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**Testing methods for determination
of metallic elements in highly
purified water**

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee, as the result of proposal for revision of Japanese Industrial Standard submitted by the Japan Industrial Water Association (JIWA)/the Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14. Consequently **JIS K 0553 : 1995** is replaced with this Standard.

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Testing methods for determination of metallic elements in highly purified water

1 Scope This Japanese Industrial Standard specifies testing methods for determination of metallic elements (sodium, potassium, calcium, magnesium, copper, zinc, lead, cadmium, nickel, cobalt, manganese, chromium, aluminum, and iron) in highly purified water.

Remarks : These methods can also be applied to the determination of metallic elements contained in refined pure water, besides in highly purified water.

2 Normative references The standards listed in Attached Table 1 contain provisions which, through reference in this Standard, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

3 Common matters Common matters shall be as follows:

- a) **General rules** The general matters common to chemical analysis shall be in accordance with **JIS K 0050**.
- b) **Definitions** For the purposes of this Standard, definitions of **JIS K 0101**, **JIS K 0102**, **JIS K 0133**, **JIS K 0211** or **JIS K 0215** shall apply.
- c) **Methods for high frequency plasma atomic emission spectrometry** Methods for inductively coupled plasma atomic emission spectrometry (hereafter referred to as "ICP atomic emission spectrometry") common to general matters shall be in accordance with **JIS K 0116**.
- d) **Electrothermal type atomic absorption spectrometry** The general matters common to the electrothermal type atomic absorption spectrometry (hereafter referred to as "electrothermal atomic absorptiometry") shall be in accordance with **JIS K 0121**.
- e) **Ion chromatography** The general matters common to the ion chromatography shall be in accordance with **JIS K 0127**.
- f) **High frequency plasma mass spectrometry** The general matters common to high frequency plasma mass spectrometry shall be in accordance with **JIS K 0133**.
- g) **Ranges of determination** Respective determination ranges for electrothermal atomic absorptiometry, ICP atomic emission spectrometry, high frequency plasma mass spectrometry, ion chromatography, of the metallic element being determined, shall be shown by its concentration in the sample ($\mu\text{g/L}$ or ng/L).
- h) **Repeatability** Repeatability shall be expressed by the coefficient of variation (%)⁽¹⁾ which has been obtained in repetition tests carried out within the determination range of each testing method.

Note (1) Coefficient of variation (%) = $\frac{\sigma}{\bar{x}} \times 100$

where, σ : standard deviation
 $\bar{x}$: average

- i) **Water** Water **A2** or **A3** specified in **JIS K 0557** shall be employed and they shall not interfere with the determination of each metallic element. If otherwise specified in relevant clauses, it shall be followed.
- j) **Reagents** The general matters common to reagents shall be as follows:
- 1) Reagents which are specified in Japanese Industrial Standards are used. If reagents other than those specified in Japanese Industrial Standards are to be used, they shall give no hindrance to test.
 - 2) The concentration of solution of reagents is generally shown by g/L (if compounds, the mass of anhydrous compounds shall be used) or mol/L (or mmol/L). The concentration of reference solution, however, is shown by mg/ml, µg/ml, or ng/ml.
 - 3) The concentration, given in parentheses put after the name of solution of the reagents, means approximate concentration, except when it is a reference solution. For instance, sodium hydrogen sulfite solution (100 g/L) means the sodium hydrogen sulfite solution with about 100 g/L concentration.
 - 4) The concentration of liquid reagent is, according to **JIS K 0050**, expressed by its mixing ratio with water [reagent ($a + b$)]. This expression means “ a ” ml of reagent is mixed with “ b ” ml of water, and is used for such as hydrochloric acid or nitric acid. However, it is expressed only by the reagent name when it is used without dilution.
 - 5) The name of reagents are principally coordinated with the nomenclature of compounds specified by the Chemical Society of Japan, based on the nomenclature system for inorganic compounds and for organic compounds prescribed by the International Union of Pure and Applied Chemistry (IUPAC), and with nomenclature system for **JIS** reagents.
 - 6) When handling reagent, waste water, or others, be sufficiently careful according to the laws and regulations concerned.
- k) **Glassware** Glassware provided in **JIS R 3503** and **JIS R 3505** shall be used, unless otherwise specified. In case of using the heating procedure, the glassware made of quartz glass (or borosilicate glass-1 specified in **JIS R 3503**) shall be employed.

The desiccant used in a desiccator shall be silicagel⁽²⁾ unless otherwise specified.

Note (2) Use silicagel desiccant for packing, type A class 1, specified in **JIS Z 0701**.

- l) **Working curve (electrothermal atomic absorptiometry, ICP atomic emission spectrometry, high frequency plasma mass spectrometry, and ion chromatography)** When a working curve is to be prepared, divide into 4 to 6 steps the determination range shown in the testing method, and take reference solution so as to agree with these steps. The working curve shall be prepared within the range of determination.

For electrothermal atomic absorptiometry, ICP atomic emission spectrometry, high frequency plasma mass spectrometry, and ion chromatography, newly prepared working curves shall be used in determination of a sample. In the case where the same test is successively carried out on more than one samples, indicated values shall be confirmed by using the reference solutions during the test as appropriate.

- m) **Environment for test** This test should be carried out in the environment where cleanliness class is 3 or higher specified in **JIS B 9920** (for example, in a clean room).
- n) **Marking of results** If there are 2 or more testing methods, the names of the testing methods shall be noted.

Remarks : In either case of sampling or test, it is important to pay the utmost care and attention so that the sample is not contaminated during any procedure. Pay attention to the shape, material and washing method of tools used. Give careful attention so that pollution may not come from the analyst. Use of gloves for the clean room is recommended.

