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**Methods for determination of nitrogen
oxides 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 Association Committee as the result of proposal for revision of Japanese Industrial Standard submitted by Japan Environmental Measurement and Chemical Analysis Association (JEMCA)/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 0104: 2000** is replaced with this Standard.

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Methods for determination of nitrogen oxides in flue gas

Introduction

This Japanese Industrial Standard has been prepared based on the first edition of ISO 11564 published in 1998 with some modifications of the technical contents by addition of the matters not specified in the corresponding International Standard and deletion of parts of the corresponding matters.

The portions with continuous sidelines or dotted underlines in this Standard are the matters in which the contents of the corresponding International Standard have been modified. A list of modifications with the explanations is given in Annex JB. Annex JA specifies the matters not in the corresponding International Standard.

1 Scope

This Standard specifies the methods to determine nitrogen oxides contained in flue gas.

The flue gasses stated in this Standard are defined as the gases which are exhausted into a flue, chimney, duct, etc. from such processes as fuel combustion, metal surface treatment, inorganic and organic chemical reaction and denitration process.

NOTE : The International Standard corresponding to this Standard and the symbol of degree of correspondence are as follows.

ISO 11564:1998 *Stationary source emissions—Determination of the mass concentration of nitrogen oxides—Naphthylethylenediamine photometric method* (MOD)

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

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

JIS B 7982	<i>Automated measuring systems and analyzers for nitrogen oxides in flue gas</i>
JIS K 0050	<i>General rules for chemical analysis</i>
JIS K 0055	<i>General rules for calibration method of gas analyzer</i>
JIS K 0095	<i>Methods for sampling of flue gas</i>
JIS K 0115	<i>General rules for molecular absorptiometric analysis</i>

JIS K 0127	<i>General rules for ion chromatographic analysis</i>
JIS K 0211	<i>Technical terms for analytical chemistry (General part)</i>
JIS K 0212	<i>Technical terms for analytical chemistry (optical part)</i>
JIS K 0213	<i>Technical terms for analytical chemistry (Electrochemistry part)</i>
JIS K 0214	<i>Technical terms for analytical chemistry (Chromatography part)</i>
JIS K 0215	<i>Technical terms for analytical chemistry (Analytical instrument part)</i>
JIS K 0216	<i>Technical terms for analytical chemistry (Environmental part)</i>
JIS K 0557	<i>Water used for industrial water and wastewater analysis</i>
JIS K 1101	<i>Oxygen</i>
JIS K 1107	<i>Nitrogen</i>
JIS K 8013	<i>Zinc powder (Reagent)</i>
JIS K 8019	<i>Sodium nitrite (Reagent)</i>
JIS K 8032	<i>Acetonitrile (Reagent)</i>
JIS K 8085	<i>Ammonia solution (Reagent)</i>
JIS K 8180	<i>Hydrochloric acid (Reagent)</i>
JIS K 8197	<i>N-1-Naphthylethylenediamine dihydrochloride (Reagent)</i>
JIS K 8230	<i>Hydrogen peroxide (Reagent)</i>
JIS K 8267	<i>Sodium formate (Reagent)</i>
JIS K 8295	<i>Glycerol (Reagent)</i>
JIS K 8355	<i>Acetic acid (Reagent)</i>
JIS K 8371	<i>Sodium acetate trihydrate (Reagent)</i>
JIS K 8548	<i>Potassium nitrate (Reagent)</i>
JIS K 8574	<i>Potassium hydroxide (Reagent)</i>
JIS K 8576	<i>Sodium hydroxide (Reagent)</i>
JIS K 8586	<i>Sulfanilic acid (Reagent)</i>
JIS K 8622	<i>Sodium hydrogen carbonate (Reagent)</i>
JIS K 8625	<i>Sodium carbonate (Reagent)</i>
JIS K 8741	<i>Sulfuric acid, fuming (Reagent)</i>
JIS K 8798	<i>Phenol (Reagent)</i>
JIS K 8863	<i>Boric acid (Reagent)</i>
JIS K 8866	<i>Sodium tetraborate decahydrate (Reagent)</i>
JIS K 8951	<i>Sulfuric acid (Reagent)</i>

