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**Testing methods for determination
of trace components in diluent gas
and zero 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 the Chemicals Evaluation and Research Institute, Japan (CERI)/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 0225 : 1990** is replaced with this Standard.

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the original JIS is to be the final authority.

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Testing methods for determination of trace components in diluent gas and zero gas

1 Scope This Japanese Industrial Standard specifies testing methods for determination of trace components of nitrogen oxide, sulfur dioxide, carbon monoxide, carbon dioxide, methane, oxygen, and moisture in diluent gas to be used for manufacturing of standard gas and in zero gas to be employed for calibration of zero point of instrument.

2 Normative references The following standards 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.

- JIS B 7952 *Continuous analyzers for sulfur dioxide in ambient air*
- JIS B 7953 *Continuous analysers for oxides of nitrogen in ambient air*
- JIS C 1302 *Insulation resistance testers*
- JIS G 3459 *Stainless steel pipes*
- JIS K 0032 *Nitrite ion standard solution*
- JIS K 0050 *General rules for chemical analysis*
- JIS K 0055 *General rules for calibration method of gas analyzer*
- JIS K 0103 *Methods for determination of sulfur oxides in flue gas*
- JIS K 0114 *General rules for gas chromatographic analysis*
- JIS K 0115 *General rules for molecular absorptiometric analysis*
- JIS K 0151 *Non-dispersive infrared gas analyzer*
- JIS K 0211 *Technical terms for analytical chemistry (General part)*
- JIS K 0512 *Hydrogen*
- JIS K 0557 *Water used for industrial water and wastewater analysis*
- JIS K 1107 *High purity nitrogen*
- JIS K 8197 *N-1-Naphthylethylenediamine dihydrochloride*
- JIS K 8230 *Hydrogen peroxide*
- JIS K 8247 *Potassium permanganate*
- JIS K 8355 *Acetic acid*
- JIS K 8586 *Sulfanilic acid*
- JIS K 8951 *Sulfuric acid*
- JIS Z 8103 *Glossary of terms used in measurement*
- JIS Z 8401 *Guide to the rounding of numbers*

3 Definitions Definitions of main terms used in this Standard shall be in accordance with **JIS K 0211** and **JIS Z 8103**, and the following:

- a) **diluent gas** The nitrogen or air of suitable quality to be used for dilution of standard gas of high concentration when low concentration standard gas is manufactured, which does not contain such component to cause aging of manufactured standard gas or to give affect to the adjusted value of the manufactured standard gas.
- b) **zero gas** The nitrogen or air to be used for calibration of the zero point of instrument, which does not contain such component as to give affect the measured value.
- c) **sample gas** Generic names of diluent gas and zero gas.
- d) **nitrogen** The gas whose quality is grade 1 or better specified in **JIS K 1107** and filled in a high pressure vessel.
- e) **air** The air whose oxygen concentration is 19 vol % to 23 vol % and filled in a high pressure vessel.
- f) **nitrogen oxide** Total amount of nitrogen monoxide and nitrogen dioxide.

4 Measurement methods and minimum limit of determination Measurement methods and minimum limit of determination for each concentration of the components in sample gas are in accordance with Table 1.

Table 1 Determination methods and minimum limit of determination

Component	Determination method	Minimum limit of determination (vol ppm)
Nitrogen oxide	The method using a nitrogen oxide analyser by a Chemiluminescence	0.005
	Saltzman absorptiometry	0.005
Sulfur dioxide	The method using a sulfur dioxide analyser by an ultraviolet fluorometric method	0.005
	Ion chromatography	0.005
Carbon monoxide	Gas chromatography (attached with a hydrogen-flame ionization detector) ⁽¹⁾	0.05
	The method using an infrared gas analyser	0.05
Carbon dioxide	Gas chromatography (attached with a hydrogen-flame ionization detector) ⁽¹⁾	0.05
	The method using an infrared gas analyser	0.05
Methane	Gas chromatography (attached with a hydrogen-flame ionization detector)	0.05
Oxygen ⁽²⁾	The method using a galvanic cell type oxygen analyser	0.1
	Yellow phosphorus emission type analysis method	0.1

Table 1 (concluded)

Component	Determination method	Minimum limit of determination (vol ppm)
Moisture	The method using an electrostatic capacity type moisture meter	2
	The method using a dew point hygrometer	2 (dew point – 72 °C)

Notes (1) In the gas chromatography (attached with a hydrogen flame ionization detector), a methanation reaction apparatus is necessary.

