



JAPANESE
INDUSTRIAL
STANDARD

Translated and Published by
Japanese Standards Association

JIS Z 3920 : 2011

(JWES/JSA)

**Methods for chemical analysis of welding
fumes**

ICS 25.160.20

Reference number : JIS Z 3920 : 2011 (E)

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Z 3920 : 2011

Date of Establishment: 1978-09-01

Date of Revision: 2011-03-22

Date of Public Notice in Official Gazette: 2011-03-22

Investigated by: Japanese Industrial Standards Committee

Standards Board

Technical Committee on Welding

JIS Z 3920 : 2011, First English edition published in 2013-07

Translated and published by: Japanese Standards Association
4-1-24, Akasaka, Minato-ku, Tokyo, 107-8440 JAPAN

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by The Japan Welding Engineering Society (JWES)/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 Z 3920:1991** is replaced with this Standard.

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Methods for chemical analysis of welding fumes

Introduction

This Japanese Industrial Standard was established in 1978 and has gone through 2 revisions to this day. The last revision was made in 1991, and the revision at this time is to correspond to the advances in analytical technology and the changes in welding materials afterwards.

The main points of revision are as follows.

- a) Chromium (VI), barium and silicon (total silicon and crystalline silica) which have not been designated as the target elements for determination are added.
- b) For the determination method of metal elements, ICP atomic emission spectrometry, ascorbic acid reduction potassium iodate back titration method, flame atomic absorption spectrometry, diphenylcarbazide absorptiometry and ion chromatography and diphenylcarbazide absorptiometry, molybdosilicate blue absorptiometry, X-ray diffractometry, etc. are totally reviewed.

1 Scope

This Standard specifies the determination methods of iron, manganese, copper, nickel, vanadium, cobalt, lead, zinc, aluminium, cadmium, silver, barium, chromium, chromium (VI), fluorine, silicon, crystalline silica and phosphorus contained in welding fumes generated at the time of welding, dusts suspended in the welding work environment and dusts in the breathing zone of welding workers (hereafter, referred to as "fumes").

In this Standard, the welding indicates the arc welding and the brazing.

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 K 0050 *General rules for chemical analysis*

JIS K 0115 *General rules for molecular absorptiometric analysis*

JIS K 0116 *General rules for atomic emission spectrometry*

JIS K 0121 *General rules for atomic absorption spectrometry*

JIS K 0127 *General rules for ion chromatographic analysis*

JIS K 0901 *Form, size and performance testing methods of filtration media for collecting airborne particulate matters*

JIS K 0970 *Piston operated micro-volumetric apparatus*

JIS K 8005 *Reference materials for volumetric analysis*

JIS K 9901 *Highly purified nitric acid*

JIS Z 3001-1 *Welding and allied processes — Vocabulary — Part 1 : General*

JIS Z 3001-2 *Welding and allied processes — Vocabulary — Part 2 : Welding processes*

JIS Z 3001-3 *Welding and allied processes — Vocabulary — Part 3 : Soldering and brazing*

JIS Z 3001-4 *Welding and allied processes — Vocabulary — Part 4 : Imperfections in fusion welding*

JIS Z 3930 *Determination of emission rate of particulate fume in arc welding*

JIS Z 3950 *Methods of measurement for airborne dust concentration in welding environment*

3 Terms and definitions

For the purposes of this Standard, the terms and definitions given in JIS Z 3001 series, and the following terms and definitions apply.

3.1 sample for analysis

the whole or a part of fumes collected for analysis

3.2 original solution

solution prepared so that acids and the like are added to the sample for analysis followed by heat decomposition, extraction, etc., then the liquid amount thereof is made definite

3.3 sample solution

solution prepared so that the original solution is partly taken, chemical treatments such as reagent addition, extraction, washing, adjustment of acidity or alkalinity are carried out, and made ready for the introduction to the analyzer

3.4 blank test

test in which the whole analysis operations are carried out exactly according to the actual procedure for the sample by using the solution containing no target element (usually tested without the sample) to evaluate the result, which is supposed to be zero

Normally, the true value is determined by subtracting the blank test value from the actual measured value.

4 General matters

General matters common in this Standard are as follows.

- a) General common matters of the chemical analysis shall be as specified in JIS K 0050, JIS K 0115, JIS K 0116, JISK 0121 and JIS K 0127.

- b) Unless otherwise specified, water to be used in this Standard shall be of A1 or A2 specified in 7.1 of JIS K 0050.

5 Element to be determined and determination method

The element to be determined and the determination method shall be as given in table 1.

6 Sampling method and pretreatment method of fumes

6.1 Sampling method of fumes

6.1.1 Filtration media

The filtration media used for the sampling of fumes shall be as follows.

- a) The filtration media shall be such that the collection efficiency according to the performance test method specified in 5.2 of JIS K 0901 is 95 % or more for aerosol of 0.3 μm in particle diameter, the initial pressure loss is low, the increase of pressure loss by the collection of fumes is low and the hygroscopic property is low.
- b) When determining elements in fumes other than chromium (VI), total silicon and crystalline silica, the filtration media made of glass fibres or quartz fibres shall be used.
- c) The filtration media used for the determination of chromium (VI) in fumes shall be as follows.
- 1) When the sampling of fumes is carried out according to 6.1.3 a) or b), polyvinyl chloride (PVC) membrane filter, polyfluoroethylene (PFE) membrane filter, etc. shall be used.
 - 2) When the sampling of fumes is carried out according to 6.1.3 c), quartz fibre filtration media shall be used.
 - 3) The filtration media using cellulose, glass fibre filtration media, etc. which may react with chromium (VI) shall not be used.
- d) The filtration media used for the determination of total silicon in fumes shall be as follows.
- 1) When the sampling of fumes is carried out according to 6.1.3 a) or b), polyvinyl chloride (PVC) membrane filter or polyfluoroethylene (PFE) membrane filter shall be used.
 - 2) When the sampling of fumes is carried out according to 6.1.3 c), polytetrafluoroethylene (PTFE) filter paper, etc. shall be used.
 - 3) The filtration media which contain silicon such as filtration media made of glass fibres or filtration media made of quartz fibres shall not be used.
- e) The filtration media used for the determination of crystalline silica in fumes shall be as follows.
- 1) When the sampling of fumes is carried out according to 6.1.3 a) or b), fluororesin

treated glass fibre filter shall be used.

- 2) When the sampling of fumes is carried out according to 6.1.3 c), the filtration media of glass fibres or quartz fibres shall be used.

Table 1 Element to be determined and determination method

Welding method	Element to be determined	Determination method					
		Ascorbic acid reduction potassium iodate back titration method	Absorptiometry	Flame atomic absorption spectrometry	Electric heating atomic absorption spectrometry	ICP atomic emission spectrometry	X-ray diffractometry method
Arc welding	Iron	○	○ ^{a)}	○		○	
	Manganese			○		○	
	Copper			○		○	
	Nickel			○		○	
	Vanadium			○		○	
	Cobalt			○		○	
	Lead			○		○	
	Zinc			○		○	
	Aluminium			○		○	
	Barium					○	
	Chromium	Total Cr		○		○	
		Cr(VI)	○ ^{b) c)}	○			
	Fluorine		○ ^{d)}				
	Silicate	Total silicate	○ ^{e)}				
		Crystalline silica					○
Brazing	Copper			○	○	○	
	Zinc			○	○	○	
	Cadmium			○	○	○	
	Silver			○	○	○	
	Fluorine		○ ^{d)}				
	Phosphorus		○ ^{f)}				
NOTE : ○ in table indicates the determination method applicable to the determination of each element. Notes a) Chloride extraction separation and sulfosalicylic acid absorptiometry b) Diphenylcarbazide absorptiometry c) Ion chromatography separation and diphenylcarbazide absorptiometry d) Thermal hydrolysis separation and lanthanum-alizarin complexone absorptiometry e) Molybdosilicate blue absorptiometry f) Molybdovanadophosphoric acid absorptiometry							

6.1.2 Sampling amount of fumes

The sampling amount of fumes shall be as follows.

