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**Iron and steel-Method for spark discharge atomic  
emission spectrometric analysis**

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## Iron and steel-Method for spark discharge atomic emission spectrometric analysis

**1 Scope** This Standard specifies the method for atomic emission spectrometric analysis by spark discharge of iron and steel and shall be applicable to the quantitative determination of respective components shown in Table 1. However, the quantitative determination of nitrogen shall be applicable to only steel.

**Remarks:** The iron in this Standard means pig iron, cast iron and the like, and the steel means carbon steel, low alloy steel, high alloy steel and the like.

**Table 1**                      **Components to be applied and determination range**

Component	Determination range % (m/m)	
Carbon	0.001	or over up to and incl. 5.5
Silicon	0.002	or over up to and incl. 6
Manganese	0.003	or over up to and incl. 30
Phosphorus	0.000 5	or over up to and incl. 1.0
Sulfur	0.000 2	or over up to and incl. 0.5
Nickel	0.002	or over up to and incl. 40
Chromium	0.002	or over up to and incl. 40
Molybdenum	0.001	or over up to and incl. 10
Copper	0.001	or over up to and incl. 6
Tungsten	0.01	or over up to and incl. 25
Vanadium	0.001	or over up to and incl. 6
Cobalt	0.001	or over up to and incl. 20
Titanium	0.000 5	or over up to and incl. 3
Aluminium	0.001	or over up to and incl. 5
Arsenic	0.001	or over up to and incl. 0.3
Tin	0.000 6	or over up to and incl. 0.3
Boron	0.000 05	or over up to and incl. 0.5
Nitrogen	0.001	or over up to and incl. 0.15.
Lead	0.001	or over up to and incl. 0.5
Zirconium	0.001	or over up to and incl. 1
Niobium	0.001	or over up to and incl. 2
Magnesium	0.001	or over up to and incl. 0.2
Calcium	0.000 1	or over up to and incl. 0.01
Tantalum	0.02	or over up to and incl. 0.2
Antimony	0.008	or over up to and incl.0.5.
Selenium	0.003	or over up to and incl. 0.1
Tellurium	0.003	or over up to and incl. 0.1

Lanthanum	0.002	or over up to and incl. 0.05
Cerium	0.005	or over up to and incl. 0.05

**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 G 0417 *Steel and iron-Sampling and preparation of samples for the determination of chemical composition*

JIS G 1201 *Iron and steel-General rules for analytical methods*

JIS K 0116 *General rules for atomic emission spectrometry*

JIS K 0211 *Technical terms for analytical chemistry (General part)*

JIS K 0212 *Technical terms for analytical chemistry (optical part)*

JIS K 0215 *Technical terms for analytical chemistry (analytical instrument part)*

JIS R 6001 *Bonded abrasive grain sizes*

**3 Definitions** For the purposes of this Standard, the definitions given in **JIS K 0116, JIS K 0211, JIS K 0212, JIS K 0215** and the following definitions apply.

- a) **measured value of emission strength** In the case of the emission strength method, the emission strength of quantitative component of the sample obtained by atomic emission spectrometry. In the case of the strength ratio method, the ratio of the emission strength of quantitative component of the sample to that of the internal standard element (iron, in general).
- b) **specific time integration method** The method in which the determination is carried out by integrating the strength of emitted spectral line for a specific time at the measurement of emission strength and then converting it to a digital signal value.
- c) **pulse distribution analysis (PDA method)** The method in which the emission strength is converted to a digital signal value for every single pulse at the measurement of emission strength and determined by using the numerical value (mean value, median value, etc.) treated statistically of the whole signal values of the pulse measured.
- d) **metallurgical hysteresis** The hysteresis of the sample such as the solidifying speed of melt sample, the heating temperature of heat treatment, rolling, forging, etc., influences the measured value of emission strength depending on the form of the metallic structure, precipitate, or intervening material, even if the chemical compositions of test portion are the same.

**4 General items** The general items required in analysis shall be in accordance with **JIS G 1201 and JIS K 0116**

**5 Summary** After cutting-off or cutting of the sample, it is finished to a plane surface by grinding or polishing, fixed to the sample support of emission spectrophotometer to make an electrode, and a spark is generated by using silver or tungsten as the counter electrode. The spectral line is then resolved by a spectroscope and the strength of the spectral line of the quantitative component of the sample is measured.

## 6 Equipment and analytical condition

**6.1 Emission spectrophotometer** The emission spectrophotometer shall be in accordance with 1.2 of Annex (normative), and shall be as follows:

- a) **Counter electrode** Mould the top end of silver rod or tungsten rod of 1 mm. to 7 mm diameter to a cone of 20° to 120° in angle or a truncated cone having a plane surface of 1 mm diameter by a moulding machine.
- b) **Argon** It is at least 99.99 % (m/m) in purity with a small amount of impurities such as oxygen, hydrocarbon, nitrogen. Since the purity of argon will influence greatly the quantitative value, in the case of supplying it to the equipment by using a cylinder, when the lot of the cylinders is changed or the residual quantity has reduced, confirm the determination result according to clause 12.

**6.2 Adjustment of equipment** The adjustment of equipment shall be in accordance with 1.3 of Annex (normative).

**6.3 Equipment performance reference** The equipment performance reference shall be as follows:

- a) For the emission spectrophotometer adjusted according to 6.2, the analytical condition (analytical line, excitation condition, photometry condition, etc.) shall be set so that the repeatability and sensitivity become adequate.
- b) The repeatability shall be not more than the tolerance on repeatability standard deviation shown in Table 2 and Table 3.  
The repeatability means the standard deviation of quantitative independent values obtained from the measured values of at least 6 measurements of the emission strength of a homogeneous sample, for example, the reference material of iron and steel for instrument analysis carried out continuously according to the procedure of clause 9.
- c) The checking of the equipment performance reference, in addition to those periodicals, shall be carried out every time the analytical condition is changed or the condition of equipment is changed by repairs, adjustments, etc.

Table 2 Repeatability standard deviation tolerance (steel)

Unit: % (m/m)

Component	Range of component content		Repeatability standard deviation tolerance (1)
Carbon	0.013	or over to and excl. 0.14	$3.0 \times (0.013\ 08 \times C \% + 0.000\ 45)$
	0.14	or over up to and incl. 0.49	$3.0 \times (0.001\ 98 \times C \% + 0.002\ 01)$ .
Silicon	0.10	or over up to and incl. 1.42	$3.0 \times (0.009\ 40 \times Si \% - 0.000\ 38)$
Manganese	0.12	or over up to and incl. 1.79	$3.0 \times (0.005\ 08 \times Mn \% + 0.000\ 11)$
Phosphorus	0.004	or over up to and incl. 0.038	$3.0 \times (0.012\ 75 \times P \% + 0.000\ 09)$
Sulfur	0.002	or over up to and incl. 0.041	$3.0 \times (0.026\ 30 \times S \% + 0.000\ 06)$
Nickel	0.015	or over to and excl. 4.00	$3.0 \times (0.005\ 98 \times Ni \% + 0.000\ 34)$
	4.00	or over up to and incl. 20.6	$3.0 \times (0.007\ 40 \times Ni \% - 0.005\ 33)$
Chromium	0.011	or over to and excl. 3.3	$3.0 \times (0.004\ 13 \times Cr \% + 0.000\ 43)$
	3.3	or over to and excl. 15.0	$3.0 \times (0.001\ 48 \times Cr \% + 0.009\ 20)$
	15.0	or over up to and incl. 25.6	$3.0 \times (0.008\ 20 \times Cr \% - 0.091\ 60)$
Molybdenum	0.010	or over up to and incl. 2.43	$3.0 \times (0.006\ 03 \times Mo \% + 0.000\ 16)$
Copper	0.024	or over up to and incl. 0.49	$3.0 \times (0.007\ 19 \times Cu \% + 0.000\ 25)$
Vanadium	0.010	or over up to and incl. 0.40	$3.0 \times (0.004\ 13 \times V \% + 0.000\ 09)$
Cobalt	0.013	or over up to and incl. 0.27	$3.0 \times (0.002\ 44 \times Co \% + 0.000\ 29)$
Titanium	0.012	or over up to and incl. 0.10	$3.0 \times (0.009\ 27 \times Ti \% + 0.000\ 01)$
Arsenic	0.005	or over up to and incl. 0.046	$3.0 \times (0.004\ 74 \times As \% + 0.000\ 24)$
Tin	0.006	or over up to and incl. 0.066	$3.0 \times (0.008\ 75 \times Sn \% + 0.000\ 08)$
Boron	0.0014	or over up to and incl. 0.007	$3.0 \times (0.004\ 73 \times B \% + 0.000\ 03)$
Nitrogen	0.001	or over up to and incl. 0.15	$3.0 \times (0.009\ 99 \times N \% + 0.000\ 39)$
Zirconium	0.008	or over up to and incl. 0.039	$3.0 \times (0.020\ 45 \times Zr \% + 0.000\ 06)$
Niobium	0.010	or over up to and incl. 0.050	$3.0 \times (0.003\ 08 \times Nb \% + 0.000\ 26)$
Calcium	0.000 6	or over up to and incl. 0.0029	$3.0 \times (0.022\ 23 \times Ca \% + 0.000\ 02)$

