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Methods for determination of metals in flue gas

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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 Japan Environmental Sanitation Center (JESC)/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 0083 : 1997** is replaced with this Standard.

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Methods for determination of metals in flue gas

1 Scope This Japanese Industrial Standard specifies the methods for determination of cadmium, lead, nickel, manganese, vanadium, chromium, beryllium, arsenic and selenium in particulate substances, and arsenic and selenium in gaseous substances among the metals which exist in the gas exhausted from a flue, chimney, or duct, due to such processes as burning of fuels or other materials, and refining, working and physicochemical-treatment of metals.

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

3 General For general matters of analysis, the following respective standards shall be referred to **JIS K 0095** and **JIS Z 8808** for the sampling method of sample gas, **JIS K 0050** for chemical analysis, **JIS K 0121** for atomic absorption spectrometry and electrothermal atomic absorption spectrometry, **JIS K 0115** for absorptiometry, **JIS K 0116** for inductively-coupled plasma emission spectrometry (hereafter referred to as “ICP emission spectrometry”), **JIS K 0120** for fluorophotometry and **JIS K 0102** for inductively-coupled plasma mass spectrometry (hereafter referred to as “ICP mass spectrometry”).

4 Object substances and classification of analysis methods The object substances and analysis methods in this Standard are as specified in table 1.

The sampling method shall generally be in accordance with the method specified in **5.1**, but when test items are for arsenic or selenium and when test target is gaseous component like mainly hydrides, follow the method specified in **5.2**.

Table 1 Object substances and classification of analysis methods

Object substances	Analysis methods
Cadmium	Flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry, ICP mass spectrometry
Lead	Flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry, ICP mass spectrometry
Nickel	Dimethylglyoxime absorptiometry, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry, ICP mass spectrometry
Manganese	Periodic acid absorptiometry, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry, ICP mass spectrometry
Vanadium	<i>N</i> -benzoyl- <i>N</i> -phenylhydroxylamine absorptiometry, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry, ICP mass spectrometry
Chromium	Diphenylcarbazide absorptiometry, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry, ICP mass spectrometry
Beryllium	Flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry, ICP mass spectrometry
Arsenic	Silver diethyldithiocarbamate absorptiometry, hydride-generation atomic absorption spectrometry, electrothermal atomic absorption spectrometry, hydride-generation ICP emission spectrometry, ICP mass spectrometry
Selenium	3,3'-diaminobenzidine absorptiometry, hydride-generation atomic absorption spectrometry, electrothermal atomic absorption spectrometry, diamino-naphthalene fluorophotometry, hydride-generation ICP emission spectrometry, ICP mass spectrometry

5 Sampling methods

5.1 Sampling methods for cadmium, lead, nickel, manganese, vanadium, chromium, beryllium, arsenic and selenium

5.1.1 Selection of measuring position The measuring position shall be in accordance with 4.1 of JIS Z 8808.

5.1.2 Selection of measuring point The measuring point shall be in accordance with 4.3 of JIS Z 8808.

5.1.3 Sampling apparatus The sampling apparatus shall be either (1) ordinary-type sampling apparatus or (2) balanced-type sampling apparatus both of which are specified in 8.1 of JIS Z 8808, and which are connected with a gas absorbing part.

The gas absorbing part is the part to catch target components which have been gasified by vapourization, and as shown in figure 1 to figure 4-2, is inserted between dust-collecting part and gas-sucking part. When the temperature of flue gas is sufficiently lower than the expected melting point of compounds and it has been confirmed in accordance with the sampling method specified in this Standard that the apparatus

is free from any leakage of fume or mist compounds, no insertion of the gas absorbing part is needed.

- a) **Sampling apparatus** Sampling apparatus shall be composed of dust collecting part, gas absorbing part, gas sucking part, and measuring device for sucking flow rate. The dust collecting part is classified into No. 1 type and No. 2 type depending on the position where a dust collector has stood; No. 1 type sets the dust collector in a duct and No. 2 type sets the dust collector out of a duct. Either of the two types may be used.

The constructional example of ordinary-type sampling apparatus is shown in figure 1 in case of No. 1 type, and in figure 2 in case of No. 2 type. The constructional example of equilibrium type sampling apparatus is shown in figure 3 in the case of manual sampling and in figures 4-1 and 4-2 in the case of automatic sampling.

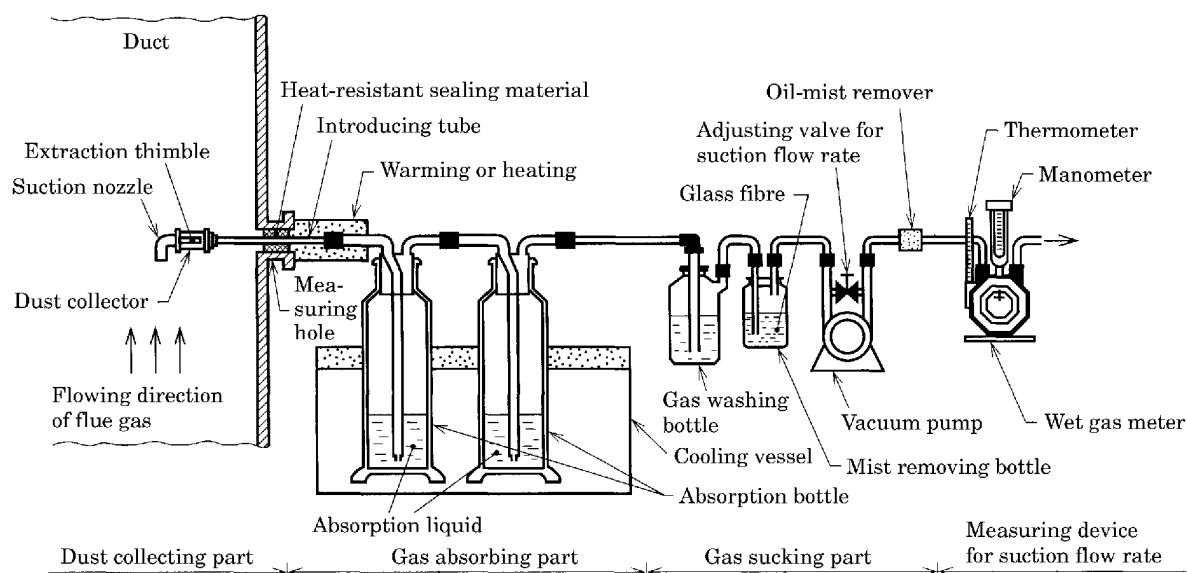


Figure 1 Constructional example of ordinary-type sampling apparatus (No. 1 type)

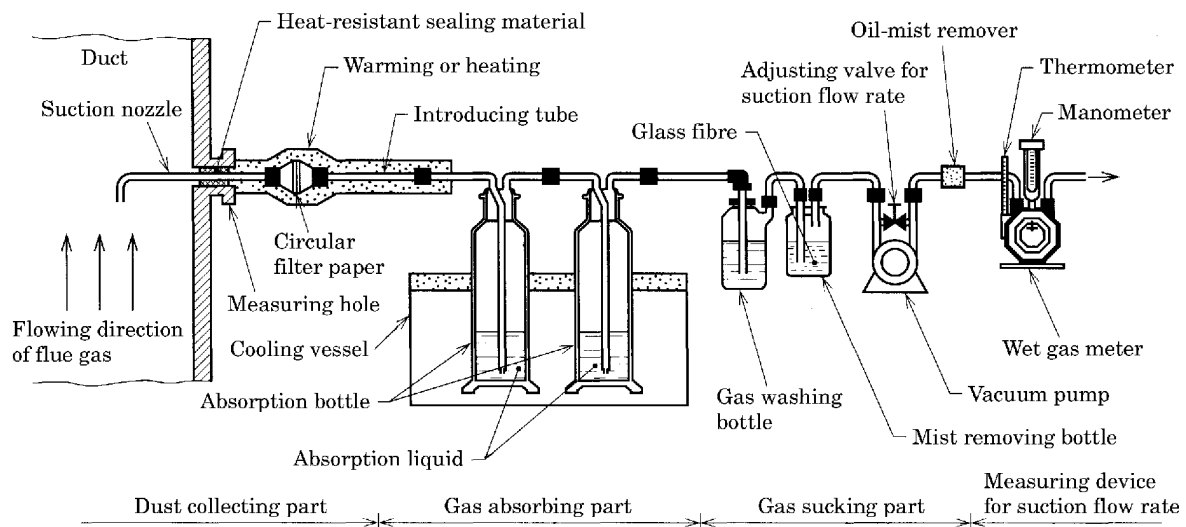


Figure 2 Constructional example of ordinary-type sampling apparatus (No. 2 type)

