- (7) Where potassium chloride solution (saturated) is used for the liquid internal cylinder, attention should be paid since the drop of the liquid temperature may cause crystallization of potassium chloride and increase the resistance owing to its sticking.
- (8) Because potassium nitrate solution (100 g/L) in external cylinder more or less mingles with potassium chloride solution in internal cylinder, the liquid in external cylinder should also be periodically exchanged.
- (9) See Note  $(^{15})$  in clause 34.
- (10) See Note (16) in clause 34.
- (<sup>11</sup>) See Note (<sup>17</sup>) in clause 34. When the liquid temperature is 10 "C to 30 °C, the response time of a chloride ion-selective electrode is about 1 min or less in the case of the chloride concentration Cl<sup>-</sup> 5 mg/L or more.
- (<sup>12</sup>) Potential discrepancy between chloride ion reference solution (Cl<sup>-</sup> 10 mg/L) and chloride ion reference solution (Cl<sup>-</sup> 1000 mg/L) falls in the range of 110 mV to 120 mV (25 "C), and the working curve shows linearity between Cl<sup>-</sup> 5 mg/L to 1000 mg/L concentration of chloride ion.
- $(^{13})$  See Note  $(^{19})$  in clause 34.
- d) **Operation** The operation shall be carried out as follows:
  - 1) Place 100 ml of sample(<sup>14</sup>)(<sup>15</sup>) in a measuring container, add 10 ml of acetate buffer solution (pH 5), and adjust the temperature of the liquid to within  $\pm 1$  "C of the temperature noted in c) 4).
  - Carry out the procedures in c) 2) to 4)<sup>(13)</sup>, find the concentration of chloride ion on the working curve and calculate the concentration of chloride ion (Cl<sup>-</sup> mg/L) in the sample.
    - Notes (<sup>14</sup>) Adjust beforehand the pH of sample to about 5 by adding sodium hydroxide solution (40g/L) [prepared in accordance with 21 a) 3)] when the sample shows acidity, and adding acetic acid (1+10) (prepared using acetate acid specified in JIS K 8355) when it shows alkalinity.
      - (<sup>15</sup>) When sample contains sulfide ion, previously add zinc acetate solution (100 g/L) (prepared by 12 g of dissolving zinc acetate dihydrate specified in **JIS K** 8356 in water to make 100 ml), filtrate the fixed sulfide ion through filter paper, and adjust the pH of the filtrate to about 5.
    - NOTES 5 In the case of an ion densitometer, use chloride ion reference solution (Cl<sup>-</sup> 10 mg/L) and chloride ion reference solution (Cl<sup>-</sup> 1000 mg/L), carry out the procedures in c) 2) and 3), and adjust the reading on the ion densitometer to Cl<sup>-</sup> 10 mg/L and Cl<sup>-</sup> 1000 mg/L. Furthermore, confirm the reading on the ion densitometer using chloride ion reference solution (Cl<sup>-</sup> 5 mg/L) and chloride ion reference solution (Cl<sup>-</sup> 100 mg/L).

6 The permissible limits of main coexisting materials are shown by the maximum ratio as follows:

7 Potentiometric titration by chloride ion-selective electrode Place 100 ml of sample in a beaker, adjust its pH to about 7. Using a chloride ion-selective electrode or silver ion-selective electrode, titrate the sample with 10 mmol/L to 100 mmol/L silver nitrate solution while measuring the electric potential according to the procedures in c )2) to 4), and draw the titration curve to find an end point. When the halide ion is coexistent, the inflection point shown on titration curve makes the order of iodide ion, bromide ion, and chloride ion. Obtain an end point from each inflection point, and calculate the concentration of each ion. One milliliter of 10 mmol/L silver nitrate solution is equivalent to 1.269 mg of iodide ion, 0.799 mg of bromide ion, and **0.354** 5 mg of chloride ion.

**35.3** Ion chromatography Chloride ion in sample shall be determined by ion chromatography. Fluoride ion, nitrite ion, nitrate ion, phosphate ion, bromide ion and sulfate ion can be also determined simultaneously or singly according to this method. However, for determination of nitrite ion, nitrate ion, phosphate ion or bromide ion, the test is immediately carried out without performing the preservation treatment in **3.3.** When the test can not be carried out immediately, the sample shall be preserved in a dark place maintained at 0 "C to 10 "C and tested as quickly as possible.