- a) **Case of sampling of fumes according to 6.1.3 a) or b)** The sampling amount of fumes shall be about 10 mg. The sampling amount of fumes for the case of brazing shall be about 1 mg.
- b) **Case of sampling of fumes according to 6.1.3 c)** The sampling amount of fumes shall be about 100 mg. The sampling amount of fumes for the case of brazing shall be about 10 mg. Also, the sampling amount of fumes when determining iron in fumes according to the method of 7.1 a) shall be the amount sufficient for weighing the amount of sample for analysis specified in table 2 according to the iron content rate in fumes.

6.1.3 Sampling of fumes

The sampling of fumes shall be carried out according to any of the following.

- a) **Sampling of fumes in welding work environment**
 - 1) Fumes shall be sampled according to the method using the low volume air sampler specified in 5.1.1 of JIS Z 3950 or 5.2 of JIS Z 3950.
 - 2) The sampling amount of fumes shall be the mass calculated to the digit of 0.1 mg by subtracting the mass of filtration media before sampling of fumes from the mass of filtration media after sampling.
 - 3) The sampled fumes including the filtration media shall be used as the sample for analysis.
- b) **Sampling of fumes of personal exposure**
 - 1) Fumes shall be sampled by the method using the filtration material specified in 6.3.1 of JIS Z 3950 or 6.4 of JIS Z 3950.
 - 2) The sampling amount of fumes shall be the mass calculated to the digit of 0.1 mg by subtracting the mass of filtration media before sampling of fumes from the mass of filtration media after sampling.
 - 3) The sampled fumes including the filtration media shall be used as the sample for analysis.
- c) **Sampling of fumes during measurement of amount of fumes generated** The sampling of fumes during the measurement of amount of fumes generated shall be either of the following.
 - 1) **Case of fumes from arc welding**
 - 1.1) Fumes shall be sampled according to the method using the high volume air sampler specified in 4.3 of JIS Z 3930.
 - 1.2) The sampling amount of fumes shall be the mass calculated to the digit of 0.1 mg by subtracting the mass of filtration media before sampling of fumes from the mass of filtration media after sampling.

- 1.3) The sample for analysis shall be prepared so that a part of sampled fumes (10 mg or more) on the filtration media are swept off by brush, etc. carefully so as not to contaminate a part of filtration media and brush, and kept in a desiccator for several hours.

2) Case of fumes from brazing

- 2.1) Fumes shall be sampled according to the method using the high volume air sampler specified in 4.3 of JIS Z 3930.
- 2.2) The sampling amount of fumes shall be the mass obtained to the digit of 0.1 mg by subtracting the mass of filtration media before sampling of fumes from the mass of filtration media after sampling.
- 2.3) The sample for analysis shall be the fumes collected on the filtration media together with the filtration media.

6.2 Pretreatment method of sample for analysis

6.2.1 Application

The pretreatment method specified herein applies to the pretreatment of the sample for analysis when determining each element specified in table 1. However, the pretreatment methods of the sample for analysis of iron [when determining according to the method of 7.1 a)], chromium (VI), fluorine, total silicon, crystalline silica and phosphorus are specified in respective determination methods, and the pretreatment specified herein does not apply.

6.2.2 Reagents

6.2.2.1 Hydrochloric acid (1 + 1)

6.2.2.2 Nitric acid (1 + 1, 1 + 2)

6.2.2.3 Perchloric acid

6.2.2.4 Hydrofluoric acid

6.2.2.5 Sodium carbonate (anhydrous)

6.2.3 Preparation of original solution and blank test solution

6.2.3.1 Preparation of original solution

The procedure of preparation of original solution shall be either of the following.

a) Case of sampling of fumes according to 6.1.3 a), b) or c) 2)

1) Case of fumes from arc welding

- 1.1) Transfer the sample for analysis obtained in 6.1.3 a) 3) or b) 3) into the platinum crucible (e.g., No. 50) or platinum dish (e.g., No. 50). Add 6 ml of nitric acid (1 + 1), 5 ml of hydrogen peroxide and 10 ml of hydrofluoric acid, and heat gently to decompose the fumes and filtration media.
- 1.2) Heat furthermore to generate white smoke of hydrogen peroxide and evaporate until the liquid amount becomes 2 ml to 3 ml.

- 1.3) Allow it to cool to the room temperature, add 10 ml of hydrochloric acid (1 + 1) to dissolve salts, then cool it to the ordinary temperature.

When undissolved materials are recognized, filter them with the filter paper (Class 5C), wash them and the filter paper well with warm water, then stock the filtrate and washings together (solution A). Put undissolved materials and filter paper into the platinum crucible (e.g., No. 20), heat gently to dry the filter paper, and ignite to ash the filter paper. Add 1.0 g of sodium carbonate (anhydrous), ignite to fuse, then allow it to cool to the room temperature. Add small amount of water and heat it to dissolve the fuse. Carefully drip hydrochloric acid (1 + 1) to make the solution slight acidity, cool it to the ordinary temperature, and join it with the solution A stored by using small amount of water.

- 1.4) Transfer 100 ml of the solution into the volumetric flask by using water, dilute it to the marked line to prepare the original solution.

2) Case of fumes from brazing

- 2.1) Put the sample for analysis obtained in 6.1.3 a) 3), b) 3) or c) 2) 2.3) into the beaker (200 ml). Add 40 ml of nitric acid (1 + 2), cover it with a watch glass and heat gently to decompose fumes.

The sample for analysis is cut into small pieces with ceramic scissors, if necessary, and put in the beaker (200 ml).

- 2.2) After cooling to the room temperature, wash the lower surface of watch glass and the inner wall of beaker and remove the watch glass, filtrate the solution with the filter paper (Class 5A), wash the filtration media and the filter paper with water sufficiently, and join the filtrate and the washings.
- 2.3) After cooling to the ordinary temperature, transfer the solution into a 100 ml of volumetric flask by using water and dilute it to the marked line with water to prepare the original solution.
- b) **Case of sampling of fumes according to 6.1.3 c) 1)** Weigh out about 10 mg of sample for analysis obtained in 6.1.3 c) 1) 1.3) accurately to the digit of 0.1 mg and transfer it into the platinum crucible (e.g., No. 50) or the platinum dish (e.g., No. 50). Add 6 ml of nitric acid (1 + 1), 5 ml of perchloric acid and 10 ml of hydrofluoric acid, and heat gently to decompose. Hereafter, carry out the procedures according to 1.2) to 1.4) of a) 1).

6.2.3.2 Preparation of blank test solution

The procedure of preparation of blank test solution shall be either of the following.

- a) **Case of sampling of fumes according to 6.1.3 a), b) or c) 2)** Use the same filtration media as that used for the sampling of fumes in 6.1.3 a), b) or c) 2) instead of the sample for analysis, the same procedures according to 6.2.3.1 a) 1) or 2) are carried out in parallel with the sample for analysis, and the solution obtained is used as the blank test solution.
- b) **Case of sampling of fumes according to 6.1.3 c) 1)** The same procedures according

to **6.2.3.1 b)** are carried out without using the sample solution in parallel with the sample for analysis, and the solution obtained is used as the blank test solution.

7 Iron determination method

7.1 Classification of determination method

The determination method of iron shall be any of the following.

The ascorbic acid reduction potassium iodate back titration method is applicable to the sample for analysis taken according to **6.1.3 c) 1)** only.

