Slide 1

−1
Sample collection, preservation, and storage

Slide 2

1. Sample collection
   - Sample collection will typical of water quality.
2. Sample container
   - Generally collect samples in clean plastic or glass bottles.
   - Collect samples bottles acid-washed, tap water and distilled water - washed
   - When Specific amount, it is specified in each clause.

Slide 3

3. Handling of sample
   - Carry out the test, unless otherwise specified on the whole amount contained in the Sample.
   - When sample contains suspensoid, take the sample for test after sufficient agitation to get uniform condition.
   - When testing anion, however, unless otherwise specified, use the sample which has been filtreated.
   - When finding the whole amount, it is specified in each clause.
   - Where only the target in determined, immediately after sampling , and take the filtrate for the sample after discarding.

Slide 4

4. Preservation, and storage of sample
   - Carry out the test, unless otherwise specified immediately after sampling.
   - When preservation is needed instead of immediate test, treat it as follows, and carry out the test, as soon as possible.
   - When storing in cold place, take care not to freeze it.
   - Preservation shall be carried out as follows.

   Preservation shall be kept in a dark place at 4

Slide 5

A) Kept in a dark place at 4 .

Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air.

COD(Cr)   (analyzed within 24 hours)
BOD   (analyzed within 24 hours)
Surfactants (analyzed within 24 hours)
NO_3-N   (analyzed within 24 hours)
NO_2-N   (analyzed within 24-48 hours)
PO_4^{3+} (analyzed within 24 hours)
Sulfide   (analyzed within 24 hours)
Cr^{6+} (analyzed within 24 hours)

Slide 6

B) If chlorine is ptesent, add 0.1 N sodium thiosulfate. Add sulfuric acid pH to 2 or less), and kept in a dark place at 4 .

   NH_3-N   (analyzed within 28 hours)

C) Add nitric acid pH to 2 or less), and kept in a dark place at 4 .

   T-Cr   (analyzed within 6 months at room temperature)
   Hardness (analyzed within 6 months at 4)

D) Adding hydrochloric acid   pH to 4 or less), and kept in a dark place at 10   .

Collect samples in clean glass bottles.

Collect samples bottles acid-washed, tap water and distilled water – washed, solvent-washed.

Oil & grease   (analyzed within 2-3 days)

Thank You for Your Kind Attention

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Slide 1 (title slide): _[blank title boxes]_

Spectropotometer

Light source part → Wavelength selection part (optical filter) → Sample part → [Detector → Amplifier] Photometry part → Signal Processing part
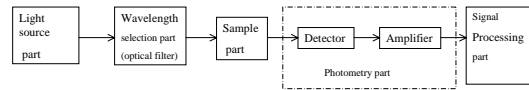
Figure 1 example of photoelectric photometer

A) Light source part

The light source part is composed of an emitter for light sources, a power source for lighting, a light condensing system, etc.

Emitter for light sources. The emitter for light sources shall be as follows:

- Tungsten lamp: used at a long wavelength range of 320 nm or over
- Halogen lamp: used at a long wavelength range of 320 nm or over
- Deuterium lamp: used at a wavelength range from 160 nm to 400 nm
- Low pressure mercury lamp: many emission lines from 253.65 nm to 579.07 nm used as a light source
- Other light sources: A xenon lamp, a high luminance LED, a laser,etc. can be used.

Power source for lighting. This shall have a function to power a light source and to keep its luminance stable.

Light condensing system. This system is composed of a light condensing mirror and a light condensing lens.

B) Wavelength selection part

The wavelength selection part uses one or more monochromater, etc.

C) Sample part

In the case of the double beam method, the target sample and reference sample shall be fixed in optical path, and in the case of the single beam method, either target sample or reference sample can be fixed in it , and is composed of an absorption-cell holder.

Absorption cell.

This is for for keeping constant the optical length of target sample such as a gas or liquid, and should have high transmissibility in the range of the measuring wevelength and be high in anticorrosiveness to the target sample.

there are types such as square cell, cylinder cell, micro cell, and flow cell.

Absorption-cell holder.

This is for fixing an absorption cell placed in optical path, and keeping constant the optical length of target sample.

D) Photometry part

This is composed of a detector and an amplifier.

Detector. This is a transducer to change proportionally the intensity of incident lightto electric signal, and a detector such as a photomultiplier, a photodiode, a photoconductive cell, a photocell, or a phototube isused.

Amplifier. This is for amplifying the electric signal from the detector up to such a magnitude that it is easy to be processed in the subsequent signal processing system.

E) Signal processing part

This is to separate and output the signal needed for measurement, and signal processing is classified into analog processing and digital one.

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
$A = \log_{10} I_0 / I_l = \log_{10} 1/T = -\log_{10} I_l / I_0$
$A = \log_{10} 100/\%T = 2 - \log_{10} \%T$
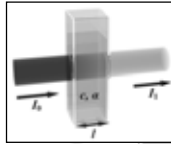
7

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 that has passed through a sample (transmitted light intensity),

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 :

$$A = \log_{10} I_l / I_0 = c\,l$$

8

Here:

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.

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3. Working curve method

Measure absorbance of several samples in which the concentration of analyte is known and differs each other, and prepare the working curve expressed by the relation curve between the concentration of analyte and absorbance.

Then, carry out the measurement of target sample, calculate the concentration of analyte contained in the sample making use of the relation curve, and determine it.

For the actual procedure, prepare the solution for working curve preparation according to the description in each individual standard, and measure absorbance of the solution.

Prepare the working curve by graduating the concentration of analyte in the sample for workind curve on an abscissa and absorbance on an ordinate.

An example of working curve is shown in figure 2.

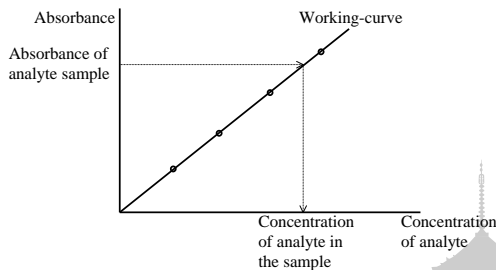Making use of the working curve, obtain the concentration of analyte.

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Figure 2 Example of working curve

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4. Standard addition method

pipette a certain amount of 4 or more samples out of the same sample solution to be determined, and except one sample add the solution where the concentration of analyte has been known into three or more sample solutions so as to let each concentration stepwise differ.

If necessary, treat these 4 or more solution with colouring operation, and then make them to be definite volume for measurement, and measure absorbance.

Calculate respectively the concentration of analyte, and graduate the increment of concentration of analyte owing to adding of standard solution on an abscissa and absorbance on an ordinate to prepare the relation curve.

The intersecting point of the relation curve and the abscissa(point X in figure 3) gives the concentration or quantity of the analyte.

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Absorbance

Increment of absorbance owing to adding of standard solution

Absorbance by sample solution

X

Increment of concentration of analyte owing to adding of standard solution

Figure 3 Example of standard addition curve

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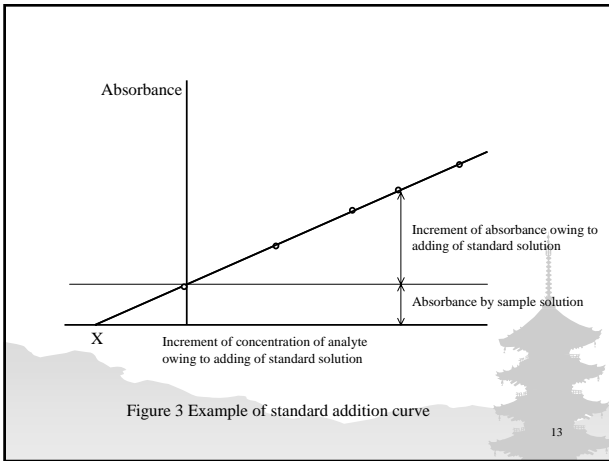
Thank You for Your Kind Attention

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interference Elimination mechanism of coloring

a

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1. NH$_3$-N

interference Elimination．

- If the sample contained a residue of [CL_2]deal it with [$Na_2S_2O_3$]
- BY distillation ammonia gas will be formed .we can get it by using absorption solution as [H_3BO_3]
- If the sample contained volatile organic matters we can volatilize it by distillation ,but before that should control PH not more 2

mechanism of coloring

- It happens according to NESLAR reaction

$2HgI_4^{2-}$ $4OH^-$ NH_4^+ $O{<}^{Hg}_{Hg}{>}NH_2I$ $7I^-$ $3H_2O$

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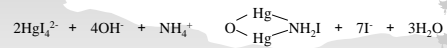
2. NO$_2$-N

interference Elimination．

- Mostly there is no interference .but if the sample contained muddiness should filtrate it
- By oxidize the nitrification microbe which existed in nature NO_2 WILL change to NO_3
- If there is strong oxide or dioxide it will affected the sample
- In the case of high alkali(600mg/L or more)

Concentration will decrease according to the change of PH

mechanism of coloring

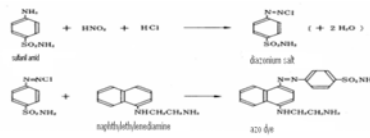- It happens according to NAPHTYLETHY LENEDI AMINE

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3. NO$_3$-N

interference Elimination．

- Mostly there is no interference .but if the sample contained muddiness should filtrate it
- By oxidize the nitrification microbe which existed in nature NO_3WILL change to NO_2
- If the sample contained [Fe]deal it with[EDTA]
- If the sample contained oil should deal it with hexane

mechanism of coloring

- By [Cd-Cu]NO_3 will be deoxidized toNO_2 ,and yellow color assume when reacting to flexible acid

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4. PO$_4^{3-}$

Elimination interference．

- Mostly there is no interference .but if the sample contained muddiness should filtrate it
- If the sample contained high concentration of [Fe]should deal it with Ascorbic acid
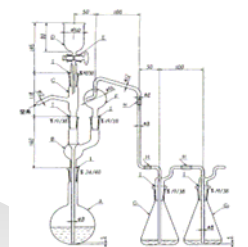
mechanism of coloring

- [Mo] as blue color will assume

---

5. Sulfide

interference Elimination．

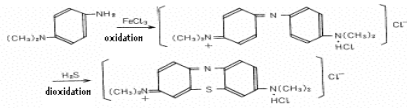- When we ventilate the sample by oxidation ,H_2S will volatilize so should be careful
- By adding ZaCO_3, ZnS   will be fixed   Then hydrogen sulfide will be formed ,and we can collect it by absorption solution .look at the shape below .

---

mechanism of coloring

- Methylene blue will be formed

---

6. Surfactants

interference Elimination.

- Existing [Cl⁻,ClO₄⁻,IO₄]give low value .
- The separation between Benzene &water is difficult .so there is tow ways.

The physical one: we can separate the tow phases by vibration and centrifugal Separation .

The chemical one :by using Na_2SO_4 or HCL .

mechanism of coloring

- Alkyl benzene sulfonate,chain alkylate sulfonate ester

React to crystal violet assume (blue color) then we can measure it By absorbance intensity.

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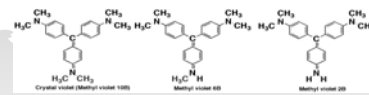
7. Hardness

interference Elimination.

- [Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}]affect the sample

mechanism of coloring

- The KALGAMITreagent colors with red, purple ,blue colors.
  when adding EDTA it react to[Ca,Mg] and assume chelate complex color vanishing [Ca,Mg]color….(blank)
  Then add EGTA react to [Ca]and make a colored chelate complex vanishing its color (Mg hardness).

---

8. Cr^{6+}

interference Elimination.

- When Putting sulfuric acid and ethanol in the sample Cr^{6+}dioxeded to Cr^{3+}

(blank)

- mechanism of coloring
  - Diphenyl carbazide assume as following

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9. T-Cr

interference Elimination.

- If the sample contained organic matters add H2SO4 then heat it

mechanism of coloring

2 Cr^{3+}	2MnO^{4+}	3H_2O	$Cr_2O_7^{2-}$	2MnO_2	6H^+	
2MnO^{4+}	5NO_2^-	6H^+	2Mn^{2-}	5NO_3^-	3H_2O	
MnO_2	NO_2^-	2H^+	Mn^{2-}	NO_3^-	H_2O	
2NO_2^-	$CO(NH_2)_2$	2H^+	CO_2	2N_2	3H_2O	

Thank You for Your Kind Attention

Cr^{6+}	T−Cr	Hardness	NO$_3^-$−N (MR)	NO$_3^-$−N (HR)
No. 1560	No. 1580	Mg No. 2020	No. 2520	No. 2530
0～0.700mg/L	0～0.700mg/L	Ca No. 2010	0～5.0mg/L	0～30.0mg/L
540 nm	540 nm	0～4.00mg/L	400 nm	500 nm
1−inch Cell	1−inch Cell	522 nm	1−inch Cell	1−inch Cell
		1−inch Cell		

Cr^{6+} (No. 1560)

Blank

- 10mL of Sample (Cell)
  ↓
- Cell holder in set.
  ↓
- ZERO

Measuremnt

- 10mL of Sample (Cell)
  ↓ ←Chroma Ver 3
- Swirl to mix
  ↓
- Wait 8 min.
  ↓
- Cell holder in set.
  ↓
- Read of result

T−Cr (No. 1580)

Blank

- 25mL of Sample (Cell)
  ↓
- Cell holder in set.
  ↓
- ZERO

Measuremnt

- 25mL of Sample (Cell)
  ↓ ←Chromium 1
- Swirl to mix
  ↓
- Boiling 5 min.
  ↓
- Cool by tap water
  ↓ ←Chromium 2
- Swirl to mix
  ↓ ←Acid Reagent
- Swirl to mix
  ↓ ←Chroma Ver 3
- Swirl to mix
  ↓
- Wait 5 min.
  ↓
- Cell holder in set.
  ↓
- Read of result

Hardness

Measuremnt

- Mg No. 2020
  ↓
- 100mL of Sample (Cylinder)
  ↓ ← 1 mL of Ca & Mg Indicator Sol.
- Several times to mix
  ↓ ← 1 mL of Alkali Sol.
- Several times to mix
  ↓
- Divide 25 mL into three samples ① ② ③ (Cell)
  ↓
- ① Mg Blank (Cell)
  ↓ ← 1 drop of EDTA
- Swirl to mix
  ↓
- Cell holder in set.
  ↓
- ZERO (Mg)
  ↓
- ② Mg Measuremnt & Ca Blank (Cell)
  ↓ ← 1 drop of EGTA
- Swirl to mix
  ↓
- Cell holder in set.
  ↓
- Read of result (Mg)
  ↓
- Ca No. 2010
  ↓
- ZERO (Ca)
  ↓
- ③ Ca Measuremnt (Cell)
  ↓
- Cell holder in set.
  ↓
- Read of result (Ca)

NO$_3^-$−N (MR) (No. 2520)

Blank

- 10mL of Sample (Cell)
  ↓
- Cell holder in set.
  ↓
- ZERO

Measuremnt

- 10mL of Sample (Cell)
  ↓ ←Nitra Ver 5 Nitrate
- Shake 1 min.
  ↓
- Wait 5 min.
  ↓
- Cell holder in set.
  ↓
- Read of result

NO$_3^-$−N (HR) (No. 2530)

Blank

- 10mL of Sample (Cell)
  ↓
- Cell holder in set.
  ↓
- ZERO

Measuremnt

- 10mL of Sample (Cell)
  ↓ ←Nitra Ver 5 Nitrate
- Shake 1 min.
  ↓
- Wait 5 min.
  ↓
- Cell holder in set.
  ↓
- Read of result

2/2

NO_2^--N	NH_3-N	PO_4^{3-}	Sulfide (S^{2-})	Surfactants
No. 2610	No. 2400	Mg No. 3025	No. 3500	No. 1850
0～0.300mg/L	0～2.500mg/L	0～2.500mg/L	0～0.800mg/L	0～0.275mg/L
507 nm	425 nm	890 nm	665 nm	605 nm
1-inch Cell	1-inch Cell	1-inch Cell	1-inch Cell	1-inch Cell

Column 1: NO_2^--N

Blank

10mL of Sample (Cell)
↓
Cell holder in set.
↓
ZERO

Measuremnt

10mL of Sample (Cell)
↓ ←Nitra Ver 3 Nitrate
Shake to dissolve
↓
Wait 20 min.
↓
Cell holder in set.
↓
Read of result

Column 2: NH_3-N

Blank

25mL of Distilled water (Cylinder)
↓ ← 3drop of Mineral Stabilizer
Several times to mix
↓ ← 3drop of polyvinyl Alcohol
Several times to mix
↓ ← 1 mL of Nessler Reagent
Several times to mix
↓
Remove into cell
↓
Cell holder in set.
↓
ZERO

Measuremnt

25mL of Sample (Cylinder)
↓ ← 3drop of Mineral Stabilizer
Several times to mix
↓ ← 3drop of polyvinyl Alcohol
Several times to mix
↓ ← 1 mL of Nessler Reagent
Several times to mix
↓
Remove into cell
↓
Cell holder in set.
↓
Read of result

Column 3: PO_4^{3-}

Blank

10mL of Sample (Cell)
↓
Cell holder in set.
↓
ZERO

Measuremnt

10mL of Sample (Cell)
↓ ←Phos Ver 3 Phosphate
Swirl to mix
↓
Wait 2 min.
↓
Cell holder in set.
↓
Read of result

Column 4: Sulfide (S^{2-})

Blank

25mL of Distilled water (Cell)
↓ ← 1 mL of Sulfide 1
Swirl to mix
↓ ← 1 mL of Sulfide 2
Swirl to mix
↓
Wait 5 min.
↓
Cell holder in set.
↓
ZERO

Measuremnt

25mL of Sample (Cell)
↓ ← 1 mL of Sulfide 1
Swirl to mix
↓ ← 1 mL of Sulfide 2
Swirl to mix
↓
Wait 5 min.
↓
Cell holder in set.
↓
Read of result

Column 5: Surfactants

Blank

10mL of Benzene (Cell)
↓
Cell holder in set.
↓
ZERO

Measuremnt

300mL of Sample (Separatory funnel)
↓ ←10 mL of Sulfate Buffer Sol.
Shake 5 sec.
↓ ←Detergents Reagent
Shake to dissolve
↓ ←30 mL of Benzene
Shake 1 min.
↓
Wait 30 min.
↓
Drain of water layer
↓
Benzene layer into cell
↓
Cell holder in set.
↓
Read of result

Standard

Solution

of

Japan

1. T–Cr & Cr^{6+} Std. Sol. (100mg/L as Cr)

K$_2$Cr$_2$O$_7$
150℃, 1hr; Dry

↓

in Desiccator; cool

↓

K$_2$Cr$_2$O$_7$ (100%): 0.283 g

↓

dissolve in water and water to make total 1L

K$_2$Cr$_2$O$_7$: 294.2   Cr : 52
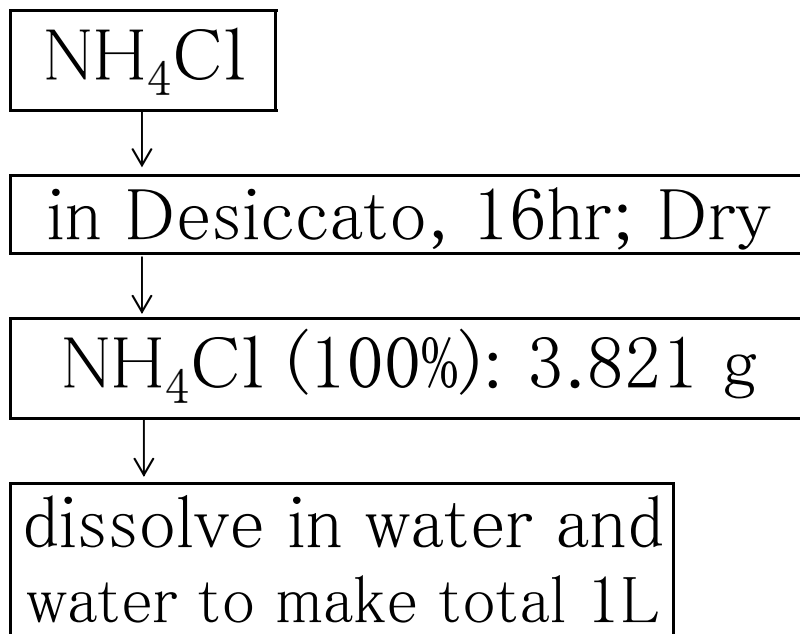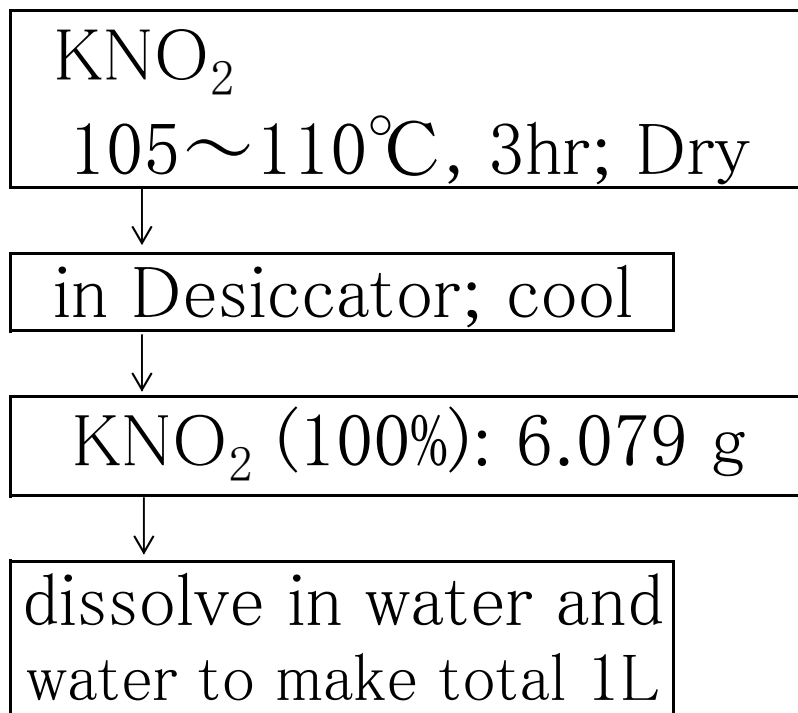
$\frac{1}{2}$ K$_2$Cr$_2$O$_7$: 147.1

