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SECOND DRAFT PROPOSAL FOR THE DETERMINATION OF MAJOR ELEMENTS OF ASH OF SOLID MINERAL FUELS (CLASSICAL & INSTRUMENTAL METHOD)

W.J. Montgomery

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INTRODUCTION

1. Scope and Field of Application

- 1.1. This proposal specifies the methods to be adopted for analysis of ash derived from solid mineral fuels. It can also be applied to ash derived from semi-coke and coke obtained from brown coals and lignites.
- 1.2 Methods of determination of the following ash components are described:
- a) silicon calculated as silica (SiO_2);
 - b) iron calculated as ferric oxide (Fe_2O_3);
 - c) titanium calculated as titanic oxide (TiO_2);
 - d) aluminum calculated as aluminum oxide (Al_2O_3);
 - e) calcium calculated as calcium oxide (CaO);
 - f) magnesium calculated as magnesium oxide (MgO);
 - g) manganese calculated as manganous-manganic oxide (Mn_3O_4);
 - h) sodium calculated as sodium oxide (Na_2O);
 - i) potassium calculated as potassium oxide (K_2O);
 - j) sulphur calculated as sulphur trioxide (SO_3);
 - k) phosphorous calculated as phosphorous pentoxide (P_2O_5).
- 1.3 This proposal is applicable in the coal, energy, metallurgical and building materials industries as well as in others where it is necessary to know the chemical composition of ash, this composition reflecting the constitution of the original mineral matter of the fuel tested. The knowledge of this composition permits the selection of the proper method of coal and ash utilization for given purposes. The chemical constitution of ash of the fuel has an influence on its fusion temperature, which in turn influences the run of ovens.

2. Reference

ISO 1171, Determination of Ash of Solid Mineral Fuels

3. Summary of Methods

In these methods, ash is prepared in accordance with ISO 1171 and ground to pass 0.063 mm square mesh sieve.

- 3.1 SiO_2 Fusion with Na_2CO_3 - Dehydration by treatment with HClO_4 - Gravimetric
- 3.2 Fe_2O_3 Decomposition with HNO_3 , HF , H_2SO_4 - Fusion with $\text{K}_2\text{S}_2\text{O}_7$ - Separation of hydroxides - Dissolution in HCl - Reduction with SnCl_2 - Titration with $\text{K}_2\text{Cr}_2\text{O}_7$ - Volumetric
- 3.3 Al_2O_3 Decomposition with HF , HNO_3 , H_2SO_4 - Fusion with $\text{K}_2\text{S}_2\text{O}_7$ - Separation of hydroxides - Dissolution in HCl - Separation of heavy metals with DDTc - Titration with EDTA - Zn - Volumetric
- 3.4 TiO_2 Fusion with Sodium peroxide - Digestion of melt with H_2O and HCl - Reduction of Fe, etc. - Development of colour with Diantipyrylmethane - Spectrophotometric
- 3.5 CaO & MgO Fusion with Na_2CO_3 - Dehydration by treatment with HClO_4 - Separation of SiO_2 - Separation of Fe, Al, etc. with NH_4OH - Titration with EDTA - Volumetric
- 3.6 SO_3 Digestion with HCl - Precipitation of BaSO_4 - Weighing Gravimetric
- 3.7 P_2O_5
- 3.7.1 Decomposition with HNO_3 , HF , HClO_4 - Fusion of residue with $\text{K}_2\text{S}_2\text{O}_7$ - Separation of hydroxide and ferric phosphate - Dissolution in HCl - Reduction of Fe - Formation of Molybdenum Blue - Spectrophotometric
- 3.7.2 Formation of Phospho-vanadomolybdate Yellow - Spectrophotometric
- 3.7.3 Precipitation of Phosphomolybdate - Dissolution with NaOH in excess - Titration with HNO_3 -

- 3.8 MnO Decomposition with HNO_3 , HF, and HClO_4 - Dissolution in water - Addition of H_2SO_4 and H_3PO_4 - Oxidation with Sodium periodate - MnO_4^- - Spectrophotometric
- 3.9 Na_2O Method 1
Decomposition with HCl, HF and HClO_4 - Separation of Fe by extraction with MIBK - Separation of Fe, Al, Ti etc. as hydroxides - Separation of Ca as oxalate - Dilution -
&
 K_2O Atomization with Oxygen and Hydrogen - Flamephotometric
- Method 2
Decomposition with HCl, HF and HClO_4 - Dilution - Atomization with air - C_2H_2 - Atomic absorption Spectrophotometric

4. Preparation of Ash for Analysis

4.1 Preparation of Ash

The Ash for analysis is prepared from the analysis sample of fuel by the methods described in ISO 1171, or is taken from the industrial hearths. Grind the Ash in an agate mortar to pass a 0.063 mm square mesh test sieve and store in an airtight jar.

When some coals are incinerated at the conditions outlined in ISO 1171, it is possible that a significant proportion of the more volatile constituents, for example, sodium, is lost. To avoid risk of this occurring, coals rich in such elements may be incinerated at 500°C . The temperature variation and the ash content at that temperature must be recorded when reporting results.

4.2 Determination of Loss in Mass on Heating

4.2.1 Procedure

Weigh in a platinum crucible of about 40 ml capacity, with an accuracy of 0.2 mg about 1 g of ash prepared according to 4.1. Insert the crucible with ash in a muffle furnace and heat at $815 \pm 10^\circ\text{C}$ until the difference between the results of two weighings is less than 0.4 mg.

4.2.2 Calculation of Results

The loss in mass on heating, X, as a percentage by mass, is given by the formula:

$$X = \frac{(m_0 - m_1) \times 100}{m_0}$$

where

m_0 is the mass, in grams, of ash taken;

m_1 is the mass, in grams, of ash after heating.

- DETERMINATION OF SILICON DIOXIDE - GRAVIMETRIC METHOD

1. PRINCIPLE

Decomposition of the test portion by fusion with sodium carbonate. Dissolution of the melt in hydrochloric acid, treatment with perchloric acid to dehydrate hydrous silicon dioxide and filtration. Treatment of the filtrate in the same way. Collection of the precipitates, ignition and weighing as impure silicon dioxide. Treatment of the impure silicon dioxide with sulphuric and hydrofluoric acids. Determination of the silicon dioxide by weight loss.

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents throughout the analysis. All reagents shall be of recognized analytical reagent quality.

- 2.1 Hydrochloric acid (d=1.19)
- 2.2 Hydrochloric acid, dilute 1+4
- 2.3 Hydrochloric acid, dilute 1+10
- 2.4 Perchloric acid (60%, d=1.54: or 70%, d=1.67)
- 2.5 Hydrofluoric acid (40%, d=1.15)
- 2.6 Sulphuric acid (d=1.84)
- 2.7 Sulphuric acid, dilute 1+1
- 2.8 Sodium carbonate, anhydrous

3. APPARATUS Ordinary laboratory equipment

4. SAMPLING AND SAMPLE PREPARATION (See Section 4 of Introduction)

5. PROCEDURE

- 5.1 Test portion - Weigh, to the nearest 0.0001g, 0.250g of the test sample

5.2 Determination

5.2.1 Decomposition of the test portion

Place the test portion (5.1) in a 30 ml platinum crucible. Add 5 g of sodium carbonate (2.8), mix thoroughly, and fuse at 900 to 1000°C while occasionally swirling the crucible gently. After no particles of sample float on the surface of melt, continue fusion for 30 to 40 min. Remove the crucible from the source of heat and cool. Transfer the crucible to 500 ml beaker, add 70 ml of hydrochloric acid (1+4) (2.2), and dissolve the melt. Rinse the crucible with water and remove from the solution.

5.2.2 Dehydration and separation

Add 50 ml of perchloric acid (2.4). Slowly heat the beaker to fume slightly, and evaporate to dense white fumes of perchloric acid, using a watch glass cover. Heat for about 15 min. so that the acid refluxes down the walls of the beaker and cool. Add 50 ml of hydrochloric acid (1+4) (2.2), filter through a medium-texture filter paper without delay. With a rubber-capped policeman, remove any residue inside the beaker and transfer it on the filter paper. Wash with warm hydrochloric acid (1+10) (2.3) 2 to 3 times, and then with warm water until the washings show no acid reaction. Finally, wash with warm water 2 to 3 times. Transfer the precipitate with the filter paper in a 30ml platinum crucible and preserve.

5.2.3 Recovery of residual silicon dioxide

Collect the filtrate and washings in a 500 ml beaker. Evaporate the solution, cover the beaker and heat to the dense white fumes of perchloric acid. Maintain a steady refluxing of the acid on the walls of the beaker for about 15 minutes. Allow the beaker to cool. Add 50 ml of hydrochloric acid (1+4) (2.2), filter with a close-texture filter paper without delay. With a rubber-capped policeman, remove any residue inside the beaker and transfer it to the filter paper. Wash with warm hydrochloric acid (1+10) (2.3) 2 to 3 times, and then with warm water until the washings shown no acid reaction. Finally, wash with warm water 2 to 3 times. Combine the precipitate with that

in the platinum crucible (5.2.2) above.

5.2.4 Determination

Gently heat the precipitate in the platinum crucible until the filter paper is thoroughly charred, and then ignite to constant mass at 1000 to 1100°C. After cooling in a desiccator, weigh the platinum crucible with impure silicon dioxide. Moisten the impure silicon dioxide in the crucible with sulphuric acid (1+1) (2.7), add 5 ml of hydrofluoric acid (2.5), heat gently to remove silicon dioxide and sulphuric acid, and ignite to constant mass at 1000 to 1100°C. After cooling in a desiccator, weigh the platinum crucible.

6. EXPRESSION OF RESULTS

6.1 Calculation of silicon dioxide content.

The silicon dioxide content, as percentage by mass, is calculated from the following formula

$$\text{SiO}_2\% \text{ (m/m)} = \frac{m_1 - m_2}{m} \times 100$$

where

m_1 is the mass, in grams, of the platinum crucible plus impure silicon dioxide;

m_2 is the mass, in grams, of the platinum crucible plus the residue;

m is the mass, in grams, of the test portion.

- DETERMINATION OF FERRIC OXIDE - VOLUMETRIC METHOD

1. PRINCIPLE

Decomposition of the test portion by treatment with hydrofluoric, nitric and sulphuric acids and by fusion with sodium pyrosulphate. Dissolution of the melt in hydrochloric acid, precipitation of iron with ammonia solution and redissolution of the precipitate in hydrochloric acid. Reduction of trivalent iron in the solution, using stannous chloride. Oxidation of excess reductant with mercuric chloride. Titration of the reduced iron with potassium dichromate solution, using sodium diphenylaminesulphonate as indicator.

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout the analysis. All reagents shall be of recognized analytical reagent quality.