The accuracy and precision of measurement differ generally depending on the type of ion by the influence of sample matrix. For the confirmation of this, it is recommended that the reference solution be added and the recovery measured.

Anion		With suppressor mg/L	Without suppressor mg/L
Chloride	$(Cl^{-})$	0.1 Lo 25	0.5 to 25
Fluoride	( <b>F</b> <sup>-</sup> )	0.05 to 20	0.1 to 20
Nitrous acid	$(NO_2^-)$	0.1 to 25	0.5 to 25
Nitric acid	(NO <sub>3</sub> <sup>-</sup> )	0.1 Io 50	0.5 to 50
Phosphoricacid	$(PO_4^{3-})$	0.1 to 50	0.5 to 50
Bromide	(Br <sup>-</sup> )	0.1 Lo 50	0.5 to 50
Sulfuric acid	$(\mathrm{SO_4}^{2^-})$	0.2 Lo 100	1 to 100

Table 35.1Example of determination range of anion according to<br/>ion chromatography

NOTE : The measurement range differs depending on the detector, quantity of sample poured, exchange capacity of column and so on.

a) **Reagents** The following reagents shall be used:

- 1) Water, of A2 or A3 specified in JIS K 0557.
- 2) Eluent Eluent<sup>(16)</sup> differs according to the type of apparatus and the type of anion-exchanger packed in a separation column. Therefore the eluent capable of separating each of fluoride ion, chloride ion, nitrite ion, nitrate ion, phosphate ion, bromide ion and sulfate ion with resolution **1.3** or more is used. The verification of resolution shall be in accordance with NOTE 8.

It is recommended that the eluent be deaerated or prepared by using the deaerated water. The countermeasure shall be taken so as to prevent the eluent from the dissolution of new gas during operation.

- **3) Reclaiming solution** The reclaiming solution<sup>(17)</sup> is used when suppressor is used; it differs according to the type of apparatus and suppressor used. Therefore, combine it with the separation column in advance, and carry out the operation in NOTE 8 to verify the performance of reclaiming solution.
- 4) Chloride ion reference solution (Cl<sup>-</sup> 1 mg/ml), in accordance with 35.2 a)
  2).
- 5) Chloride ion reference solution (Cl<sup>-</sup> 0.1 mg/ml) Place 10 ml of chloride ion reference solution (Cl<sup>-</sup> 1 mg/ml) in a 100-ml volumetric flask, and add water to the mark.
- 6) Fluoride ion reference solution (F<sup>-</sup> 1 mg/ml) Place sodium fluoride of the reference solution for volumetric analysis specified in JIS K 8005 in platinum dish, heat at 500 "C for approximately 1h and allow to cool in a desiccator. Weigh out 2.210 g of this to NaF 100 %, dissolve in a small amount of water, transfer to a 1000-ml volumetric flask and add water to the mark. Pour it into a polyethylene bottle to preserve.
- 7) Fluoride ion reference solution ( $\mathbf{F}^- 0.01 \text{ mg/ml}$ ) Place 1 ml of fluoride ion reference solution ( $\mathbf{F}^- 1 \text{ mg/ml}$ ) in a 100-ml volumetric flask and add water to the mark.
- 8) Nitrite ion reference solution (NO<sub>2</sub><sup>-</sup> 1 mg/ml) Heat sodium nitrite specified in JIS K 8019 at 105 "C to 110 °C for approximately 4 h, allow to cool in a desiccator, and then obtain the purity of sodium nitrite(<sup>18</sup>). Take sodium nitrite equivalent to 1.500 g to NaNO<sub>2</sub> 100%, dissolve in a small amount of water, transfer to a 1000-ml volumetric flask and add water to the mark. Prepare this solution immediately before use.
- 9) Nitrite ion reference solution (NO<sub>2</sub><sup>-</sup> 0.1 mg/ml) Place 10 ml of nitrite ion reference solution (NO<sub>2</sub><sup>-</sup> 1 mg/ml) in a 100-ml volumetric flask and add water to the mark. Prepare this solution immediately before use.
- 10) Nitrate ion reference solution (NO<sub>3</sub><sup>-</sup> 1 mg/ml) Heat potassium nitrate specified in JIS K 8548 at 105 °C±2 °C for about 2 h and allow to cool in a desiccator. Take 1.631g of this, dissolve in small amount of water, and after transferring to a 1000-ml volumetric flask, add water to the mark. Store in a dark place at 0 "C to 10 °C.
- 11) Nitrate ion reference solution (NO<sub>3</sub><sup>-</sup> 0.1 mg/ml) Place 10 ml of nitrate ion reference solution (NO<sub>3</sub><sup>-</sup> 1 mg/ml) in a 100-ml volumetric flask and add water to the mark. Prepare this solution immediately before use.