- a) **Ascorbic acid reduction potassium iodate back titration method** This method is applicable to the determination of iron of 6 mg or over to and including 100 mg in the sample solution.

This method is applicable to the sample for analysis taken according to **6.1.3 c) 1)** only.

- b) **Chloride extraction separation and sulfosalicylic acid absorption spectrometry** This method is applicable to the determination of iron of which the concentration in the sample solution is 1 µg /ml or over to and including 10 µg/ml.
- c) **Flame atomic absorption spectrometry** This method is applicable to the determination of iron of which the concentration in the sample solution is 0.3 µg /ml or over to and including 6 µg/ml.
- d) **ICP atomic emission spectroscopy** This method is applicable to the determination of iron of which the concentration in the sample solution is 0.1 µg /ml or over to and including 5 µg/ml.

7.2 Ascorbic acid reduction potassium iodate back titration method

7.2.1 Summary

Decompose the sample for analysis with hydrochloric acid and tin chloride (II), oxidizes iron to iron (III) by adding hydrogen peroxide, then boil to decompose the residual hydrogen peroxide. Reduce iron (III) to iron (II) by adding a definite amount of ascorbic acid reference solution, and titrate excessive ascorbic acid with potassium iodate reference solution.

7.2.2 Reagents

7.2.2.1 Hydrochloric acid (1 + 1)

7.2.2.2 Hydrogen peroxide

7.2.2.3 Sodium fluoride

7.2.2.4 Tin chloride (II) solution

Dissolve 130 g of metal tin [99.9 % or over (mass fraction)] in hydrochloric acid, make the liquid amount 1 000 ml with hydrochloric acid, and store this solution in a brown bottle.

7.2.2.5 Ascorbic acid reference solution

Dissolve 9 g of L (+) – ascorbic acid in water, add about 100 mg of disodium dihydrogen ethylenediamine tetraacetate dihydrate and 4 ml of formic acid, transfer the solution into a 1 000 ml volumetric flask by using water, and dilute it to the marked line with water. Obtain the factor of this solution by the following operation at every service.

Take 10.0 ml of ascorbic acid reference solution into a beaker (300 ml), make the liquid amount about 150 ml with water, add 10 ml of hydrochloric acid (1 + 1) and 2 ml of starch solution (7.2.2.7) as the indicator, and titrate it with potassium iodate reference solution (7.2.2.6). Obtain the used amount of potassium iodate solution by taking the point where the colour of solution becomes faint blue as the end point, and obtain the factor of ascorbic acid reference solution.

$$F = \frac{V}{10}$$

where, F : factor of ascorbic acid reference solution
 V : used amount of potassium iodate reference solution (ml)

7.2.2.6 Potassium iodate reference solution

Dissolve 3.567 g of potassium iodate, which is preliminarily dried at 120 °C to 140 °C for 90 min to 120 min and allowed to cool to the ordinary temperature in a desiccator, and 10 g of potassium iodide in 200 ml of sodium hydroxide solution (5 g/L), transfer the solution into a 1 000 ml volumetric flask by using water, and dilute it to the marked line with water. One ml of this solution corresponds to 0.005 585 g of iron.

7.2.2.7 Starch solution

After stirring 1 g of starch (soluble) with about 10 ml of water, add this into 100 ml hot water stirring. After boiling the solution about 1 min, allow it to cool to the room temperature, and use the supernatant. Prepare this solution at every service.

7.2.3 Operation

7.2.3.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following procedure.

- a) Weigh out the sample for analysis obtained in 6.1.3 c) 1) 1.3) of the amount specified in table 2 according to the iron content rate thereof, and transfer it into a beaker (300 ml). Add 15 ml of hydrochloric acid (1 + 1) and 5 ml of tin chloride (II) solution (7.2.2.4), cover it with a watch glass, heat it to the extent of not boiling, and decompose it by sometimes shaking gently to mix.

When undissolved residues or suspension are recognized in the solution, add a suitable amount of sodium fluoride (100 mg or under).

- b) Wash the lower surface of watch glass and the inner wall of beaker with small amount of water, add warm water to make the liquid amount about 80 ml. Add 1 ml of hydrogen peroxide, heat it again, and completely decompose the residual hydrogen peroxide by boiling for several minutes. Wash the lower surface of watch

glass and the inner wall of beaker with small amount of hot water, and remove the watch glass.

Table 2 Amount of sample for analysis weighed out and addition amount of ascorbic acid reference solution

Iron content rate in sample for analysis % (mass fraction)	Amount of sample for analysis mg	Addition amount of ascorbic acid reference solution ml
2 or over to and excl. 10	300	10.0
10 or over to and excl. 30	200	15.0
30 or over to and excl. 60	100	15.0
60 or over	100	20.0

7.2.3.2 Titration

Add the amount specified in table 2 of ascorbic acid reference solution (7.2.2.5) to the sample solution (hot solution) obtained in 7.2.3.1 b), make the liquid amount 200 ml with water, immerse in the running water for about 10 min, and cool it to the room temperature. Next, add 2 ml of starch solution (7.2.2.7) as the indicator, and titrate with potassium iodate reference solution (7.2.2.6). Obtain the used amount of ascorbic acid reference solution by taking the point where the colour of solution becomes faint blue as the end point.

7.2.4 Blank test

A blank test is not carried out.

7.2.5 Calculation

The iron content rate in the fumes shall be calculated according to the following formula.

$$Fe = \frac{(V_1 \times F - V_2) \times 0.005\,585}{m} \times 100$$

- where,
- Fe : iron content rate in fumes sampled in 6.1.3 c) 1)
[% (mass fraction)]
 - V_1 : amount of ascorbic acid reference solution added in
7.2.3.2 (ml)
 - F : factor of ascorbic acid reference solution
 - V_2 : used amount of potassium iodate reference solution ob-
tained in 7.2.3.2 (ml)
 - m : amount of sample for analysis weighed out in 7.2.3.1 a)
(g)

7.3 Chloride extraction separation and sulfosalicylic acid absorption spectrometry

7.3.1 Summary

Decompose the sample for analysis with nitric acid, perchloric acid and hydrofluoric acid. Add hydrochloric acid, extract the chloride complex of generated iron (III) with

3-methylbutyl acetate and 4-methyl-2-pentanone, back extract it with water, add sulfosalicylic acid to generate sulfosalicylic acid iron complex, and measure the absorbance by using a photometer.

7.3.2 Reagents

7.3.2.1 Hydrochloric acid

7.3.2.2 Aqueous ammonia (1 + 1)

7.3.2.3 Ammonium chloride solution (100 g/L)

7.3.2.4 Sulfosalicylic acid solution

Dissolve 50 g of 5-sulfosalicylic acid dihydrate in water, and make the liquid amount 1 000 ml.

7.3.2.5 Mixed solvent

Mix 3-methylbutyl acetate and 4-methyl-2-pentanone in equal amount.

7.3.2.6 Iron reference solution (100 µg/ml)

Accurately weigh out 1.00 g of iron [99.9 % or over (mass fraction)], transfer it into a beaker (200 ml), add 50 ml of hydrochloric acid (1 + 1), cover it with a watch glass, and decompose iron by heating. After allowing it to cool to the ordinary temperature, wash the lower surface of watch glass and inner wall of beaker with water, transfer the solution into a 1 000 ml volumetric flask by using water, and dilute it to the marked line with water as the stock solution (Fe : 1 000 µg/ml). Take 10.0 ml of this stock solution into a 100 ml volumetric flask, add 5 ml of hydrochloric acid (1 + 1), and dilute it to the marked line with water at every service to prepare the iron reference solution.

7.3.3 Operation

7.3.3.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following procedure.