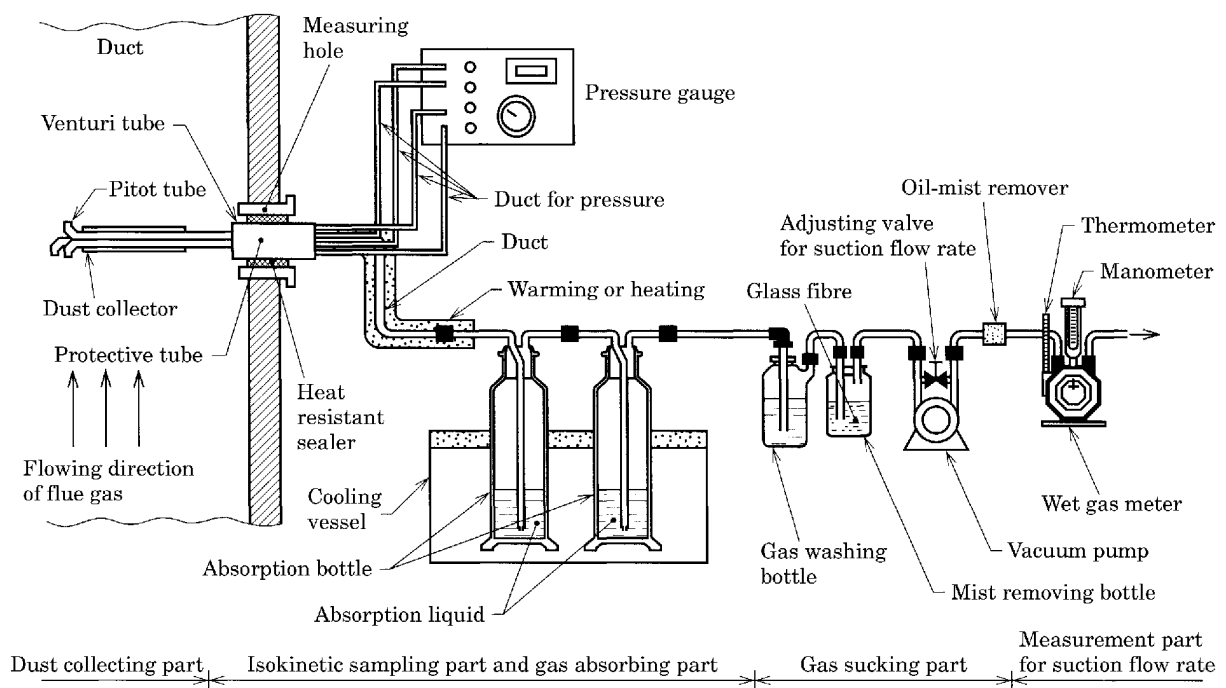


Figure 3 Example of construction for equilibrium type manual sampling apparatus (dynamic pressure type)

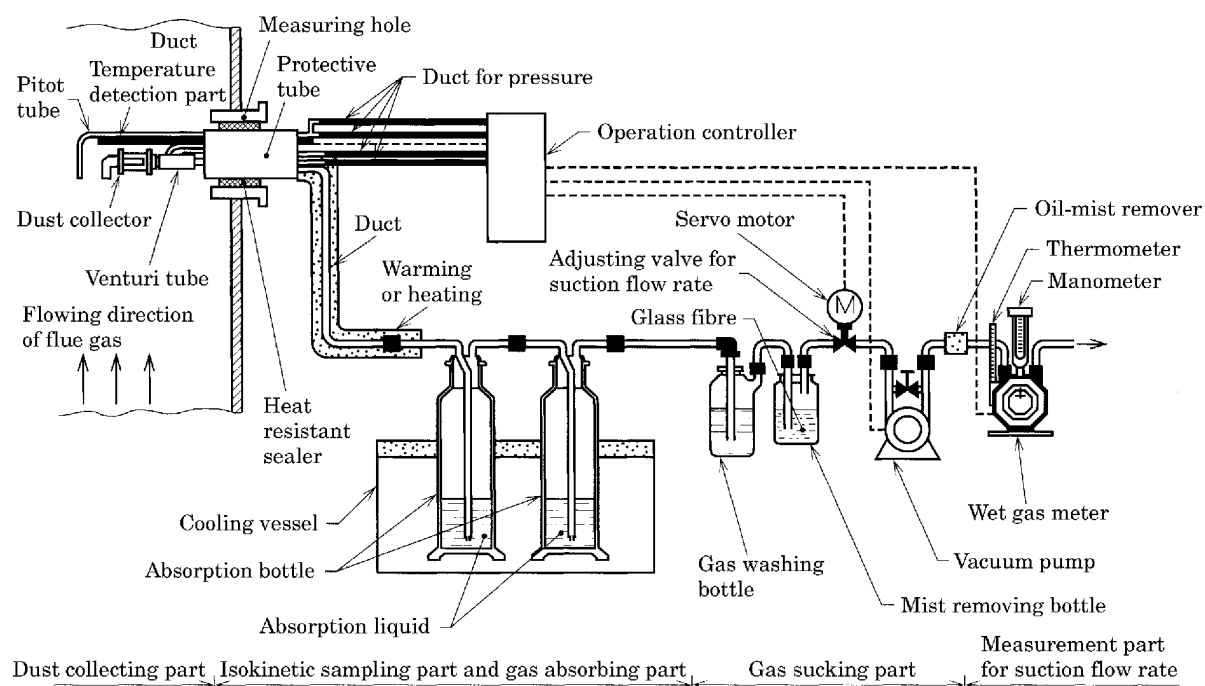


Figure 4-1 Example of construction for equilibrium type automatic sampling apparatus (dynamic pressure type)

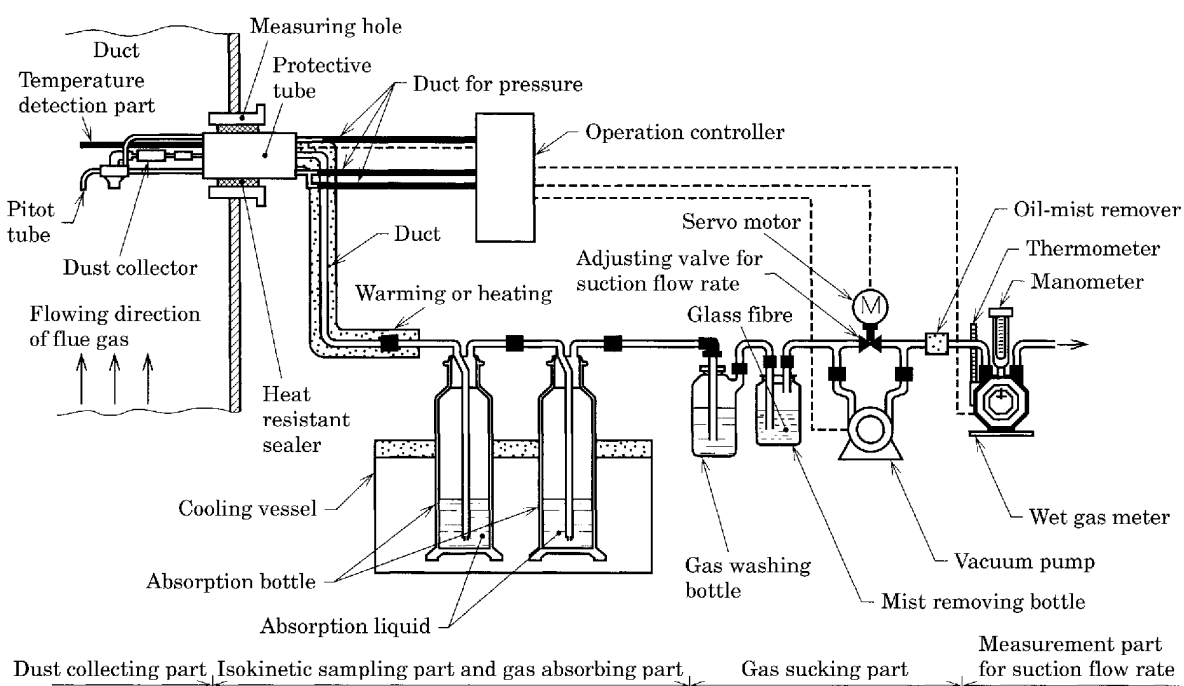


Figure 4-2 Example of construction for equilibrium type automatic sampling apparatus (static pressure type)

- b) **Dust collecting part** Follow the specification stated in 8.3.1 (2) and 8.3.2 (2) of JIS Z 8808. The suction nozzle made of stainless steel shall not be used because it may compromise the analysis.

- 1) **Dust collector** The dust collector shall be the one employing filter paper specified in 8.3.1 (2.2) of JIS Z 8808. The filter paper shall be selected among the filter papers whose collecting rate, pressure loss, moisture-absorbing rate, and content of testing target have been ascertained according to the performance test methods specified in JIS K 0901 which are for filtering materials used for dust sample.
- 2) **Suction nozzle** An example of suction nozzle is shown in figure 5. In this case, the material shall be in accordance with 6.2 of JIS K 0095. The construction shall be in accordance with 8.3.1 (2.1) of JIS Z 8808. Wash previously the suction nozzle with water, and store it after drying.

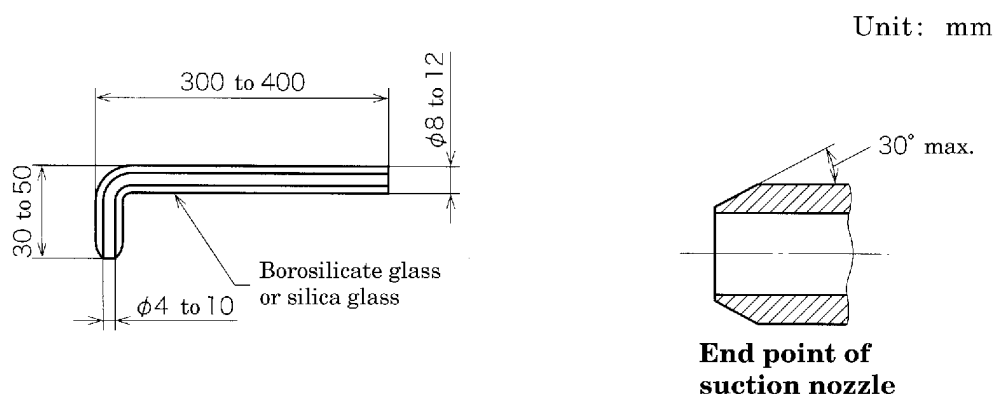


Figure 5 Suction nozzle (example)

- 3) **Introducing tube** The introducing tube connects a dust collector with a gas absorption bottle, and shall be in accordance with 6.6 of JIS K 0095. Its material shall be in accordance with 6.2 of JIS K 0095⁽¹⁾.
- Note ⁽¹⁾ Generally, use borosilicate glass.
- 4) **Insulating and heating of introducing tube and dust collector** If necessary, these are heated or thermally insulated so as not to allow moisture in flue gas to condense on the introducing tube, dust collector or others.
- c) **Gas absorbing part** The gas absorbing part is composed of absorption bottles and a cooling vessel.

