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A new method of total sulfur estimation in coal/coke, lime/dolime by UV-VIS spectrophotometer

D.G. Annapurna

Essar Steel India Ltd., Hazira, Surat, Gujarat State, (INDIA)

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ABSTRACT

Sulfur estimation in COAL/COKE, LIME/DOLIME is very important in Iron & Steel making process. Conventionally it is estimated by Gravimetric and Combustion methods. A new & rapid semi instrumental method is developed and also cost effective compared to other expensive analytical instrumental techniques. This method of Sulfur estimation is also applicable to Limestone, Dolomite and Ladle Furnace (LF) Slag also.

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KEYWORDS

Total sulfur in coal, coke;
Sulfur in limestone, dolomite;
Sulfur in calcined lime, dolime;
Sulfur in ladle furnace slag;
A new method of sulfur in coal,
coke, lime, dolime and
limestone, dolomite;
Total sulfur in coal & coke by
U.V – VIS spectrophotometer.

INTRODUCTION

The most popular method of total Sulfur in Coal/ Coke is estimated by gravimetric method with ESCHKA mixture^[2]. In literature, few more methods described Bomb washing^[3] and High temperature Combustion method^[4]. Determination of forms of Sulfur in Coal along with other elements by X ray Fluorescence^[6] In raw and calcined forms of Limestone and dolomite Sulfur estimation by LECO Sulfur determinator^[5] Forms of Sulfur in Coals and related materials by Eschka Digestion and Inductively coupled Plasma atomic emission spectrometry^[7].

In ESCHKA method^[2]

Sample 1 gm and 4 gm ESCHKA mixture (2 parts of calcined dolime MgO and 1 part of Sodium carbonate) heating in muffle furnace extracted in water and estimated as BaSO₄ with BaCl₂ solution by gravimetric method.

Bomb washing method^[3]

After using an Oxygen bomb Calorimeter to determine Calorific value is washed with water to dissolve the Sulfate which remains in the solid residue. The wash water is then titrated to neutralize the acids that were formed by combustion of Sulfur and Chlorine compounds and filter to remove the extraneous solids. BaCl₂ is then added to the filter water to precipitate the Sulfur as BaSO₄.

High temperature combustion methods^[4]

In each of these methods, the Coal is first burned in a tube furnace at 1350 degree Celsius in a stream of Oxygen to convert the Sulfur completely in gaseous oxides. The quantity of these oxides in the gaseous combustion products is determined by Acid, base titration or Iodometric method or Infrared absorption by Sulfur determinator.

The conventional gravimetric method is accurate but has limitation of more time consuming and also very

low sulfur < 0.1% is also not possible. This rapid new method is semi instrument technique and very accurate compared with Gravimetric method even < 0.1 % Sulfur estimation is also possible. In this method the instrument UV-VIS is more cost effective when compared to other analytical instruments. XRF is very expensive and sample required is 20-30 gm where as this new method required only 1.0 gm. This method is giving good results for total sulfur in Coal/Coke, Lime/Dolime, Limestone, Dolomite and LF Slag samples.

Brief procedure

This method is semi instrument technique. Till sample dissolution and oxidation with Bromine is same like normal gravimetric method. Here reagent Barium chloride addition is at room temperature and estimation by UV-VIS spectrometer in 30 minutes time where as Gravimetric method over night settling of precipitate and followed by filtration and igniting from ambient temperature to high temperature.

EXPERIMENTAL PROCEDURE

Reagents required: All are pure analytical grade reagents.

1. 5% Bromine in Methanol solvent.
2. Conc.HCl
3. Conc. HNO₃
4. Barium chloride crystals BaCl₂
5. Glycerol
6. Ethanol
7. Sodium chloride
8. Magnesium oxide powder MgO.
9. Ammonia solution.
10. Sodium sulfate anhydrous.

Preparation of conditioning agent^[1]

Dissolve 75 gm Sodium chloride in 200ml distilled water. Add 30ml Conc.HCl with stirring. Add 50ml Glycerol and 100ml Ethanol with constant stirring. Make up this mixture with water up to 500ml volumetric flask. Preserve this conditioning agent in refrigerator below 20 degree Celsius.

Total sulfur in coal and coke

Take 1.0 gm sample in a 50 ml porcelain /platinum crucible mix with pure Magnesium oxide (MgO) pow-

der 3.0 gm and cover with 1.0gmMgO and keep crucible in muffle furnace. Carry out the same procedure only with MgO 4.0gm without Coal sample. Raise the temperature till 700 degree Celsius. Incinerate for one hour and remove from furnace and mix with spatula again keep in furnace and raise the temperature till 850 degree Celsius. Keep one more hour in furnace to ensure all carbon particles burnt. Remove from furnace cool and extract in 500ml beaker with water. To this add 5ml Bromine solution and allow reacting on hot plate. This reaction oxidizes completely sulfur compounds to sulfate form. Add 5ml Concentrate HNO₃ followed by 5ml Concentrate HCl. Allow this mixture to react for 10 minutes on hot plate till Bromine evaporate. Cool the mixture and dilute with water and add concentrate Ammonia till Litmus paper blue. Acidify with 1:1 HCl till litmus paper to red. Add 0.5ml more. Filter off un dissolved solids with filter paper. Collect filtrate in 250ml volumetric flask and make up to the mark with distilled water. Take 50ml aliquot in 100ml volumetric flask add 5ml conditioning agent 0.5gm BaCl₂ crystals. Make up with distilled water up to the mark and do the blank without BaCl₂. Note the absorbance at 420 nm between 20 to 30 minutes Sulfur in sample absorbance minus pure MgO absorbance. Keep one primary standard (reference) sample along with sample.