JIS K 8983	<i>Copper (II) sulfate pentahydrate (Reagent)</i>
JIS K 9066	<i>Sulfanilamide (Reagent)</i>
JIS K 9704	<i>2-Amino-2-hydroxymethyl-1,3-propanediol (Reagent)</i>
JIS K 9808	<i>2-Bis (2-hydroxyethyl)amino-2-hydroxymethyl-1,3-propanediol (Bis-Tris)</i>
JIS P 3801	<i>Filter paper (for chemical analysis)</i>
JIS T 3201	<i>Glass syringes</i>
JIS Z 8808	<i>Methods of measuring dust concentration in flue gas</i>

3 Terms and definitions

For the purposes of this Standard, the terms and definitions given in JIS K 0211, JIS K 0212, JIS K 0213, JIS K 0214, JIS K 0215 and JIS K 0216 apply.

4 General matters

The general matters shall be as follows.

- The general matters common to the chemical analysis shall be as specified in JIS K 0050.
- The general matters common to the flue gas sampling method shall be as specified in JIS K 0095.
- The general matters common to the ion chromatography shall be as specified in JIS K 0127.
- The general matters common to the molecular absorptiometric analysis shall be as specified in JIS K 0115.
- Water to be used for the analyses shall be of A2 or A3 specified in clause 4 of JIS K 0557 or the equivalent.
- Reagents with the highest grade or the appropriate quality in the relevant JIS, if any, shall be used. However, if any relevant JIS does not exist, reagents of a quality adequate for the analysis shall be used.
- Reference solution for which the preparing method is specified for respective test items, which is traceable or which is diluted to a definite concentration shall be used.
- Apparatus and implements which have the specified functions shall be used.
- Flue gas used for an analysis of nitrogen oxides, the absorbing solution of the flue gas, etc. shall not be disposed improperly.

NOTE : For traceable reagents, JCSS-marked reagents specified in the national measurement standard (Measurement Law, Article 134) are applicable.

5 Type and summary of analysis methods

The type and summary of analysis methods shall be as follows.

- Chemical analysis** The type and summary of analysis methods shall be as given in table 1.

Table 1 Type and summary of analysis methods

Type of analysis methods	Summary of analysis methods				Applicable condition
	Outline	Sampling	Determination range ^{a)} vol ppm (mg/m ³)	Target gas for analysis	
Zinc reduction naphthylethyl-enediamine absorptiometry (hereafter referred to as "Zn-NEDA method".)	Make nitrogen oxides in the sample gas oxidize with ozone, and absorb into the absorption solution to be converted to nitrate ion. After making this nitrate ion be reduced to nitrite ion with zinc powder, add sulfanilamide and naphthylethylenediamine solution for colouring and measure the absorbance (545 nm).	Evacuated flask method or syringe method Absorption solution: 0.005 mol/L sulfuric acid Quantity of solution: 20 ml	Evacuated flask method: 1 to 50 (2 to 100) Syringe method: 5 to 250 (10 to 510)	NO + NO ₂	
Naphthyl-ethylenediamine absorptiometry (hereafter referred to as "NEDA method".)	Make nitrogen oxides in the sample gas absorb into the alkaline absorption solution to be converted to nitrite ion. Add sulfanilamide and naphthylethylenediamine dihydrochloride solution for colouring and measure the absorbance (545 nm).	Evacuated flask method or syringe method Absorption solution: alkaline hydrogen peroxide solution- sodium formate solution Quantity of solution: 50 ml	Evacuated flask method: 3 to 500 (5 to 1 000) Syringe method: 7 to 1 200 (13 to 2 500)	NO + NO ₂	
Ion chromatography	Make nitrogen oxides in the sample gas oxidize with ozone or oxygen, absorb into the absorption solution to be converted to nitrate ion. Introduce it into an ion chromatograph, and record its chromatogram.	Evacuated flask method or syringe method Absorption solution: 0.005 mol/L sulfuric acid-hydrogen peroxide solution (1+99) Quantity of solution: 20 ml	Evacuated flask method: 4 to 1 400 (8 to 2 800) Syringe method: 19 to 7 200 (39 to 14 000)	NO + NO ₂	
Phenol disulfonic acid absorptiometry (hereafter referred to as "PDS method".)	Make nitrogen oxides in the sample gas oxidize with ozone or oxygen, and absorb into the absorption solution to be converted to nitrate ion. Add phenol disulfonic acid for colouring and measure the absorbance (400 nm).	Evacuated flask method or syringe method Absorption solution: 0.005 mol/L sulfuric acid-hydrogen peroxide solution (1+99) Quantity of solution: 20 ml	Evacuated flask method: 10 to 300 (20 to 620) Syringe method: 12 to 4 200 (24 to 8 400)	NO + NO ₂	See 7.4.1.
Saltzman absorptiometry	Pass nitrogen dioxide in the sample gas through the absorption colouring liquid for colouring and measure the absorbance (545 nm).	Absorption bottle method Absorption colouring liquid: sulfanilic acid-naphthylethyl-enediamine acetic acid solution Quantity of solution: 25 ml	5 to 200 (10 to 400)	NO ₂	See 7.5.1.
Note ^{a)} Indicates the following volume of the sample gas when sampling: about 1 000 ml in case of evacuated flask (1 L). However, 500 ml in case of NEDA method, 200 ml in case of the syringe (200 ml), 100 ml in case of absorption bottle. In case of NEDA method, when the concentration exceeds 1 000 mg/m ³ , the sample solution for analysis can be measured up to 5 000 mg/m ³ by diluting or taking partly.					