4 Sampling Sampling shall be as follows:

4.1 Reagents Reagent shall be as follows:

- a) **Nitric acid (0.2 mol/L)** Prepare it with nitric acid specified in **JIS K 8541** and water of class **A2**.
- b) **Nitric acid (1+1)** Prepare it with nitric acid which is high purity reagent specified in **JIS K 9901** or that of equivalent grade, and water of class **A3**.

4.2 Sample container The container which is airtight and made of quartz glass, polymethylpentene, polyethylene, polypropylene, polystyrene or the like, shall be employed.

4.3 Washing of a sample container Washing method of a sample container shall be as follows:

- a) Fill a sample container with nitric acid (0.2 mol/L), stopper it closely, after allowing to stand for 16 h or longer, discard nitric acid (0.2 mol/L) and wash the container with class **A2** water.
- b) Pour **A2** water into a sample container to about a quarter of its volume, stopper it, and shake vigorously for about 30 s to wash. Repeat this procedure five times.
- c) Fill the container with **A3** water (or that of equivalent grade to water to be tested) stopper it closely, allow it to stand for 16 h or longer, and discard the water.
- d) Fill the container with the same water as c), stopper it closely and allow to stand until sampling.

4.4 Operation Operation shall be as follows:

- a) Wash sufficiently the outlet of water purifying apparatus or the end of sampling valve⁽¹⁾ of main piping with the water to be tested, and install a sample

introducing pipe (made of soft synthetic resin) whose inside and outside has been sufficiently washed with **A2** water previously⁽²⁾.

Notes (1) Use a sampling valve made of corrosion resistant material.

(2) When a sample introducing pipe has long length, let the sample flow out to completely displace the water from the sampling valve to the end of sample introducing pipe, and then further let the sample flow out freely for about 5 min continuously. When main piping is employed, it is recommended to flow out the sample always at the rate of about 1 L/min from the sampling valve.

- b) Discard the water in a sample container, pour water to be tested in it to approximately a quarter of its volume, stopper it, and shake vigorously to wash for approximately 30 s. Repeat this procedure five times.
- c) Let the end of a sample introducing pipe touch the bottom of a sample container, flow out sample of about 5 times the volume of sample container, take out the sample introducing pipe, add nitric acid (1+1) at the rate of 1 ml per 1 L of sample⁽³⁾, and stopper it closely after thoroughly washing the stopper by using the sample.

Note (3) When sodium and potassium are determined by the ion chromatography, the sample to which nitric acid (1+1) is not added shall be used.

5 Sodium (Na) Sodium shall be determined by electrothermal atomic absorptiometry, high frequency plasma mass spectrometry, or ion chromatography.

5.1 Electrothermal atomic absorptiometry After sample has been concentrated, measure atomic absorbance caused by sodium at the wavelength of 589.0 nm and determine sodium concentration by electrothermal atomic absorptiometry.

Determination range: Na 5 ng/L to 50 ng/L⁽¹⁾

Precision of repeatability: 10 % to 30 %⁽¹⁾

Note (1) This is the value of original sample in the case that the volume of the sample was concentrated to about $\frac{1}{50}$ according to the procedure in **5.1.3**. It varies depending on apparatus and measuring conditions.

5.1.1 Reagents Reagents shall be as follows:

- a) **Water** **A3** water or refined water⁽²⁾ whose quality is equal to this. The fitness of water shall be confirmed by the blank test for the metallic elements to be determined without the concentration. This water is used for preparation and the operation of the reagent.

Note (2) In the case of distilling, apparatus without elution of metallic element to be determined shall be employed.

- b) **Nitric acid (1+1)** It shall be in accordance with **4.1 b)**.

- c) **Sodium reference solution (100 µgNa/ml)** Heat sodium chloride, which is a reference material for volumetric analysis, specified in **JIS K 8005** at 600 °C for 1 h and allow it to cool in a desiccator. Weigh 0.254 g from NaCl 100 %, dissolve it in a small volume of water, transfer the solution into 1 000 ml volumetric flask, and add water up to the marked line. Store it in a polyethylene bottle.

- d) **Sodium reference solution (1 µgNa/ml)** Take 5 ml of sodium reference solution (100 µgNa/ml) in a 500 ml volumetric flask, and add water up to the marked line. Prepare it when it is needed.
- e) **Sodium reference solution (10 ngNa/ml)** Take 5 ml of sodium reference solution (1 µgNa/ml) in a 500 ml volumetric flask, and add water up to the marked line. Prepare it when it is needed.

5.1.2 Implements and apparatus Implements and apparatus shall be as follows:

- a) **Concentration apparatus** It is a reduced pressure type made of fused silica. The capacity of the sample container is about 1 L.
- b) **Electrothermal atomic absorptiometer** One capable of background correction is used.
- c) **Heating element** It is made of graphite, or refractory metal.
- d) **Sodium hollow cathode lamp**
- e) **Flow gas** Argon class 2 specified in **JIS K 1105**⁽³⁾.
Note ⁽³⁾ When a heating body made of refractory metal is used, add hydrogen class 2 of 2 volume, specified in **JIS K 0512**, into the argon of 5 volume.
- f) **Micropipette** Piston operated micro-volumetric apparatus for 20 µl to 50 µl liquid specified in **JIS K 0970** or automatic injector.

