

Determination of Forms of Sulfur in Coal

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INTRODUCTION

The need for low-sulfur coal has assumed major proportions. Shortages of other fossil fuels, restrictions on sulfur oxide emissions, and technical problems associated with the use of high-sulfur coals in newly proposed coal conversion processes are contributing to the crisis. It is now apparent not only to coal specialists but also to others that the emission standards and technical problems associated with high sulfur content of bituminous coals are contributing greatly to the severity of the fuel shortages in the United States. Consequently, it is appropriate to discuss old and new methods of evaluating the sulfur status of coal and to reexamine some of the problems associated with their application.

Free sulfur as such does not occur in coal to any significant extent. Sulfur is present in coal in organically bound combinations, in inorganic compounds mainly as pyrite (FeS_2), and especially in weathered coals as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and as ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). In a few coals, significant amounts of other inorganic sulfates and sulfides, e.g. barite (BaSO_4) and sphalerite (ZnS), (1,2) which normally occur only in trace concentrations, may be present.

The three forms of sulfur commonly measured in coal are sulfate, pyritic, and organic. Although less frequently determined than total sulfur, they are, perhaps, the most significant in terms of coal utilization. Of the two predominant sulfur forms, pyritic and organic, the former can be partially removed by conventional gravity coal cleaning procedures prior to combustion, but the latter cannot. The amount of pyritic sulfur in Illinois coals and the percentages of it that can be removed with reasonable coal recovery (80%) were recently reported by Helfinstine et al. (3,4). For 64 coals, they found that the total sulfur removed as pyrite in laboratory washing studies varied from about 10 to 65%. The pyritic sulfur that was removed with 80% coal recovery varied from about 10 to 90% and averaged about 60%.

Although significant amounts of pyritic sulfur can usually be removed by physical means, very finely divided or framboidal pyrite is not amenable to reduction by such treatment. For complete removal of pyritic sulfur, a combination of physical and chemical extraction methods is usually required. Methods of this type are currently being developed, but these have not been employed on an industrial scale (5).

Similar methods for the reduction of organic sulfur, without destruction of the coal molecule itself, have not been developed. Even if 100% of the pyritic sulfur were removed from all the Illinois coals produced, only about 15% would meet current environmental standards without supplementary controls (3,4).

Because the degree to which sulfur can be reduced in coal is primarily a function of the forms of sulfur contained in the coal, analytical methods for their accurate determination are essential.

ASTM FORMS OF SULFUR INVESTIGATION

Committee D-5 on Coal and Coke, of the American Society for Testing and Materials (ASTM), began a study of methods for the determination of forms of sulfur in coal in 1957. This study eventually led to the current Standard Method D-2492,

Forms of Sulfur in Coal (6). In this procedure, total sulfur and only two of its three forms - sulfate and pyritic - are determined. The third form, organic sulfur, is calculated by difference:

$$\text{Organic S} = \text{Total S} - (\text{sulfate S} + \text{pyritic S}).$$

For this method, it is not only essential to obtain accurate values for sulfate and pyritic sulfur forms, it is also necessary to obtain accurate total sulfur values. Any errors made in total, pyritic, or sulfate sulfur determinations will be cumulative in the organic sulfur calculation. Unfortunately, there are no published methods for the direct determination of organic sulfur that will permit the sum of independently determined values for the three forms of sulfur to be checked against an independently determined total sulfur value. This has led to a number of problems, which will be discussed in more detail later.

A flow sheet for ASTM Standard Method D-2492, Forms of Sulfur in Coal, is given in Figure 1. The method is based on the different solubilities of sulfate and pyritic sulfur in HCl and HNO₃. Sulfate sulfur is soluble in dilute HCl, both sulfate and pyritic forms of sulfur are soluble in HNO₃, and organic sulfur is insoluble in the acids. Pyritic sulfur is generally determined by extracting the coal residue from the sulfate sulfur determination (Figure 1), although it may also be determined on a separate coal sample if corrections for the sulfate sulfur or iron are made. Pyrite is oxidized by HNO₃ to ferric iron and sulfate, but it is the ferric iron associated with the pyrite that is usually determined rather than the sulfur (Figure 1). The HNO₃ extraction may oxidize small amounts of organic matter that contains sulfur. This would be erroneously determined as part of the pyritic sulfur. Organic sulfur is calculated by difference as previously described.

During the ASTM round-robin testing of this method, large amounts of data were generated and subsequently compiled by Krumin (7,8,9,10) for Committee D-5. The results and conclusions of this study are unavailable in published form, but a brief summary of its nature and the conclusions drawn are as follows*.

