

JIS

JAPANESE INDUSTRIAL STANDARD

Methods for Analysis of
Coal Ash and Coke Ash

JIS M 8815-1976
(Reaffirmed: 1984)

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Methods for Analysis of Coal Ash
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1. General Rules

1.1 Scope This Japanese Industrial Standard specifies the methods for analysis of the ashes of coals, hereinafter referred to as the "coal ash", and ashes of cokes, hereinafter referred to as the "coke ash".

The coal ash or coke ash in this standard means the ashes of the first class and of the second class, as follows:

- (1) Ashes of First Class Those ashes of the air dried samples of coals and cokes which have been incinerated under the incinerating conditions specified in 3. of JIS M 8812.
- (2) Ashes of Second Class Those ashes which have been produced by the combustion of coals or cokes in stoking equipments.

1.2 Analysis Items The analysis items specified in this standard shall be as given in the following:

- (1) Total moisture in the ashes of the second class
- (2) Unburnt matter in the ashes of the second class
- (3) Silicon dioxide
- (4) Ferric oxide
- (5) Aluminium oxide
- (6) Calcium oxide
- (7) Magnesium oxide
- (8) Sulfur trioxide
- (9) Phosphorus pentaoxide

Remark: The methods for analysis of manganese oxide, titanium dioxide, vanadium pentaoxide, sodium oxide and potassium oxide are specified as Reference Methods.

Applicable Standards: See page 51.

1.3 General Matters The general matters in common with the methods for analysis, unless otherwise specified, shall be in accordance with JIS K 0050.

In addition, the general matters in common with the absorptiometry and atomic absorption spectrochemical analysis shall be in accordance with JIS K 0115 and JIS K 0121, respectively.

1.4 Number of Times of Analyses

1.4.1 The total moisture of the ashes of the second class shall be determined by repeating 2 times of analyses in accordance with the method described in 3.

1.4.2 Unburnt matter content (%) shall be determined by repeating 2 times of analyses in accordance with the method described in 4.

1.4.3 The contents (%) of silicon dioxide, ferric oxide, aluminium oxide, calcium oxide, magnesium oxide, sulfur trioxide, and phosphorus pentaoxide shall be determined by repeating 2 times of analyses using the samples for analyses prepared in accordance with 2.5.

1.5 Blank Test In the determination of 7 items given in 1.4.3, blank tests shall be carried out through out the whole operations for correcting contents in percent.

1.6 Expression of Analysis Results

1.6.1 The individual values which has been obtained in 2 times of determination are called as measured values, and when the difference between these values is less than the tolerance within-laboratory of Table 2 to Table 5, the mean value shall be obtained to consider this as a reporting value.

1.6.2 The measured values and the reporting values shall be rounded-off to the places given in Table 1 in accordance with JIS Z 8401.

Table 1

Analysis item	Measured value	Reporting value
Total moisture in ash of the second class	2 places of decimals	1 place of decimal
Unburnt matter in ash of the second class	2 places of decimals	1 place of decimal
Silicon dioxide	2 places of decimals	1 place of decimal
Ferric oxide	2 places of decimals	2 places of decimals
Aluminium oxide	2 places of decimals	2 places of decimals
Calcium oxide	2 places of decimals	2 places of decimals
Magnesium oxide	2 places of decimals	2 places of decimals
Sulfur trioxide	2 places of decimals	2 places of decimals
Phosphorus pentaoxide	3 places of decimals	2 places of decimals

1.6.3 Bases for Indication of Analysis Results The indicating method of the bases shall be as given in the following:

- (1) The total moisture in the ash of the second class shall be indicated by an arrival basis percentage (percentage to the sample of at time of sampling of a gross sample).
- (2) The unburnt matter content (%) shall be indicated by an anhydrous basis percentage or an arrival basis percentage in accordance with the procedure described in 4. When to indicate the unburnt matter content (%), the name of basis shall be appended.
- (3) The contents of silicon dioxide, ferric oxide, aluminium oxide, calcium oxide, magnesium oxide, sulfur trioxide, and phosphorus pentaoxide shall be indicated by percentages to the samples for analysis ⁽¹⁾.

Note ⁽¹⁾ Namely, these are indicated by anhydrous and unburnt matter bases.