In addition to the methods as specified in table 1, the simultaneous analysis of nitrogen oxides, sulfur oxides and hydrogen chloride by ion chromatography is specified in Annex JA.

- b) **Automated measuring method** The automated measuring method for nitrogen oxides in flue gas shall be in accordance with the method specified in **JIS B 7982**.

6 Method of gas sampling

The sampling method of sample gas to be used for chemical analysis shall be in accordance with the evacuated flask method, the syringe method and the absorption bottle method.

Choose the spot where representative sample gas for analysis can be taken, sample principally at least twice the sample gas at shorter intervals at the same sampling spot, and use all of them for analysis.

6.1 Evacuated flask method

The evacuated flask method shall be as follows.

This method shall be applied to Zn-NEDA method, NEDA method, ion chromatography and PDS method.

6.1.1 Preparation of reagents and reagent solution

a) Reagents

- 1) **Sulfuric acid** Specified in **JIS K 8951**.
- 2) **Copper (II) sulfate pentahydrate** Specified in **JIS K 8983**.
- 3) **Sodium hydroxide** Specified in **JIS K 8576**.
- 4) **Sodium carbonate** Specified in **JIS K 8625**.
- 5) **Sodium formate** Specified in **JIS K 8267**.
- 6) **Hydrogen peroxide** Specified in **JIS K 8230**.
- 7) **Oxygen** Specified in **JIS K 1101**.

b) Preparation of reagent solution

- 1) **Sulfuric acid (1+17)**
- 2) **Copper (II) sulfate solution** Dissolve 1 g of copper (II) sulfate pentahydrate in water, transfer it into a 1 000 ml one-mark volumetric flask and add water up to the marked line. Take 10 ml of this solution into a 100 ml one-mark volumetric flask and add water up to the marked line.
- 3) **Sodium hydroxide solution (40 g/L)** For filling the washing bottle. Dissolve 4 g of sodium hydroxide in water to make 100 ml.
- 4) **Absorption solution** Use any of the following solution.
 - 4.1) **In case of zinc reduction naphthylethylenediamine absorptiometry (Zn-NEDA method)**

0.005 mol/l sulfuric acid Take about 800 ml of water into a 1 000 ml one-mark volumetric flask add 5 ml of sulfuric acid (1+17) and then add water up to the marked line.

4.2) **In case of naphthylethylenediamine method (NEDA method)**

Alkaline hydrogen peroxide solution- sodium formate solution Dissolve 48 g of sodium hydroxide, 40 g of sodium carbonate and 5 mg of sodium formate in about 800 ml of water; add 20 ml of hydrogen peroxide solution (30 %) and then transfer it into a 1 000 ml one-mark volumetric flask while rinsing, add water up to the marked line.

4.3) **In case of ion chromatography**

0.005 mol/L sulfuric acid-hydrogen peroxide solution (1+99) Take about 800 ml of water into a 1 000 ml one-mark volumetric flask, add 5 ml of sulfuric acid (1+17) and 10 ml of hydrogen peroxide solution and then add water up to the marked line.