Note (1) For the elementary symbol for each component, followed by %, the mean value of the quantitative values [% (m/m)] obtained during the procedure of determining the repeatability of each component in 6.3 b) is inserted.

**Table 3 Repeatability standard deviation tolerance (iron)**

Unit: % (m/m)

Component	Range of component content		Repeatability standard deviation tolerance (1)
Carbon.	2.2	or over up to and incl. 4.32	$3.0 \times (0.005\ 01 \times C \% + 0.002\ 9)$
Silicon	0.32	or over to and excl. 1.60	$3.0 \times (0.006\ 09 \times Si \% + 0.001\ 7).$
	1.60	or over up to and incl. 3.44	$3.0 \times (0.014\ 59 \times Si \% - 0.011\ 8).$
Manganese	0.18	or over up to and incl. 2.42	$3.0 \times (0.003\ 92 \times Mn \% + 0.001\ 3)$
Phosphorus	0.010	or over up to and incl. 0.57	$3.0 \times (0.010\ 40 \times P \% + 0.000\ 3)$
Sulfur	0.003	or over up to and incl. 0.23	$3.0 \times (0.032\ 82 \times S \% + 0.000\ 2)$
Nickel	0.03	or over up to and incl. 5.27	$3.0 \times (0.008\ 26 \times Ni \% + 0.0001)$
Chromium	0.02	or over up to and incl. 2.11	$3.0 \times (0.006\ 42 \times Cr \% + 0.000\ 2)$
Copper	0.02	or over up to and incl. 2.11	$3.0 \times (0.046\ 70 \times Cu \% + 0.000\ 3)$
Titanium	0.009	or over up to and incl. 0.17	$3.0 \times (0.018\ 66 \times Ti \% - 0.000\ 1)$

**6.4 Analytical condition** The analytical condition shall be set so as to satisfy the equipment performance reference depending on the classification of the test portion, the coexisting components, the classification of simultaneous quantitative component of the sample and the content of quantitative component of the sample. The examples of the analytical conditions and the related matters are shown in Table 4 to Table 7. The emission strength becomes in some cases unstable immediately after exchanging to a newly moulded counter electrode and under the condition of discharge repeated multiple times. Therefore, the range of number of times for analysis, in which an emission strength is stably obtained shall be previously investigated.

**Table 4 An example of analytical condition**

Item	Contents
Pressure in spectroscope	2.7 Pa max.
Reciprocal linear dispersion of spectroscope	1 nm/mm max.
Inlet slit width	20 $\mu$ m to 50 $\mu$ m
Photometry method	Specific time integration method. Time resolved PDA photometry
Gap between test portion and counter electrode	4.0 mm to 6.0 mm
Flow rate of argon gas at the time of emission	4 L/min to 18 L/min
Wavelength of analytical line	See Table 5
Excitation condition and discharge condition	See Table 6 and Table 7

Table 5 An example of analytical line and internal standard line

Component	Wavelength of analytical line nm	Component	Wavelength of analytical line nm
Carbon	C I 156.14	Aluminium	Al I 808.22
	C I 165.81		Al I 394.40
	C I 193.09		Al I 396.15
Silicon	Si I 212.42	Arsenic	As I 197.26
	Si I 251.61		As I 228.81
	Si I 288.16		As I 234.98
Manganese	Mn II 290.02	Tin	Sn I 189.99
	Mn II 293.81		Sn I 317.50
Phosphorus	P I 177.50		Sn I 326.23
	P I 178.29	Boron	B I 182.58
	P I 214.91		B I 182.6
Sulfur	S I 180.73		B II 206.72
	Nickel		Ni II 225.39
		Ni II 227.02	B I 249.68
Ni II 227.73		Nitrogen	N I 149.26
Ni II 231.60			Lead
Ni I 341.48		Pb I 283.31	
Ni II 248.79		Pb I 405.78	
Chromium	Cr II 265.85	Zirconium	Zr II 339.20
	Cr II 267.72		Zr II 343.82
	Cr II 276.65	Niobium	Nb II 319.50
	Cr II 286.09		Nb II 320.63
	Cr II 286.26	Magnesium	Mg II 279.55
	Cr II 298.92		Mg II 280.27
	Cr I 428.97	Calcium	Ca II 393.37
Molybdenum	Mo II 202.03		Ca II 396.85
	Mo II 277.54	Tantalum	Ta II 240.06
	Mo II 281.62		Antimony
	Mo I 313.26	Selenium	Se I 196.09
	Mo I 317.03	Tellurium	Te I 214.28
	Mo I 386.41	Lanthanum	La II 408.67



Table 5 (concluded)

Component	Wavelength of analytical line nm	Component	Wavelength of analytical line nm	
Copper	Cu II 213.60	Cerium	Ce II 413.76	
	Cu II 224.26		Iron (internal standard line)	Fe II 170.20
	Cu I 327.40			Fe II 261.49
Tungsten	W II 209.86			Fe II 271.44
	W II 210.32			Fe I 287.23
	W II 220.45			Fe I II 287.53
	W II 239.71			Fe I 296.69
	W I 400.88			Fe II 322.77
Vanadium	V II 310.23			Fe I 353.66
	V II 311.07			Fe I 871.99
	V II 437.92			Fe I 382.04
Cobalt	Co II 228.62		Fe I 393.03	
	Co II 258.03		Fe I 438.35	
	Co I 345.35	Fe I 440.48		
Titanium	Ti II 323.45			
	Ti II 324.20			
	Ti II 337.28			

Table 6 An example of excitation condition

No.	Excitation condition					Remarks
	Secondary voltage E (V)	Electrostatic capacity C ( $\mu$ F)	Self-induction L ( $\mu$ H)	Secondary resistance R ( $\Omega$ )	Frequency f (Hz)	
I	300 to 1 000	2 to 12	3 to 35	Residue to 5	200 to 600	Mainly applied to predischage
II	300 to 1 000	2 to 20	(1) 10, 140 (2) 20, 160	Residue to 10	40 to 500	Mainly applied to the determination of phosphorous, sulfur, boron, aluminium and tin.
III	300 to 700	1.5 to 2.5	5 to 20	Residue to 10	40 to 500	Mainly applied to the determination of components other than mentioned above
IV	300 to 500	(1) 4, 2, 2 (2) 2, 2, 2	(1) 2, 20, 140 (2) 2, 2, 150 (3) 2, 22, 142 (4) 8, 16, 198	Residue	40 to 500	Excitation source used for determination of one pulse of emission strength based on the division of time

V	300 to 850	0.5 to 2.5	5 to 180	Residue to 10	40 to 500	Applied to the removal of adhered matter at the top of the counter electrode.
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Table 7 An example of discharge condition