1.7 Methods for Application of Tolerance

1.7.1 Methods for Application When the difference between the measured values of 2 times of analyses in repetition exceeds the tolerance of 1.7.2, operations shall be carried out again from the beginning. However, when a simple total moisture measuring method is employed, because repetition is not allowed if it has exceeded the tolerance, the mean value is taken as the reporting value, and the difference between the two measured values shall be appended.

- Remarks 1. When the 2 measured values or reporting values straddle over two divisions, the tolerance of a division to which the mean value of the 2 measured values (one place of decimal) or the mean value of the two reporting values corresponds is applicable.
2. The between-laboratory tolerance in Table 3 is applicable in the case where the two laboratories have employed the same analysis method respectively. For example, in analysis of phosphorus, in the case where one laboratory has employed a volumetric method and another has employed an absorptiometry, the between-laboratory tolerances of respective methods are not applicable.

1.7.2 Tolerances The tolerances shall be as given in the following:

- (1) Regarding the total moisture in the ashes of the second class, these shall be in accordance with 9.2.1 of JIS M 8810, as appropriate.
- (2) Regarding the unburnt matter content (anhydrous base), these shall be in accordance with Table 2.

Table 2. Tolerances
Unit: %

Within-laboratory (measured value)	Between-laboratory (reporting value)
0.40	0.8

- (3) Regarding silicon dioxide, ferric oxide, aluminium oxide, calcium oxide, and magnesium oxide, these shall be in accordance with Table 3.

Table 3. Tolerances
Unit: %

Item	Within-laboratory (measured value)	Between-laboratory (reporting value)
Silicon dioxide	0.85	1.15
Ferric oxide	0.35	0.95
Aluminium oxide	0.50	1.10
Calcium oxide	0.25	0.60
Magnesium oxide	0.15	0.15

- (4) Regarding sulfur trioxide, these shall be in accordance with Table 4.

Table 4. Tolerances

Unit: %

Division %	Within-laboratory (measured value)	Between-laboratory (reporting value)
2.50 max.	0.10	0.15
2.51 to 4.00	0.20	0.30
4.01 min.	0.25	0.40

- (5) Regarding phosphorus pentaoxide, these shall be in accordance with Table 5.

Table 5. Tolerances

Unit: %

Method of determination	Division	Within-laboratory (measured value)	Between-laboratory (reporting value)
Molybdate blue absorptiometry (abbreviation: MB)	0.20 max.	0.020	0.04
	0.21 to 0.50	0.050	0.07
	0.51 to 1.00	0.070	0.07
	1.01 to 1.50	0.070	0.15
	1.51 min.	0.130	0.16
Vanado-molybdate yellow absorptiometry (abbreviation: VY)	0.20 max.	0.020	0.02
	0.21 to 0.50	0.050	0.10
	0.51 to 1.00	0.050	0.10
	1.01 to 1.50	0.090	0.10
	1.51 min.	0.110	0.49
Volumetric method (abbreviation: VO)	0.20 max.	0.020	0.07
	0.21 to 0.50	0.040	0.24
	0.51 to 1.00	0.110	0.24
	1.01 to 1.50	0.110	0.27
	1.51 min.	0.110	0.27

2. Sampling Method and Handling Method

2.1 Original Sample for Ashes of First Class The original sample of the ashes for the first class shall be the air dried sample prepared in accordance with 4. of JIS M 8811 from a lot of coals or cokes.

Remark: In the case of the coals, it may be prepared into an equilibrium-humidity sample.

2.2 Incinerating Conditions of Ashes of First Class The incinerated sample of the ashes of the first class shall be made incinerating the original sample prepared in accordance with 2.1 under the incinerating conditions specified in 3. of JIS M 8812. The amount of the ash shall be determined with reference to the masses of samples to be weighed out for respective components to be determined.

Remark: Particularly the preparing method of ash to be used in the determination of the sulfur trioxide has considerable influence on an analysis value, the incinerating conditions specified in 3. of JIS M 8813, namely the following conditions shall be observed stringently.