1) Five coal samples containing from 1.6 to 24% sulfur, each ground to pass a -60 mesh and -200 mesh-sieve, and analyzed by five different laboratories gave essentially the same results for forms of sulfur. Thus, the use of -60 mesh coal was recommended.

2) Further studies using methods originally developed by Powell and Parr (11) and Powell (12) were conducted by 24 laboratories, each analyzing two coals in triplicate and using the coal extraction and method variations given in Table I. In all cases, organic sulfur was determined by differences. Results of this study are summarized in Table I. Table II presents the results of the t-test of means, and Table III presents results of the F-test of variances as performed on the data determined by the various methods for sulfate and pyritic sulfur in coal samples designated S-1 and S-2. Conclusions were drawn by Krumin (10) and presented at the meeting of ASTM Committee D-5, January 30, 1961:

Total Sulfur-Eschka Method (ASTM D-3177). Deviations in the data reported by the various laboratories were within, or exceeded by only a small amount (0.01 to 0.05%), ASTM limits for maximum deviations of results.

Sulfate Sulfur (ASTM D-2492). The results determined by the two methods Sulfate Sulfur, Short Extraction and Sulfate Sulfur, Long Extraction are in close agreement, and are characterized by almost identical values for the standard deviation, repeatability and reproducibility. The great advantages of the 30-minute extraction procedure over the 40-hour technique make the method Sulfate Sulfur, Short Extraction the more suitable method for use in the routine analysis of coal.

* Permission to summarize this work was granted by the Executive Committee of ASTM Committee D-5 on Coal and Coke.

TABLE I. STATISTICAL EVALUATION*

Experimental procedure	Sample	Meant data (%)	Standard deviation	Repeat-ability	Reproduc-ibility
Total Sulfur	S-1	2.93	0.0945	0.0610	0.2514
	S-2	2.94	0.0846	0.0928	0.2142
Sulfate Sulfur,	S-1	0.08	0.0131	0.0196	0.0311
HCl Short Extraction (30 min.)	S-2	0.16	0.0124	0.0214	0.0322
Sulfate Sulfur	S-1	0.08	0.0115	0.0196	0.0339
HCl Long Extraction (40 hrs., 60° C)	S-2	0.15	0.0124	0.0191	0.0316
Pyritic Sulfur, Short	S-1	1.75	0.1799	0.1412	0.4412
HNO ₃ Extraction (reflux, 30 min.), Gravimetric Determination	S-2	1.62	0.1637	0.14555	0.4069
Pyritic Sulfur, Long	S-1	1.74	0.1952	0.1614	0.5085
HNO ₃ Extraction (24 hrs., room temp.), Gravimetric Determination	S-2	1.59	0.1228	0.1460	0.3359
Pyritic Sulfur, Short	S-1	1.74	0.1553	0.1198	0.4119
HNO ₃ Extraction (reflux, 30 min.), Titrimetric Determination of Iron	S-2	1.58	0.0943	0.1213	0.2516
Pyritic Sulfur, Long	S-1	1.85	0.1027	0.0922	0.2815
HNO ₃ Extraction (24 hrs., room temp.), Titrimetric Determination of Iron	S-2	1.59	0.0974	0.0998	0.2553

*After a thesis by E. Fasig, Jr., Engineering and Experiment Station, Ohio State University, Columbus, OH.

†Moisture-free.

TABLE II. RESULTS OF THE T-TEST OF MEANS*

Method of determination	Sample	Degrees of freedom	Calculated value of t	Critical value or range of t
Sulfate Sulfur, Long vs. Short Extractions	S-1	102	0.790	2.000 to 1.980
	S-2	100	4.475	2.000 to 1.980
Pyritic Sulfur, Short Extraction, Gravimetric vs. Titrimetric Determinations	S-1	70	0.106	2.000 to 1.980
	S-2	70	1.505	2.000 to 1.980
Pyritic Sulfur, Long Extraction, Gravimetric vs. Titrimetric Determinations	S-1	76	3.371	2.000 to 1.980
	S-2	72	0.007	2.000 to 1.980
Pyritic Sulfur, Short vs. Long Extractions, Gravimetric Determination	S-1	86	0.126	2.000 to 1.980
	S-2	83	0.953	2.000 to 1.980
Pyritic Sulfur Short vs. Long Extractions, Titrimetric Determination	S-1	60	3.768	2.000
	S-2	59	0.552	2.008 to 2.000

*After a thesis by E. Fasig, Jr., Engineering Experiment Station, Ohio State University, Columbus, OH.