5.1.3 Concentration procedure Concentration procedure shall be as follows:

- a) Add 500 ml of sample, whose mass has been measured (to the nearest 0.1 g), into the sample container of a concentration apparatus⁽⁴⁾.
Note ⁽⁴⁾ Give careful attention so that pollution may not come from the analyst. Use of gloves for the clean room is recommended.
- b) Start the concentration apparatus, keep a water bath at 75 °C to 80 °C and concentrate the solution to about 10 ml.
- c) Weigh the mass of the sample container of concentration apparatus (to the nearest 0.1 g), calculate the difference between the mass thus obtained and the mass of the original sample container, and take it as the volume of sample after the concentration operation. The concentration factor is calculated with the following formula:

$$\frac{\text{Volume of sample used for concentration (ml)}}{\text{Volume of sample after concentration (ml)}}$$

Remarks 1 Instead of carrying out concentration under reduced pressure, it is permissible to directly concentrate in a clean room of cleanliness class 3 or more (or in a clean bench) specified in **JIS B 9920**. In this case, the operation ^(1*) shall be as follows:

Add 200 ml of sample in a 500 ml beaker made of quartz glass or polytetrafluoroethylene ^(2*), heat it on a hot plate just under boiling point, until the volume of about 50 ml is obtained, then add 300 ml of sample, heat it successively until the volume of about 10 ml

volume is obtained, and allow it to cool. The volume of sample after concentration and concentration factor are calculated according to **5.3.1 c**).

Notes (1*) It shall be in accordance with Note (4).

(2*) Some products may elute metal elements from it, therefore, carry out previously a blank test, and use the product which gives no influence on the test.

5.1.4 Operation Operation shall be as follows:

- a) Set an electrothermal atomic absorptiometer standby for running, inject a certain amount of the sample concentrated by **5.1.3** (for instance, 50 μ l) into the heating element with a micropipette, perform drying, ashing, atomizing according to clause **6** of **JIS K 0121**⁽⁵⁾ and measure the atomic absorbance of sodium at wavelength 589.0 nm and read⁽⁷⁾ the indicated value⁽⁶⁾.

Notes (5) The condition of drying, ashing, and atomization varies according to the apparatus. Moreover, it varies depending on the injection volume of the sample.

(6) Absorbance or its proportional value.

(7) If necessary, repeat the operation of **a**) three times or more and confirm that the indicated values agree with each other.

- b) For a blank test, without injecting sample, carry out the procedure of **a**), read indicated value⁽⁵⁾, and correct the indicated value obtained on the sample.
- c) Obtain sodium concentration (ngNa/L) with the working curve and calculate the concentration of sodium (ngNa/L) in the sample by using a concentration factor.

Working curve Take stepwise 2.5 ml to 25 ml of sodium reference solution (10 ngNa/ml) into as many 100 ml volumetric flasks, add nitric acid (1+1) so that each solution is of the same acid concentration as the concentrated sample and add water to the marked line. Carry out the procedures of **a**), without performing concentration, for these solutions. Separately, for a blank test, add nitric acid (1+1) to the water used in this procedure until it is of the same acid concentration as the sample and carry out the procedure of **a**) without performing concentration. After correcting the indicated value obtained for each reference solution, prepare the relation curve between the concentration of sodium (ngNa/L) and indicated value. The working curve shall be drawn up when sample is measured.

Remarks 2 Instead of concentrating the sample by **5.1.3**, an alternative method may be employed where a certain amount of the sample (for instance, 50 μ l) is injected into the heating element with a micropipette and dried, and again the same amount of the sample is injected to be dried. The sample may be determined after concentrating by repeating this operation up to 10 times, ashing and atomizing it.

- 3 When a sample whose sodium concentration is 50 ng/L or more is examined, take a proper quantity (500 ml or less) according to the procedure of **5.1.3**, concentrate it to approximately 10 ml and examine it.

5.2 High frequency plasma mass spectrometry Atomize a sample into the high frequency plasma, measure the ion current in m/z of sodium (mass/charge numbers) and determine the sodium concentration.

Determination range: Na 20 ng/L to 2 000 ng/L⁽⁸⁾

Precision of repeatability: 5 % to 20 %⁽⁸⁾

Note ⁽⁸⁾ It varies depending on the apparatus and the measurement condition.

5.2.1 Reagents Reagents shall be as follows:

- a) **Water** It shall be in accordance with 5.1.1 a).
- b) **Nitric acid (1+1)** It shall be in accordance with 4.1 b).
- c) **Mixed reference solution** [(20 ngNa, 20 ngMg, 10 ngCu, 20 ngZn, 5 ngPb, 5 ngCd, 10 ngNi, 10 ngCo, 10 ngMn, 10 ngCr, 10 ngAl)/ml]⁽⁹⁾ Take 10 ml of sodium reference solution (1 µgNa/ml) specified in 5.1.1 d), 10 ml of magnesium reference solution (1 µgMg/ml) specified in 8.1.1 d), 5 ml of copper reference solution (1 µgCu/ml) specified in 9.1.1 e), 10 ml of zinc reference solution (1 µgZn/ml) specified in 10.1.1 e), 2.5 ml of lead reference solution (1 µgPb/ml) specified in 11.1.1 d), 2.5 ml of cadmium reference solution (1 µgCd/ml) specified in 12.1.1 d), 5 ml of nickel reference solution (1 µgNi/ml) specified in 13.1.1 d), 5 ml of cobalt reference solution (1 µgCo/ml) specified in 14.1.1 d), 5 ml of manganese reference solution (1 µgMn/ml) specified in 15.1.1 f), 5 ml of chromium reference solution (1 µgCr/ml) specified in 16.1.1 d), and 5 ml of aluminum reference solution (1 µgAl/ml) specified in 17.1.1 d), into a 500 ml volumetric flask, add 0.5 ml of nitric acid (1+1), and add water up to the marked line. Prepare it when it is needed.