4.4) **In case of phenol disulfonic acid absorptiometry (PDS method)**

0.05 mol/L sulfuric acid-hydrogen peroxide solution (1+99) Take about 800 ml of water into a 1 000 ml one-mark volumetric flask, add 50 ml of sulfuric acid (1+17) and 10 ml of hydrogen peroxide solution, and then add water up to the marked line.

6.1.2 Implements and apparatus

a) Gas sampling implements

- 1) **Evacuated flask for gas sampling** As shown in figure 1, having a three-way cock, about 1 000 ml in capacity [hereafter referred to as “evacuated flask (E)”] ¹⁾. Its unobstructed capacity shall have been obtained from the mass which was weighed when filling the evacuated flask (E) with water in accordance with Annex H of JIS K 0050. The flask shown in c) of figure 1 is for the case of sampling using the evacuated flask with two cocks in NEDA method.
- 2) **Syringe for injecting absorption solution** As specified in JIS T 3201, having 20 ml or 100 ml capacity [hereafter referred to as “syringe (L)”].
- 3) **Syringe for adding oxygen or ozone** As specified in JIS T 3201, having 200 ml capacity [hereafter referred to as “syringe (M)”].

Note ¹⁾ When using the flask shown in b) of figure 1, care shall be taken not to allow the grease used to enter the flask.

b) Pressure meter

- 1) **Manometer** U-shaped open tube mercury manometer, capable of measuring pressure difference of about 27 kPa or one capable of obtaining the value equivalent to that, or closed tube mercury manometer or one capable of obtaining the value equivalent to that.
- 2) **Pressure meter** The mercury type capable of measuring 0.1 kPa to 100 kPa or one capable of obtaining the value equivalent to that. This pressure meter is used for NEDA method.

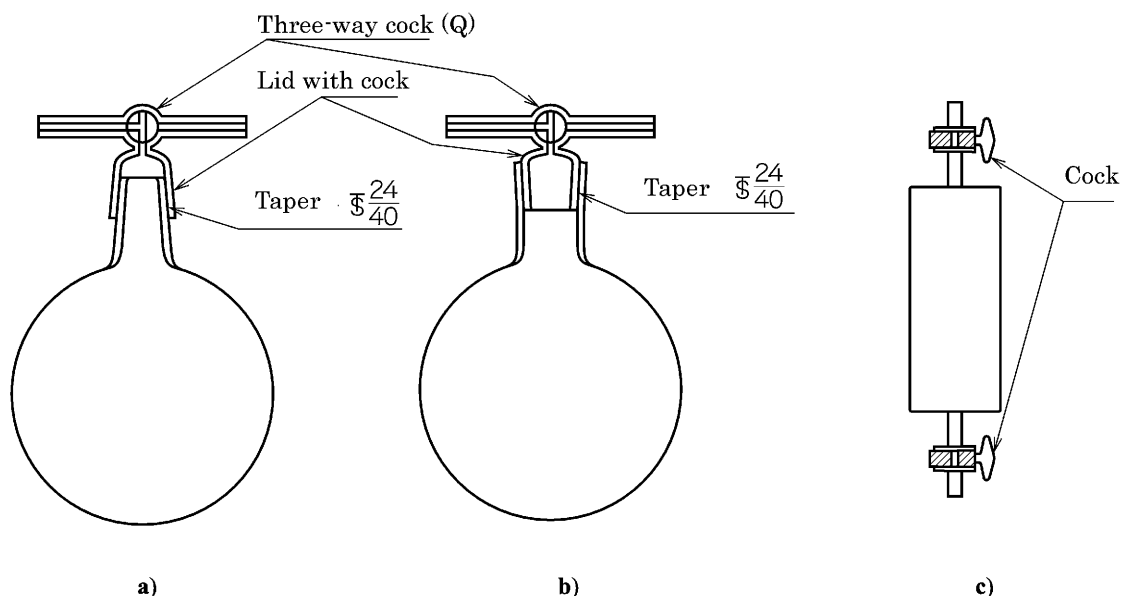


Figure 1 Example of evacuated flask for gas sampling (capacity of about 1 L)

c) **Sampling apparatus for sample gas** The apparatus, constructed as shown in figure 2, shall be equipped with the following conditions.

- 1) The sampling probe shall be made of the material, resisting corrosive gas contained in flue gas, such as glass tube quartz glass tube, or polytetrafluoroethylene tube.
- 2) In order to prevent dust from mixing into sample gas, plug suitable filter medium at end of sampling tube or at suitable place.