- 1) **Reagents** The reagents shall be as follows:

Nitric acid (1+13), prepared using nitric acid specified in JIS K 8541.

Hydrochloric acid (1+13), prepared using hydrochloric acid specified in JIS K 8180.

- 2) **Absorption bottle** The absorption bottle measures 250 ml to 300 ml in capacity, and its example is shown in figure 6 (its material shall be borosilicate glass). In advance, wash it with nitric acid (1+13) or hydrochloric acid (1+13), then rinse with water, and dry it. Prepare 2 or more absorption bottles⁽²⁾, and use the following absorption liquids accordance to the items to be analyzed.

Note (2) When the third and after absorption bottles are used, it shall be confirmed that there is no leakage of fume or mist-type compounds in them according to the determination procedures similar to the case of the first and the second absorption bottles. When the determined value at the third and after absorption bottles is larger than that of a blank test, this result shall be added to the value given by the first and second bottles. As necessity demands, install a back-up filter at the latter step of an absorption bottle to catch fume or mist-type compounds, and determine it similarly to other one.

2.1) **Absorption liquid of cadmium, lead, nickel, manganese, vanadium, chromium, and beryllium** Place 50 ml of nitric acid (1+13) or hydrochloric acid (1+13) respectively into each absorption bottle⁽³⁾.

Note (3) When ICP mass spectrometry is used for the analytical method, nitric acid (1+13) is used for the absorption liquid.

2.2) **Absorption liquid of arsenic** Place 50 ml of water respectively into each absorption bottle.

2.3) **Absorption liquid of selenium** Place 50 ml of nitric acid (1+13) respectively into each absorption bottle.

Unit: mm

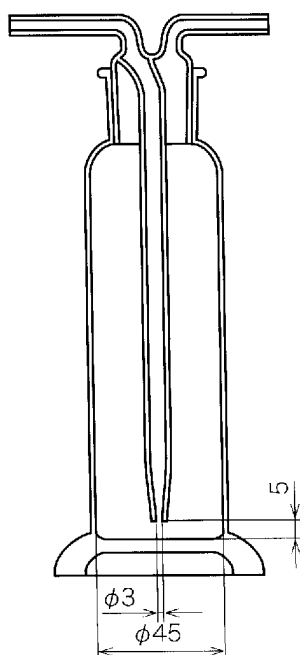


Figure 6 Absorption bottle (example)

3) **Cooling vessel** The cooling vessel contains absorption bottles, and can keep the absorption liquid at 0 °C to 10 °C⁽⁴⁾.

Note (4) Generally, put ice in it to cool.

5.1.4 Sampling The sampling shall be in accordance with the specification in clause 9 of JIS Z 8808.

- a) **Classification of sampling methods** Sampling method shall be either (1) (Method of each point sampling) or (2) (Method of traverse sampling) among the methods specified in 9.2 of JIS Z 8808⁽⁵⁾.

Note (5) Generally, method of traverse sampling is used.

- b) **Preparation of sampling** The preparation of sampling shall be as follows:

- 1) **Calculation of suction flow rate for isokinetic sampling** When ordinary-type sampling apparatus is used, it can be obtained by the calculation formula specified in 9.3.1 of JIS Z 8808⁽⁶⁾.

Note (6) Generally, the pressure of gas meter and temperature used in this calculation are those given when the moisture content in flue gas was measured, but when the moisture content in high-temperature flue gas is measured, considering the cooling effect caused by the installment of a gas absorbing part, it is preferable to make measurement under the condition that the gas absorbing part has been installed in the rear of the absorption bottles.

- 2) **Preparation of dust collector** The preparation of dust collector shall be in accordance with the specification in 9.3.2 of JIS Z 8808. Except when the measurement of dust concentration is carried out at the same time as the determination, such procedures as the drying and weighing of filter paper are unnecessary.

- 3) **Preparation of gas absorption bottle** Into gas absorption bottles, place respectively 50 ml of absorption liquid specified in 5.1.3 c) 1) depending on the analytical ingredient, introduce the gas which comes from a dust collector, and prepare to catch the analytical ingredient contained in gas in the absorption liquid⁽⁷⁾.

Note (7) The volume of a absorption bottle shall be decided according to the flow rate of isokinetic sampling. In case of large quantity of flow rate, the bottle shall be replaced by larger capacity one, and the amount of absorption liquid shall be adjusted so that the nozzle of the absorption bottle is immersed in the surface of absorption liquid. In the case of violent foaming, an anti-foaming plate may be used.

- c) **Sampling** Carry out sampling by using the sampling apparatus shown in figures 1 to 4-2 following the specification in 9.4 of JIS Z 8808.
- d) **Measurement of quantity of sucked gas** The gas quantity sucked in for sampling shall be measured according to 9.5 of JIS Z 8808.

5.2 Sampling method for gaseous compound such as arsenic hydride, hydrogen selenide or others

5.2.1 Selection of measuring position The measuring position shall be in accordance with 5.1 of JIS K 0095.

5.2.2 Selection of measuring point The measuring point shall be in accordance with 5.2 of JIS K 0095.

5.2.3 Sampling apparatus The sampling apparatus shall be as follows:

- a) **Construction of sampling apparatus** The construction of sampling apparatus shall be in accordance with 6.1 of JIS K 0095. The construction of sampling apparatus is shown in figure 7.
- b) **Sampling tube** The sampling tube shall be as specified in 6.3 of JIS K 0095. Its material shall be in accordance with 6.2 of JIS K 0095⁽⁸⁾. Wash previously the sampling tube with water, and store it after drying⁽⁹⁾.

Notes (8) Generally, use such as borosilicate glass, silica glass, tetrafluoroethylene resin.

- (9) When there is the possibility that moisture is condensed, the distance from the sampling tube to the cock (P1) is warmed or heated. When the distance from the sampling tube to the absorption bottle is short, it is not required to fix a bypass at the distance from P1 to P2 in figure 7.

- c) **Filtering material** In order to prevent mixing soot and dust with sample gas, insert suitable filtering material at the end or midway of the sampling tube⁽¹⁰⁾.

Note (10) Generally, use silica wool or alkali-free glass wool.

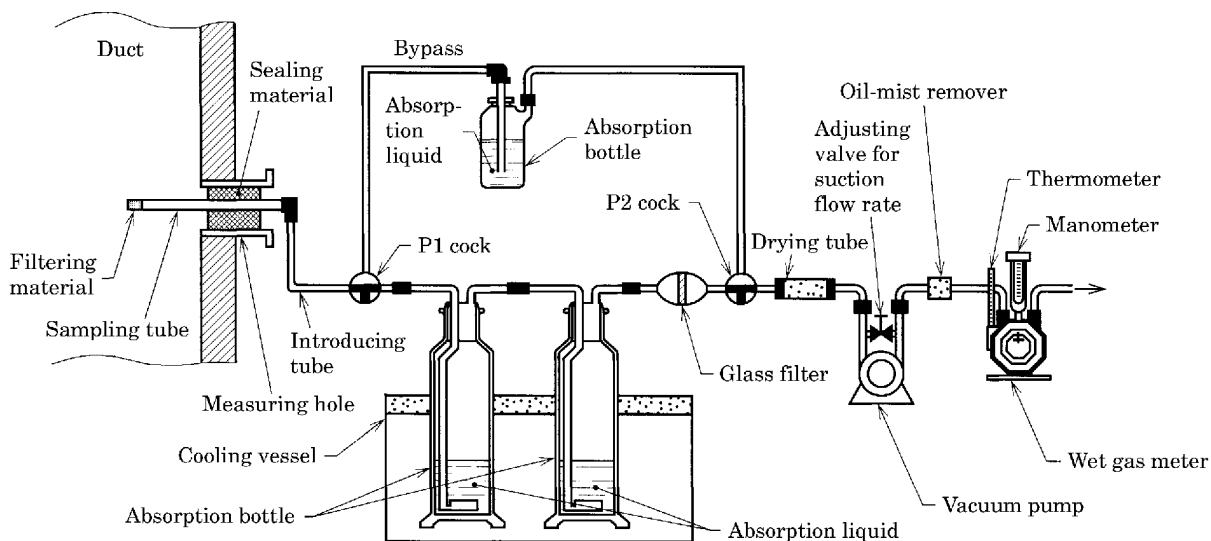


Figure 7 Constructional example of sampling apparatus

- d) **Absorption bottle** The absorption bottle measures 250 ml to 300 ml in capacity, and its example is shown in figure 8. In this case, its material shall be borosilicate glass. In advance, wash it with nitric acid (1+13) or hydrochloric acid (1+13), rinse with water, and dry it. Prepare 2 or more absorption bottles⁽²⁾, and use the following absorption liquids.

- 1) **Absorption liquid for arsenic hydride and gaseous arsenic compounds, etc.** Place 50 ml of absorption liquid (dissolve 0.5 g of potassium permanganate specified in JIS K 8247 in water to make total 100 ml) respectively into each absorption bottle.

