- 1) Perform the procedure in **52.3 d**) **1**), except that the atomization (⁷) temperature shall be 2 200 °C to 3 000 °C, and the wavelength used shall be 309.3 nm.
- 2) Perform the procedure in 52.3 d) 2) as a blank test.
- 3) Determine the amount of aluminium by reference to the working curve and calculate the concentration of aluminium (Al μ g/L) in the sample.

Note $(^{7})$ See Note $(^{9})$ to clause **52**.

- e) **Working curve** The working curve shall be prepared as follows.
 - 1) Place a series of aliquots in stepwise increment ranging from 2 ml to 20 ml of aluminium reference solution (Al 1 μ g/ml) in as many 100-ml volumetric flasks. Add acid to each of these solutions until the acid concentration is the same as that of the sample treated according to c) 1) and add water to the mark. Perform the procedure in d) 1) using these solutions.
 - 2) Perform the procedures in **52.3** e) 2) and 3) and plot the relation curve between the amount of aluminium (Al) and the reading on the apparatus. Prepare the working curve at the time of measurement of sample.

58.4 ICP atomic emission spectrometry After pretreated, the sample is sprayed into an inductively coupled plasma through the sample introducing part, and the emission made by aluminium is measured at the wavelength of 309.271 nm to determine aluminium. By this method, the elements given in table 58.1 can be simultaneously determined. Table 58.1 gives examples of measuring wavelength, determination range and repeatability of each target element.

Target element	Measuring wavelength nm	Determination range μg/L	Repeatability %
Aluminium (Al)	309.271	80 to 4 000	2 to 10
Chromium (Cr)	206.149	20 to 4 000	2 to 10
Molybdenum (Mo)	202.030	40 to 4 000	2 to 10
Vanadium (V)	309.311	20 to 2 000	2 to 10
Yttrium (Y) **	371.029	_	_

Table 58.1Example of measuring wavelength, determination range
and repeatability *

Notes * The values shown may vary according to the type of apparatus used and measurement conditions applied.

- ** Internal standard element. Besides yttrium (Y) given above, indium (In) and ytterbium (Yb) can also be used.
- a) **Reagents** The following reagents shall be used.
 - 1) Nitric acid (1+1), prepared using nitric acid in JIS K 8541.
 - 2) Aluminium reference solution (Al 20 μg/ml) Place 10 ml of the aluminium reference solution (Al 0.5 mg/ml) in 58.2 a) 2) in a 250-ml volumetric flask, add 5 ml of nitric acid (1+1), and add water to the mark.

- 3) Chromium reference solution (Cr 0.1 mg/ml) Heat potassium dichromate of reference material for volumetric analysis specified in JIS K 8005 at 150 °C for about 1 h, and allow to cool in a desiccator. Take 0.283 g of $K_2Cr_2O_7$ (100%) and dissolve in a small volume of water. Transfer into a 1 000-ml volumetric flask, and add water to the mark.
- 4) **Chromium reference solution (Cr 10 μg/ml)** Place 50 ml of the chromium reference solution (Cr 0.1 mg/ml) in a 500-ml volumetric flask, and after adding 10 ml of nitric acid (1+1), add water to the mark.
- 5) **Molybdenum reference solution (Mo 0.1 mg/ml)** Dissolve 0.184 g of the hexaammonium heptamolybdate tetrahydrate specified in **JIS K 8905** in a small volume of water. Transfer into a 1 000-ml volumetric flask, and add water to the mark.
- 6) **Molybdenum reference solution (Mo 20 μg/ml)** Place 20 ml of the molybdenum reference solution (Mo 0.1 mg/ml) in a 100-ml volumetric flask and add water to the mark.
- 7) Vanadium reference solution (V 0.1 mg/ml) Take 0.230 g of ammonium vanadate (V) specified in JIS K 8747 and dissolve in 10 ml of sulfuric acid (1+1) [specified in 5.4 a) 2)] and 200 ml of hot water. After allowing to cool, transfer into a 1 000-ml volumetric flask and add water to the mark.
- 8) **Vanadium reference solution (V 10 \mug/ml)** Place 10 ml of the vanadium reference solution (V 0.1 mg/ml) in a 100-ml volumetric flask, add 2 ml of nitric acid (1+1), and add water to the mark.
- b) Apparatus, as specified in **52.4** b).
- c) **Preparatory operation** The preparatory operation shall be carried out as follows.
 - 1) Treat the sample as shown in **5.5**. However, the method in **5.3** shall not be applied for determination of chromium.
 - NOTE 8 When the pretreated sample has high concentration of alkali metal ion, alkaline earth metal ion, etc., but has low concentration of aluminium, perform determination as follows: using 100 ml of the sample, perform the procedures given in **58.1 c**) **1**) to **5**) replacing chloroform with 3-methyl-1-butanol (isoamyl alcohol) specified in **JIS K 8051**, and transfer the 3-methy-1-butanol layer into a test tube with a ground stopper. In this case, the procedure of removing moisture content through addition of sodium sulfate given in **58.1 c**) **6**) may be omitted.
- d) **Procedure** The test procedure shall be as specified in **52.4** d). The emission intensity of each of the metal elements at the wavelengths shown in table 58.1 shall be measured.
- e) Working curve See 52.4 e) $(^8)$.
 - Note (8) When the preparatory operation is carried out according to NOTE 8, and 3-methyl-1-butanol layer is sprayed as it is, the preparation of working curve shall be as follows.