(2) The measurement of oxygen shall be carried out only when the sample gas is nitrogen.

Remarks : Because an example of the measurement methods and minimum limits of determination are shown in Table 1, the following methods may be employed.

- The methods according to the analytical method of flue gas specified in **JIS**, or the measuring method of continuous analyser for ambient air.
- Accuracy of methods are at least equivalent to those of measurement method shown in Table 1 and confirmed.

5 Measurement of the nitrogen oxide concentration

5.1 The nitrogen oxide analyser using a Chemiluminescence

5.1.1 Apparatuses, instruments and gases The apparatuses, instruments and gases shall be as follows and the constitution of the apparatus is shown in Fig. 1.

- Nitrogen oxide analyser by using a Chemiluminescence** The analyser among those specified in 7.2.2 of **JIS B 7953** and having 0 vol ppm to 0.1 vol ppm range.
- Preparation apparatus of calibration gas** The preparation apparatus of the calibration gas shall be a dilution apparatus with the dilution ratio mixed mode. The materials of its parts to touch the gas are used SUS304 or SUS316 specified in **JIS G 3459** or materials of their adsorptivity and reactivity are at least equivalent to those of stainless steels.
- Nitrogen oxide removing instrument** The nitrogen oxide removing instrument is a stainless-steel U tube of 10 mm to 15 mm in inside diameter and 800 mm to 1 000 mm in length, filled uniformly with 50 g or more of synthetic zeolite (particle size range 177 µm to 250 µm) and activated. This instrument is used by cooling with liquefied argon.

A zero gas purifier which is confirmed the performance at least equivalent to the above instrument may be employed.

- Piping and valves** As the materials of piping and valves, those made of SUS304 or SUS316 specified in **JIS G 3459** shall be used. Further, the piping and valves are to be connected as short as possible so that the play spaces do not generate.

- e) **Pressure regulator** The pressure regulator is a regulator having automatic pressure regulating mechanism, and the material of the part to be touched the gas shall use that of a little or neglectible for adsorptivity and reactivity.
- f) **Refining gas** The refining gases are the ones to be used for diluting the nitrogen monoxide standard gas to a certain concentration when preparing calibration gas of nitrogen monoxide. The nitrogen filled in high-pressure gas vessel for the sample gas is nitrogen, or air filled in the high-pressure gas vessel, for the sample gas is air, is passed through the nitrogen oxide removing apparatus shall be employed.
- g) **Nitrogen monoxide standard gas** The nitrogen monoxide whose concentration is 0.1 vol ppm to 100 vol ppm.

Remarks : The nitrogen monoxide standard gas cited here means the nitrogen monoxide standard gas for practical use or specified secondary standard gas of nitrogen monoxide which are provided by the standard supply system (traceability system) based on the regulations of measurement.

