Project

14 DFEAs	Damascus, Homs, Aleppo	Damascus DFEA
Basic Water Quality Analysis 1 pH 2 Water Temperature 3 Color 4 TDS 5 DO 6 SS 7 CODcr 8 BOD_5 9 NO_3-N 10 PO_4 11 Cl^- (not Cl_2) 12 NH_3-N 13 EC 14 Turbidity	Basic Water Quality Analysis Air Quality Analysis 1 SOx 2 NOx 3 TSP 4 PM10 5 Pb	Basic Water Quality Analysis Air Quality Analysis Chemical & Biological Water Quality Analysis (Oil, Coliform, Heavy metals, etc.)

2

2. Equipment and Instrument provided by JICA

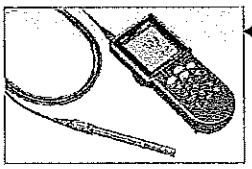
pH, Temp., SS, Color, NO_3-N, PO_4, NH_3-N

COD_{Cr} →

BOD_5 →

pH meter | Colorimeter

3



DO →

Turbidity →

Cl⁻ →

EC & TDS →

Reagents, Glassware, Computer, Digital Camera and others

4

1.Introduction of Water Quality Monitoring (WQM)

1) Definition of WQM

ISO: "The programmed process of sampling, measurement and subsequent recording or signaling, or both, of various water characteristics, often with the aim of assessing conformity to specified objectives.

5

2) Necessity and Importance of WQM

8 Environment tragedies in the world

5 tragedies – air pollution (London, England; 1948-1963; around 10,000 deaths)

2 tragedies – water pollution (*Mina Mata disease* and *Itai-Itai disease*, Japan; 1930'-70'; around 300 deaths)

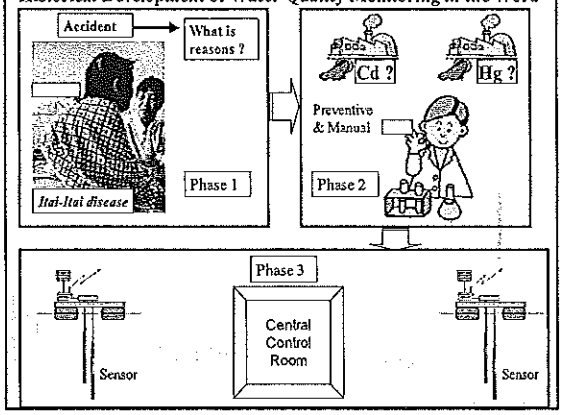
Historical Development of Water Quality Monitoring in the World

Phase 1: **Accident survey** (1950', passive monitoring)

Phase 2: **Pollution sources monitoring** (1960'-70', initiative)

Phase 3: **Water environmental quality monitoring** (1980'~present, automatic monitoring, GIS, RS, GPS)

Historical Development of Water Quality Monitoring in the Word

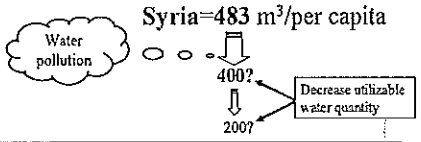


2) Necessity and Importance of WQM

- Freshwater resource:

Average of the world=**7,342** m^3/per capita

Syria=**483** m^3/per capita



- Protect human health
- Evaluation of environmental quality
- Environmental protection policies, plan and management (local and national levels)

WQM: Eye of Water Environmental Protection

3) Water Pollution Sources

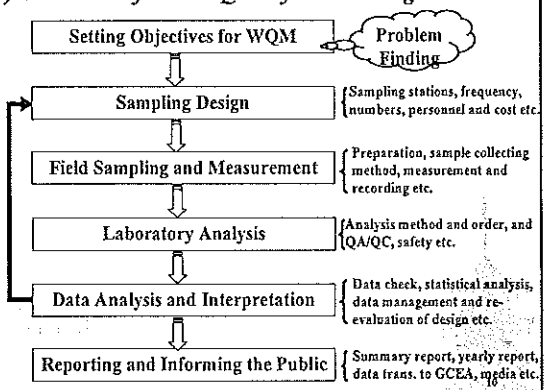
1) Industry Wastewater (point source)
(acid, alkali, organic substances, heavy metals, toxic substances etc.)

2) Domestic Wastewater (point source)
(organic substances, pathogenic organism etc.)