TABLE III. RESULTS OF THE F-TEST OF VARIANCES*

Method of determination	Sample	Degrees of Freedom		Calculated value of F	Critical range, F
		numerator	denominator		
Sulfate Sulfur, Long vs. Short Extractions	S-1	1	102	1.73	4.00 to 3.92
	S-2	1	100	26.97	4.00 to 3.92
Pyritic Sulfur, Long and Short Extractions	S-1	3	146	6.87	2.68 to 2.60
	Gravimetric and Titrimetric Determinations	S-2	3	142	2.96

*After a thesis by E. Fasig, Jr., Engineering Experiment Station, Ohio State University, Columbus, OH.

Pyritic Sulfur (ASTM D-2492). Data determined by four methods (Table 1), were, for all cases except one, in close agreement with each other and were characterized by values of standard deviation, repeatability, and reproducibility, all of which were very similar. The precision of the titrimetric technique was better than that of the gravimetric procedure as shown by the values of standard deviation and reproducibility shown in Table I. Since the precision and results of the various methods are so similar, the advantages of the short, 30-minute extraction procedure over the long, 40-hour technique, and the greater ease and speed of the titrimetric determination in comparison with the gravimetric procedure make the method Pyritic Sulfur, Short Extraction, Titrimetric Determination the most suitable for use in the routine analysis of coal.

TOTAL SULFUR

The need for accurate methods of determining total sulfur in coal was previously noted. The Eschka and bomb washing procedures are the two most commonly used methods in the United States, both of which are given in ASTM D-3177 (6).

The Eschka procedure consists of thoroughly mixing coal with Eschka mixture (2 parts calcined MgO and 1 part anhydrous Na₂CO₃) and ashing it in a muffle furnace at 800° C. The ashed coal is leached with hot water, filtered, and the sulfur is determined gravimetrically in the filtrate. This method is rapid when carried out on large batches of samples; it is most accurate when used for coals containing no more than 6 or 7% sulfur.

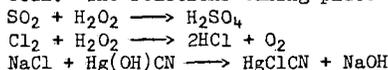
The bomb washing procedure is convenient for laboratories that make frequent coal calorimetric determinations as described in ASTM D-2015 (6). After cooling and careful venting, the bomb used for a calorific determination is thoroughly washed with water, and the sulfur is then gravimetrically determined in the bomb washings. This method gives excellent results when used for the analysis of coals containing no more than 4% sulfur.

A third method in common use, but which was dropped as an ASTM standard in 1974, is the peroxide bomb method (13). In this method, coal is fused with Na₂O₂ in a special bomb. Following dissolution of the melt, sulfur is usually determined gravimetrically. This procedure is especially useful for the determination of high sulfur concentrations up to 30 or 40%. The difficulties and precautions required for the correct use of these three methods have been described by Selvig and Fieldner (14) and Rees (15).

There are at least three other less frequently used procedures: The high-temperature combustion method (16), which has been approved by ASTM Committee D-5 and will probably be published in 1975; the Leco or induction furnace method, which was tested by ASTM Committee D-5 with unsatisfactory results (17); and X-ray fluorescence methods.

The high-temperature combustion procedure is most useful for the rapid (30 min. per sample) determination of total sulfur in a small batch of less than 8 or 10 samples. Under these conditions, it is much more rapid than the Eschka method; however, when samples are analyzed in larger groups (20 to 30 samples), the Eschka procedure is preferred over the high-temperature combustion method.

The high-temperature combustion method for determining total sulfur in coal is based on the procedure of Mott and Wilkinson (18) in which a weighed coal sample is burned in a tube furnace in a stream of oxygen at a temperature of 1350° C. The sulfur oxides and chlorine formed are absorbed in H₂O₂ solution yielding HCl and H₂SO₄. The total acid content is determined by titration with NaOH, and the amount of NaCl resulting from the titration of the HCl is converted to NaOH with a solution of mercuric oxycyanide (Hg(OH)CN). This NaOH is determined titrimetrically and used to correct the sulfur value, which is equivalent to the amount of H₂SO₄ formed during combustion of the coal. The reactions taking place are as follows:



The method is accurate for both low and high sulfur concentrations.

Finally, X-ray fluorescence has been used for determining total sulfur in coal (19,20,21). Ruch et al. (1) have recently described a method of preparing pressed coal samples, which may be used for the determination of a variety of major, minor, and trace elements, including sulfur, in whole coal. Their sulfur values for more than 100 coals showed good agreement with those determined by the ASTM standard Eschka procedure (Ruch, p. 15). The economy and speed of such X-ray fluorescence methods, when used for multiple determinations (e.g. Al, Si, Ca, Mg, Fe, K, Ti, P, and S) in the same prepared coal sample, are probably unsurpassed by any other method. The relative standard deviation for sulfur, as determined by the X-ray fluorescence method of Ruch et al. (1) is 0.5%.