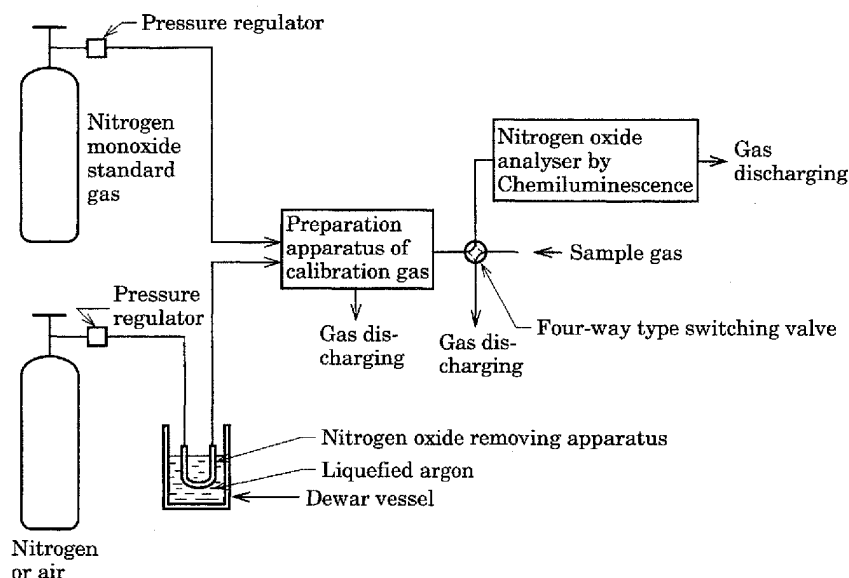


Fig. 1 Constitution of nitrogen oxide measuring apparatus (example)

5.1.2 Calibration and measurement

5.1.2.1 For flow passage selector system In case of employing the flow passage selector system, it shall be as follows.

- a) Change the passage of the instrument to nitrogen monoxide measuring passage, introduce the refining gas through the calibration gas refining apparatus at a flow rate specified to the instrument, and after the indication is stabilized, carry out zero point adjustment.
- b) Change the passage of the instrument to the nitrogen oxides measuring passage, and confirm that there is no variation in indication⁽³⁾. Thereafter, again change the passage to the nitrogen monoxide measuring passage.

Note ⁽³⁾ The limit of variation is ± 1 vol ppb.

- c) By using a preparation apparatus of the calibration gas, generate the nitrogen monoxide calibration gas corresponding to 90 % to 100 % of measuring scale range of the instrument, introduce this at the flow rate specified to the instrument, and after the indication is stabilized, carry out the span adjustment.
- d) Change the passage of the instrument to the nitrogen oxide measuring passage and confirm that there is no variation in indication⁽³⁾. Thereafter, again change the passage of the instrument to the nitrogen oxide measuring passage.
- e) Prepare the calibration curve according to **5.3.2** of **JIS K 0055**.
- f) Change the passage of the instrument to the nitrogen oxide as measuring passage, operate four-way type switching valve, and introduce the sample gas at a flow rate specified to the instrument. After the indication is stabilized, read out the value and obtain the nitrogen oxide concentration in the sample gas with the calibration curve prepared in e).

5.1.2.2 For optical path selector system and two passage two optical path system In cases of optical path selector system and two passage two optical path system shall be as follows.

- a) Introduce the refining nitrogen through preparing apparatus of the calibration gas at a flow rate specified to the instrument, and after stabilizing of the indications of nitrogen monoxide measuring passage and nitrogen oxide measuring passage, carry out zero adjustment respectively.
- b) By using preparing apparatus of a calibration gas, generate the nitrogen monoxide calibration gas corresponding to 90 % to 100 % of the measuring scale range of instrument, introduce this at the flow rate specified to the instrument, and after the indications of the nitrogen monoxide measuring pass and the nitrogen oxide measuring pass is stabilized, carry out the span adjustment.
- c) According to **5.3.2** of **JIS K 0055**, prepare the calibration curve.
- d) Operate four-way type switching valve, and introduce the sample gas at a flow rate specified to the instrument. After the indication of the nitrogen oxide measuring pass is stabilized, read out the value and obtain the nitrogen oxide concentration in the sample gas with the calibration curve prepared in c).

5.1.3 Indication of results Obtain the nitrogen oxide concentration (vol ppm) to four places of decimals, and, according to **JIS Z 8401**, round off to three places of decimals to indication. However, in the case where the nitrogen oxide concentration is less than 0.005 0 vol ppm, take as less than 0.005 vol ppm.

5.2 Saltzman absorptiometry

5.2.1 Summary This is a method that nitrogen monoxide and nitrogen dioxide included in the sample gas are determined simultaneously by the absorptiometry using with colour former (Saltzman reagent).