- a) Take a part of the original solution obtained in 6.2.3.1 a) 1) 1.4) or b) so that the amount of iron is 0.1 mg to 1.0 mg, and transfer it into a separatory funnel (200 ml).
- b) Add 25 ml of hydrochloric acid, then add water to make the liquid amount 50 ml. After allowing it to cool to the room temperature, add 50 ml of mixed solvent (7.3.2.5), shake it vigorously to mix for 3 min, and allow it to stand so as to be separated into two layers. Discard the lower water phase. Shake the separatory funnel to separate the water phase on the inner wall of it to remove the water completely.
- c) Add 30 ml of water to the organic phase, and shake it vigorously to mix for about 3 min. After allowing it to stand so as to be separated into two layers, transfer the lower water phase into a beaker (100 ml). Add small amount of water to the separatory funnel, and transfer the water phase remained in the leg part, etc. of separatory funnel.

ratory funnel to the beaker containing the previous water phase using water. Discard the organic phase.

- d) Evaporate the mixed solvent contaminated in the water phase by heating the solution, and remove it until the mixed solvent is not recognized on the solution surface. After cooling to the ordinary temperature, transfer the solution into a 100 ml volumetric flask by using water, and make the liquid amount to about 50 ml.
- e) Add 10 ml of ammonium chloride and 5 ml of sulfosalicylic acid solution (7.3.2.4), drip aqueous ammonia (1 + 1) until the colour of solution changes from red violet to yellow, and add 0.2 ml to 0.4 ml thereof excessively. After cooling to the ordinary temperature, dilute it to the marked line with water.

7.3.3.2 Measurement of absorbance

Take a part of the solution obtained in 7.3.3.1 e) in an absorption cell (10 mm) of the photometer, and measure the absorbance in the neighbourhood of 420 nm in wavelength by taking water as the contrast solution.

7.3.4 Blank test

Take the same amount of blank test solution obtained in 6.2.3.2 a) or b) as that partly taken in 7.3.3.1 a) from the original solution, and transfer it into a separatory funnel (200 ml). Hereafter, carry out the same operations as those of the original solution according to the procedures of 7.3.3.1 b) to 7.3.3.2 in parallel with the original solution.

7.3.5 Preparation of working curve

Take 0 ml to 10.0 ml (0 mg to 1.0 mg as iron) of iron reference solution (7.3.2.6) to several separatory funnels (200 ml) in a stepwise manner. Hereafter, carry out the same operations as those of the original solution according to the procedures of 7.3.3.1 b) to 7.3.3.2 in parallel with the original solution, prepare the relation line between the obtained absorbance and the amount of iron, translate the relation line so as to pass the origin, and take it as the working curve.

7.3.6 Calculation

The calculation shall be according to either of the following.

- a) **Case of sampling of fumes according to 6.1.3 a) or b)** The amount of iron is obtained from the absorbances obtained in 7.3.3.2 and 7.3.4, and the working curve prepared in 7.3.5. The iron content rate in the fumes shall be calculated according to the following formula.

$$Fe = \frac{(A_1 - A_2)}{m_1 \times \frac{B_1}{100}} \times 100$$

where, Fe : iron content rate in fumes [% (mass fraction)]
 A_1 : detected amount of iron in sample solution (mg)
 A_2 : detected amount of iron in blank test solution (mg)

m_1 : sampling amount of fumes obtained in 6.1.3 a) 2) or b) 2) (mg)

B_1 : aliquot of original solution and amount of blank test solution taken in 7.3.3.1 a) and 7.3.4 respectively (ml)

- b) **Case of sampling of fumes according to 6.1.3 c) 1)** The amount of iron is obtained from the absorbances obtained in 7.3.3.2 and 7.3.4, and the working curve prepared in 7.3.5. The iron content rate in the fumes shall be calculated according to the following formula.

$$Fe = \frac{(A_1 - A_2)}{m_2 \times \frac{B_1}{100}} \times 100$$

where, Fe : iron content rate in fumes [% (mass fraction)]

A_1 : detected amount of iron in sample solution (mg)

A_2 : detected amount of iron in blank test solution (mg)

m_2 : amount of sample for analysis weighed out in 6.2.3.1 b) (mg)

B_1 : aliquot of original solution and amount of blank test solution taken in 7.3.3.1 a) and 7.3.4 respectively (ml)

7.4 Flame atomic absorption spectrometry

7.4.1 Summary

Decompose the sample for analysis with nitric acid, perchloric acid and hydrofluoric acid. Add hydrochloric acid, and spray the solution into the air-acetylene flame of atomic absorption spectrophotometer, and measure the absorbance.

7.4.2 Reagents

7.4.2.1 Hydrochloric acid (1 + 1)

7.4.2.2 Iron reference solution (Fe : 100 µg/ml)

Weigh out 0.100 g of iron [not less than 99.9 % (mass fraction)], transfer it into a beaker (100 ml), add 10 ml of nitric acid (1 + 1), cover it with a watch glass and decompose iron by heating. After cooling to the ordinary temperature, wash the lower surface of the watch glass and the inner wall of beaker with water, and remove the watch glass. Transfer the solution into a 1 000 ml volumetric flask by using water, add 40 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

7.4.2.3 Iron reference solution (Fe : 10 µg/ml)

Take 10.0 ml of iron reference solution (7.4.2.2) into a 100 ml volumetric flask at every service, add 5 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

7.4.3 Operation

7.4.3.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following

procedure.

- a) Take a part of the original solution obtained in 6.2.3.1 a) 1) 1.4) or b) so that the amount of iron is 30 µg to 600 µg, and transfer it into a 100 ml volumetric flask.
- b) Add 10 ml of hydrochloric acid (1 + 1), and dilute it to the marked line with water.

7.4.3.2 Measurement of absorbance

Spray a part of the solution obtained in 7.4.3.1 b) into the air-acetylene flame adjusted to zero value with water, and measure the absorbance at the wavelength of 248.3 nm.

7.4.4 Blank test

Take the same amount of blank test solution obtained in 6.2.3.2 a) or b) as that partly taken in 7.4.3.1 a) from the original solution, and transfer it into a 100 ml volumetric flask. Hereafter, carry out the same operations as those of the original solution according to the procedures of 7.4.3.1 b) and 7.4.3.2 in parallel with the original solution.

7.4.5 Preparation of working curve

Take several amounts of the iron reference solution (7.4.2.2) and/or the iron reference solution (7.4.2.3) (0 µg to 600 µg as iron) to several 100 ml volumetric flasks in a stepwise manner. Hereafter, carry out the same operations as those of the original solution according to the procedures of 7.4.3.1 b) and 7.4.3.2 in parallel with the original solution, prepare the relation line between the obtained absorbance and the amount of iron, translate the relation line so as to pass the origin, and take it as the working curve.

7.4.6 Calculation

The calculation shall be according to either of the following.

- a) **Case of sampling of fumes according to 6.1.3 a) or b)** The amount of iron is obtained from the absorbances obtained in 7.4.3.2 and 7.4.4, and the working curve prepared in 7.4.5. The iron content rate in the fumes shall be calculated according to the following formula.

$$Fe = \frac{(A_1 - A_2)}{m_1 \times \frac{B_2}{100}} \times 100$$

- where,
- Fe : iron content rate in fumes [% (mass fraction)]
 - A_1 : detected amount of iron in sample solution (mg)
 - A_2 : detected amount of iron in blank test solution (mg)
 - m_1 : sampling amount of fumes obtained in 6.1.3 a) 2) or b) 2) (mg)
 - B_2 : aliquot of original solution and amount of blank test solution taken in 7.4.3.1 a) and 7.4.4 respectively (ml)

- b) **Case of sampling of fumes according to 6.1.3 c) 1)** The amount of iron is obtained

from the absorbances obtained in 7.4.3.2 and 7.4.4, and the working curve prepared in 7.4.5. The iron content rate in the fumes shall be calculated according to the following formula.

$$Fe = \frac{(A_1 - A_2)}{m_2 \times \frac{B_2}{100}} \times 100$$

where, Fe : iron content rate in fumes [% (mass fraction)]
 A_1 : detected amount of iron in sample solution (mg)
 A_2 : detected amount of iron in blank test solution (mg)
 m_2 : amount of sample for analysis weighed out in 6.2.3.1 b) (mg)
 B_2 : aliquot of original solution and amount of blank test solution taken in 7.4.3.1 a) and 7.4.4 respectively (ml)

7.5 ICP atomic emission spectroscopy

7.5.1 Summary

Decompose the sample for analysis with nitric acid, perchloric acid and hydrofluoric acid. Spray the solution into the argon plasma of ICP atomic emission spectrophotometer, and measure the emission intensity.