Note ⁽⁹⁾ For metal elements, a mixed reference solution of the metal elements to be determined, or a single metal reference solution may be prepared and used.

5.2.2 Apparatus Apparatus shall be as follows:

- a) **High frequency plasma mass spectrometer**

Remarks 4 In some high frequency plasma mass spectrometers, a quadrupole type mass spectrometer or a magnetic field type double settling mass spectrometer is used as a mass separation part.

- 5 For the atomization of the sample, the supersonic nebulizer or an apparatus having equal performance to this may be used. In this case, the lower limit of determination range can be lowered by one decimal place, provided that memory effect is paid attention to and sufficient washing carried out.

- b) **Gas** It is used for the plasma formation and the sample introduction, etc. The gas of the high purity nitrogen class 2 specified in JIS K 1107 or the argon class 2 specified in JIS K 1105⁽¹⁰⁾ shall be used.

Note ⁽¹⁰⁾ Other than the above gas, sometimes mixed gas which is composed of helium, either one of oxygen or nitrogen and argon is employed.

5.2.3 Operation Operation shall be as follows:

- a) Set a high frequency plasma mass spectrometer standby for running, spray sample into high frequency plasma through a sample introducing part according to clause 12 of **JIS K 0133**, and read the indicated value⁽¹¹⁾ given at the m/z (mass/charge number) of sodium.

Note ⁽¹¹⁾ The value of ionic current given at m/z (mass/charge number) of target element, or the value proportionated to it.

- b) For a blank test, carry out the procedure in a) using water⁽¹²⁾. Correct the indicated value obtained on the sample⁽¹¹⁾.

Note ⁽¹²⁾ In the case of determination around the lower limit of determination range, where the indicated value by water is not negligible, measure the blank-test value of the apparatus and correct the indicated value obtained on the sample, which shall be done as follows:

Concentrate water by about 5 times and 10 times of concentration factor according to 5.1.3, and carry out the procedure in a) on these waters to obtain indicated values. Plot these values on the paper on which concentration factor has graduated along abscissa and indicated value along ordinate, and elongate the line tying these two points to make it intersect the ordinate. The indicated value corresponding to this point intersecting with ordinate (zero value of abscissa) is referred to as a blank-test value of the apparatus.

- c) On the working curve, find the concentration of sodium (ngNa/L), and calculate the concentration of sodium (ngNa/L) in the sample.

Working curve Take stepwise 0.1 ml to 10 ml of mixed reference solution [(20 ngNa, 20 ngMg, 10 ngCu, 20 ngZn, 5 ngPb, 5 ngCd, 10 ngNi, 10 ngCo, 10 ngMn, 10 ngCr, 10 ngAl)/ml]⁽⁹⁾ into 100 ml volumetric flasks, add nitric acid (1+1) so that each solution is of the same acid concentration as the sample (about 0.1 ml usually), and add water up to the marked line. Carry out the procedure in a) on these solutions. Separately, for a blank test, add nitric acid (1+1) to the same water as used in this operation until it is of the same acid concentration as the sample, carry out the procedure in a), correct each indicated value which has been measured on the reference solution of sodium, and plot the relation curve between the concentration of sodium (ngNa/L) and indicated value⁽¹³⁾. Prepare the working curve when sample is measured.

Note ⁽¹³⁾ When more than one element is to be simultaneously determined, the working curve shall be prepared under the test condition of each metal element.

Remarks 6 The minimum limit of determination can be lowered by using a sample concentrated according to 5.1.3.

5.3 Ion chromatography After sodium in sample has been concentrated in a concentration column, determine it according to ion chromatography.

Determination range: Na 50 ng/L to 1 000 ng/L⁽⁸⁾

Precision of repeatability: 5 % to 20 %⁽⁸⁾

5.3.1 Reagents Reagents shall be as follows:

- a) **Water** A2 or A3 water or the water purified to the same quality level as these. In advance, confirm its usability by practicing a blank test with a working curve. Use this water when preparing reagent solution and when carrying out the operation.
- b) **Eluent** The type of eluent varies according to the kinds of apparatus and of cation exchanger packed in separation column, therefore, it shall be necessary to confirm the condition of separation in advance according to the procedure shown in Note ⁽¹⁴⁾.
- c) **Regenerant** Regenerant is needed when a suppressor is used, but the type of regenerant depends on the kinds of apparatus and of suppressor. In advance, combine the suppressor and separation column, and carry out the procedure in Note ⁽¹⁴⁾ to confirm the performance of regenerant.
- d) **Cation mixed reference solution [(5 ngNa, 10 ngK)/ml]**⁽⁹⁾ Take 2.5 ml of sodium reference solution (1 µgNa/ml) specified in 5.1.1 d) and 5 ml of potassium reference solution (1 µgK/ml) specified in 6.1.1 c) into a 500 ml volumetric flask, and add water up to the marked line. Prepare it when it is needed.

Note ⁽¹⁴⁾ Flow the eluent into the separation column by constant flow rate (for instance, 1 ml/min to 2 ml/min), inject a certain amount of cation mixed reference solution [(1 µgNa, 2 µgK)/ml] (for instance, 100 µl) into this column and obtain a chromatogram, and employ the separation column that each cation can be separated (separation level about 1.3). It is preferable to confirm the performance of the separation column regularly by above method.

Mixed reference solution of cation [(1 µgNa, 2 µgK)/ml] shall be prepared as follows:

Take 1 ml of sodium reference solution (10 µgNa/ml) of 5.1.1 c) and 2 ml of potassium reference solution (10 µgK/ml) of 6.1.1 b) into a 100 ml volumetric flask and add water to the marked line.