- 2) **Absorption liquid for hydrogen selenide and gaseous selenium compounds, etc.** Place 50 ml of hydrobromic acid saturated with bromine (mix one volume of hydrobromic acid specified in **JIS K 8509** and 12 volumes of water, and saturate this solution with bromine specified in **JIS K 8529**) respectively into each absorption bottle.
- e) **Cooling vessel** The cooling vessel contains absorption bottles, and can keep the temperature of absorption liquid at 0 °C to 10 °C⁽⁴⁾.

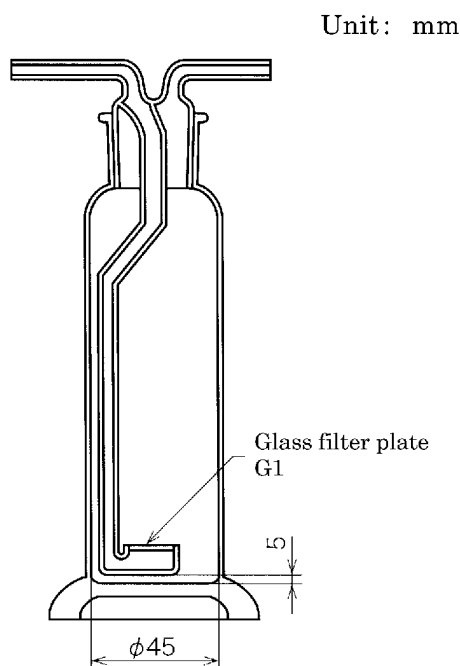


Figure 8 Absorption bottle (example)

5.2.4 Sampling Sampling shall be carried out using a sampling apparatus as shown in figure 7, and shall be in accordance with clause 7 of **JIS K 0095**.

- a) **Measurement of quantity of sucked gas** The quantity of gas sucked into sample shall be measured according to 7.3.6 of **JIS K 0095**. The sampling flow rate shall be approximately 1 L/min.

6 Preparation of sample solution

6.1 Sample solution preparation of cadmium, lead, nickel, manganese, and vanadium

6.1.1 Reagents The reagents shall be as follows:

- a) **Nitric acid (1+1)**, prepared using nitric acid specified in **JIS K 8541**.
- b) **Hydrogen peroxide**, specified in **JIS K 8230**.
- c) **Hydrochloric acid (2+98)**, prepared using hydrochloric acid specified in **JIS K 8180**.

6.1.2 Procedures The procedures shall be as follows:

- a) In the case of sampling on filter paper alone without absorption bottle
- 1) Cut the filter paper with collected material⁽¹¹⁾ from sample gas into suitable size, put them in a 200 ml beaker, add 30 ml of nitric acid (1+1) and 5 ml of hydrogen peroxide, cover it with a watch glass, and heat it for 1 h on a hot plate or boiling water bath.
 - 2) After allowing it to cool to room temperature, wash the watch glass with 10 ml of warm water, and filtrate washings through filter paper Grade 5B. Then, filtrate the supernatant through the filter paper in 1) with care so that as many solid particles as possible remain in the beaker.
 - 3) Add 20 ml of nitric acid (1+1) onto the residue in the beaker, and heat it for 10 min on a hot plate or boiling water bath.
 - 4) After cooling, filtrate it through the filter paper in 1), wash the residue in the beaker with warm water, and filtrate it through the filter paper in 1). Transfer every filtrate into a 100 ml beaker.
 - 5) Evaporate it to dryness on a water bath.
 - 6) Add 10 ml of warm hydrochloric acid (2+98), heat it on a hot plate or boiling water bath to dissolve, allow it to cool, transfer it into a 100 ml measuring flask, add water up to the marked line, and make it sample solution⁽¹²⁾.
 - 7) Separately, take filter paper, carry out the procedures from 1) to 6) on a filter paper, and prepare the solution for blank test.

Notes ⁽¹¹⁾ Collect all materials stuck inside of the tube from suction nozzle to filter paper using a suitable method. For instance, shake out the stuck material from the cylinder, and wash it with a small amount of hydrochloric acid (2+98) or small amount of nitric acid (2+98) in the case of ICP mass spectrometry, and collect all of them into a beaker. In case of chromium, collect it without using water or water solution.

⁽¹²⁾ For ICP mass spectrometry, warm nitric acid (2+98) shall be used.

NOTE : See Annex (normative).

- b) In the case of sampling both by filter paper and by absorption in solution by setting an absorption bottle
- 1) Treat the filter paper with the collected material⁽¹¹⁾ from sample gas similarly to the procedures in a) 1) to a) 4).
 - 2) On the other hand, pour the solution in the absorption bottle into a 300 ml beaker, wash the introducing tube and the absorption bottle with 10 ml to 20 ml of water, put the washings into the 300 ml beaker, add 10 ml of nitric acid (1+1) and 5 ml of hydrogen peroxide, and heat on a hot plate or boiling water bath nearly to dryness.
 - 3) When organic matter is hardly decomposed, repeat the procedure of 2) until the solution turns pale yellow or colourless, filtrate the contents, put the filtrate in the 100 ml beaker of a) 4), wash the residue in the 300 ml beaker with a small amount of water, and put the washings into the 100 ml beaker after filtration.

- 4) Thereafter, follow the procedures from **a) 5)** to **a) 6)**.
- 5) Separately, carry out the same procedures as the procedures from **1)** to **4)** on filter paper and absorption liquid, and prepare the solution for blank test.

NOTE : See Annex (normative).

6.2 Preparation of chromium sample solution

6.2.1 Reagents The reagents shall be as follows:

- a) **Sulfuric acid (1+2)**, prepared using sulfuric acid specified in **JIS K 8951**.
- b) **Hydrofluoric acid**, specified in **JIS K 8819**.
- c) **Sodium carbonate**, specified in **JIS K 8625**.
- d) **Sodium nitrate**, specified in **JIS K 8562**.
- e) **Nitric acid (1+1)**, prepared using nitric acid specified in **JIS K 8541**.

6.2.2 Implements and apparatus The implements and apparatus shall be as follows:

- a) **Porcelain crucible**
- b) **Platinum crucible**, with 20 ml to 30 ml capacity.
- c) **Electric furnace**

6.2.3 Procedures The procedures shall be as follows:

- a) In the case of sampling on filter paper alone without an absorption bottle
 - 1) Cut the filter paper, on which collected material⁽¹¹⁾ from sample gas sticks, into suitable size, put them in a porcelain crucible, raise gradually its temperature in an electric furnace up to 550 °C and keep it for 2 h⁽¹³⁾.
 - 2) Transfer the contents in the porcelain crucible into a platinum crucible. Add gradually several drops of sulfuric acid and 20 ml of hydrofluoric acid⁽¹⁴⁾, and heat it in a draft chamber on a hot plate until white fume of sulfuric acid appears. After allowing it to cool, add 10 ml of hydrofluoric acid, and heat again up until white fume by sulfuric acid almost disappears. Then, raise gradually the temperature of the platinum crucible by direct heating until no white fume of sulfuric acid appears, and allow it to cool.
 - 3) Add 5 g of sodium carbonate and 0.3 g of sodium nitrate in the platinum crucible, mix them well, put a cover on it, heat directly to raise gradually its temperature, when it gets about 900 °C, sometimes shake the crucible to mix them well, and further heat for about 20 min.
 - 4) After cooling it, add warm water into the platinum crucible, and transfer the melt⁽¹⁵⁾ into a 200 ml beaker.

- 5) Heat the beaker on a water bath to leach chromate out. Filtrate it through filter paper Grade 5B⁽¹⁶⁾, and wash the residue on the filter paper with warm water⁽¹⁷⁾.
- 6) Put together filtrate and washings, and neutralize it with sulfuric acid (1+2). Evaporate it⁽¹⁸⁾, allow it to cool, transfer it into a 100 ml measuring flask, add water up to the marked line, and make it sample solution.
- 7) Separately, take a filter paper, carry out the same procedures as the procedures from 1) to 6)⁽¹⁹⁾, and prepare the solution for blank test.

Notes ⁽¹³⁾ Ashing operation of analysis sample is carried out to ash the organic matters in sample, and this operation can prevent the loss of melt and the damage of platinum crucible caused by violent reaction due to decomposition of organic matters while making alkali fusion.

⁽¹⁴⁾ The hydrofluoric-acid treatment on the ashed sample has the purpose to accelerate the subsequent fusion reaction by expelling and removing silicic acid as silicon tetrafluoride. The heating to emit white fume of sulfuric acid shall be done with care not to make bumping, and the temperature of the hot plate shall be also observed.

⁽¹⁵⁾ When it is difficult to take out alkali melt from platinum crucible with warm water, place the platinum crucible and its cover in a 200 ml beaker in which about 50 ml warm water has been put, and carry out the procedures in 5). Before filtration, take out the crucible and cover after washing them with water. Add washings into the beaker.

⁽¹⁶⁾ Long duration for filtration easily results in negative error, so it is preferable to make filtration at 70 °C to 80 °C.

⁽¹⁷⁾ When it is apprehended that chromium content remains in undissolved residue, dry the undissolved residue together with filter paper, retry ashing procedure, and again carry out melting procedures on this ash.

⁽¹⁸⁾ When quantity of liquid exceeds 100 ml, concentration process is needed, but when the totaled quantity of filtrate and washings is 80 ml or less, this process is not needed.

⁽¹⁹⁾ In this time, the heating procedure in 3) is continued just until the content of crucible becomes melting condition.

NOTE : When methods other than absorptiometry are adopted for determination, the following procedures, instead of the procedures in 6) and 7), shall be carried out.