- 2.1 Hydrochloric acid (d=1.19)
- 2.2 Hydrochloric acid, dilute 1+3
- 2.3 Hydrochloric acid, dilute 1+9
- 2.4 Nitric acid (d=1.42)
- 2.5 Hydrofluoric acid (40%, d=1.13)
- 2.6 Sulphuric acid (d=1.84)
- 2.7 Sulphuric acid, dilute 1+1
- 2.8 Phosphoric acid (d=1.70)
- 2.9 Acid mixture

Pour 150 ml of sulphuric acid (2.6) into about 500 ml of water with stirring thoroughly, add 150 ml of phosphoric acid (2.8), cool to room temperature and dilute a whole volume to 1000 ml with water.

- 2.10 Ammonia solution (d=0.9)
- 2.11 Ammonia solution, dilute 1+1
- 2.12 Ammonium chloride, solution

Dissolve 10 g of ammonium chloride in 500 ml of water and make slightly alkaline with several drops of ammonia solution (1+1) (2.11)

- 2.13 Sodium pyrosulphate or potassium pyrosulphate

2.14 Stannous chloride, solution

Take 200 ml of hydrochloric acid (2.1) into a 1 l beaker, and add 100 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) into it bit by bit while heating on boiling water bath to dissolve the salt. After cooling, dilute to 1000 ml with water. Preserve the solution in a brown bottle, adding granular tin.

2.15 Mercuric chloride, saturated solution, about 5% (w/v)

2.16 Potassium bichromate, standard solution, N/30

Weigh exactly 1.635 g of crystalline potassium bichromate (Standard reagent for quantitative analysis), place it in a 300 ml beaker and dissolve it in about 100 ml of water. Transfer it to a 1000 ml volumetric flask and dilute to mark with water. In this case, calculate the equivalent value of N/30 solution with the purity indicated for standard reagent without standardization.

2.17 Ammonium ferrous sulphate, standard solution, N/30

Weigh 13 g of ammonium ferrous sulphate $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, add 30 ml of sulphuric acid (1+1) (2.7) and about 700 ml of water, and then dissolve it with stirring, and dilute to 1000 ml with water.

2.18 Methyl red, solution

Dissolve 0.20 g of methyl red in 90 ml of ethyl alcohol, 95% (V/V), and dilute to 100 ml with water

2.19 Sodium diphenylaminesulphonate, solution, 0.2% (w/v)

Preserve it in brown bottle. Barium salt is allowed instead of this reagent.

3. APPARATUS Ordinary laboratory equipment

4. SAMPLING AND SAMPLE PREPARATION (See Section 4 of Introduction)

5. PROCEDURE

5.1 Test portion. Weigh, to the nearest 0.0001 g, 0.250 g of the test sample

5.2 Determination

5.2.1 Decomposition of the test portion

Place the test portion (5.1) in a 30 ml platinum crucible. Add 15 ml of hydrofluoric acid (2.5) and 5 ml of nitric acid (2.4), and dissolve gradually by heating cautiously, without splashing, stir occasionally

by means of a platinum wire. After evaporating to a volume below 5 ml, add 2 ml of sulphuric acid (1+1) (2.7), and heat gradually until all of sulphuric acid is fumed off. Add 5 g of sodium pyrosulphate (2.13), at first heat gradually, and then raise the temperature, fuse to melt in red heat. After cooling, transfer the crucible into a 200 ml beaker, add about 70 ml of hydrochloric acid (1+9) (2.3) and heat gradually to dissolve the melt. Rinse the crucible with water and remove. Add a few drops of nitric acid (2.4) and heat to boil for 1 to 2 min., and then removing the beaker from the source of heat, allow to cool for a few minutes.

5.2.2 Separation

Add a few drops of methyl red solution (2.18) as indicator to the solution, and then add ammonia solution (1+1) (2.11) drop by drop while stirring. When light pink colour disappears, add 1 to 2 drops of ammonia solution (1+1) (2.11) in excess. After heating to boil the solution for a few minutes, remove from the source of heat. After allowing the precipitate to settle, filter off through a rapid filter paper and wash with warm ammonium chloride solution (2.12) 4 to 5 times.

Keeping the filter paper on the filter, wash down most of the precipitate from the filter to the original beaker. Setting the beaker under the funnel, pour 30 ml of hot hydrochloric acid (1+3) (2.2) onto the filter paper to dissolve the hydroxides, and further, wash out the filter paper with hot hydrochloric acid (1+9) (2.3) 4 to 5 times, and finally with warm ammonium chloride solution (2.12) until acid disappears.

Discard the filter paper. Heat the beaker to dissolve hydroxides completely, and then cool to room temperature. Transfer to a 250 ml volumetric flask, dilute to volume and mix.

5.2.3 Reduction

Take a 100 ml aliquot of the solution from the volumetric flask into a 500 ml beaker. After adding 10 ml of hydrochloric acid (2.1), heat the solution over 80°C . Immediately add stannous chloride solution (2.14) drop by drop, while swirling the solution. When the yellow colour of the ferric chloride has disappeared, add one additional

drop of the stannous chloride solution. Next wash the inside wall of the beaker with water and cool below room temperature in a water cooler. Add all at once 10 ml of mercuric chloride solution (2.15) mix thoroughly, and allow the solution to stand for 3 to 5 minutes.

5.2.4 Titration

Add 30 ml of acid mixture (2.9) dilute to about 300 ml with water. Add a few drops of sodium diphenylaminesulphonate solution (2.19) as indicator, and titrate the solution with the standard potassium bichromate solution (2.16). The end point is reached when the green colour of the solution changes to bluish green and a final drop of the titrant imparts a violet colour.

5.2.5 Blank determination

Carry out all operations as for the test portion until 5.2.2. Transfer a 100 ml aliquot of the solution from the volumetric flask to another 500 ml beaker. Add 10 ml of hydrochloric acid (2.1) and heat the solution over 80°C. Immediately add stannous chloride solution (2.14), drop by drop, while swirling the liquid in the beaker. When the yellow colour of the ferric chloride has disappeared, add one additional drop of the stannous chloride solution. Next wash the inside wall of the beaker with water and cool below room temperature in a water cooler. Add all at once 10 ml of mercuric chloride solution (2.15) mix thoroughly, and allow the solution to stand 3 to 5 minutes. Add 30 ml of acid mixture (2.9) and 10 ml of the standard ammonium ferrous sulphate solution (2.17) exactly, and dilute to about 300 ml with water. Add a few drops of sodium diphenylaminesulphonate solution (2.19) as indicator and titrate the solution with the standard potassium bichromate solution (2.16) as 5.2.4. (A ml). Add 30 ml of acid mixture (2.9) and 10 ml of the standard ammonium ferrous sulphate solution (2.17) precisely to another 500 ml beaker, dilute to 300 ml with water and titrate as 5.2.4. (B ml). Subtracting the (B ml) from (A ml), the value of the blank determination (V_2) (shown below) is obtained.

6. EXPRESSION OF RESULTS

6.1 Calculation of ferric oxide content

The ferric oxide content, as percentage by mass, is calculated from the following formula:

$$\text{Fe}_2\text{O}_3\% (\text{m/m}) = \frac{(v_1 - v_2) \times 0.1862}{m \times L} \times 1.4297$$

where

v_1 is the volume, in millilitres, of the standard potassium bichromate solution (2.16) consumed for the test portion;

v_2 is the volume, in millilitres, of the standard potassium bichromate solution (2.16) consumed for the blank test;

m is the mass, in grams, of the test portion;

L is the volume fraction of the aliquot.

DETERMINATION OF ALUMINIUM OXIDE - VOLUMETRIC METHODS

1. PRINCIPLE

Decomposition of the test portion by treatment with nitric, hydrofluoric and sulphuric acids and by fusion with potassium pyrosulphate. Dissolution of the melt in hydrochloric acid. Adjustment of the pH with acetic acid and ammonia solution, and separation of heavy metals by extraction with sodium diethyldithiocarbamate and chloroform. Formation of EDTA-Al complex by reaction with EDTA, and titration of the excess of EDTA with standard zinc solution.

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout the analysis. All reagents shall be of recognized analytical reagent quality.

- 2.1 Hydrochloric acid (d=1.19)
- 2.2 Hydrochloric acid, dilute 1+1
- 2.3 Hydrochloric acid, dilute 1+9
- 2.4 Nitric acid (d=1.42)
- 2.5 Hydrofluoric acid (40%, d=1.13)
- 2.6 Sulphuric acid (d=1.84)
- 2.7 Sulphuric acid, dilute 1+1
- 2.8 Acetic acid (d=1.06)
- 2.9 Acetic acid, dilute 1+1
- 2.10 Ammonia solution, (d=0.9)
- 2.11 Ammonia solution, dilute 1+1
- 2.12 Potassium pyrosulphate or sodium pyrosulphate
- 2.13 Sodium diethyldithiocarbamate (DDTC) solution, 50g/l, a fresh solution shall be prepared daily.
- 2.14 Chloroform
- 2.15 Zinc, standard solution, 0.01M

Dissolve 0.6537 g of pure zinc metal with 10 ml of hydrochloric acid (1+1) (2.2), add 5 ml of acetic acid (2.8) and adjust the pH to 6.0 ± 0.2 with ammonia solution (1+1) (2.11). Allow the solution to cool and dilute with water to exactly 1000 ml in a volumetric flask. If

the surface of pure zinc metal used is oxidized, wash the metal surface with hydrochloric acid (1+1) (2.2), water and acetone, in this order, and weigh it after drying for approximately 5 min. under 110°C.

- 2.16 Disodium ethylenediaminetetraacetate (EDTA), standard solution, 0.01M.

Dissolve 3.7225 g of EDTA dihydrate with water and dilute to 1000 ml. Standardize this solution against the zinc standard solution (0.01M). Take a 25 ml aliquot of this solution (2.16) into a 300 ml beaker, add 10 ml of acetic acid (1+1) (2.9) and about 50 ml of water and adjust the pH to 6.0 ± 0.2 with ammonia solution (1+1) (2.11). Add a few drops of xylenol orange solution (2.17) and titrate with standard zinc solution (0.01 M) (2.15). The end point is reached when the slight red colour of the solution appears with a final drop of standard zinc solution. Record the volume of standard zinc solution (0.01 M) (2.15) used and calculate the factor of this solution (2.16) from the following formula:

$$f = \frac{v_1}{v_2}$$

where

f is the factor of 0.01M EDTA standard solution;

v_1 is the volume, in millilitres, of standard zinc solution consumed;

v_2 is the volume, in millilitres, of standard EDTA solution taken.

- 2.17 Xylenol orange solution, 1g/l

3. APPARATUS Ordinary laboratory equipment

4. SAMPLING AND SAMPLE PREPARATION (See Section 4 of Introduction)

5. PROCEDURE

- 5.1 Test portion - Weigh, to the nearest 0.0001 g, 0.250 g of the test sample.

5.2 Determination

5.2.1 Decomposition of the test portion

Place the test portion (5.1) in a 30 ml platinum crucible. Add 15 ml of hydrofluoric acid (2.5) and 5 ml of nitric acid (2.4). Heating carefully and with occasional stirring with a platinum wire to avoid bumping, decompose the test portion gradually. After evaporating to about 5 ml, add 2 ml of sulphuric acid (1+1) (2.7), heat gradually to white fumes of sulphuric acid and continue heating until all of sulphuric acid is fumed off.