Dilute the aluminium reference solution (Al 20 μ g/ml) to an adequate concentration (Al 1 μ g/ml to 4 μ g/ml). Place a series of aliquots of this solution in stepwise increment in as many 100-ml volumetric flasks, and after making 100 ml with water, carry out the procedures given in NOTE 8 and **52.4 d**) **1**) and **2**) similarly to the sample. Prepare the relation curve between the amount of aluminium (Al) and the emission intensity.

58.5 ICP mass spectrometry See 52.5.

59 Nickel (Ni) For the determination of nickel, the dimethylglyoxime absorptiometry, flame atomic absorption spectrometry, ICP atomic emission spectrometry or ICP mass spectrometry is applied.

The flame atomic absorption spectrometry and the ICP atomic emission spectrometry described in this clause are in consistency with the first edition of **ISO 8288** published in 1986, and the first edition of **ISO 11885** published in 1996, respectively.

NOTE : The corresponding International Standards relevant to these test methods are as follows.

The symbols which denote the degree of correspondence in the contents between the relevant International Standards and **JIS** are IDT (identical), MOD (modified), and NEQ (not equivalent) according to **ISO/IEC Guide 21-1**.

ISO 8288:1986 Water quality—Determination of cobalt, nickel, copper, zinc, cadmium and lead—Flame atomic absorption spectrometric methods (MOD)

ISO 11885:1996 Water quality—Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy (MOD)

59.1 Dimethylglyoxime absorptiometry Citrate is added to the sample, and after the sample is made faint alkaline with ammonia solution, 2,3-butanedionedioxime (dimethylglyoxime) is added to produce nickel complex. The produced nickel complex is extracted with chloroform, followed by back-extraction with diluted hydrochloric acid. To the obtained extraction solution, bromine and ammonia solution is added to oxidize nickel, and after 2,3-butanedionedioxime is added again, the absorbance of the generated reddish brown nickel complex is measured to determine nickel.

Determination range: Ni 2 μ g to 50 μ g

Repeatability: 2 % to 10 %

- a) **Reagents** The following reagents shall be used.
 - Hydrochloric acid (1+20), prepared using the hydrochloric acid specified in JIS K 8180.
 - 2) Ammonia solution (1+1) and (1+5), prepared using the ammonia solution specified in JIS K 8085.
 - 3) **Bromine water (saturated)** Add 3 ml to 4 ml of bromine specified in **JIS K 8529** to 100 ml of water, shake vigorously to mix, and after allowing to stand, employ its supernatant.
 - 4) **Diammonium hydrogen citrate solution (100 g/L)** Dissolve 10 g of diammonium hydrogen citrate specified in **JIS K 8284** in about 80 ml of water, adjust the pH to about 7 by adding dropwise the ammonia solution (1+1), and add water to make 100 ml.
 - 5) Phenolphthalein solution (5 g/L), in accordance with NOTE 2 to clause 15.
 - 6) Ethanol solution of dimethylglyoxime (10 g/L) Dissolve 1 g of dimethylglyoxime specified in JIS K 8498 in ethanol (95) specified in JIS K 8102 to make 100 ml.