$\frac{1}{2}$ K$_2$Cr$_2$O$_7$: Cr = χ mg : 100 mg

147.1 : 52 = χ mg : 100 mg

$$\chi \text{ mg} = \frac{147.1 \times 100 \text{ mg}}{52}$$

χ mg = 283 mg = 0.283 g

2. NH$_3$-N Std. Sol.
(1000mg/L as NH$_3$-N)

$$\boxed{\text{NH}_4\text{Cl}}$$

$$\downarrow$$

$$\boxed{\text{in Desiccato, 16hr; Dry}}$$

$$\downarrow$$

$$\boxed{\text{NH}_4\text{Cl (100\%): 3.821 g}}$$

$$\downarrow$$

$$\boxed{\text{dissolve in water and water to make total 1L}}$$
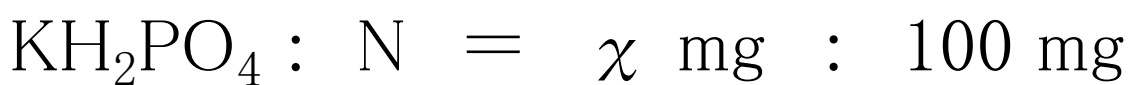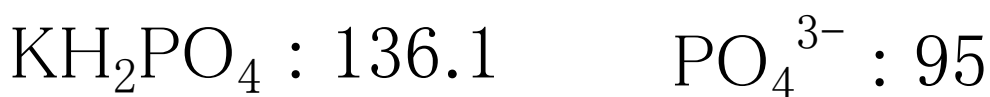
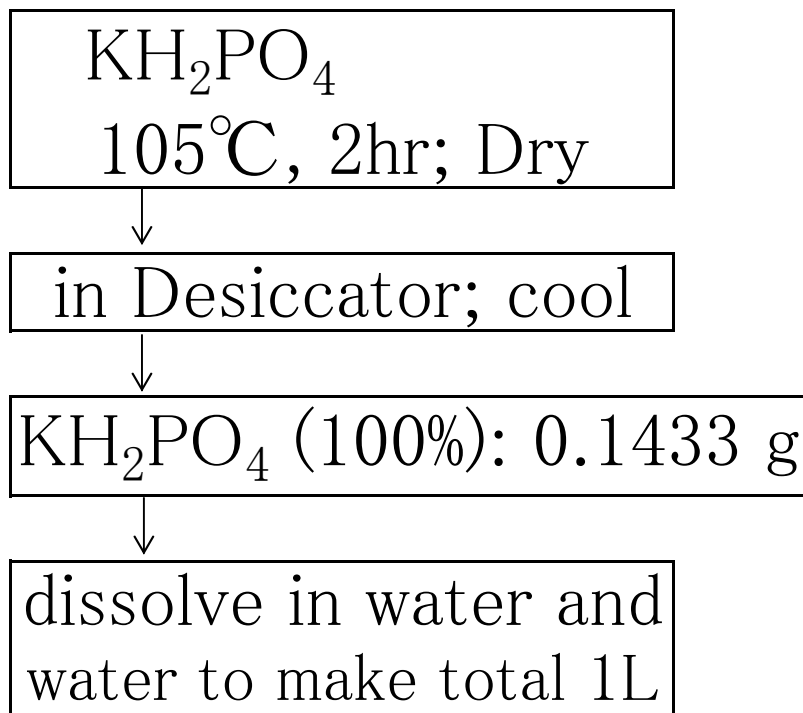NH$_4$Cl : 53.5   N : 14

NH$_4$Cl : N $=$ χ mg : 1000 mg

53.5 : 14 $=$ χ mg : 1000 mg

$$\chi \text{ mg} = \frac{53.5 \times 1000 \text{ mg}}{14}$$

$$\chi \text{ mg} = 3821 \text{ mg} = 3.821 \text{ g}$$

3. NO_3−N Std. Sol.
(1000mg/L as NO_3−N)

KNO_3
 105～110℃, 3hr; Dry

in Desiccator; cool

KNO_3 (100%): 7.221 g

dissolve in water and
water to make total 1L
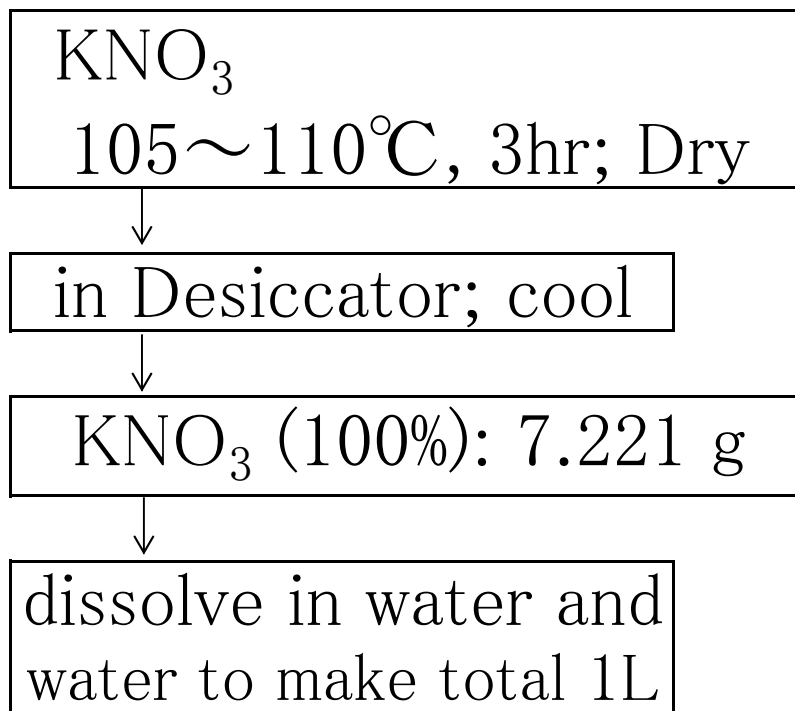
KNO_3 : 101.1   N : 14

KNO_3 : N = x mg : 1000 mg

101.1 : 14 = x mg : 1000 mg

$$x \text{ mg} = \frac{101.1 \times 1000 \text{ mg}}{14}$$

$$x \text{ mg} = 7221 \text{ mg} = 7.221 \text{ g}$$

4-①. NO$_2$-N Std. Sol.
(1000mg/L as NO$_2$-N)

KNO$_2$
105~110℃, 3hr; Dry

↓

in Desiccator; cool

↓

KNO$_2$ (100%): 6.079 g

↓

dissolve in water and water to make total 1L

KNO$_2$: 85.1   N : 14

KNO$_2$: N = x mg : 1000 mg

85.1 : 14 = x mg : 1000 mg

$$x \text{ mg} = \frac{85.1 \times 1000 \text{ mg}}{14}$$

$$x \text{ mg} = 6079 \text{ mg} = 6.079 \text{ g}$$

4-②. NO$_2$-N Std. Sol.
(1000mg/L as NO$_2$-N)

NaNO$_2$
   105~110℃, 4hr; Dry

$\downarrow$

in Desiccator; cool

$\downarrow$

NaNO$_2$ (100%): 4.929 g

$\downarrow$

dissolve in water and
water to make total 1L
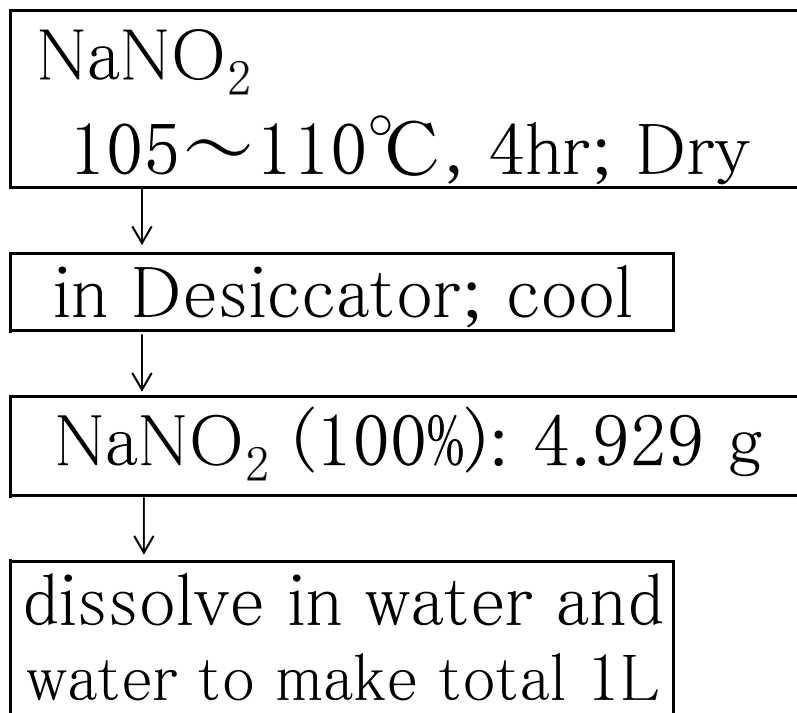
NaNO$_2$: 69   N : 14

NaNO$_2$: N = χ mg : 1000 mg

69 : 14 = χ mg : 1000 mg

$$\chi \text{ mg} = \frac{69 \times 1000 \text{ mg}}{14}$$

$$\chi \text{ mg} = 4929 \text{ mg} = 4.929 \text{ g}$$

5. PO_4^{3-} Std. Sol.
($100mg/L$ as PO_4^{3-})

$$\boxed{\begin{array}{l} KH_2PO_4 \\ \quad 105℃, \ 2hr; \ Dry \end{array}}$$

$$\downarrow$$

$$\boxed{\text{in Desiccator; cool}}$$

$$\downarrow$$

$$\boxed{KH_2PO_4 \ (100\%): \ 0.1433 \ g}$$

$$\downarrow$$

$$\boxed{\begin{array}{l} \text{dissolve in water and} \\ \text{water to make total 1L} \end{array}}$$

$KH_2PO_4 : 136.1 \qquad PO_4^{3-} : 95$

$KH_2PO_4 : \ N \ = \ \chi \ mg \ : \ 100 \ mg$

$136.1 \ : \ 95 \ = \ \chi \ mg \ : \ 100 \ mg$

$$\chi \ mg \ = \frac{136.1 \ \times \ 100 \ mg}{95}$$

$$\chi \ mg \ = \ 143.3 \ mg \ = \ 0.1433 \ g$$

6. Sulfide Std. Sol.
(About 1000mg/L as S^{2-})

NaS・9H2O   About 7.6 g

$\downarrow$

Wash its surface with a little water

$\downarrow$

Filter paper to remove moisture

$\downarrow$

Dissolve in Dissolved-oxygen-free water and make total 1L
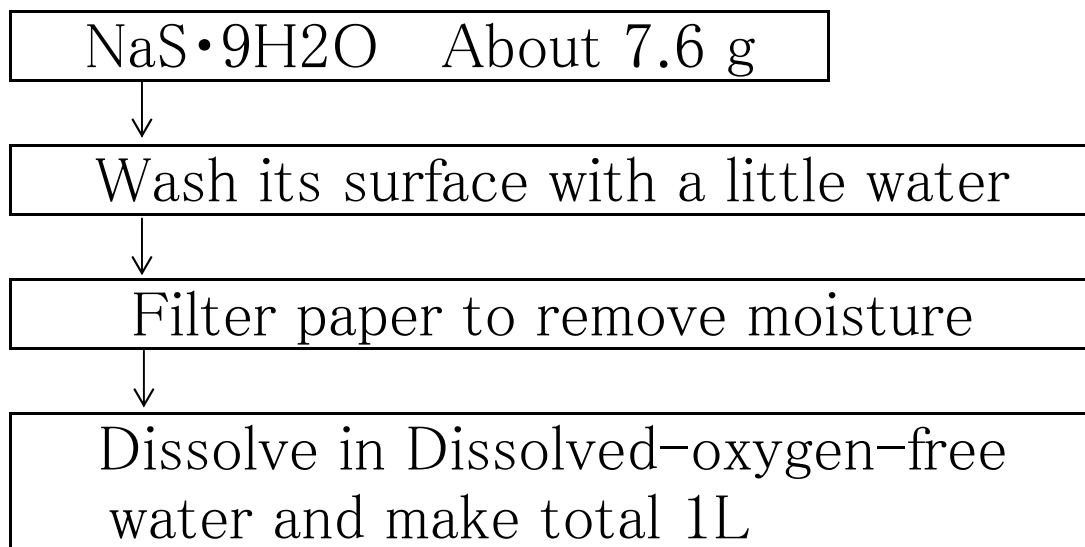
1) Standardization
① About 1000mg/L as S^{2-}

0.05mol/L I_2 sol.   20 mL

$\downarrow \longleftarrow$ (1+1)HCl 0.5 mL

$\longleftarrow$ About 1000mg/L as S^{2-} 10 mL

Stopper and mix

$\downarrow$

Stand for several min.

$\downarrow$

0.1mol/L $Na_2S_2O_3$ sol. Titrate

color : brown $\rightarrow$ yellow

$\downarrow \longleftarrow$ (10g/L) Starch sol. 1 mL

0.1mol/L $Na_2S_2O_3$ sol. Titrate

color : blue $\rightarrow$ color less

$\rightarrow$ 0.1mol/L $Na_2S_2O_3$ sol. Total Titrate (a mL)

② Blank

```
┌─────────────────────────────────────┐
│   0.05mol/L I₂ sol.    20 mL         │
└─────────────────────────────────────┘
        │ ←───(1+1)HCl  0.2 mL
        ▼
┌─────────────────────────────────────┐
│   Stopper and mix                    │
└─────────────────────────────────────┘
        ▼
┌─────────────────────────────────────┐
│   Stand for several min.             │
└─────────────────────────────────────┘
        ▼
┌─────────────────────────────────────┐
│   0.1mol/L Na₂S₂O₃ sol. Titrate      │
└─────────────────────────────────────┘
              ┌──────────────────────────┐
              │  color : brown → yellow   │
              └──────────────────────────┘
        │ ←───(10g/L) Starch sol.  1 mL
        ▼
┌─────────────────────────────────────┐
│   0.1mol/L Na₂S₂O₃ sol. Titrate      │
└─────────────────────────────────────┘
              ┌──────────────────────────┐
              │ color : blue → color less │
              └──────────────────────────┘
        ▶  0.1mol/L Na₂S₂O₃ sol. Total Titrate (b mL)
```

$$S = (b - a) \times f \times \frac{1000}{20} \times 1.603$$

S : Sulfide conc. (mg/L as S^{2-})

a : 0.1mol/L $Na_2S_2O_3$ sol. Needed for
    titration (mL)

b : Blank to 0.1mol/L $Na_2S_2O_3$ sol. Needed
    for titration (mL)

f : Factor for 0.1mol/L $Na_2S_2O_3$ sol.

1.603 : 1mL of 0.1mol/L $Na_2S_2O_3$ sol. : S^{2-} (mg)

2) Prepare to dissolved-oxygen-free water

Water
Boil water
for 5 min.

Dissolved–oxygen–free water

Alkarin pyrogallol sol.
e.g. (30%)KOH and
(15%)pyrogallol

equipment set and cool
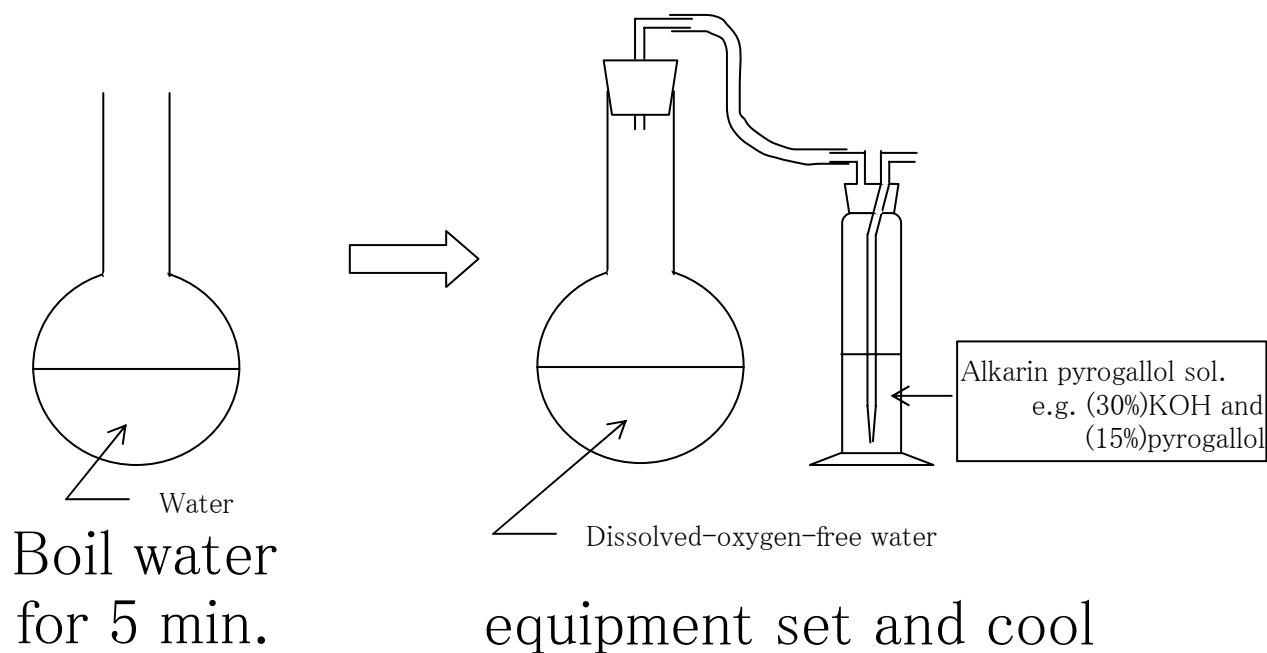
3) Prepare to 0.05mol/L I_2 sol.

KI 45 g		I_2 13 g

water 100 mL
dissolve

water 100 mL
dissolve

Mix

water to make total 1L

4) Factor for 0.1mol/L $Na_2S_2O_3$ sol.