Take filtrate and washings into a 200 ml beaker, add 20 ml of nitric acid (1+1), evaporate it⁽²⁰⁾, allow it to cool, transfer it into a 100 ml measuring flask, add water up to the marked line, and make it the sample solution.

Separately, carry out the same procedures⁽¹⁹⁾ as above on a filter paper, and prepare the solution for blank test.

Note ⁽²⁰⁾ Boiling shall be carried out to expel carbon dioxide, dissolve completely, and the quantity of solution shall be made 80 ml or less.

- b) In the case of sampling both by filter paper and by absorption in absorption solution by setting an absorption bottle
- 1) Treat the filter paper, on which the collected material⁽¹¹⁾ from sample gas sticks, as shown in the procedures in **a) 1)**, and transfer the contents in the crucible into a platinum crucible.
 - 2) On the other hand, put the solution kept in the absorption bottle into a 300 ml beaker, wash the introducing tube and absorption bottle with 10 ml to 20 ml of water, transfer the washings into the 300 ml beaker, add 10 ml of nitric acid (1+1) and 1 ml of sulfuric acid (1+2), and heat it on a hot plate to near dryness. In this time, when organic matter is hard to decompose, add 10 ml of nitric acid (1+1) until the liquid becomes pale yellow or colourless, heat it on a hot plate to near dryness, and repeat these procedures. After cooling, put the contents into the platinum crucible in **1)**.
 - 3) Add gradually 20 ml of hydrofluoric acid⁽¹⁴⁾ into the platinum crucible, and heat it in a draft chamber on a hot plate until white fume of sulfuric acid appears. After allowing it to cool, add 10 ml of hydrofluoric acid, and heat again until white fume by sulfuric acid almost disappears. Then, raise gradually the temperature of the platinum crucible by direct heating until no white fume of sulfuric acid appears, and allow it to cool.
 - 4) Thereafter, follow the procedures from **a) 3)** to **a) 6)**.
 - 5) Separately, carry out the same procedures from **1)** to **4)** on filter paper and absorption liquid to prepare the solution for blank test.

Information : Taken sample may be treated as follows to prepare sample solution.

Cut filter paper, on which collected material from sample gas sticks, into suitable size, put them in a nickel crucible, then heat it in an electric furnace by gradual raising of temperature finally up to 550 °C for 2 h. After cooling it, add about 5 g of sodium peroxide, mix them well, additionally add a little amount of sodium peroxide so as to cover the surface, heat it by flame of a burner directly and gently at initial stage, then heat strongly after it melts, and keep it red-hot molten state for about 3 min (but avoid to make it very high temperature), then allow it to cool.

Place the crucible into a 300 ml beaker in which 50 ml of water has been put, add little by little carefully 50 ml of warm water, and heat it to leach the contents out. Then, take out the crucible while washing it with water, add sodium peroxide little by little while shake the leached liquid, heat it to boil, and oxidize completely chromium to chromium (VI) and simultaneously decompose excessive sodium peroxide.

Transfer the solution together with precipitate into a 250 ml measuring flask, add water up to the marked line, shake it sufficiently, and allow it to stand. Filtrate supernatant solution through filter paper Grade 5B, discard initial 10 ml filtrate, and make the next filtrate sample solution.

Separately, carry out similar procedures on a filter paper, and prepare the solution for blank test.

When sample wash taken owing to both depositing on filter paper and absorbing in the liquid by setting an absorption bottle, prepare the sample solution and blank-test solution according to the procedure in **b**).

Instead of a nickel crucible, an iron, alumina, or zirconia crucible may be used. The tongs for crucible made of stainless steel shall not be used.

6.3 Preparation of beryllium sample solution

6.3.1 Reagents The reagents shall be as follows:

- a) **Nitric acid**, specified in **JIS K 8541**.
- b) **Hydrofluoric acid**, specified in **JIS K 8819**.
- c) **Sulfuric acid**, specified in **JIS K 8951**.
- d) **Perchloric acid (60 %)**, specified in **JIS K 8223**.
- e) **Hydrochloric acid (2+1)**, prepared using hydrochloric acid specified in **JIS K 8180**.

6.3.2 Procedures The procedures shall be as follows:

- a) In the case of sampling on filter paper alone without an absorption bottle
 - 1) Cut the filter paper, on which collected material⁽¹⁾ from sample gas sticks, into suitable size, put them into a 100 ml tetrafluoroethylene resin beaker, add 30 ml of nitric acid, 10 ml of hydrofluoric acid, and 2 ml of sulfuric acid, and heat it gently on a hot plate until white fume of sulfuric acid emits.
 - 2) After cooling it, add 10 ml of nitric acid and 5 ml of perchloric acid (60 %), and heat it with gradual raising of temperature until dense white fume of sulfuric acid appears.
 - 3) When organic matter in sample is hardly decomposed, repeat the procedures in **2**) until the solution turns pale yellow or colourless, and then evaporate it to dryness.
 - 4) After cooling it, add 10 ml of hydrochloric acid (2+1), cover it with a watch glass, heat it on a water bath to dissolve for about 1 h, filtrate it through filter paper Grade 5A, and transfer the filtrate into a 50 ml measuring flask. Wash the residue on the filter paper with water, put the washings together with filtrate, add water up to the marked line, and make this solution sample solution⁽²⁾.
 - 5) Separately, carry out the same procedures as the procedures from **1**) to **4**) on a filter paper, and prepare the solution for blank test.

Note ⁽²⁾ For ICP mass spectrometry, nitric acid (2+1) shall be used.

- b) In the case of sampling both by filter paper and by absorption in absorption solution by setting an absorption bottle
- 1) Cut the filter paper, on which collected material⁽¹¹⁾ from sample gas sticks, into suitable size, put them into a 100 ml tetrafluoroethylene resin beaker, add 30 ml of nitric acid, 10 ml of hydrofluoric acid, and 2 ml of sulfuric acid, heat it gently on a hot plate until white fume of sulfuric acid appears, and allow it to cool.
 - 2) On the other hand, put the solution kept in the absorption bottle into a 300 ml beaker, wash the introducing tube and absorption bottle with 10 ml to 20 ml of water, transfer the washings into the 300 ml beaker, and heat it on a hot plate to condense it until it becomes about 50 ml. Transfer the contents into the 100 ml tetrafluoroethylene resin beaker in 1), wash it with a little amount of water, and put the washings into the 100 ml tetrafluoroethylene resin beaker.
 - 3) Thereafter, follow the procedures from a) 2) to a) 4).
 - 4) Separately, carry out the same procedures as the procedures from 1) to 3) on a filter paper and absorption liquid, and prepare the solution for blank test.

6.4 Preparation of arsenic and selenium sample solutions

6.4.1 Reagents The reagents shall be as follows:

- a) **Nitric acid**, specified in **JIS K 8541**.
- b) **Sulfuric acid (1+1)**, prepared using sulfuric acid specified in **JIS K 8951**.
- c) **Perchloric acid (60 %)**, specified in **JIS K 8223**.

6.4.2 Procedures The procedures shall be as follows:

- a) Cut the filter paper, on which collected material⁽¹¹⁾ from sample gas sticks, into suitable size, put them into a 250 ml beaker, add 50 ml of nitric acid and 5 ml of sulfuric acid (1+1), heat gently for 10 min to decompose it, add 25 ml of warm water, allow it to stand, and transfer its supernatant into another 300 ml beaker.
- b) Add 50 ml of nitric acid onto residue in the 250 ml beaker, heat it with gradual raising temperature for 10 min, add 25 ml of warm water, filtrate it through filter paper Grade 5A, and put the filtrate into the 300 ml beaker in a).
- c) On the other hand, place the solution kept in the absorption bottle into the 300 ml beaker mentioned above, wash the introducing tube and absorption bottle with 10 ml to 20 ml water, and put the washings into the 300 ml beaker.
- d) Add 5 ml of nitric acid and 5 ml of perchloric acid (60 %), heat it with gradual raising temperature, cover it with a watch glass when white fume of perchloric acid appears, and decompose organic matter while keeping perchloric acid flowing down on the wall of the beaker.
- e) When organic matter in sample is hardly decomposed, repeat the procedures in d) until the solution turns pale yellow or colourless⁽²²⁾. Wash the wall of the

beaker with a small amount of water, and decompose the organic matter until white fume appears again.

- f) After cooling it, add 100 ml of water to dissolve soluble salts, filtrate it through filter paper Grade 5A, and transfer filtrate into a 250 ml measuring flask. Wash the residue on filter paper with water, put the washings and filtrate together, add water up to the marked line, and make this solution the sample solution.
- g) Separately, carry out the procedures in **a)** to **f)** on filter paper and absorption liquid, and prepare the solution for blank test.

Note ⁽²²⁾ Added quantity of nitric acid and perchloric acid shall be the same in the case for the preparation of blank-test solution.

6.5 Preparation of gaseous arsenic compound and gaseous selenium compound (arsenic hydride, hydrogen selenide) sample solutions

6.5.1 Reagents The reagents shall be as follows:

- a) **Hydroxylammonium chloride solution (100 g/L)**, prepared by dissolving 10 g of hydroxylammonium chloride specified in **JIS K 8201** in water to make total 100 ml⁽²³⁾.

Note ⁽²³⁾ When ICP mass spectrometry is used for the analytical method, it shall be carried out after confirming that it is not influenced by the molecular ion of argon chlorine (ArCl).

- b) **Hydrochloric acid (1+120)**, prepared using hydrochloric acid specified in **JIS K 8180**⁽²⁴⁾.

Note ⁽²⁴⁾ For ICP mass spectrometry, nitric acid (1+120) shall be used.

