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REDUCTION METHODS IN
THE DETERMINATION OF
FORMS OF SULFUR IN COAL

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ABSTRACT

Results obtained by analyzing nine coals for varieties of sulfur by two methods—a reduction method in which lithium aluminum hydride (LAH) was used and the ASTM standard oxidation method—were compared to evaluate the effectiveness of the methods for quantitative removal and subsequent determination of pyrite. Total iron and total sulfur were determined by X-ray fluorescence analysis of the whole coal. Each coal was ground to three different sizes (-60 mesh, -200 mesh, and -400 mesh) for a study of the effects of particle size.

The two methods produce comparable and reliable results in the determination of sulfur varieties in coal. Pyritic sulfur is quantitatively removed by both procedures and, therefore, does not inflate calculated and/or determined organic sulfur values. Particle size was found to be a determining factor in the quantitative reduction and subsequent determination of pyrite by the LAH method.

INTRODUCTION

Recent concern for the environment has increased interest in the reliability of methods routinely used to determine varieties of sulfur in coal. The most commonly used procedure (ASTM D-271 and D-2492) is summarized in the Appendix.

Some doubt exists as to whether in the ASTM method the removal of finely-dispersed pyrite by extraction with nitric acid is actually quantitative (Rees, 1966). Incomplete removal of pyrite would result not only in low

values for pyritic sulfur but also in erroneously high values for organic sulfur. The effect the nitric acid used in ASTM D-2492 has upon the organic constituents of coal (Rees, 1966) also is open to debate. If any organic material is oxidized by the nitric acid treatment, some of the organic sulfur might go into solution. The determination of organic sulfur by Eschka fusion (ASTM D-271) on the residue remaining from the pyritic sulfur extraction would then be erroneously low.

In the ASTM procedures, a theoretical organic sulfur value is calculated from the formula, % organic sulfur = % total sulfur - (% sulfate sulfur + % pyritic sulfur). Calculated values of organic sulfur depend on quantitative pyrite removal, whereas Eschka-determined values for organic sulfur depend not only on quantitative pyrite removal but also on the nonreactivity of nitric acid with the organic constituents. Therefore, agreement of the Eschka-determined value and the calculated value does not prove that either is correct.

For this project, a reduction method for determining pyritic sulfur in coal was adapted from a method used on shales by Smith, Young, and Lawlor (1964). Results from this method were compared with those from the ASTM oxidative method to determine whether or not the extraction of the pyrite in the ASTM method is complete, whether or not the organic matter is significantly affected by the nitric acid, and whether or not reliable values for organic sulfur can be obtained either by computation or by the Eschka determination.

In a study of the varieties of sulfur present in oil shale, Smith, Young, and Lawlor (1964) employed a reduction method using lithium aluminum hydride (LAH), an extremely effective reducing agent that Gaylord (1956) had indicated would not attack the organic constituents in shale. Lawlor, Fester, and Robinson (1963) later reported that quantitative reduction of pyrite in shale was possible. Although Belcher and Spooner (1941) indicated that reduction methods in general were unsatisfactory for coal, Radmacher and Mohrhauer (1953) showed that good results could be obtained with stronger reducing conditions and coal of a smaller particle size. Therefore, the influence of coal particle size on the analyzed values was studied in this project.

Because agreement of values obtained by the two different methods would not in itself prove that all of the pyrite had been removed from the coal, additional evidence was needed. X-ray fluorescence analysis, as described by Ruch, Gluskoter, and Shimp (1973), was used to determine the total amount of iron in the coal. Total iron content was also determined as the sum of the iron removed by hydrochloric acid digestion of the coal during removal of sulfate sulfur and of the iron removed by nitric acid digestion in the extraction of pyritic sulfur. Agreement of the two total iron values would indicate that the nitric acid digestion of pyrite (FeS_2) in the ASTM method was complete. Total sulfur was also determined by X-ray fluorescence analysis. When these results are compared with the total sulfur values determined by the ASTM procedure and considered in conjunction with data obtained from the varieties-of-sulfur determinations obtained by the two methods, any errors in the methods used should be evident.