17/13

KIO_3 (Purity b %)

$$\boxed{130^{\circ}\text{C, 2hr; Dry}}$$

$$\downarrow$$

$$\boxed{\text{in Desiccator; cool}}$$

$$\downarrow$$

$$\boxed{\text{KIO}_3 \text{ (100\%): 0.72 g}} \quad (\text{a g})$$

$$\downarrow$$

$$\boxed{\begin{array}{c}\text{dissolve in water and}\\ \text{water to make total 200mL}\end{array}}$$

$$\downarrow$$

$$\boxed{20 \text{ mL}}$$

$$\downarrow \longleftarrow \text{KI 2 g}$$

$$\longleftarrow (1+5)\text{H}_2\text{SO}_4 \text{ 5 mL}$$

$$\boxed{\text{Stopper and mix}}$$

$$\downarrow$$

$$\boxed{\text{Stand for several min.}}$$

$$\downarrow \longleftarrow \text{Water 100 mL}$$

$$\boxed{0.1\text{mol/L Na}_2\text{S}_2\text{O}_3 \text{ sol. Titrate}}$$

$$\boxed{\text{color : brown} \rightarrow \text{yellow}}$$

$$\downarrow \longleftarrow (10\text{g/L}) \text{ Starch sol. 1 mL}$$

$$\boxed{0.1\text{mol/L Na}_2\text{S}_2\text{O}_3 \text{ sol. Titrate}}$$

$$\boxed{\text{color : blue} \rightarrow \text{color less}}$$

$$\cdots\!\!\rightarrow 0.1\text{mol/L Na}_2\text{S}_2\text{O}_3 \text{ sol. Total Titrate } (\chi \text{ mL})$$

$$f \;=\; a \times \frac{b}{100} \underset{18/13}{\times} \frac{20}{200} \times \frac{1}{\chi \times 0.0214}$$

f : Factor for 0.1mol/L $Na_2S_2O_3$ sol.

a : KIO_3 （ g ）

b : KIO_3 （ Purity ％ ）

χ : 0.1mol/L $Na_2S_2O_3$ sol. Needed for titration (mL)

0.0214 : 1mL of 0.1mol/L $Na_2S_2O_3$ sol. : KIO_3 （ g ）

7. Surfactant Std. Sol.
〔1000mg/L as $NaO^3SO(CH_2)_{11}CH_3$〕

Sodium dodecyl sulfate
$NaO_3SO(CH_2)_{11}CH_3$ (100%)

↓

0.1433 g

↓

dissolve in water and
water to make total 1L

Standard

Solution

of Oil

Oil meter range : 0 to 200 mg/L

Standard material : B − heavy oil

Specific gravity : 0.895 g/mL

Concentration of Standard sol. :

$$200 \text{ mg/L} = 200 \text{ mg/1000 mL}$$

··

① Prepare to standard sol. (make to 200 mL)

$$\frac{200 \text{ mg}}{5} \Big/ \frac{1000 \text{ mL}}{5} = 40 \text{ mg/200 mL}$$

$$\frac{40 \text{ mg/200 mL}}{0.895 \text{ g/mL}} = 44.7 \ \mu\text{L/200 mL}$$

② Prepare to standard sol. (make to 100 mL)

$$\frac{200 \text{ mg}}{10} \Big/ \frac{1000 \text{ mL}}{10} = 20 \text{ mg/100 mL}$$

$$\frac{20 \text{ mg/100 mL}}{0.895 \text{ g/mL}} = 22.3 \ \mu\text{L/100 mL}$$

$$\text{Water layer} \xrightarrow{\text{Oil}} \text{Solvent layer}$$
$$\text{Extract}$$

$$C \times V = C' \times V'$$

$$C \times 20 \text{ mL} = C' \times 10 \text{ mL}$$

$$C = C' \times \frac{10}{20}$$

$$C = C' \times \frac{1}{2}$$

C : Concentration of oil in sample (mg/L)

V : Volume of sample (mL)

C' : Concentration of oil in solvent (mg/L)

V' : Volume of solvent (mL)

Therfore program of span :

$$C = 200 \text{ mg/L} \times \frac{1}{2} = 100 \text{ mg/L}$$

Oil & Grease

Gravimetric method

of Japan

0il & Grease   Gravimetric method

Sampling   (1＋1)HCl to pH4 ↓

$$(Sample ＋ Bottle)g － (Bottle)g ＝ (Sample)g$$
$$\fallingdotseq (Sample)mL$$

Sample

Hexane 25 mL wash

bottle

Sample

Hexane

repeat extract one more time

Hexane layer

Sample

Water layer

Extract
mix and sheick

$$(Oil＆Grease)mg/L ＝ \frac{(Oil＆Grease)mg}{(Sample)mL} × 1000$$

Water layer

Hexane layer

Sample

$$(Oil＆Grease ＋ Beaker)mg － (Beaker)mg$$
$$＝(Oil＆Grease)mg$$

Water layer

Hexane layer

Water

Hexane layer

Water layer

Hexane layer wash by water

Water layer
drain

Volatilize of Hexane layer
(80℃)

Hexane layer

0il & Grease

Correlation Coefficient

Correlation coefficient

$$r = \sum_{i=1}^{n} \frac{(x_i - \overline{x}) \times (y_i - \overline{y})}{n \times \sigma_x \times \sigma_y}$$

r : Correlation coefficient

x_i : x date

y_i : y date

$\overline{x}$: x average

$\overline{y}$: y average

n : Number of date

σ_x: x standard deviation

σ_y : y standard deviation

$$\sigma_x = \sqrt{\frac{\Sigma (x_i - x)^2}{n}}$$

$$\sigma_y = \sqrt{\frac{\Sigma (y_i - y)^2}{n}}$$

$$-1 \geqq r \geqq 1$$

$$r^2 \leqq 1$$
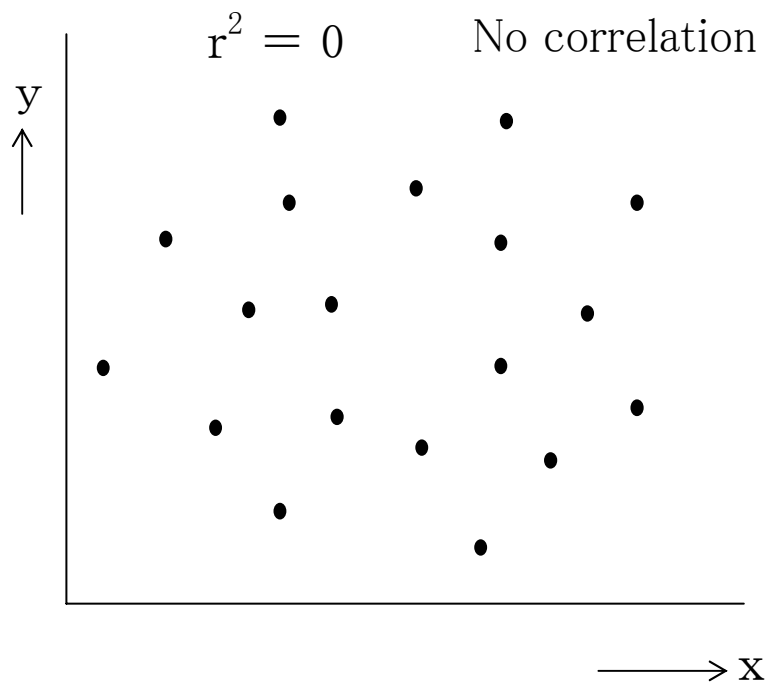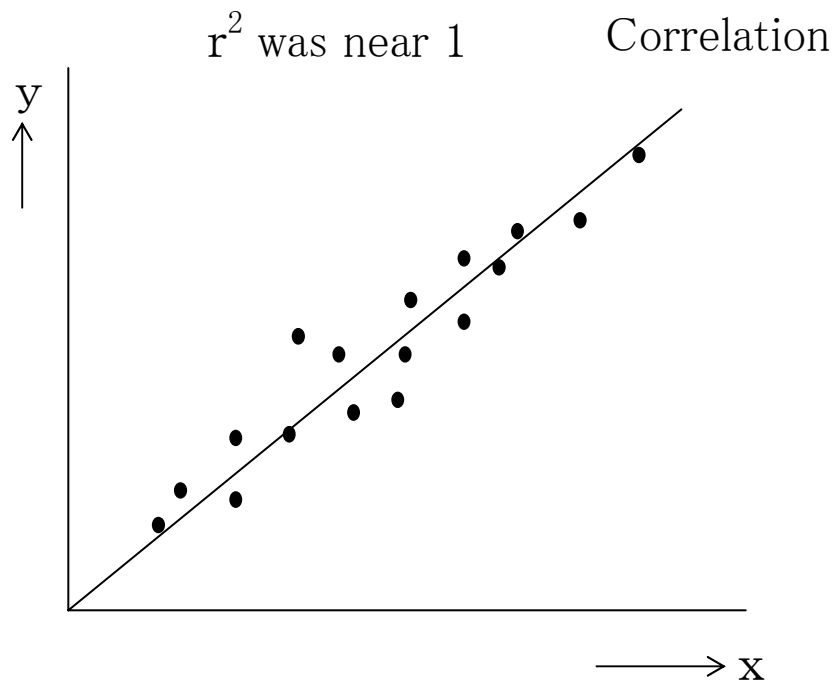
r^2 was near 1   Correlation

$r^2 = 0$ No correlation

Slide 1

Lecture Training for
Chemical & Biological Water Quality
Analysis - 2

Lecture -

Chemical reactions mechanism of coloring

2007 November

Kazuki SAKAE

The JICA Expert Team

1

Slide 2

1. NH_3-N

  1 Chemical reactions. (mechanism of coloring)

$$2K_2HgI_4 + NH_3 + 3KOH \rightarrow Hg_2OINH_2 + 7KI + 2H_2O$$
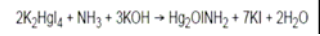
  2 Reagents

    Product Name: Mineral Stabilizer
    Catalog Number: 2376626
    Composition: Sodium Citrate
             Potassium Sodium Tartrate
             Demineralized Water
    Product Name: Polyvinyl Alcohol Dispersing Agent
    Catalog Number: 2376526
    Composition: Polyvinyl Alcohol
             Demineralized Water
             Other components, each

2

Slide 3

Product Name: Nessler Reagent
Catalog Number: 2119449
Composition: Sodium Hydroxide
           Mercuric Iodide
           Sodium Iodide
           Demineralized Water
           Other component

3

Slide 4

2. NO_2-N

  1 Chemical reactions. (mechanism of coloring)

4

Slide 5
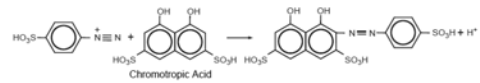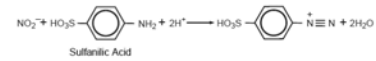
  2 Reagents

    Product Name: NitriVer ® 3 Nitrite Reagent
    Catalog Number: 2107169
    Composition: Chromatropic Acid, Disodium salt
           Sodium Sulfanilate
           Potassium Pyrosulfate
           Potassium Phosphate, Monobasic
           1,2-Cyclohexanediaminetetraacetic Acid Trisodium Salt

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Slide 6

3. NO_3-N

  1 Chemical reactions. (mechanism of coloring)
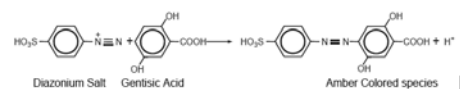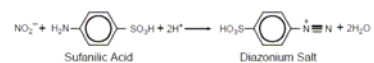
6

2 Reagents

Product Name: NitraVer ® 5 Nitrate Reagent

Catalog Number: 2106169

Composition: Potassium Phosphate, Monobasic

Magnesium Sulfate

Cadmium

Gentisic Acid

Sulfanilic Acid

Other components, each

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4. PO_4^{3-}

1 Chemical reactions. (mechanism of coloring)

[Mo] as blue color will assume

2 Reagents

Product Name: PhosVer ® 3 Phosphate Reagent

Catalog Number: 2106069

Composition: Potassium Pyrosulfate

Ascorbic Acid

Sodium Molybdate

Other components, each

---

5. Sulfide

1 Chemical reactions. (mechanism of coloring)
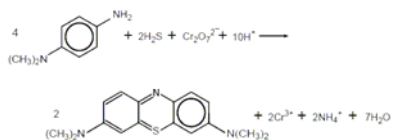
2 Reagents

Product Name: Sulfide 1 Reagent

Catalog Number: 181632

Composition: N,N-dimethyl-p-phenylenediamine

Sulfuric Acid

Demineralized Water

Other component

Product Name: Sulfide 2 Reagent

Catalog Number: 181732

Composition: Potassium Dichromate

Demineralized Water

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6. Surfactants

1 Chemical reactions. (mechanism of coloring)

Alkyl benzene sulfonate,chain alkylate sulfonate ester
React to crystal violet assume (blue color) then we can measure it
By absorbance intensity.

crystal violet
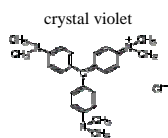
2 Reagents

Product Name: Buffer Solution, Sulfate Type

Catalog Number: 45249

Composition: Sodium Bisulfate

Sodium Sulfate

Demineralized Water

Product Name: Detergents Reagent Powder Pillows

Catalog Number: 100868

Composition: Crystal Violet Dye

Sodium Chloride

Other component

Product Name: Benzene

Catalog Number: 1444017

Composition: Benzene

7. Hardness

1 Chemical reactions. (mechanism of coloring)

Calmagte (Blue)   Calmagte-Mg Complex (Wine Red)

EDTA-Ethylenediaminetetraacetic Acid

EGTA
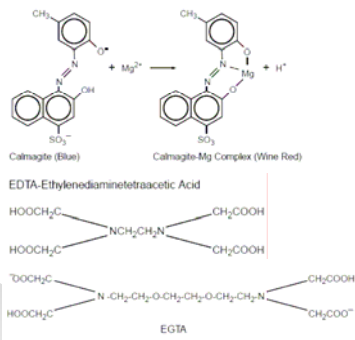
13

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2 Reagents

Product Name: Calcium and Magnesium Indicator Solution
Catalog Number: 2241832
Composition: Propionic acid
        Demineralized Water
        Other component (Calmagite etc.)
Product Name: Alkali Solution for Calcium and Magnesium Test
Catalog Number: 2241732
Composition: Sodium Hydroxide
        Nitrilotriethanol
        Demineralized Water
Product Name: EDTA Solution 1M
Catalog Number: 2241926
Composition: EDTA Tetrasodium Salt
        Demineralized Water
        Other component

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Product Name: EGTA Solution
Catalog Number: 2229726
Composition: ethyleneglycol-bis (2-aminoethylether)-N,N,N',N'-
        tetraacetic acid (EGTA)
        Sodium Hydroxide
        Demineralized Water

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8. Cr^{6+}

1 Chemical reactions. (mechanism of coloring)

1,5-diphenylcarbohydrazide
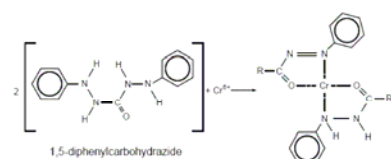
2 Reagents

Product Name: ChromaVer® 3 Chromium Reagent
Catalog Number: 12710-99
Composition: Potassium Pyrosulfate
        Magnesium Sulfate
        1,5-Diphenylcarbohydrazide

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9. T-Cr

1 Chemical reactions. (mechanism of coloring)

$$2Cr^{3+} + 3\,OBr^- + 10\,OH^- \rightarrow 2CrO_4^{2-} + 3Br^- + 5H_2O$$

1,5-diphenylcarbohydrazide
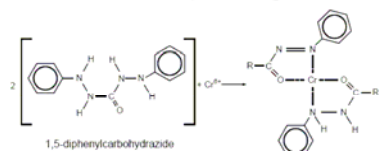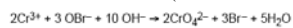
2 Reagents

Product Name: Chromium 1 Reagent
Catalog Number: 2043-99
Composition: Lithium Hypobromite
        Lithium Hydroxide, Anhydrous
        Sodium Sulfate

17

Product Name: Chromium 2 Reagent
Catalog Number: 2044-99
Composition: 5-Sulfosalicylic Acid
        1,2-Cyclohexanediaminetetraacetic Acid Trisodium Salt
        Sodium Sulfate
Product Name: Acid Reagent
Catalog Number: 2126-99
Composition:Potassium Pyrosulfate

Product Name: ChromaVer® 3 Chromium Reagent
Catalog Number: 12066-99
Composition: Potassium Pyrosulfate
        Magnesium Sulfate
        1,5-Diphenylcarbohydrazide

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Thank You for Your Kind Attention

19

Lecture Training for
Chemical & Biological Water Qualty
Analysis - 2

Lectuer - 2

Handling of the sample of the environmental analysis

2007 November

Kazuki SAKAE

The JICA Ekpert Team

1

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1. The feature of an environmental analysis

Environmental sample: Various

Water quality		High concentration Source
Soil	×	
Atmosphere		Low concentration (Environmental sample)

It exists with forms various moreover by heterogeneous many ingredients.

A related factor is various and it is a change with the passage of time.

The concentration range of the quality of a subject is wide.

2

A sampling is difficult. Representation nature of a sample

The necessity with a variation of analyzing many samples quickly.

There are multi-ingredient simultaneous analysis and a fixed quantity of necessity.

The dependability to an analytical instrument is large.

The optimal analysis method needs to be chosen by the object sample (a matrix and coexistence ingredient) or an item.

Sociality is strong and data goes out of control.

Analytical data are asked for objectivity and accuracy.

3

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2. What is required of an environmental analyst

Capability to grasp the essence, the actual condition, and the analysis purpose of a sample clearly, and to select the optimal sampling, sample preservation, and the analysis method

Discovery, and its knowledge and skill of the problem produced in process of the pretreatment of a sample, or preparation operation which are coped with and solved

Technology in which performances, such as the feature of an analytical instrument and a fault, can be had full knowledge of and mastered

Capability which evaluates analytical data and is managed

It trains daily with the pride of a professional.

Self-study

4

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3. Offer of reliable data
Environmental measurement analysis flow

The purpose of measurement	For what purpose are measurement and analysis conducted?
Examination of a measuring method	What is necessity because of the purpose?
Sampling	If it carries out, how is the sample appropriate for the purpose extractable?
Preservation of a sample	For preventing change deterioration of the sample extracted also including the conveyance method?
Measurement and analysis	The point in measurement analytical practice?
Equipment management	In order to make the state of apparatus best?
Traceability	Is there any Traceability of a standard substance?
Data management	Validity of the obtained data?
The check of analytical data	The check by persons other than a person in charge?
Report	The existence check of the clerical error of a report matter?

5

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4. An environmental measurement analytical-skills person's ethics norm

1. Duty as an engineer
We the engineers give top priority to public safety, health, and welfare through the right environmental measurement analysis business.

2. Observance of a statute
We the engineers observe all the statutes and carry out business based on a social norm and social good sense.

3. Improvement in knowledge and technology
We the engineers make an effort to raise one's technology, speciality nature and able nature, and prestige, and utilize the skill and knowledge for a social activity and philanthropy.

4. Observance of the range of qualification and authority
We the engineers provide service of professionals only in the domain to which the qualification and authority which oneself holds reach.

5. Evasion of interest conflict
We the engineers avoid the situation where it becomes impossible to fulfill duty as an engineer oneself, with a belief and courage.

6

5. The foundation of a sampling

1 Importance of a sampling

(1) The purpose of a chemical analysis

The average of the analytical value of the whole substance is decided.

It asks for concentration distribution of the quality of a subject of the whole substance.
It opts for partial contamination of a substance.

The sampling method changes with analysis purposes.

(2) When the examination sample does not represent the substance of a basis

However good the analysis method may be, as for the result measured even if analyzed carefully however, the characteristics of the substance of a basis are not shown.

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(3) Sampling error

A sampling error can be rectified by neither the standard substance nor a measurement standard, but always causes error generating.

(4) The result obtained by the sampling is a value representing the whole.

You have to carry out under those skilled who understand the general background of the analysis and who can sample, or its command.

What can be sampled correctly is those who were specialized in education and training about an experienced analyzer or sampling.

It is a typical trap to entrust the employee in which education is make light of the importance of a sampling procedure, and unripe and insufficient.

8

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(5) The important matter in a sampling plan and implementation

The procedure suitable for the purpose

Average concentration
Distribution of an object component
Contamination of a specific component

Homogeneity

Even if it looks uniformly, it is careful to consider that it is uniform.

The characteristics of the purpose component are taken into consideration.

Volatility - Light   Heat stability - Chemical reactivity

Sampling planning
An extraction instrument and equipment selection
A container and storage
In a microanalysis with a possibility that the purpose component may stick to a sample container, an acid, an antioxidant, etc. are added for stabilization.

9

Record of a sampling

The followed procedure is clearly recorded so that a sampling process can be repeated strictly.

When an experiment station does not sample itself

It is irresponsible in a sampling stage.

The received sample is analyzed as it is.

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(6) Other notes

The thing in contact with a sample is that the surface is inactivity.
Contamination by the metal and the plasticizer which are eluted from a container and a plug.

Leakage of the sample from a container, mixing of a contaminant

Sample label
What is not damaged by being important "document" (fading, breakage), but is equal to adhesion of a sample and a reagent.

Storage of a sample
The place which was pure so that there might not be contamination, crossing contamination, and label damage, and was arranged.
As occasion demands, environment monitoring (example temperature) is carried out.

Sample handling
The procedure documented about storage and disposal
Suitable education, training

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2 The notes of a sampling

(1) The purpose of a sampling   Measurement / analysis purpose

Environmental measurement
Actual condition grasp of the target environment
Conformity evaluation to bases, such as environmental standards
Specification of a pollution source, diffusion evaluation from a pollution source
Investigation of the influence and contamination by a specific enterprise and construction

Drainage from a place of business
The observance situation of bases, such as an effluent standard, a conformity check
Water quality grasp for every process for water disposal management

Quality control, schedule controlling
Characteristics grasp of a lot
Important characteristics grasp of quality control and schedule controlling

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(2) The main specification about a sampling, the regulating method.

to Japan

Object		Specification, the regulating method
Industrial water and an industrial liquid waste		The sampling method of industrial water and an industrial liquid waste (JIS K 0094)
Exhaust gas		The exhaust gas sampling method (JIS K 0095) In addition, it is every item by the individual specification for every item. The individual extraction method is specified.
Industrial waste		The sampling method of industrial waste JIS K 0060
Soil Pollution Control Measures Law relation	Soil	Soil Pollution Control Measures Law enforcement regulations (The environmental ministerial ordinance No. 29 /2002)
	Gas in a soil, and groundwater	The method of the extraction concerning soil gas investigation, and measurement (The Ministry of Environment notification No. 16 /2003)
Dioxin	Factory city water Industrial liquid waste	The sampling method of industrial water and an industrial liquid waste (JIS K 0094) and The dioxin measuring method in industrial water and an industrial liquid waste (JIS K 0312)
	Exhaust gas	The exhaust gas sampling method (JIS K 0095) and The measuring method of the dioxin in an exhaust gas (JIS K 0311)

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Object	Specification, the regulating method
Deposit	Deposit examination method
Sewer	Sewer test method
Tap water	The ministerial ordinance about a water quality standard About the points of concern
Waterworks	Waterworks test method

Furthermore, various manuals are enacted for every object from the Environment Agency, the Ministry of Environment, etc.