- 12) Phosphate ion reference solution ( $PO_4^{3-} 1 mg/ml$ ) Heat potassium dihydrogenphosphate specified in JIS K 9007 (for pH reference solution) at  $105 \degree C \pm 2$  "C for about 2 h and allow to cool in a desiccator. Take 1.433 g of this, dissolve in water, and after transferring to a 1000-ml volumetric flask, add water to the mark. Store this solution in a dark place at 0 "C to 10 "C.
- 13) **Phosphate ion reference solution** ( $\mathbf{PO_4^{3^-} 0.1 \text{ mg/ml}}$ ) Place 10 ml of phosphate ion reference solution ( $\mathbf{PO_4^{3^-} 1 mg/ml}$ ) in a 100-ml volumetric flask, and add water to the mark.
- 14) Bromide ion reference solution (Br<sup>-</sup> 1 mg/ml) Heat potassium bromide specified in JIS K 8506 at 105 °C for about 4 h and allow to cool in a desiccator. Take 1.489 g of this (1.00 g as bromide), dissolve in small amount of water, and after transferring to a 1000-ml volumetric flask, add water to the mark.
- 15) **Bromide ion reference solution** (**Br**<sup>-</sup> **0.1 mg/ml**) Place 10 ml of bromide ion reference solution (**Br**<sup>-</sup> 1mg/ml) in a 100-ml volumetric flask and add water to the mark. Prepare this solution immediately before use.
- 16) Sulfate ion reference solution  $(SO_4^2 \ 1 \ mg/ml)$  Heat potassium sulfate specified in JIS K 8962 at approximately 700 °C for about 30 min, and allow to cool in a desiccator. Take 1.815 g of this, dissolve in small amount of water, and after transferring to a 1000-ml volumetric flask, add water to the mark.
- 17) Sulfate ion reference solution  $(SO_4^{2^-} 0.1 \text{ mg/ml})$  Place 10 ml of sulfate ion reference solution  $(SO_4^{2^-} 1 \text{ mg/ml})$  in a 100-ml volumetric flask and add water to the mark. Prepare this solution immediately before use.
  - Notes (<sup>16</sup>) When an ultraviolet absorption detector is to be used, the eluent shall be without absorption in ultraviolet part. If the detector is equipped with a suppressor, the eluent of carbonate base may be also used.
    - (<sup>17</sup>) For example, sulfuric acid (12.5 mmol/L) [prepared by making 25 ml of sulfuric acid (0.5 mmol/L) (prepared by adding 30 ml of sulfuric acid specified in **JIS K 8951** little by little to 500 ml of water, cooling, and then making 1L with water) 1 L with water] is used.
    - (<sup>18</sup>) The purity shall be obtained in accordance with **JIS K** 8019.
- b) **Implement and apparatus** The implement and apparatus to be used shall be as follows:
  - 1) **Ion chromatograph,** of either the type combining a separation column with a suppressor<sup>(19)</sup> or the type consisting only of a separation column, which satisfies the following conditions and is capable of separating and determining fluoride ion, chloride ion, nitrite ion, nitrate ion, phosphate ion, bromide ion, and sulfate ion.
  - 1.1) **Separation column,** made of stainless steel or synthetic resin<sup>(20)</sup>, and packed with strongly basic anion exchanger (surface coated type or totally porous silica type)<sup>(21)</sup>.