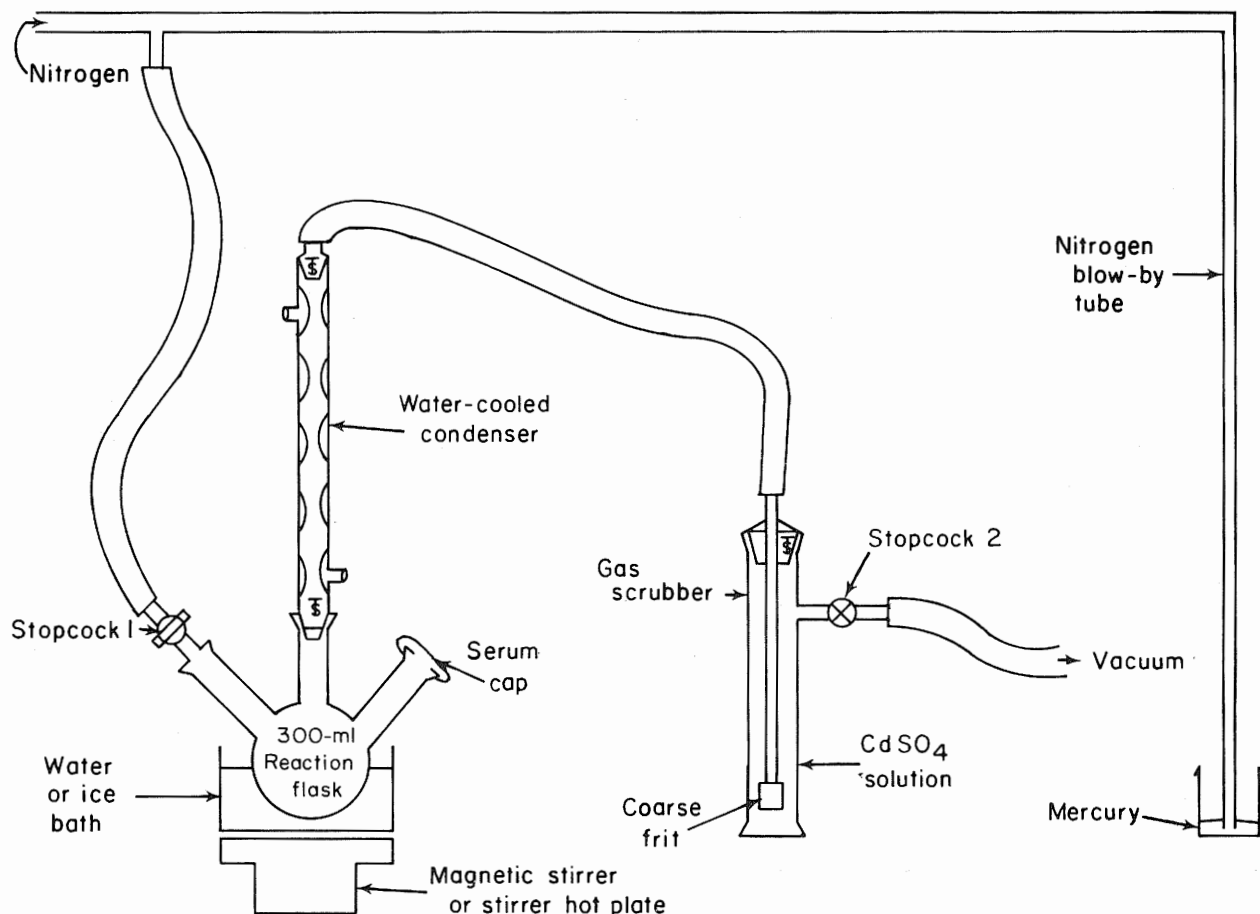


Fig. 1 - Apparatus used for reduction process.

PREPARATION OF LABORATORY SAMPLES

Each of the nine coal samples studied was ground to pass a -60-mesh screen. One split of each -60-mesh sample was hand-ground to pass a -200-mesh screen, and a second split was placed in a tungsten carbide capsule along with a tungsten carbide pellet and was shaken at high speed for 1 hour in a motorized Spex mixer mill. The resultant fraction passed a -400-mesh screen.