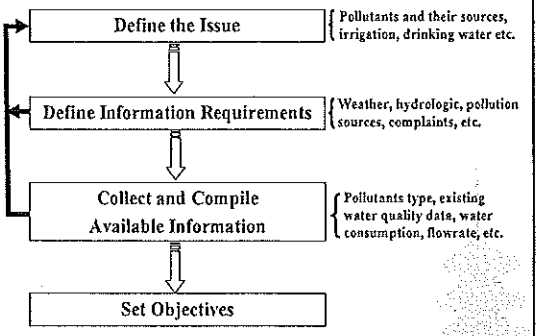
3) Agricultural Waster (no-point source, runoff)
(fertilizer, pesticides, livestock excreta etc.)

4) Others (hospital wastewater, acid rain etc.)

4) Structure of Water Quality Monitoring Plan

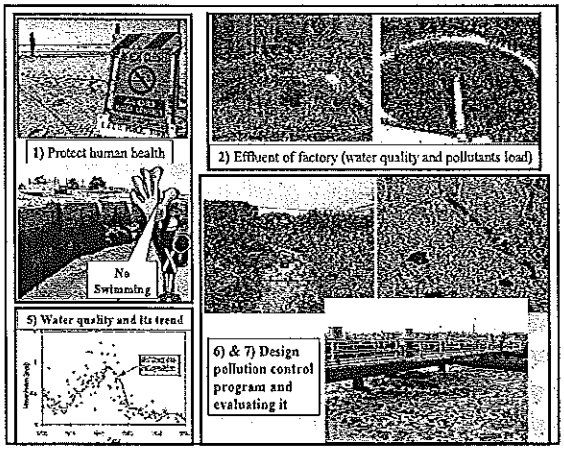


2. Setting Water Quality Monitoring Plan Objectives



Objectives of Water Quality Monitoring Plan

1) Protect human health (next slide)
2) Checking whether effluent from factories comply with industrial wastewater discharge standard (next)
3) Determining whether water bodies meet environmental standards
4) Screening for potential water quality problems
5) Grasping water quality and trends over time (next slide)
6) Design pollution prevention or control programs
7) Assessing program goals and effectiveness
8) Responding to emergencies
9) Others (e.g. handling of complaints, EIA, educating citizens etc.)



Environmental Quality Standard - Rivers, Japan

class	Item: Water use	Standard value: pH	BOD	SS	DO	Total coliform
AA	Water supply class 1, conservation of natural environment and uses listed in A-E	6.5-8.5	1 mg/l or less	25 mg/l or less	7.5 mg/l or more	50 MPN/100ml or less
A	Water supply class 2, fishery class 1, bathing and uses listed in B-E	6.5-8.5	2 mg/l or less	25 mg/l or less	7.5 mg/l or more	1000 MPN/100ml or less
B	Water supply class 3, fisheryclass 2 and uses listed in C-E	6.5-8.5	3 mg/l or less	25 mg/l or less	5 mg/l or more	5000 MPN/100ml or less
C	Fishery class 3, Industrial water class 1 and uses listed in D-E	6.5-8.5	5 mg/l or less	50 mg/l or less	5 mg/l or more	-
D	Industrial water class 2, agricultural water and uses listed in E	6.0-8.5	8 mg/l or less	100 mg/l or less	2 mg/l or more	-
E	Industry water class 3, and conservation of environment	6.0-8.5	10 mg/l or less	Floating Matter such as garbage should not be observed	2 mg/l or more	-

Drinking Water Resource | Water Treatment (SS<25) | Actual Condition of Rivers

Swimming (pH6.5-8.5) | Fishery (DO>5) | Agriculture (SS) | Daily Life (odor→BOD 10)

Environmental Quality Standard – Lakes, Japan

This Project ⇒ COD_{Cr}=2 to 3COD_{Mn}

class	Item: Water use	Standard value: pH	COD	SS	DO	Total coliform
AA	Water supply class 1, fishery class 1, conservation of natural environment, and uses listed in A-C	6.5-8.5	1 mg/l or less	1 mg/l or less	7.5 mg/l or more	50 MPN/100ml or less
A	Water supply class 2, and 3, fishery class 2, bathing and uses listed in B-C	6.5-8.5	3 mg/l or less	5 mg/l or less	7.5 mg/l or more	1000 MPN/100ml or less
B	Fishery class 3, industrial water class 1, agricultural water and uses listed in C	6.5-8.5	5 mg/l or less	15 mg/l or	5 mg/l or more	-
C	Industrial water class 2, and conservation of the environment	6.0-8.5	8 mg/l or less	Floating matter such as garbage not be observed	2 mg/l or more	-