- 1.2) **Detector** Electric conductivity detector or ultraviolet absorption detector. However, the ultraviolet absorption detector is used for the individual or simultaneous measurement of nitrite ion, nitrate ion and bromide ion.
- 1.3) Recorder, in accordance with JIS K 0127.
- 2) **Microsyringe,** of a suitable capacity of  $50 \,\mu$ l to  $200 \,\mu$ l, or an automatic injecting device.
  - Notes (<sup>19</sup>) This is for exchanging cation in eluent for hydrogen ion, and is the cation exchange membrane (including both membrane type and electrodialysis type) having ion-exchange capability sufficient for the cation concentration in eluent or is packed with cation-exchanger which has the similar performance to this. For the electrodialysis type, use an effluent from the detector (a solution discharged from the detector) as the reclaiming solution.
    - (<sup>20</sup>) For instance, made of ethylene tetrafluoride resin, polyetheretherketone, etc.
    - (<sup>21</sup>) See NOTE 8.
  - NOTE 8 The performance of ion chromatograph shall be such that the resolution (R) is 1.3 or more. It is recommended to verify it periodically. For obtaining the resolution, let flow the eluent at a definite flow rate (for example, 1ml/min to 2 ml/min), prepare the anion mixed solution with the concentration of which the peak height of chromatogram becomes approximately the same degree, and prepare the chromatogram to calculate the resolution according to the following formula:

$$R = \frac{2 \times (t_{R2} - t_{R1})}{W_1 + W_2}$$

where,  $t_{R1}$ : retention time of the first peak (s)

- $t_{R2}$ : retention time of the second peak (s)
- $W_1$ : peak width of the first peak (s)
- $W_2$ : peak width of the second peak (s)
- cj **Preparatory operation** The preparatory operation shall be carried out as follows:
  - 1) Filtrate the sample in accordance with **3.2**.
  - 2) When the sample has electric conductivity of  $10 \text{ mS/m} (100 \mu\text{S/cm}) (25 \text{ °C})$  or more, dilute it with water at a decided ratio to make its conductivity not more than 10 mS/m.
- d) **Operation** The operation shall be carried out as follows:
  - $1_j$  Get an ion chromatograph ready for running, and flow the eluent in a separation column at a specified rate (for instance, 1 ml/min to 2 ml/min). In the case of an apparatus equipped with a suppressor, flow the reclaiming solution at a specified rate.

- 2) Inject a specified amount (for instance, 50  $\mu$ l to 200  $\mu$ l) of the sample pretreated at **c**) using a microsyringe<sup>(22)</sup> into the ion chromatograph and record chromatogram.
- 3) Note the reading('') of the peak(<sup>23</sup>) corresponding to each target ion on the chromatogram.
- 4) In the case of diluting the sample, for a blank test, take the same amount of water as that of the sample, carry out the procedures in 1) to 4) and correct the reading<sup>(24)</sup> obtained on the sample.
- 5) Find the amount of each target ion on the working curve, and calculate the concentration of each target ion (mg/L) in the sample.
  - Notes (<sup>22</sup>) The same microsyringe as used in preparation of working curve shall be used.
    - (<sup>23</sup>) The chromatogram is recorded by using a definite amount (50µl to 200 µl) of anion mixed reference solution [for example, ( $F^- 5 \mu g$ ,  $Cl^- 10 \mu g$ ,  $NO_2^- 10 \mu g$ ,  $NO_3^- 10 \mu g$ , POP-  $10 \mu g$ ,  $Br^- 10 \mu g$  and  $SO_4^{2-} 10 \mu g$ )/ml] and the position of peak corresponding to the retention time of each ion are confirmed beforehand.
    - <sup>(24)</sup> Peak height or peak area.
- e) Working curve The working curve shall be prepared as follows:
  - 1) Take an adequate quantity of each of **a**) **4**) to **17**) and prepare the mixed diluted reference solution containing the measurement target ion and having a concentration higher than the measurement concentration range( $^{25}$ ).
  - 2) Dilute this mixed diluted reference solution in four to five steps and prepare the mixed diluted reference solution for preparing the working curve.
  - 3) Carry out the operation of d) 1) to 4) on the mixed diluted reference solution for preparing each working curve, and note  $(^{26})$  the reading  $(^{24})$  of the peak corresponding to each ion.
  - 4) Separately, for a blank test, carry out the procedures of d) 1) to 4) on water, and correct the reading values corresponding to each ion. Then, for respective ions, plot the concentration on the abscissa and the reading value on the ordinate to prepare the relation curve<sup>(27)</sup>.
    - Notes (<sup>25</sup>) In the case of the measurement of single ion or the measurement of only limited multiple ions, it is recommended that the necessary mixed reference solution and the mixed reference solution containing necessary anion are prepared.
      - (<sup>26</sup>) Example of allowable rate of respective interfering ions in each ion is shown in table *35.2*.
      - (<sup>27</sup>) The working curve does not necessarily indicate the linear relation depending on the composition of eluent and the type of measurement target ion.