		Predischarge	Determination of phosphorus, sulfur, boron, aluminium, tin	Determination of component other than those mentioned to the left	Cleaning of counter electrode
Application example 1	Discharge order	1	2	3	4
	Excitation condition <sup>(2)</sup>	Any one of I to IV	II	III	V
	Number of pre-discharges	700 to 3 000	100 to 500	100 to 500	10 to 600
	Number of measurement pulses	-	1 000 to 2 000	1000 to 2 000	-
Application example 2	Discharge order	None	1	2	3
	Excitation condition <sup>(2)</sup>		II	III	V
	Number of pre-discharges		700 to 3 000	100 to 500	10 to 600
	Number of measurement pulses		1000 to 2 000	1000 to 2 000	
Application example 3	Discharge order	None	1		2
	Excitation condition <sup>(2)</sup>		IV		V
	Number of pre-discharges		700 to 3 000		10 to 600
	Number of measurement pulses		1000 to 2 000		-

**Note <sup>(2)</sup>** That indicates No. of excitation condition in Table 6.

## 7 Reference material for preparation of working curve, sample for calibration of working curve and test portion

**7.1 Reference material for preparation of working curve** The reference material for preparation of working curve shall be as follows:

a) **Certified reference material of iron and steel for instrument analysis** It shall be the sufficiently homogeneous reference material of iron and steel for instrument analysis with the certified value for one or more components. However, the metallurgical hysteresis of the certified reference material is in some cases, different from that of the test portion and it is required that the working curve is corrected by using the reference material of iron

and steel for instrument analysis which is analogous to the test portion in metallurgical hysteresis and chemical composition, when used as the reference material for preparation. of the working curve.

b) **Reference material of iron and steel for instrument analysis** It shall be homogeneous, analogous to the test portion in metallurgical hysteresis and chemical composition, and the reference value of quantitative component of the sample shall be determined by using the method for chemical analysis specified officially in Japanese Industrial Standard and the like, and the accuracy shall be certified by the certified reference material of iron and steel for analysis (). When there is chemical is not such 1 official standard as that, the reference value shall be decided by using the method for chemical analysis which has been technically confirmed and formulated in documents in the analytical laboratory. When the reference value of reference material of iron and steel for instrument analysis is determined, it is required to confirm that the quantitative value satisfies (4) the tolerance by analysing the certified reference material of iron and steel for chemical analysis in parallel. When there is not such a standard as that, the reference used shall be formulated in documents.

Notes (3) It is the sufficiently homogeneous reference material of iron and steel for chemical analysis with the certified value for one or more components.

(4) The details of the judgement method shall be in accordance with **JIS G 1201**.

**7.2 Sample for calibration of working curve** It is the sample to be daily used in order to carry out the confirmation and calibration of working curve, and if it is the certified reference material of iron and steel for instrument analysis or any sample with homogeneity equivalent to that, it is not required that the sample is analogous in metallurgical hysteresis and chemical composition. This sample may also be used for the judgement of equipment performance reference.

**7.3 Test portion** The test portion shall be sampled according to **JIS G 0417**.

**8 Preparation of test portion** For the preparation of test portion, the test portion shall be cut off according to **JIS G 0417** or processed by using a cutting machine to the shape () of not less than 20 mm in the diameter of analytical surface and not less than 3 mm in thickness, and the analytical surface shall be prepared to a plane surface (6) by a grinding or polishing machine.

For the molten pig iron, the test portion shall be prepared so that the part of white cast iron is made to be the analytical surface. In the case of using an abrasive belt and a grinder, the grain size of abrasives for sample preparation shall be # 36 to # 240 specified in JIS R 6001. Some types of abrasives may depend on quality of material of abrasive grains, contaminate the analytical surface, causing to influence the quantitative value. Therefore, the quality of material shall be selected so as to suit the purpose. The raising of the sample temperature at the time of preparation of test portion will influence the quantitative value in some cases depending on the emission condition, therefore it is required to always keep the preparation conditions at a constant temperature.

**Notes** (5) In the case of a sample under 20 mm in diameter, or under 3 mm in thickness, the auxiliary metal fittings shall be used.

(6) The abrasives and cutting machine shall be controlled so that the discharge surface of the sample is finished to be flat and smooth, and its roughness uniform.

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**9. Operation** The operation shall be in accordance with **JIS K 0116**, and shall be in accordance with either of the following.

**a) Emission strength method**

- 1) Fix the counter electrode **[6.1 a)]** and the test portion prepared in clause 8 to the sample support of analytical equipment adjusted according to 6.2.
- 2) Start the emission under the analytical condition decided according to 6.4, and measure the emission strength.
- 3) Take the emission strength obtained in 2) as the measured value of emission strength.

**b) Strength ratio method**

- 1) Follow the procedures of 1) and 2) in a).
- 2) Obtain the ratio of the emission strength of quantitative component of the sample obtained in 2) in a) to the emission strength of internal standard element, and take it as the measured value of emission strength.

**10 Preparation of working curve** The preparation of working curve shall be in accordance with any one following.

- a) Preparation of working curve by type Prepare (7) not less than four types of reference materials for preparation of working curve which are analogous to the test portion in metallurgical hysteresis and chemical composition and in which the range of quantitative component of the sample content can be divided approximately equally. Carry out the measurement of emission strength under the same condition as in test portion according to the procedure of a) in clause 9 or b) in clause 9, and obtain the relation curve from any one of formula (1), formula (2), or formula (8) from the measured value of emission strength obtained and the reference value of quantitative component of the sample. The working curve (8) shall be taken from the relation curve.

$$W_i = a_1 I_i + b_1$$

$$W_i = a_2 I_i^2 + b_2 I_i + c_2$$

$$W_i = a_n I_i^n + b_n I_i^{(n-1)} + c_n$$

where,  $W_i$ : Reference value of quantitative component of the sample,  $i$ , of reference material for preparation of working curve % (m/m)

$I_i$ : measured value of emission strength of quantitative component of the sample,  $i$ , of reference material for preparation of working curve.

$a_1, b_1$  : constant term

$a_2, b_2, c_2$  : constant term

$a_n, b_n, c_n$  : constant term

Note (7) A series of certified reference materials of iron and steel for instrument analysis or a series of reference materials of iron and steel for instrument analysis which have different metallurgical hysteresis and/or chemical composition from the test portion may be used. However, in such a case, the reference material of iron and steel for instrument analysis analogous to the test portion in metallurgical hysteresis and chemical composition is analyzed by using the working curve already obtained, the bias of quantitative value from the reference value is obtained and the working curve is made by correcting so as to minimize the bias.

(8) The working curve may be prepared by dividing the range of content justifiably.

b) **Preparation of reference working curve** (9) The preparation of reference working curve shall be carried out according to the following procedure:

Note (9) For example, the overlap correction factor of spectral line specified in the following may be used when the components of test portion, which is analogous to the reference material for preparation of working curve in metallurgical hysteresis and different in chemical composition, is determined by correcting the influence of coexisting component and iron quantity.

1) **Calculation of overlap correction factor of spectral line** (10) Measure the emission strength of the quantitative component of the sample,  $i$ , of a series of Fe- $i$  binary dimensional reference materials of iron and steel (11) composed of iron and quantitative component of the sample,  $i$ , according to the procedure of a) in clause 9 or b) in clause 9. For the relation of this measured value of emission strength to the reference value of quantitative component of the sample,  $i$ , the Fe- $i$  binary dimensional working curve shall be taken. Next, measure the emission strength of quantitative component of the sample,  $i$ , at the analytical line by using a series of Fe- $j$  binary dimensional reference materials of iron and steel composed of iron and component,  $j$ , under the same condition as the Fe- $i$  binary dimensional reference material of iron and steel and obtain the apparent quantitative value,  $\Delta X_1$  (12), equivalent to the quantitative value,  $i$ , from the measured value of emission strength and the Fe- $i$  binary dimensional working curve. Carry out the primary regression calculation on the relation of this  $\Delta X_1$  to the content of coexisting component,  $j$ , by the method of least squares, and obtain the overlap correction factor,  $l_j$ , of spectral line according to formula (4),

$$\Delta X_1 = l_j \cdot W_j + C \dots\dots\dots (4)$$

where,  $\Delta X_1$ : apparent quantitative value of quantitative component of the sample,  $i$ , of Fe- $j$  binary dimensional reference material of iron and steel % (m/m)

$W_j$  : reference value of quantitative component of the sample,  $j$ , of Fe- $j$  binary dimensional reference material of iron and steel % (m/m)

$l_j$  : overlap correction factor of spectral line of coexisting component,  $j$ , to quantitative component of the

$C$  : constant term

Notes (10) It is the correction factor indicating the rate of the influence of coexisting component to the quantitative value of quantitative component of the sample. In other words, it is the factor correcting the influence amount of coexisting component, j, to the quantitative component of the sample, i, when the spectral line of quantitative component of the sample, i, is overlapped

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by the spectral line of coexisting component, j, and the apparent emission strength of quantitative component of the sample, i, indicates the higher value than the actual strength.