6.5.2 Procedures The procedures shall be as follows:

- a) Transfer the contents in an absorption bottle, in which sample was caught, into a 250 ml measuring flask, wash the absorption bottle, introducing tube and the like with water, put the washings into the measuring flask, add drop by drop hydroxylammonium chloride solution (100 g/L) until colour of bromine disappears, and add hydrochloric acid (1+120) up to the marked line⁽²⁵⁾. Make this solution the sample solution.

Note ⁽²⁵⁾ For ICP mass spectrometry, nitric acid (1+120) shall be used.

- b) Separately, carry out the procedures in **a)** on absorption liquid, and prepare the solution for blank test.

7 Determination of cadmium For determination of cadmium, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry or ICP mass spectrometry shall be applied.

7.1 Flame atomic absorption spectrometry Spray the sample solution in acetylene—air flame, measure the atomic absorption caused by cadmium at 228.8 nm wavelength, and determine cadmium.

Determination range: Cd 0.05 mg/L to 2 mg/L

Repeatability: 2 % to 10 % by variation coefficient (depending on apparatus and measuring condition)

a) **Reagents** The reagents shall be as follows:

- 1) **Cadmium reference solution (Cd 0.1 mg/ml)**, prepared as follows: take 0.100 g of cadmium (not less than 99.9 %) and dissolve in 20 ml of nitric acid (1+1). Expel nitrogen oxide by boiling, and then after allowing it to cool, transfer it into a 1 000 ml volumetric flask, and add water up to the marked line. Alternatively, use Cd100 of the cadmium reference solution specified in **JIS K 0012**.
- 2) **Cadmium reference solution (Cd 10 µg/ml)**, prepared by taking 50 ml of cadmium reference solution (Cd 0.1 mg/ml) prepared in 1) in a 500 ml measuring flask, adding 10 ml of nitric acid (1+1), and adding water up to the marked line.

b) **Implement and apparatus** The implement and apparatus shall be as follows:

- 1) **Apparatus for flame atomic absorption spectrometry**
- 2) **Cadmium hollow cathode lamp**

c) **Procedures** The procedures shall be as follows:

- 1) Spray the sample solution prepared in **6.1** in flame according to clause **6** of **JIS K 0121**, and read the indicated value⁽²⁶⁾ at 228.8 nm wavelength.
- 2) For blank test, carry out the procedures in 1) on blank-test solution in the same manner as done on the test solution, and correct the indicated value obtained on sample solution.
- 3) On the working curve, obtain the amount of cadmium, and calculate the concentration of cadmium (Cd mg/L) in sample solution. The working curve shall be prepared as follows.

Working curve Take stepwise from 0.5 ml to 20 ml⁽²⁷⁾ of cadmium reference solution (Cd 10 µg/ml) into as many 100 ml measuring flasks, add respectively acid to make them the same condition as sample solution, and add water up to the marked line⁽²⁸⁾. Carry out the procedures in 1) on these solutions. Separately, as a blank test, add acid to water to make this the same condition as reference solution that was used for working-curve preparation, carry out the procedures in 1), correct the indicated value obtained on reference solution, and plot the relation curve between the amount of cadmium (Cd) and the indicated value. Prepare the working curve when sample solution is measured.

Notes ⁽²⁶⁾ Absorbance or its proportionated value.

⁽²⁷⁾ When solvent extraction is adopted, the quantity of cadmium reference solution (Cd 10 µg/ml) shall be suitably lessened.

⁽²⁸⁾ When, according to NOTE 1 or NOTE 2, butyl acetate layer, 4-methyl-2-pentanone layer, or 2,6-diethyl-4-heptanone layer is directly sprayed, the method to prepare working curve shall be as follows.

Dilute cadmium reference solution (Cd 10 µg/ml) to suitable concentration (Cd 0.1 µg/ml to Cd 1 µg/ml), take stepwise 0.5 ml to 20 ml of this solution, make these solutions about 100 ml, carry out the same procedures at NOTE 1 or NOTE 2 and **1**) and **2**) as those for sample solution, and plot the relation curve between the amount of cadmium (Cd) and indicated value.

NOTES 1 Take a suitable quantity of sample solution, add 10 ml of diammonium hydrogen citrate solution (100 mg/L) and 2 or 3 drops of meta-cresol purple solution (1 g/L) for an indicator, and add aqueous ammonia (1+1) until the solution gives faint purple colour.

Add 5 ml of sodium diethyldithiocarbamate solution (10 g/L), shake it, add 20 ml of butyl acetate specified in **JIS K 8377**, shake it vigorously for 1 min, and allow it to stand. Separate butyl acetate layer and put it in a 100 ml beaker. Add 5 ml of butyl acetate in water layer and repeat the extraction process. Put extracted butyl acetate layer into the beaker above.

Spray either the extracted butyl acetate layer added with butyl acetate to make liquid quantity definite or directly the butyl acetate layer which is once extracted under the specified extraction condition, and carry out atomic absorption spectrometry. Instead of butyl acetate, 4-methyl-2-pentanone (methylisobutyl ketone) specified in **JIS K 8903** may be used.

2 Take a suitable quantity of sample solution, and adjust its pH as 3.5 to 4.0. Add 20 ml of ammonium sulfate solution (saturated). Add 5 ml of ammonium 1-pyrrolidinecarbodithioate (ammonium pyrrolidine-*N*-dithiocarbamate) (APDC) solution (10 g/L), shake it gently, and allow it to stand for 3 min. Then, add 10 ml of 4-methyl-2-pentanone specified in **JIS K 8903**, shake it vigorously for 3 min, and separate completely water layer and organic layer. In organic layer, not only cadmium but also nickel, lead and so on are contained.

Instead of 4-methyl-2-pentanone, 2,6-dimethyl-4-heptanone (DIBK) may be used. In this case, because there is almost no mutual miscibility between water and 2,6-dimethyl-4-heptanone, smaller addition shall suffice.

3 When a lot of zinc, copper, or others is contained in sample solution, add hydrobromic acid specified in **JIS K 8509** into a suitable quantity of sample solution to make it about 0.5 mol/L hydrobromic acid solution, take its 50 ml, add 10 ml of 4-methyl-2-pentanone solution of trioctyl amine (1 vol %), shake it, and extract cadmium. The extracted 4-methyl-2-pentanone layer shall be sprayed as it is to carry out atomic absorption spectrometry.

4 Existence of a large amount of halogenide of alkali metals gives positive error due to its molecular absorption or light scattering. In such a case, either previously separate the cadmium or employ the background correcting device.

7.2 Electrothermal atomic absorption spectrometry After the sample is pre-treated, palladium nitrate (II) shall be added as matrix modifier, be atomized in an electric furnace, and the atomic absorbance due to cadmium be measured at 228.8 nm wavelength and cadmium shall be determined according to the standard addition method.

Determination range: Cd 0.5 µg/L to 10 µg/L

Repeatability: 2 % to 10 % by variation coefficient (varies depending on the apparatus and measurement condition)

NOTE : This method is easily influenced by the class and concentration of existing acid or salt. It shall therefore be applied only to the samples which are little influenced by these and the samples shall be prepared such that the concentration of acid will stay constant during the measurement.

a) **Reagents** The reagents shall be as follows:

- 1) **Water**, of A3 specified in **JIS K 0557**. Confirm prior to use that it will be of no hindrance to the analysis by a blank test with respect to the element to be determined.
- 2) **Nitric acid (1+1)**, prepared by using the high purity grade reagent of nitric acid specified in **JIS K 9901**.
- 3) **Palladium nitrate (II) solution (Pd 1 000 µg/ml)**, of matrix modifier for atomic absorption spectrometry, diluted for use.
- 4) **Cadmium reference solution (Cd 0.1 µg/ml)**, prepared by taking 10 ml of cadmium reference solution (Cd 10 µg/ml) in **7.1 a) 2)** in a 1 000 ml volumetric flask, adding 20 ml of nitric acid (1+1), and then adding water up to the marked line.

b) **Implements and apparatus** The implements and apparatus shall be as follows:

- 1) **Apparatus for electrothermal atomic absorption spectrometry**, of electrothermal system and capable of correcting the background.
- 2) **Heating unit**, of graphite or heat resistant metal.
- 3) **Cadmium hollow cathode lamp**
- 4) **Flow gas**, of Grade 2 of argon specified in **JIS K 1105**.
- 5) **Micropipette**, 10 µl to 500 µl of piston operated micro-volumetric apparatus specified in **JIS K 0970** or automatic injection apparatus.

c) **Preparatory operations** The preparatory operations shall be as follows:

- 1) Treat the sample according to **6.1**.

d) **Procedures** The procedures shall be as follows:

- 1) Take an appropriate amount of the sample, on which the preparatory operations in **c)** have been carried out, in 20 ml volumetric flasks respectively. Prepare one sample without the cadmium reference solution (Cd 0.1 µg/ml)

and another sample to which the said cadmium reference solution has been added stepwise not less than in three concentrations in the range between 0.1 ml and 2 ml. Add nitric acid (1+1) to each of these solutions so that they are uniform in the acid concentration. Add water up to the marked line.

- 2) Inject a definite amount (for example, 10 μL to 50 μL) of this solution and the same volume of palladium nitrate (II) solution (Pd 1 000 $\mu\text{g}/\text{ml}$) in an electroheating furnace by using a micropipette or an automatic injection apparatus. Carry out drying (for 30 s to 40 s at 100 °C to 120 °C), ashing (for 30 s to 40 s at 500 °C to 800 °C) and atomizing⁽²⁹⁾ (for 3 s to 6 s at 1 600 °C to 2 200 °C) according to clause 6 of **JIS K 0121** and read the indicated value⁽³⁰⁾ at 228.8 nm wavelength.
- 3) For the blank test, carry out the operation in 1) on the blank test solution in a similar manner to the sample solution and correct the indicated value obtained on the sample solution.