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(3) The sampling of a water quality sample   JIS K 0094

In addition, sampling of dissolved oxygen, a hexane extraction substance, a microbiological examination, a volatile organic compound (VOC), etc. is based on individual methods, such as JIS K 0101, JIS K 0102, JIS K 0125, and the Environment Agency notification.

Scope
    Industrial water   Waterworks water   Waterworks-for-industrial-use water   River water   Lake water   Groundwater   Sea water
    Industrial liquid waste

Sample container

Common stopper polyethylene bottle   PE

    Polypropylene bottle (PP) or Polycarbonate bottle (PC). A stopper is made into a bottle and this quality of the material.   any ommon stopper
    PE bottle is a tendency of adhesion and adsorption about suspended matter, P compound, an organic substance, heavy metal, etc.

Colorlessness is a plug glass bottle.

    Depending on Na, K, B, SiO2, aluminum, and a kind, a little As(es) and Zn(s) elute a glass bottle.
The 1st class of hard glass has few amounts of elutions.

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The washing procedure of a sample container

Tap water washes and, subsequently refining water washes.

Washing according to object

Metallic elements, an organic substance	) It washes by hot-Nitric acid (1+10) or hot-Hydrochloric acid (1+5).) Nitric acid (1+65) is filled, an airtight stopper is carried out, and it is 16 hours or more.) Refining water washes enough.
Except the above Anion etc.	) Refining water is filled, an airtight stopper is carried out, and it is 16 hours or more.) Refining water washes enough.

The airtight stopper of the sample container after washing is carried out after discharging water, and it is saved.

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Extraction by a water sampler

Water sampler	The extraction method
Sample container	Direct extraction) The water of an extraction place washes a container 3 to 4 times.) A container is sunk calmly, it extracts until it is filled to the brim with water, and it is an airtight stopper.
A bucket, a ladle with a handle	Extraction of surface water A bucket attaches a rope if needed. PE or the product made from PP notices a little good products made from SUS about a metaled elution.) The water of an extraction place washes a water sampler.) The water of an extraction place is drawn up with a water sampler, and it is a sample container quickly. it washes -- putting in until it is filled to the brim with water -- an airtight stopper

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Water sampler	The extraction method
A high funnel water sampler	Sampling of each depth can be performed. Unsuitable for a dissolved gas component and reduction nature goods, in order that the air and sample water in a sample container may replace at the time of extraction) The sample container washed with the water of the extraction place is attached.) hanging and lowering -- business -- with a rope, it sinks calmly to extraction depth.) The chain for open is lengthened and open the stopper, it is neglected for a while, and a sample is extracted.) The chain for open is loosened, a plug is carried out, and it pulls up.) A sample container is removed and it is an airtight stopper. Full of water

18

3

Water sampler	The extraction method
Van Dawn Water sampler	Sampling of each depth can be performed. ）The water of an extraction place washes the cylinder of a water sampler, an up-and-down lid, and buckets. ）It sinks calmly to predetermined depth with the rope for hanging, and depth is checked. ）A water sampler is made to go up and down 2 to 3 times, and the water in a cylinder is fully replaced. ）A water sampler is pulled up, after failing a messenger and closing an up-and-down lid. ）The pinch cock of an inner tube is loosened and a sample is moved to a bucket after washing a bucket by a part of sample. ）Agitating a sample, by this sample, it passes and the airtight stopper of the sample container is carried out until it becomes washing full of water one to twice.

19

The other extraction methods
）Automatic extraction equipment
　　Intermittent extraction equipment
　　　　Water quality meter linkage extraction system, Regular extraction system
　　Composite sample extraction equipment
　　　　Mixed sample extraction equipment
　　Intensive extraction piping system

）Extraction by an extraction valve
　　Extraction using the extraction valve installed in piping and equipment

20

Preservation processing of a sample
The sample which conducts ion chromatographic analysis is immediately examined after extraction, without carrying out preservation processing.

Preservation processing	Analysis item
It saves in dark place and 0 to 10　degree.	COD　　COD COD$_{OH}$　BOD　TOC TOD　Surfactant
It is pH 2-3　Hydrochloric acid or sulfuric acid added. 　It saves in the dark place and 0 to 10　degree. 　As long as it is short days, 0 to 10　degree and dark place preservation may be sufficient in the state as it is, without carrying out preservation processing.	NH　NO Organic –N　Total-N
Chloroform added (1mL /L), it saves in a 0 to 10　degree place 　As long as it is short days, 0 to 10　degree and dark place preservation may be sufficient in the state as it is, without carrying out preservation processing.	NO

21

Preservation processing	Analysis item
pH about 10　NaOH 200 /L Added or Granular NaOH is added　2 to 4 Grain /L．	Br
pH about 12　NaOH 200 /L　Addition or Granular NaOH is added　4 to 6 Grain /L．	CN　S
When oxidizing quality substances, such as residual chlorine, live together 　L(+)-ascorbic acid added and they are after reduction and pH About 12	CN
It extracts into DO measurement bottle and is basic zinc carbonate suspension. You may add (about 2 mL(s) / 100mL).	S
pH is set to about 4 (phosphoric acid added), and they are CuSO$_4$ with 5H$_2$O 1g/L added, it saves in dark place and 0 to 10　degree.	Phenol

22

Preservation processing	Analysis item
Weak acidity　Hydrochloric acid added	Agricultural chemicals (Parathion　Methyl parathion　EPN Pentachlorophenol, etc.
Chloroform is added in the neutral state (about 5 mL/L), it saves in dark place and 0 to 10　degree. 　As long as it is for one to two days, it may not add but a 0 to10　degree dark place may be sufficient.	phosphorus
pH about 2　Sulfuric acid or nitric acid addition	Total phosphorus
Filtering through a filter paper (No.5C), the first filtrate throwing away about 50 mL, and making subsequent filtrate into a sample, the following carries out the same preservation processing as a (phosphorus).	Dissolved phosphorus

23

Preservation processing	Analysis item
pH about 1　Nitric acid added	Cu,Zn,Pb,Cd,Mn,Fe,Al, Ni,As,Cr,Hg,Se,etc.
pH about 1　Hydrochloric acid (for arsenic analysis) added	As 　An organic substance, nitrate salt etc. it does not contain, when an oxidizer is not used for nitric acid with pretreatment
It saves in dark place and 0 to 10　degree.	Cr　）
Filtering through a filter paper (No.5C), the first filtrate throwing away about 50 mL, and making subsequent filtrate into a sample pH about 1　Nitric acid added	Dissolved of Metallic elements

24

The extraction method classified by kind of a sample

Industrial liquid waste - 1

Feature	）What is discharged from a factory and a place of business, carries out purification processing of product processing cleaned waste liquid, cooling waste water, boiler waste water, etc. which are discharged from each production process with liquid-waste-treatment equipment with operation, and is discharged outside a factory etc. ）Water quality differs from amount of water on a scale of a type of industry, a product kind, and an enterprise etc., and there are a change with the passage of time and a seasonal variation by the cycle variation of operation.
Extraction point	）The exhaust port of a factory and a place of business ）The sewage measure of a drainage canal and a drainage pipe way, final adjustment tub, liquid-waste-treatment institution exit which drainage of this water quality can extract when extraction for an exhaust port is difficult ）When examining the waste water for every process, it sets up according to the purpose.
Extraction time and frequency	）The usual operating hours and the operation time of liquid-waste-treatment equipment are taken into consideration. ）Frequency is set up according to the purpose.

25

Industrial liquid waste - 2

The extraction method	）When having fallen from a drainage canal and a drainage pipe way It is a sample container and they are direct or a bucket, and a ladle with a handle. ）When discharged from the drainage canal (drain) and the drainage pipe way It is a sample container and they are direct or a bucket, and a ladle with a handle. External water flows backwards and is careful by change of a water level. ）Extraction from a sewage measure and a final adjustment tub A bucket and a ladle with a handle ）Extraction at a liquid-waste-treatment institution exit When there is extraction equipment JIS K 0094　It is based on the 4.3rd clause. When there is no extraction equipment It is a sample container and they are direct or a bucket, and a ladle with a handle.

26

Factory city water　River water　- 1

Feature	）It changes with geographical and geology conditions of a valley, and is water quality change further by artificial conditions, such as inflow of water supply of climate conditions, such as rain, and various city water, and drainage from the household and an industrial liquid waste, and river-development construction. ）In many of rivers, since a minor river flows together and is formed, the water quality of a minor river is also a change factor. ）In an admiration tidewater region, they are the influence of the ebb and flow of tide, and the difference in the water quality of surface water and lower layer water.
Extraction point	）It extracts from this depth at the point which the place of business which water supply is water supplying. ）The point which water quality change of river water can foreknow is selected beforehand. ）It is the place which the branch flowing in and drainage are fully mixing when extracting directly from a river. ）It is desirable to extract and compare also in right-and-left both banks in the position of twenty percent of total depth of water in a center flow part (portion with the largest flow rate about the unit area of a cross section .... the deepest part), when broad.

27

Factory city water　River water　- 2

Extraction time and Frequency	）When the place of business etc. is operating and water supplying in the usual state ）The day where fine weather continued comparatively and water quality was stabilized By the purpose, it is after rain at the time of rain. ）At the time of the ebb tide whose ebb and flow of tide are not intense in an admiration tidewater region The influence of sea water may be investigated for the purpose. ）Usually, when investigating 3 to 4 times/day, and the change during a day, it is two to 4 time interval.

28

Factory city water　River water　- 3

The extraction method	）When there is sluice piping JIS K 0094　It is based on 4.2 4.3 clause. ）When there is no sluice piping In a riverside and the central part of a flow, since the flow velocity differs from the amount of suspended solids, generally a flow extracts in the uniform central part. a) Extraction by on foot It is a sample container and they are direct or a bucket, and a ladle with a handle. b) Extraction from onboard A bow is turned to the upper stream so that there may be no artificial pollution. Surface water It is a sample container and they are direct or a bucket, and a ladle with a handle. Each depth A high funnel water sampler or Van Dawn water sampler c) Extraction from a bridge It extracts in the lower stream without the turbulent flow by a bridge beam. Surface water It is a sample container and they are direct or a bucket, and a ladle with a handle. Each depth A high funnel water sampler or Van Dawn water sampler e) Extraction by extraction equipment JIS K 0094　It is based on the 4.2nd clause.

29

Factory city water　Groundwater　- 1

Feature	）Subsoil water　River water, Lake water permeates underground.　,　Free groundwater　It flows near the surface of the earth, Azai door　, Artesian water　It is in a deep stratum, Fukai door　It is alike and is divided. ）Subsoil water As compared with river water, an organic substance, NH4, and phosphorus concentration generally it is low. Free groundwater It is easy to be influenced by rain and a biological activity, and water quality also changes easily. Artesian water Although geology influence is received, there is little water quality change. ）There is little contact with the atmosphere, and since dissolved oxygen is consumed by microbe activity etc. and water quality change is produced in contact with air with many reduction nature states (anaerobic state), contact with air is avoided at the time of extraction.
Extraction point	A storage pump exit or sand separation equipment exits, such as a factory and a place of business

30

Factory city water Groundwater - 2	
Extraction time and frequency	）When the place of business etc. is pumping up water in the usual state ）When water quality change is expected, it decides each time. ）At a suspended well door, water quality of extraction of a state may not usually be fixed at the time of superfluous pumping and too little pumping. 　At a suspended well door, it extracts after several hour pumping according to the usual operational status. ）As for artesian water, water quality may change by large change of a pump discharge. ）Since subsoil water and free groundwater tend to be influenced by river water etc., it is cautious of extraction time and frequency.
The extraction method	）When there is a sampling valve 　JIS K 0094 It is based on 4.2 and the 4.3rd clause. ）Extraction from a storage pump exit and a sand separation equipment exit 　It is a sample container and they are direct or a bucket, and a ladle with a handle. ）From a well to direct extraction (when a water sampler can be put in) 　A high funnel water sampler or Van Dawn water sampler

Thank You for Your Kind Attention

Lecture Training for
Chemical & Biological Water Quality
Analysis - 2

Lecture - 3
Analytical skills

2007 November

Kazuki SAKAE

The JICA Expert Team

1

Before beginning analysis.

Precision and accuracy.

Measurement accurate [why] is called for.

The foundations of a quality control.

The general quality control performed with an analysis organ.

2

Precision and accuracy

"Precision" ?

The grade of the variation in an observed value.

The grade of coincidence between the independent test results repeated under the defined conditions.

"Accuracy"?

The average enough acquired from many test results.

The grade of coincidence with an accepted reference value (a theoretical value, a certified value, or an expectation value).

3

Why is accurate measurement called for?

Establishment of the traceability of the measurement analysis value in international and the country.
Justice on commercial transactions, such as export and import.

Data service which a visitor has satisfied.

Social trust of an organization.

Technical acquisition, and education and training without the gap between individuals.

Failure is allowed by neither of the positions.
Introduction of quality control systems, such as Quality ISO and GLP.

4

The foundations of a quality control.

Self-control.
Maintenance of precision cannot be performed unless everyday life and action are managed.
Poor health, Home disagreement, Lack of sleep, etc.

Station management.
A quality control is impossible in the office which cannot be committed in comfort.
Discord between poor business performance and the personnel, will understanding etc of the hierarchical order.

Analysis environment management.
Maintenance of precision cannot be performed in the environment where the laboratory is not commanded intentionally.
A reagent and instrument management, instrument maintenance, housekeeping etc.

5

The general quality control performed with an analysis organ.

Internal quality control.
The quality control performed within an engine   It carries out periodically   .

External quality control.
Participation to the quality control joint experiment which an external engine conducts.

It is important to feed back results of an investigation and to strive for improvement in a technique.
Strengthening of a quality assurance system.

6

About accurate analysis environment.

Environmental pollution management.

Management of a test device.

Water used by a chemical analysis.

Management of a reagent.

Selection of a measurement method.

Management of analyser.

7

Environmental pollution management.

Thoroughness in a laboratory of 6S.
   Arrangement , Order , Cleaning , Upbringing
      Appearance   , Clean , Manners

Defecation within a draft.

The pollution control of atmosphere.
   Indoor contamination by a volatile component.
   Handling of a high concentration sample.

8

For preventing environmental pollution.

Analyser etc.

   Electronic balance etc.
      The level of analysis accuracy is known only by
      seeing the balance environment of the laboratory!

   The sample and reagent of a measuring object are falling
   on the body of a balance absolutely. It is a container, a
   powder paper, etc. of a receptacle so that there may be
   nothing. Use it correctly.

   When you fall, wipe off promptly, and take measures so
   that contamination does not arise.

9

They are also reagent chemicals if the equipment circumference
is not always beautiful.   Grade falls below in the first class.

A reagent spoon should measure and don't touch a hand at a
picking part.

When you fold a powder paper, don't pollute by hand.

Don't pollute the interior of a reagent vessel with your hand etc.

The reagent measured too much is not returned to the original
container by any means, is pollution-free, and ensure and
discard insurance.

10

Don't neglect glassware, such as a volumetric flask, a
graduated cylinder, a transfer pipet, and a measuring pipet,
as they are in sink after use, but it is tap water, rinse it, and
wash it promptly.
   As it is, by oneself, pipets turn a mouthpiece down to the
   cylinder of a penetrant remover, and put it in to it, after
   washing in cold water.

   Since it will become difficult to take the soil which
   adhered in the container if it dries, strive for prevention
   of an early rinse and inner wall desiccation.

11

Unless a soil can come off easily, by oneself, a medicine
spoon, a spatula, etc. are after washing and pure water,
rinse them with tap water, wipe off moisture by wiper , and
return it to the original storage place.
   When desiccation is bad, after applying a little pure
   ethanol, vaporization of the alcohol is carried out and it
   dries.

   If it carries out [put / into the plastic bucket of sink /
   continue], it will rust, shortly after the container which
   uses an acid enters. Since contamination by other matter
   is also considered, medicine spoon relations are by
   themselves. It washes and returns. [after-use]

12

2

Defecation within a draft.

Wiping within a draft is performed briskly.
    Until it reaches not only a working plane but head lining
    and a side face.
An unnecessary object is not placed into a draft.
    It is toughness to a lumber room about a draft.

By adhesion of an acid, the instrument neglected in a draft
inside and the interior corrodes, and rust is generated.
It becomes a sample for metal analysis with the cause of
mixing and contamination.

The inside of a draft pollutes by evapotranspiration of PCB.
It becomes a cause of contamination to a subsequent sample.

13

In addition to this

When you leave a laboratory, touch a hand
fundamentally at the knob of washing deer doors. A
white robe is left after removing in a laboratory.

An outside in white is making it inside-out,
extracting a sleeve and putting on the corner of the
subject etc. since the reagent's has adhered in that
case.

Use neither makeup nor a colon. These are
chemicals, and since many matter which we make
the measuring object is contained, they cause
contamination.

Moreover, since it becomes remarkable disturbance
especially in the case of the judgment of an odor,
avoid the stinking powerful cosmetics.

14

The hair of hair and a dress are caught in equipment and
the instrument of a laboratory, and are kept from serving
as generation causes, such as accident.

Wear glasses as occasion demands, a mask, etc. at the
time of the work using a poisonous substance, strong acid,
and strong alkali, and perform test operation.
Attend an examination after putting on as knowledge
whether there is any toxicity the reagent which he is
taking charge of, and whose sample are how much.

15

Management of a test device

Chemical-analysis appliance implement.

The volumeter for glass chemistry.

Characteristics of plastics.

Cleaning method.

16

Chemical-analysis appliance implement

Kind   Glassware for chemical analyses

Glass beaker   Soda-lime glass , Hard glass , PYREX
Erlenmeyer flask
Color comparison tube
Evaporating dish   Porcelain , Glass
Plastic instrument   Polyethylene , Vinyl chloride , Teflon ,
                    Polo propylene etc.
Rubber goods   Rubber stopper , Syringe , Safety pipeter
                    etc.
Metal goods   Crucible Spatula Pincette Platinum
                 basin etc.
In addition to this   Filter paper Solid phase column etc.

17

The volumeter for glass chemistry

Kind   Glass volumeter
    Buret   Measuring pipet
    Whole pipet   Volumetric flask
    Graduated cylinder

Common conditions etc.
    The volume of a volumeter is determined with
    water.
    Standard temperature: 20   degrees
    There is distinction of the object for carriers and
    delivery volume.
       E(Eingus) or TC(To Contain)
   A(Ausguss) or TD(To Deliver)

18

3

Characteristics of plastics

The kind of resin	Polyvinyl chloride	Polyethylene	Polypropylene	Fluororesin	Polycarbonate
Cable address	PVC	PE	PP	PTFE	PC
20% hydrochloric acid					
30% nitric acid					
Aqua regia		×			×
20% hydrofluoric acid					
30% sulfuric acid					
10% sodium hydroxide					
Liquid ammonia					
Ethanol					
Acetone	×				×
Hexane		×			
Chloroform	×	×	×		×
Heat-resisting property Continuous duty temperature	66 - 79	82 ~ 100 Low density 121 High density	121 - 160	288	121

It is completely or almost uninfluential.
Although it has the influence of some, it is equal to use enough with conditions.
It is better not to use it if possible.
× Since it is greatly influential, it is not suitable for use.