EXPERIMENTAL

ASTM Methods (Appendix 1)

Total sulfur is first determined for each coal fraction by the Eschka fusion method, D-271. Forms of sulfur are next determined according to the procedures in D-2492. Acid-extractable iron content is computed as the sum of pyritic iron and iron soluble in hydrochloric acid. The latter iron is titrated in the same manner as pyritic iron. Total iron and total sulfur contents are also determined by X-ray fluorescence analysis.

Pyritic Sulfur by LAH Reduction

A sample of coal is chosen that will yield between 10 and 20 mg of pyritic sulfur. Sulfate sulfur and iron soluble in hydrochloric acid are removed from the coal sample as indicated in ASTM D-2492. The residue of the coal in the filter paper is dried overnight at approximately 80° C. A funnel with stem is inserted into the center neck of a 300-ml, 3-necked reaction flask (fig. 1), and the filter paper containing the sample is placed in the funnel. A spatula is used to tear the paper into small pieces, which are allowed to fall into the flask along with the coal. A teflon-coated magnetic stirring bar is placed in the flask.

Approximately 1 gram of lithium aluminum hydride (LAH) powder is very carefully added to the flask through the funnel. Precautions are taken to ensure that the LAH does not come into contact with moisture. Fifty milliliters of tetrahydrofuran, which has been dried over 4A molecular sieves, is then poured through the funnel, washing any adhering particles of sample or LAH into the flask.

The flask is topped with a water-cooled condenser, and the contents are stirred and refluxed for 30 minutes (a bath temperature of 80° C maintains proper refluxing). Stopcock 1 (fig. 1) is closed during the refluxing and a serum cap seals the third neck of the flask. An ice bath is then placed under the reaction flask and magnetic stirring is resumed. A 250-ml portion of the cadmium sulfate (CdSO_4) solution (36 grams per liter of water) is poured into the gas scrubber. The scrubber system is then connected to the top of the condenser with rubber tubing, as shown in figure 1. Nitrogen flow is started at a rate slow enough to produce only an occasional gas bubble on the surface of the mercury sealing the end of the blow-by tube.

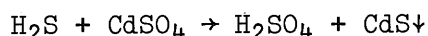
Stopcock 1 (fig. 1) is opened fully. Stopcock 2 is opened gradually until a vigorous bubbling of nitrogen through the cadmium sulfate solution is established. The tank pressure is regulated to maintain atmospheric pressure in the system, as is evidenced by the level of mercury in the blow-by tube.

With the contents of the flask still being stirred and cooled in the ice bath, a 50-ml portion of water is added very slowly through the serum cap from a syringe. After the first 5 ml have been added drop by drop from a small needle, the reaction in the flask subsides sufficiently to allow the rest of the water to be introduced more conveniently from a larger needle. A 50-ml volume of 30 percent hydrochloric acid is then added through the serum cap.

The ice bath is replaced by the hot water bath on the stirrer hot plate, and the contents of the flask are again refluxed. The hydrogen sulfide liberated at this point begins to react with the cadmium sulfate in the gas scrubber, and the solution takes on the yellow color of cadmium sulfide (CdS).

After 30 minutes of refluxing, no traces of hydrogen sulfide should be detected within the system, except in cases where a proper sweep of gases cannot be maintained through the gas scrubber. Cadmium sulfide tends to accumulate within the pores of the frit, hindering the gas flow, and must be removed between experiments.

The gas scrubber is removed, and the cadmium sulfate solution containing the suspended cadmium sulfide is transferred to a 400-ml beaker. The sulfuric acid that forms during the reaction



is titrated to a pH of 5.25 by adding 0.1N sodium hydroxide. Near the equivalence point, a minute is allowed for equilibration of the sample between dropwise additions of the sodium hydroxide solution. Pyritic sulfur is computed by the equation:

$$\text{SP} = \frac{1.6033 \times V \times N}{W}$$

where

Sp = wt % pyritic sulfur
V = volume of NaOH in milliliters
N = normality of NaOH
W = sample wt in grams.