The concentration of nitrogen dioxide is determined by measuring the absorbance of colour former, after absorbing nitrogen dioxide by passing through the constant

flow rate of the sampling gas into the constant volume of colour former during constant time. Because nitrogen monoxide cannot react to the colour, after it is converted to nitrogen dioxide with the oxidizer and is measured with the same procedures as that of nitrogen dioxide.

5.2.2 Reagents Reagents shall be as follows:

- a) **Water** Class A2 specified in **JIS K 0557**.
- b) **Acetic acid** Specified in **JIS K 8355**.
- c) **Sulfanilic acid** Specified in **JIS K 8586**.
- d) **Potassium permanganate** Specified in **JIS K 8247**.
- e) **Sulfuric acid** Specified in **JIS K 8951**.
- f) **Nitrite ion standard solution (reference solution)** Specified in **JIS K 0032**.
- g) **Nitrogen dioxide standard solution** (5.80 $\mu\text{NO}_2/\text{ml}$) Diluted nitrite ion standard solution with water and prepared to 10 mgNO_2/L . 1 ml of this nitrogen dioxide standard solution is equal to 5.80 μNO_2 (at 0 °C, 101.32 kPa).
- h) **N-1-naphthyl ethylenediamine dihydrochloride** Specified in **JIS K 8197**.
- i) **N-1-naphthyl ethylenediamine dihydrochloride solution** (1 g/L) Dissolve 0.1 g of N-1-naphthyl ethylenediamine dihydrochloride into 100 ml of water.
- j) **Colour former** Dissolve 5 g of sulfanilic acid into approximately 900 ml of hot water containing 50 ml of acetic acid. After cooling, add 50 ml of N-1-naphthyl ethylenediamine dihydrochloride solution (1 g/L) and dilute to total 1 000 ml. This solution shall be stored in a brown coloured bottle.
- k) **Oxidizing reagent** Dissolve 25 g of potassium permanganate into approximately 900 ml of water, add 25 g of concentrated sulfuric acid or 52 ml sulfuric acid (1+3) and dilute into 1 L with water.

5.2.3 Sampling apparatus of the sample gas An example of the sampling apparatus of the sample gas shall be in Fig. 2.

5.2.4 Sampling of sample gas Sampling of sample gas shall be as follows:

- a) Prepare 2 absorption bottles. One of them is used for nitrogen dioxide gas sampling and others for nitrogen monoxide gas sampling. Put 10 ml of the colour former solution into each bottle.

Absorption bottle with glass filter whose maximum pore size is 60 μm shall be employed.

- b) Put 10 ml of oxidizing agent into oxidizing bottle and introduce air during approximately 60 min before measurement.

The oxidizing bottle which is used ordinarily and equipped with nozzle of 1 mm in diameter shall be employed.

- c) Turn a three-way cock to the gas outlet side (⊥) and purge the inner of piping with the sample gas. Gas flow rate shall be regulated to 0.4 L/min or under with a pressure regulator. After regulating, turn off the valve of sample gas cylinder and turn the three-way cock to the absorption bottle side (└).
- d) After reading the indication of a gas meter, open the valve of sample gas cylinder, pass the sample gas through the absorption bottle and take the sample gas. After sampling of the designated volume of sample gas, turn off the valve of sample gas cylinder and read the indication of the gas meter. Suction flow rate of sample gas shall be approximately maximum 0.4 L/min. An aim of minimum limit of determination is approximately 0.005 vol ppm at 24 L of suction flow rate.