19

Cleaning method

New glassware   Alkalinity is removed.
  One nights are soaked in hydrochloric acid (1+30).
    Water   Purified water
Volumeter   When drying, heat is not applied by any means.
Since heavy metal, oil, a precipitate, etc. are adhering or sticking to a bottom or a wall, immediately after use, it washes with one cleaning method of the degrees, and the glassware used for the examination is dried.
  1. Washing by water
  2. Washing by the detergent or a cleanser
  3. Washing by the mixture of nitric acid and oxygenated water
  4. Washing by an organic solvent
  5. Washing by an ultrasonic washing machine
When dirty, it will attach to a drug solution several days.
The cleaning method appropriate for the purposes to be used, such as an object for organic analyses and an object for inorganic analyses, is chosen.
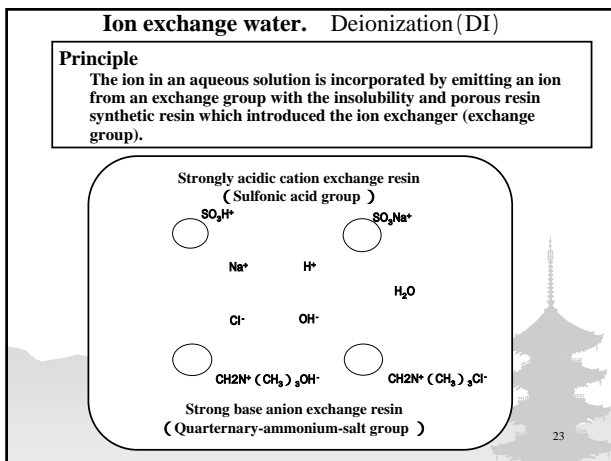
20

It uses by a chemical analysis.   "Water"

The amount of ions

[cm(25)]

21
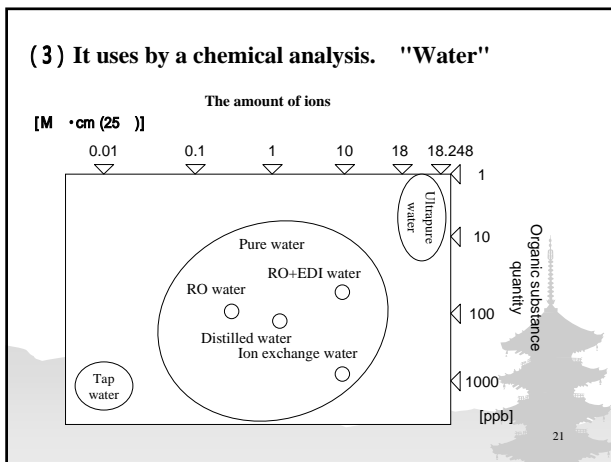
The definition of pure water

The Pure water (theoretical pure water) which consists of only H_2O also as a basis.
Moreover, the water which processed using a certain purification technique is pointed out.
As compared with ultrapure water, the treated water beyond specific resistance 1   cm with low cleanliness is pointed out these days in many cases.

The definition of ultrapure water

The high purity water which is obtained combining all the component engineerings about purification and which approached H_2O infinite is said.
The latest ultrapure water is specific resistance 18   cm, and a particle number below 20-piece/cm³ (0.1 micrometer of diameters), viable cell count below 0.01-piece/cm³ and TOC (total organic carbon) It has the characteristics of 0.1 mg/dm³.

22

Ion exchange water.   Deionization DI

Principle
The ion in an aqueous solution is incorporated by emitting an ion from an exchange group with the insolubility and porous resin synthetic resin which introduced the ion exchanger (exchange group).

Strongly acidic cation exchange resin
Sulfonic acid group

Strong base anion exchange resin
Quarternary-ammonium-salt group

23

The description of ion exchange water

Strong point
It is the water from which inorganic ion was removed.

Demerit
There is water quality change according to the exchange capacity of resin.
The organic substance (PSA) of resin origin may be contained.
A microorganism propagates and may be polluted with the resin surface.
Grains may be mixing by breakage of resin etc.

Selectivity is so high that the valence of an ion becomes large.
Selectivity is so high that an atomic number is large if the valence is the same.
It is very easy to stick to the organic substance with large molecular weight.

24

4

Distillation.   Distilled Water DW

How to pick out water from the solution in which the impurity is intermingled using the physical properties (= boiling point) of water.

Cooling water
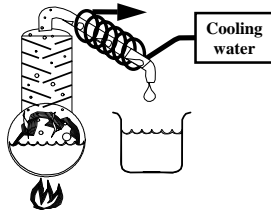
The description of distilled water

Strong point
The underwater impurity is removed generally.

Demerit
In order that the entrainment of raw water may occur, water quality deteriorates.
Water quality deteriorates according to the contamination from environment.
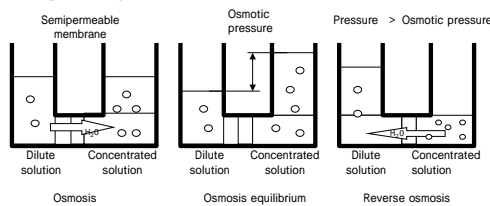The matter of a low boiling point is hard to be removed.

It is hard to remove volatile high elements (Pb, B, Zn, etc.).
It is hard to remove the organic substance which has volatility.

26

RO water.

Water refined using the reverse osmosis (Reverse Osmosis (RO)) film.

A solvent is the method of separating by the semipermeable membrane which does not let solute pass although it lets it pass, applying a larger pressure than the osmotic pressure to generate, and making a solvent penetrating.

Semipermeable membrane

Osmotic pressure

Pressure   Osmotic pressure

Dilute solution   Concentrated solution

Dilute solution   Concentrated solution

Dilute solution   Concentrated solution

Osmosis   Osmosis equilibrium   Reverse osmosis

The description of RO water

Strong point
The underwater impurity is removed generally.

Demerit
The water quality refined is influenced by the water quality of raw water.

28

Management of a reagent

Specification of a reagent

Common reagent
Super grade , 1st class
Particular application reagent
For pH measurement , For ultimate analyses ,
For HPLC , Dioxin analytical grade etc.
The standard reagent for volumetric analyses
Sodium chloride , Sodium carbonate ,
Sodium fluoride etc.
The standard solution by a mensuration traceability system   It manufactures by an authorization contractor ,
With the badge of JCSS , PH standard ,
Ion standard solution , Metal standard solution

What is necessary is just a super grade and a 1st class anything.
The grade (it is cautious of impurity labeling) according to the experimental purpose is chosen.

29

Storage of a reagent

A deleterious substance and poison record the amount used and use time.

Reagents lock and keep it.

A reagent shelf is fixed to a floor.

The reagent which reacts easily is not put on the same shelf.

Storage according to the characteristics of the reagent is performed. (Protection from light, refrigeration, etc.)

If handling and storage are bad, it is not only dangerous, but it will become a cause of deterioration or contamination.

30

Selection of a measurement method

The selection of a measurement method and the identification of validity according to the request purpose of starting measurement analysis

Observance of applicable laws and regulations

A standardized work sheet (SOP) is drawn up based on the selected method.

Management of analyser

Periodical maintenance check

   Inspection standard

      Daily check book

      Routine inspection book

   It creates and manages for every instrument.

**The check of a calibration curve, a retention time, etc.**

Molecular-spectrum analytical method

（ ）Absorptiometric method

- **From the amount of the light which a sample solution absorbs to quantitative analysis**
  - **About the light which a sample absorbs**
  - **Relation between the absorption of light and sample concentration?**
- **About light**
  - **Ultraviolet radiation and a visible radiation?**
    - **Ultraviolet radiation UV, ultra-violet 200 - 380 nm**
    - **Visible radiation VIS, visible light 380 - 780 nm**
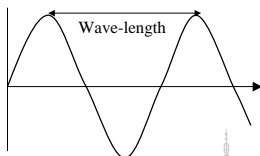   - **Infrared radiation IR, Infrared 780nm - 1000 μ m 1mm**

The matter absorbs the light of specific wavelength.

Color Ring
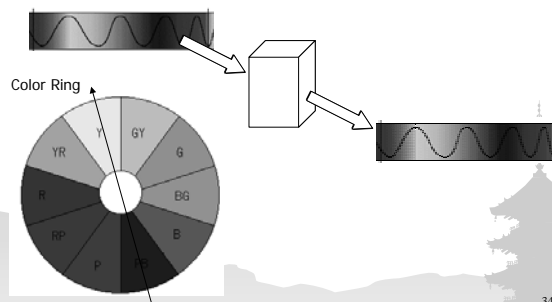
The foundation of an absorptiometric method

- **Wave-length**

  Wave-length

  - **Unit   nm = 10^{-9} m**
  - **Energy changes with wavelength.**
    - $E = h\nu$
      - h: Plank constant
      - ν: Frequency (Hz)
    - $\nu = c/l$
      - c: Velocity in the inside of the vacuum of light

Wavelength and light

Region	Color	Complementary color	
Void ultra-violet region			
			200
Ultra-violet region			
			380
		Complementary color	
	Purple	Yellowish green	
	Blue	Yellow	450
	Verdigris	Orange	
	Greenish blue	Red	
Visible region	Green	Purplish red	500
	Yellowish green	Purple	
	Yellow	Blue	
	Orange	Verdigris	600
	Red	Greenish blue	780
Near infrared region			

Each wavelength band name, color tone, and complementary color of a visible region

Transmittance and absorbance
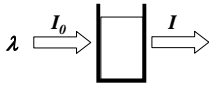
$$\frac{I}{I_0} = t \qquad 0 \leq t \leq 1$$

$$T(\%) = 100 \cdot t \qquad 0 \leq T \leq 100$$

$$A = -\log t = -\log \frac{I}{I_0}$$

37

Lambert-Beer low

- **Lambert low**
  - Absorbance A is the layer length of a cell. It is proportional to l.
  - $A = k \cdot l$
- **Beer low**
  - Absorbance A is concentration of a sample. It is proportional to c.
  - $A = k' \cdot c$
- **Lambert-Beer low**
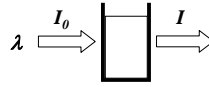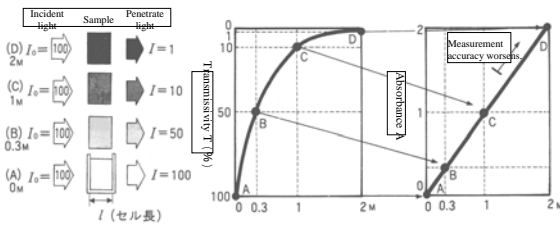 - $A = a \cdot c \cdot l$
    - **a:** extinction coefficient

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Dependability of absorbance

Incident light	Sample	Penetrate light
(D) $I_0 = 100$, 2_M		$I = 1$
(C) $I_0 = 100$, 1_M		$I = 10$
(B) $I_0 = 100$, 0.3_M		$I = 50$
(A) $I_0 = 100$, 0_M		$I = 100$

l (セル長)

The relation of the transmittance and absorbance of the light of various concentration samples

- **Usually, it measures so that it may fit in the range of 0-1.0.**

39

The advantage of an absorptiometric method

- **Sensibility is high.**
  - The sharp organic color reagent is developed and a solvent extraction method is used together in many cases.
- **It is accurate.**
- **Operation is possible in fixed quantity in ease and a short time.**
- **Selectivity is high.**
  - The high coloration indicator of selectivity, a masking reagent, an extraction method, etc. are used together, and disturbance of a coexistence component is removed.

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Calibration curve

- **Instrumental-analysis methods are "it not being concentration absolutely" but "relative concentration."**
  A calibration curve is created using a standard sample.

Example   Absorptiometric method

Reference standard

A_1 A_2 A_3 A_4 A_5 A_6 A_7

Absorbance
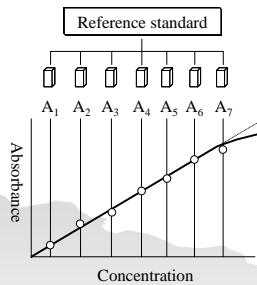
Concentration

- Reference standard
  - The solution of gradual concentration
  - Each absorbance measurement
  - Calibration curve creation
    - Test range determination
- Absorbance measurement of a sample solution
  - It plots to a calibration curve and is concentration determination.

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- **Quality control   Validation**
  That the state of equipment is only good tends to attract attention.
  It is an indispensable thing that the equipment state is kept good.
  It is more important than it to secure the dependability of a calibration curve.
  However good equipment may be, if the treatment of a calibration curve is unsuitable, the dependability of an observed value is not securable.

- **A setup of a par point   Mark and a ratio of concentration**

- **Dependability of the concentration adjustment of a standard solution**

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（　）The kind of calibration curve

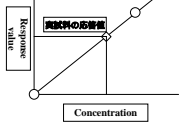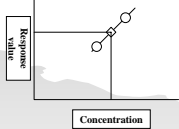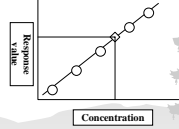**One-point calibration curve method**
When there is correlation good to a certain concentration

Response value / Concentration

Two-point calibration curve method

Response value / Concentration

Multipoint calibration curve method

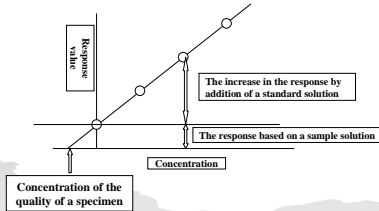Response value / Concentration

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Standard addition method

When it has the influence of the matrix in a sample.

A sample is divided into four or more pieces, and one piece is excluded a criterion is added by gradual concentration in the remaining solutions.

Response value

The increase in the response by addition of a standard solution

The response based on a sample solution

Concentration

Concentration of the quality of a specimen

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The trouble of a calibration curve

If the large range is taken, it does not correlate linearly.
If the range is narrowed, there is certainly a part which can take good correlation.

The definition of good correlation.
Tolerance of the error in measurement.

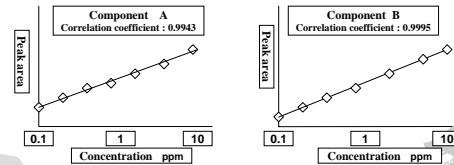Envelope "wide"　　"Correlation" seems to be good even if shifted to some extent.

Envelope "strict"　　The density range it can consider that correlates is also narrow.

45

A calibration curve and a correlation coefficient

Although a "correlation coefficient" may be used for verification of a calibration curve, making the value of a correlation coefficient into the absolute index by which "a mutually related degree" is evaluated has many problems.
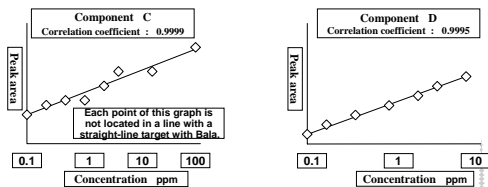
Example　　Comparison of the calibration curve with same how to take a point

Component A
Correlation coefficient : 0.9943
Peak area
0.1 | 1 | 10
Concentration　ppm

Component B
Correlation coefficient : 0.9995
Peak area
0.1 | 1 | 10
Concentration　ppm

A correlation coefficient is effective to some extent, when how to take a density range and a point compares the calibration curve which was completely in agreement.

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Example　　Comparison of the calibration curve from which how to take a point differs.

Component C
Correlation coefficient : 0.9999
Peak area
Each point of this graph is not located in a line with a straight-line target with Bala.
0.1 | 1 | 10 | 100
Concentration　ppm

Component D
Correlation coefficient : 0.9995
Peak area
0.1 | 1 | 10
Concentration　ppm

Meaningless, even if the value of a correlation coefficient compares the calibration curve from which how to take a density range and a point is different.
If a density range becomes large also with comparable variation especially, a correlation coefficient will approach "1."
(in inside of the density range to be used) A calibration curve is created in the narrowest possible range.
Fixed in the ratio between each point in the case of a multipoint calibration curve.
The ratio between each point is set to 2 or 2.5.

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Dependability of standard solution concentration

Calibration curve creation　　Preparation of a standard solution
Standard solution concentration　　Generally, they are several mg/L
It is difficult to prepare directly from a powder reagent.
Usually, the "par undiluted solution" of 1000 mg/L concentration is once diluted from preparation and it, and the "standard solution" of the predetermined range is prepared.

When preparing by oneself from a powder reagent.
➢ A delivery basis of a powder reagent　Purity and its dependability
➢ The impurity of pure water　A kind and concentration
➢ Dependability of the balance used for weighing capacity
➢ Dependability of the flask used at the time of the dissolution (Tolerance) etc.

When preparing with a g.m.b. par undiluted solution.
➢ That by which traceability, such as JCSS, was established is used.

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Thank You for Your Kind Attention

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Slide 1

Lecture Training for
Chemical & Biological Water Qualty
Analysis - 2

Lectuer - 4

For accurate measurement

2007 November

Kazuki SAKAE

The JICA Ekpert Team

1

Slide 2

. **Traceability**

About the traceability of measurement

The decided test result which is usually the national standard or the international standards through a chain of comparison without a break and which may be associated par or the par property which all the uncertainties were written.

If the path of operation is traced back from an analysis result, it specifies including uncertainty that it can follow to a national standard.

Reservation of international circulation of a test result. One-Stop-Testing

2

Slide 3

The traceability system based on mensuration
- Measuring par supply system
- Double-feature of a proofreading undertaker registration system
- A standard substance with a JCSS badge and a calibration certificate are national standards.   It is shown that it is a tracer bull.

Analysis is the operation or the technique which gets to know the component of the matter, or a presentation, and detects and identifies them.

In order to change into the amount of substance the electrical signal acquired from measuring apparatus, a signal is proportional to the amount of standard substances as which the charateristic value was determined.

In a chemical analysis, a standard substance is dramatically important.
- Traceability of a standard substance

3

Slide 4

. **Standard substance**

Reference Material   RM
- Uniform matter or material in which the charateristic value was decided.
  - Justice of an instrument
  - Evaluation of a measuring method
  - Market-making of the matter

Certified Reference Material   CRM
- The standard substance in which the certificate of attestation by the attestation organization and an engine was attached.
- What the charateristic value decided.
- That by which traceability was established.
- What was written.
- That by which validation is established.

Certified reference material of JCSS
Standard gas   Standard solution   A certificate with a JCSS logo mark

4

Slide 5

. **Handling of data**

3.1 Self-control of an analytical value

1   Validation of analytical method
Check by investigation that each requirement is satisfied to the particular application to mean, and prepare an objective proof.   ISO/IEC17025
- Sampling
- Handling, transportation, storage, preparation
- Analysis environment
- Instrument
- Analyst
- Presumption of uncertainty
- Statistical techniques of data analysis

5

Slide 6

2   Self-control of an analytical value

At a measuring proof enterprise, analytical values are goods.

A reliable analytical value is calculated.

The analytical practice as a standard operation procedure (SOP) trusts it.   A sexual high value is not necessarily guaranteed.

The dependability of an analysis result is always considered and analyzed.

Objective self-control of an analytical value is important.

6

3 Outliers in an environmental assessment

When a measurement analysis result exceeds a regulation value etc.

(A right value, outliers, and suitable judgment is searched for.

When judged with outliers from comparison with the past data.

When judged with outliers by comparison with an item with other correlation.

When being statistically judged with outliers by a cross check etc.

7

---

4 One spot of outliers presumption

A blank value is high.

➢ Possibility that there is a problem in a process.

Is it influence at all the measurement results which are series?
Only blank value.

➢ In order to lose the abnormalities in a blank value, the check of each prior factor and everyday management are required.

Practical use of a control chart

An analytical value is high.

➢ Contamination — Environment, a laboratory, an instrument, a cell, water, a reagent, etc.

➢ Fixed quantity — The factor of a standard solution, a calculation mistake, etc.

➢ Measurement — Disturbance on equipment instability and measurement etc.

The early detection and the cure against outliers are important.

8

An analytical value is low.

➢ Loss of an analytical object component
➢ The loss in pretreatment
➢ The condition of a sample
➢ Fixed quantity — The factor of a standard solution, a calculation mistake, etc.
➢ Measurement — An addition failure of a reagent, matrix interference, equipment instability, etc.

The early detection and the cure against outliers are important.

9

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5 Outliers management of everyday regular analysis

Shewhart's control chart

➢ Did the process suit the state where it was often managed?

➢ Is work done as the set-up criterion or directions?
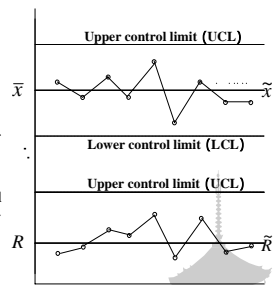
$\bar{x} - R$ Control chart

Average $\bar{x}$, The range of dispersion R

The state managed

➢ A point is in the inside of an upper control limit (UCL) and a lower control limit (LCL).

➢ Even if a point is in the inside of the control limit, there is no bias in how for points to be scattered.

➢ It uses for the data of a sample analyzed regularly, and analytical-data management of the standard sample for a check.

Upper control limit UCL

$\bar{x}$ .... $\tilde{x}$

Lower control limit LCL

Upper control limit UCL

R $\tilde{R}$

The example of a control chart

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6 Management by a check sample etc.

Parallel simultaneous analysis of a commercial standard sample.

➢ Japan Society for Analytical Chemistry JSAC
➢ National Institute for Environmental Studies NIES
➢ National Institute of Advanced Industrial Science and Technology measuring par synthesis center NMIJ

The amount management of recovery by standard substance addition.

➢ Parallel analysis of the sample which added the analysis standard substance is conducted, and the validity of analytical practice is judged in the amount of recovery of loadings (rate).

Management by a joint experiment.

➢ Accidental, when the same sample is analyzed by the same method in a separate chemical laboratory Is the same result obtained within the limits of an error?
➢ Z score

Management by double measurement.

➢ Two or more observed values [identical test items] Is an error in tolerance?

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3.2 Calculation of an observed value etc.

1 Significant figure

Addition and subtraction.

➢ A result is doubled with the number of digits of the more inaccurate one.

Multiplication and division.

➢ A result is doubled with the number of digits with a smaller significant figure.

➢ It asks in the middle of operation treatment under 1-2 figures of a significant figure, and the adequate significant figure after the end of operation makes it suit.