5.3.2 Instrument and apparatus Instrument and apparatus shall be as follows:

- a) **Concentration apparatus**, satisfying the following conditions, and being capable of connecting with an ion chromatograph.
 - 1) **Sample injecting pump**, capable of getting flow rate of 1 ml/min to 5 ml/min.
 - 2) **Concentration column**, consisting of a pipe for column made of synthetic resin⁽¹⁵⁾ packed with cation exchanger.
- Note ⁽¹⁵⁾ For instance, they are made of polytetrafluoroethylene or polyether-etherketone.
- b) **Ion chromatograph** Either of the type combining separation column and suppressor, or the type separation column only may be used as long as it satisfies the following conditions and is capable of determining sodium and potassium separately.

- 1) **Separation column** It shall consist of a pipe for column made of stainless steel or synthetic resin⁽¹⁵⁾, packed⁽¹⁴⁾ with strong cation exchanger (surface-layer coated type or porous silica type).
 - 2) **Suppressor** It is a converter for exchanging anion in eluent with hydroxide ion, made of strong alkaline anion exchange membrane or the anion exchanger with equal performance to the above etc.
 - 3) **Detector** Electric conductivity detector
- c) **Recorder** It shall be in accordance with 4.2 f) of JIS K 0127.

5.3.3 Operation Operation shall be as follows:

- a) Set an ion chromatograph standby for running, and flow eluent in a concentration column and separation column at a certain flow rate (for instance, 1 ml/min to 2 ml/min) beforehand. In case that suppressor is used, flow the regenerant in the suppressor at the specified flow rate beforehand.
- b) Switch the flow route to stop the eluent flow into the concentration column, inject a certain quantity of sample (for instance, a certain quantity from 40 ml to 50 ml)⁽¹⁶⁾ into the concentration column with a sample injecting pump, concentrate it, then, switch again the flow route to regain the condition in a), send the concentrated sample into a separation column after the component has been eluted, and record its chromatogram.

Note ⁽¹⁶⁾ When the sample in which the concentration of sodium is 1 µgNa/L or more is tested, a certain quantity of sample of 40 ml or less is used.

- c) Find the peak corresponding to sodium on the chromatogram, and read its indicated value⁽¹⁷⁾.

Note ⁽¹⁷⁾ Peak height or peak area.

- d) Find the amount of sodium (ngNa) with the working curve, and calculate the concentration of sodium (µgNa/L) in sample.

Working curve Take stepwise from 1 ml to 20 ml of cation mixed reference solution [(5 ngNa, 10 ngK)/ml]⁽⁹⁾ into as many 100 ml volumetric flasks, and add water up to the marked line. Carry out the operation from a) to c) on these solutions, and read indicated value⁽¹⁷⁾ corresponding to each amount of sodium. Separately, for a blank test, carry out the operation from a) to c) on the same water as used for the above procedure, correct each indicated value corresponding to the amount of sodium, and prepare the relation curve between the amount of sodium (ngNa) and indicated value⁽¹⁸⁾. Prepare the working curve when sample is measured.

Note ⁽¹⁸⁾ When sodium and potassium are examined at the same time, the working curve of each metal element shall be prepared.

Remarks 7 If the cation (such as calcium or magnesium), which has strong affinity to packings in a separation column, exists in sample, it would gradually lower separative ability owing to its adsorption into packings. Therefore, the column shall be washed periodically by injecting the eluent which is prepared to have a concentration

about 10 times that of eluent into a separation column, in the same way as the case of sample.

- 8 Because a separation column lowers its performance by its continuous use, it shall be confirmed by the periodical procedure in Note ⁽¹⁴⁾. When the performance is lowered, prepare the solution which is of a concentration about 10 times that of eluent, wash the column, confirm it by the procedure in Note ⁽¹⁴⁾, and when it does not recover performance, replace it with new one.

6 Potassium (K) Potassium shall be determined by applying electrothermal atomic absorptiometry, high frequency plasma mass spectrometry or ion chromatography.

6.1 Electrothermal atomic absorptiometry After sample has been concentrated, potassium shall be determined by the electrothermal atomic absorptiometry by measuring atomic absorbance at the wavelength of 766.5 nm or 769.9 nm of potassium.

Determination range: K 5 ng/L to 50 ng/L⁽¹⁾

Precision of repeatability: 10 % to 30 %⁽¹⁾

Note ⁽¹⁾ It shall be in accordance with Note ⁽¹⁾ of clause 5.

6.1.1 Reagents Reagents shall be as follows:

- a) **Water** It shall be in accordance with 5.1.1 a).
- b) **Potassium reference solution (100 µgK/ml)** Heat potassium chloride for measuring electric conductivity specified in JIS K 8121 at 500 °C for about 4 h, and allow it to cool in a desiccator. Dissolve 0.191 g of it in a small amount of water, transfer it into a 1 000 ml volumetric flask, and add water up to the marked line. Store it in a polyethylene bottle.
- c) **Potassium reference solution (1 µgK/ml)** Take 5 ml of potassium reference solution (100 µgK/ml) into a 500 ml volumetric flask, and add water up to the marked line. Prepare it when it is needed.
- d) **Potassium reference solution (10 ngK/ml)** Take 5 ml of potassium reference solution (1 µgK/ml) into a 500 ml volumetric flask, and add water up to the marked line. Prepare it when it is needed.

6.1.2 Instruments and apparatus Instruments and apparatus shall be as follows:

- a) **Electrothermal atomic absorptiometer** It is capable of background correction.
- b) **Heating element** It is made of graphite, or refractory metal.
- c) **Potassium hollow cathode lamp**
- d) **Flow gas** It shall be in accordance with 5.1.2 e).
- e) **Micropipette** It shall be in accordance with 5.1.2 f).