7.5.2 Reagents

7.5.2.1 Iron reference solution (Fe : 100 µg/ml)

In accordance with 7.4.2.2.

7.5.2.2 Iron reference solution (Fe : 10 µg/ml)

In accordance with 7.4.2.3.

7.5.3 Operation

7.5.3.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following procedure.

- Take a part of the original solution obtained in 6.2.3.1 a) 1) 1.4) or b) so that the amount of iron is 10 µg to 500 µg, and transfer it into a 100 ml volumetric flask.
- Add water to dilute it to the marked line.

7.5.3.2 Measurement of emission intensity

Spray a part of the solution obtained in 7.5.3.1 b) into argon plasma of ICP atomic emission spectrophotometer, and measure the emission intensity at the wavelength of 238.204 nm.

In the case where the emission intensity of iron at 238.204 nm is affected by coexisting elements, other unaffected wavelength for measurement shall be selected. If necessary, the background correction shall be carried out. The necessity of other unaffected wavelength selection and/or background correction shall be determined accord-

ing to the preliminary measurement.

7.5.4 Blank test

Take the same amount of blank test solution obtained in 6.2.3.2 a) or b) as that partly taken in 7.5.3.1 a) from the original solution, and transfer it into a 100 ml volumetric flask. Hereafter, carry out the same operations as those of the original solution according to the procedures of 7.5.3.1 b) and 7.5.3.2 in parallel with the original solution.

7.5.5 Preparation of working curve

Take several amounts of the iron reference solution (7.5.2.1) and/or the iron reference solution (7.5.2.2) (0 µg to 500 µg as iron) to several 100 ml volumetric flasks in a stepwise manner. Hereafter, carry out the same operations as those of the original solution according to the procedures of 7.5.3.1 b) and 7.5.3.2 in parallel with the original solution, prepare the relation line between the obtained emission intensity and the amount of iron, translate the relation line so as to pass the origin, and take it as the working curve.

7.5.6 Calculation

The calculation shall be according to either of the following.

- a) **Case of sampling of fumes according to 6.1.3 a) or b)** The amount of iron is obtained from the emission intensities obtained in 7.5.3.2 and 7.5.4, and the working curve prepared in 7.5.5. The iron content rate in the fumes shall be calculated according to the following formula.

$$Fe = \frac{(A_1 - A_2)}{m_1 \times \frac{B_3}{100}} \times 100$$

- where, Fe : iron content rate in fumes [% (mass fraction)]
 A_1 : detected amount of iron in sample solution (mg)
 A_2 : detected amount of iron in blank test solution (mg)
 m_1 : sampling amount of fumes obtained in 6.1.3 a) 2) or b) 2) (mg)
 B_3 : aliquot of original solution and amount of blank test solution taken in 7.5.3.1 a) and 7.5.4 respectively (ml)

- b) **Case of sampling of fumes according to 6.1.3 c) 1)** The amount of iron is obtained from the emission intensities obtained in 7.5.3.2 and 7.5.4, and the working curve prepared in 7.5.5. The iron content rate in the fumes shall be calculated according to the following formula.

$$Fe = \frac{(A_1 - A_2)}{m_2 \times \frac{B_3}{100}} \times 100$$

- where, Fe : iron content rate in fumes [% (mass fraction)]
 A_1 : detected amount of iron in sample solution (mg)

- A_2 : detected amount of iron in blank test solution (mg)
 m_2 : amount of sample for analysis weighed out in 6.2.3.1 b) (mg)
 B_3 : aliquot of original solution and amount of blank test solution taken in 7.5.3.1 a) and 7.5.4 respectively (ml)

8 Manganese determination method

8.1 Classification of determination method

The determination method of manganese shall be either of the following.

- a) **Flame atomic absorption spectrometry** This method is applicable to the determination of manganese of which the concentration in the sample solution is 0.1 µg/ml or over to and including 50 µg/ml.
- b) **ICP atomic emission spectroscopy** This method is applicable to the determination of manganese of which the concentration in the sample solution is 0.05 µg/ml or over to and including 50 µg/ml.

8.2 Flame atomic absorption spectrometry

8.2.1 Summary

Decompose the sample for analysis with nitric acid, perchloric acid and hydrofluoric acid. Add hydrochloric acid, and spray the solution into the air-acetylene flame of atomic absorption spectrophotometer, and measure the absorbance.

8.2.2 Reagents

8.2.2.1 Hydrochloric acid (1 + 1)

8.2.2.2 Manganese reference solution (Mn : 100 µg/ml)

Weigh out 0.100 g of manganese [not less than 99.9 % (mass fraction)], transfer it into a beaker (100 ml), add 10 ml of nitric acid (1 + 1), cover it with a watch glass, and decompose manganese by heating. After cooling to the ordinary temperature, wash the lower surface of the watch glass and the inner wall of beaker with water, and remove the watch glass. Transfer the solution into a 1 000 ml volumetric flask by using water, add 40 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

8.2.2.3 Manganese reference solution (Mn : 10 µg/ml)

Take 10.0 ml of manganese reference solution (8.2.2.2) into a 100 ml volumetric flask at every service, add 5 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

8.2.3 Operation

8.2.3.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following procedure.

- a) Take a part of the original solution obtained in of 6.2.3.1 a) 1) 1.4) or b) so that the

amount of manganese is 10 µg to 500 µg, and transfer it into a 100 ml volumetric flask.

b) Add 10 ml of hydrochloric acid (1 + 1), and dilute it to the marked line with water.

8.2.3.2 Measurement of absorbance

Spray a part of the solution obtained in 8.2.3.1 b) into the air-acetylene flame adjusted to zero value with water, and measure the absorbance at the wavelength of 279.5 nm.

8.2.4 Blank test

Take the same amount of blank test solution obtained in 6.2.3.2 a) or b) as that partly taken in 8.2.3.1 a) from the original solution, and transfer it into a 100 ml volumetric flask. Hereafter, carry out the same operations as those of the original solution according to the procedures of 8.2.3.1 b) and 8.2.3.2 in parallel with the original solution.

8.2.5 Preparation of working curve

Take several amounts of the manganese reference solution (8.2.2.2) and/or the manganese reference solution (8.2.2.3) (0 µg to 500 µg as manganese) to several 100 ml volumetric flasks in a stepwise manner. Hereafter, carry out the same operations as those of the original solution according to the procedures of 8.2.3.1 b) and 8.2.3.2 in parallel with the original solution, prepare the relation line between the obtained absorbance and the amount of manganese, translate the relation line so as to pass the origin, and take it as the working curve.