Direct Determination of Organic Sulfur

Following the pyritic sulfur determination, the contents of the reaction flask are filtered and washed with several portions of hot water. The residue and filter paper are dried at room temperature for several days. The filter cake containing the bulk of the residue can then be lifted from the filter paper. The cake is broken up as well as possible in a 50-ml porcelain crucible and mixed with about 3 grams of Eschka's Mixture. The filter paper is cut up and placed in the same crucible and the total contents are well covered with another 3 to 6 grams of Eschka's Mixture. The remainder of the procedure is identical to that for total sulfur (ASTM D-271 from paragraph 20.2). The direct determination of organic sulfur on the residue from the pyritic sulfur determination by the ASTM method is carried out in the same manner.

RESULTS AND DISCUSSION

Results of the analyses appear in table 1. Theoretical values for organic sulfur were calculated for both the LAH and ASTM methods, using the proper pyritic sulfur values for each method, and the ASTM total sulfur and sulfate sulfur values. Limits of repeatability for these methods, as given in ASTM, part 19, 1972, are included in table 1. The repeatability for the LAH method was determined from replicate samples in our laboratories. The standard deviations for the X-ray method were taken from tables presented in Ruch, Gluskoter, and Shimp (1973).

Table 1 shows that coal particle size had no significant effect on the amount of total sulfur determined by Eschka fusion. Furthermore, the total sulfur values obtained by X-ray fluorescence analysis agree well with those obtained by the ASTM method. Table 1 also shows that coal particle size had no effect on the sulfate sulfur results.

In the ASTM procedure for the determination of varieties of sulfur, the sulfate sulfur is first removed from the coal by hydrochloric acid extraction,