Notes ⁽²⁹⁾ The conditions of drying, ashing, atomizing vary depending on apparatus, and in some cases, also vary depending on the injection amount of sample and the concentration of existing salts.

⁽³⁰⁾ The operation in 2) is repeated at least three times continuously and it shall be confirmed that the indicated values coincide.

7.3 ICP emission spectrometry Spray the sample solution into inductively coupled plasma, measure the emission by cadmium at 214.438 nm wavelength, and determine cadmium.

Determination range: Cd 0.008 mg/L to 2 mg/L

Repeatability: 2 % to 10 % by variation coefficient (depending on apparatus and measuring condition)

a) **Reagents** The reagents shall be as follows:

- 1) **Cadmium reference solution (Cd 8 $\mu\text{g}/\text{ml}$)**, prepared by taking 40 ml of cadmium reference solution (Cd 0.1 mg/ml) prepared in **7.1 a) 1)** into a 500 ml measuring flask, adding 10 ml of nitric acid (1+1), and adding water up to the marked line.
- 2) **Mixed reference solution [(Cd 8 μg , Pb 10 μg , Ni 10 μg , Mn 10 μg)/ml]**, prepared as follows: take 40 ml of cadmium reference solution (Cd 0.1 mg/ml) in **7.1 a) 1)**, 50 ml of lead reference solution (Pb 0.1 mg/ml) in **8.1 a) 1)**, 50 ml of nickel reference solution (Ni 0.1 mg/ml) in **9.1 a) 9)**, 50 ml of manganese reference solution (Mn 0.1 mg/ml) in **10.1 a) 4)** into each 500 ml measuring flask, add 3 ml of nitric acid (1+1), and add water up to the marked line. Prepare this solution when it is needed.

b) **Apparatus** Apparatus for ICP emission spectrometry

c) **Procedures** The procedures shall be as follows:

- 1) Spray the sample solution prepared in **6.1** into a plasma torch according to clause 5 of **JIS K 0116**, and measure the emission intensity at 214.439 nm wavelength⁽³¹⁾ ⁽³²⁾ ⁽³³⁾.

- 2) For a blank test, carry out the procedures in 1) on blank-test solution in the same manner as done on the sample solution, and correct the emission intensity obtained on sample solution.
- 3) On the working curve, obtain the amount of cadmium, and calculate the concentration (Cd mg/L) of cadmium in sample solution. The working curve shall be prepared as follows.

Working curve Take stepwise from 0.1 ml to 25 ml⁽³⁴⁾ ⁽³⁵⁾ of cadmium reference solution (Cd 8 µg/ml) into as many 100 ml measuring flasks, add respectively acid to make them the same condition as sample solution, and add water up to the marked line. Carry out the procedures in 1) on these solution. Separately, carry out a blank test using water by adding acid to it to make it the same condition as the reference solution used for working-curve preparation, carry out the procedures in 1), correct the emission intensity obtained on reference solution, and plot the relation curve between the amount of cadmium (Cd) and the emission intensity. Prepare the working curve when sample solution is measured.

Notes ⁽³¹⁾ Internal standard method is also available. When the internal standard method is adopted, take suitable quantity of sample solution into a 100 ml measuring flask, add 10 ml of yttrium solution (Y 50 µg/ml) [Weigh 0.318 g of yttrium (III) oxide, dissolve it in 5 ml of hydrochloric acid specified in **JIS K 8180** with heating, after cooling it, transfer it into a 250 ml measuring flask, and add water up to the marked line. Take 10 ml of this solution into a 200 ml measuring flask, and add water up to the marked line.], add acid to make it the same condition as the sample solution prepared in c) 1), and add water up to the marked line. Carry out the spray procedures on this solution as shown in c) 1), measure the emission intensity at 214.438 nm and 371.029 nm (yttrium) wavelength, and obtain the emission-intensity ratio of cadmium to yttrium.

Separately, take stepwise from 0.1 ml to 25 ml of cadmium reference solution (Cd 8 µg/ml) into as many 100 ml measuring flasks, add respectively 10 ml of yttrium solution (Y 50 µg/ml), add acid to make them the same condition as the sample solution in c) 1), and add water up to the marked line. Carry out the spray procedures on these solutions as specified in c) 1), measure its emission intensity at 214.438 nm and 371.029 nm wavelength, plot the relation curve between cadmium concentration and the emission-intensity ratio of cadmium to yttrium, and make it a working curve. On this working curve, obtain the amount of cadmium corresponding to the emission-intensity ratio that was obtained from sample solution, and calculate the concentration of cadmium (Cd mg/ml) in sample solution.

- ⁽³²⁾ When high concentration of salt in sample solution prevents applying of working-curve method, the standard additional method which is specified in 5.8.3 (2) of **JIS K 0116** can be applied. In this case, however, background correction is necessary for every kind of sample solution.

- (³³) When the apparatus is capable of using high order spectral line, the high order spectral line may be used. If the accuracy and correctness are certified, other wavelength may be used.
- (³⁴) The working curve, which is applicable when xylene layer is directly sprayed after the procedures in NOTE were carried out, shall be prepared as follows; dilute cadmium reference solution (Cd 8 µg/ml) to get suitable concentration (Cd 0.1 µg/ml to Cd 0.8 µg/ml), take stepwise from 0.1 ml to 25 ml of the solution, make them a definite quantity, carry out the same procedures in NOTE and c) 1) and 2) as those for sample solution, and plot the relation curve between the amount of cadmium (Cd) and emission intensity.
- (³⁵) When cadmium, lead, nickel, and manganese are simultaneously tested, use the mixed reference solution in a) 2), and prepare the working curve under the test condition of each metal element.

NOTE : When sodium, potassium, magnesium, calcium and the like in sample solution have high concentration and cadmium is rather low, the following procedures are also serviceable for measurement.

Take a suitable quantity of sample solution in a beaker, add 10 ml of acetic acid-sodium acetate buffer solution (pH 5) [Dissolve 19.2 g of sodium acetate trihydrate specified in **JIS K 8371** and 3.4 ml of acetic acid specified in **JIS K 8355** in water to make total 1 L.], and control its pH to be 5.2 by adding aqueous ammonia (1+1) or nitric acid (1+10). Transfer this solution into 1 L (or 200 ml to 500 ml) separatory funnel, add 2 ml of ammonium 1-pyrrolidine-carbodithioate solution (20 g/L) and 2 ml of methanol solution of hexamethyl-eneammonium hexamethylene-carbamodithioate (hexamethyleneammonium hexamethylenedithiocarbamate) (20 g/L), mix them, add definite quantity (5 ml to 20 ml) of xylene specified in **JIS K 8271**, shake vigorously for about 5 min, and allow it to stand. Discard the water layer, put the xylene layer in a ground stoppered test tube, and use it for determination of cadmium. This solution is also available for determination of cadmium, lead, nickel, manganese, and vanadium.

The acetic acid—sodium acetate buffer solution (pH 5) to be used for this procedure shall be refined owing to shaking the mixture of this solution, 2 ml of ammonium 1-pyrrolidinecarbodithioate solution (20 g/L), 2 ml of methanol solution of hexamethyleneammonium hexamethylene-carbamodithioate (20 g/L) and 5 ml to 20 ml of xylene, before it is used.

7.4 ICP mass spectrometry The internal standard material is added to the sample solution, sprayed in inductively coupled plasma through the sample introducing part, and the ion currents in the respective mass/number of charges of cadmium and internal standard material are measured and cadmium is determined by obtaining the ratio of the ion current of cadmium to the ion current of the internal standard material.

Determination range: Cd 0.5 µg/L to 25 µg/L, Cd 10 µg/L to 500 µg/L

Repeatability: 2 % to 10 % by variation coefficient (varies depending on the apparatus and the measuring conditions)

a) **Reagents** The reagents shall be as follows:

- 1) **Water**, of A3 specified in **JIS K 0557**. Confirm prior to use that it will be no hindrance to the analysis by a blank test with respect to the element to be determined.
- 2) **Nitric acid**, specified in **JIS K 8541**.
- 3) **Yttrium solution (Y 1 µg/ml)**, prepared by taking 20 ml of yttrium solution (Y 50 µg/ml) as described in Note ⁽³¹⁾ of **7.3** in a 1 000 ml volumetric flask, adding 1.5 ml of nitric acid (1+1) and adding water to the marked line. This solution shall be prepared newly for each use. The adequate internal standard material other than yttrium may be used as specified in Note ⁽³⁷⁾ of **7.4**.
- 4) **Cadmium reference solution (Cd 1 µg/ml)**, prepared by taking 10 ml of cadmium reference solution (Cd 0.1 mg/ml) of **7.1 a) 1** in a 1 000 ml volumetric flask, adding 20 ml of nitric acid (1+1), and then adding water up to the marked line.
- 5) **Cadmium reference solution (Cd 50 ng/ml)**, prepared by taking 50 ml of cadmium reference solution (Cd 1 µg/ml) of **4** in a 1 000 ml volumetric flask, adding 3 ml of nitric acid (1+1), and then adding water up to the marked line. This solution shall be prepared newly for each use.
- 6) **Mixed reference solution [(Cd 1 µg, Pb 1 µg, Ni 1 µg, Mn 1 µg, V 1 µg)/ml]**, prepared as follows: take 10 ml of cadmium reference solution (Cd 0.1 mg/ml) of **7.1 a) 1**, 10 ml of lead reference solution (Pb 0.1 mg/ml) of **8.1 a) 1**, 10 ml of nickel reference solution (Ni 0.1 mg/ml) of **9.1 a) 9**, 10 ml of manganese reference solution (Mn 0.1 mg/ml) of **10.1 a) 4** and 10 ml of vanadium reference solution (V 0.1 mg/ml) of **11.1 a) 5** in a 1 000 ml volumetric flask respectively, add 1.5 ml of nitric acid (1+1), and then add water up to the marked line. This solution shall be prepared newly for each use.
- 7) **Mixed reference solution [(Cd 50 ng, Pb 50 ng, Ni 50 ng, Mn 50 ng, V 50 ng)/ml]**, prepared as follows: take 5 ml of cadmium reference solution (Cd 10 µg/ml) of **7.1 a) 2**, 5 ml of lead reference solution (Pb 10 µg/ml) of **8.1 a) 2**, 5 ml of nickel reference solution (Ni 10 µg/ml) of **9.2 a) 1**, 5 ml of manganese reference solution (Mn 10 µg/ml) of **10.2 a) 1**, and 5 ml of vanadium reference solution (V 10 µg/ml) of **11.4 a) 1** in a 1 000 ml volumetric flask respectively, add 1.5 ml of nitric acid (1+1), and then add water up to the marked line. This solution shall be prepared newly for each use.

b) **Apparatus** An ICP mass spectrometer apparatus shall be used.