- 7) Sodium hydroxide solution of dimethylglyoxime (10 g/L) Dissolve 1 g of dimethylglyoxime specified in **JIS K 8498** in the sodium hydroxide solution (10 g/L) (prepared by using sodium hydroxide specified in **JIS K 8576**) and add the sodium hydroxide solution (10 g/L) to make 100 ml. If undissolved matter is found, filtrate it.
- 8) Chloroform, as specified in JIS K 8322.
- 9) Nickel reference solution (Ni 0.1 mg/ml), in accordance with 52.4 a) 14).
- 10) Nickel reference solution (Ni 5 μg/ml) Place 50 ml of the nickel reference solution (Ni 0.1 mg/ml) in a 1 000-ml volumetric flask, add 20 ml of nitric acid (1+1) [specified in 58.4 a) 1)] and add water to the mark.
- b) **Implement and apparatus** The following implement and apparatus shall be used.
 - 1) Separatory funnel
 - 2) **Photometer** Spectrophotometer or photoelectric photometer
- c) $\ensuremath{\,{\rm Procedure}}$ The test procedure shall be as follows.
 - 1) Place a suitable volume $(^1)$ (containing 2 µg to 50 µg as Ni) of the sample which has been pretreated according to clause **5** in a separatory funnel, and add 5 ml of the diammonium hydrogen citrate solution (100 g/L) and two or three drops of the phenolphthalein solution (5 g/L) $(^2)$ as an indicator. Then add dropwise the ammonia solution (1+5) until the solution turns faint red, and add two or three more drops of the ammonia solution (1+5) and water to make about 100 ml.
 - 2) Add 2 ml of the ethanol solution of dimethylglyoxime (10 g/L) and 10 ml of chloroform, and after shaking vigorously for about 1 min and allowing to stand, transfer the chloroform layer into another separatory funnel. Add 5 ml of chloroform to the water layer, shake vigorously for about 1 min to extract, and after allowing to stand, take the chloroform layer, and join it to the above separatory funnel. Repeat this procedure once.
 - 3) Add 10 ml to 20 ml of the ammonia solution (1+50) (prepared using ammonia solution specified in **JIS K 8085**) to the separatory funnel containing the chloroform layer, shake for about 30 s, and after allowing to stand, transfer the chloroform layer to another separatory funnel.
 - Add 10 ml of hydrochloric acid (1+20) to the separatory funnel containing the chloroform layer, shake vigorously for about 1 min, and back-extract nickel. After allowing to stand, transfer the chloroform layer into another separatory funnel. Add again 5 ml of hydrochloric acid (1+20) to the chloroform layer, and repeat back-extraction. Discard the chloroform layer, join this water layer to the above water layer, and transfer it into a 25-ml volumetric flask.
 - 5) Add 2 ml of bromine water (saturated), shake to mix, and allow to stand for about 1 min. Then neutralize it by adding the ammonia solution (1+1), and after adding excess 2 ml of the ammonia solution (1+1), cool it to room temperature or lower using running water.