- (1) Thickness of sample layer (0.1 g/cm^2 or under)
- (2) Ventilation
- (3) Speed of temperature rise (1 h from a room temperature to 500°C , and 30 to 60 min from 500°C to 815°C)
- (4) Heating time at 815°C (The perfect incineration is to be confirmed by carrying out a strong heating operation again, as required.)

However, in the preparation of the ash to be used for the determinations of other components, it is not necessary to observe the requirements so strictly as given in the foregoing.

2.3 Original Sample of Ashes of Second Class The original sample of the ashes of the second class shall be the sample prepared to the particle size of $250 \mu\text{m}$ or under, being collected from the lot of the ashes of the second class generally in accordance with JIS M 8811, as appropriate. However, in the case where a gross sample is in humid condition, it shall be dried at 150°C or under, prior to preparation, to such an extent that it is not impedimental in pulverizing.

2.4 Incinerating Conditions of Ashes of Second Class The incinerated samples of the ash of the second class shall be made, incinerating the original sample prepared in accordance with 2.3 in accordance with 2.2, as appropriate.

2.5 Preparing Method of Analysis Sample Crush the incinerated sample prepared in accordance with 2.2 or 2.4 to fines (approximately $74 \mu\text{m}$ or under) until tactile impression of coarse particles with fingertips becomes intangible, using a special steel crusher or an agate mortar so as to prevent mingling of foreign matters such as iron and the like. Transfer this into a porcelain dish or platinum dish, and put it into a muffle furnace which has been heated at $815 \pm 10^\circ\text{C}$, and heat for 30 min or over ⁽¹⁾. Transfer into the flat weighing bottle of approximately 50 mm in diameter ⁽²⁾, apply a lid and put it in a desiccator, and cool to ordinary temperature ⁽³⁾.

- Notes (1) In the meantime, this shall be stirred up with a platinum wire and the like so that no unburnt matter is remained. Whether any unburnt matter is remained or not can be discriminated by moistening the ash with a small amount of water or alcohol. If any unburnt matter presents, black spots are observed.
- (2) If the sample has been cooled to room temperature before being transferred into the weighing bottle, the sample which has been contained in the weighing bottle shall be dried for 1 h at $107 \pm 2^\circ\text{C}$, and then the weighing bottle is applied with the lid and is put into the desiccator.
- (3) In the case where an analysis sample which has lapsed 48 h or over after preparation is used, it shall be used after drying for 1 h at $107 \pm 2^\circ\text{C}$.

3. Determination for Total Moisture of Ashes of Second Class

If the ash of the second class is in humid condition, and in the case where its total moisture is required to know, it shall be determined in accordance with 5. of JIS M 8811, as appropriate (measuring method of total moisture). The total moisture W_* (%) which has been obtained in this manner shall be indicated on the arrival basis.

4. Determination of Unburnt Matter

An unburnt matter is frequently contained in the ash of the second class. The unburnt matter content (%) shall be obtained according to the following procedures:

Regarding the original sample of the ashes of the second class prepared in accordance with 2.3, determine the percentage loss L (%) when it has been heated at 815°C in accordance with the operations of 3.3.2 (in the case of cokes) of JIS M 8812, and in parallel to this, determine its moisture W_* (%) in accordance with 2. (determination of moisture) of the same standard, and calculate the unburnt matter content (%) in accordance with either one of the following formula (1) and formula (2). The unburnt matter content (%) shall be indicated by an anhydrous basis or arrival basis, and be appended with the name of basis, without fail.

- (1) Unburnt matter content (converted value to anhydrous basis)

$$\text{Unburnt} \quad \text{Anhydrous} \quad (\%) = (L - W_*) \times \frac{100}{100 - W_*} \dots\dots\dots (1)$$

(2) Unburnt matter content (converted value to arrival basis)

$$\begin{aligned} \text{Unburnt}^{\text{Arrival}} (\%) &= \text{Unburnt matter}^{\text{Anhydrous}} (\%) \times \frac{100 - W_w}{100} \\ &= (L - W_a) \times \frac{100 - W_w}{100 - W_a} \dots\dots\dots (2) \end{aligned}$$

where W_w : total moisture of the ash of the second class obtained in accordance with the method stated in 3. (%)

5. Determination of Silicon Dioxide

5.1 Classification of Method The determination of the silicon dioxide in the coal ash and coke ash shall be in accordance with the gravimetric method.

