

**A STANDARD ADDITIONS METHOD FOR THE MEASUREMENT OF SULFATE
PRODUCED DURING THE DETERMINATION OF SULFUR FORMS IN COAL
USING PERCHLORIC ACID**

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INTRODUCTION

A reaction scheme has been developed and tested at the Ames National Laboratory for the direct determination of the sulfur forms in coal (1). The variable oxidizing power of perchloric acid was used to selectively dissolve the various sulfur-containing components and convert them to sulfate for turbidimetric measurement. Sulfate was extracted with a perchloric acid solution boiling at 120°C. Pyrite was then determined by reacting the residue from the previous step with a perchloric acid solution boiling at 155°C. From the second residue, organic sulfur was oxidized with a 9:1 solution of concentrated perchloric acid and concentrated phosphoric acid boiling at 205°C. The phosphoric acid was used to prevent foaming of the mixture during the heating process. In all three steps, sulfur-containing gases were trapped in 15 percent hydrogen peroxide. Sulfate was then determined in the trap and in the aqueous solution by precipitation as barium sulfate followed by turbidimetric measurement. For some coals, the total sulfur recovered was slightly less than the total sulfur in the coal as determined by the ASTM procedure. Generally, the recoveries were on the order of 0.2 to 0.4 percent low out of a total sulfur content of about five percent. Possible explanations included: 1) the incomplete absorption of sulfur-containing gases by the neutral peroxide trap, 2) the dissolution of some organosulfur compounds at 155°C without being converted to the measurable sulfate form, and 3) the incomplete precipitation of barium sulfate during turbidimetric analysis due to the high acidity of the solutions.

It is possible that acidic gases, such as hydrogen sulfide or sulfur dioxide, might not be completely trapped by neutral hydrogen peroxide. Therefore, in order to test the first hypothesis, the oxidations were run using a peroxide trap made basic with ammonium hydroxide. Sulfate was then determined as before. The filtrate solution from the 155°C reaction was yellow-brown due to the dissolution of some organic material. Upon standing, a brown precipitate formed in these solutions. Dilution which occurred during filtration caused the perchloric acid to become more aqueous resulting in the precipitation of some organic material. To test the second hypothesis, the

precipitate was filtered and oxidized with perchloric acid boiling at 203°C in the Bethge apparatus with a peroxide trap. Sulfate was then measured by the turbidimetric method as above. Also, 5 mL aliquots from the 155°C filtrate were oxidized with hydrogen peroxide and again sulfate was measured turbidimetrically. To test the third hypothesis, sulfate was measured using a standard additions technique in which aliquots of a standard sodium sulfate solution were added to the test samples and sulfate was measured turbidimetrically.

EXPERIMENTAL

The coal used in this study was obtained from the Kentucky #9 seam and was ground to minus 100 mesh. A modified Bethge apparatus was used to maintain a constant boiling mixture. The Bethge apparatus has been described previously by McGowan and Markuszewski (2). The system was fitted with a gas trap, containing 15 percent hydrogen peroxide to collect sulfur-containing gases and convert them to sulfate, and with a nitrogen purge line.

A Note on Safety. The use of perchloric acid alone as an oxidizing agent for organic materials always poses a hazard. In this study, all reactions were performed in a hood and behind an explosion shield. In order to minimize the possibility of a fire or explosion, the authors urge that extreme caution be used anytime perchloric acid alone is used as an oxidizing agent. The authors recommend that reactions be performed at low temperatures first and that small amounts of organic material be employed.

Reaction Procedure. For each oxidation experiment, perchloric acid was added to the Bethge apparatus and the boiling point was adjusted to the desired temperature. By varying the initial amount of perchloric acid added, a final volume of approximately 50 mL was obtained. The boiling point could be increased by removing reflux condensate from the condenser. The boiling point could be decreased by adding water through the top of the apparatus. The 15 percent hydrogen peroxide trap was attached to the apparatus for each oxidation. Nitrogen was used as a purge gas. A weighed 1-g sample of coal was added to the flask. The sample was reacted with perchloric acid boiling at 120°C (actual reaction temperatures were noted in each step) for 45 min. The reaction mixture was filtered. The residue from the previous step was reacted with a perchloric acid solution boiling at 155°C for 1.5 hrs. The reaction mixture was filtered. The residue from above was reacted for 1 hr. with a 9:1 solution of concentrated perchloric acid and concentrated phosphoric acid boiling at 205°C. The phosphoric acid was added to inhibit foaming during the reaction. The reaction mixture was filtered and any residue was discarded. The filtrate from each of the three reactions was diluted to 250 mL. Each of the peroxide trap solutions was boiled to insure oxidation of the sulfur to sulfate and to reduce the volume to about 25 mL. The trap samples were then diluted to 50 mL. In each fraction, sulfate was determined by precipitation with barium and the turbidity of the resultant

barium sulfate suspension was measured spectrophotometrically using a calibration curve. For the solutions that were colored, the absorbance of the sample without the added barium was measured and subtracted from the absorbance of the test solutions. Sulfate in the coal sample was determined as sulfate in the filtrate, and sulfide in the coal was determined from the sulfate accumulated in the peroxide trap after the 120°C reaction. Pyritic sulfur was determined from the sulfate in the filtrate and peroxide trap after the reaction at 155°C. Organic sulfur was determined in the filtrate and in the peroxide trap after the reaction at 205°C. Total sulfur in the coal was determined by reacting 0.1-g samples of the coal with the perchloric acid and phosphoric acid mixture.