6.1.3 Operation Operation shall be as follows:

- a) Set an electrothermal atomic absorptiometer standby for running, inject a certain quantity of sample (for instance, 50 μ l), which has been concentrated according to 5.1.3, into a heating element with a micropipette, dry, ash and atomize it⁽²⁾ according to clause 6 of JIS K 0121, measure the atomic absorbance by potassium at the wavelength of 766.5 nm or 769.9 nm, and read⁽⁴⁾ its indicated value⁽³⁾.

Notes ⁽²⁾ It shall be in accordance with Note ⁽⁵⁾ of clause 5.

⁽³⁾ It shall be in accordance with Note ⁽⁶⁾ of clause 5.

⁽⁴⁾ It shall be in accordance with Note ⁽⁷⁾ of clause 5.

- b) For a blank test, without injecting sample, carry out the procedure according to a), read indicated value⁽³⁾, and correct the indicated value obtained on the sample.
- c) Obtain the concentration of potassium (ngK/L) with the working curve and calculate the concentration of potassium (ngK/L) in the sample by using a concentration factor.

Working curve Take stepwise 2.5 ml to 25 ml of potassium reference solution (10 ngK/ml) into as many 100 ml volumetric flasks, add nitric acid (1+1) so that each solution is of the same acid concentration as the concentrated sample and add water to the marked line. Carry out the operation in a) on these solutions without concentrating. Separately, for a blank test, add nitric acid (1+1) to the same water as used in the above procedure until it is of the same acid concentration as the concentrated sample, carry out the operation in a) without performing concentration, read indicated value, correct each indicated value which has been measured on the reference solution of potassium, and prepare the relation curve between the concentration of potassium (ngK/L) and indicated value. Prepare the working curve when sample is measured.

Remarks 1 It shall be in accordance with Remarks 2 of clause 5.

- 2 When the sample whose potassium concentration is 50 ng/L or more is examined, take a proper quantity (500 ml or less) according to the procedure of 5.1.3, concentrate it to approximately 10 ml and examine it.

6.2 High frequency plasma mass spectrometry Atomize a sample into the high frequency plasma, measure the ion current in m/z of potassium (mass/charge number) and determine potassium.

Determination range: K 20 ng/L to 2 000 ng/L⁽⁵⁾

Precision of repeatability: 5 % to 20 %⁽⁵⁾

Note ⁽⁵⁾ It shall be in accordance with Note ⁽⁸⁾ of clause 5.

6.2.1 Reagent Reagent shall be as follows:

- a) **Water** It shall be in accordance with 5.1.1 a).
- b) **Nitric acid (1+1)** It shall be in accordance with 4.1 b).
- c) **Mixed reference solution [(20 ngK, 20 ngCa, 10 ngFe)/ml]**⁽⁶⁾ Take 2 ml of potassium reference solution (1 μ gK/ml) described in 6.1.1 c), 2 ml of calcium reference solution, (1 μ gCa/ml) described in 7.1.1 d), 1 ml of iron reference solution (1 μ gFe/ml) described in 18.1.1 d), into a 100 ml volumetric flask, add

0.1 ml of nitric acid (1+1), and add water up to the marked line. This solution shall be prepared when it is used.

Note ⁽⁶⁾ It shall be in accordance with Note ⁽⁹⁾ of clause 5.

6.2.2 Apparatus Apparatus shall be as follows:

- a) **High frequency plasma mass spectrometer** The high frequency plasma mass spectrometer shall be such that the interference by a molecular ion peaks such as ArH, Ar, and ArO can be decreased in determination of potassium, calcium, and iron, etc.

Remarks 3 It shall be in accordance with Remarks 4 of clause 5.

4 It shall be in accordance with Remarks 5 of clause 5.

5 As a method of decreasing interference, there are apparatus for system to lower the temperature of plasma and for other systems.

6 Even with the plasma temperature lower, other metal elements can be determined at the same time. But, the minimum limit of determination rises.

- b) **Gas** It shall be in accordance with 5.2.2 b).

6.2.3 Operation Operation shall be as follows:

- a) Set a high frequency plasma mass spectrometer standby for running, atomize the sample into the high frequency plasma according to clause 12 of JIS K 0133 through the sample introduction part, and read the indicated value⁽⁷⁾ in m/z of potassium.

Note ⁽⁷⁾ It shall be in accordance with Note ⁽¹¹⁾ of clause 5.

- b) Carry out the procedure in a) by using water, obtain the blank test value⁽⁸⁾ of the apparatus and correct the indicated value⁽⁷⁾ obtained on the sample.

Note ⁽⁸⁾ It shall be in accordance with Note ⁽¹²⁾ of clause 5.

- c) Obtain concentration of potassium (ngK/L) with the calibration curve, and calculate concentration of potassium (ngK/L) in the sample.

Working curve Take stepwise 0.1 ml to 10 ml of mixed reference solution [(20 ngK, 20 ngCa, 10 ngFe)/ml]⁽⁶⁾ into as many 100 ml volumetric flasks, add nitric acid (1+1) so that each solution is of the same acid concentration as the sample (about 0.1 ml usually), and add water up to the marked line. Carry out the procedures of a) for these solutions. Separately, for a blank test, add nitric acid (1+1) to the water used in this procedure until it is of the same acid concentration as the sample and carry out the procedure of a) for each solution. After correcting the indicated value obtained for each reference solution, prepare the relation curve between the concentration of potassium (ngK/L) and indicated value⁽⁹⁾. The working curve shall be drawn up when sample is prepared for analysis.