5.2 Summary The sample is melted with sodium carbonate, and the melt is dissolved in hydrochloric acid. This is treated with perchloric acid to dehydrate silicic acid, and filter out precipitates to preserve. The silicic acid in the filtrate is recovered and is combined with the main precipitates, and this is ignited and is incinerated to produce anhydrous silicic acid. To this hydrofluoric acid and sulfuric acid is added, to vaporize silicon dioxide, and its loss is obtained.

5.3 Reagents The reagents shall be in accordance with the following:

- (1) Hydrochloric acid (1 + 4) (1 + 10)
- (2) Perchloric acid
- (3) Hydrofluoric acid
- (4) Sulfuric acid (1 + 1)
- (5) Anhydrous sodium carbonate

5.4 Amount of Sample to Be Weighed Out For the sample, 0.250 g shall be weighed out to the nearest 0.1 mg.

5.5 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) Weigh out the sample and transfer it into a platinum crucible (No. 25). Add 5 g of the anhydrous sodium carbonate to this, and mix well. Heat this to melt at 900 to 1000°C, lightly shake the crucible from time to time, and after it has been melted down continue melting for 30 to 40 min. Take it down from heat source, after cooling put it into a beaker (500 ml), add 70 ml of the hydrochloric acid (1 + 4), and dissolve the melt. Remove this by washing the crucible with water, and add 50 ml of the perchloric acid.

- (2) Heat (¹) this slowly, cover with a watch glass when white fume has begun to generate slightly, continue heating, allow to generate the dense vapour of the perchloric acid, and after the heating has been continued for approx. 15 min to an extent that the inside of the beaker turns transparent, and further to flows back along the wall of the beaker, cool.
- (3) Add 50 ml of the hydrochloric acid (1 + 4), and immediately filter using filter paper (Class 5 A). Scrape off adhered matters from the inside wall of the beaker using a glass rod with rubber tube, and transfer the total amount onto the filter paper. At first, wash 2 to 3 times using the warm hydrochloric acid (1 + 10), and next wash with warm water until acid in washings vanishes, and further wash 2 to 3 times. Preserve the precipitates together with the filter paper in a platinum crucible (No. 25). Receive the filtrate and washings in a beaker (500 ml).
- (4) Heat the beaker, and dehydrate the silicic acid which has been leaked into the filtrate in accordance with the same operations as (2). Add 50 ml of the hydrochloric acid (1 + 4), and recover the dehydrated silicic acid, by carrying out the same operations as (3) using filter paper (Class 5 C), and put the precipitates together with the filter paper into the platinum crucible containing the main precipitates which has been preserved in the foregoing operation. Preserve the filtrates and washings, if these are required to be subjected to the determinations of the ferric oxide, aluminium oxide, calcium oxide and magnesium oxide.
- (5) Heat slowly the platinum crucible in which the precipitates have been contained, and after these have been incinerated, ignite to a constant mass at 1000°C to 1100°C. Cool in a desiccator and weigh the mass of the platinum crucible containing impure silicon dioxide. Next, drip the fufuric acid (1 + 1) into the crucible to moisten the residue, add approx. 5 ml of the hydrofluoric acid, heat carefully allow the silicon dioxide and the sulfuric acid to evaporate, with preventing these from scattering. Ignite this platinum crucible at 1000°C to 1100°C to attain a constant mass, and after it has been cooled in a desiccator, weigh the mass of the platinum crucible.

5.6 Calculation Calculate the silicon dioxide content from the following formula:

$$\text{Silicon dioxide (\%)} = \frac{w_1 - w_2}{W} \times 100$$

where w_1 : mass of platinum crucible containing impure silicon dioxide (g)

w_2 : mass of platinum crucible containing impure residue (g)

W : weighed out amount of the sample (g)

Note (1) According to the type of the sample, it is liable to be scattered due to bumping, so that sufficient care shall be taken in regulating heating.