TABLE 1—CONCENTRATION OF IRON AND VARIETIES OF SULFUR IN NINE ILLINOIS COALS

| Sample and size | Total iron (%) | | Total | | Sulfur (%) | | | | | | | |
|------------------------|----------------|------------------------------------|---------------|------------------------------------|----------------------------------|---------------|--------------|---------------|-----------------------|---------------|-----------------------|--|
| | ASTM ±0.05 | X-ray fluores- ence ±0.04 | ASTM ±0.10 | X-ray fluores- ence ±0.10 | SO ₄ ASTM ±0.02 | Pyritic | | | Calculated organic | | Determined organic | |
| | | | | | | ASTM ±0.05 | LAH ±0.05 | ASTM ±0.10 | LAH ±0.10 | ASTM ±0.20 | LAH ±0.20 | |
| <u>Randolph Co. I</u> | | | | | | | | | | | | |
| -60 | 0.38 | 0.49 | 2.45 | 2.65 | 0.05 | 0.37 | 0.15 | 2.03 | 2.25 | 1.77 | 1.52 | |
| -200 | 0.41 | 0.49 | 2.44 | 2.51 | 0.05 | 0.41 | 0.30 | 1.98 | 2.09 | 1.72 | 1.50 | |
| -400 | 0.42 | 0.52 | 2.48 | 2.50 | 0.04 | 0.43 | 0.40 | 2.01 | 2.04 | 1.79 | 1.97 | |
| <u>Randolph Co. II</u> | | | | | | | | | | | | |
| -60 | 1.17 | 1.14 | 3.04 | 3.10 | 0.13 | 1.15 | 0.93 | 1.76 | 1.98 | 1.34 | 1.84 | |
| -200 | 1.23 | 1.22 | 3.07 | 3.15 | 0.14 | 1.20 | 1.02 | 1.73 | 1.91 | 1.42 | 1.64 | |
| -400 | 1.25 | 1.26 | 3.09 | 3.16 | 0.15 | 1.20 | 1.12 | 1.74 | 1.82 | 1.47 | 1.63 | |
| <u>C-17965</u> | | | | | | | | | | | | |
| -60 | 1.04 | 1.05 | 1.91 | 1.96 | 0.26 | 0.83 | 0.72 | 0.82 | 0.93 | 0.84 | 0.81 | |
| -200 | 1.10 | 1.09 | 1.92 | 1.97 | 0.27 | 0.90 | 0.84 | 0.75 | 0.81 | 0.82 | 0.72 | |
| -400 | 1.06 | 1.05 | 1.91 | 1.96 | 0.27 | 0.92 | 0.91 | 0.72 | 0.73 | 0.81 | 0.67 | |
| <u>C-16718</u> | | | | | | | | | | | | |
| -60 | 2.12 | 2.13 | 3.08 | 3.13 | 0.91 | 1.25 | 1.15 | 0.82 | 1.02 | 0.90 | 0.94 | |
| -200 | 2.07 | 2.19 | 3.17 | 3.19 | 0.91 | 1.25 | 1.22 | 1.01 | 1.04 | 0.89 | 0.90 | |
| -400 | 2.03 | 1.98 | 3.11 | 3.18 | 0.93 | 1.29 | 1.30 | 0.89 | 0.85 | 0.88 | 0.82 | |
| <u>C-18039</u> | | | | | | | | | | | | |
| -60 | 2.15 | 2.17 | 4.11 | 3.92 | trace | 2.36 | 1.95 | 1.75 | 2.16 | 1.80 | 1.48 | |
| -200 | 2.23 | 2.28 | 4.20 | 3.99 | 0.01 | 2.45 | 2.11 | 1.74 | 2.08 | 1.61 | 1.34 | |
| -400 | 2.26 | 2.41 | 4.18 | 4.07 | 0.01 | 2.44 | 2.30 | 1.73 | 1.87 | 1.59 | 1.45 | |
| <u>C-18060</u> | | | | | | | | | | | | |
| -60 | 1.16 | 0.97 | 1.12 | 1.20 | 0.01 | 0.64 | 0.49 | 0.47 | 0.62 | 0.34 | 0.72 | |
| -200 | 1.15 | 0.95 | 1.12 | 1.16 | 0.01 | 0.61 | 0.53 | 0.50 | 0.58 | 0.38 | 0.67 | |
| -400 | 0.93 | 1.05 | 1.14 | 1.13 | 0.01 | 0.61 | 0.56 | 0.52 | 0.57 | 0.41 | 0.64 | |
| <u>C-18067</u> | | | | | | | | | | | | |
| -60 | 4.28 | 3.80 | 7.48 | 7.25 | 0.02 | 4.82 | 4.08 | 2.64 | 3.38 | 2.50 | 2.24 | |
| -200 | 4.26 | 4.28 | 7.53 | 7.45 | 0.02 | 4.76 | 4.44 | 2.75 | 3.07 | 2.48 | 2.21 | |
| -400 | 4.30 | 4.52 | 7.52 | 7.63 | 0.02 | 4.79 | 4.60 | 2.71 | 2.90 | 2.54 | 2.51 | |
| <u>C-18068</u> | | | | | | | | | | | | |
| -60 | 2.32 | 1.79 | 4.82 | 4.42 | 0.04 | 2.41 | 2.05 | 2.37 | 2.73 | 2.25 | 2.23 | |
| -200 | 2.54 | 2.09 | 4.54 | 4.35 | 0.05 | 2.67 | 2.51 | 1.82 | 1.98 | 2.16 | 1.91 | |
| -400 | 2.90 | 2.36 | 4.44 | 4.48 | 0.06 | 2.56 | 2.51 | 1.82 | 1.87 | 2.08 | 2.24 | |
| <u>C-17167</u> | | | | | | | | | | | | |
| -60 | 1.24 | 1.23 | 2.91 | 3.05 | 0.40 | 0.94 | 0.77 | 1.57 | 1.74 | 1.37 | 1.45 | |
| -200 | 1.29 | 1.31 | 2.95 | 3.09 | 0.39 | 0.92 | 0.88 | 1.75 | 1.68 | 1.26 | 1.25 | |
| -400 | 1.30 | 1.31 | 2.93 | 3.07 | 0.39 | 0.93 | 0.93 | 1.61 | 1.61 | 1.19 | 1.31 | |

for otherwise it would be dissolved by the nitric acid treatment used subsequently in the procedure for determining pyritic sulfur. However, in the LAH reduction of pyrite, the sulfate sulfur is unaffected and need not be removed prior to the determination of pyritic sulfur. Coal from which sulfate sulfur had already been removed was used in this work because it was available as a product of the sulfate-sulfur determination.