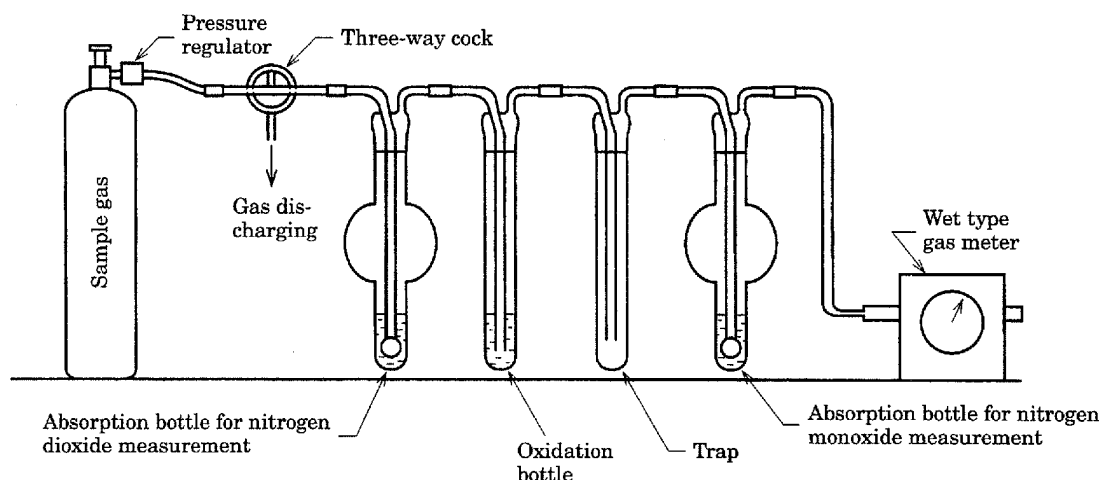


Fig. 2 An example of apparatus for sampling gas (example)

5.2.5 Procedures of determination After blowing the sample gas for 20 min, transfer colour developed solutions of each absorption bottle into 10 mm cell respectively and measure an absorbance at near 545 nm in wavelength according to **JIS K 0115**. Colour former solution is used as reference solution. Then, obtain the volume of nitrogen dioxide and nitrogen oxide with calibration curve.

5.2.6 Preparation of a calibration curve Add correctly stepwise 0 ml to 1.5 ml of nitrogen dioxide standard solution into a 10 ml volumetric flask, and dilute the solution with the colour former solution up to the marked line. After being allowed to stand for 20 min at ordinary temperature, measure the absorbance according to the procedure **5.2.5** and obtain a correlation curve between the concentration of nitrogen dioxide and the absorbance.

5.2.7 Calculation Calculate the concentration of nitrogen dioxide or nitrogen monoxide in the sample gas with the following formula:

- a) **Conversion to sampling volume of sample gas**

$$V_s = V \times \frac{273}{273 + t} \times \frac{P_a + P_m - P_v}{101.32}$$

where, V_s : sampling volume of sample gas (L) (0 °C, 101.32 kPa)

V : volume of suction gas (L)
 P_a : atmospheric pressure (kPa)
 P_m : gauge pressure of a gas meter (kPa)
 t : temperature of a gas meter (°C)
 P_v : saturated vapor pressure at t °C (kPa)

b) **Calculation of nitrogen dioxide or nitrogen monoxide**

$$C = \frac{V}{V_s}$$

where, C : concentration of nitrogen dioxide or nitrogen monoxide (vol ppm)
 V : nitrogen dioxide or nitrogen monoxide obtained with the calibration curve (μl)

5.2.8 Indication of results In accordance with 5.1.3.

6 Determination of sulfur dioxide

6.1 The method of a sulfur dioxide analyser by an ultraviolet fluorometric method

6.1.1 Apparatuses, instruments and gases The apparatuses, instrument and gases shall be as follows. The composition of measurement system is shown in Fig. 3.

- a) **Sulfur dioxide analyser ultraviolet fluorometric** The analyser is based on the ultraviolet fluorometric system specified in **JIS B 7952**, having 0 vol ppm to 0.1 vol ppm range.
- b) **Preparation apparatus of calibration gas** The apparatus is in accordance with 5.1.1 b).
- c) **Sulfur oxides removing apparatus** The sulfur oxides removing apparatus is a stainless steel cylinder tube of 20 mm to 30 mm in inner diameter, and 800 mm to 1 000 mm in length, filled with synthetic zeolite (particle size range 177 μm to 250 μm) of 50 g or more and activated.