2 Rules for rounding of numerical values

Treatment of "5" is the point. JIS Z8401

When the integral multiple nearest to the given number is one, it is the same as rounding off.

Example 12.251 12.3

When there are two near adjacent integral multiples equal to the given number

At the time of 5 Even times are chosen. (Rule A

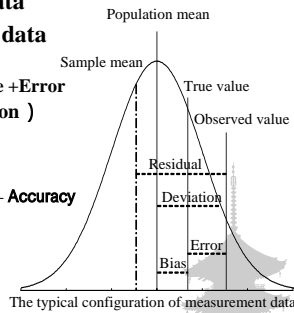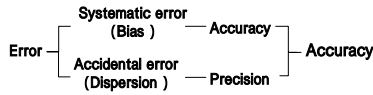Example 12.25 12.2 12.35 12.4

Slight roundness is ended in one step.

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2

3.3 Statistical handling of data

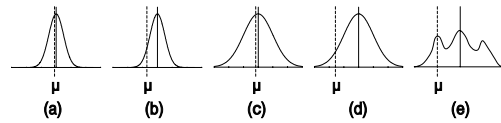### 1 Statistical handling of data

Data is grasped objective.

Observed value　　True value +Error

Bias , Dispersion

```
Systematic error
Bias                    Accuracy
Error                                    Accuracy
Accidental error        Precision
Dispersion
```

The typical configuration of measurement data

Population mean
Sample mean
True value
Observed value
Residual
Deviation
Error
Bias

---

2 Distribution of data and a kind with error

μ (a)　μ (b)　μ (c)　μ (d)　μ (e)

The example of distribution of data

(a) A state with good precision and accuracy.
　　Ideal conditions.
(b) The state whose accuracy is poor although precision is good.
　　It is required to investigate the deviation of analyser and the
　　purity of a reagent and to make a systematic error small.
(c) The state whose precision is poor although accuracy is good.
　　It is required to take the measures which raise precision.
(d) A state also with poor precision and accuracy.
　　It is required to take the measures described in Above (b) and (c).
(e) The state where the analytical method is not managed.
　　It is required to improve analytical work so that the crest of
　　distribution may be set to one.

---

3 Frequency and a histogram

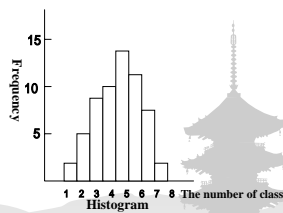**How to express distribution of data.**

Histogram

What divided the range of an observed value into some sections (class), and made pillar-shaped frequency of occurrence (frequency) of the observed value to each class

Frequency

The number of data included in each class

The related table of the class of an observed value, and frequency

The number of class	Threshold value		Central value	Frequency
1	14.75	14.95	14.85	2
2	14.95	15.15	15.05	5
3	15.15	15.35	15.25	9
4	15.35	15.55	15.45	10
5	15.55	15.75	15.65	14
6	15.75	15.95	15.85	11
7	15.95	16.15	16.05	7
8	16.15	16.35	16.25	2

Histogram

---

4 How to carry out quantity front [of the distribution of data]

Statistics showing a core.

- mean
- median
- mode

Statistics about scatter

- Maximum
- Minimum
- Range
- Residual　Sum of squares
- Sample　Dispersion
- Sample　Standard deviation
- Coefficient of variation
- The 1st and 3rd quartiles

Example computation of the amount of key statistics

Statistics	A notation, a formula	Remarks
The number of data	n	
Average	$\overline{x} = \dfrac{x_1 + x_2 + x_3 \cdots\cdots + x_n}{n} = \sum\limits_{i=1}^{n} x_i / n$	The notation of population mean is mu.
The maximum, the minimum	x_{max} , x_{min}	
Range	$R = x_{max} - x_{min}$	
Sum of squares	$S = (x_1 - \overline{x})^2 + (x_2 - \overline{x})^2 \cdots\cdots + (x_n - \overline{x})^2 = \sum\limits_{i=1}^{n}(x_i - \overline{x})^2$	The sum of squares of a residual
Sample　Dispersion or a mean square	$s^2 = V = S/(n-1) = \sum\limits_{i=1}^{n}(x_i - \overline{x})^2 /(n-1)$	Population variance ^{2} is broken by n.
Sample　Standard deviation	$s = \sqrt{S/(n-1)} = \sqrt{\sum\limits_{i=1}^{n}(x_i - \overline{x})^2 /(n-1)}$	The population standard deviation　is broken by n.
Coefficient of variation	$CV = s/\overline{x}$	% Display in many cases.
Standardization regular variate	$u_i = \dfrac{x_i - \overline{x}}{s}$	The converted value to a standard normal distribution z is also often used instead of u.
Median (median)	$\widetilde{x}$　The median when arranging in order of magnitude	n=If the number is even, it is the central average of two pieces.
The 1st and 3rd quartile	$Q_1　Q_3$　The value it arranges [value] in order of magnitude and for which it comes to 25 and 75% of location	Q_2 is a median.
Interquartile range	$IRQ = Q_3 - Q_1$　It is also called a between range for about 4 minutes.	0.7413　IRQ is Equivalent to S.
Percentile (percentile)	The value for which it comes to the location of arbitrary % when it arranges in order of magnitude	50 percentiles are medians.

---

5 A population and a sample

Population

- The ensemble having all the characteristics of the measuring object

Sample

- The part sampled from the population for measurement

6 Distribution of statistics

Normal distribution

- When the frequency of occurrence of the data x obtained by measuring independently many times is drawn on a graph, distribution of being symmetrical and a temple bell type centering on the average mu as shown in a drawing is shown in many cases.
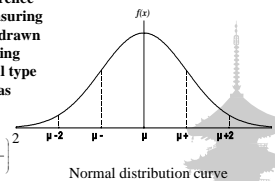
$$f(x) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

μ-2　μ-　μ　μ+　μ+2

Normal distribution curve

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The example of the area (probability) of the normal distribution curve lower part

k value	Between $\mu \pm k$	Outside of $\mu \pm$	μ
0	0.0000	1.0000	0.5000
1	0.6827	0.3173	0.1587
1.645	0.9000	0.1000	0.0500
1.960	0.9500	0.0500	0.0250
2	0.9545	0.0455	0.0228
2.576	0.9900	0.0100	0.0050
3	0.9973	0.0027	0.00135

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Slide 20

7 Correlation coefficient

Correlation analysis

➢ The analytical method in the case of two or more variables becoming a set and changing simultaneously
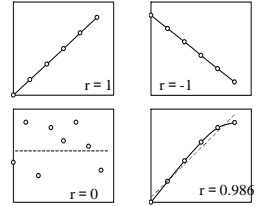
Correlation coefficient: r

➢ The grade of the correlation matrix between 2 variates is shown.

$$r = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}}$$
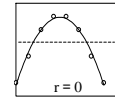
The related example of a correlation coefficient and linearity

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8 Uncertainty

About uncertainty

➢ The parameter by which dispersion in the value which may be rationally connected to measurand is characterized.
This is appended to a test result.

➢ Doubt which exists about any test results with the uncertainty of measurement

How to express uncertainty

➢ It displays by the section and a confidence level.

An error and uncertainty

Error   : The difference of an observed value and a "true value"

Uncertainty : What displayed the doubt of the observed value numerically

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Slide 22

The example of a factor of the uncertainty of analytical practice.

**Sampling**

➢ Homogeneity , The kind of sampling , The physical state of bulk , Temperature　Pressure influence

Sample preparation

➢ Homogenization , Desiccation , Grinding , Dissolution , Extraction , Contamination , Concentration , Dilution error

The device calibration by certified reference material (CRM) or a standard substance (RM)

➢ Uncertainty of (C)RM , Compatibility of a sample and (C)RM , Proofreading precision by (C)RM , Precision of equipment

Analysis

➢ An operator's specificity , Interference of a matrix etc. , Reagent purity , A setup of an equipment parameter , Precision for every measurement

Data processing

➢ Equalization , Rounding-off and omission , Statistics , Algorithm

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Slide 23

9 Test for outliers

The method of Grubbs

➢ The method which assumed that data followed normal distribution.

➢ Standardized variate

$$u = \frac{\left| x - \bar{x} \right|}{s}$$

u value of a doubtful value u value of a rejection limit

$\longrightarrow$ Outliers, rejection

➢ The inclination to be easy to be influenced by outliers and for a judgment to become indefinite

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Slide 24

Z score

➢ The method which is not assumed that data distributes normally.

➢ It is hard to be influenced by outliers and a judgment is clear.

➢ Calculation of the Z score of a report value.

Z ＝ x－x / 0.7413× IQR

IQR=Q₃－Q₁

x　Each observed value   x　Median

IQR　Interquartile range

Q1: The 1st quartile   Q3　The 3rd quartile

The acceptance criterion of a Z score

|Z|　3   Dissatisfied

3　|Z|　2   It is doubtful.

|Z|　2   Satisfactory

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Slide 25

> **Calculation of the Z score between offices (Z$_B$), and the Z score in an office (Z$_w$)**

  Two data, *A* and *B*

  $S = A + B / 2$

  $D = A - B / 2 \qquad A \quad B$

  $Z_B = S - \bar{S} / 0.7413 \times IQR(S)$

  $Z_w = (D - \bar{D}) / 0.7413 \times IQR(D)$

  $Z_B \quad Z_B \quad 3$ **It inclines toward the larger one.**

  $Z_B \quad -3$ **It inclines toward the smaller one.**

  $Z_W \quad |Z_W| \quad 3$ **Dispersion is large.**

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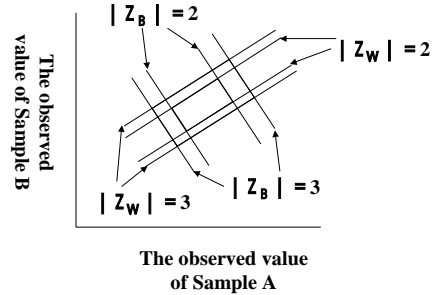
Compound evaluation figure
The median of Sample A   In the case of the median of Sample B

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Slide 27

Partition	Change between places Z$_B$	Change within a station Z$_W$	Evaluation
	Z 3	Z 3	A bias is in the smaller one and dispersion is also large. It may be pulled by A or B.
	Z 3	Z 3	
	Z 3	Z 3	A bias is in the larger one and dispersion is also large. It may be pulled by A or B.
	Z 3	Z 3	
	Z 3	3 Z 3	Although a bias is in the smaller one, there is little dispersion.
	Z 3	3 Z 3	Although a bias is in the larger one, there is little dispersion.
	3 Z 3	Z 3	Although there is no bias, there is little dispersion. A or B may be greatly separated.
	3 Z 3	Z 3	
	2 |Z| 3	2 |Z| 3	A bias, dispersion, or both have a doubtful point.
	|Z| 2	|Z| 2	There is also no bias and there is also no dispersion.

Evaluation of the partition of a scatter diagram

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Slide 28

Thank You for Your Kind Attention

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Accuracy management

1. Outline

In order to secure fixed accuracy when conducting measurement and analysis, you have to do a series of work under exact accuracy management from sample extraction to transportation, a pretreatment, analysis, and a fixed quantity. Therefore, the standard of ISO (International Organization for Stsndardization), Concepts, such as a guide and GLP (Good Laboratory Practice), are taken in, and a system is built, and it inquires, before conducting measurement and analysis about the matter shown below.
　　　(1) Standard Operating Procedure's
　　　(2) Reservation of reliability (Validasion)
　　　(3) Evaluation of the reliability of measurement

2. Standard Operating Procedure's

Before conducting measurement and analysis, standard work sequence is created in advance.
　　Especially when measuring and analyzing by methods other than the thing applicable to "the work which has on quality", and "the work done daily", and a public test method, it certainly creates.
　　In consideration of reservation of reliability etc., standard work sequence is concretely intelligible and common knowledge thoroughness is carried out at the persons concerned. Next, a key point is shown.
　　　①　The turning point of success or failure (The part which influences precision greatly)
　　　②　Safety (dangerous portion)
　　　③　The ease of doing (Point)

By creating standard work sequence and standardizing work, management of the following matter is also expectable in addition to accuracy management.
　　　①　Quality　　⇒　Reduction in a mistake
　　　②　Ｃｏｓｔ　　⇒　Optimal location and allocation of an instrument and a facility
　　　③　Time for delivery ⇒　Management of time 、Aid assistance of a staff
　　　④　Insurance　⇒　Improvement in work insurance
　　　⑤　Productivity　⇒　Examination of automation etc.
　　　⑥　Management　⇒　Technical improvement, maintenance, and succession（Cover the limitation of OJT. ）

The demerit of standard work sequence is also understood, and adaptable nature in the spot is not checked or it does not become conservative. Understand the limit which can do a standard (Standard), and when you manage the sample which contains a matrix variously like an environmental sample, don't lose pliability.
　　When the measurement / analysis method, and apparatus and equipment are changed, standard work sequence is reexamined and the contents are changed if needed.

3. Reservation of Reliability (Validation)

Standard work sequence is created about evaluation of the validity of the sample extraction in

the various measurement / analysis methods, and the measurement / analysis method, and the performance of an instrument and equipment, and the contents of control of maintenance, and the reliability is examined in advance. Reliability and validity are expressed as each application limit (time base range), an error, uncertainty, etc.

Generally the object of validation has various classifications. The contents of method validation (method validation) are shown below.

a. Validation of a principle

Validity in the principle of the measurement / analysis method, such as collection efficiency of the sharpness of the reaction using coloring by a chemical reaction like absorption photometry, the selectivity of the separation ability and the detector of chromatograph in the case of gas analysis, and a sampling agent.

b. Validation of a procedure

Validity in the actual procedure implementation of the contents of the representation nature of the determination of the sample extraction place and time which suited the purpose of measurement and analysis, or a method and a sample, storage and conveyance of a sample, preliminary treatment, or the pretreatment, a plan, exact operation of quality and a fixed quantity, etc.

c. Validation, such as an instrument, equipment, and a reagent

Validity [in / several kinds / the control of maintenance of a hard side], such as adjustment and a condition setup of the grade of a reagent, and measurement and an analytical instrument, a clean lab, environment of other institution and equipment, etc. which manage [maintenance management of a sampling set, and / preparation of an instrument and], and are used.

d. Calibration

Reservation of the reliability in proofreading operations, such as use of the standard substance in which traceability was carried out and the contents were decided.

In addition, reliability, such as computer software incidental to the personnel's capability, and measurement and an analytical instrument, is also checked.

[Uncertainty]   Uncertainty shows doubt and does not show the gap from a true value. Uncertainty is estimated as composition of the zone of ambiguity and is shown by the width incidental to the result.

It is more practical to estimate the following uncertainty, since the factor by operation of sampling, pretreatment, etc. is large in environmental measurement and analysis in many cases.
　　① Collection efficiency at the time of sampling, etc. and variation of double measurement and analysis
　　② A blank check and compensation
　　③ The identification of the bias by a standard substance
　　④ The check of the variation by repetition measurement

4. Evaluation of Reliability of Measurement

In order to evaluate the numerical value of measurement / analysis result, the reliability of the whole process is managed and the enforcement state of measurement and analysis is supervised, and it must be utilized as an examination material in the case of the determination of a report value at the same time it perceives and feeds back abnormalities.

The index of general surveillance is shown below.

① Stability of equipment:　Adjustment states, such as sensitivity change of a detector, inclination of an analytical curve, etc.

② Check of a minimum-limit-of-detection value and a determination limit value: Standard deviation of inclination, the linearity and the relative sensitivity coefficient of an analytical curve, the sensitivity of the least concentration of a standard substance, blank concentration and an operation blank value, and a travel blank value etc.

③ Operation blank measurement and analysis

④ Travel blank measurement and analysis

⑤ Double measurement and analysis

⑥ Others:　Recovery rate measurement, sensitivity check in the setting position of an automatic-meter-reading machine and an on-site measuring instrument, etc.

As a periodical surveillance index, the sample for control which added the standard substance as internal accuracy management is measured and analyzed periodically. Or it participates in the external accuracy management enterprise and skill examination which a third party carries out, and management data is obtained.

5. Management and Record, and Report of Data

If a problem occurs from evaluation of the dependability of measurement, measurement and the analyzed result will serve as treatment of a missing measurement.Everyday monitoring is ensured so that missing measurement may not be issued. It is important to fully examine and report the circumstances, when a problem occurs, and to use for recurrence prevention. Even when there is no problem in particular, all the information is certainly recorded as examination and retroactivity of the contents can be performed later.

It arranges and the record about accuracy management is kept so that it may be easy to take a statistical total and verification.

6. Concrete Accuracy Management

6.1 The Special Feature of a Quality Control and Environmental Measuring

(1) The precondition of environmental measurement and analysis

The following recognition is required of accuracy management of the measurement and analysis of environment.

① Maintenance of measurement apparatus and equipments, and maintenance of apparatus accuracy

② Recognition of the tolerance of a measuring machine (pipet buret - in addition to this)

③ The degree conditions of cleanness of an analysis laboratory (when conducting super-microanalysis)
④ Reservation of quality, such as an examination reagent
⑤ Traceability of the standard substance for measurement / analysis
⑥ The handling of a sample, and the technique of preservation
⑦ The degree of the education and training of the engineer of environmental measurement and analysis

(2)   They are important influence conditions to environmental measurement / analysis sample, environmental measurement conditions, and data.

a. Validation of a principle

① Water Quality
Environmental water: According to samples, such as a season, the weather (at the time of extraction the weather situation before – extraction, especially rain), flux, water temperature, the flow velocity (current; a current, a deep pool), depth of water (sampling water level), extraction time, an extraction point, the quality of a bottom and a coast situation, plankton, bacteria.
Drainage: Time, amount of water, the operating condition of a place of business, relation with rain, etc.
Groundwater: Extraction time, a pumping situation, extraction conditions (a strainer position, the extraction method, etc.).
② Air Quality
Environmental Air: The operation situation of a season, the weather (a wind direction, wind velocity, weather, temperature), an investigation position, and a neighborhood place of business, means-of-transportation organization situation, etc.
Exhaust gas: The situation of work of taking out temperature and an exhaust gas, the sample extraction method.
③ Bad smell: Climate condition (a wind direction, wind velocity, temperature, humidity) etc.
④ Soil pollution investigation: Sample extraction conditions influence remarkably. Investigation of the past history suitable for the investigation purpose and an investigation point.
✦ Handling of the sample after an extraction part, the extraction method, and extraction.
✦ Selection of the sample which suited the investigation purpose for each the investigation of every.
✦ Prudent prior examination of extraction conditions.
⑤ N o i s e : Spatial relationship of an industrial noise, aircraft noise, a traffic noise (a railroad and an automobile), a measured region, a location, meteorological conditions (wind direction, a wind speed, atmospheric temperature, humidity, etc.), a structure, a forest tree tree, etc., etc., the measurement technique.
⑥ Vibration: A position, geology foundation conditions, the measurement technique.

⑦ Land subsidence: Groundwater level measurement time, the level measurement technique.

⑧ Waste relations: Selection of the sample suitable for the investigation purpose, a reduction.

⑨ Others: If measurement conditions are not clear, even if managed with sufficient accuracy, value will be reduced by environmental measurement.

b. Consideration of a statute and a social situation

① It is careful of whether a sample and measurement / analysis conditions suit the sample extraction conditions provided in the statute.

② It is cautious also of the social situation at the time of measurement and analysis, and deal with a sample.

c. 1 time of character of a sample and measurement

It is recognized as environmental measurement not having reproducibility, thinks that there are not a sample and the measurement conditions that measurement and analysis are the same again only at once, and is dealt with carefully. The sample after measurement / analysis which remained is kept in a cool place, without throwing away (it is useful for examination of data).

d. How to round a significant figure and a numerical value

Since it is meaningless even if it takes out a numerical value lower than a determination limit value with the technique of measurement and analysis, by concentration, extraction, etc., it pulls up to a determination limit value, and measurement and analysis are conducted.

In order to arrange data, data (numerical value) is rounded about [effective], judging from a statute etc.