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Environmental Quality Standard – Lakes, Japan

class	Item: Water use	Standard value: Total Nitrogen	Total Phosphorus
I	Conservation of natural environment and uses listed in II-V	0.1 mg/l or less	0.005 mg/l or less
II	Water supply classes 1, 2 and 3 (except special type), Fishery class 1, bathing and uses listed in III-V	0.2 mg/l or less	0.01 mg/l or less
III	Water supply class 3 (special type) and uses listed in IV-V	0.4 mg/l or less	0.03 mg/l or less
IV	Fishery class 2 and uses listed in V	0.6 mg/l or less	0.05 mg/l or less
V	Fishery class 3, Industrial, agricultural water and conservation of the environment	1 mg/l or less	0.1 mg/l or less

Eutrophication Control

Environmental Quality Standard – Coast, Japan

class	Item: Water use	COD_{Mn} Standard value: pH	COD	DO	Total Coliform	Nitrogen Extracts (oil materials)
A	Fishery class 1, bathing, conservation of the natural environment, and uses listed in B-C	7.8-8.3	2 mg/l or less	7.5 mg/l or less	1000 MPN/100ml or less	Not detectable
B	Fishery class 2, Industrial water and the uses listed in C	7.8-8.3	3 mg/l or less le	5 mg/l or less	-	Not detectable
C	Conservation of the environment	7.0-8.3	8 mg/l or less	2 mg/l or less	-	

class	Item: Water use	Standard value: Total Nitrogen	Total Phosphorus
I	Conservation of the natural environment and uses listed in II-IV Except Fishery classes 2 and 3)	0.2 mg/l or less	0.02 mg/l or less
II	Fishery class 1, bathing and the uses listed in III-IV Except Fishery class 2 and 3)	0.3 mg/l or less	0.03 mg/l or less
III	Fishery class 2 and the uses listed in IV Except Fishery class 3)	0.6 mg/l or less	0.05 mg/l or less
IV	Fishery class 3, Industrial water, and conservation of habitats environment for marine life	1 mg/l or less	0.09 mg/l or less

Water Quality Standard for Industrial Wastewater Discharging into Public Sewer System – Syria & Japan

No	Parameter	Unit	Max Admissible Concentration (Syria)	Max Admissible Concentration (Japan)
1	pH	pH Unit	6.5 - 9.5	5.0 - 9.0 (5.7 - 8.7)*
2	Water Temp.	℃	35	45 (40)
3	Color	Unit	-	-
4	TDS	mg/l	2,000	-
5	DO	mg/l	-	-
6	SS	mg/l	500	600 (300)
7	COD_{Cr}	mg/l	1,600	-
8	BOD_5	mg/l	800	600 (300)
9	NO_3^-	mg/l	-	-
10	PO_4^{3-}	mg/l	20	(T-P) 32 (20)
11	Cl^-	mg/l	600	-
12	NH_3-N	mg/l	100	(T-N) 240 (150)
13	EC	μS/cm	-	-
14	Turbidity	NTU	-	-

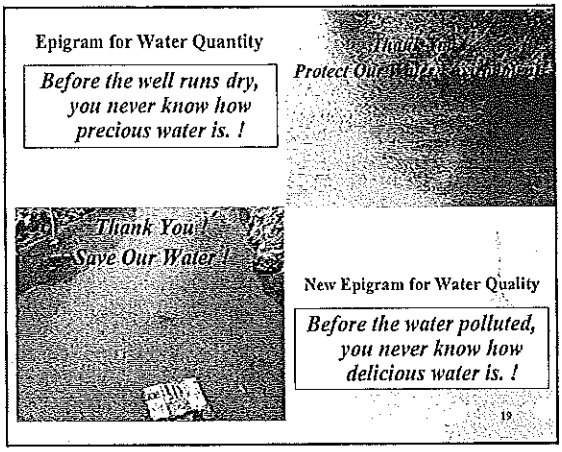
Check it !

* ( ): Applying for manufacturing industry and gas supply industry

18

Epigram for Water Quantity

Before the well runs dry, you never know how precious water is. !



New Epigram for Water Quality

Before the water polluted, you never know how delicious water is. !

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