Add 5 g of potassium pyrosulphate (2.12), heat slowly at first, then raise the temperature gradually and fuse at red heat. After cooling, transfer the crucible to a 200 ml beaker, add about 70 ml of hydrochloric acid (1+9) (2.3), heat slowly to dissolve the melt. After washing with water, the crucible is removed. Then add a few drops of nitric acid (2.4), heat to boil for 1 to 2 minutes. Remove the beaker from the source of heat and cool to room temperature. Transfer the solution to a 250 ml volumetric flask, dilute to volume with water and mix.

5.2.2 Extraction

Take a 25 ml aliquot of the solution, transfer to a 100 ml beaker, add 10 ml of acetic acid (1+1) (2.9) and adjust the pH of the solution to 2.8 - 3.0 with ammonia solution (1+1) (2.11). Transfer the solution to a 200 - 300 ml separating funnel, add 20 ml of chloroform (2.14) and 20 ml of DDTC solution (2.13) and begin shaking the funnel within 5 seconds. After shaking vigorously for about 1 minute, allow the liquid to separate into two layers and discard the lower organic layer. In order to collect the dirty organic drops floating on the liquid surface, add about 5 ml of chloroform (2.14) to the separating funnel, shake for 1 minute, allow to separate into two layers and discard the lower layer. Repeat the extraction above mentioned, but using 10 ml of DDTC solution (2.13). Finally, wash the stem and cock of the funnel with about 2 ml of chloroform (2.14). Transfer the aqueous layer in the separating funnel to a 300 ml beaker, rinse the inside of the funnel with small portion of water and combine with the contents of the beaker.

5.2.3 Titration

Add the volume of standard EDTA solution (2.16) according to the classification of Table 1.

Table 1

% Al ₂ O ₃ presumed	ml 0.01M standard EDTA solution added
up to 30	25
30 to 40	35
over 40	1.5 fold over against equivalent

After boiling the solution for about 10 min., remove from the source of heat, add 10 ml of ammonia solution (1+1) (2.11) and cool below room temperature in a water cooler. Then, adjust the pH to 6.0 ± 0.2 with hydrochloric acid (1+9) (2.3). Add a few drops of xylenol orange solution (2.17) as indicator and titrate with standard zinc solution (2.15) until the colour of the solution changes to a slight pink colour with the last drop.

6. EXPRESSION OF RESULTS

6.1 Calculation of aluminum oxide content

The aluminum oxide content, as percentage by mass, is calculated from the following formula:

$$\text{Al}_2\text{O}_3\% (\text{m/m}) = \frac{(V_1 \times f - V_2) \times 0.000510}{m \times L} \times 100 = \frac{(V_1 \times f - V_2) \times 0.0510}{m \times L}$$

where

v_1 is the volume, in millilitres, of standard EDTA solution (2.16) added;

v_2 is the volume, in millilitres, of standard zinc solution (2.15) consumed;

f is the factor of standard EDTA solution (2.16) against 0.01M;

m is the mass, in grams, of the test portion;

L is the volume fraction of the aliquot.

DETERMINATION OF CALCIUM OXIDE AND MAGNESIUM OXIDE - VOLUMETRIC METHOD

1. PRINCIPLE

Decomposition of the test portion by fusion with sodium carbonate. Dissolution of the melt in hydrochloric acid, treatment with perchloric acid and filtration of insoluble residue, the filtrate being reserved as the main solution (Solution A). Elimination of silica in insoluble residue by treatment with sulphuric acid and hydrofluoric acid and decomposition of impurities by fusion with sodium pyrosulphate. Dissolution of the melt in hydrochloric acid (Solution B) and combination with the main solution. Precipitation of hydroxides of iron, aluminum, etc. with ammonia solution and filtration (Solution C).

(Determination of Calcium Oxide)

Aliquotation of Solution C, precipitation of magnesium hydroxide by adjustment of the pH with sodium hydroxide, masking of the interfering elements with potassium cyanide and titration with EDTA using NN indicator (V_1).

Calculation of the percentage of calcium oxide from V_1 .

(Determination of Magnesium Oxide)

Aliquotation of Solution C, adjustment of the pH with ammonia solution masking of the interfering elements with potassium cyanide and titration with EDTA using EBT indicator (V_2).

Calculation of the percentage of magnesium oxide from $(V_2 - V_1)$

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout the analysis. All reagents shall be recognized analytical reagent quality.

- 2.1 Hydrochloric acid (d=1.19)
- 2.2 Hydrochloric acid, dilute 1+4
- 2.3 Hydrochloric acid, dilute 1+10
- 2.4 Perchloric acid (60%, d=1.54 : or 70%, d=1.67)
- 2.5 Hydrofluoric acid (40%, d=1.13)

- 2.6 Sulphuric acid (d=1.84)
 2.7 Sulphuric acid, dilute 1+1
 2.8 Sodium hydroxide solution, 280g/l
 2.9 Ammonia solution (d=0.9)
 2.10 Ammonia solution, dilute 1+1
 2.11 Sodium carbonate, anhydrous
 2.12 Sodium pyrosulphate
 2.13 Ammonium chloride solution

Dissolve about 10 g of ammonium chloride with about 500 ml of water and render slightly alkaline with a few drops of ammonia solution.

- 2.14 Potassium cyanide solution, 200g/l
 2.15 Disodium ethylenediaminetetraacetate (EDTA), standard solution, 0.01M
 Dissolve 3.7225 g of EDTA dihydrate with water and dilute to 1000 ml. Standardize this solution against standard zinc solution (0.01M). Take a 25 ml aliquot of this solution (2.15) into a 300 ml beaker, add 10 ml of acetic acid (1+1) and about 50 ml of water and adjust the pH to 6.0 ± 0.2 with ammonia solution (1+1) (2.10). Add a few drops of xylenol orange solution (2.20) and titrate with standard zinc solution (2.16). The end point is reached when the slight red colour of the solution appears with a final drop of 0.01M standard zinc solution. Record the volume of standard zinc solution used and calculate the factor of this solution (2.15) from the following formula:

$$f = \frac{v_1}{V_2}$$

where

f is the factor of standard EDTA solution;

v_1 is the volume, in millilitres, of standard zinc solution consumed;

v_2 is the volume, in millilitres, of standard EDTA solution aliquot.

- 2.16 Zinc, standard solution, 0.01M

Dissolve 0.6537 g of pure zinc metal with 10 ml of hydrochloric acid (1+1), add 5 ml of acetic acid and adjust the pH to 6.0 ± 0.2 with ammonia solution (1+1) (2.10). Allow the solution to cool and dilute with water to exactly 1000 ml in a volumetric flask.

2.17 Methyl red solution

Dissolve 0.20 g of methyl red powder in 90 ml of ethyl alcohol, 95% (v/v) and dilute with water to 100 ml.

2.18 NN indicator

Dilute 0.10 g of 1-(2-hydroxy-4-sulfo-1-naphthylazo)-2-hydroxy-3-naphthoic acid with 10 g of potassium nitrate and grind.

2.19 EBT solution

Dissolve 0.20 g of sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate with 15 ml of triethanolamine and 5 ml of ethyl alcohol, 95% (v/v).

2.20 Xylenol orange solution, 1g/l

3. APPARATUS Ordinary laboratory equipment

4. SAMPLING AND SAMPLE PREPARATION (See Section 4 of Introduction)

5. PROCEDURE

5.1 Test portion - Weigh, to the nearest 0.0001g, 0.250g of the test sample sample

5.2 Determination

5.2.1 Decomposition of the test portion

Place the test portion in a 30 ml platinum crucible, add 5 g of sodium carbonate (2.11) and mix. Heat the crucible at 900-1000°C to fuse the ash and continue the fusion for 30-40 min. After cooling, place the crucible in a 500 ml beaker, add 70 ml of hydrochloric acid (1+4) (2.2) to dissolve the melt. Rinse and remove the crucible. Add 50 ml of perchloric acid (2.4), heat gently, cover the beaker with a watch glass when the solution begins to fume slightly and evaporate to dense white fumes of perchloric acid. Maintain a steady refluxing of the acid on the walls of the beaker for about 15 min. Allow the beaker to cool, add 50 ml of hydrochloric acid (1+4) (2.2) to dissolve soluble salts.

Filter the solution through a medium-texture paper (see note) and wash the filter, first with small portions of warm hydrochloric acid (1+10) (2.3) 2 to 3 times, second with warm water until the washings are no longer acid and then more 2 to 3 times. Preserve the residue

on the filter.

Combine the filtrate and washings in a 500 ml beaker, cover with a watch glass, and heat the solution to dense white fumes of perchloric acid and maintain a steady refluxing of perchloric acid on the walls of the beaker for about 15 min. Proceed again as described in the preceding paragraph, to recover residual silicon dioxide. Store the filtrate and washings for the determination of calcium oxide and magnesium oxide (Solution A).

(NOTE) Insoluble hydrous silicon dioxide will adhere to the bottom of the beaker and will not be removed by spraying with a jet of water. This must be scraped off with a rubber-capped glass rod (policeman).

5.2.2. Treatment of residue

Place the two precipitates with filters in a platinum crucible, heat gently to dry, ash the filter paper, and ignite at a high temperature, e.g. 800°C. Moisten the residue in the crucible with sulphuric acid (1+1) (2.7), add 5 ml of hydrofluoric acid (2.5), heat gently to remove silicon dioxide and sulphuric acid and ignite at a high temperature, e.g. 800°C.

After cooling, add about 1 g of sodium pyrosulphate (2.12) in the platinum crucible and fuse gently until a clear melt is obtained. Cool the crucible, add about 15 ml of water and a few drops of hydrochloric acid (2.1) and heat gently to dissolve the melt (Solution B). Evaporate the Solution A, cover the beaker and heat to dense white fumes of perchloric acid. After cooling, add about 100 ml of water and the Solution B to dissolve the salts.

5.2.3 Separation

Add a few drops of methyl red solution (2.17), make this solution to slight alkalinity by the addition of ammonia solution (1+1) (2.11). Heat the solution until the boiling begins and remove from the source of heat. Allow the precipitate to settle, then collect it on a rapid filter paper. Wash the inside wall of the beaker 1 time and the precipitate 1 time, respectively, with warm ammonium chloride solution (2.13).

Collect the filtrate and washings in a 500 ml beaker. Wash the precipitate back into the original beaker with a small quantity of water.

Add 5 ml of hydrochloric acid (1+4) (2.2) and heat to dissolve the hydroxides. Dilute to about 50 ml with water. Add a few drops of methyl red solution (2.17), adjust this solution to slight alkalinity by the addition of ammonia solution (1+1) (2.10).

Heat the solution until the boiling begins and remove from the source of heat. Allow the precipitate to settle, then collect it on the original filter paper. Wash the precipitate 3 to 4 times with warm ammonium chloride solution (2.13). Collect the filtrate into the 500 ml beaker containing the filtrate and washings from the previous precipitation. Discard the precipitate. Evaporate the solution to less than 200 ml. cool, transfer to 250 ml volumetric flask and dilute to 250 ml with water, and mix thoroughly (Solution C).