6. 2 Accuracy and a True Value

(1) Correspondence relations, such as a term

The term on measurement accuracy is shown in the next table.

table 1. Terminological correspondence relation table

	JIS Z 8402 (1991) ISO 5745 (1994)	Old things JIS Z 8402 (1974) Old things ISO 5745 (1981)	JIS Z 8402 (1991) Quality control term	JIS Z 8402 (1991) Measurement term
The grade of variation	precision	precision	precision	precision
The grade of bias	trueness	accuracy	accuracy	accuracy
Both comprehensive concept	accuracy			overall accuracy

(2) A kind with error

a. Dispersion and reliance

When the difference of a true value and measured value is an error and roughly divides by

measurement and analysis, they are two kinds, variation and bias . However, the true value is unknown and presumes a true value as a substitute as compared with a standard (a reference solution, a standard substance). (Figure 1. variation and correctness   Reference)

exactitude (degree which

Gol
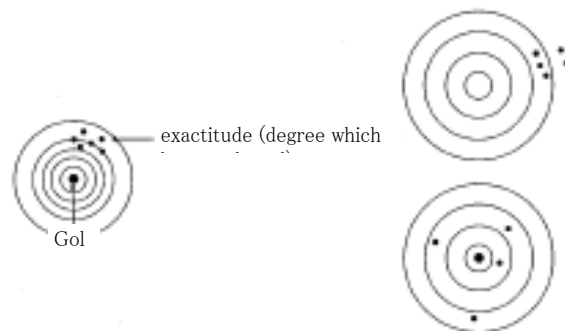
figure 1. Variation   Correctness

b. The method of another classification of a kind with error

If an error is seen a little in more detail, it can classify into five kinds. (Figure 2. Five kinds of errors   Reference)

	Accuracy	+	True value	+	precision
	Good		Good		Good
	Good		Defect		Defect
	Defect		Good		Defect
	Defect		Defect		Defect
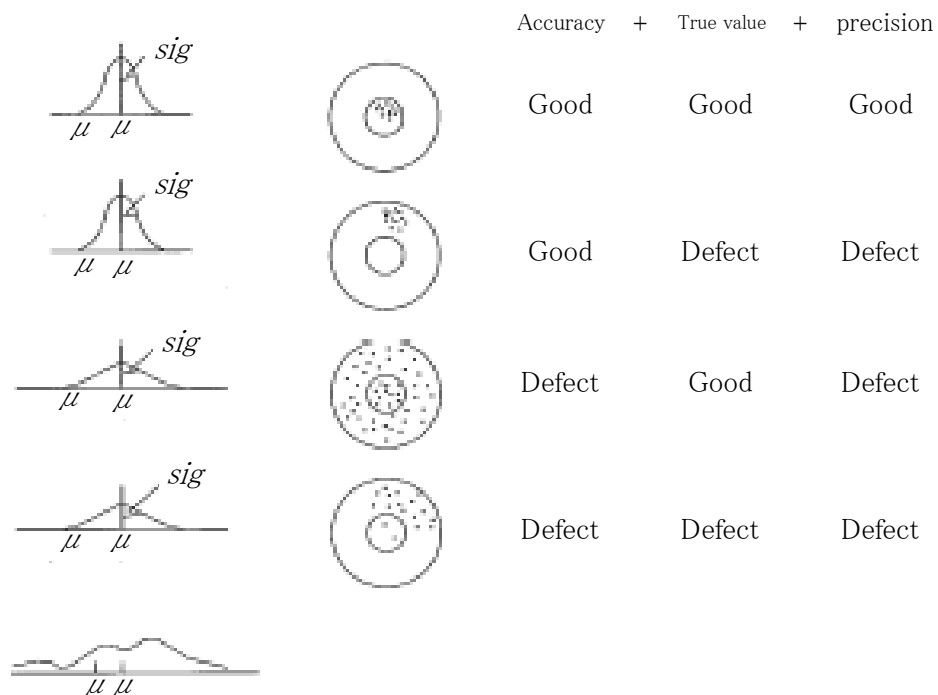
figure 2. Five kinds of errors

6. 3 Statistical Work of Data

(1) Handling of an abnormal value

When some data exists, when incorrect measurement has not clarified, especially an abnormal value (value which cannot be treated as the same group on the occasion of statistical works, such as average value) authorizes data, and removes (the removed value is also saved). The official approval methods include the method of Dixon, the method of Grubbs, the method of Pearson and Stepfens, etc.

(2) Average value

When the group of data is a normal distribution, using in quest of average value is useful. However, an error uses average value at the time of the distributed type of log normal distribution or others.

(3) Use of regular establishment paper

Data is plotted on regular establishment paper, and he is a data group of a well-shaped normal distribution, so that it is close to a straight line. As long as it is a straight line mostly, you may calculate as a normal distribution.

(4) Use of logarithm regular establishment paper

Data is plotted on logarithm regular establishment paper, and he is a data group of well-shaped log normal distribution, so that it is close to a straight line.

(5) A normal distribution and log normal distribution

In the case of a normal distribution, the range of standard deviation is between [average value]+ [standard deviation] and [average value]–[standard deviation], and, in the case of log normal distribution, it is between [average value]x [standard deviation] and [average value]/ [standard deviation].

(6) Standard deviation and a coefficient of variation

A coefficient of variation (CV%) breaks [standard deviation] by [average value], and expresses it as x100%. When a coefficient of variation is small, measurement accuracy may become good, but this is a time of concentration being the almost same grade. If concentration becomes low, a coefficient of variation will go up exponentially and will worsen.

(7) Correlation

a. Correlation coefficient (gamma)

The ranges of a correlation coefficient (gamma) are +1>=-0 – >=-1.
The definition of a correlation coefficient is as follows.

$$\gamma = \frac{Sxy}{\sqrt{SxSy}}$$

The residual square sum of Variables x and y and Sxy of Sx and Sy are the sums of the product of the residual of x, and the residual of y here, respectively.

$$Sx = \text{sigma}(x_i-\bar{x})^2 = \sum_{i=1}^{n} x_i{}^2 \ \llcorner\_\text{Supe}\_ \ ^{-(\Sigma x_i)^2} / n$$

$$Sy = \text{sigma}(y_i-\bar{y})^2 = \sum_{i=1}^{n} y_i{}^2 \ \llcorner\_\text{Supe}\_ \ ^{-(\Sigma y_i)^2} / n$$

$$Sxy = \text{sigma}(x_i-\bar{x})(y_i-\bar{y}) = \sum x_i y_i - (\Sigma(\Sigma y_i) y_i)/ n \qquad {}_{i=1}^{n} \quad {}_{i=1}^{n}$$

b. Rank correlation

When not adapting oneself to ordinary correlation functions with which distribution of sensory analysis, a color, hardness, the data that is hard to express for a numerical value directly, and a numerical value was confusedly and roughly different widely in environmental-related investigation, such as scatter, examination of rank correlation is also one technique.

The method of an easy examination of rank correlation asks for a rank correlation coefficient by the following formula, and judges it by a rank correlation coefficient (γ) official approval table.

$$\text{Rank correlation coefficient}\ (\gamma) = 1 - \frac{6 \times \Sigma\,(\text{The difference of ranking})^2}{n(n^2\text{-}1)}$$

Table 2.   Rank correlation coefficient （γ）Assay table

n	Percentage of risk		n	Percentage of risk		n	Percentage of risk	
	5% γ	1% γ		5% γ	1% γ		5% γ	1% γ
4	1.000	–	10	0.564	0.746	22	0.359	0.503
5	0.900	1.000	12	0.506	0.712	24	0.343	0.485
6	0.829	0.943	14	0.456	0.645	26	0.329	0.465
7	0.714	0.893	16	0.425	0.601	28	0.317	0.448
8	0.643	0.833	18	0.339	0.564	30	0.306	0.432
9	0.600	0.783	20	0.377	0.534			

7. Self-Control of Measurement and Analytical Value

7. 1 Self-Control of Measurement and an Analytical Value

An analyzer conducts measurement and analysis according to a standard operations list (SOP). However, as for the equipment, the instrument, the institution, reagent, analyzer, etc. who uses it, the result as expected does not necessarily get by daily delicate difference.

Each one repeats the education of safety, and measurement and analysis, and an analyzer strives for the rise of skill, after receiving the education of safety, and measurement and analysis. Measurement and analysis of are always done with a question at measurement / analysis result of

operation of series, such as a pretreatment, preparation operation, measurement by apparatus, and calculation of a result. Self-control of measurement and an analytical value is important, and effective in quick processing of an abnormal value.

7. 2 Self-Control of an Analytical Value

The following two cases can be considered in the abnormal value in environmental measurement and analysis.

① Measurement / analysis result of having exceeded regulation values, such as an environmental standards value and an effluent standard value

② Measurement / analysis result which processed the result of a cross check this statistically and was judged to be an abnormal value

When a report value exceeds a regulation value, action concerning water disposal is needed. A report value always corrects an analyzer and things are required. However, it is also a fact that the error is included in measurement and an analytical value.

An analyzer controls himself an analytical value and endeavors bringing speeding up of the correspondence to the abnormal value of (1), and the abnormal value of (2) close to zero.

7. 3 One Spot of Outlier Presumption

(1)   A blank value is high.

When a blank value is high in everyday measurement and analysis, the cause is checked as an abnormal value. It is considered whether only the blank value's having polluted with a certain cause or a reagent polluted, and all the examination systems were polluted similarly.

If it redoes from a sampling again, it will cost many labors, time, and cost. Moreover, it becomes missing measurement when it cannot measure again and analyze. Therefore, while it is important to manage a blank value and it checks each factor in advance, the circumstances of abnormalities are examined and it uses for recurrence prevention. If data is stored and a control chart is created, it will be useful for examination of an abnormal value.

(2)   Measurement and an analytical value are high.

When measurement and an analytical value are high, it is presumed that it is based on contamination etc. The overlap of the error based on the fall of the slope of an analytical curve and the instability of equipment, the ingredient for measurement / analysis, and a spectral line due to the contamination from poor washing, such as contamination from environment and a testing laboratory, a container, a use instrument, the contamination from the container under test preservation, the contamination from water and a reagent, and the fall of the factor of a reference solution etc. a sample There are many factors by calculation mistakes, such as a dilution error when diluting, and a dilution rate, and the measurement / analysis method.

Poor processing and river water of industrial waste water are polluted [whether it is an abnormal value and] artificially, and the sample itself needs to judge correctly whether it is high concentration.

An analyzer operates it according to a standard operations list (SOP), and raises skill.

Moreover, it is cautious of sensitivity change of the range of an application sample, the concentration range of an analytical curve, and measurement / analysis equipment and the check of stability, and the reaction change under operation. Self analytical skills are managed and an abnormal value is distinguished. If data is stored and a control chart is created, it will be useful for examination of an abnormal value.

(3)　Measurement and an analytical value are low.

When an analytical value is low, loss of measurement and an analytical object component is presumed. Adsorption, an addition failure of a reagent, the lack of loadings of a masking reagent, pH of the sample at the time of the poor pH adjustment at the time of extraction and ion exchange, and a coexistence component receive interference in vaporization and the preservation container which oxidizes and serves as insolubility in the phase of pretreatment of a sample, and it originates in housekeeping operation, such as poor extraction / separation, and becomes a low value.

By poor manufacture of an analytical curve reference solution, the slope of an analytical curve becomes large and the concentration of a sample becomes low. When the matrix concentration of a sample exceeds acceptable concentration highly and differs from the matrix of an analytical curve, it becomes a low value by matrix interference. It becomes a low value according to many factors which originate in the measurement / analysis method by change of measurement / analysis equipment etc. when measurement and the analytical value of an analytical curve and a sample have a difference. It is important to carry out early detection of the abnormal value, and to implement a measure by self-control.

7.4　Outlier Management of Everyday Regular Measurement and Analysis（x-Rs Control Chart ）

When conducting measurement and analysis periodically, and measurement and an analytical value (x) control chart are used and also drainage, river water, a flue exhaust gas, etc. create simultaneously a moving range (Rs; difference between adjacent measurement and analytical value) control chart, they are intelligible.

Measurement and an analytical value (x) control chart draw a pair of control limit lines which show a control limit up and down by making average value (x) of x into a central line. It asks for an upper part control limit (UCL) by [x]+ [2.66xRs], and it asks for a lower part control limit (LCL) by [x]+ [2.66xRs]. A moving range (Rs) control chart makes the average value (Rs) of Rs a central line, and an upper part control limit (UCL) serves as [3.27xRs]. A lower part control limit (LCL) does not think by a moving range (Rs) control chart.

7.5　Management by a Check Sample etc.

(1)　Management by the parallel coincidence measurement and analysis of a check sample (internal accuracy management)

Acid etc. is added in the factory effluent or river water which is conducting measurement and

analysis every day, it makes a market in it, and the inhouse check sample made uniformly stable during the period is produced.

It parallel-measures, a sample and a check sample are analyzed, measurement and analytical value, and value price offered of a check sample are compared, and self analysis is managed.

(2)   Management by the amount of recoveries (rate) which carried out standard addition

The sample which carried out standard addition is parallel measured and analyzed, a sample and a sample are asked for the amount of recoveries (rate) which carried out standard addition, and measurement / analysis result is judged. A recovery rate is low, or when variation is large, there is interference by the matrix and a coexistence ingredient, and measurement and an analysis method need a pretreatment and to be inquired.

(3)   Management by the external accuracy management enterprise or skill examination

It participates in the external accuracy management enterprise and skill examination which are carried out on a scale of a city, a prefecture, or a country, and evaluation diagnosis of its measurement and analytical value is carried out. A cause is studied when measurement / analysis result is unusual.

7. 6 Management by Double Measurement and Analysis (Indoor Parallel Examination)

Double measurement and analysis measure 2-3 pieces so that a sample may become the same, and it conducts same measurement and analysis. Since the same operation is performed, a result is obtained in an error span. It follows and double measurement and the analysis can evaluate the whole system of measurement and analysis. It manages by whether a result is in tolerance level with error by double measurement and analysis.

7. 7 The factor of outlier

When an abnormal value is acquired, it is necessary to check a check to see it became unusual in process of a thing with the unusual sample itself, and measurement and analysis. a cause -- the sample which can be saved [that it is unknown and] conducts remeasurement and analysis (if it can do, double measurement and analysis are desirable) within the period when a preservation state is good.

Variation probes an error factor, when unusually large, the cause of interference is studied, it is inquired and established and measurement and an analysis method are re-analyzed.

In water quality change, such as increase of an object ingredient, a matrix, and a coexistence ingredient, increase of waste water concentration and the amount of waste water, the management defect of a processing institution, etc. measure again and analyze after examination of measurement and an analysis method, and establishment by factory effluent analysis.

(1)   When measurement / analysis result is high

① Contamination: Instruments, such as beaker pipettes, such as a sampling container, water and reagents, a testing laboratory, draft, etc.
② Measurement and analytical instrument: The inaccuracy of background correction, duplication of a spectral line, instability of equipment, etc.

③ Calibration curve: Positive [accompanying the fall of analytical curve concentration / the fall of a slope, unsuitable positive / of sample concentration and analytical curve concentration]

④ Errors in calculation: Errors in calculation of the concentration rate and dilution rate at the time of sample concentration calculation

(2)　When measurement / analysis result is low

① Loss of the quality of an analysis subject: While measuring and analyzing from sample extraction, the mistake in vaporization and deterioration, sample decomposition insufficiency, and an addition order of a reagent, the shortage of concentration of a masking agent, and pH and liquefaction are not the optimal, and extraction and decomposition are insufficient.

② Measurement and analytical instrument: A minimum-limit-of-detection value and the determination limit value of the instability of equipment and a background are highly unsuitable.

③ An analytical curve and sample matrix concentration: When the matrix concentration in a sample is high as compared with an analytical curve

④ Analytical curve: Increase of the slope by the difference in the potency of the reference solution for analytical curves

⑤ Errors in calculation: Errors in calculation of the concentration rate and dilution rate at the time of sample concentration calculation

(3)　Measurement / analysis result is a barracks case.

When the measurement / analysis method is the same and the variation in the result which the same analyzer analyzed is large, application by the measurement / analysis method is an object for unsuitable, inquires and examines the measurement / analysis method, and is established.

7. 8 The Cure Against Outlier

(1)　The analytical curve concentration range, and measurement and an analytical value

It quantifies to the concentration of the quality of measurement / analysis subject within the analytical curve (straight line region) by the reference solution used for proofreading of measurement / analysis equipment.

When a high-concentration sample is diluted with a low-concentration analytical curve and it measured and analyzes, if the dilution rate of a slight difference is great, a fixed-quantity result will serve as a big difference. Therefore, the concentration range of an analytical curve and the nature concentration of measurement / analysis subject are measured and analyzed by proper concentration.

(2)　Matching of a matrix

The matrix ingredient and concentration of an analytical curve and a sample are made the same.

(3) Standard addition method

The matrix of various samples differs from a coexistence ingredient like an environmental sample. In order to - [qualitative] Quantify the matrix and a coexistence ingredient, a labor, time, and cost are required. In such a case, a standard addition method is used. The analytical curve is premised on being able to ignore through a zero point and not affecting measurement and an analytical value when an object ingredient is not included in a sample with a standard addition method.

(4) Internal standard method

When an interference according [the ingredient for measurement / analysis] to coexistence ingredients, such as a matrix, is presumed, an internal standard addition method is used. An object ingredient and an internal standard substance select the substance which receives the same interference by the matrix and a coexistence ingredient to an internal standard substance, and it asks for the rate that an object ingredient receives interference, from the rate that an internal standard receives interference.

(5) Standard addition method-matrix modifier addition method

An electric heating type atomic absorption method tends to receive interference by the matrix and a coexistence ingredient, and applies it to a comparatively pure sample.

(6) Background correction mechanism

A background compensation mechanism rectifies a background proper according to an equipment instructions manual.

(7) Addition of an interference depressant

An interference depressant is added when an object ingredient receives interference by the matrix and a coexistence ingredient. When measuring calcium (Ca) by a frame atomic absorption method, a lantern (La) etc. is used as interference depressants, such as aluminum (aluminum), Lynn acid, and sulfuric acid.

(8) Addition of a matrix modifier

an electric heating type atomic absorption method tends to receive interference by the matrix and a coexistence component, reduces interference of a matrix, and adds the stability of an object component to a measure sake. Palladium nitrate (II) is used as a matrix modifier.

(9) Selection of a spectral line

In an analysis method with many spectral lines, such as ICP emission spectrometry and ICP mass spectrometry, there is an optical interference of a coexistence ingredient, another spectral lines, such as a high order line which does not receive interference, are measured, and optical interference is avoided.

(10) The specificity of a standard operation procedure (SOP), and removal of an

interferent component

The capability which an object ingredient can measure and analyze correctly under coexistence of a matrix, a coexistence ingredient, etc. is the singularity of a standard operations list, and needs to examine and prove suiting the purpose beforehand. Acceptable concentration is also examined and examined and a scope is also clarified.

a. How to remove interference

The interference by the matrix and a coexistence component changes with measurement and analytical instruments. Many methods, such as selection of a background correction mechanism and a spectrum line, internal standardization, a standard addition method, an interference inhibitor, and the matrix modifier method, are used.

b. Chemical abstraction method

① Solvent extraction method: How to separate and condense an object ingredient by a solvent extraction method from a matrix and a coexistence ingredient
- Multi-ingredient simultaneous sampling process
- Single ingredient sampling process

② Ionic exchange method: Separate an object ingredient by ionic exchange.
- Adsorption separation of a matrix and the coexistence ingredient is carried out, and flow out an object ingredient.
- An object ingredient is adsorbed, and a matrix and a coexistence ingredient are flowed out, and flow out an object ingredient after separation.

③ Coprecipitation abstraction method: The precipitation separation method using a coprecipitater
- carry out coprecipitation of the object component by a coprecipitater -- carrying out another -- a matrix and a coexistence component, and separation
- Coprecipitation of a matrix and the coexistence component is carried out, it dissociates, and filtrate recovers an object component.

④ Solid phase sampling process: Adsorption concentration of the object ingredient is carried out, and a matrix and a coexistence ingredient are flowed into a solid phase column, and flow an object ingredient into it after separation.

⑤ Column chromatographic separation method: Separate an object component, and a matrix and a coexistence component by column chromatograph.
- Adsorption separation of the coexistence ingredient is carried out, and flow out an object ingredient.
- Adsorption concentration of the object ingredient is carried out, and a matrix and a coexistence ingredient are flowed out, and flow out an object ingredient after separation.

⑥ Others: Separation, separation of mercury steam, and a matrix and a coexistence ingredient, separation by a headspace method, separation by the purge trap method, and an object ingredient are methylated as a hydrogenation thing by reduction evaporation, and measure by a gas chromatograph.

7. 9 A Minimum Limit of Detection and a Determination Limit

When carrying out a quantitative analysis using an analytical curve, it is necessary to check that the minimum limit of detection and the determination limit are filling the concentration for the purpose of measurement / analysis.

Usually, the standard deviation (S_B) of an operation blank value (Y_B) is measured, and let that to which the value which added one 3 times the value of this to the blank value added one 10 times the value of this with the minimum-limit-of-detection value be a determination limit value.

If expressed with a measurement value standard (Y value)

Minimum-limit-of-detection value : $Y_B + 3 \times S_B$

Determination limit value : $Y_B + 10 \times S_B$

This is corrected and displayed on a concentration standard (x value).

When converting concentration after pulling a blank value from the measured value of a sample, it calculates by $3xS_B$ and $10xS_B$, without applying a blank value to a minimum-limit-of-detection value and a determination limit value.

7.10 A minimum Limit of Detection and a Determination Limit

A linear expression is almost a calibration curve is a regression line by a least squares method.

An absorbance equimeasure constant value is taken along the axis of ordinate of a grid sheet, concentration is taken along an axis of abscissa, it plots, and a relation line is created. A correlation matrix is searched for from the variation in the point on a relation line, and it is shown that it is a primary regression line, so that a correlation coefficient is [one] near.