(11) It is the reference material of iron and steel of which the main component is iron and to which only one quantitative component of the sample is added. It contains, other component the content of which is absolute minimum.

(12) When the influence of the quantitative component of the sample, i, contained in Fe-j binary dimensional reference material of iron and steel cannot be ignored, it is required to calculate the correction factor,  $l_j$ , after the content of quantitative component of the sample, i, is subtracted from the apparent quantitative value.

**2) Calculation of estimated reference value** Calculate  $X_i$ , by using the reference value,  $W_i$  (13), of quantitative component of the sample, i, of the reference material for preparation of working curve (multi-dimensional), the reference value,  $W_j$ (18), of coexisting component, j, and the correction factor,  $l_j$ , obtained in 1) according to formula (5), and make it the estimated reference value of quantitative component of the sample, i, of the reference material for preparation of working curve (multi-dimensional).

$$X_i = W_i + \sum l_j \cdot W_j \dots\dots\dots (5)$$

**Note (13)** In the case of the correction of iron quantity, the values (ratio of iron quantity),  $W_i$ ,  $W_j$  obtained by dividing the content by the rate of iron content ( $W_{Fe}$ ) shall be used.

$$W_i' = W_i / (W_{Fe} / 100)$$

$$W_j' = W_j / (W_{Fe} / 100)$$

3) Preparation of reference working curve Concerning the reference material for preparation of working curve (multi-dimensional) from which the estimated reference value,  $X_1$ , is obtained in 2), follow the procedure of a) in clause 9 or b) in clause 9 under the same condition as that of the test portion, obtain the relation formula of any one of formula (6), formula (7) or formula (8) from the measured value. of emission strength of quantitative component of the sample obtained and the estimated reference value,  $X_1$ , and take it as the reference working curve (14).

$$X_i = a_{11} + b_1 \dots\dots\dots (6)$$

$$X_i = a_2 l_i^2 + b_2 l_i + C_2 \dots\dots\dots (7)$$

$$X_i = a_n l_i^n + b_n l_i^{(n-1)} + C_2 \dots\dots\dots (8)$$

where,  $X_i$  : estimated reference value of quantitative component of the sample, i, of the reference material for preparation of working curve obtained in 2) % (m/m)

$l_i$  : measured value of emission strength of quantitative component of the sample, i, of the reference material for preparation of working curve

- a<sub>1</sub>, b<sub>1</sub> : constant term  
a<sub>2</sub>, b<sub>2</sub>, C<sub>2</sub> : constant term  
a<sub>n</sub>, b<sub>n</sub>, c<sub>n</sub> : constant term

Note (14) The reference working curve does not completely conform to the real binary dimensional working curve in some cases because of the micro error caused by the approximation of working curve, etc.

C) Preparation of reference working curve by type <sup>(15)</sup> Carry out the procedure of b) for every metallurgical hysteresis or every suitable component content so as to minimize the error of quantitative value, obtain the relation formula of I to  $\hat{A}_1$ , and take it as the reference working curve by type.

**Note (15)** This reference working curve shall be used when the accuracy within tolerance cannot be obtained for the quantitative value obtained by the working curve of a) and the reference working curve of b), and when the correction of the influence of coexisting component or the influence of variation in iron quantity is carried out for every metallurgical hysteresis of test portion or every suitable component content.

**11 Verification of working curve** The reference material for preparation of working curve analogous to the test portion in metallurgical hysteresis and chemical composition shall be determined in the range of component content in Table 8 or Table 9, and it shall be confirmed that the quantitative value is within the counter reference material tolerance in Table 8 or Table 9. If not satisfied, the fractionalization of working curve by type, the division of concentration range of working curve or the change to reference working curve by type from reference working curve, etc. shall be investigated.

Table 8 Counter reference material tolerance (steel)

Unit: % (m/m)

Component	Range of component content	Counter reference material tolerance (10)
Carbon	0.013 or over to and excl. 0.12	2.0 x (0.039 26 x C % + 0.002 64)
	0.12 or over up to and incl. 0.49	2.0 x (0.025 67 x C % + 0.004 26)
Silicon	0.10 or over up to and incl. 1.42	2.0x (0.025 98 x Si % + 0.003 20)
Manganese	0.12 or over up to and incl. 1.79	2.0 (0.018 00 x Mn % + 0.004 05)
Phosphorus	0.004 or over up to and incl. 0.038	2.0 x (0.041 48x P% + 0.000 80)
Sulfur	0.002 or over up to and incl. 0.041	2.0 x (0.067 98 x S% + 0.000 36)
Nickel	0.015 or over to and excl. 4.00	2.0 x (0.016 38 x Ni % + 0.001 55)
	4.00 or over up to and incl. 20.6	2.0x (0.047 18 x Ni % - 0.121 44)
Chromium	0.011 or over to and excl. 1.02	2.0 x (0.020 64 x Cr % + 0.003 09)
	1.02 or over to and excl. 15.0	2.0 x (0.015 85 x Cr % + 0.008 48)
	15.0 or over up to and incl. 25.6	2.0 x (0.041 39 x Cr % - 0.382 18)
Molybdenum	0.010 or over up to and incl. 2.43	2.0 x (0.022 50 x Mo % + 0.003 81)
Copper	0.024 or over up to and incl. 0.49	2.0 x (0.025 16 x Cu % + 0.001 31)
Vanadium	0.010 or over up to and incl. 0.40	2.0 x (0.018 74 x V% + 0.001 17)
Cobalt	0.018 or over up to and incl. 0.27	2.0x (0.034 77 x Co % + 0.001 50)
Titanium	0.012 or over to and excl. 0.05	2.0 x (0.023 04 x Ti% + 0.001 16)
	0.05 or over up to and incl. 0.10	2.0 x (0.015 00 x Ti % + 0.001 43)
Aluminium	0.005 or over up to and incl. 0.078	2.0x (0.017 69 x Al % + 0.001 56)
Arsenic	0.005 or over up to and incl. 0.046	2.0 x (0.028 34 x As % + 0.001 05)
Tin	0.006 or over up to and incl. 0.066	2.0x (0.023 83 x Sn % + 0.000 89)
Boron	0.001 4 or over up to and incl. 0.007	2.0 X (0.049 28 x B % + 0.000 09)
Nitrogen	0.001 or over to and excl. 0.015	2.0x (0.031 58 x N% + 0.000 25)
	0.015 or over up to and incl. 0.070	2.0x (0.018 68 x N % + 0.000 63)
Zirconium	0.008 or over up to and incl. 0.039	2.0x (0.028 40 x Zr % + 0.002 57)
Niobium	0.010 or over up to and incl. 0.050	2.0 (0.015 00xNb % + 0.001 71)
Calcium	0.000 6 or over up to and incl. 0.0029	2.0x (0.053 57 x Ca % + 0.000 14)
Antimony	0.008 or over up to and incl. 0.019	2.0 x (0.091 67 x Sb % + 0.003 90)
Tungsten	0.001 or over to and excl. 0.05	2.0 x (0.212 01xW% + 0.000 71)
Lead	0.05 or over to and excl. 1	2.0 (0.078 64 x Pb % + 0.007 63)
Magnesium	1 or over up to and incl. 25	2.0 x (0.024 73 x Mg % + 0.056 19)
Tantalum		
Selenium		
Tellurium		
Lanthanum		
Cerium		



Note (16) For the elementary symbol for each component or X, followed by %, the quantitative value of the component is inserted {% (m/m)}

**Table 9 Counter reference material tolerance (iron)**

Unit: % (m/m)