8.2.6 Calculation

The calculation shall be according to either of the following.

a) **Case of sampling of fumes according to 6.1.3 a) or b)** The amount of manganese is obtained from the absorbances obtained in 8.2.3.2 and 8.2.4, and the working curve prepared in 8.2.5. The manganese content rate in the fumes shall be calculated according to the following formula.

$$Mn = \frac{(A_3 - A_4)}{m_1 \times \frac{B_4}{100}} \times 100$$

where, Mn : manganese content rate in fumes [% (mass fraction)]
 A_3 : detected amount of manganese in sample solution (mg)
 A_4 : detected amount of manganese in blank test solution (mg)
 m_1 : sampling amount of fumes obtained in 6.1.3 a) 2) or b) 2) (mg)
 B_4 : aliquot of original solution and amount of blank test solution taken in 8.2.3.1 a) and 8.2.4 respectively (ml)

b) **Case of sampling of fumes according to 6.1.3 c) 1)** The amount of manganese is obtained from the absorbances obtained in 8.2.3.2 and 8.2.4, and the working curve

prepared in 8.2.5. The manganese content rate in the fumes shall be calculated according to the following formula.

$$Mn = \frac{(A_3 - A_4)}{m_2 \times \frac{B_4}{100}} \times 100$$

where, Mn : manganese content rate in fumes [% (mass fraction)]
 A_3 : detected amount of manganese in sample solution (mg)
 A_4 : detected amount of manganese in blank test solution (mg)
 m_2 : amount of sample for analysis weighed out in 6.2.3.1 b) (mg)
 B_4 : aliquot of original solution and amount of blank test solution taken in 8.2.3.1 a) and 8.2.4 respectively (ml)

8.3 ICP atomic emission spectroscopy

8.3.1 Summary

Decompose the sample for analysis with nitric acid, perchloric acid and hydrofluoric acid. Spray the solution into the argon plasma of ICP atomic emission spectrophotometer, and measure the emission intensity.

8.3.2 Reagents

8.3.2.1 Manganese reference solution (Mn : 200 µg/ml)

Weigh out 0.200 g of manganese [not less than 99.9 % (mass fraction)], transfer it into a beaker (100 ml), add 10 ml of nitric acid (1 + 1), cover it with a watch glass and decompose manganese by heating. After cooling to the ordinary temperature, wash the lower surface of the watch glass and the inner wall of beaker with water, and remove the watch glass. Transfer the solution into a 1 000 ml volumetric flask by using water, add 40 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

8.3.2.2 Manganese reference solution (Mn : 10 µg/ml)

Take 5.0 ml of manganese reference solution (8.3.2.1) into a 100 ml volumetric flask at every service, add 5 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

8.3.2.3 Manganese reference solution (Mn : 1.0 µg/ml)

Take 10.0 ml of manganese reference solution (8.3.2.2) into a 100 ml volumetric flask at every service, add 5 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

8.3.3 Operation

8.3.3.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following procedure.

a) Take a part of the original solution obtained in 6.2.3.1 a) 1) 1.4) or b) so that the

amount of manganese is 5 µg to 5 000 µg, and transfer it into a 100 ml volumetric flask.

b) Add water to dilute it to the marked line.

8.3.3.2 Measurement of emission intensity

Spray a part of the solution obtained in 8.3.3.1 b) into argon plasma of ICP atomic emission spectrophotometer, and measure the emission intensity at the wavelength of 257.610 nm.

In the case where the emission intensity of manganese at 257.610 nm is affected by coexisting elements, other unaffected wavelength for measurement shall be selected. If necessary, the background correction shall be carried out. The necessity of other unaffected wavelength selection and/or background correction shall be determined according to the preliminary measurement.

8.3.4 Blank test

Take the same amount of blank test solution obtained in 6.2.3.2 a) or b) as that partly taken in 8.3.3.1 a) from the original solution, and transfer it into a 100 ml volumetric flask. Hereafter, carry out the same operations as those of the original solution according to the procedures of 8.3.3.1 b) and 8.3.3.2 in parallel with the original solution.

8.3.5 Preparation of working curve

Take several amounts of the manganese reference solution (8.3.2.1), the manganese reference solution (8.3.2.2) and/or the manganese reference solution (8.3.2.3) (0 µg to 5 000 µg as manganese) to several 100 ml volumetric flasks in a stepwise manner. Hereafter, carry out the same operations as those of the original solution according to the procedures of 8.3.3.1 b) and 8.3.3.2 in parallel with the original solution, prepare the relation line between the obtained emission intensity and the amount of manganese, translate the relation line so as to pass the origin, and take it as the working curve.

8.3.6 Calculation

The calculation shall be according to either of the following.

a) **Case of sampling of fumes according to 6.1.3 a) or b)** The amount of manganese is obtained from the emission intensities obtained in 8.3.3.2 and 8.3.4, and the working curve prepared in 8.3.5. The manganese content rate in the fumes shall be calculated according to the following formula.

$$Mn = \frac{(A_3 - A_4)}{m_1 \times \frac{B_5}{100}} \times 100$$

where, Mn : manganese content rate in fumes [% (mass fraction)]
 A_3 : detected amount of manganese in sample solution (mg)
 A_4 : detected amount of manganese in blank test solution (mg)

m_1 : sampling amount of fumes obtained in 6.1.3 a) 2) or b) 2) (mg)

B_5 : aliquot of original solution and amount of blank test solution taken in 8.3.3.1 a) and 8.3.4 respectively (ml)

- b) **Case of sampling of fumes according to 6.1.3 c) 1)** The amount of manganese is obtained from the emission intensities obtained in 8.3.3.2 and 8.3.4, and the working curve prepared in 8.3.5. The manganese content rate in the fumes shall be calculated according to the following formula.

$$Mn = \frac{(A_3 - A_4)}{m_2 \times \frac{B_5}{100}} \times 100$$

where, Mn : manganese content rate in fumes [% (mass fraction)]

A_3 : detected amount of manganese in sample solution (mg)

A_4 : detected amount of manganese in blank test solution (mg)

m_2 : amount of sample for analysis weighed out in 6.2.3.1 b) (mg)

B_5 : aliquot of original solution and amount of blank test solution taken in 8.3.3.1 a) and 8.3.4 respectively (ml)

9 Copper determination method

9.1 Classification of determination method

The determination method of copper shall be any of the following.

The electrothermal atomic absorption spectrometry is only applicable to the original solution prepared according to 6.2.3.1 a) 2).

- a) **Flame atomic absorption spectrometry** This method is applicable to the determination of copper of which the concentration in the sample solution is 0.1 µg/ml or over to and including 5 µg/ml.
- b) **Electrothermal atomic absorption spectrometry** This method is applicable to the determination of copper of which the concentration in the sample solution is 0.005 µg/ml or over to and including 0.1 µg/ml. In the case where the absorbance of copper is affected by coexisting elements, salts and the like in the sample solution, the working curve method specified in this method shall not be applied.
- c) **ICP atomic emission spectroscopy** This method is applicable to the determination of copper of which the concentration in the sample solution is 0.1 µg/ml or over to and including 50 µg/ml.

9.2 Flame atomic absorption spectrometry

9.2.1 Summary

Decompose the sample for analysis with nitric acid, perchloric acid and hydrofluoric acid, or nitric acid. Add hydrochloric acid, and spray the solution into the air-acetylene flame of atomic absorption spectrophotometer, and measure the absorbance.

9.2.2 Reagents

9.2.2.1 Hydrochloric acid (1 + 1)

9.2.2.2 Copper reference solution (Cu : 100 µg/ml)

Weigh out 0.100 g of copper [not less than 99.9 % (mass fraction)], transfer it into a beaker (100 ml), add 10 ml of nitric acid (1 + 1), cover it with a watch glass and decompose copper by heating. After cooling to the ordinary temperature, wash the lower surface of the watch glass and the inner wall of beaker with water, and remove the watch glass. Transfer the solution into a 1 000 ml volumetric flask by using water, add 40 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

9.2.2.3 Copper reference solution (Cu : 10 µg/ml)

Take 10.0 ml of copper reference solution (9.2.2.2) into a 100 ml volumetric flask at every service, add 5 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

9.2.3 Operation

9.2.3.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following procedure.