- Remarks 1. When an extreme accuracy is not required in the determination of the silicon dioxide, the leaked amount of silicic acid may be either neglect by omitting the operation of (4), or the approximate value of leaked amount of silicic acid which is grasped experimentally may be added to the main silicon dioxide content, as a correction value. When the operation of (4) is to be omitted as mentioned in the foregoing, the filter paper to be used in (3) shall be changed to Class 5 C.
2. When any wooden part is provided in the construction of draft, the perchloric acid shall not be used. In this case, approximately half an amount of the sulfuric acid (1 + 1) as the consumption of the perchloric acid shall be used. However, the determinations of the calcium oxide and magnesium oxide shall not be conducted from the liquid on which the dehydration of silicic acid has been made by using the sulfuric acid.

6. Determination of Ferric Oxide

6.1 Classification of Method The determination of the ferric oxide in the coal ash and coke ash shall be in accordance with stannous chloride reduction-potassium dichromate titration method.

6.2 Summary The sample is decomposed with nitric acid, hydrofluoric acid and sulfuric acid, and is melted with potassium pyrosulfate, the melt is dissolved with hydrochloric acid, and the hydroxides of iron and other are separated with aqueous ammonia. Precipitates are dissolved with hydrochloric acid, and are reduced with stannous chloride. The excessive stannous salt is oxidized with mercuric chloride to adjust the density of acidity, and titration is made with potassium dichromate solution using sodium-diphenylamine-sulfonate as an indicator.

6.3 Reagents The reagents shall be in accordance with the following:

- (1) Hydrochloric acid (1 + 3), (1 + 9)
- (2) Nitric acid
- (3) Hydrofluoric acid
- (4) Sulfuric acid (1 + 1)
- (5) Mixed acid While pouring 150 ml of sulfuric acid into approx. 500 ml of water, stir well and add 150 ml of phosphoric acid, and dilute with water to total quantity of 1000 ml.
- (6) Aqueous ammonia (1 + 1)
- (7) Washing water Dissolve 10 g of ammonium chloride with 500 ml of water, and drip aqueous ammonia until weak alkalinity in respect to methyl red is obtained.
- (8) Potassium pyrosulfate For this reagent, sodium salt may also be used.
- (9) Stannous chloride solution Pour 200 ml of hydrochloric acid into a beaker (1000 ml), add 100 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), bit by bit, while heating on a water bath to dissolve, after cooling dilute to 1000 ml with water. Add small amount of granular tin in this solution, and store in a brown bottle.
- (10) Mercuric chloride solution (saturated, approx. 5 w/v %)
- (11) N/30 potassium dichromate standard solution (1.635 g $\text{K}_2\text{Cr}_2\text{O}_7/\text{l}$) Weigh out correctly 1.635 g of crystalline potassium dichromate (standard reagent for volumetric analysis) into a beaker (300 ml), dissolve with approx. 100 ml of water, transfer into a 1000 ml measuring flask, and dilute up to the marked line. In this case, the purity marked on the standard reagent, as it is, is used as the titer in respect to N/30, and standardization shall not be performed.
- (12) N/30 ferrous ammonium sulfate standard solution Weigh out 13 g of ferrous ammonium sulfate [$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$], add 30 ml of sulfuric acid (1 + 1) and approx. 700 ml of water, stir to dissolve, further add water to make up to a total quantity of 1000 ml.

- (13) Methyl Red solution Dissolve 0.20 g of Methyl Red with 90 ml of ethyl alcohol (95 v/v %), and dilute with water to make up to a total quantity of 100 ml.
- (14) Sodium-diphenylamine-sulfonate solution (0.20 w/v %) Store this in a brown bottle. For this reagent, barium salt may also be used.