Note ⁽⁹⁾ When two or more metal elements among potassium, calcium, and iron, are measured at the same time, the working curve of each metal element shall be prepared.

Remarks 7 It shall be in accordance with Remarks 6 of clause 5.

6.3 Ion chromatography After potassium in sample has been concentrated in a concentration column, determine it according to ion chromatography.

Determination range: K 0.1 µg/L to 2 µg/L⁽¹⁰⁾

Precision of repeatability: 5 % to 20 %⁽¹⁰⁾

Note ⁽¹⁰⁾ It shall be in accordance with Note ⁽⁸⁾ of clause 5.

6.3.1 Reagents Reagents shall be as follows:

- a) **Water** It shall be in accordance with 5.3.1 a).
- b) **Eluent** It shall be in accordance with 5.3.1 b).
- c) **Regenerant** It shall be in accordance with 5.3.1 c).
- d) **Cation mixed reference solution [(5 ngNa, 10 ngK)/ml]** It shall be in accordance with 5.3.1 d).

6.3.2 Instruments and apparatus Instruments and apparatus shall be according to 5.3.2.

6.3.3 Operation Operation shall be as follows:

- a) Carry out the procedure specified in 5.3.3 a) and b)⁽¹¹⁾.
Note ⁽¹¹⁾ When the sample whose potassium concentration is 2 µg/L or more is examined, the certain volume (40 ml or less) shall be used.
- b) Find the peak due to potassium on the chromatogram, and read its indicated value⁽¹²⁾.
Note ⁽¹²⁾ It shall be in accordance with Note ⁽¹⁷⁾ of clause 5.
- c) Find the amount of potassium (ngK) with the working curve, and calculate the concentration of potassium (µgK/L) in sample.

Working curve Take stepwise from 1 ml to 20 ml of cation mixed reference solution [(5 ngNa, 10 ngK)/ml]⁽⁶⁾ into as many 100 ml volumetric flasks, and add water up to the marked line. Carry out the operation a) and b) on these solutions, and read indicated value⁽¹²⁾ corresponding to each amount of potassium. Separately, for a blank test, carry out the operation a) and b) on the same water as used for the above procedure, correct each indicated value corresponding to the amount of potassium, and prepare the relation curve between the amount of potassium (ngK) and indicated value⁽¹³⁾. The working curve shall be drawn up when sample is measured.

Note ⁽¹³⁾ It shall be in accordance with Note ⁽¹⁸⁾ of clause 5.

Remarks 8 It shall be in accordance with Remarks 7 of clause 5.

9 It shall be in accordance with Remarks 8 of clause 5.

7 Calcium (Ca) Calcium shall be determined by applying electrothermal atomic absorptiometry, ICP atomic emission spectrometry, or high frequency plasma mass spectrometry.

7.1 Electrothermal atomic absorptiometry After sample has been concentrated, calcium shall be determined by the electrothermal atomic absorptiometry by measuring atomic absorbance at the wavelength of 422.7 nm of calcium.

Determination range: Ca 5 ng/L to 50 ng/L⁽¹⁾

Precision of repeatability: 10 % to 30 %⁽¹⁾

Note ⁽¹⁾ It shall be in accordance with Note ⁽¹⁾ of clause 5.

7.1.1 Reagents Reagents shall be as follows:

- a) **Water** It shall be in accordance with 5.1.1 a).
- b) **Nitric acid (1+1)** It shall be in accordance with 4.1 b).
- c) **Calcium reference solution (100 µgCa/ml)** Heat calcium carbonate specified in JIS K 8617 at 180 °C for about 1 h and allow it to cool in a desiccator. Take 0.125 g of it and disperse it in about 50 ml of water, and add 5 ml of nitric acid (1+1) to dissolve it. Heat it for several minutes just under boiling point. After cooling it, transfer it into a 500 ml volumetric flask, and add water up to the marked line.
- d) **Calcium reference solution (1 µgCa/ml)** Take 5 ml of calcium reference solution (100 µgCa/ml) into a 500 ml volumetric flask, and add water up to the marked line. Prepare it when it is needed.
- e) **Calcium reference solution (10 ngCa/ml)** Take 5 ml of calcium reference solution (1 µgCa/ml) into a 500 ml volumetric flask, and add water up to the marked line. Prepare it when it is needed.

7.1.2 Instrument and apparatus Instrument and apparatus shall be as follows:

- a) **Electrothermal atomic absorptiometer** One that is capable of background correction.
- b) **Heating element** It is made of graphite, or refractory metal.
- c) **Calcium hollow cathode lamp**
- d) **Flow gas** It shall be in accordance with 5.1.2 e).
- e) **Micropipette** It shall be in accordance with 5.1.2 f).

7.1.3 Operation Operation shall be as follows:

- a) Set an electrothermal atomic absorptiometer standby for running, inject a certain quantity of sample (for instance, 50 µl), which has been concentrated as shown in 5.1.3, into a heating element with a micropipette according to clause 6 of JIS K 0121, dry, ash, and atomize it⁽²⁾, measure the atomic absorbance of calcium at the wavelength of 422.7 nm, and read⁽⁴⁾ its indicated value⁽³⁾.

Notes ⁽²⁾ It shall be in accordance with Note ⁽⁵⁾ of clause 5.

⁽³⁾ It shall be in accordance with Note ⁽⁶⁾ of clause 5.

⁽⁴⁾ It shall be in accordance with Note ⁽⁷⁾ of clause 5.