Component	Range of component content	Counter reference material tolerance (16)
Carbon	2.02 or over up to and incl. 4.32	$2.0 \times (0.018\ 06 \times C \% + 0.096\ 3)$
Silicon	0.82 or over up to and incl. 3.44	$2.0 \times (0.024\ 21 \times Si \% + 0.010\ 2)$
Manganese	0.18 or over to and excl. 0.93	$2.0 \times (0.016\ 20 \times Mn \% + 0.003\ 3)$
	0.93 or over up to and incl. 2.42	$2.0 \times (0.021\ 34 \times Mn \% - 0.001\ 5)$
Phosphorus	0.010 or over up to and incl. 0.57	$2.0 \times (0.015\ 36 \times P \% + 0.002\ 1)$
Sulfur	0.003 or over up to and incl. 0.23	$2.0 \times (0.056\ 10 \times S \% + 0.001\ 2)$
Nickel	0.03 or over to and excl. 1.70	$2.0 \times (0.010\ 25 \times Ni \% + 0.002\ 7)$
	1.70 or over up to and incl. 5.27	$2.0 \times (0.032\ 48 \times Ni \% - 0.035\ 1)$
Chromium	0.02 or over up to and incl. 2.11	$2.0 \times (0.018\ 23 \times Cr \% + 0.000\ 9)$
Copper	0.02 or over up to and incl. 2.11	$2.0 \times (0.025\ 73 \times Cu \% + 0.000\ 8)$
Titanium	0.009 or over up to and incl. 0.17	$2.0 \times (0.038\ 94 \times Ti \% + 0.000\ 9)$
Tungsten	0.001 or over to and excl. 0.05	$2.0 \times (0.212\ 01 \times X \% + 0.000\ 71)$
Lead	0.05 or over to and excl. 1	$2.0 \times (0.073\ 64 \times X \% + 0.007\ 63)$
Magnesium	1 or over up to and incl. 25	$2.0 \times (0.024\ 73 \times X \% + 0.056\ 19)$
Tantalum		
Selenium		
Tellurium		
Lanthanum		
Cerium		

**12 Calibration of working curve** The calibration of working curve shall be as follows:

- a) The reference material for preparation of working curve shall be periodically determined, and it shall be confirmed that the quantitative value satisfies the counter reference material tolerance shown in Table 8 or Table 9 or the sample for calibration of working curve is periodically determined and the difference from the desired value (17) at the time of calibration is within the laboratory reproducibility limit shown in Table 10 or Table 11. The confirmation by the former shall be surely carried out at a specific frequency. When those are not satisfied and the variation factor in equipment as shown in the following 1) to 9) arises, the working curve shall be calibrated.

Note (17) It means the temporary value of each quantitative component of the sample obtained by analyzing repeatedly the sample for calibration of working curve by using the working curve at the initial step of preparation of working curve and after verification.

- 1) Case of the sudden change in voltage of power supply.

- 2) Case of degradation of vacuum in spectroscope
- 3) Case of cleaning of condensation lens or protective quartz plate
- 4) Case of changing of the lot of argon gas cylinder
- 5) Case of exchanging of the abrasives for sample preparation
- 6) Case of exchanging of counter electrode

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- 7) Case of adjusting of relative position of inlet slit to spectral line
- 8) Case of carrying out of repairs and adjustment of equipment
- 9) Case of a long term pause of analysis

b) The calibration of working curve, for example, shall be in accordance with the following method.

The change of the measured value of emission strength from the time of preparation of working curve shall be corrected (18) by using the two samples for calibration of working curve in the neighbourhood of the upper limit and the lower limit in the range of content in working curve according to formula (9).

$$I_i = \alpha \cdot I_i' + \beta \quad (9)$$

where,  $I_i$ : strength of quantitative component of the sample, i, of test portion after corrected

$$\alpha = (I_{iH} - I_{iL}) / (I_{iH}' - I_{iL}')$$

$I_i'$ : uncorrected strength of quantitative component of the sample, i, of test portion

$$\beta = I_{iH} - \alpha \cdot I_{iH}'$$

$I_{iH}$ : measured value of emission strength of the sample for preparation of working curve at high concentration side at the time of preparation of working curve

$I_{iL}$ : measured value of emission strength of the sample for preparation of working curve at low concentration side at the time of preparation of working curve

$I_{iH}'$ : measured value of emission strength of the sample for preparation of working curve at high concentration side at the time of determination

$I_{iL}'$ : measured value of emission strength of the sample for preparation of working curve at low concentration side at the time of determination

Note (18) It is treated as the calibration for the measured value of emission strength of test portion in the calculation, however the effect of calibrate working curve is the same.

- c) After calibrating the working curve, it shall be confirmed that the quantitative value satisfies the counter reference material tolerance shown in Table 8 or Table 9 by determining the reference material for preparation of working curve or the difference from the desired value (17) at the time of calibration satisfies the within laboratory-reproducibility limit shown in Table 10 or Table 11 by determining the sample for calibration of working curve. The confirmation by the former shall be surely carried out at a specified frequency.
- d) When the condition of e) is not satisfied by calibration, another working curve shall be prepared according to clause 10 and then verified according to clause 11.

**Table 10 Within-laboratory-reproducibility limit (steel)**

Unit: % (m/m)

Component	Range of component content		Within-laboratory-reproducibility limit (1)
Carbon	0.013	or over to and excl. 0.12	$2.0 \times (0.027\ 21 \times C \% + 0.001\ 32)$
	0.12	or over up to and incl. 0.49	$2.0 \times (0.016\ 09 \times C \% + 0.002\ 63)$
Silicon	0.10	or over up to and incl. 1.42	$2.0 \times (0.017\ 94 \times Si \% + 0.000\ 31)$
Manganese	0.12	or over up to and incl. 1.79	$2.0 \times (0.010\ 85 \times Mn \% + 0.001\ 53)$
Phosphorus	0.004	or over up to and incl. 0.038	$2.0 \times (0.025\ 81 \times P \% + 0.000\ 17)$
Sulfur	0.002	or over up to and incl. 0.041	$2.0 \times (0.043\ 75 \times S \% + 0.000\ 24)$
Nickel	0.015	or over to and excl. 4.00	$2.0 \times (0.010\ 21 \times Ni \% + 0.001\ 03)$
	4.00	or over up to and incl. 20.6	$2.0 \times (0.029\ 97 \times Ni \% - 0.078\ 02)$
Chromium	0.011	or over up to and incl. 1.02	$2.0 \times (0.008\ 00 \times Cr \% + 0.002\ 15)$
	1.02	or over up to and incl. 15.0	$2.0 \times (0.010\ 44 \times Cr \% - 0.001\ 46)$
	15.0	or over up to and incl. 25.8	$2.0 \times (0.027\ 66 \times Cr \% - 0.259\ 90)$
Molybdenum	0.010	or over up to and incl. 2.43	$2.0 \times (0.012\ 55 \times Mo \% + 0.001\ 01)$
Copper	0.024	or over up to and incl. 0.49	$2.0 \times (0.016\ 76 \times Cu \% + 0.000\ 86)$
Vanadium	0.010	or over up to and incl. 0.40	$2.0 \times (0.009\ 91 \times V \% + 0.000\ 18)$
Cobalt	0.018	or over up to and incl. 0.27	$2.0 \times (0.012\ 20 \times Co \% + 0.000\ 86)$
Titanium	0.012	or over to and excl. 0.05	$2.0 \times (0.015\ 55 \times Ti \% + 0.000\ 16)$
	0.05	or over up to and incl. 0.10	$2.0 \times (0.008\ 20 \times Ti \% + 0.000\ 52)$
Aluminium	0.005	or over up to and incl. 0.073	$2.0 \times (0.008\ 20 \times Al \% + 0.000\ 85)$
Arsenic	0.005	or over up to and incl. 0.046	$2.0 \times (0.009\ 39 \times As \% + 0.000\ 42)$
Tin	0.006	or over up to and incl. 0.066	$2.0 \times (0.007\ 79 \times Sn \% + 0.000\ 21)$
Boron	0.001 4	or over up to and incl. 0.007	$2.0 \times (0.008\ 79 \times B \% + 0.000\ 05)$
Nitrogen	0.001	or over up to and incl. 0.015	$2.0 \times (0.009\ 79 \times N \% + 0.000\ 19)$
	0.015	or over up to and incl. 0.070	$2.0 \times (0.004\ 53 \times N \% + 0.000\ 38)$
Zirconium	0.008	or over up to and incl. 0.039	$2.0 \times (0.014\ 52 \times Zr \% + 0.000\ 21)$
Niobium	0.010	or over up to and incl. 0.050	$2.0 \times (0.007\ 13 \times Nb \% + 0.000\ 55)$
Calcium	0.000 6	or over up to and incl. 0.002 9	$2.0 \times (0.021\ 38 \times Ca \% + 0.000\ 08)$
Antimony	0.008	or over up to and incl. 0.019	$2.0 \times (0.046\ 50 \times Sb \% + 0.002\ 63)$