7.11   Conclusion

In accuracy management of measurement and analysis, it is important to secure reliability. Therefore, the system which took in concepts, such as ISO and GLP, needs to be built. It is important to fix standard work sequence, to strive for reservation of reliability, and to evaluate reliability.

An analyzer controls himself, and it is effective to manage one's skill, when securing the reliability of measurement and an analytical value, and it can profit by it as examination data when an abnormal value occurs.

Check, inspection records, etc. (every day, a commuter's ticket, and emergency), such as control log (an acquisition date, term of validity, manufacture, etc.) of the reagent used in everyday measurement and analysis, equipment, equipment, apparatus, are created and kept. Moreover, the standards (a standard machine, a standard substance, etc.) to be used keep record using the thing used as traceability. It can profit also by these records as examination data when an abnormal value occurs.

It is important to perform reexamination of a system and standard work sequence periodically, and to change if needed.

Normal distribution or Laplace-Gauss distribution
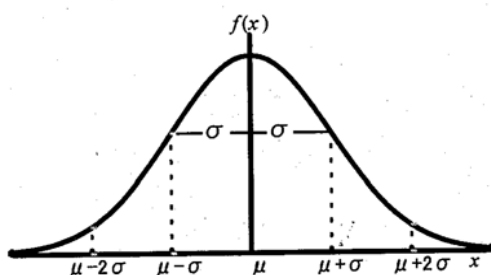
$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}(\frac{x-\mu}{\sigma})^2}$$

x   : random variable
f(x) : probability density function
μ   : population mean
e   : Natural number (2.71828···)
σ   : populationstandard deviation
σ^2 : population variance

$x = \mu \pm \sigma$ →The point of inflexion of a
                        probability density curve

The example of the area (probability) of the normal distribution curve lower part

k	μ±k	μ±kσ out	>μ±kσ
0	0.0000	1.0000	0.5000
1	0.6827	0.3173	0.1587
1.645	0.9000	0.1000	0.0500
1.960	0.9500	0.0500	0.0250
2	0.9545	0.0455	0.0228
2.576	0.9900	0.0100	0.0050
3	0.9973	0.0027	0.00135

Various normal distribution is changed into standardized normal distribution.
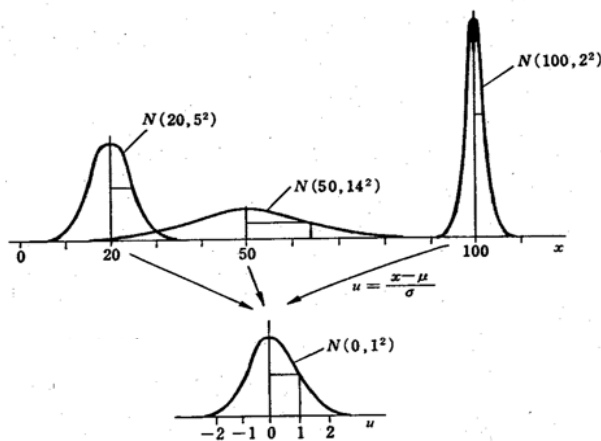
$$u = \frac{x - \mu}{\sigma}$$

u : standardized random variable
x : random variable
μ : population mean
σ : population standard deviation

u = k

$$u = \frac{x - \bar{x}}{s}$$

u : standardized random variable
x : random variable
$\bar{x}$: sample mean

Example computation which asks for the upper part probability of normal distribution

Normal distribution   μ : 80.2   σ : 9.0

How much is the probability that the data exceeding 95 will appear?

$$u = \frac{x - \mu}{\sigma} = \frac{95 - 80.2}{9.0} = 1.644$$

k = 1.644   Upper piece side probability: 0.050 (5%)

Normal-distribution table

The probability that x will take the value more than
$\mu + k\sigma$

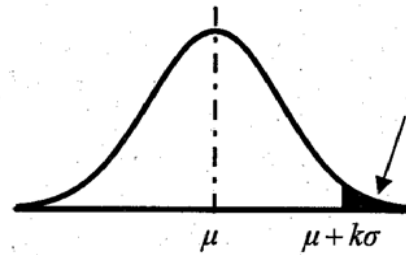| k	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
0.0	.500 0	.496 0	.492 0	.488 0	.484 0	.480 1	.476 1	.472 1	.468 1	.464 1
0.1	.460 2	.456 2	.452 2	.448 3	.444 3	.440 4	.436 4	.432 5	.428 6	.424 7
0.2	.420 7	.416 8	.412 9	.409 0	.405 2	.401 3	.397 4	.393 6	.389 7	.385 9
0.3	.382 1	.378 3	.374 5	.370 7	.366 9	.363 2	.359 4	.355 7	.352 0	.348 3
0.4	.344 6	.340 9	.337 2	.333 6	.330 0	.326 4	.322 8	.319 2	.315 6	.312 1
0.5	.308 5	.305 0	.301 5	.298 1	.294 6	.291 2	.287 7	.284 3	.281 0	.277 6
0.6	.274 3	.270 9	.267 6	.264 3	.261 1	.257 8	.254 6	.251 4	.248 3	.245 1
0.7	.242 0	.238 9	.235 8	.232 7	.229 6	.226 6	.223 6	.220 6	.217 7	.214 8
0.8	.211 9	.209 0	.206 1	.203 3	.200 5	.197 7	.194 9	.192 2	.189 4	.186 7
0.9	.184 1	.181 4	.178 8	.176 2	.173 6	.171 1	.168 5	.166 0	.163 5	.161 1
1.0	.158 7	.156 2	.153 9	.151 5	.149 2	.146 9	.144 6	.142 3	.140 1	.137 9
1.1	.135 7	.133 5	.131 4	.129 2	.127 1	.125 1	.123 0	.121 0	.119 0	.117 0
1.2	.115 1	.113 1	.111 2	.109 3	.107 5	.105 6	.103 8	.102 0	.100 3	.098 5
1.3	.096 8	.095 1	.093 4	.091 8	.090 1	.088 5	.086 9	.085 3	.083 8	.082 3
1.4	.080 8	.079 3	.077 8	.076 4	.074 9	.073 5	.072 1	.070 8	.069 4	.068 1
1.5	.066 8	.065 5	.064 3	.063 0	.061 8	.060 6	.059 4	.058 2	.057 1	.055 9
1.6	.054 8	.053 7	.052 6	.051 6	.050 5	.049 5	.048 5	.047 5	.046 5	.045 5
1.7	.044 6	.043 6	.042 7	.041 8	.040 9	.040 1	.039 2	.038 4	.037 5	.036 7
1.8	.035 9	.035 1	.034 4	.033 6	.032 9	.032 2	.031 4	.030 7	.030 1	.029 4
1.9	.028 7	.028 1	.027 4	.026 8	.026 2	.025 6	.025 0	.024 4	.023 9	.023 3
2.0	.022 8	.022 2	.021 7	.021 2	.020 7	.020 2	.019 7	.019 2	.018 8	.018 3
2.1	.017 9	.017 4	.017 0	.016 6	.016 2	.015 8	.015 4	.015 0	.014 6	.014 3
2.2	.013 9	.013 6	.013 2	.012 9	.012 5	.012 2	.011 9	.011 6	.011 3	.011 0
2.3	.010 7	.010 4	.010 2	.009 9	.009 6	.009 4	.009 1	.008 9	.008 7	.008 4
2.4	.008 2	.008 0	.007 8	.007 5	.007 3	.007 1	.006 9	.006 8	.006 6	.006 4
2.5	.006 2	.006 0	.005 9	.005 7	.005 5	.005 4	.005 2	.005 1	.004 9	.004 8
2.6	.004 7	.004 5	.004 4	.004 3	.004 1	.004 0	.003 9	.003 8	.003 7	.003 6
2.7	.003 5	.003 4	.003 3	.003 2	.003 1	.003 0	.002 9	.002 8	.002 7	.002 6
2.8	.002 6	.002 5	.002 4	.002 3	.002 3	.002 2	.002 1	.002 1	.002 0	.001 9
2.9	.001 9	.001 8	.001 8	.001 7	.001 6	.001 6	.001 5	.001 5	.001 4	.001 4
3.0	.001 3	.001 3	.001 3	.001 2	.001 2	.001 1	.001 1	.001 1	.001 0	.001 0
3.1	.001 0	.000 9	.000 9	.000 9	.000 8	.000 8	.000 8	.000 8	.000 7	.000 7
3.2	.000 7	.000 7	.000 6	.000 6	.000 6	.000 6	.000 6	.000 5	.000 5	.000 5
3.3	.000 5	.000 5	.000 5	.000 4	.000 4	.000 4	.000 4	.000 4	.000 4	.000 3
3.4	.000 3	.000 3	.000 3	.000 3	.000 3	.000 3	.000 3	.000 3	.000 3	.000 2
3.5	.000 2	.000 2	.000 2	.000 2	.000 2	.000 2	.000 2	.000 2	.000 2	.000 2
3.6	.000 2	.000 2	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1
3.7	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1
3.8	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1	.000 1
3.9	.000 0	.000 0	.000 0	.000 0	.000 0	.000 0	.000 0	.000 0	.000 0	.000 0

Null hypothesis test (The method of Grubbs)

No.	date	u
1	133	1.1725
2	134	1.0377
3	134	1.0377
4	134	1.0377
5	135	0.903
6	135	0.903
7	139	0.3639
8	140	0.2291
9	140	0.2291
10	140	0.2291
11	141	0.0943
12	142	0.0404
13	142	0.0404
14	144	0.31
15	144	0.31
16	147	0.7143
17	147	0.7143
18	149	0.9838
19	150	1.1186
20	164	3.0054
n	20	
x (average)	141.7	
s	7.42	

No.	date	u
1	0.342	1.53
2	0.4	1.2016
3	0.42	1.0883
4	0.463	0.8448
5	0.48	0.7486
6	0.499	0.641
7	0.51	0.5787
8	0.511	0.573
9	0.534	0.4428
10	0.552	0.3409
11	0.555	0.3239
12	0.59	0.1257
13	0.593	0.1087
14	0.617	0.0272
15	0.626	0.0781
16	0.631	0.1065
17	0.653	0.231
18	0.654	0.2367
19	0.67	0.3273
20	0.71	0.5538
21	0.74	0.7237
22	0.746	0.7576
23	0.762	0.8482
24	0.808	1.1087
25	1.24	3.5549
n	25	
x (average)	0.6122	
s	0.1766	

$u = |x - \bar{x}| / s$

u: Null hypothesis test value
x: Date
$\bar{x}$: Average
s: Standard deviation
n: Nummber of date

Null hypothesis test value (The method of Grubbs)   α＝Level of significance

n数	α=0.05	0.025	0.01	0.005	n数	α=0.05	0.025	0.01	0.005
3	1.153	1.155	1.155	1.155	30	2.745	2.908	3.103	3.236
4	1.463	1.481	1.492	1.496	31	2.759	2.924	3.119	3.253
5	1.672	1.715	1.749	1.764	32	2.773	2.938	3.135	3.270
6	1.822	1.887	1.944	1.973	33	2.786	2.952	3.150	3.286
7	1.938	2.020	2.097	2.139	34	2.799	2.965	3.164	3.301
8	2.032	2.126	2.221	2.274	35	2.811	2.979	3.178	3.316
9	2.110	2.215	2.323	2.387	36	2.823	2.991	3.191	3.330
10	2.176	2.290	2.410	2.482	37	2.835	3.003	3.204	3.343
11	2.234	2.355	2.485	2.564	38	2.846	3.014	3.216	3.356
12	2.285	2.412	2.550	2.636	39	2.857	3.025	3.228	3.369
13	2.331	2.462	2.607	2.699	40	2.866	3.036	3.240	3.381
14	2.371	2.507	2.659	2.755	41	2.877	3.046	3.251	3.393
15	2.409	2.549	2.705	2.806	42	2.887	3.057	3.261	3.404
16	2.443	2.585	2.747	2.852	43	2.896	3.067	3.271	3.415
17	2.475	2.620	2.785	2.894	44	2.905	3.075	3.282	3.425
18	2.504	2.651	2.821	2.932	45	2.914	3.085	3.292	3.435
19	2.532	2.681	2.854	2.968	46	2.923	3.094	3.302	3.445
20	2.557	2.709	2.884	3.001	47	2.931	3.103	3.310	3.455
21	2.580	2.733	2.912	3.031	48	2.940	3.111	3.319	3.464
22	2.603	2.758	2.939	3.060	49	2.948	3.120	3.329	3.474
23	2.624	2.781	2.963	3.087	50	2.956	3.128	3.336	3.483
24	2.644	2.802	2.987	3.112	60	3.025	3.199	3.411	3.560
25	2.663	2.822	3.009	3.135	70	3.082	3.257	3.471	3.622
26	2.681	2.841	3.029	3.157	80	3.130	3.305	3.521	3.673
27	2.698	2.859	3.049	3.178	90	3.171	3.347	3.563	3.716
28	2.714	2.876	3.068	3.199	100	3.207	3.383	3.600	3.754
29	2.730	2.893	3.085	3.218					

The example of evaluation of the outliers of 2 sample data

No.	A	B	S	D	Z_B	Z_W
L1	20.1	26	32.6	4.2	−4.84	−0.64
L2	64.2	35.2	70.3	−20.5	0.19	−6.52
L3	33.7	41.1	52.9	5.2	−2.13	−0.4
L4	12.3	42.4	38.7	21.3	−4.03	3.43
L5	38.7	43.1	57.8	3.1	−1.48	−0.9
L6	43.3	43.2	61.2	−0.1	−1.03	−1.67
L7	45.8	43.7	63.3	−1.5	−0.75	−2
L8	44.9	43.8	62.7	−0.8	−0.83	−1.83
L9	29.1	44.8	52.3	11.1	−2.21	1
L10	40.5	45.5	60.8	3.5	−1.08	−0.81
L11	44.4	47.3	64.8	2.1	−0.55	−1.14
L12	34.4	48.3	58.5	9.8	−1.39	0.69
L13	49.2	52.5	71.9	2.3	0.4	−1.1
L14	44	52.6	68.3	6.1	−0.08	−0.19
L15	42.9	52.7	67.6	6.9	−0.17	0
L16	44.4	53	68.9	6.1	0	−0.19
L17	41.3	53.4	67	8.6	−0.25	0.4
L18	45.8	54.1	70.6	5.9	0.23	−0.24
L19	44.1	54.7	69.9	7.5	0.13	0.14
L20	49.6	55.9	74.6	4.5	0.76	−0.57
L21	43.3	56.1	70.3	9.1	0.19	0.52
L22	44.7	56.1	71.3	8.1	0.32	0.29
L23	44.6	56.3	71.3	8.3	0.32	0.33
L24	46.5	56.9	73.1	7.4	0.56	0.12
L25	41.7	58.3	70.7	11.7	0.24	1.14
L26	46.6	59.3	74.9	9	0.8	0.5
L27	46.1	61.4	76	10.8	0.95	0.93
L28	46.7	61.5	76.5	10.5	1.01	0.86
L29	39.4	77.1	82.4	26.7	1.8	4.71
Σ	1212.3	1476.3	1901.2	186.9		
$\overline{x}$ (average)	41.803	50.907	65.56	6.44		
s	9.32	9.573	10.85	7.8		
$\widetilde{x}$ (median)	44.1	52.7	68.9	6.9		
Q_3	45.8	56.1	71.3	9.1		
Q_1	40.5	43.8	61.2	3.5		
$0.7413 \times IQR$	3.9	9.1	7.5	4.2		

No. : Laboratory
A : Data 1
B : Data 2
Σ : Total
$\overline{x}$: Average
s : Standard deviation
$\widetilde{x}$: Median
Q_3 : Quartile 75%
Q_1 : Quartile 25%
Z_B : Z score of between laboratory
Z_W : Z score of within laboratory

$$S = (A+B)/(\sqrt{2})$$
$$D = (B-A)/(\sqrt{2}) \quad \widetilde{A} > \widetilde{B}$$
$$IQR(S) = S_{Q3} - S_{Q1}$$
$$IQR(D) = D_{Q3} - D_{Q1}$$
$$Z_B = (S - \widetilde{S})/\{0.7413 \times IQR(S)\}$$
$$Z_W = (D - \widetilde{D})/\{0.7413 \times IQR(D)\}$$
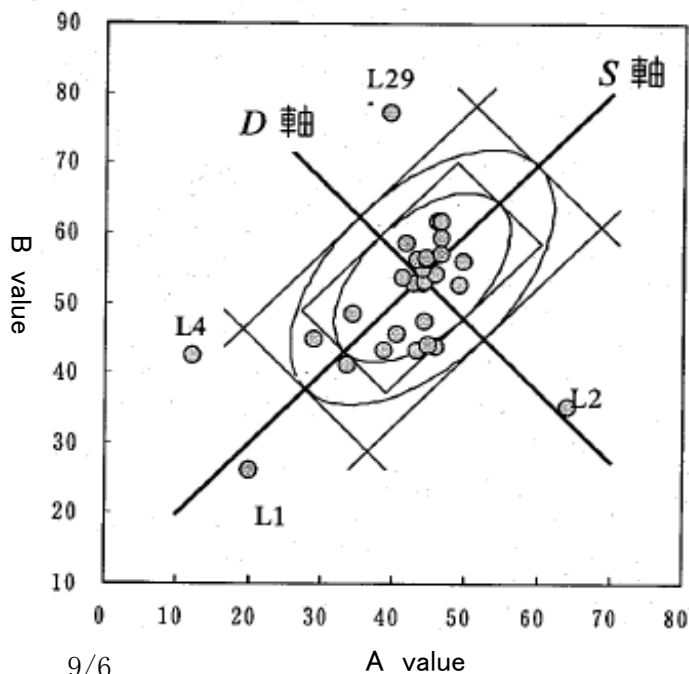
$Z_B=$	0
$S=(A+B)/\sqrt{2}=$	68.9
A+B=	97.43931

$Zw=$	0
$D=(B-A)/\sqrt{2}=$	6.9
B−A=	9.758074

$Z_B=$	−2
$S=(A+B)/\sqrt{2}=$	53.9
A+B=	76.22611

$Zw=$	−2
$D=(B-A)/\sqrt{2}=$	−1.5
B−A=	−2.12132

$Z_B=$	2
$S=(A+B)/\sqrt{2}=$	83.9
A+B=	118.6525

$Zw=$	2
$D=(B-A)/\sqrt{2}=$	15.3
B−A=	21.63747

$Z_B=$	−3
$S=(A+B)/\sqrt{2}=$	46.4
A+B=	65.61951

$Zw=$	−3
$D=(B-A)/\sqrt{2}=$	−5.7
B−A=	−8.06102

$Z_B=$	3
$S=(A+B)/\sqrt{2}=$	91.4
A+B=	129.2591

$Zw=$	3
$D=(B-A)/\sqrt{2}=$	19.5
B−A=	27.57716

Sulfaide in sample

Cl$_2$	NH$_3$−N	NH$_3$−N
DPD Method	Salicylate Method	Salicylate Method
No. 1450	No. 2455	No. 2455
0〜2.00mg/L	0〜0.800mg/L	0〜0.800mg/L
530 nm	655 nm	655 nm
1−inch Cell	1−inch Cell	1−inch Cell

Column 1 — Cl$_2$

Blank

| 10mL of Sample | (Cell)
↓
| Cell holder in set. |
↓
| ZERO |

Measuremnt

| 10mL of Sample | (Cell)
↓ ←DPD Free Chlorine
| Swirl to mix |
↓
| Cell holder in set. |
↓
| Read of result |

Column 2 — NH$_3$−N

Blank

| 10mL of Distilled water | (Cell)
↓ ← Ammonia Salicylate Powder
| Swirl to mix |
↓
| Wait 3 min. |
↓ ← Ammonia Cyanurate Powder
| Swirl to mix |
↓
| Wait 15 min. |
↓
| Cell holder in set. |
↓
| ZERO |

Measuremnt

| 10mL of Sample | (Cell)
↓ ← Ammonia Salicylate Powder
| Swirl to mix |
↓
| Wait 3 min. |
↓ ← Ammonia Cyanurate Powder
| Swirl to mix |
↓
| Wait 15 min. |
↓
| Cell holder in set. |
↓
| Read of result |

Column 3 — NH$_3$−N (Sulfaide in sample)

Blank

| 10mL of Distilled water | (Cell)
↓ ← Ammonia Salicylate Powder
| Swirl to mix |
↓
| Wait 3 min. |
↓ ← Ammonia Cyanurate Powder
| Swirl to mix |
↓
| Wait 15 min. |
↓
| Cell holder in set. |
↓
| ZERO |

Measuremnt

| 350mL of Sample | (Beaker)
↓ ← Sulfide Inhibitor Reagent
↓   Powder Pillows
| Swirl to mix |

| 10mL of Sample | (Cell)
↓ ← Ammonia Salicylate Powder
| Swirl to mix |
↓
| Wait 3 min. |
↓ ← Ammonia Cyanurate Powder
| Swirl to mix |
↓
| Wait 15 min. |
↓
| Cell holder in set. |
↓
| Read of result |