5.2.4. Determination of Calcium Oxide

Take a 100 ml aliquot of Solution C into a 300 ml beaker and adjust the pH to 12.5-13.5 with sodium hydroxide solution (2.8). Add 5 ml of potassium cyanide solution (2.14), mix and allow the solution to stand for 5 min. Add 0.05-0.1 g of the NN indicator (2.18) and titrate with standard EDTA solution (2.15). The end point is reached when the red colour of the solution disappears and the blue colour appears with a final drop of standard EDTA solution (2.15). Record the volume of standard EDTA solution (2.15) used (V_1) and calculate the percentage of calcium oxide from formula (1) in 6.1.

5.2.5. Determination of magnesium oxide

Take a 100 ml aliquot of Solution C into a 300 ml beaker and adjust the pH to 9.5-10.5 with ammonia solution (2.9). Add 5 ml of potassium cyanide solution (2.14), mix and allow the solution to stand for 2 or 3 minutes.

Add a few drops of EBT solution (2.19) and titrate with standard EDTA solution (2.15). The end point is reached when the slight red colour of the solution disappears and the blue colour appears with a final drop of standard EDTA solution (2.15). Record the volume of standard EDTA solution (2.15) used (V_2) and calculate the percentage of magnesium oxide from formula (2) in 6.2.

6. EXPRESSION OF RESULTS

6.1 Calculation of calcium oxide content

The calcium oxide content, as a percentage by mass, is calculated from the following formula:

$$\text{Ca O \% (m/m)} = \frac{V_1 \times f \times 0.05608}{m \times \frac{100}{250}} = \frac{V_1 \times f \times 0.1402}{m} \quad (1)$$

where

v_1 is the volume, in millilitres, of standard EDTA solution (2.15) consumed;

f is the factor of 0.01M standard EDTA solution (2.15)

m is the mass, in grams, of the test portion.

6.2 Calculation of magnesium oxide content

The magnesium oxide content, as a percentage by mass, is calculated from the following formula:

$$\text{MgO \% (m/m)} = \frac{(V_2 - V_1) \times f \times 0.04032}{m \times \frac{100}{250}} = \frac{(V_2 - V_1) \times f \times 0.1008}{m} \quad (2)$$

where

V_1 is the volume, in millilitres, of standard EDTA solution (2.15) consumed for calcium oxide determination;

V_2 is the volume, in millilitres, of standard EDTA solution (2.15) consumed for calcium oxide plus magnesium oxide determination;

f is the factor of 0.01M standard EDTA solution (2.15),

m is the mass, in grams, of the test portion.

DETERMINATION OF SULPHUR TRIOXIDE - GRAVIMETRIC METHOD

1. PRINCIPLE

Dissolution of sulphate in the test portion by digestion with hydrochloric acid. Precipitation of barium sulphate by treatment with barium chloride, filtration and weighing.

(NOTE) It has been noted that low sulphur values may occur in coals high in lead and barium.

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout analysis. All reagents shall be of recognized analytical reagent quality.

- 2.1 Hydrochloric acid (d=1.19)
- 2.2 Hydrochloric acid, dilute 1+3
- 2.3 Ammonia solution (d=0.9)
- 2.4 Ammonia solution, dilute 1+1
- 2.5 Barium chloride solution, 85g/l
- 2.6 Methyl orange solution, 1g/l
- 2.7 Silver nitrate solution, 20g/l

3. APPARATUS Ordinary Laboratory equipment

4. SAMPLING AND SAMPLE PREPARATION (See Section 4 of Introduction)

5. PROCEDURE

5.1 Test portion - Weigh, to the nearest 0.0001 g, approximately 0.2 to 0.5 g of the test sample.

5.2 Determination

5.2.1 Dissolution of sulphate in the test portion

Place the test portion (5.1) in a 500 ml beaker. Add 20 ml of hydrochloric acid (1+3) (2.2) and cover the beaker with a watch glass. Heat and boil gently for 15-20 minutes. Filter the hot solution through a medium-texture filter paper, collect the filtrate and washings in a 500 ml beaker and dilute to about 150 ml with water.

5.2.2 Precipitation and filtration of barium sulphate

Add 2-3 drops of methyl orange solution (2.6) as indicator. Neutralize with ammonia solution (1+1) (2.4) using a pipet or buret until the colour of solution changes from red to orange. Then add 1ml of hydrochloric acid (2.1).

(Note 1) In this case, if any precipitate is formed, add 1 or 2 drops of hydrochloric acid (2.1) to re-dissolve the precipitate.

Dilute to 250 ml with water. Heat the covered beaker until the solution boils and then reduce the heating slightly until ebullition ceases. Add 10 ml of the warm barium chloride solution (2.5) using a pipet, so that barium chloride solution falls into the center of the hot solution, which is being stirred.

Maintain the solution just below boiling point for one hour, or allow to stand at room temperature for 12 hours or longer. Filter supernatant liquid through a close-texture filter paper. Add a small portion of warm water to the beaker containing the precipitate after stirring, allow the beaker to stand to settle the precipitate. Pour the upper clear portion of the solution on the filter and repeat the procedure several times. Add a small portion of warm water to the beaker containing the precipitate, stir and pour the precipitate and washings on the filter. Wash down the inside of the beaker with a fine stream of wash water, and pour the washings on the filter.

(NOTE 2) It is preferable to use a policeman (rubber-capped glass rod) to polish down the inside of the beaker and stirrer before pouring the solution into the beaker.

Wash the filter paper with water until the last 20 ml of the washings give not more than a faint opalescence with silver nitrate solution (2.7).

(NOTE 3) Total volume of washing water used should be kept to less than 250 ml.

5.2.3 Gravimetric determination

Place the wet filter paper and precipitate in a previously ignited and weighed platinum crucible. Open the door of an electrically heated muffle furnace, which has with a sufficient ventilation,

maintained at 700 to 800°C. Place the crucible almost closed with a platinum lid in a lower temperature zone of the furnace, and take off the lid after carbonization of the filter paper. Insert the crucible into the hottest zone of the furnace, and maintain it for 20 minutes. Allow the crucible to cool in a desiccator and weigh accurately.

5.2.4 Blank test

Carry out blank tests twice or more under the same conditions as for the test portion, but omitting the test portion. The mean value (m_2) (shown below) of the weights of barium sulphate found in the blank determinations is used to correct the weights of barium sulphate found in the determinations.

6. EXPRESSION OF RESULTS

6.1 Calculation of sulphur trioxide content

The sulphur trioxide content, as percentage by mass, is calculated from the following formula:

$$SO_3 \text{ \% (m/m)} = \frac{(m_1 - m_2) \times 0.3430}{m} \times 100 = \frac{m_1 - m_2}{m} \times 34.30$$

where

m_1 is the mass, in grams, of barium sulphate found in the test portion.

m_2 is the mass, in grams, of barium sulphate found in the blank test;

m is the mass, in grams, of the test portion

DETERMINATION OF PHOSPHOUS PENTOXIDE

Spectrophotometric or Volumetric Method

1. PRINCIPLE

1.1. Method 1: Spectrophotometric method by molybdenum blue

Decomposition of the test portion by treatment with nitric, hydrofluoric and perchloric acids, and the residue being filtered off, ignited, fused with potassium pyrosulphate. Dissolution of the melt in hydrochloric acid, addition of ferric chloride and collection of the phosphorus by precipitation with ammonia solution, dissolution in hydrochloric acid and combination with the main solution. Reduction of iron, etc. in the solution with sodium sulphite, and formation of molybdenum blue with ammonium molybdate and hydrazine sulphate. The colour intensity of the molybdenum blue is measured spectrophotometrically at a wave length of about 660 nm or 825 nm.

1.2 Method 2: Spectrophotometric method by phospho-vanado-molybdate yellow

Decomposition of the test portion by treatment with nitric, hydrofluoric and perchloric acids, and the residue being filtered off, ignited fused with potassium pyrosulphate. Dissolution of the melt in hydrochloric acid, addition of ferric chloride and collection of the phosphorus by precipitation with ammonia solution, dissolution in hydrochloric acid and combination with the main solution. Formation of phospho-vanado-molybdate yellow with ammonium molybdate and ammonium metavanadate. The colour intensity of the phospho-vanado-molybdate yellow is measured spectrophotometrically at a wavelength of about 430 nm.

1.3 Method 3: Volumetric Method

Decomposition of test portion by treatment with nitric, hydrofluoric and perchloric acids, and the residue being filtered off, ignited, fused with potassium pyrosulphate. Dissolution of the melt in hydrochloric acid, addition of ferric chloride and collection of the phosphorus by precipitation with ammonia solution, dissolution in hydrochloric acid and combination with the main solution. Evaporation to fumes of perchloric acid, dissolution of the salts in water, neutralization with ammonia solution and adjustment of the acidity with nitric acid. Addition of ammonium molybdate to the solution and collection by filtration of the yellow precipitates of ammonium phosphomolybdate.

Washing free of acid and dissolution in a slight excess of sodium hydroxide, the excess being titrated with nitric acid.

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout the analysis. All reagents shall be of recognized analytical reagent quality.

	Method
2.1 Hydrochloric acid (d=1.19)	1, 2 and 3
2.2 Hydrochloric acid, dilute 1+1	1, 2 and 3
2.3 Hydrochloric acid, dilute 2+100	1, 2 and 3
2.4 Nitric acid (d=1.42)	1, 2 and 3
2.5 Nitric acid, dilute 2+100	3
2.6 Nitric acid, dilute 2+10000	3
Dilute nitric acid (2+100) (2.5) to 100 times of the original volume with water	
2.7 Perchloric acid (60%, d=1.54; or 70%, d=1.67)	1, 2 and 3
2.8 Perchloric acid, dilute 1+1	1 and 2
2.9 Hydrofluoric acid (40%, d=1.13)	1, 2 and 3
2.10 Ammonia solution (d=0.9)	1, 2 and 3
2.11 Ammonium nitrate	3
2.12 Potassium nitrate solution, 10g/l	3
2.13 Sodium sulphite solution, 50g/l	1
2.14 Sodium carbonate, anhydrous	1 and 2
2.15 Sodium carbonate solution, 20g/l	1 and 2
2.16 Potassium pyrosulphate	1, 2 and 3
2.17 Mixed reagent for Method 1	1

Solution A: Dissolve 20 g of ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in about 100 ml of warm water, add 600 ml of sulphuric acid (1+1), cool and dilute to 1000 ml with water.

Solution B: Dissolve 1.5 g of hydrazine sulphate in water and dilute to 1000 ml with water. Prepare the mixed reagent, each time just before use; mix Solution A,

Solution B and water in the ratio of 25 ml : 10 ml : 65 ml.

2.18 Mixed reagent for Method 2

Solution A: Dissolve 40 g of ammonium molybdate

$[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ in water and dilute to 1000 ml.