**Note (19)** The elementary symbol of each component means the quantitative value of The Component {% (m/m)}

**Table 11 Within-laboratory-reproducibility limit (iron)****Unit: % (m/m)**

component	Range of component content	Within-laboratory-reproducibility limit (19)
Carbon	2.02 or over up to and incl. 4.32	$2.0 \times (0.01120 \times C \% + 0.0650)$
Silicon	0.32 or over up to and incl. 3.44	$2.0 \times (0.01592 \times Si \% + 0.0063)$
Manganese	0.18 or over to and excl. 0.93	$2.0 \times (0.00735 \times Mn \% + 0.0012)$
	0.93 or over up to and incl. 2.42	$2.0 \times (0.01520 \times Mn \% - 0.0061)$
Phosphorus	0.010 or over up to and incl. 0.57	$2.0 \times (0.01037 \times P \% + 0.0013)$
Sulfur	0.003 or over up to and incl. 0.23	$2.0 \times (0.03478 \times S \% + 0.0008)$
Nickel	0.03 or over to and excl. 1.70	$2.0 \times (0.00609 \times Ni \% + 0.0017)$
	1.70 or over up to and incl. 5.27	$2.0 \times (0.02161 \times Ni \% - 0.0244)$
Chromium	0.02 or over up to and incl. 2.11	$2.0 \times (0.01100 \times Cr \% + 0.0005)$
Copper	0.02 or over up to and incl. 2.11	$2.0 \times (0.01521 \times Cu \% + 0.0006)$
Titanium	0.009 or over up to and incl. 0.17	$2.0 \times (0.01543 \times Ti \% + 0.0006)$

**13 Calculation** The calculation shall be in accordance with any one of the following:

a) **Case of using the reference working curve by type** Obtain  $W_i$ , from the measured value of emission strength,  $I_i$ , obtained in clause 9 and the working curve prepared in 10 a) and calibrated in clause 12, and take it as the quantitative value of quantitative component of the sample,  $i$ , in the sample.

b) **Case of using the reference working curve or the reference working curve by type**

**1) Case of emission strength method**

**1.1) Calculation of uncorrected quantitative value** Obtain  $X_i$ , from the measured value of emission strength,  $I_i$ , obtained in 9 a) and the working curve prepared in 10 b) 3) and calibrated in clause 12, and take it as the uncorrected quantitative value,  $X_1$ .

**1.2) Calculation of quantitative value** Calculate the quantitative value by using  $X_i$ ; obtained in 1.1) and  $I_j$  obtained in 10 b) 1) according to the following formula (10).

$$\hat{W}_i = X_i - \sum I_j \cdot W_j \quad (10)$$

where,  $\hat{W}_i$ : quantitative value of quantitative component of the sample,  $i$ , in the test portion % (m/m)

$X_i$ : uncorrected quantitative value of quantitative component of the sample,  $i$ , in the test portion obtained in 1.1) % (m/m)

$W_j$ : content of coexisting component,  $j$ , in the test portion % (m/m)(20)

**Note (20)** Since the correction calculation is carried out by using the product of coexisting component and the uncorrected quantitative value of quantitative component of the sample, therefore, it is required to

know the content of coexisting component. For this content of coexisting component, the quantitative value obtained by other method or atomic emission spectrometric analysis shall be used.

## 2) Case of strength ratio method

**2.1) Calculation of uncorrected quantitative value** Obtain  $X_i$  from the measured value of emission strength,  $I$ , obtained in 9 b) and the working curve prepared in 10 b) 3) and calibrated in clause 12, and take it as the uncorrected quantitative value,  $X_{i1}$ .

**2.2) Calculation of quantitative value** Calculate the quantitative value (<sup>21</sup>) by using  $X_i$ , obtained in 2.1) and  $I_j$  obtained in 10 b) 1) according to formula (10).

**Note** (<sup>21</sup>) In the case of correcting the iron quantity according to Note (13), calculate  $W_i$  according to formula (11), and take it as the quantitative value.

$$\hat{W}_i = \hat{W}_i - \hat{W}_{Fe}/100 \quad (11)$$

Where,  $\hat{W}_i$ : quantitative value of quantitative component of the sample,  $i$ , in the test portion % (m/m)

$\hat{W}_i$ : quantitative value after correction of iron quantity of quantitative component of the sample,  $i$ , in the test portion % (m/m)

$\hat{W}_{Fe}$ : content of iron in the test portion % (m/m) The quantitative value obtained by other method or the approximate value obtained according to the following formula (12) shall be used.

$$\hat{W}_{Fe} = \frac{100 - \Sigma W_{non}}{100 + \Sigma_{cor}} = 100 \quad (12)$$

Where,  $\Sigma W_{non}$  the sum of quantitative value of coexisting component obtained by other method or the sum of quantitative value,  $W$ , % (m/m), of component before correction of iron quantity

$\Sigma W_{cor}$  the sum of quantitative value,  $W$ , % (m/m), before correction of iron quantity in the component to be corrected of iron quantity