6.4 Amount of Sample to Be Weighed Out For the sample, 0.250 g shall be weighed out to the nearest 0.1 mg.

6.5 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) Weigh out the sample, and transfer into a platinum crucible (No. 25). Add 15 ml of the hydrofluoric acid and 5 ml of the nitric acid to this, regulate heating carefully so as not to cause bumping, stir up with a piece of platinum wire from time to time, and decompose gradually. When the liquid quantity becomes 5 ml or under, add 2 ml of the sulfuric acid (1 + 1), slowly heat succeedingly (¹), allow to general white fume of sulfuric acid, and continue heating until the white fume ceases to generate.
- (2) Add 5 g of the potassium pyrosulfate, at first heat slowly, gradually increase temperature, and melt at a red heat condition. After cooling, put the crucible in a beaker (200 ml), add approx. 70 ml of the hydrochloric acid (1 + 9), and heat slowly to dissolve the melt. Wash the crucible with water, and remove (²). Add 2 to 3 drops of the nitric acid to this and heat, and after it has been boiled for 1 to 2 min, take it down from the heat source, and cool for several minutes.
- (3) Add 2 to 3 drops of Methyl Red as an indicator, stir up to mix while dripping the aqueous ammonia (1 + 1), and after weak red colour has vanished, add in excess of 1 to 2 drops. Heat, and after this has been boiled for 2 to 3 min take down from the heat source, wait until the precipitates settle, filter using filter paper (Class 5 A), and wash 4 to 5 times with warm washing water (³). Wash off the larger part of the precipitates, as the filter being attached to a funnel, into the original beaker, pour 30 ml of the hot hydrochloric acid (1 + 3) over the filter paper, receiving with the beaker underneath the funnel, to dissolve residual hydroxides, and next wash with 4 to 5 times with the warm hydrochloric acid (1 + 9), and lastly wash with warm water until the acidity vanishes. Discard the filter paper. Heat the beaker, and after the hydroxides have been dissolved, cool to room temperature, transfer this into a 250 ml measuring flask, and dilute with water up to the marked line.
- (4) Separately take 100 ml from this and pour it into a beaker (500 ml). Add 10 ml of the hydrochloric acid, heat at approx. 80°C or over, and shake up to mix while dripping the stannous chloride solution. When yellow colour has begun to fade, shake up well carefully adding drip by drip, and after the yellow colour has vanished add one drip excessively, wash the inside wall of the beaker with water, and cool down to room temperature or under in running water.

- (5) Add 10 ml of the mercuric chloride solution all at once, immediately after this has been shaken up to mix, leave for 3 to 5 min. Add 30 ml of the mixed acid and dilute with water to approx. 300 ml, add 2 to 3 drops of the sodium diphenylamine sulfonate solution as the indicator, titrate this using the N/30 potassium-dichromate standard solution, and take the point when its colour has turned purple as the end point.
- (6) The blank test shall be carried out as follows ⁽⁴⁾.

Operate the operations up to (3) in the same manners as in the sample. Separately take 100 ml from this, and pour it into a beaker (500 ml). Add 10 ml of the hydrochloric acid to this, heat to approx. 80°C or over, add 1 drop of the stannous chloride solution, wash the inside wall of the beaker with water, and cool, in running water, to room temperature or under. Add 10 ml of the mercuric chloride solution and immediately shake up to mix, and leave for 3 to 5 min as it is. Add accurately 30 ml of the mixed acid and 10 ml of the N/30 ferrous ammonium sulfate solution to this, dilute with water to approx. 300 ml, add 2 to 3 drops of the sodium diphenylamine sulfonate solution as the indicator, and titrate in the same operation as in (5). Take accurately 30 ml of the mixed acid and 10 ml of the N/30 ferrous ammonium sulfate solution in another beaker, dilute with water to 300 ml, and titrate in the same manner.

Consider the subtracted value of the consumption of the N/30 potassium dichromate standard solution consumed only in the N/30 ferrous ammonium sulfate solution from the amount of the N/30 potassium dichromate standard solution consumed in the blank test solution as the blank test value.

6.6 Calculation Calculate the ferric oxide content from the following formula:

$$\text{Ferric oxide (\%)} = \frac{(V_1 - V_2) \times 0.001862}{W \times L} \times 1.4297 \times 100$$

where V_1 : consumption of the N/30 potassium dichromate standard solution in (5) (ml)

V_2 : amount of solution of blank test value obtained in (6) (ml)

W : weighed out amount of the sample (g)

L : separating rate, 100 ml herein

Notes ⁽¹⁾ Because it is liable to be scattered due to bumping, depending on the characteristics of the sample, heating shall be regulated with sufficient care.