Solution B: Dissolve 2 g of ammonium metavanadate (NH_4VO_3) in perchloric acid (1+3) and dilute with perchloric acid (1+3) to 1000 ml. Prepare the mixed reagent, each time just before use, mixing the equal volumes of each of the above two solutions.

2.19 Ammonium molybdate solution

3

Dissolve 40g of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ in 300 ml of warm water and 80ml of ammonia solution, cool and pour little by little into 600ml of nitric acid (1+1), while stirring nitric acid (1+1) all the time.

2.20 Dephosphorized ferric chloride solution

1 and 2

Weigh 0.300g of pure iron into a 300ml beaker, add 10ml of hydrochloric acid, cover the beaker with a watch glass and heat gently to decompose.

After having added 3 ml of nitric acid to oxidize ferrous ions, add 5 ml of perchloric acid, heat to evaporate sufficiently to white fumes and cool. Transfer the solution to a 100 ml separating funnel with 20 ml of hydrochloric acid (10+6). Add 20 ml of methyl isobutyl ketone and shake vigorously for about 1 minute. Allow to stand for separation into two layers and discard the lower layer. Add 20 ml of water to the separating funnel, shake the funnel vigorously for about 1 minute, allow to stand separating the contents into two layers, and then draw off the under layer into a 300 ml beaker. Add 5 ml of water to the separating funnel and after a similar operation, separate the lower layer into the 300 ml beaker collected previously. Boil the combined under layers, to expel the dissolved methyl isobutyl ketone, add 5 ml of nitric acid and 10 ml of perchloric acid and heat to evaporate. When dense white fumes of perchloric acid have started, cool, add 10 ml of hydrochloric acid and heat to dissolve. Add a few drops of nitric acid to oxidize, boil and cool. Dilute with water to exactly 100 ml.

Exactly 10ml of this solution shall be added to make the blank value constant.

2.21 Ferric chloride solution

3

Dissolve 0.300g of pure iron whose phosphorus content is extremely low in 10ml of hydrochloric acid by heating, oxidize by adding a few drops of nitric acid, boil, cool and dilute to exactly 100 ml with water. Exactly 10 ml of this solution shall be added to make the blank value constant.

2.22 Phosphorus pentoxide, standard solution $20\mu\text{g P}_2\text{O}_5/\text{ml}$

1 and 2

Dry sodium bihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) at 110° to constant mass and cool to room temperature in a desiccator. Weigh exactly 0.338g of the dried and cooled sodium bihydrogen phosphate, dissolve in water and dilute to exactly 1000ml to obtain the stock solution ($200\mu\text{g P}_2\text{O}_5/\text{ml}$). Take a 50ml aliquot of the stock solution into a 500ml volumetric flask, dilute to volume to obtain the phosphorus pentoxide standard solution ($20\mu\text{g P}_2\text{O}_5/\text{ml}$). Standardize the standard solution by the following procedures:

Using two 300 ml erlenmeyer flasks, transfer a 10 ml aliquot of phosphorus pentoxide stock solution into the first flask and add 2.000g of pure iron. Add 2.000g of pure iron only into the second flask. Add 20ml of nitric acid and 10ml of water to the first flask, and 20ml of nitric acid and 20ml of water to the second flask. Heat both flasks to dissolve the pure iron. After boiling the solutions to remove nitrogen oxides add potassium permanganate solution (20g/l) immediately little by little several times and boil to produce the precipitate of manganese dioxide. Add small crystals of ferrous ammonium sulphate [$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$] little by little, while shaking the flask. After having decomposed the precipitate of manganese dioxide, boil to oxidize the excess of iron (II) ions. Then, follow the procedures as described in 5.3.4 and subsequent clauses, and obtain the quantity of phosphorus pentoxide contained in 1 ml of the phosphorus pentoxide standard solution.

$$f = (V_1 - V_2) \times 0.00309$$

where

f is the mass, in milligrams, of phosphorus pentoxide contained in 1ml of the standard phosphorus pentoxide solution;

V_1 is the volume, in millilitres, of the standard sodium hydroxide solution (0.1N) consumed to determine phosphorus pentoxide in the first flask;

V_2 is the volume, in millilitres, of the standard sodium hydroxide solution (0.1N) consumed to determine phosphorus pentoxide in the second flask.

- 2.23 Sodium hydroxide, standard solution, 0.1N 3
Dissolve 4 g of sodium hydroxide in 1 l of freshly boiled and cooled water. Standardize this solution against either sulphamic acid or potassium hydrogen phthalate.
- 2.24 Nitric acid, standard solution, 0.1N 3
Dilute 6.5 ml of nitric acid (2.4) with water to 1 l.
Standardization of the solution: Accurately measure 25ml of the standard sodium hydroxide solution (2.23) and titrate with the nitric acid solution, using phenolphthalein solution (2.25) as indicator, correct the normality to exactly 0.1N by adding water or 1N nitric acid.
- 2.25 Phenolphthalein solution 3
Dissolve 0.10g of powdered phenolphthalein in 90ml of ethyl alcohol, 95% (v/v), and dilute with water to 100ml.
- 2.26 Ammonium thiocyanate solution, 100g/l 3
- 2.27 Sulphurous acid water, 6% v/v 3
3. APPARATUS Ordinary laboratory equipment and spectrophotometer
4. SAMPLING AND SAMPLE PREPARATION See Section 4 of Introduction.
5. PROCEDURE
- 5.1 Method 1: Spectrophotometric method by Molybdenum blue
- 5.1.1 Test Portion
Weigh, to the nearest 0.0001g, 0.200g of the test sample.
- 5.1.2 Decomposition of the test portion
Place the test portion (5.1.1) in a 80ml platinum dish, add 10ml

of nitric acid (2.4), 5ml of hydrofluoric acid (2.9) and 10ml of perchloric acid (2.7), and heat to decompose. Continue heating for evaporation, and evolve dense white fumes of perchloric acid sufficiently. Remove from the source of heat and cool. Add about 50ml of warm water, heat to dissolve the soluble salts, filter through a medium-texture filter paper containing filter paper pulp to separate the insoluble residue and wash with warm water thoroughly. Collect the filtrate and washings into a 300ml beaker and preserve as a main solution.

5.1.3 Treatment of residue

Transfer the insoluble residue with the filter paper into a 30ml platinum crucible, dry and ignite to ash. After cooling, add about 1g of potassium pyrosulfate (2.16), heat slowly at first, raise the temperature gradually to dull red and fuse. After cooling, transfer the crucible to a 300ml beaker, add about 30ml of warm water containing about 5ml of hydrochloric acid (2.1), and heat until the melt dissolves. Remove the crucible from the solution, after washing with warm water.

Add exactly 10ml of the dephosphorized ferric chloride solution (2.20), add ammonia solution (2.10) in small portions while stirring, until the solution is slightly alkaline, to precipitate ferric hydroxide and ferric phosphate. Boil the solution for about 2 min., then remove from the source of heat. Allow the precipitate to settle, filter through a rapid filter paper and wash with warm water. Discard the filtrate and washings. Place the beaker containing the main solution from 5.1.2 under the funnel. Dissolve the precipitate by pouring onto the paper about 10ml of warm hydrochloric acid (1+1) (2.2). Wash with warm hydrochloric acid (2+100) (2.3). Evaporate the solution in the covered beaker to dense white fumes of perchloric acid. Remove the beaker from the source of heat, cool, add about 50ml of water and warm to dissolve the salts. If any insoluble residue is noticed, filter the solution with a close-texture filter paper and wash with warm water. Transfer the filtrate and washings to a 100ml volumetric flask, cool, dilute with water to volume and mix.

5.1.4 Determination

From this solution, pipette an aliquot in accordance with Table 2 according to the content of phosphorus pentoxide, into a 100 ml volumetric flask; add 2 ml of perchloric acid (1+1) (2.8) and 5ml of sodium sulphite solution (2.13), mix and wait until the colour of the solution shows no further change due to the reduction of ferric to ferrous salts. If the iron (III) ions are not reduced completely after mixing for a few minutes it is recommended that the solution be heated to complete the reduction.

Table 2

% P ₂ O ₅ presumed	ml aliquot
up to 0.25	20
0.2 up to 1.0	10
1.0 over	5

(Note) When a new 100ml volumetric flask is to be used, fill with water and place in boiling water bath for 10 min. Cool in a water cooler. Repeat the procedure several times. Use it after the change of the volume has become slight.

Add 25ml of the mixed reagent for Method 1 (2.17) and heat for 10 min. in the boiling water bath. Cool to room temperature, dilute to volume with water and mix. Transfer a part of this solution to a 10mm photometric cell and measure the absorbance with reference to water using a wavelength of 660 or 825nm. Determine the amount of phosphorus pentoxide from the absorbance by using the calibration curve preliminarily prepared as instructed in 5.1.5. Calculate the percentage of phosphorus pentoxide from formula in 6.1.(1).

5.1.5 Preparation of calibration curve

Take 0 to 15ml aliquots in steps from the standard phosphorus pentoxide solution (2.22), each into a series of 100ml volumetric flasks and add water to make each about 20ml.

Add 2ml of perchloric acid (1+1) (2.8) and 5ml of sodium sulphite solution (2.13), mix, add 25ml of the mixed reagent for Method 1 and heat for 10 min. in a boiling water bath. Cool to room temperature and dilute each to the mark of the flask. Transfer a portion

from each of the solutions into the 10mm photometric cell and measure as described above. Plot the relationship between the amount of phosphorus pentoxide added and absorbance to prepare the calibration curve.

Remarks 1. When the test portion contains 30mg or more of titanium oxide, the following procedure should be followed:

Place the test portion into a 30ml platinum crucible, add 10ml of nitric acid (2.4) and then 5ml of hydrofluoric acid (2.9) slowly in drops. Heat to decompose. After decomposition, evaporate to dryness on the hot plate and cool. Add about 3g of sodium carbonate (2.14), heat slowly at first and then raise the temperature gradually to fuse completely.

After cooling, transfer the crucible with the melt into a 300ml beaker, add about 100ml of warm water, stir gently, detach the melt from the crucible and remove after washing with water.

Boil the solution for a while to dissolve the soluble salts, filter through a medium-texture filter paper and wash thoroughly with warm sodium carbonate solution (2.15). Discard the residue. Transfer the filtrate and washings into a 500ml beaker, add hydrochloric acid (2.1) to acidify the solution definitely and decompose carbonates. Add exactly 10ml of the dephosphorized ferric chloride solution (2.20), and while mixing the solution, add ammonia solution (2.10) drop by drop until ferric phosphate, ferric hydroxide, etc. are precipitated and the solution is slightly alkaline. Boil gently for about 2 min., remove from the source of heat and allow to settle the precipitates of ferric phosphate, ferric hydroxide, etc. Filter with a rapid filter paper, wash with warm water and discard the filtrate and washings. Pour about 10ml of warm hydrochloric acid (1+1) (2.2) onto the filter paper to dissolve the precipitates, wash with warm water and collect the solution and washings into a 300ml beaker. Cover with a watch glass, add 10 ml of perchloric acid (2.7), heat sufficiently to evaporate and evolve dense white fumes.