- 6) Add 2 ml of the sodium hydroxide solution of dimethylglyoxime (10 g/L), shake to mix until nickel develops color, and add water to the mark.
- 7) Transfer a part of this solution into an absorption cell, and measure its absorbance near the wavelength of 450 nm.
- 8) For a blank test, using about 50 ml of water, carry out the procedures in 1) to 7) to measure its absorbance, and correct the measured absorbance of the sample.
- 9) Determine the amount of nickel by reference to the working curve, and calculate the concentration of nickel (Ni μ g/L) in the sample.
 - Notes (¹) In the case of samples containing no organic matter or turbidity, of which the nickel concentration is low, carry out the procedure in **5.1** using a suitable volume, up to 500 ml, of the sample, and then determine nickel according to **1**) to **8**). In this case, use the whole volume of sample which has been pretreated, and employ the same volume of reagents as that used in **1**) to **6**). Prepare the working curve according to the procedure similar to that of the sample.
 - (²) Litmus test paper may be used.
- d) **Working curve** The working curve shall be prepared as follows.
 - 1) Place a series of aliquots in stepwise increment ranging from 0.4 ml to 10 ml of the nickel reference solution (Ni 5 μ g/ml) in as many 25-ml volumetric flasks. Perform the procedures in c) 5) to 8) and plot the relation curve between the amount of nickel (Ni) and the absorbance.

59.2 Flame atomic absorption spectrometry After pretreated, the sample is sprayed into an acetylene-air flame, and the atomic absorption made by nickel is measured at the wavelength of 232.0 nm to determine nickel.

Determination range: Ni 0.3 mg/L to 6 mg/L

Repeatability: 2% to 10% (subject to variation depending on the type of apparatus used and the measuring conditions applied)

- a) **Reagent** The following reagent shall be used.
 - 1) Nickel reference solution (Ni 10 μ g/ml), in accordance with 52.4 a) 15).
- b) Apparatus, as specified in 52.2 b).
- c) **Preparatory operation** The preparatory operation shall be carried out as follows.
 - 1) Treat sample as shown in clause **5**.
 - NOTE 1 In the case of a sample containing low nickel concentration and no substance interfering with extraction, perform the preparatory operation according to the procedure given in NOTE 4, NOTE 5 or NOTE 6 to clause **52**. Alternatively, the sample may be treated with the following procedure to determine nickel.

Place 100 ml of the sample in a beaker, add 5 ml of hydrochloric acid specified in **JIS K 8180**, boil for about 5 min, and allow to cool. Carry out the procedures in **59.1 c**) **1**) to **3**), turn nickel into dimethylglyoxime complex, and extract it in chloroform layer. Put together the chloroform layers, add 10 ml of hydrochloric acid (1+20) [as specified in **59.1 a**) **1**)], and shake to back-extract nickel. Separate the water layer, and add 5 ml of hydrochloric acid (1+20) to the chloroform layer to make backextraction again. Put together all the back-extracted solutions, transfer it to a 25-ml volumetric flask, and add water to the mark.

- d) **Procedure** The test procedure shall be as follows.
 - 1) Perform the procedure in **52.2** d) 1), except that the wavelength used shall be 232.0 nm.
 - 2) For a blank test, perform the procedure in **52.2 d**) **2**).
 - 3) Determine the amount of nickel by reference to the working curve, and calculate the concentration of nickel (Ni mg/L) in the sample.
- e) **Working curve** The working curve shall be prepared as follows.
 - 1) Place a series of aliquots in stepwise increment ranging from 3 ml to 60 ml $(^3)$ of the nickel reference solution (Ni 10 µg/ml) in as many 100-ml volumetric flasks. Add acid to each of these solutions until the acid concentration is the same as that of the sample treated according to **c**) **1**) and add water to the mark.
 - 2) Perform the procedures in **52.2** e) 2) and 3), and plot the relation curve between the amount of nickel (Ni) and the reading on the apparatus. Prepare the working curve at the time of measurement of the sample.
 - Note (³) When a solvent extraction method is adopted as the preparatory operation, suitably reduce the volume of nickel reference solution.

59.3 ICP atomic emission spectrometry See 52.4.

59.4 ICP mass spectrometry See 52.5.

60 Cobalt (Co) For the determination of cobalt, the nitroso R salt absorptiometry, flame atomic absorption spectrometry, ICP atomic emission spectrometry or ICP mass spectrometry is applied.

The flame atomic absorption spectrometry and the ICP atomic emission spectrometry described in this clause are in consistency with the first edition of **ISO 8288** published in 1986, and the first edition of **ISO 11885** published in 1996, respectively.

NOTE : The corresponding International Standards relevant to these test methods are as follows.