- a) Take a part of the original solution obtained in 6.2.3.1 a) 1) 1.4) or 2) 2.3), or 6.2.3.1 b) so that the amount of copper is 10 µg to 500 µg, and transfer it into a 100 ml volumetric flask.
- b) Add 10 ml of hydrochloric acid (1 + 1), and dilute it to the marked line with water.

When the original solution is prepared in accordance with 6.2.3.1 a) 2), dilute the solution to the marked line with water without adding 10 ml of hydrochloric acid (1 + 1).

9.2.3.2 Measurement of absorbance

Spray a part of the solution obtained in 9.2.3.1 b) into the air-acetylene flame adjusted to zero value with water, and measure the absorbance at the wavelength of 324.8 nm.

9.2.4 Blank test

Take the same amount of blank test solution obtained in 6.2.3.2 a) or b) as that partly taken in 9.2.3.1 a) from the original solution, and transfer it into a 100 ml volumetric flask. Hereafter, carry out the same operations as those of the original solution according to the procedures of 9.2.3.1 b) and 9.2.3.2 in parallel with the original solution.

9.2.5 Preparation of working curve

Take several amounts of the copper reference solution (9.2.2.2) and/or the copper reference solution (9.2.2.3) (0 µg to 500 µg as copper) to several 100 ml volumetric flasks in a stepwise manner. Hereafter, carry out the same operations as those of the original

solution according to the procedures of **9.2.3.1 b)** and **9.2.3.2** in parallel with the original solution, prepare the relation line between the obtained absorbance and the amount of copper, translate the relation line so as to pass the origin, and take it as the working curve.

9.2.6 Calculation

The calculation shall be according to either of the following.

- a) **Case of sampling of fumes according to 6.1.3 a), b) or c) 2)** The amount of copper is obtained from the absorbances obtained in **9.2.3.2** and **9.2.4**, and the working curve prepared in **9.2.5**. The copper content rate in the fumes shall be calculated according to the following formula.

$$Cu = \frac{(A_5 - A_6)}{m_3 \times \frac{B_6}{100}} \times 100$$

where, Cu : copper content rate in fumes [% (mass fraction)]
 A_5 : detected amount of copper in sample solution (mg)
 A_6 : detected amount of copper in blank test solution (mg)
 m_3 : sampling amount of fumes obtained in **6.1.3 a) 2), b) 2) or c) 2) 2.2)** (mg)
 B_6 : aliquot of original solution and amount of blank test solution taken in **9.2.3.1 a)** and **9.2.4** respectively (ml)

- b) **Case of sampling of fumes according to 6.1.3 c) 1)** The amount of copper is obtained from the absorbances obtained in **9.2.3.2** and **9.2.4**, and the working curve prepared in **9.2.5**. The copper content rate in the fumes shall be calculated according to the following formula.

$$Cu = \frac{(A_5 - A_6)}{m_2 \times \frac{B_6}{100}} \times 100$$

where, Cu : copper content rate in fumes [% (mass fraction)]
 A_5 : detected amount of copper in sample solution (mg)
 A_6 : detected amount of copper in blank test solution (mg)
 m_2 : amount of sample for analysis weighed out in **6.2.3.1 b)** (mg)
 B_6 : aliquot of original solution and amount of blank test solution taken in **9.2.3.1 a)** and **9.2.4** respectively (ml)

9.3 Electrothermal atomic absorption spectrometry

9.3.1 Summary

Decompose the sample for analysis with nitric acid. Add nitric acid, inject the solution into the electrical furnace of the electrothermal atomic absorption spectrometer, and measure the absorbance.

9.3.2 Water

For water used in the preparation of reagents and determination procedures, that of A3 specified in 7.1 of JIS K 0050 shall be used.

9.3.3 Reagents

9.3.3.1 Nitric acid (1 + 1)

Prepare it by using nitric acid (JIS K 9901).

9.3.3.2 Copper reference solution (Cu : 1.0 µg/ml)

Weigh out 0.100 g of copper [not less than 99.9 % (mass fraction)], transfer it into a beaker (100 ml), add 10 ml of nitric acid (1 + 1) [prepared by using nitric acid (JIS K 9901)], cover it with a watch glass and decompose copper by heating. After cooling to the ordinary temperature, wash the lower surface of the watch glass and the inner wall of beaker with water (9.3.2), and remove the watch glass. Transfer the solution into a 1 000 ml volumetric flask by using water, add 40 ml of nitric acid (1 + 1) [prepared by using nitric acid (JIS K 9901)], and dilute it to the marked line with water to prepare the stock solution (Cu: 100 µg/ml). Take 1.0 ml of this stock solution into a 100 ml volumetric flask at every service, add 2 ml of nitric acid (1 + 1) [prepared by using nitric acid (JIS K 9901)], and dilute it to the marked line with water (9.3.2).

9.3.3.3 Copper reference solution (Cu : 0.1 µg/ml)

Take 10.0 ml of copper reference solution (9.3.3.2) into a 100 ml volumetric flask at every service, add 2 ml of nitric acid (1 + 1) [prepared by using nitric acid (JIS K 9901)], and dilute it to the marked line with water (9.3.2).

9.3.4 Instrument

9.3.4.1 Micropipette

That of piston operated micro-volumetric apparatus specified in JIS K 0970, or automatic injection device shall be used.

9.3.5 Operation

9.3.5.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following procedure.

a) Case of determination according to working curve method

- 1) Take a part of the original solution obtained in 6.2.3.1 a) 2) 2.3) so that the amount of copper is 0.5 µg to 10 µg, and transfer it into a 100 ml volumetric flask.
- 2) Add 10 ml of hydrochloric acid (1 + 1) (9.3.3.1), and dilute it to the marked line with water (9.3.2).

b) Case of determination according to standard addition method

- 1) Prepare four or more 100 ml volumetric flasks, and take the same amount of the original solution obtained in 6.2.3.1 a) 2) 2.3), respectively.

The aliquot of original solution shall be so that the amount of copper in it is not

under 0.5 µg.

- 2) Add the copper reference solution (9.3.3.2) and/or the copper reference solution (9.3.3.3) to volumetric flasks other than one so that the amount of copper is 0.5 µg to 10 µg in the solution of each flask in a stepwise manner. Then, add 10 ml of hydrochloric acid (1 + 1) (9.3.3.1), and dilute it to the marked line with water (9.3.2).

9.3.5.2 Measurement of absorbance

The measurement of absorbance shall be carried out according to the following procedure.

a) Case of determination according to working curve method

- 1) Inject a part (for example, 10 µl to 50 µl) of the solution obtained in 9.3.5.1 a) 2) with micropipette (9.3.4.1) into the electric furnace of electrothermal atomic absorption spectrometer.
- 2) Carry out drying (for 30 s to 40 s at 100 °C to 120 °C), incinerating (for 30 s to 40 s at 600 °C to 1 000 °C) and atomizing (for 4 s to 6 s at 2 000 °C to 2 700 °C), and measure the absorbance at 324.8 nm in wavelength.

On the absorbance measurement, the background correction shall be carried out. As the conditions of drying, incinerating and atomizing differ depending on the apparatus, injection amount of sample solution, concentration of salts in the sample solution, etc., the optimized conditions shall be obtained beforehand.

b) Case of determination according to standard addition method

- 1) Inject a part (for example, 10 µl to 50 µl) of the solution obtained in 9.3.5.1 b) 2) with micropipette (9.3.4.1) into the electric furnace of electrothermal atomic absorption spectrometer.
- 2) Carry out the operation of a) 2).

9.3.6 Blank test

The blank test shall be either of the following.