## NOTES 9 Interference substance

- a) The organic acid such as monocarboxylic acid and dicarboxylic acid can interfere with the determination of inorganic anion.
- b) When the buffering eluent (for example, carbonate/hydrogen carbonate) is used, the determination is not influenced when the pH of sample is in the range from 2 to 9.
- c) When there is a great difference in concentrations between the anions (fluoride ion, chloride ion, nitrite ion, nitrate ion, phosphate ion, bromide ion and sulfate ion), the typical crossing sensitivity interference due to incomplete separation can be caused. The determination of chloride ion, when the concentration of fluoride ion is high, is susceptible to interference.

## d) Influence of coexisting ion on each ion

- 1) When the concentration of chloride ion is 1mg/L, nitrite ion of up to 200 mg/L will not interfere.
- 2) When the concentration of nitrite ion is 1 mg/L, chloride ion of up to 50 mg/L, bromide ion of up to 200 mg/L and sulfate ion of up to 500 mg/L will not interfere.
- 3) When the concentration of nitrate ion is 1mg/L, bromide ion of up to 200 mg/L and sulfate ion of up to 500 mg/L will not interfere.
- 4) When the concentration of bromide ion is 1mg/L, nitrite ion of up to 200 mg/L will not interfere.
- 5) When the concentration of sulfate ion is 1 mg/L, bromide ion of up to 200 mg/L and nitrate ion of up to 400 mg/L will not interfere.
- e) The determination of sulfate ion can be easily affected by interference of iodide ion or thiosulfate ion of high concentration.
- f) Sulfide ion, which can cause the determination error of sulfate ion, should be separated through filtering after adding zinc acetate solution and precipitating.
- 10 The performance of a separation column can deteriorate after successive use and should be checked periodically according to the procedure in NOTE S.

If the column performance is found to have deteriorated, prepare a solution of a concentration about 10 times that of the eluent and inject it into the separation column for washing. Check the performance according to NOTE 8, and if the performance has not recovered, replace the column with a new one.

Because suspensoid or organic substances (such as protein, oils, surface active agents) in sample gradually lower the performance by contamination, if the sample contains suspensoid, eliminate it according to the preparatory operation stated in  $\mathbf{c}$ ) prior to test.

In the case of the sample containing organic substances, filtrate it through an ultrafilter membrane to remove organic substances as completely as possible prior to test.

If the sample contains anions (such as iodide ion, chromate ion) which have strong affinity with the packing material in a separation column, because they lower the separative performance gradually by adsorbing onto the packing material, prepare a solution of a concentration 5 times to 10 times that of the eluent, and inject it into the separation column, similarly to the case of sample, so as to wash it.

Additionally, if the oxidizing substance or reducing substance is coexistent, the separative performance of a separation column lowers. In this case, the dilution of the sample with water at a definite rate is expected to prevent some of the adverse influence on the sample.

- 11 When the concentrations of nitrite ion, nitrate ion, and phosphate ion are expressed by nitrite nitrogen, nitrate nitrogen and phosphate phosphorus, the following conversion formula shall be used:
  - a) Nitrite nitrogen (NOT-N mg/L) = Nitrite ion (NO<sub>2</sub><sup>-</sup> mg/L) × 0.304 5
  - b) Nitrate nitrogen (NO<sub>3</sub><sup>-</sup>-N mg/L) = Nitrate ion (NO<sub>3</sub><sup>-</sup> mg/L) x 0.225 9
  - c) Phosphate phosphorus (PO<sub>4</sub><sup>3-</sup>-P mg/L) = Phosphate ion (PO<sub>4</sub><sup>3-</sup> mg/L) × 0.326 1

<b>Table 35.2</b>	Example of	cross-sensitivity	of anion
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[Detection: Electric conductivity (CD) and direct ultraviolet absorption]