The symbols which denote the degree of correspondence in the contents between the relevant International Standards and **JIS** are IDT (identical), MOD (modified), and NEQ (not equivalent) according to **ISO/IEC Guide 21-1**.

ISO 8288:1986 Water quality—Determination of cobalt, nickel, copper, zinc, cadmium and lead—Flame atomic absorption spectrometric methods (MOD)

ISO 11885:1996 Water quality—Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy (MOD)

60.1 Nitroso R salt absorptiometry Citrate is added to the sample, and after the sample is made faint alkaline with ammonia solution, diethyldithiocarbamic acid sodium (diethylcarbamodithio acid sodium salt) is added to it to produce cobalt complex, which is then extracted with butyl acetate. The butyl acetate layer is evaporated to dryness, and the obtained residue is decomposed with nitric acid and sulfuric acid. This is dissolved in water, the pH is adjusted to 6 with sodium acetate, and nitroso R salt (3-hydroxy-4-nitroso-2,7-naphthalenedisulfonic acid disodium salt) is added to generate cobalt complex. The absorbance of the generated cobalt complex is measured to determine cobalt.

Determination range: Co 1 µg to 30 µg

Repeatability: 2% to 10%

- a) **Reagents** The following reagents shall be used.
 - 1) Nitric acid, specified in JIS K 8541.
 - 2) Sulfuric acid (1+1), in accordance with 5.4 a) 2).
 - Ammonia solution (1+1), prepared using the ammonia solution specified in JIS K 8085.
 - 4) Diammonium hydrogen citrate solution (100 g/L), in accordance with 52.1 a) 3).
 - 5) Sodium acetate solution (200 g/L) Dissolve 33.2 g of sodium acetate trihydrate specified in JIS K 8371 in water to make 100 ml.
 - 6) **Diethyldithiocarbamic acid sodium salt solution (20 g/L)** Dissolve 2.6 g of sodium *N*,*N*-diethyldithiocarbamate trihydrate specified in **JIS K 8454** in water to make 100 ml. Store this solution in a colored bottle, and do not use after a lapse of 2 weeks or more from preparation.

- 7) Metacresol purple solution (1 g/L), in accordance with 52.1 a) 6).
- 8) Nitroso R salt solution (2 g/L) Dissolve 0.2 g of 1-nitroso-2-naphthol-3,6disulfonic acid disodium salt (nitroso R salt) in water to make 100 ml.
- 9) Butyl acetate, specified in JIS K 8377.
- 10) Cobalt reference solution (Co 0.1 mg/ml), in accordance with 52.4 a) 16).
- 11) Cobalt reference solution (Co $2 \mu g/ml$) Place 20 ml of the cobalt reference solution (Co 0.1 mg/ml) in a 1 000-ml volumetric flask, add 20 ml of nitric acid (1+1) [as specified in 58.4 a) 1)], and add water to the mark.
- b) **Implement and apparatus** The following implement and apparatus shall be used.
 - 1) Separatory funnel, of 100 ml capacity.
 - 2) **Photometer** Spectrophotometer or photoelectric photometer
- c) **Procedure** The test procedure shall be as follows.
 - Place a suitable volume (containing 1 µg to 30 µg as Co) of the sample, which has been treated according to clause 5, in a 100-ml separatory funnel, and add 5 ml of the diammonium hydrogen citrate solution (100 g/L) and two or three drops of the metacresol purple solution (1 g/L). Then add the ammonia solution (1+1) until it turns faint purple, and add water to make about 50 ml.
 - 2) Add 3 ml ⁽¹⁾ of the diethyldithiocarbamic acid sodium salt solution (20 g/L), shake to mix, then add 10 ml of butyl acetate, shake to mix for about 2 min, and allow to stand.
 - 3) Separate the butyl acetate layer and transfer it into a 100-ml beaker. Add 10 ml of butyl acetate to the water layer to make re-extraction, and join this butyl acetate layer to the above butyl acetate in the beaker.
 - 4) Heat the butyl acetate layer gently, and evaporate nearly to dryness. Add 3 ml of nitric acid and 1 ml of sulfuric acid (1+1) to the residue, and heat it to decompose organic matter as well as to expel almost all acid.
 - 5) Add 10 ml of water to dissolve, and add the sodium acetate solution (200 g/L) to adjust its pH to 5 to 6 using a pH test paper.
 - 6) Add 1 ml (²) of the nitroso R salt solution (2 g/L), and boil it for about 1 min. Add 2 ml of nitric acid, boil for about 1 min, and cool it quickly with running water.
 - 7) Transfer it into a 25 ml-volumetric flask, and add water to the mark.
 - 8) Transfer a part of this solution into an absorption cell, and measure its absorbance near the wavelength of 420 nm.
 - 9) For a blank test, using 10 ml of water, carry out the procedures in **5**) to **8**), and correct the measured absorbance of the sample.
 - 10) Determine the amount of cobalt by reference to the working curve, and calculate the concentration of cobalt (Co μ g/L) in the sample.