- b) For a blank test, without injecting sample, carry out the procedure according to **a)**, read indicated value⁽³⁾, and correct the indicated value obtained on the sample.
- c) Find the concentration of calcium (ngCa/L) with the working curve, and calculate the concentration of calcium (ngCa/L) in the sample by using concentration factor.

Working curve Take stepwise 2.5 ml to 25 ml of calcium reference solution (10 ngCa/ml) into as many 100 ml volumetric flasks, add nitric acid (1+1) so that each solution is of the same acid concentration as the concentrated sample and add water to the marked line. Carry out the procedure **a)**, without performing concentration, for these solutions. Separately, for a blank test, add nitric acid (1+1) to the water used in this procedure until it is of the same acid concentration as the concentrated sample, carry out the procedure of **a)** without performing concentration. After correcting the indicated value obtained for each reference solution, prepare the relation curve between the concentration of calcium (ngCa/L) and indicated value. Prepare the working curve when sample is measured.

Remarks 1 It shall be in accordance with Remarks 2 of clause 5.

- 2 When the sample, whose concentration of calcium is 50 ng/L or more, is tested, take suitable quantity of sample (500 ml or less), carry out the procedure in 5.1.3 to concentrate it to about 10 ml, and test it.

7.2 ICP atomic emission spectrometry After sample has been concentrated, spray it into a high frequency plasma through a sample introducing part, and measure emission by calcium at the wavelength of 393.367 nm, to determine calcium.

Determination range: Ca 0.4 ng/L to 20 ng/L⁽⁵⁾

Precision of repeatability: 5 % to 20 %⁽⁵⁾

Note ⁽⁵⁾ It shall be in accordance with Note (1) of clause 5.

7.2.1 Reagents Reagents shall be as follows:

- a) **Water** It shall be in accordance with 5.1.1 a).
- b) **Nitric acid (1+1)** It shall be in accordance with 4.1 b).
- c) **Mixed reference solution [(10 ngCa, 10 ngMg, 250 ngCu, 250 ngZn, 250 ngCd, 100 ngMn, 250 ngFe)/ml]⁽⁶⁾** Take 5 ml of calcium reference solution (1 µgCa/ml) specified in 7.1.1 d), 5 ml of magnesium reference solution (1 µgMg/ml) specified in 8.1.1 d), 5 ml of copper reference solution (25 µgCu/ml) specified in 9.2.1 c), 5 ml of zinc reference solution (25 µgZn/ml) specified in 10.2.1 c), 5 ml of cadmium reference solution (25 µgCd/ml) specified in 12.2.1 c), 5 ml of manganese reference solution (10 µgMn/ml) specified in 15.2.1 c), 5 ml of iron reference solution (25 µgFe/ml) specified in 18.2.1 c), into a 500 ml volumetric flask, add 0.5 ml of nitric acid (1+1), and add water up to the marked line. Prepare it when it is needed.

Note ⁽⁶⁾ It shall be in accordance with Note (9) of clause 5.

7.2.2 Instrument and apparatus Instrument and apparatus shall be as follows:

- a) **ICP atomic emission spectrometer** One that is capable of correction of background is used.

- b) **Ultrasonic nebulizer**⁽⁷⁾

Note (7) Other nebulizer which has equal performance to this may be used.

7.2.3 Operation Operation shall be as follows:

- a) Set an ICP atomic emission spectrometer ready for determination, spray the sample, which has been concentrated as shown in 5.1.3, according to 5.8 of JIS K 0116 into a high frequency plasma through a sample introducing part, and measure emission intensity at the wavelength of 393.367 nm⁽⁸⁾.

Note (8) When the apparatus which provides high-order spectral line can be employed, the high-order spectral line may be serviceable. When its accuracy and precision have been confirmed beforehand, other wavelengths may be also used.

- b) For a blank test, spray water into a high frequency plasma, measure emission intensity at the wavelength of 393.367 nm⁽⁹⁾, and correct the emission intensity obtained on sample.

Note (9) When the emission intensity of a blank test is large, or when determination is carried out near the lower limit of determination range, carry out the operation according to Note (12) of clause 5, and obtain the blank test value of the apparatus.

- c) Obtain calcium concentration (ngCa/L) with the working curve and calculate the concentration of calcium (ngCa/L) in the sample by using a concentration factor.

Working curve Take stepwise 0.2 ml to 10 ml of mixed reference solution [(10 ngCa, 10 ngMg, 250 ngCu, 250 ngZn, 250 ngCd, 100 ngMn, 250 ngFe)/ml]⁽⁶⁾ into as many 100 ml volumetric flasks, add nitric acid (1+1) so that each solution is of the same acid concentration as the sample (about 0.1 ml usually), and add water up to the marked line. Carry out the procedure in a) on these solutions. Separately, for a blank test, add nitric acid (1+1) to the same water as used in this operation until it is of the same acid concentration as the sample, carry out the procedure in a), correct the emission intensity which has been obtained from each calcium reference solution, and prepare the relation curve between the concentration of calcium (ngCa/L) and emission intensity⁽¹⁰⁾. Prepare the working curve when sample is measured.

Note (10) When more than one metal element is to be simultaneously determined, the working curves shall be prepared for each metal element under respective test conditions. When the concentrations of copper, zinc, cadmium, iron are 500 ng/L to 1 000 ng/L, 0.2 ml to 20 ml of mixed reference solution [(10 ngCa, 10 ngMg, 250 ngCu, 250 ngZn, 250 ngCd, 100 ngMn, 250 ngFe)/ml] shall be employed.

Remarks 3 When the sample, whose concentration of calcium is 20 ng/L or more, is tested, take a suitable quantity of sample (500 ml or less), carry out the procedure in 5.1.3 to concentrate it to about 10 ml, and test it.