To test the first hypothesis, the above reaction scheme was performed using a 15 percent hydrogen peroxide trap which was made basic by the addition of 15 mL of concentrated ammonium hydroxide. To test the second hypothesis, the precipitate from the 155°C reaction was filtered and reacted with boiling concentrated perchloric acid. Sulfate was measured in the trap and in the reaction solution. Also, sulfate was measured using a 5.0 mL aliquot of the supernatant solution from the 155°C reaction. Another 5.0 mL aliquot from the same solution was then oxidized with 30 percent hydrogen peroxide, followed by the measurement of sulfate. To test the third hypothesis, a standard additions method was applied to the turbidimetric method used to measure sulfate. Amounts of 0.0, 0.1, 0.2 and 0.3 mL of a standard sodium sulfate solution which contained 0.62 g of sulfur/L were added to the appropriate volume of each solution, and the turbidity of each solution was measured as before.

RESULTS

The sulfate results from the oxidations run with the neutral trap on the Kentucky #9 coal appear in Table 1. The total sulfur, determined using the ASTM procedure, for this sample also appears in Table 1. The results with the basic trap, using a different split of this same sample of coal, appear in Table 2. The total sulfur for this sample was determined using the perchloric acid method (1). The sulfur recoveries, although still slightly low when using the basic hydrogen peroxide trap, were comparable to previous results, indicating that the neutral trap does an adequate job of absorbing the sulfur-containing gases. The results for the oxidations of the precipitate formed in the solutions from the 155°C reactions are presented in Table 3. No additional sulfur was recovered from these precipitates. The results for sulfur found in the solutions from the 155°C reactions, before and after oxidation with hydrogen peroxide, are presented in Table 4. Some additional sulfur (<0.1%) was recovered, although not enough to account for the low sulfur recoveries. Based on previous work (1-3), it was suspected that some sulfur might be lost in this step but that it would be small. It was interesting that additional sulfur was recovered from the aqueous solution and not from the precipitate formed from that solution. This would indicate that the dissolved

organosulfur compounds remained soluble while other organic compounds precipitated under the more aqueous conditions. Possibly the organosulfur compounds formed under these mildly oxidizing conditions were sulfonic acids and thus more soluble.

The sulfur recovery results using the standard additions technique on the Kentucky #9 coal appear in Table 5. The sulfur recoveries for this experiment were very close to the total sulfur in the coal. When these results were compared to the corresponding results for the same coal in Table 2, a slight increase was observed for each sulfur form (except sulfide). This indicated that there could be a systematic error in the turbidimetric technique used to measure sulfate. This error apparently involved the inability to match the conditions of the calibration curve to the matrix effects of the samples.

CONCLUSIONS

The neutral hydrogen peroxide trap is sufficient to trap sulfur-containing gases. Only a small amount of sulfur is converted to a soluble organosulfur compound at 155°C and is not measured as sulfate by the turbidimetric technique. Sulfur recoveries using the standard additions method are comparable to the total sulfur measured in the coal.

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TABLES

TABLE 1. Sulfur forms (in percent) determined for the Kentucky #9 coal using the perchloric acid procedure and a neutral trap

<u>SULFUR FORM</u>	1	2	3	4	AVG.
SULFATE	0.30	0.31	0.30	0.34	0.31
SULFIDE	0.02	0.03	0.01	0.00	0.02
PYRITE	2.81	2.70	2.80	2.83	2.79
ORGANIC	<u>1.36</u>	<u>1.41</u>	<u>1.24</u>	<u>1.47</u>	<u>1.37</u>
RECOVERY	4.49	4.45	4.35	4.64	4.48
TOTAL SULFUR (by the ASTM procedure)					4.86

TABLE 2. Sulfur forms (in percent) determined for the Kentucky #9 coal using the perchloric acid procedure and an ammoniacal trap

<u>SULFUR FORM</u>	1	2	3	4	AVG.
SULFATE	0.38	0.40	0.37	0.42	0.39
SULFIDE	0.14	0.01	0.03	-	0.06
PYRITE	2.69	2.91	2.91	2.46	2.74
ORGANIC	<u>1.32</u>	<u>1.31</u>	<u>1.56</u>	<u>1.48</u>	<u>1.42</u>
RECOVERY	4.53	4.63	4.87	4.36	4.60
TOTAL SULFUR (by the perchloric/phosphoric acid procedure)					4.96

Table 3. Sulfur (in percent) in precipitates from the solutions after the 155°C reactions

<u>FRACTION FROM</u>	1	2	3
FILTRATE	0.00	0.00	0.00
TRAP	0.00	0.00	0.00

TABLE 4. Sulfur (in percent) recovered from solutions after the 155°C reactions

<u>SOLUTION</u>	1	2	3
BEFORE H ₂ O ₂ OXIDATION	0.37	0.62	0.53
AFTER H ₂ O ₂ OXIDATION	<u>0.46</u>	<u>0.67</u>	<u>0.61</u>
ADDITIONAL SULFUR	0.09	0.05	0.08

TABLE 5. Sulfur forms (in percent) determined for the Kentucky #9 coal when sulfate was measured using standard additions

<u>SULFUR FORM</u>	1	2	AVG.
SULFATE	0.69	0.39	0.54
SULFIDE	0.01	0.01	0.01
PYRITE	2.81	2.91	2.86
ORGANIC	<u>1.52</u>	<u>1.56</u>	<u>1.54</u>
RECOVERY	5.03	4.87	4.95
TOTAL SULFUR (by the perchloric/phosphoric acid procedure)	4.96		