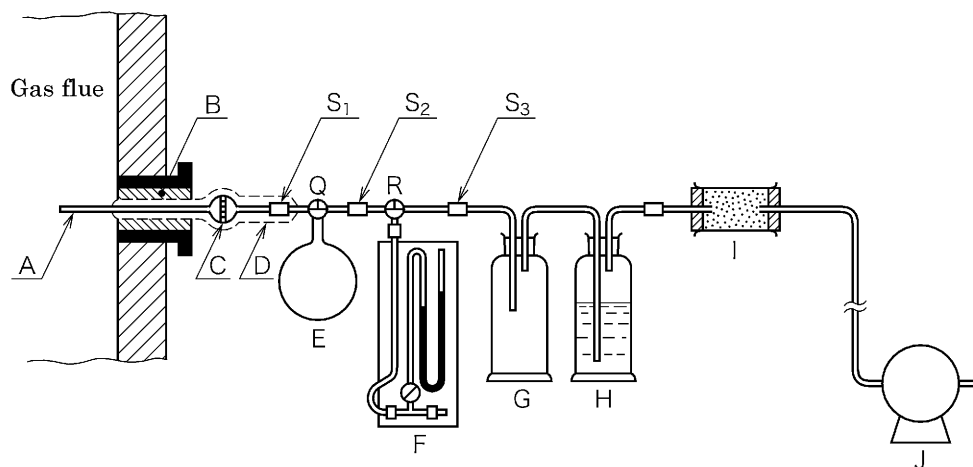
In addition, the example of filter materials when attaching them to the outside of the gas flue using the sampling apparatus shown in b) of figure 2 according to NEDA method shall be given in figure 3.

Use the filter material, making no chemical reaction with the components in flue gas, such as silica wool, or alkaliless glass wool.

- 3) In order to prevent the moisture contained in the sample gas from being condensed, provide a device to heat the place from gas sampling tube to three-way cock (Q).

In addition, to connect these parts, use commonly ground connecting tube, silicone rubber tube or polytetrafluoroethylene resin tube. Set up the line of piping as short as possible, and if it is apprehended that moisture will condense, heat to about 120 °C along the tube from the sampling tube to three-way cock (Q).

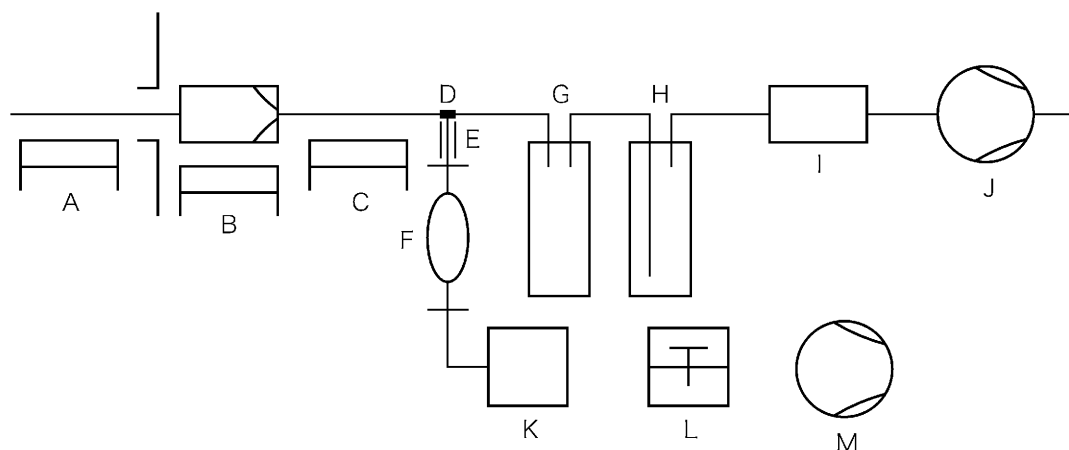
- 4) Set up the whole apparatus so that there is no leakage at any connection.