Remove from the source of heat, allow to cool for a while, add about 50ml of warm water and heat to dissolve soluble salts. Transfer the solution into a 100ml volumetric flask with water, cool to room temperature, dilute to volume with water and mix. Then, obtain the

phosphorus pentoxide content according to the procedure specified in 5.1.4 and subsequent clauses.

5.2 Method 2: Spectrophotometric method by phosphovanado-molybdate yellow

5.2.1 Test portion

Weigh, to the nearest 0.0001g, 0.500g of the test sample.

5.2.2 Decomposition of the test portion

Decompose the test portion (5.2.1) according to the procedure specified in 5.1.2, but the volume of nitric acid (2.4) used should be 15ml.

5.2.3 Treatment of residue

Treat the residue according to the procedure specified in 5.1.3. But the volume of solution diluted should be made 250ml.

5.2.4 Determination

From this solution, take a 50ml aliquot into a 100ml volumetric flask, add 3ml of perchloric acid (1+1) (2.8), adjust the temperature of the solution to 20 to 30°C, add 10ml of the mixed reagent for Method 2 (2.18), dilute to volume and mix. Allow to stand for about 10 min. Transfer a part of this solution into a 10mm photometric cell and measure the absorbance with reference to water using a wave length of 430nm. Determine the amount of phosphorus pentoxide from the absorbance by using the calibration curve preliminarily prepared as instructed in 5.2.5. Calculate the percentage of phosphorus pentoxide from formula in 6.1 (2).

5.2.5 Preparation of calibration curve

Take 0 to 25ml aliquots in steps from the standard phosphorus pentoxide solution (2.22), each into a series of 100ml beakers, add 10ml of perchloric acid (2.7), heat to dense white fumes of perchloric acid and evaporate to about 3ml. Remove from the source of heat, cool, transfer each of them to a series of 250ml volumetric flasks with water, dilute to volume and mix. Treat according to the procedure of 5.2.4 and measure the absorbance. Plot the relationship between the amount of phosphorus pentoxide added and absorbance to prepare the calibration curve, but allow to stand for about 20min. before measuring absorbance.

(Note) Colour development of a sample solution will reach its maximum in about 10min., however on the standard phosphorus pentoxide

solution which does not include iron, the color development after 10 min. is insufficient and it is necessary to leave for 20 min.

Remarks 2 When the content of titanium oxide in the test portion is high, the following procedures should be followed:

Treat the test portion according to the procedure of Remark 1. But the volume of solution diluted should be made 250ml, and then obtain the phosphorus pentoxide content according to the procedure specified in 5.2.4 and subsequent clauses.

5.3 Method 3: Volumetric method

5.3.1 Test portion

Weigh, to the nearest 0.0001g, the test portion in accordance with Table 3.

Table 3

% P ₂ O ₅ presumed	g Mass of test portion
up to 0.2	1.0
0.2 up to 1.0	0.5
1.0 over	0.2

5.3.2 Decomposition of the test portion

Place the test portion (5.3.1) in a 80ml platinum dish, add nitric acid (2.4) according to Table 4, then 5ml of hydrofluoric acid (2.9) and 10ml of perchloric acid (2.7), and heat to decompose. Continue heating until dense white fumes of perchloric acid evolve sufficiently. Remove from the source of heat and cool. Add about 50ml of warm water, heat to dissolve the soluble salts, filter through a medium-texture filter paper containing filter paper pulp to separate the insoluble residue and wash with warm nitric acid (2+100) (2.5) until the washings show no iron reaction (note 1) and collect the filtrate and washings into a 300ml beaker to preserve as a main solution.

Table 4

g Weight of the test portion	ml Volume of nitric acid to be added
1.0	15
0.5	15
0.2	10

(Note 1) Take 1 to 2 drops of the washings on a spot plate and a drop of ammonium thiocyanate solution (2.26) to detect the presence of iron ions.

5.3.3 Treatment of residue

Transfer the insoluble residue with the filter paper into a 30ml platinum crucible, dry and ignite to ash. After cooling, add about 1g of potassium pyrosulphate (2.16), heat slowly at first, raise the temperature gradually to dull red and fuse. After cooling, transfer the crucible to a 300ml beaker, add about 30ml of warm water containing about 5 ml of hydrochloric acid (2.1), and heat until the melt dissolves. Withdraw the crucible, remove it after washing with warm water.

Add exactly 10ml of ferric chloride solution (2.21), add ammonia solution (2.10) in small portions until the solution is slightly alkaline, to precipitate ferric hydroxide and ferric phosphate, while stirring. Boil the solution for about 2 min., then remove from the source of heat. Allow the precipitate to settle, filter through a rapid filter paper and wash with warm water. Discard the filtrate and washings. Place the beaker containing the main solution from 5.3.2 under the funnel. Dissolve the precipitate by pouring onto the paper about 10ml of warm hydrochloric acid (1+1) (2.2). Wash with warm hydrochloric acid (2+100) (2.3). Heat to evaporate and continue heating until fumed and condensed perchloric acid refluxes on the wall of the beaker for about 3 min. Remove from the source of heat and after cooling, add about 50ml of warm water and swirl gently to dissolve soluble salts. Transfer to a 500ml erlenmeyer flask with small portions of water, adjust the volume to about 60ml by evaporating and cool to room temperature.

5.3.4 Precipitation and treatment of precipitate

Add ammonia solution (2.10) until a small precipitate of ferric hydroxide persists after shaking or stirring. Add nitric acid (2.4) until the precipitate just dissolves and then 5ml in excess. Add about 3g ammonium nitrate (2.11), shake to dissolve and dilute to about 100ml with water. Add 100ml of ammonium molybdate solution (2.19), heat to about 50°C by dipping in the warm water bath of 50°C,

remove the flask from the bath, stopper and shake the flask vigorously for 3 min., allow to stand for 30 to 60 min. in room temperature to settle the precipitate of ammonium phospho-molybdate. Filter the precipitate through a small close-texture filter paper (note 2), wash the flask and the precipitate with nitric acid (2+100) (2.5) until the washings show no iron reaction (note 1), then wash with nitric acid (2+10000) (2.6) the insides of the flask 3 times and the precipitate 5 times, and further wash with potassium nitrate solution (2.12) the insides of the flask 2 times and the precipitate 1 time, respectively. Discard the filtrate and washings.

(Note 2) For filtering off the precipitate of ammonium phospho-molybdate, filter paper pulp may be used instead of filter paper. Cut rapid filter paper into small pieces, place into a flask, add an appropriate quantity of water, shake vigorously to pulp completely.

5.3.5 Titration

Return the precipitate with the filter paper to the original flask, add 50ml of freshly boiled cold water and shake to disintegrate the paper. Add a measured volume of standard sodium hydroxide solution (2.23) in excess and shake the mixture to dissolve the yellow precipitate. Add a few drops of phenolphthalein solution (2.25) as indicator and titrate the excess sodium hydroxide with the standard nitric acid solution (2.24), until the red color of the solution just disappears with a final drop of the titrant.

Remarks 3. When the test portion contains 30mg or more of titanium oxide, the following procedures should be followed:

Weigh, to the nearest 0.0001g, 0.5g of the test portion, place in a 30ml platinum crucible, add 10ml of nitric acid (2.4) and then 5ml of hydrofluoric acid (2.9) slowly in drops. Heat to decompose. After decomposition, evaporate to dryness on the hot plate and cool. Add about 3g of sodium carbonate (2.14), heat slowly at first and then raise the temperature gradually to fuse completely. After cooling, transfer the crucible with the melt into a 300ml beaker add about 100ml of warm water, stir gently, detach the melt from the crucible and remove after washing with water. Boil the solution for a while to dissolve the soluble salts, filter with a medium-texture filter paper and wash thoroughly with warm sodium carbonate solution (2.15).

Discard the residue. Transfer the filtrate and washings into a 500ml beaker, add hydrochloric acid (2.1) to acidify the solution definitely and decompose carbonates. Add exactly 10ml of ferric chloride solution (2.21), and while shaking, add ammonia solution (2.10) drop by drop until ferric phosphate, ferric hydroxide, etc. are precipitated and the solution is slightly alkaline. Boil gently for about 2 min., remove from the source of heat and allow to settle the precipitates of ferric phosphate, ferric hydroxide, etc. Filter with a rapid filter paper, wash with warm water and discard the filtrate and washings. Pour about 10ml of warm hydrochloric acid (1+1)(2.2) onto the filter paper to dissolve the precipitates, wash with warm water and collect the solution and washings into a 300ml beaker. Cover with a watch glass, add 10ml of perchloric acid (2.7), heat to evaporate and continue heating until fumed and condensed perchloric acid reflux down along the wall of the beaker for about 10 min. or more. Remove from the source of heat and after cooling, add about 50ml of warm water and swirl gently to dissolve soluble salts. Transfer to a 500ml erlenmeyer flask with small portions of water, adjust the volume to about 60ml by evaporating and cool to room temperature. Treat the solution according to the procedures 5.3.4 and 5.3.5.

Remarks 4. When the test portion contains 4mg or more of vanadium pentoxide (V_2O_5), the following procedures should be followed:

Treat the test portion according to 5.3.2 and 5.3.3. Add ammonia solution (2.10) until a small precipitate of ferric hydroxide persists after shaking or stirring. Add nitric acid (2.4) until the precipitate just dissolves and then 5ml in excess. Add about 3g ammonium nitrate (2.11), shake to dissolve and dilute to about 100ml with water. Heat the solution to about 40°C, add 10ml of sulphurous acid water (2.27) shake to mix for reduction of vanadium, cool to 30°C or under, add 80ml of ammonium molybdate solution (2.19) at 30°C, shake to mix thoroughly for about 5 min., and allow to stand overnight at 20 to 30°C in order to allow the precipitate of ammonium phospho-molybdate to settle. Filter the precipitate through a small, close-texture filter paper (Note 2), wash the flask and the precipitate with nitric acid (2+100) (2.5) until the washings show no iron reaction (Note 1), then wash with nitric acid (2+10000)(2.6) the insides of the flask 3 times and the

precipitate 5 times, and further wash with potassium nitrate solution (2.12) the insides of the flask 2 times and the precipitate 1 time. Treat the precipitate according to the procedure 5.3.5.

6. EXPRESSION OF RESULTS

6.1 Calculation of phosphorus pentoxide content

The phosphorus pentoxide content, as percentage by mass, is calculated from the following formula:

(Method 1)

$$P_2O_5 \text{ \% (m/m)} = \frac{m_1 \times 10^{-1}}{m \times L} \quad (1)$$

where

m_1 is the mass, in milligrams, of phosphorus pentoxide found in the aliquot of sample solution in Table 2 (5.1.4);

L is the volume fraction of the aliquot;

m is the mass, in grams, of the test portion.