A sample of coal (C-17167) was used to verify the fact that the LAH reduction of pyritic sulfur could be performed prior to sulfate sulfur removal without affecting the results. The sample was treated according to the LAH reduction procedure, following which an additional 50 ml-portion of 50 percent hydrochloric acid was added to the reaction flask; the mixture was then boiled for 20 minutes to dissolve the sulfate sulfur. After the contents of the flask had been filtered and the sulfate precipitated as barium sulfate, the percentage of sulfate sulfur was found to be identical (0.40 percent) to that found when sulfate sulfur was determined first (table 1). If pyritic sulfur is determined first by the LAH reduction method, the aforementioned overnight drying procedure following sulfate sulfur removal can be eliminated.

The results for pyritic sulfur determined by the ASTM method (table 1) show only slight differences for the various coal particle size fractions. The small differences are more likely due to mechanical segregation of the heavy pyrite particles during grinding than to actual particle size differences.

In contrast, the pyritic sulfur values obtained by the LAH reduction method show a general increase as coal particle size decreases (table 1). The LAH pyritic sulfur values determined for the -400-mesh fraction are not significantly lower than those obtained by the ASTM method. Therefore, the smaller the coal particle size, the more complete is the chemical reduction of pyrite, and at -400 mesh reduction is essentially complete, if the ASTM values can be assumed to be accurate.

Owing to the physical limits of grinding and screening techniques, it is difficult to obtain samples much finer than -400 mesh. However, because virtually total pyrite recovery is achieved within experimental error at -400 mesh, it is logical to assume that the apparent bias will be eliminated with further reduction in particle size.

Studies have shown that some coals contain significant quantities of nonpyritic sulfide (Ruch, Gluskoter, and Shimp, 1973) and that it usually occurs in conjunction with high zinc concentrations (as high as 5000 ppm). In the LAH method the pyrite (FeS_2) is first reduced to sulfide (FeS). Any nonpyritic sulfide present in the coal will contribute to the LAH pyritic sulfur value when the chemical reduction of pyrite is carried out prior to sulfate removal. This is true only when the reduction step is done first, as some nonpyritic sulfide is lost in the hydrochloric acid digestion for sulfate sulfur (ASTM). The ASTM method for pyritic sulfur measures only the pyritic iron. Consequently, a pyritic sulfur value determined by the LAH method that is higher than one determined by the ASTM method would be a measure of the amount of nonpyritic sulfide present in the coal.

The loss of nonpyritic sulfides as hydrogen sulfide in the hydrochloric acid digestion of sulfate sulfur (ASTM) would result in this sulfide's

being determined as neither sulfate nor pyritic sulfur. The organic sulfur value, calculated as the difference between the total sulfur and the sulphate + pyritic sulfur values, would then be erroneously high.

As previously mentioned, theoretical organic sulfur values were computed from both the LAH and ASTM pyritic sulfur values. They were also determined directly by Eschka fusion of the residues from both the LAH and ASTM pyritic sulfur determinations. With several exceptions, table 1 shows that directly determined organic sulfur values were generally lower than theoretical values for both the LAH and the ASTM residues. Some loss of sample would not be surprising in the filtration, drying, and transferral of the residue to Eschka sulfur crucibles. The filter cake could not be finely ground without loss of sample, and the occurrence of large particles may have prevented complete reaction of the residue.

The values for total iron determined by X-ray fluorescence and ASTM acid-extractable iron agree well and show no significant variations with particle size (table 1). The variation in sample C-18068 probably reflects inhomogeneous splits of the original sample. The agreement of total iron values from the two methods means that all the iron in the coals has been accounted for as hydrochloric acid-soluble and pyritic iron. Therefore, no pyrite remains in the coal residue after the pyritic sulfur determination to interfere with the determination of organic sulfur.