- | | |
|--|--|
| A : Gas sampling tube | G : Vacant bottle (to prevent back flow) |
| B : Thermal insulating material | H : Washing bottle [containing sodium hydroxide solution (40 g/L)] |
| C : Filter material | I : Drying pump ^{a)} |
| D : Heater | J : Suction pump |
| E : Gas sampling evacuated flask [evacuated flask (E)] | Q, R : Three-way cocks |
| F : Closed tube mercury manometer | S ₁ , S ₂ , S ₃ : Silicone rubber tubes |

Note ^{a)} For desiccant, use granular silica gel or calcium chloride.

a) Zn-NEDA method, ion chromatography, PDS method



- | | |
|--|--|
| A : Sampling probe | H : Washing bottle [containing sodium hydroxide solution (40 g/L)] |
| B : Filter material | I : Drying tube ^{a)} |
| C : Sampling line | J : Suction pump |
| D : T-piece | K : Pressure meter |
| E : Capillary | L : Thermometer |
| F : Gas sampling flask | M : Vacuum pump |
| G : Vacant bottle (to prevent back-flow) | |

b) NEDA method

Figure 2 Example of sampling apparatus of sample gas

Unit: mm

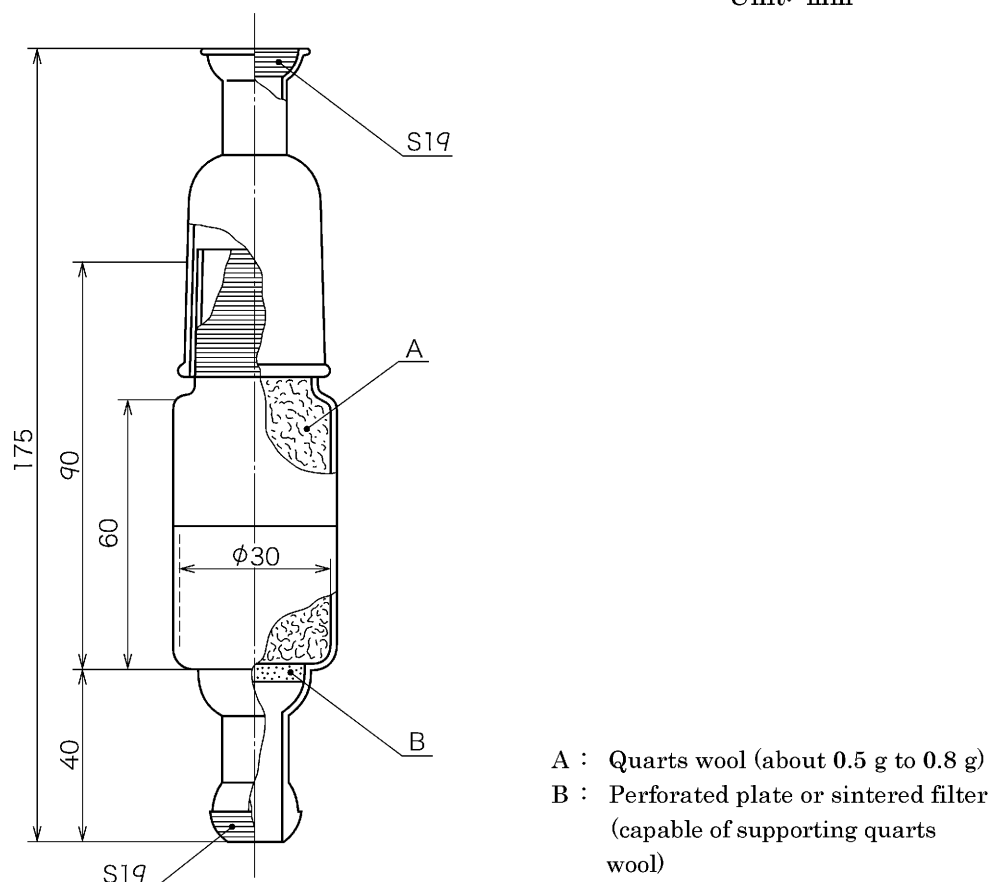
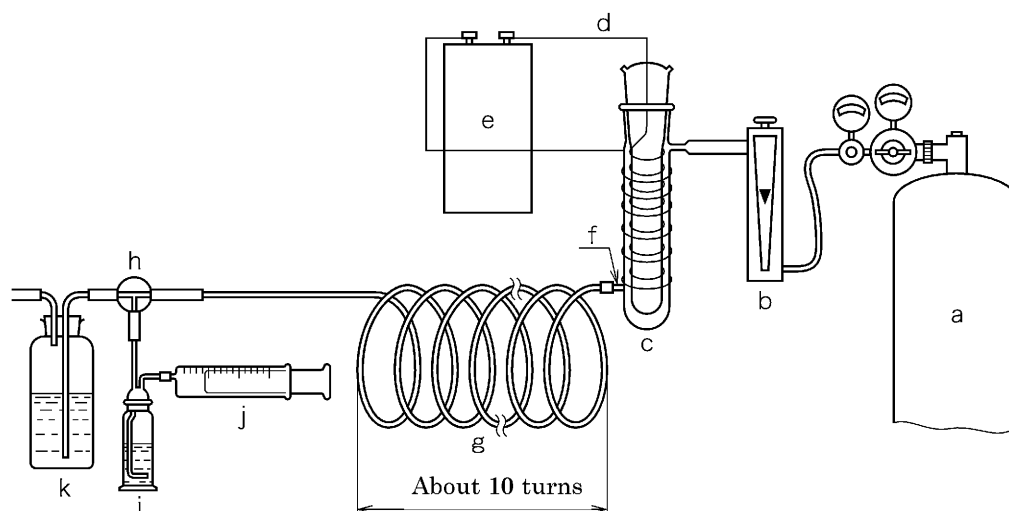