(Method 2)

$$P_2O_5 \text{ \% (m/m)} = \frac{m_1 \times 10^{-1}}{m} \quad (2)$$

where

m_1 is the mass, in milligrams, of phosphorus pentoxide obtained from the calibration curve (5.2.5);

m is the mass, in grams, of the test portion.

(Method 3)

$$P_2O_5 \text{ \% (m/m)} = \frac{(V_1 \times f_1 - V_2 \times f_2) \times 0.0309}{m} \quad (3)$$

where

V_1 is the volume, in millilitres, of the standard sodium hydroxide solution;

V_2 is the volume, in millilitres, of the standard nitric acid solution;

f_1 is the factor of the standard sodium hydroxide solution against 0.1N;

f_2 is the factor of the standard nitric acid solution against 0.1N;

m is the mass, in grams, of the test portion.

DETERMINATION OF MANGANESE OXIDE - SPECTROPHOTOMETRIC METHOD

1. PRINCIPLE

Decomposition of the test portion by treatment with hydrofluoric, nitric and perchloric acids and evaporation to fumes of perchloric acid. Dissolution of the salts in water and filtration of the solution. Adjustment of acidity by addition of sulphuric and phosphoric acids. Oxidation of manganese to permanganic acid with sodium periodate and measurement of absorbance based on permanganic acid.

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout the analysis. All reagents shall be of recognized analytical reagent quality.

2. 1 Nitric acid (d=1.42)
2. 2 Perchloric acid (60%, d=1.67)
2. 3 Hydrofluoric acid (40%, d=1.13)
2. 4 Sulphuric acid (d=1.84)
2. 5 Sulphuric acid, dilute 1+1
2. 6 Phosphoric acid (d=1.70)
2. 7 Acid Mixture Add 150ml of phosphoric acid (2.6) into 750ml of water, pour 100ml of sulphuric acid (2.4) slowly, while stirring thoroughly and cool to room temperature.
2. 8 Sodium meta-periodate solution, 50g/l
2. 9 Sodium nitrite solution, 100g/l
- 2.10 Urea solution, 100g/l
- 2.11 Hydrogen peroxide solution, dilute 1+9
- 2.12 Manganese standard solution
 - 2.12.1 Stock solution, 1.0mg MnO/ml
Transfer exactly 0.775 g of pure manganese metal (purity: 99.95% or over) to a 300ml beaker, add 10ml of nitric acid (2.1) and 20ml of sulphuric acid (1+1) (2.5) and heat it to dissolve the metal, and evaporate it until dense white fumes of sulphuric acid are evolved for 10 minutes. After cooling it to room temperature, add about 100ml of water and warm to dissolve the salt and cool to room temperature again. Transfer the solution into a 1000ml volumetric flask with small portions of water, dilute to volume with water and mix.

2.12.2 Standard solution, 0.10mg MnO/ml

Take a portion of the stock solution (2.12.1), which contains 1.0mg of manganese oxide (MnO) in 1ml, dilute it exactly with water to 10 times in volume to prepare manganese standard solution.

3. APPARATUS Ordinary laboratory equipment and spectrophotometer

4. SAMPLING AND SAMPLE PREPARATION (See Section 4 of Introduction)

5. PROCEDURE

5.1 Test portion Weigh, to the nearest 0.0002g, 1.000g of the test sample

5.2 Determination

5.2.1 Decomposition of the test portion

Place the test portion (5.1) into a 100ml platinum dish, add 20ml of nitric acid (2.1) and 10ml of hydrofluoric acid (2.3), and heat gently without boiling to decompose, sometimes swirling the dish slowly. Add 15ml of perchloric acid (2.2), continue heating until the white fumes of perchloric acid appear, and increase heating to continue evolution of dense white fumes of perchloric acid for 10 minutes. After cooling, add 50ml of water and a few drops of hydrogen peroxide solution (2.11), and cover with a watch glass. Heat the dish and boil the solution to decompose an excess of hydrogen peroxide. Filter the solution through a medium-texture filter paper into a 200ml beaker. Wash the dish and the filter paper with warm water until the washings used show no acid reaction. Evaporate the filtrate and washings in the beaker to concentrate to about 80ml. Allow to cool, transfer the solution to a 100ml volumetric flask, dilute to volume with water and mix.

5.2.2 Oxidation of manganese to permanganic acid

Transfer a 20ml or 50ml of aliquot of the solution from the volumetric flask, according to whether the presumed content of manganese oxide in the sample is 0.2% and over or below, into a 300ml beaker, add 30ml of acid mixture (2.7), and adjust the volume of the solution to about 60ml by addition of water or evaporation. Add 10ml of sodium meta-periodate solution (2.8), and cover with a watch glass. Heat and oxidize manganese ions to permanganic acid, and continue heating to keep just boiling of the solution for at least 5 minutes. Cool below room temperature in a water cooler, and

add 10ml of urea solution (2.10), then transfer into a 100ml volumetric flask. Dilute to volume with water and mix.

5.2.3 Measurement of absorbance

Transfer a portion of the solution to a cell (light path : 10mm) and measure the absorbance of the solution against water as reference using a wavelength of about 530 nm.

Next, add sodium nitrite solution (2.9) drop by drop to the solution in the volumetric flask, while shaking vigorously, until reddish purple based on permanganic acid just disappear. Without delay, transfer a portion of the faded solution to a cell (light path : 10mm) and measure the absorbance of the solution in the same manner as above mentioned.

Read out amount of manganese oxide, expressed in mass, corresponding to the difference between the absorbance obtained according to the paragraph 1st and 2nd of this clause from the calibration curve prepared previously in accordance with clause 5.2.4 shown below.

5.2.4 Preparation of calibration curve

Transfer 0 to 20ml of standard solution (2.12.2) in steps to a series of 300ml beakers, add 30ml of acid mixture (2.7) to each of them, dilute each of the solutions with water to about 60ml.

Then, treat them according to the paragraph 2nd of clause 5.2.2 and thereafter. Plot the relationship between the amount of manganese oxide and the absorbance to prepare the calibration curve.

6. EXPRESSION OF RESULTS

6.1 Calculation of manganese oxide content

The manganese oxide content, as percentage by mass, is calculated from the following formula:

$$\text{MnO \% (m/m)} = \frac{m_1 \times 10^{-1}}{m \times L}$$

where

m_1 is the mass, in milligrams, of manganese oxide found in the aliquot of sample solution,

L is the volume fraction of the aliquot;

m is the mass, in grams, of the test portion.

(Mn_3O_4) Manganese Oxide content may be obtained by multiplying 1.075 times Manganese Oxide content.

DETERMINATION OF TITANIUM OXIDE - SPECTROPHOTOMETRIC METHOD

1. PRINCIPLE

Fusion of the test portion with sodium peroxide and dissolution of the melt in hydrochloric acid and water. Reduction of ferric ions and so on with ascorbic acid and adjustment of acidity. Formation of titanium-diantipyrylmethane complex and measurement of its' absorbance using a wavelength of about 386nm.

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout the analysis. All reagents shall be of recognized analytical reagent quality.

2. 1 Hydrochloric acid (d=1.19)
2. 2 Hydrochloric acid, dilute 1+1
2. 3 Sulphuric acid, dilute 1+1
2. 4 Sulphuric acid, dilute 1+9
2. 5 Hydrogen peroxide (30%)
2. 6 Sodium peroxide
2. 7 Potassium pyrosulphate
2. 8 Diantipyrylmethane solution, 15 g/l

Place 15g of diantipyrylmethane in a 1000ml beaker containing 30ml of sulphuric acid (1+1) (2.3) and 300ml of water, stir gently until diantipyrylmethane has been dissolved, and then dilute to 1000ml with water. Filter, if necessary, and store in a dark-coloured bottle.

2. 9 Ascorbic acid solution, 10 g/l

Freshly prepare as needed.

- 2.10 Titanium dioxide standard solution

- 2.10.1 Stock solution, 200 μ g TiO₂/ml

Place exactly 0.2000g of titanium dioxide (purity : 99.5% or over) in a 30ml platinum crucible, add 5g of potassium pyrosulphate, heat gently at first to expel moisture. Then, increase gradually heating to melt down quietly the potassium pyrosulphate, keep the bottom of the crucible in dark red until clear melt is obtained and allow to cool. Transfer the crucible with the cold melt into a 300ml beaker, add 50ml of sulphuric acid (1+9)(2.4), followed by heating the

beaker to dissolve the cold melt and remove the crucible after washing with sulphuric acid (1+9)(2.4).

Allow to cool the solution, transfer it to a 1000ml volumetric flask, dilute to volume with sulphuric acid (1+9)(2.4) and mix.

2.10.2 Standard solution, 40 μ g TiO₂/ml

Take a given aliquot of the stock solution (2.10.1), dilute exactly to 5 times of its volume with sulphuric acid (1+9)(2.4) and mix.

3. APPARATUS Ordinary laboratory equipment and spectrophotometer

4. SAMPLING AND SAMPLE PREPARATION (See Section 4 of Introduction)

5. PROCEDURE

5.1 Test Portion Weigh, to the nearest 0.0002g, 0.500g of the test sample

5.2 Determination

5.2.1 Decomposition of the test portion

Place the test portion (5.1) in a 30ml sintered - alumina crucible, mix it with 5g of sodium peroxide (2.6), and cover the surface of the mixture with small amount of sodium peroxide (2.6). Heat it gradually at first to expel moisture, increase heating to dark red to melt it down quietly and allow to cool. Transfer the crucible with cold melt to a 200ml beaker, add gradually 40ml of warm water and 20ml of hydrochloric acid (2.1) to dissolve the melt and take out the crucible after washing with warm water.

Heat the solution to boiling to decompose hydrogen peroxide. If the solution is turbid, add a few drops of hydrogen peroxide (2.5) and boil for a few minutes. Allow to cool, transfer the solution to a 200ml volumetric flask, dilute to volume with water and mix.

5.2.2 Formation of titanium-diantipyrylmethane complex

Place an aliquot of the solution, which corresponds to 10 μ g to 300 μ g of titanium dioxide, into a 50ml volumetric flask, add 8ml of ascorbic acid solution (2.9) and swirl the flask thoroughly to reduce ferric completely to ferrous salt. Add 8 ml of hydrochloric acid (1+1) (2.2) and 20ml of diantipyrylmethane solution (2.8), dilute to volume with water, mix and allow to stand for 20 minutes.

5.2.3 Measurement of absorbance

Transfer a portion of the solution to a cell (light path : 10mm), and measure the absorbance of the solution against water as reference using

a wavelength of about 385nm.

Read out amount of titanium dioxide, in mass, corresponding to the obtained absorbance from calibration curve prepared previously.

5.2.4 Preparation of calibration curve

Place 1 ml to 8 ml of standard solution (2.10.2) in steps in a series of 50 ml volumetric flasks, add 8 ml of hydrochloric acid (1+1)(2.2) and 20 ml of diantipyrylmethane solution (2.8), dilute to volume with water and mix. After allowing to stand for 20min, measure the absorbances of the solutions against water as mentioned in clause 5.2.3. Then, plot the relationship between the amount of titanium dioxide and the absorbance to prepare the calibration curve.