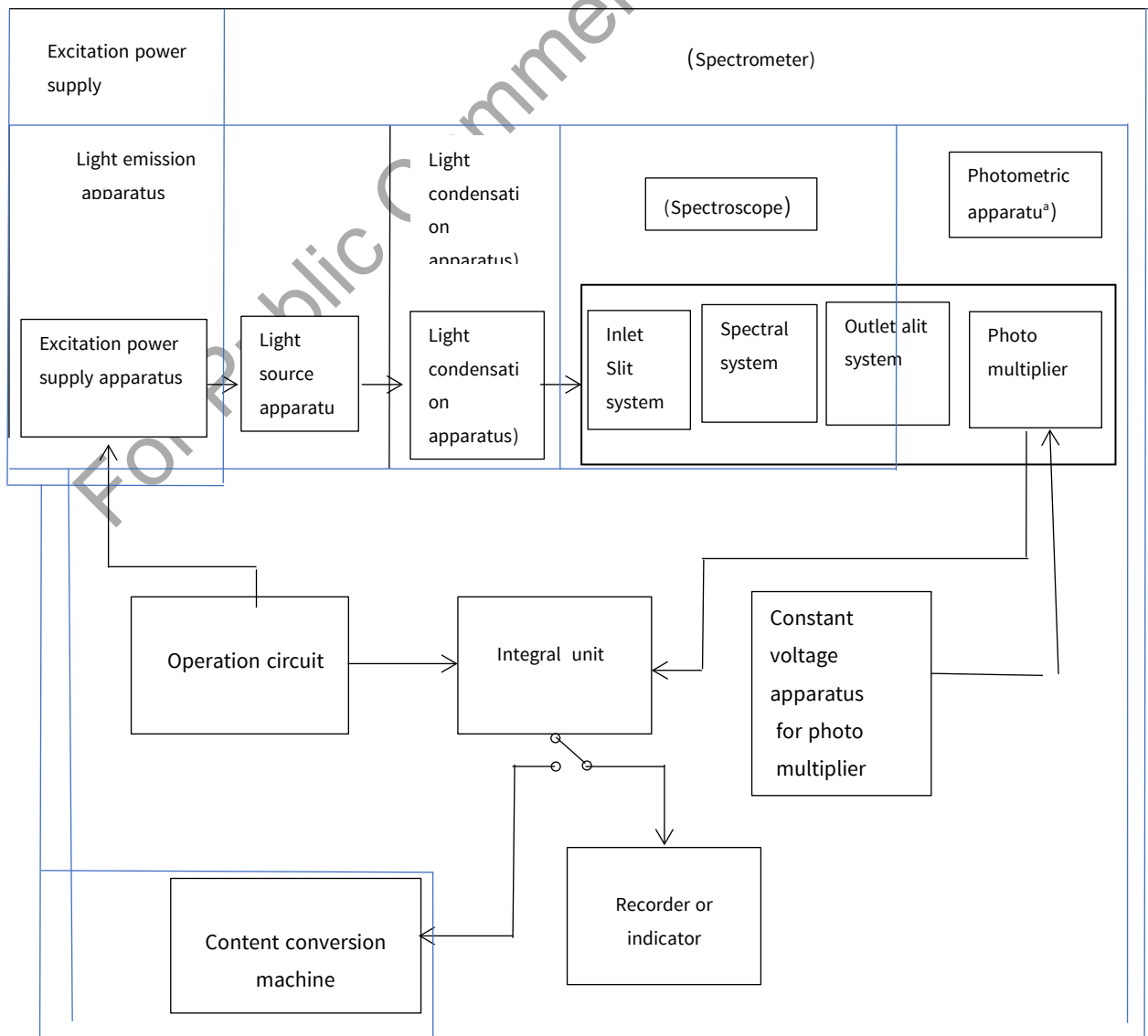
**Annex (normative)**

**Spark discharge emission spectrophotometer**

**1 Equipment**

**1.1 Summary of equipment** The spark discharge emission spectrophotometer shall be composed of the excitation power supply part, the light source part, the light condensation part, the spectral part, the light receiving part, and the photometric part. In the excitation power supply part, the light is emitted by supplying the excitation source to the light source part. In the light condensation part, the light is condensed and introduced to the spectral part. In the spectral part, the incident light is resolved to the spectral lines of respective elements and received in the light receiving part. In the photometric part, the strength of incident spectral lines of respective elements in the light receiving part is photo electrically measured and indicated, recorded or displayed by converting the measured value into the content of element.

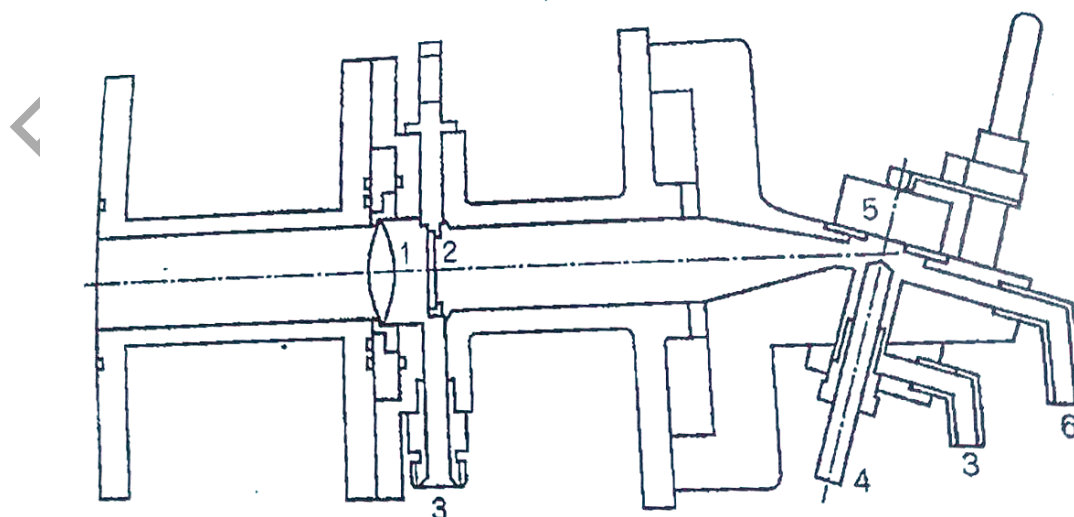
**1.2 Constitution of equipment** The equipment shall be constituted by the following unit apparatus. An example is shown in Annex Fig. 1.



**Annex Fig. 1 An example of constitution chart of spark discharge emission spectrophotometer**

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- a) **Excitation power supply apparatus** shall be the apparatus capable of supplying the power to the light source part, by which the sample is evaporated to vapour by discharging and excited to emission. Any one of the following shall be used:
- 1) **Direct current high voltage spark (DC HVS) power supply apparatus**, capable of raising the voltage to approximately 10 kV or over by a high voltage transformer, charging to a condenser by rectifying with a rectifying tube or a rectifier and discharging it successively by a synchronous breaker;
  - 2) **Alternating current high voltage spark (AC HVS) power supply apparatus**, capable of raising the voltage to approximately 10 kV or over by a high voltage transformer, charging to a condenser and controlling the discharge by using the control gap arranged in series or in parallel to analytical gap or the synchronous breaker arranged in series;
  - 3) **Low voltage condenser discharge power supply apparatus**, capable of charging a condenser of large capacity to approximately 1 kV at most and then carrying out the ignition by high voltage spark discharge.
- b) **Light source apparatus shall be the apparatus** in which the support of sample electrode and counter electrode, the control of emission atmosphere by using the specific gas, the water cooling of electrode holding part, etc. are possible for the purpose of making the sample the light source by discharging to emission. Either of the following shall be used:
- 1) **Electrode support for plane sample**, capable of holding usually a plane sample not less than 20 mm in diameter and of controlling the flow rate by a flowmeter and an automatic valve at the time of using argon etc. in emission atmosphere (An example is shown in Annex Fig. 2.); **Remarks:** That of structure capable of supporting a cylindrical sample also may be used.



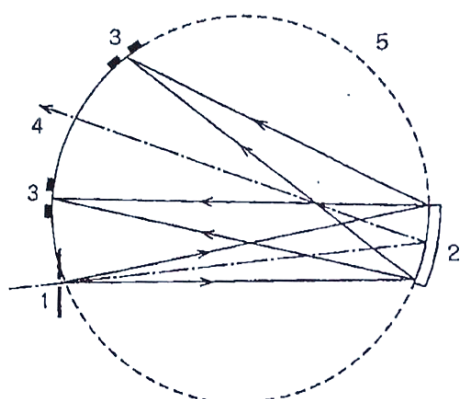
- |   |                         |   |                          |   |                           |
|---|-------------------------|---|--------------------------|---|---------------------------|
| 1 | condensation lens       | 3 | Inflow hole of argon gas | 5 | Sample                    |
| 2 | Protective quartz plate | 4 | counter electrode        | 6 | Outflow hole of argon gas |

**Annex Fig . 2 An example of electrode support for plane sample**

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- 2) **Electrode support for cylindrical sample**, capable of holding usually a cylindrical sample not more than 20 mm in diameter and of projecting the electrode for the adjustment of electrode position, and of water-cooling for the prevention of overheating at the electrode holding part.
- c) **Light condensation apparatus shall be the apparatus** capable of condensing the light from the light source to enter into the spectral system by using a condensation lens system. For the condensation lens system, either of the following shall be used:
- 1) **Collimator image formation method**, in which one piece of condensation lens is placed in the front of inlet slit, the inlet slit is uniformly irradiated by condensing the light from the light source, and the image is formed on the collimator;
  - 2) **Cylindrical lens image formation method**, in which a slender image is formed on the inlet slit vertically by using one piece of cylindrical lens. Furthermore, one piece of cylindrical lens is placed just in front of the slit and a slender image is formed horizontally on the collimator. Remarks: For the spectrometer, the collimator image formation method is usually used.
- d) **Spectroscope** shall be the apparatus composed of an inlet slit system, a spectral system and an outlet slit system in which the incident light from the inlet slit system is resolved to a spectrum in the spectral system and is able to be sorted to the spectral line of respective element by the outlet slit system. Usually a vacuum system in which the inside of apparatus is used under vacuum conditions, or the normal pressure system which is used under normal pressure are used.
- 1) **Inlet slit system** It is composed of an inlet slit and its position adjustment mechanism, and the slit width is fixed or variable. Usually, the fixed type is used.
  - 2) **Spectral system** It shall be capable of resolving to spectrum by using a diffraction grating or a prism. Usually, the spectral system by diffraction grating is used. For the spectral system by diffraction grating, a concave diffraction grating or a plane diffraction grating shall be provided, and there are Paschen-Runge type, Eagle type etc. for the concave diffraction grating and Ebert type for the plane diffraction grating. Usually, Paschen-Runge type spectral system is used.