Figure 3 Example of particle filter

- d) **Ozone generator** As illustrated in figure 4, capable of obtaining ozone concentration of about 1 ml /100 ml. It shall have the least production of nitrogen oxides, and the variation of production amount shall be very small.

Upon generating ozone, nitrogen oxides generate at the same time. Since the nitrogen oxides thus generated must be removed by converting fully to dinitrogen pentaoxide (N_2O_5) through the reaction with ozone, they shall be forced to pass through the polytetrafluoroethylene tube (g) of about 10 m in length and furthermore the bottle (i) containing sodium hydroxide solution (40 g/L) to absorb nitrogen oxides. In addition, the sodium hydroxide solution (40 g/L), when showing a high value in the blank test, shall be replaced with the fresh solution.



- | | |
|--|---|
| a : High pressure vessel containing oxygen | g : Ethylene tetrafluoride resin tube for oxidation of nitrogen oxides (for example, a coil of about 10 turns made of a tube of 6 mm in inside diameter, 8 mm in outside diameter and 10 m in length) |
| b : Flow meter | h : Three-way cock |
| c : Ozone generating bottle | i : Bottle for absorbing nitrogen oxides, containing sodium hydroxide solution (40 g/L) |
| d : Copper wire (1 mm in diameter) | j : Ozone adding syringe (M) |
| e : Neon transformer | k : Water seal bottle |
| f : Inlet of ozone-containing oxygen | |

Figure 4 Example of ozone generator

6.1.3 Procedures for sampling

The procedures for sampling shall be carried out as follows.

However, in case of NEDA method, the procedures in a) and b) shall not be carried out. Furthermore, in case of sampling with the evacuated flask with two cocks in accordance with NEDA method, the sampling by using the apparatus constructed as shown in b) of figure 2 shall be performed, but the procedures for sampling shall be carried out in accordance with the method described in the following.

In addition, symbols shown in following shall be in accordance with a) of figure 2.

- a) Remove the lid with cock from the dried evacuated flask (E), inject 20 ml of any absorption solution specified in 4) of b) of 6.1.1 for each analysis method with a syringe (L: see figure 7) or with a pipette, and put the lid with cock on the evacuated flask (E).

The lid and cock of the evacuated flask (E) shall not be greased too much. Fluorocarbon type of grease, etc. which is inactive against nitrogen oxides shall be used.

- b) Connect the evacuated flask (E) to the vacuum pump as shown in figure 2. Open the three-way cock (Q) to the side of the vacuum pump [⊕²⁾], reduce the pressure in the evacuated flask (E) until the absorption solution boils, and then close the three-way cock (Q) (⊕).

Since it does not always boil, shake the flask gently in that case.

Note ²⁾ The directions of the cocks shown hereinafter are based on the arrangement of a) of figure 2.