6. ESPRESSION OF RESULTS

6.1 Calculation of titanium dioxide content

The titanium dioxide content, as percentage by mass, is calculated from the following formula:

$$\text{TiO}_2\% \text{ (m/m)} = \frac{m_1 \times 10^{-1}}{m \cdot x L}$$

where

- m_1 is the mass in milligrams, of titanium dioxide found in the aliquot of sample solution,
- L is the volume fraction of the aliquot;
- m is the mass, in grams, of the test portion.

DETERMINATION OF SODIUM OXIDE AND POTASSIUM OXIDE - FLAME
PHOTOMETRIC OR ATOMIC ABSORPTIOMETRIC METHOD

1. PRINCIPLE

1.1 Method 1 (Flame Photometric Method)

Decomposition of the test portion by treatment with hydrochloric, hydrofluoric and perchloric acids. Dissolution of the salts. Separation of most of iron by extraction with methylisobutylketone. (1)

Precipitation of iron, aluminium, titanium and others with ammonia solution and filtration off.

Precipitation of calcium with ammonium oxalate and filtration off.

Dilution of the solution to a definite volume. Aspiration of the solution to an oxygen-hydrogen flame and measurement of the intensity with a flame photometer.

1.2 Method 2 (Atomic Absorptiometric Method)

Decomposition of the test portion by treatment with hydrochloric, hydrofluoric and perchloric acids. Dissolution of the salt and dilution of the solution to a definite volume. Aspiration of the solution to an air-acetylene flame and measurement of the absorbance with an atomic absorption spectrophotometer.

2. REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout the analysis. All reagents shall be of recognized analytical reagent quality.

2.1	Hydrochloric acid (d=1.19)	Method 1 and 2
2.2	Hydrochloric acid, dilute 1+1	1
2.3	Hydrochloric acid, dilute 10+6	1
2.4	Nitric acid (d=1.42)	1
2.5	Perchloric acid (60%, d=1.54 ; or 70%, d=1.67)	1 and 2
2.6	Hydrofluoric acid (40%, d=1.13)	1 and 2
2.7	Ammonia solution (d=0.9)	1
2.8	Ammonia solution, dilute 1+1	1
2.9	Ammonium oxalate solution, saturated	1
2.10	Methylisobutylketone	1
2.11	Sodium oxide, standard solution, 200µg Na ₂ O/ml	1 and 2

(1) IF IT IS FOUND NECESSARY THE IRON MAY BE REMOVED BY THE SPECIFIED PROCEDURE)

2.11 (continued)

Dry sodium chloride (standard material for volumetric analysis) at 110°C to a constant mass and cool to room temperature in a desiccator. Weigh exactly 0.3772g of the dried and cooled sodium chloride, dissolve in water and dilute exactly to 1000ml and then preserve the solution in a polyethylene bottle.

METHOD

- | | | |
|------|---|---------|
| 2.12 | Potassium oxide, standard solution, 400µg K ₂ O/ml | 1 and 2 |
| | Dry potassium chloride at 110°C to a constant mass and cool to room temperature in a desiccator. Weigh exactly 0.6336g of the dried and cooled potassium chloride, dissolve in water, dilute exactly to 1000ml and then preserve the solution in a polyethylene bottle. | |
| 2.13 | Oxygen gas | 1 |
| 2.14 | Hydrogen gas | 1 |
| 2.15 | Compressed air | 2 |
| 2.16 | Acetylene gas | 2 |

3. APPARATUS.

Ordinary laboratory equipment and flame photometer or atomic absorption spectrophotometer.

4. SAMPLING AND SAMPLE PREPARATION (See Section 4 of Introduction)

5. PROCEDURE

5.1 Method 1 (Flame Photometric Method)

5.1.1 Test portion

Weigh, to the nearest 0.0001g, 0.200g of the test sample.

5.1.2 Decomposition of the test portion

Place the test portion (5.1.1) in a 80ml platinum dish, add 15ml of hydrochloric acid (2.1), heat and add 10ml of hydrofluoric acid (2.6) to decompose the test portion thoroughly. Add 10ml of perchloric acid (2.5), heat to evolve the dense white fumes of perchloric acid sufficiently, to evaporate hydrofluoric acid completely and to oxidize iron and others. Remove from the source of heat and cool.

5.1.3 Separation of iron and others

Dissolve the salts with hydrochloric acid (10+6) (2.3), rinse with

5.1.3 (continued)

hydrochloric acid (10+6)(2.3) to transfer into a 300ml separating funnel. Add the nearly same amount of methylisobutylketone (2.10) as the solution, shake vigorously for about 1 minute. Allow to stand for separation into two layers and separate the lower level into a 200ml quartz beaker. Furthermore add about 10ml of hydrochloric acid (10+6)(2.3) to the funnel and after a similar operation, separate the lower layer into the quartz beaker. Discard after the organic solvent is vaporized from the aqueous solution, add 5ml of nitric acid ($d=1.42$) (2.4) to decompose residual organic matter in the solution, and continue heating until perchloric acid is fumed off and completely removed. After cooling add 5ml of hydrochloric acid (1+1)(2.2), heat gently to decompose the contents, add ammonia solution (1+1)(2.8) in small portions to neutralize and add 5ml of ammonia solution (1+1)(2.8) in excess. Add 10ml of ammonium oxalate solution (2.9) and boil to form the precipitates for about 3 minutes. After cooling, rinse with water to transfer into a 100ml volumetric flask, dilute with water to volume and mix. Filter the solution through a dry medium texture filter paper in a dry 100ml quartz beaker.

5.1.4 Determination

Transfer a part of the filtrate into a cell for flame photometry, aspirate the solution to an oxygen-hydrogen flame and measure the intensity with a flame photometer using a wavelength of about 589nm for sodium and using a wavelength of about 766nm for potassium. Determine the amount of sodium oxide and potassium oxide from the intensity by using the calibration curve prepared as instructed in 5.1.5 in parallel with the test portion. Calculate the percentage of sodium oxide from formula in 6.1 (1) and potassium oxide from formula in 6.2 (1).

5.1.5 Preparation of calibration curve

Take 0 to 10ml aliquots in steps from the standard sodium oxide (2.11) and potassium oxide (2.12) solution, each into a series of 80ml platinum dishes in which 0.05g of iron without sodium and potassium is weighed respectively. Operate according to 5.1.2 to 5.1.4. Plot the relationship between the amount of sodium oxide or potassium oxide and the intensity to prepare the calibration curve.

5.2 Method 2 (Atomic Absorptiometric Method)

5.2.1 Test portion

Weigh, to the nearest 0.0001g, 0.200g of the test sample.

5.2.2 Decomposition of the test portion

Place the test portion (5.2.1) in a 80ml platinum dish, add 15ml of hydrochloric acid (2.1), heat and add 10ml of hydrofluoric acid (2.6) to decompose the test portion thoroughly. Add 10ml of perchloric acid (2.5) and heat to evaporate nearly to dry up. After cooling add 10ml of perchloric acid (2.5) and 10ml of water and heat to dissolve the salts. After cooling transfer the solution into a 100ml volumetric flask, dilute with water to the mark and mix.

5.2.3 Determination

Aspirate the solution into an air-acetylene flame and measure the absorbance with an atomic absorption spectrophotometer.

To measure the absorbance, define the analytical line according to Table 1 and then set up the lamp current value, the slit width of spectrophotometer, the pressure and the flow of acetylene gas and air. Adjust the position of the beam which transmits through the flame and measure the absorbance of the flame following the operation which is prescribed to each atomic absorption spectrophotometer. It shall be read on a recorder or a meter. When the sensitivity is insufficient, a scale magnifier would be provided to photometer shall be adjusted to the required sensitivity.

If the sensitivity is higher than required, it shall be decreased by adjusting the beam angle and others.

Table 1. Analytical line

Component	Analytical line (nm)
Sodium oxide	589.0
Potassium oxide	766.5

Determine the amount of sodium oxide and potassium oxide from the absorbance by using the calibration curve prepared as instructed in 5.2.4 in parallel with the test portion. Calculate the percentage of sodium oxide from formula in 6.1 (1) and potassium oxide from formula in 6.2 (1).

5.2.4 Preparation of calibration curve

Take 0 to 10ml aliquots in steps from the standard sodium oxide (2.11) and potassium oxide (2.12) solutions, each into a series of 80ml platinum dishes in which 0.05g of iron without sodium and potassium is placed respectively. Add 10ml of perchloric acid (2.5), heat to decompose, after cooling transfer into a 100ml volumetric flask, dilute with water to volume and mix.

Aspirate the solution to an air-acetylene flame and measure the absorbance of each component with an atomic absorption spectrophotometer.

Plot the relationship between the amount of sodium oxide or potassium oxide and absorbance to prepare the calibration curve.

6. EXPRESSION OF RESULTS

- 6.1 Calculation of sodium oxide content, as percentage by mass, is calculated from the following formula:

$$\text{Na}_2\text{O}\% \text{ (m/m)} = \frac{m_1 \times 10^{-1}}{m} \quad (1)$$

where

m_1 is the mass, in milligrams, of sodium oxide found in the test portion solution;

m is the mass, in grams, of the test portion.

- 6.2 Calculation of potassium oxide content, as percentage by mass, is calculated from the following formula:

$$\text{K}_2\text{O}\% \text{ (m/m)} = \frac{m_1 \times 10^{-1}}{m} \quad (2)$$

where

m_1 is the mass, in milligrams, of potassium oxide found in the test portion solution;

m is the mass, in grams, of the test portion.

PRECISION OF DETERMINATION

Constituents of Ash in Coal and Coke		Maximum acceptable differences between results obtained	
		in the same laboratory	in different laboratories
		% absolute	% absolute
Silicon dioxide		0.85	1.15
Ferric oxide		0.35	0.95
Aluminum oxide		0.50	1.10
Calcium oxide		0.25	0.60
Magnesium oxide		0.15	0.15
Sulphur trioxide		up to 2.50 %	0.10
		2.51 - 4.00	0.20
		4.01 over	0.25
Phosphorus pentoxide	Molybdenum Blue Spectro-photometry	up to 0.20 %	0.020
		0.21 - 0.50	0.050
		0.51 - 1.00	0.070
		1.01 - 1.50	0.070
		1.51 over	0.130
	Vanadomolybdate Yellow Spectro-photometry	up to 0.20	0.020
		0.21 - 0.50	0.050
		0.51 - 1.00	0.050
		1.01 - 1.50	0.090
		1.50 over	0.110
	Volumetric Method	up to 0.20	0.020
		0.21 - 0.50	0.040
		0.51 - 1.00	0.110
		1.01 - 1.50	0.110
		1.51 over	0.110

In the same laboratory

The results of duplicate determinations carried out at different times in the same laboratory, by the same operator, with the same apparatus, on representative portions taken from the same analysis sample, should not differ by more than the above value.

In different laboratories

The means of the results of duplicate determinations carried out separately in two different laboratories, on representative portions taken from the same analysis sample, should not differ by more than the above value.