Furthermore, a zero (calibration) gas purifier of which performance is equivalent to or superior thereto the above apparatuses and is confirmed may be employed.

- d) **Piping and valves** The piping and valves are in accordance with 5.1.1 d).
- e) **Pressure regulator** The pressure regulator is in accordance with 5.1.1 e).
- f) **Refining gas** When sulfur dioxide calibration gas is prepared, the refining gas is used for diluting the sulfur dioxide standard gas into a certain concentration. When the sample gas is nitrogen, nitrogen packed in a high pressure gas cylinder is employed. When sample gas is air, air packed in a high pressure gas cylinder is used after passing through sulfur oxide removing apparatus.

- g) **Sulfur dioxide standard gas** The sulfur dioxide standard gas whose concentration is 0.1 vol ppm to 100 vol ppm.

Remarks : Sulfur dioxide standard gas cited here means sulfur dioxide standard gas for practical use or specified secondary standard gas of sulfur dioxide which are provided by Japan Calibration Service System.

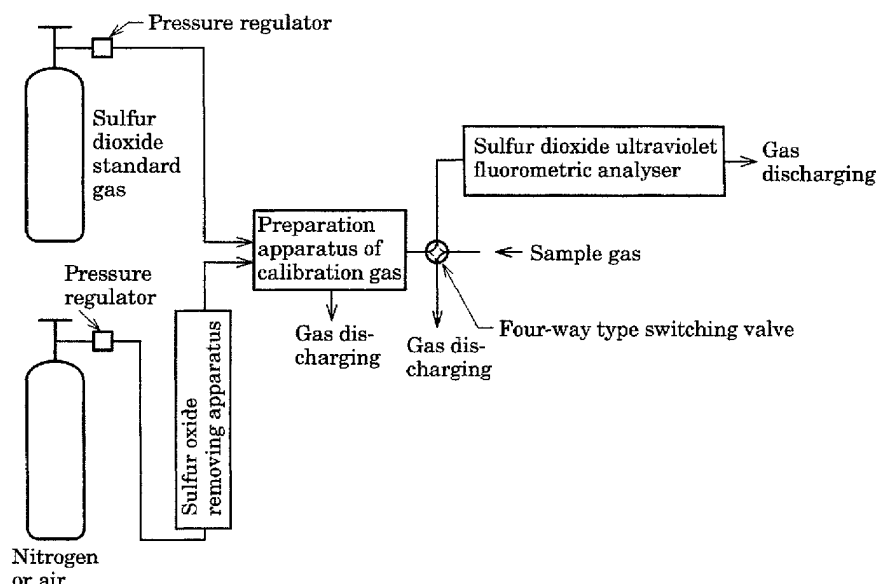


Fig. 3 Constitution of sulfur dioxide measuring apparatus
(example)

6.1.2 Calibration and determination The calibration and determination shall be carried out according to the following procedures:

- Introduce the refining gas through the preparing apparatus of calibration gas at a flow rate specified to the measuring instrument and, after the indication is stabilized, carry out the zero regulation.
- By using the preparing apparatus of calibration gas, generate sulfur dioxide calibration gas corresponding to 90 % to 100 % of measuring scale range of instrument, introduce this at a rate specified to the instrument, and, after the indication is stabilized, carry out the regulation of span.
- Prepare the calibration curve according to **5.3.2 of JIS K 0055**.
- Operate the four-way type switching valve, introduce the sample gas at a flow rate specified to the instrument, after the indication is stabilized, read out the value and obtain the sulfur dioxide concentration in sample gas with the calibration curve prepared in c).

6.1.3 Indication of results Indication of results shall be as follows:

Obtain the sulfur dioxide concentration (vol ppm) to four places of decimals, and, according to **JIS Z 8401**, round off to three places of decimals to indication. However, in case where the sulfur dioxide concentration is less than 0.005 vol ppm, mark shall be less than 0.005 vol ppm.