- c) Turn the three-way cock (R) the side of the closed tube mercury manometer (F) (⊕) [the cock (Q) directions still as shown by ⊕] and suction the sample gas with the suction pump (J) until the moisture in the tube does not condense to water.
- d) Prior to the gas sampling, turn the three-way cock (R) to the side of the evacuated flask (E) (⊕), then, turn the cock (Q) to the side of the closed tube mercury manometer (F)(⊕), and measure and record the pressure (P_1) in the evacuated flask (E). Since, in this case, there is possibility of leakage, if the pressure is 10.1 kPa or over, the ground part shall be regreased, and carry out the procedure after b) again.
- e) Return the three-way cocks (Q) and (R) to their original position (⊕, ⊕). At the same time, measure and record the ambient temperature (t) of the evacuated flask (E).
- f) Turn the three-way cock (Q) to the side of the evacuated flask (E) (⊕) to allow the sample gas to enter the evacuated flask (E), and close the cock (Q) (⊕), and stop the vacuum pump (J).

In addition, for the procedure in case of NEDA method, turn the three-way cock (R) to the side of the evacuated flask (⊕), and then turn the three-way cock (Q) to the side of the evacuated flask and the pressure meter (⊕), take the sample gas, and close the cock when the pressure becomes 10 kPa to 60 kPa according to the concentration of NO_x in the sample gas (⊕).

- g) Take the evacuated flask (E) out of the sampling apparatus of sample gas at the silicone rubber tubes (S_1 , S_2) and shake the flask for 1 min to mix.
- h) Leave the evacuated flask (E) still until it cools down to the room temperature, connect the three-way cock (Q) with the open tube mercury manometer, open the cock (Q) to the connecting side and read the mercury level difference on the manometer, find the pressure (P_t) in the evacuated flask (E), and then close the cock (Q). At the same time, measure and record the atmospheric pressure (P_a) and the ambient temperature (t) of the room. In case of NEDA method, use the pressure meter in 2) of b) of 6.1.2.

In f) and h), the absolute pressure in the flask is the atmospheric pressure reduced by the mercury level difference. If the pressure difference in the flask is positive, add it to the atmospheric pressure, and subtract if negative.

6.1.4 Preparation of sample solution for analysis

The preparation shall be carried out as follows.

- a) In case of zinc reduction naphthylethylenediamine absorptiometry (Zn-NEDA method)

- 1) As illustrated in figure 4, take 100 ml of ozone-containing oxygen produced by ozone generator into the syringe (M) for adding ozone, immediately connect the syringe (M) to the evacuated flask (E) containing the sample gas taken according to 6.1.3, open the three-way cock (Q) to the side of the syringe (M), and push the inner cylinder of the syringe (M) gently to force ozone-containing oxygen to enter the evacuated flask (E). Close the three-way cock (Q), and then remove the syringe (M).
- 2) Shake the evacuated flask (E) for 1 min to mix, and then leave it still for about 5 min. Furnish the liquid thus obtained to the analysis as the sample solution.

b) In case of naphthylethylenediamine absorptiometry (NEDA method)

- 1) Connect the syringe (L) containing 50 ml of absorption solution and 5 ml of copper sulfate solution which have been previously mixed to the three-way cock (Q) of the evacuated flask (E) with silicone rubber tube, open the three-way clock (Q) to the side of the syringe, put the mixed solution into the evacuated flask ³⁾.

In addition, when using the evacuated flask with two cocks, the absorption solution may be sucked in by the residual pressure inside the evacuated flask as shown in figure 5.

- 2) Close the three-way cock (Q), detach the syringe (L) from the evacuated flask (E), immediately shake the evacuated flask (E) vigorously for 3 min to mix, or after shaking vigorously for 1 min shake it for 2 min using a shaker.

In order to make a vapour phase reaction with NO, NO₂ and SO₂ minimized, carried out procedures from gas sampling to shaking within 5 min.

- 3) Transfer the content solution in the evacuated flask into a 100 ml one-mark volumetric flask, furthermore wash the evacuated flask (E) with 15 ml of water twice and transfer the washing solution also into the flask.
- 4) Open the stopper of the one-mark volumetric flask, and after leaving it still in the water bath at 80 °C for 30 min, take the flask out of the water bath, make it cool with running water down to the room temperature, add water up to the marked line, and then shake it with its stopper closed. Furnish the liquid thus obtained to the analysis as the sample solution.

Note ³⁾ The rubber glove should be used for protecting hands from the alkaline solution.