Mass concentration ratio Solute/interfering ion			Maximum allowable concentration of	
			mg/L	101
Br <sup>-</sup> /C1 <sup>-</sup>	1.	500		500
$Br^{-}/PO_{4}^{3-}$	1. 1.	100		100
$Br^{-}/NO_{2}^{-}$	1:	50	NO <sub>2</sub> <sup></sup>	100
$Br^{-}/SO_4^{2-}$	1:	500	SO42-	500
$Br^{-}/SO_3^{2-}$	1:	50		
Cl <sup>-</sup> /NO <sub>2</sub> <sup>-</sup>	1:	50	NO <sub>2</sub> <sup>-</sup>	5
Cl <sup>-</sup> /NO <sub>3</sub> <sup>-</sup>	1:	500	NO <sub>3</sub> <sup>-</sup>	500
$Cl^{-}/SO_4^{2-}$	1:	500	SO42-	500
NO <sub>3</sub> <sup>-</sup> /Br <sup>-</sup>	1:	100	Br <sup>-</sup>	100
NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup>	1:	500 (CD)	Cl-	500
	1:	2000 (UV)	CI-	500
$NO_{3} - /SO_{4}^{2-}$	1:	500 (CD)	SO4 <sup>2-</sup>	500
	1:	1000 (UV)	SO4 <sup>2-</sup>	500
$NO_3 - /SO_3^{2-}$	1:	50		
$NO_2^-/Cl^-$	1:	250 (CD)	C1 <sup>-</sup> (CD)	100
	1:	10000 (UV)	Cl <sup></sup> (UV)	500
$NO_{2}^{-}/PO_{4}^{3-}$	1:	50	PO <sub>4</sub> <sup>3-</sup>	20
$NO_2^{-}/NO_3^{-}$	1:	500	NO <sub>3</sub> <sup>-</sup>	500
$NO_{2}^{-}/SO_{4}^{2-}$	1:	500 (CD)	SO4 <sup>2-</sup>	500
	1:	1000 (UV)	SO4 <sup>2-</sup>	500
PO <sub>4</sub> <sup>3-</sup> /Br <sup>-</sup>	1:	100	Br <sup>-</sup>	100
PO <sub>4</sub> <sup>3-</sup> /C1 <sup>-</sup>	1:	500	C1 <sup></sup>	500
PO <sub>4</sub> <sup>3-</sup> /NO <sup>3-</sup>	1:	500	NO <sub>3</sub> <sup>-</sup>	400
$PO_4^{3-}/NO^{2-}$	1:	100	$  NO_2^-$	100
PO <sub>4</sub> <sup>3-</sup> /SO <sub>4</sub> <sup>2-</sup>	1:	100	SO4 <sup>2-</sup>	500
PO <sub>4</sub> <sup>3-</sup> /SO <sub>3</sub> <sup>2-</sup>	1:	50 ***		
$  SO_4^{2-}/Cl^-$	1:	500	Cl <sup>-</sup>	500
$SO_4^2 / NO_3^-$	1:	500	NO <sub>3</sub> <sup>-</sup>	400
$SO_4^{2-}/SO_3^{2-}$	1:	50 **		
$  SO_4^{2^-}/S_2O_3^{2^-}$	1:	500		
$  SO_4^{2-}/I^-$	1:	500		

Notes \* When the concentration of interference substance exceeds the limit, the sample is diluted.

\*\*  $SO_3^{2^-}$ , if present, always interferes.

**36 Iodide ion (I-)** For the determination of iodide ion, iodine-extraction absorptiometry or iodometry applies.

**36.1 Iodine-extraction absorptiometry** Make iodide ion react with nitrite ion under sulfuric acidity, extract the isolated iodine with chloroform, and measure its absorbance to determine iodide ion.