Preparation of plot

Prepare 100 PPM solution of anhydrous Sodium sulfate by dissolving 0.1479gm sample in 1000ml distilled water. Take 10,20,40,60 and 80ml aliquot (corresponds to 0.0333, 0.0666, 0.1332, 0.1998 and 0.2664 Sulfur) to this add 5ml conditioning agent and 0.5 gm BaCl₂ crystals. Note the absorbance at 420nm after 2 minutes by using water as blank. Plot the graph with Sulfur concentration and corresponding absorbance.

Calculation for Sulfur in Coal/Coke:(Absorbance for sample- Absorbance for MgO)/ aliquot weight.

Note

Concentration of aliquot is adjusted as per Sulfur in sample. High sulfur >2% weight of aliquot to be taken is 0.05gm.

Sulfur in limestone/dolomite

Weigh 2.0gm sample in beaker and add 1.0gm pure

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MgO 1.0gm MgO also to be taken in another beaker as blank. Add 50ml distilled water, 5ml bromine solution. Allow to react the mixture for 5 minutes on hot plate, add 5ml HNO₃ and 5ml HCl. continue the mixture on hot plate till complete dissolution. Cool the beaker and dilute the mixture with water. Add ammonia solution till litmus blue. Acidify with 1:1HCl till litmus red. Add 0.5ml excess. Filter off un dissolved particles if any. Collect filtrate in 100ml flask. Make up with water till 100ml. Take 50ml aliquot in two 100ml flasks one sample and the blank. Add conditioning agent in both the blank and sample flask; add 0.5gm Barium chloride crystals only in sample flask. Do the same procedure for pure MgO also. Treat this is also sample. Note the absorbance at 420 nm between 20-30 minutes.

Calculation

Sulfur in Limestone/Dolomite

$$\frac{\text{Absorbance of sample} - \text{Absorbance of MgO}}{\text{Aliquot weight}}$$

Sulfur in calcined lime and dolime

Weigh 1.0gm sample with 1.0 gm MgO in one beaker and only MgO 1.0gm in another beaker and do the same as above procedure for Limestone/Dolomite.

Calculation

Sulfur in Lime/Dolome

$$\frac{\text{Absorbance of sample} - \text{Absorbance of MgO}}{\text{Aliquot weight}}$$

Sulfur in LF slag

Weigh 1.0gm sample and do the same as above procedure for Limestone/Dolomite.

Calculation

Sulfur in LF Slag

$$\frac{\text{Absorbance of sample} - \text{Absorbance of MgO}}{\text{Aliquot weight}}$$

Sample	Gravimetric method	New method
Calcined Lime 1	0.32	0.31- 0.34
Calcined Lime 2	0.28	0.27-0.29
Calcined Lime 3	0.88	0.86-0.89
Calcined Lime 4	0.27	0.27
Calcined Lime 5	0.13	0.11-0.13
CalcinedDolime 1	0.1	0.08-0.10
CalcinedDolime 2	0.11	0.10-0.11
CalcinedDolime 3	0.76	0.75-0.77
CalcinedDolime 4	0.55	0.53-0.56

Primary standard	certified	obtained
Lime stone/BCS-CRM 393	0.007	0.0060-0.009
Dolomite/NCSDCI14019a	0.018	0.015-0.019
Slag /SM-4	0.11	0.09 -0.11

COALAND COKE SAMPLES

Sample	Gravimetric method	New method
Anthracite Coal	0.43	0.42-0.44
Coal	0.52	0.51 – 0.53
Coke	0.63	0.62 -0.64
Coke	0.61	0.61- 0.62
Coke breeze	0.59	0.58- 0.61
Calcined petroleum coke	0.99	0.98-1.02
Calcined petroleum coke	2.09	2.08- 2.11

LF SLAG	Gravimetric method	New method
Source A	0.53	0.51-0.54
Source A	0.24	0.22-0.25
Source A	0.44	0.43-0.45
Source A	0.78	0.75-0.77
Source A	0.42	0.40 -0.44
Source B	0.36	0.36-0.39
Source B	0.18	0.16-0.19
Source B	0.26	0.22-0.28
Source B	0.11	0.09-0.12
Source B	0.31	0.30-0.32

All Coal and Coke samples analyzed with reference primary STD

	Sulfur standard	Sulfur obtained
Coal/LECO Ref Std	0.97	0.96-1.00
Coal/LECO Ref Std	0.66	0.65-0.68
Coke AR 2772	0.76	0.76-0.80
CPC/ AR 744	2.66	2.60- 2.73

COAL SAMPLES

Coal source A	0.63
Coal source B	0.44
Coal source C	0.85
Coal source D	0.63
Coal source E	0.42
Coal source F	0.48
Coal source G	0.87

COKE SAMPLES

Coke source 1	0.41
Coke source 2	0.65
Coke source 3	0.59
Coke source 4	0.69
Coke source 5	0.71
Coke source 6	0.62

CONCLUSIONS

This new method is very fast and more accurate compared to gravimetric method. Time of analysis for single sample is 1 hour and for Coal/Coke is 8hr instead of gravimetric 16 hrs and 24 hrs respectively. The main time consuming step in Gravimetric method is BaSO₄ precipitation and filtration followed by ignition from ambient to high temperature. In this new developed method BaSO₄ estimated by UV - VIS instrument. One more advantage is UV-VIS instrument is low cost and any lab can effort compared to expensive instruments like ICP or XRF. Sample quantity required in case of Limestone, Dolomite is 1gm where as in XRF 20-30gm. Sulfur values range from 0.01 to 2.0% obtained very accurately. If sulfur value is more in sample, low aliquot weight is to be taken. All primary standard Coal/Coke samples obtained with accuracy, +/- 0.01 - 0.04 variation. In all above samples of Coal and Coke are tested against primary standard.

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