- Notes (¹) Nickel, copper, cadmium, lead, arsenic, and so on also react with diethyldithiocarbamic acid. Therefore, if the sample contains a large amount of these metals, excess diethyldithiocarbamic acid sodium salt shall be added. These metal elements also make interference by coloring with nitroso R salt, but nickel in an amount of about 30 times that of cobalt, or copper in an amount of about 20 times that of cobalt will not interfere.
 - (²) Since nitroso R salt complex of cobalt may decompose when exposed to direct sunshine, treatment after addition of nitroso R salt shall be performed avoiding direct sunshine.
- d) Working curve The working curve shall be prepared as follows.
 - 1) Place a series of aliquots in stepwise increment ranging from 0.5 ml to 15 ml of the cobalt reference solution (Co $2 \mu g/ml$) in as many 100-ml beakers, and after making each of these solutions 10 ml to 15 ml, carry out the procedures in c) 5) to 9) to measure the absorbance of each. Plot the relation curve between the amount of cobalt (Co) and its absorbance.

60.2 Flame atomic absorption spectrometry After pretreated, the sample is sprayed into an acetylene-air flame, and the atomic absorption made by cobalt is measured at the wavelength of 240.7 nm to determine cobalt.

Determination range: Co 0.5 mg/L to 10 mg/L

Repeatability: 5% to 10% (subject to variation depending on the type of apparatus used and the measuring conditions applied)

- a) **Reagent** The following reagent shall be used.
 - 1) Cobalt reference solution (Co 0.1 mg/ml), in accordance with 52.4 a) 16).
- b) Apparatus, as specified in **52.2** b).
- c) **Preparatory operation** The preparatory operation shall be carried out as follows.
 - 1) Treat the sample as shown in **5.5**.
 - NOTE 1 In the case of the sample of low cobalt concentration which contains no substance interfering with extraction, perform the preparatory operation according to the procedure given in NOTE 4, NOTE 5 or NOTE 6 to clause **52**.
- d) **Procedure** The test procedure shall be as follows.
 - 1) Perform the procedure in **52.2** d) 1), except that the wavelength used shall be 240.7 nm.
 - 2) For a blank test, perform the procedure in **52.2 d**) **2**).
 - 3) Determine the amount of cobalt by reference to the working curve, and calculate the concentration of cobalt (Co mg/L) in the sample.
- e) Working curve The working curve shall be prepared as follows.

- 1) Place a series of aliquots in stepwise increment ranging from 0.5 ml to 10 ml $(^3)$ of the cobalt reference solution (Co 0.1 mg/ml) in as many 100-ml volumetric flasks. Add acid to each of these solutions until the acid concentration is the same as that of the sample treated according to **c**) **1**) and add water to the mark.
- 2) Perform the procedures in **52.2** e) 2) and 3), and plot the relation curve between the amount of cobalt (Co) and the reading on the apparatus. Prepare the working curve at the time of measurement of the sample.
 - Note (³) When a solvent extraction method is adopted as the preparatory operation, suitably reduce the volume of cobalt reference solution.

60.3 ICP atomic emission spectrometry See 52.4.

60.4 ICP mass spectrometry See 52.5.