**Paschen-Runge type spectral system shall be as shown in Annex Fig. 3.**



- 1 Inlet slit
- 2 Concave diffraction grating
- 3 Outlet slit
- 4 Focus surface
- 5 Rowland circle



**Annex Fig. 3 Paschen-Runge type spectral system**

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- 3) Outlet slit system** It shall be composed of outlet slits, the concave reflecting mirror to form the image of the spectral line passed through outlet slit on the surface of photocathode of photomultiplier, the quartz refracting plate to enter the spectral line into the outlet slit, etc., and for the outlet slit, the width of slit shall be usually fixed, and the adequate width of slit shall be able to be selected and used depending on the degree of influence of disturbance spectral line to the analytical line as well as the inlet slit.
- e) Photometric apparatus** It shall be composed of a photomultiplier, an integral unit, a recorder, an operation circuit, etc. and able to convert the light from outlet slit to electric current by receiving it in the photomultiplier and to measure the strength of each spectral line. For the photometric method, the voltage measurement system by integral unit and recorder or the electricity quantity measurement system according to direct counting conversion shall be used.
- 1) Photomultiplier** It shall be the one in the optimum region of wavelength sensitivity to the wavelength of analytical line to be used, whose characteristics are such that the SN ratio is large, the sensitivity is high, the recovery of fatigue is quick and the voltage applied to it shall be able to be controlled depending on the strength of spectral line.
  - 2) Integral unit** It shall be composed of the groups of condensers and relays of a very small amount of leakage and hysteresis, and the signal shall be able to be input in a recorder, an indicator or a content conversion machine by charging the output current of photomultiplier.
  - 3) Recorder, indicator and content conversion machine** For the recorder and indicator, a digital displaying instrument shall be usually used which is capable of measuring the output signal of integral unit and recording and indicating the measured value usually as the relative value to the internal standard line. The content conversion machine shall have the function capable of converting automatically the relative value to the corresponding content of element.
  - 4) Operation circuit** It shall be composed of numbers of relays, switches, timers, etc., and shall be able to control the operational command to the respective parts of photometric apparatus and emission apparatus automatically.

**1.3 Adjustment of apparatus** The adjustment of apparatus shall be as follows: The apparatus shall be maintained sufficiently so that it is ready for normal operation at all times.

- a) Adjustment of emission apparatus** The adjustment of emission apparatus shall be as follows:

For the respective dimensions of circuit in excitation power supply apparatus, the flow rate of atmospheric gas in light source apparatus, etc., the adequate conditions shall be decided previously according to the classification of sample, the quantitative component of the sample, the range of determination, etc.

- 1) Preliminary electrification** Electrify previously for an adequate time until the electric actuation of excitation power supply apparatus is stabilized. If required, set the primary voltage of high voltage

transformer in the excitation power supply apparatus at the specified voltage by a voltage regulator. This primary voltage shall be sufficiently stabilized.

- 2) **Adjustment of control gap in excitation power supply apparatus** Adjust so that the discharge surface and gap of electrode are always in the specified condition by forming each of them

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periodically or adjust by means of spacers or discharge voltage so that they become the specified gap.

- 3) **Adjustment of flow rate of atmospheric gas** Adjust the flowmeter so that the flow rate is of the specified value during emission and pause.

Information: The flow rate of atmospheric gas will influence the emission of sample.

**b) Adjustment of optical system** The adjustment of optical system in light condensation apparatus and spectroscopy shall be as follows (the inspection and adjustment shall be previously carried out):

- 1) **Inspection of condensation lens and protective quartz plate** Clean them when contaminated. Inspect the existence of contamination according to the increase of integral time or the decrease of sensitivity usually.
- 2) **Adjustment of pressure in spectroscopy** For the inside pressure of vacuum type spectroscopy, maintain the vacuum of not more than 2.67 Pa.
- 3) **Adjustment of profile** Carry out the adjustment of optical system so that the analytical line enters in the normal position of outlet slit by the adjusting mechanism by using the spectral line of specific element. For the apparatus having an automatic adjustment mechanism, confirm the actuation condition.

**c) Adjustment of photometric apparatus** The inspection and adjustment of photometric apparatus shall be as follows:

- 1) **Preliminary electrification** Electrify the photometric apparatus previously for an adequate time until the measurement circuit including photo multiplier comes to operate stably.
- 2) **Determination of preliminary discharge time and number of pulses** The preliminary discharge time and the number of pulses are different according to the test portion, the classification of quantitative element, the emission condition, the analytical line pair, etc. Therefore, determine them previously and experimentally.
- 3) **Adjustment of integral time and number of pulses** The integral time and number of pulses shall be set experimentally and previously based on the analytical accuracy, required time, strength of analytical line, etc.
- 4) **Regulation for the range of measured strength** Adjust the applied voltage of each photomultiplier according to the concentration range of quantitative element and the characteristic of spectral line.

**2 Installation of equipment** At the time of installation of equipment, the installation condition according to the type of equipment shall be satisfied. Attention shall be paid to the following items:

- a) It is recommended to install the equipment in a room free from dust or corrosive gas.
- b) The inside of the analysis laboratory in which the equipment is installed shall be usually maintained at 22 °C to 25 °C in temperature of which the variation is  $\pm 1$  °C and at not more than 60% in relative humidity. However, this shall not apply to the case where the

spectroscope has the built-in constant-temperature mechanism and the insulation resistance of the electric circuit of the equipment is sufficient large with respect to the humidity.

- c) The spectroscope shall be installed at a place where the vibration is minimum and, if required, a vibration isolating common bed, rubber vibration isolator, etc. shall be used so that the spectroscope is not influenced by vibration.

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- d) It is recommended that the power supply of equipment is supplied through a constant voltage apparatus in order to keep the variation in voltage within  $\pm 1\%$  and the variation of frequency is as small as possible.
- e) For the purpose of operating the equipment stably and reducing the disturbance noise to other machinery, the exclusive earthing device not more than  $20 \Omega$  in grounding resistance shall be provided.
- f) In the case of the apparatus to supply gas to light source part, it is recommended that the stainless-steel tubes, copper tubes, etc. with clean insides are used for the piping of gas and the joint part is as short as possible.
- g) The equipment shall be installed at a place without direct exposure to the sunshine and the rays of electric light shall not enter into the collimator directly.

**3 Safety and hygiene** For the safety and hygiene when the spectrometric analysis is carried out, attention shall be paid to the following items:

- a) The electric wiring to be used shall be wholly conformed to the standards and the insulating and earthing of equipment shall be sufficiently performed.
- b) A main switch capable of breaking the whole electric circuit shall be provided.
- c) The inspection and repair of the equipment shall be carried out after the main switch has been turned off, except when this is impractical. The main switch shall be turned on/off with sufficient caution, by taking measures such as making warning call-out. The excitation power supply apparatus containing condensers in the circuit, especially, tends to be still charged with electricity for a short time after the switch is turned off, so, the inspection and repair shall be carried out after a discharge. The inspection during electrifying shall be carried out by two or more persons and it is recommended the emergency measures in case of electric shock have been clearly decided.
- d) In the inside of a room where the equipment is installed, measures shall be taken so that the room does not become filled with the toxic gas and dust generated at the time of emission of sample, the gas supplied as atmospheric gas, etc.
- e) Attention shall be paid so as not to watch the ultraviolet rays radiated from emission source directly. If required, the protector for preventing ultraviolet rays shall be used.
- f) It is recommended that the extinguishing implements are provided in the room in case of an electric fire.
- g) When the equipment which generates noise is used, it is recommended that it has a sound-absorption structure.
- h) The operation of the machine: preparation of sample shall be carried out after the method is mastered sufficiently. For the high-speed cutting-off machine, belt sander, grinder, etc., the safety cover, dust

separator, etc. shall be provided. For the operation of lathe for cutting, drilling machine, etc., gloves shall not be used. When the eyes are subjected to the danger of flying chips, an eye protector shall be worn. Removal of scraps generated from cutting and abrasion shall not be neglected.

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