Determination range:  $I^- 0.1 \text{ mg to } 5 \text{ mg}$ 

Repeatability: 3% to 10%

- a) **Reagents** The following reagents shall be used:
  - 1) Sulfuric acid (1+1), in accordance with 5.4 a) 2).
  - 2) Sodium nitrite, specified in JIS K 8019.
  - 3) Urea solution (10g/L), prepared by dissolving 1g of urea specified in JIS K 8731 in water to make total 100 ml.
  - 4) Sodium sulfate, specified in JIS K 8987.
  - 5) Chloroform, specified in JIS K 8322.
  - 6) **Iodide ion reference solution** (**I**<sup>-</sup> **1 mg/ml**) Dissolve 1.310 g of potassium iodide specified in **JIS K 8913** in a small amount of water, transfer into a 1000-ml volumetric flask, and add water to the mark.
  - 7) **Iodide ion reference solution** (**I**<sup>-</sup> **0.1 mg/ml**) Place 20 ml of iodide ion reference solution (I- 1mg/ml) in a 200-ml volumetric flask, and add water to the mark. Prepare this solution immediately before use.
- b) **Implement and apparatus** The implement and apparatus to be used shall be as follows:
  - 1) Separatory funnel, of capacity 100 ml.
  - 2) **Photometer** Spectrophotometer or photoelectric photometer
- c) **Operation** The operation shall be carried out as follows:
  - 1) Place a suitable amount(')(<sup>2</sup>) (containing 0.1 mg to 5 mg as  $I^{-}$ ) of sample in a 100-ml separatory funnel, and add water to make total about 50 ml.
  - 2) Add 1ml of sulfuric acid (1+1)[if sample is alkaline, neutralize it by adding sulfuric acid (1+1)] and 0.5 g of sodium nitrite, and agitate.
  - 3) Add 10 ml of chloroform, and after agitating vigorously for about 2 min, allow to stand.
  - **4)** Transfer the chloroform layer into another 100-ml separatory funnel. Again add 10 ml of chloroform to the water layer to extract, and join this chloroform layer to the above chloroform layer.
  - 5) Add 50 ml of urea solution (10g/L) to the separatory funnel holding the chloroform, and agitate vigorously for about 2 min to wash the chloroform layer.
  - 6) After about 5-min of standing, transfer the chloroform layer into a 50-ml Erlenmeyer flask with ground stopper containing about 1g of sodium sulfate, and agitate for dehydration.

- 7) Place a part of the chloroform layer into an absorption cell, and measure its absorbance at a wavelength near 515 nm making chloroform a reference solution.
- 8) For a blank test, using 50 ml of water, carry out the procedures in 2) to 7), and correct the absorbance measured about the sample.
- 9) Find the amount of iodide ion on the working curve, and calculate the concentration of iodide ion (I<sup>-</sup> mg/L) in the sample.
  - Notes (1) When the concentration of iodide ion is 2 mg/L or less, take a suitable amount of sample, make it alkaline by adding sodium hydroxide solution (200 g/L) (prepared by dissolving 20 g of sodium hydroxide specified in **JIS K 8576** in water to make 100 ml), and heat gently to concentrate. If turbidity takes place while concentrating, filtrate it, and carry out the procedures in and after 1).
    - (<sup>2</sup>) When a lot of organic matter coexists, take 200 ml of sample, add 2 ml or 3 ml of aluminium potassium sulfate solution (prepared by dissolving 5 g of aluminium potassium sulfate-12 water specified in **JIS K 8255** in water to make total 100 ml), and then add sodium hydroxide solution (50 g/L) (prepared by dissolving 5 g of sodium hydroxide specified in **JIS K 8576** in water to make 100 ml) until precipitate of aluminium hydroxide generates. After about 5-min standing, filtrate it, and taking a suitable amount of this filtrate, carry out the procedures in and after 1).
- d) Working curve The working curve shall be prepared as follows:
  - 1) Place several aliquots, increased stepwise from 1 ml to 50 ml, of iodide ion reference solution ( $I^- 0.1 \text{ mg/ml}$ ) in as many 100-ml separatory funnels.
  - 2) Carry out the procedures in c) 1) to 8), measure their absorbances, and plot the relation curve between the amount of iodide ion (I-) and the absorbance.
    - NOTE 1 If iodate ion is included, when sample is acidified by sulfuric acid, it turns into iodine owing to its reaction with iodide ion, therefore, the whole or a part of iodate ion is determined as iodide ion. Bromide ion causes no interference.

**36.2 Iodometry** Oxidize iodide ion by hypochlorous acid under the pH 1.3 to 2.0 into iodate ion. Decompose excess hypochlorous acid by sodium formate under the pH 3 to 7, add potassium iodide, titrate isolated iodine with sodium thiosulfate solution, and thus determine iodide ion.

Determination range: I<sup>-</sup> 0.1 mg or more

- a) **Reagents** The following reagents shall be used:
  - 1) Hydrochloric acid (1+1), prepared using the hydrochloric acid specified in JIS K 8180.
  - 2) Hydrochloric acid (1+11), prepared using the hydrochloric acid specified in JIS K 8180.