- a) **Case of determination according to working curve method** Take same amount of the blank test solution obtained in 6.2.3.2 a) as that of the original solution partly taken in 9.3.5.1 a) 1), and transfer it into a 100 ml volumetric flask. Hereafter, carry out the same operations as those of the original solution according to the procedures of 9.3.5.1 a) 2) and 9.3.5.2 a) in parallel with the original solution.
- b) **Case of determination according to standard addition method** Prepare four or more 100 ml volumetric flasks, and take the same amount of the blank test solution obtained in 6.2.3.2 a) as that of the original solution partly taken in 9.3.5.1 b) 1). Hereafter, carry out the same operations as those of the original solution according to the procedures of 9.3.5.1 b) 2) and 9.3.5.2 b) in parallel with the original solution.

9.3.7 Preparation of working curve

The preparation of working curve shall be either of the following.

- a) **Case of determination according to working curve method** Take several amounts of the copper reference solution (9.3.3.2) and/or the copper reference solution (9.3.3.3) (0 µg to 10 µg as copper) to several 100 ml volumetric flasks in a stepwise manner. Hereafter, carry out the same operations as those of the original solution according to the procedures of 9.3.5.1 a) 2) and 9.3.5.2 a) in parallel with the original solution, prepare the relation line between the obtained absorbance and the amount of copper, translate the relation line so as to pass the origin, and take it as the working curve.
- b) **Case of determination according to standard addition method**
 - 1) **Working curve for sample solution** Prepare the relation line between the absorbance obtained in 9.3.5.2 b) 2) and the amount of copper added as the copper reference solution in 9.3.5.1 b) 2), translate the relation line so as to pass the origin, and take it as the working curve.
 - 2) **Working curve for blank test solution** Prepare the relation line between the absorbance obtained in 9.3.6 b) and the amount of copper added as the copper reference solution in 9.3.6 b), translate the relation line so as to pass the origin, and take it as the working curve.

9.3.8 Calculation

The calculation shall be according to either of the following.

- a) **Case of determination according to working curve method** The amount of copper is obtained from the absorbances obtained in 9.3.5.2 a) 2) and 9.3.6 a), and the working curve prepared in 9.3.7 a). The copper content rate in the fumes shall be calculated according to the following formula.

$$Cu = \frac{(A_5 - A_6)}{m_3 \times \frac{B_7}{100}} \times 100$$

- where,
- Cu : copper content rate in fumes [% (mass fraction)]
 - A_5 : detected amount of copper in sample solution (mg)
 - A_6 : detected amount of copper in blank test solution (mg)
 - m_3 : sampling amount of fumes obtained in 6.1.3 a) 2), b) 2) or c) 2) 2.2) (mg)
 - B_7 : aliquot of original solution and amount of blank test solution taken in 9.3.5.1 a) 1) and 9.3.6 a) respectively (ml)

- b) **Case of determination according to standard addition method** The amounts of copper are respectively obtained from the absorbance of sample solution to which the copper reference solution obtained in 9.3.5.2 b) 2) is not added and the working curve prepared in 9.3.7 b) 1), and also from the absorbance of blank test solution to which the copper reference solution obtained in 9.3.6 b) is not added and the working curve prepared in 9.3.7 b) 2). The copper content rate in the fumes shall be calculated according to the following formula.

$$Cu = \frac{(A_5 - A_6)}{m_3 \times \frac{B_8}{100}} \times 100$$

where, Cu : copper content rate in fumes [% (mass fraction)]
 A_5 : detected amount of copper in sample solution (mg)
 A_6 : detected amount of copper in blank test solution (mg)
 m_3 : sampling amount of fumes obtained in 6.1.3 a) 2), b) 2) or c) 2) 2.2) of (mg)
 B_8 : aliquot of original solution and amount of blank test solution taken in 9.3.5.1 b) 1) and 9.3.6 b) respectively (ml)

9.4 ICP atomic emission spectroscopy

9.4.1 Summary

Decompose the sample for analysis with nitric acid, perchloric acid and hydrofluoric acid, or nitric acid. Spray the solution into the argon plasma of ICP atomic emission spectrophotometer, and measure the emission intensity.

9.4.2 Reagents

9.4.2.1 Copper reference solution (Cu : 200 µg/ml)

Weigh out 0.200 g of copper [not less than 99.9 % (mass fraction)], transfer it into a beaker (100 ml), add 10 ml of nitric acid (1 + 1), cover it with a watch glass and decompose copper by heating. After cooling to the ordinary temperature, wash the lower surface of the watch glass and the inner wall of beaker with water, and remove the watch glass. Transfer the solution into a 1 000 ml volumetric flask by using water, add 40 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

9.4.2.2 Copper reference solution (Cu : 10 µg/ml)

Take 5.0 ml of copper reference solution (9.4.2.1) into a 100 ml volumetric flask at every service, add 5 ml of nitric acid (1 + 1), and dilute it to the marked line with water.

9.4.3 Operation

9.4.3.1 Preparation of sample solution

The preparation of sample solution shall be carried out according to the following procedure.

- a) Take a part of the original solution obtained in 6.2.3.1 a) 1) 1.4) or 2) 2.3), or 6.2.3.1 b) so that the amount of copper is 10 µg to 5 000 µg, and transfer it into a 100 ml volumetric flask.
- b) Add water to dilute it to the marked line.

9.4.3.2 Measurement of emission intensity

Spray a part of the solution obtained in 9.4.3.1 b) into argon plasma of ICP atomic emission spectrophotometer, and measure the emission intensity at the wavelength of

324.754 nm.

In the case where the emission intensity of copper at 324.754 nm is affected by coexisting elements, other unaffected wavelength for measurement shall be selected. If necessary, the background correction shall be carried out. The necessity of other wavelength selection and/or background correction shall be determined according to the preliminary measurement.

9.4.4 Blank test

Take the same amount of blank test solution obtained in 6.2.3.2 a) or b) as that partly taken in 9.4.3.1 a) from the original solution, and transfer it into a 100 ml volumetric flask. Hereafter, carry out the same operations as those of the original solution according to the procedures of 9.4.3.1 b) and 9.4.3.2 in parallel with the original solution.

9.4.5 Preparation of working curve

Take several amounts of the copper reference solution (9.4.2.1) and/or the copper reference solution (9.4.2.2) (0 µg to 5 000 µg as copper) to several 100 ml volumetric flasks in a stepwise manner. Hereafter, carry out the same operations as those of the original solution according to the procedures of 9.4.3.1 b) and 9.3.3.2 in parallel with the original solution, prepare the relation line between the obtained emission intensity and the amount of copper, translate the relation line so as to pass the origin, and take it as the working curve.

9.4.6 Calculation

The calculation shall be according to either of the following.

- a) **Case of sampling of fumes according to 6.1.3 a), b) or c) 2)** The amount of copper is obtained from the emission intensities obtained in 9.4.3.2 and 9.4.4, and the working curve prepared in 9.4.5. The copper content rate in the fumes shall be calculated according to the following formula.

$$Cu = \frac{(A_5 - A_6)}{m_3 \times \frac{B_9}{100}} \times 100$$

where, Cu: copper content rate in fumes [% (mass fraction)]
 A_5 : detected amount of copper in sample solution (mg)
 A_6 : detected amount of copper in blank test solution (mg)
 m_3 : sampling amount of fumes obtained in 6.1.3 a) 2), b) 2) or c) 2) 2.2) (mg)
 B_9 : aliquot of original solution and amount of blank test solution taken in 9.4.3.1 a) and 9.4.4 respectively (ml)

- b) **Case of sampling of fumes according to 6.1.3 c) 1)** The amount of copper is obtained from the emission intensities obtained in 9.4.3.2 and 9.4.4, and the working curve prepared in 9.4.5. The copper content rate in the fumes shall be calculated according to the following formula.