- (2) The sample solution at this stage is required to be transparent. If any turbidity presents, it shall be operated again from the beginning. If it is known that, depending on the characteristics of the sample, the turbidity is presented on the melting of the first time, it should be preferable to operate as follows; cool after the melting with the pyrosulfate salt, add 1 ml of the sulfuric acid (1 + 1) into the crucible, heat this slowly, and remelt by increasing temperature gradually.
- (3) The filtrate and the washing at this stage may be used in the determination of the calcium oxide and magnesium oxide. However, in this case, reprecipitating operation shall be carried out in accordance with 8.5 (2) of 8. Determination of calcium oxide.
- (4) When the amount of iron in the blank test solution is extremely small, irrespective of the excessive amount of the potassium dichromate, coloration due to the diphenylamine sulfonate does not occur promptly, therefore it is liable to obtain the excessively large blank test value. Coexistence of ferrous ions makes the coloration prompt.

Remarks 1. The filtrate and washing of 5.5 (4) at the time of determination of the silicon dioxide may be used for the sample primary solution. In this case, when the determinations of the calcium oxide and magnesium oxide are to be correlated, it shall be carried out as follows:

Add approx. 1 g of the sodium pyrosulfate in the platinum crucible in which the determination of silicon dioxide has been finished by the hydrofluoric acid treatment, and after this has been fused by heating gradually allow to cool, add approx. 15 ml of water and several drops of the hydrochloric acid in the crucible, and allow the melt to dissolve by heating gradually. Receive the filtrate and washing at the time of determination of the silicon dioxide in a beaker (500 ml) and heat to generate fumes of perchloric acid, and condense until salts are deposited. After cooling, add approx. 100 ml of water, dissolve the salts, add the dissolved liquid of melt in the crucible to this to make up as a sample primary solution. When the correlation with the determinations of the calcium oxide and magnesium oxide is unnecessary, the concentration of the filtrate and washing at the time of the determination of silicon dioxide is not necessary, but is only required to melt the residue in the platinum crucible and to combine with the principal liquid.

- 2. As in the ash of compounded oil and coke in the sample containing vanadium, it shall be operated as follows:

Treat the sample in the manners as (1) to (3), take separately the sample solution of 100 ml from this, and put into a beaker (500 ml). Concentrate this by heating to approx. 30 ml of liquid quantity. After this has been cooled for a while, drip the aqueous ammonia (1 + 1), allow to generate somewhat larger amount of the hydroxides, next, stir to mix while dripping hydrochloric acid (1 + 1) until the extremely weak acidity which makes the liquid having slight turbidity is attained, and add an excess of 10 ml. Add hot water to this to make up to a liquid quantity of approx. 100 ml ⁽⁵⁾, shake up well to mix while dripping the stannous chloride solution to this; stir up well to mix at each drip when yellow colour has become faint, and add an excess of only one drop ⁽⁶⁾ after the yellow colour has vanished. Wash the inside wall of beaker with water, and cool to room temperature or under in running water. Hereafter, operate in accordance with (5) and thereafter.

Notes ⁽⁵⁾ Adjust the liquid quantity and the additional amount of the hydrochloric acid (1 + 1) so that the density of hydrochloric acid at this time becomes 0.4 to 0.6 N.

⁽⁶⁾ When an excessive additional quantity of the stannous chloride solution exceeds one drop, a part of the vanadium is reduced to the trivalent, and it results in the cause for a positive error.

7. Determination of Aluminium Oxide

7.1 Classification of Method The determination of the aluminum oxide in the coal ash and the coke ash shall be in accordance with the annexing EDTA back titration with zinc method.

7.2 Summary The sample is decomposed with hydrofluoric acid, nitric acid and sulfuric acid, and is melted with potassium pyrosulfate. The melt is dissolved with hydrochloric acid, pH is adjusted with acetic acid and aqueous ammonia, and heavy metals are extracted and eliminated with DDTC and chloroform. A defined amount of EDTA solution is added to this to generate EDTA-aluminium complex salt, and the excessive EDTA is back titrated with zinc standard solution.

7.3 Reagents The reagents shall be in accordance with the following:

- (1) Hydrochloric acid (1 + 9)
- (2) Nitric acid
- (3) Hydrofluoric acid
- (4) Sulfuric acid (1 + 1)
- (5) Acetic acid (1 + 1)
- (6) Aqueous ammonia (1 + 1)