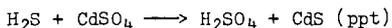
INSTRUMENTAL METHODS FOR DETERMINING PYRITIC SULFUR

The HNO₃ extraction of pyrite (FeS₂) from coal yields a solution ideal for the atomic absorption determination of iron as a measure of pyritic sulfur. Current studies of this method by ASTM Committee D-5, the U. S. Bureau of Mines, Pittsburgh, PA, and the TVA Central Chemical Laboratories, Chattanooga, TN, show good agreement between pyritic iron values determined using an atomic absorption procedure with those determined by the titrimetric methods described for pyritic iron in ASTM D-2492 (6). The method is simple and rapid, and it may soon replace currently specified ASTM standards. Care must be taken to avoid interferences from variable amounts of H₂SO₄ formed when pyrite is oxidized during extraction of the coal with HNO₃. Compensation for this matrix change can be made by adjustment of the sample size and addition of H₂SO₄ to standards, by addition of a flame buffer such as LaCl₃ to samples and standards, or both.

The determination of crystalline pyrite in coal by an X-ray diffraction method has been described by Schehl and Friedel (22). Finely ground coal samples of known pyrite concentration were used as standards in a technique that takes advantage of digital computers for measurement of the diffraction patterns, as well as for the calculation of the percentage of pyrite present in the coal sample. Background corrections due to carbon are made and quantitative results achieved by comparing the integrated intensity of a given pyrite reflection with the integrated intensity of a particular reflection from an internal standard (nickel). Acceptable precision within current ASTM tolerances was obtained for the coals studied, but interferences from reflections due to high concentrations of kaolin in coal were noted.

CHEMICAL REDUCTION METHOD FOR DETERMINING PYRITIC SULFUR

Methods involving reduction of pyrite to H_2S have also been employed for the determination of forms of sulfur (23,24,25). A reduction method (24) was recently studied by Kuhn et al. (26). This method uses lithium aluminum hydride to reduce pyritic sulfur to H_2S , which is then reacted with $CdSO_4$. The H_2SO_4 formed from the reaction



is titrated with standard base. Both sulfate and organic sulfur were determined by ASTM D-2492 procedures (6).

Major advantages of this method are that pyritic sulfur can be directly determined without danger of oxidation of the sulfur containing organic constituents, and that it can be determined without prior removal of sulfate sulfur. Further, it is extremely useful as an independent check on the accuracy of values for the forms of sulfur determined by the ASTM oxidation method.

ACCURACY OF FORMS OF SULFUR METHODS

Questions concerning the accuracy of either oxidation or reduction methods for the determination of forms of sulfur in coal generally stem from the difficulties associated with the incomplete extraction of finely-dispersed pyrite (25,27,28,29). Results of these studies have been at variance. In some cases, fine grinding of coal (-200 mesh) tended to increase the amount of pyrite extracted by HNO_3 , especially in high rank British coals (>85% carbon content). However, for U. S. coals, grinding to the usual -60 mesh particle size has been successful (7,8,9,10). Burns (30) also found fine grinding to be unnecessary for Australian coals when pyritic sulfur was extracted from the coal residue following the sulfate sulfur extraction rather than from a fresh coal sample.

These and other questions regarding the reliability of determinations of forms of sulfur were the subject of a recent investigation (26). For this study, results from the ASTM oxidative method were compared with those of a reductive method (24) to determine whether or not extraction of pyrite is complete, whether or not organic matter is significantly affected by HNO_3 extraction, and whether or not organic sulfur can be obtained either by computation or by Eschka determination of residual sulfur following HNO_3 extraction of pyritic sulfur. The influence of coal particle sizes (-60, -200, and -400 mesh) on the values determined by both methods was also studied.

Results for two coals, which are representative of the nine coals studied in this investigation, are given in Table IV. The principal conclusions are summarized as follows:

- 1) Coal particle size had no significant effect on total sulfur determined by the Eschka method (Table IV, column four).
- 2) X-ray fluorescence values for total sulfur agree well with Eschka values (Table IV, columns four and five).
- 3) Pyritic sulfur values determined by the ASTM method are not significantly influenced by coal particle size (Table IV, column seven).
- 4) For the reduction method, pyritic sulfur values in agreement with those from the ASTM procedure were obtained only when the coal was ground to -400 mesh (Table IV, columns seven and eight).
- 5) Agreement of total iron in the coals, as determined by X-ray fluorescence, with the sum of the iron determined in the ASTM HCl and HNO_3 extracts was excellent (Table IV, columns two and three). This indicates that all of the pyritic iron (sulfur) was extracted by the HNO_3 .
- 6) It was concluded that no pyritic iron remained in the residues of the nine coals studied after they were subjected to either the ASTM oxidation method or the reduction method (on -400 mesh coals only). Therefore, organic sulfur values calculated by subtracting the sum of sulfate sulfur plus pyritic sulfur from total sulfur were deemed accurate (Table IV, columns nine and ten).