Although no significant amounts of elemental sulfur are thought to occur in coal (Rees, 1966), any that might be present should be reduced to sulfide by LAH and result in erroneously high pyritic sulfur values. To test this supposition, enough elemental sulfur was added to a -400-mesh coal sample that had already been analyzed for pyritic sulfur (4.60 percent) to yield a final concentration of 0.50 percent elemental sulfur. The LAH pyritic sulfur value for the adulterated sample was 5.17 percent, indicating that reduction of the added elemental sulfur was complete within experimental error. The nitric acid digestion of the coal in the ASTM procedure should not affect elemental sulfur. Therefore, when sulfate sulfur and sulfides have been removed by hydrochloric acid digestion, the difference in the pyritic sulfur values determined by the LAH and ASTM methods should give a quantitative measure of the elemental sulfur present. This method could be used to determine elemental sulfur in coal where quantities of elemental sulfur greater than the experimental errors of the procedure are suspected.

CONCLUSIONS

When coal is ground to a very fine particle size, the values for varieties of sulfur in the coal determined by the LAH reduction method and by the ASTM procedure agree well. The two methods can be expected to produce comparable results when correct experimental conditions are maintained. The ASTM method is the more adaptable to the routine analysis of large numbers of coal samples. However, the LAH reduction method is useful when sulfides other than pyrite are present or when additional information is required.

The agreement of total iron values determined by X-ray fluorescence and by ASTM procedures indicates that essentially all of the pyrite is, in-

deed, removed from the coal samples by the ASTM method. The values determined for sulfate sulfur and pyritic sulfur by either the ASTM or LAH method must therefore be reasonably accurate. The sulfur remaining in the residue must be either organic or elemental in nature.

Because elemental sulfur is affected differently in the LAH and ASTM methods, comparison of the pyritic sulfur values determined could reveal the presence of significant quantities of elemental sulfur when the hydrochloric acid-soluble portion has first been removed. Comparison of the pyritic sulfur values obtained by the two different methods also indicates that no significant amounts of elemental and nonpyritic sulfide sulfur were present in the coals studied. The calculated values for organic sulfur from either method thus appear to be valid.

That the experimental values found for organic sulfur are lower than the theoretical (calculated) values is probably the result, in part, of mechanical loss. However, in both the LAH and ASTM methods, small quantities of organic sulfur may be dissolved or suspended in the refluxing liquid and lost. This loss does not affect the pyritic sulfur values when the analyses are performed by the methods previously described. A further study of this potential loss is being made at the Illinois State Geological Survey.

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APPENDIX

Summary of the ASTM Methods for Forms of Sulfur (D-2492) and Total Sulfur (D-271) in Coal (ASTM, part 19, 1972).

Sulfate sulfur is determined by refluxing a coal sample with dilute (2:3 H₂O) hydrochloric acid. The sulfate sulfur dissolves in the acid and, after extraction, is precipitated with barium chloride and weighed as barium sulfate.

Pyritic sulfur is determined by refluxing the coal sample with dilute nitric acid. Ferrous iron is converted to ferric iron and sulfide to sulfate, both of which are soluble in nitric acid. Ferric iron is then removed and titrated to provide a measure of pyritic sulfur. This method is used rather than precipitation of the sulfur because the extraction dissolves sulfate sulfur, pyritic sulfur, and a small amount of organic sulfur. If the extraction is done on the residue from the sulfate-sulfur extraction, the amount of iron found indicates directly the quantity of pyritic sulfur present. However, if a whole coal sample is used for this determination, it is necessary to titrate the iron removed in the sulfate-sulfur extraction of another sample and subtract it from the amount of iron determined by the nitric acid extraction.

Organic sulfur is calculated by determining the total sulfur by the Eschka method and subtracting the sum of the sulfate sulfur and pyritic sulfur values from the total sulfur value.

Total sulfur is determined by heating in a crucible a coal sample combined with Eschka's Mixture (MgO + Na₂CO₃) at 800° C. The mixture is then leached with hot water to remove the sulfur. The solution is made acid, oxidized, and the sulfur is precipitated as barium sulfate.

The barium sulfate is then recovered, dried, and weighed, and the total sulfur is calculated from the weight of barium sulfate.

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