NOTES 1 The apparatus having the performance equivalent to inductively coupled plasma as an ion source may be used.

2 It shall be confirmed that the contamination from the material of sampling cone and skimmer cone is not recognized.

c) **Procedures** The procedures shall be as follows⁽³⁶⁾ ⁽³⁷⁾:

- 1) Take an appropriate amount of sample solution (containing 0.05 µg to 50 µg as Cd) prepared in **6.1** in a 100 ml volumetric flask, add 1 ml of yttrium solution (Y 1 µg/ml), add nitric acid (1+1) so that the final concentration of

nitric acid is a definite concentration of 0.1 mol/L to 0.5 mol/L, and then add water up to the marked line.

- 2) Make the ICP mass spectrometer apparatus ready for operation, spray the solution of 1) in inductively coupled plasma through the sample introducing part, read the indicated value⁽³⁹⁾ at mass/number of charges⁽³⁸⁾ of cadmium and yttrium, and obtain the ratio of the indicated value of cadmium to the indicated value of yttrium.
- 3) Take the same amount of water as the sample for the blank test, carry out similarly the operations of 1) to 4), obtain the ratio of the indicated value of cadmium to the indicated value of yttrium, and correct the ratio of the indicated value of cadmium to yttrium obtained from the sample.
- 4) Obtain the amount of cadmium from the working curve and calculate the concentration of cadmium (Cd $\mu\text{g/L}$) in the sample.

Working curve Take 1 ml to 50 ml⁽⁴⁰⁾ of cadmium reference solution (Cd 50 ng/ml or Cd 1 $\mu\text{g/ml}$) in 100 ml volumetric flasks stepwise, add 1 ml of yttrium solution (Y 1 $\mu\text{g/ml}$), add nitric acid (1+1) so as to be the same concentration of acid as the sample of 1), and then add water up to the marked line. Carry out the operation of 2) on this solution.

Separately, add 1 ml of yttrium solution (Y 1 $\mu\text{g/ml}$) in a 100 ml volumetric flask for the blank test, add nitric acid (1+1) so that the concentration of acid is the same as the sample of 1), add water up to the marked line, correct the ratio of indicated value obtained with respect to the reference solution by carrying out the operation of 2), and then prepare the relation curve of the ratio of the indicated value to the amount of cadmium (Cd) to the indicated value of yttrium. Prepare the working curve when the sample is measured.

Notes ⁽³⁶⁾ Care shall be taken so as not to be contaminated from the analyst. Use of the rubber gloves (without dusting powder) specified in **JIS T 9107** is recommended.

⁽³⁷⁾ When the presence of interfering substances is unknown, the interference to the measured mass number of the objective element and the internal standard material can be presumed by carrying out the qualitative analysis according to ICP mass spectrometer before determination. When the interference is recognized, the reduction of interference is attempted by the alteration of internal standard material and dilution of sample or pretreatment.

⁽³⁸⁾ For the setting of mass number, table 2 should be referred to. When a stable isotope is present, the interference due to spectral interference can be presumed by carrying out the measurement by using the mass/number of charges of some isotopes. When a molecular ion interferes, the production of molecular ion may be restrained by using a collision cell and the like. When it is influenced still, the matrix to be an interference is removed by using an adequate separation method, and then the measurement is carried out.

⁽³⁹⁾ The ion current at the mass/number of charges of objective element or its proportional value.

- (40) When cadmium, lead, nickel, manganese and vanadium are simultaneously measured, it is recommended to prepare the working curve under the test conditions of respective metallic elements by using the mixed reference solution [(Cd 1 µg, Pb 1 µg, Ni 1 µg, Mn 1 µg, V 1 µg)/ml] or the mixed reference solution [(Cd 50 ng, Pb 50 ng, Ni 50 ng, Mn 50 ng, V 50 ng)/ml].

NOTE : If, by the operation in Note (37), the influence of interfering substance on the sample concerned is presumed to be negligible, the determination may be carried out by the working curve method without adding the internal standard material.

Table 2 Example of measurement mass

Name of element	Number of mass	Example of interfering ion
Cadmium	111	MoO ⁺
	114	MoO ⁺ , Sn ⁺
Lead	208	—
	206	
	207	
Nickel	58	CaO ⁺ , Sn ⁺⁺ , Fe ⁺
	60	CaO ⁺ , Sn ⁺⁺
	62	CaO ⁺ , Sn ⁺⁺
Manganese	55	KO ⁺
Vanadium	51	ClO ⁺ , ClN ⁺
Chromium	53	ClO ⁺
	52	SO ⁺ , ClOH ⁺ , ArO ⁺ , ArC ⁺
	50	SO ⁺ , Ti ⁺ , V ⁺ , ArN ⁺
Beryllium	9	—
Arsenic	75	ArCl ⁺
Selenium	78	ArAr ⁺ , NiO ⁺
	82	ZnO ⁺
	77	ArCl ⁺ , NiO ⁺

8 Determination of lead For determination of lead, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, ICP emission spectrometry or ICP mass spectrometry shall be applied.

8.1 Flame atomic absorption spectrometry Spray the sample solution in acetylene—air flame, measure the atomic absorption caused by lead at 283.3 nm wavelength, and determine lead.

Determination range: Pb 1 mg/L to 20 mg/L

Repeatability: 2 % to 10 % by variation coefficient (depending on apparatus and measuring condition)

a) **Reagents** Reagents shall be as follows:

- 1) **Lead reference solution (Pb 0.1 mg/ml)**, prepared as follows: weigh 0.100 g of lead (99.9 % or more) specified in **JIS K 8701**, dissolve it in 40 ml of nitric acid (1+3), heat it to expel nitrogen compounds, allow it to cool, transfer it into a 1 000 ml measuring flask, and add water up to the marked line; or weigh 0.160 g of lead (II) nitrate specified in **JIS K 8563**, dissolve it in the mixture of 20 ml of nitric acid (1+1) and suitable quantity of water, transfer whole solution into a 1 000 ml measuring flask, and add water up to the marked line. Alternatively, employ Pb100 of lead standard solution specified in **JIS K 0015**.
- 2) **Lead reference solution (Pb 10 µg/ml)**, prepared by taking 50 ml of lead reference solution (Pb 0.1 mg/ml) of 1) in a 500 ml measuring flask, adding 10 ml of nitric acid (1+1), and adding water up to the marked line.

b) **Implement and apparatus** Implement and apparatus shall be as follows:

- 1) **Apparatus for flame atomic absorption spectrometry**
- 2) **Lead hollow cathode lamp**

c) **Procedures** The procedures shall be follows:

- 1) Spray the sample solution prepared in **6.1** in flame according to clause **6** of **JIS K 0121**, and read the indicated value⁽²⁶⁾ at 283.3 nm wavelength.
- 2) For a blank test, carry out the procedures of 1) on blank-test solution, in the same manner as done on the sample solution, and correct the indicated value obtained on sample solution.
- 3) On the working curve, obtain the amount of lead, and calculate the concentration of lead (Pb mg/L) in sample solution. The working curve shall be prepared as follows.

Working curve Take stepwise from 1 ml to 20 ml⁽⁴¹⁾ of lead reference solution (Pb 0.1 mg/ml) into as many 100 ml measuring flasks, add to each of them acid to make them the same condition as the sample solution, and add water up to the marked line⁽⁴²⁾. Carry out the procedures of **1)** on these solutions. Separately, carry out a blank test using water by adding acid to make this the same condition as reference solution that was used for working-curve preparation, carry out the procedures in **1)**, correct the indicated value attained on reference solution, and plot the relation curve between amount of lead (Pb) and the indicated value. Prepare the working curve when sample solution is measured.

Notes ⁽⁴¹⁾ When solvent extraction is adopted, the quantity of lead reference solution (Pb 0.1 mg/ml) shall be suitably lessened.

⁽⁴²⁾ When, according to NOTE 1 or NOTE 2, butyl acetate layer, 4-methyl-2-pentanone layer, or 2,6-dimethyl-4-heptanone layer is directly sprayed, the method to prepare working curve shall be as follows.

Dilute lead reference solution (Pb 0.1 mg/ml) to suitable concentration (Pb 1 µg/ml to Pb 5 µg/ml), take stepwise 1 ml to 20 ml of this solution, make them a definite quantity, carry out the same procedures