TABLE IV. CONCENTRATION OF IRON AND VARIETIES OF SULFUR IN TWO ILLINOIS COALS

Sample and size	Total iron (%)		Total Sulfur (%)				Sulfur (%)				
	X-ray fluorescence		X-ray fluorescence		SO ₄ ASTM	Pyritic		Calculated organic		Determined organic	
	ASTM	ASTM	ASTM	ASTM		ASTM	Reduc.	ASTM	LAH	ASTM	Reduc.
<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-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

ORGANIC SULFUR

Research on the nature and removal of organic sulfur compounds from coal has been extensive (31,32,33,34,35,36). Unfortunately, none of these investigations has led to useful methods for determining varieties of organic sulfur in coal. Indeed, as previously mentioned, no methods have as yet been developed for the direct determination of total organic sulfur in the presence of inorganic sulfates and sulfides. When organic sulfur has been "determined" rather than calculated by difference, the coal was first demineralized using methods similar to those described in the International Standards Organization Recommended Method R-602 (37), or by Kuhn et al. (26) and Smith and Batts (38). In these, sulfate and pyritic sulfur are first removed by acid dissolution, oxidation and/or reduction reactions. The total sulfur determined in the coal residue is then considered to be organic sulfur. This method was found to be fairly reliable by Kuhn et al. (26), although small losses of organic sulfur were unavoidable (Table IV, columns nine through twelve). The most accurate results for organic sulfur seemed to be those which were calculated.

An interesting new approach to the purported determination of organic sulfur in coal is that of Hurley and White (39). They employed a X-ray fluorescence method to first determine total sulfur from the K β line intensity and then a line ratio technique to find the proportion of sulfate sulfur (K β' line intensity) in the total sulfur:

$$\%S_{SO_4} = \% \text{ Total } S \times (SK\beta' / SK\beta) \times M_1$$

where M_1 is the slope of a standard straight line calibration curve of the ratio (SK β' /SK β) vs. concentration. The peak shift of sulfur K β was used to determine amounts of sulfide and organic sulfur:

$$\%S_{org} = \% \text{ Total } S \times \left(\frac{\Delta SK\beta - B}{M_2} \right)$$

$$\%S_{pyr} = \% \text{ Total } S \times \left(100 - \frac{\Delta SK\beta - B}{M_2} \right)$$

where the calibration constants, M_2 and B are obtained from a straight line calibration curve of the form $Y = MX + B$. It should be noted that pyritic sulfur is a calculated difference figure, i.e., the sum of the three forms of sulfur must equal 100%. Therefore, the sulfur values are not independently determined.

NONPYRITIC SULFIDES

Studies have shown that some coals contain significant quantities of nonpyritic sulfide (1,2), and that it usually occurs in conjunction with high zinc concentrations (up to 5000 ppm). In the reduction method the pyrite (FeS₂) is first reduced to sulfide (FeS). Any nonpyritic sulfide present in the coal will contribute to the 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 HCl digestion for sulfate sulfur (ASTM). The ASTM method for pyritic sulfur measures only the pyritic iron. Consequently, a pyritic sulfur value determined by the reduction 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. In such a case, Zn concentration is also a useful measure of nonpyritic sulfide.

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 sulfate + pyritic sulfur values, would then be erroneously high.

ANALYSIS OF COAL-RELATED MATERIALS

Coal preparation and float-sink studies frequently require the determination of forms of sulfur in coal gravity fractions. Because these commonly contain 10 to 20% sulfur, care must be taken when applying methods developed for the analysis of whole coal to them. Helfinstine et al. (3,4) determined forms of sulfur in 64 Illinois coals, in their float fractions (five for each coal), and in the material that sank at a specific gravity of 1.60. These data were then used to calculate sulfur in the "raw coal" by proportionally combining the individual float-sink fractions to give values that should be equivalent to values given in the original raw coal analysis. The average difference in percent between analyzed raw coal sulfur values and those calculated from the individual analyses of float-sink fractions are -0.15, -0.05, and -0.11 for total sulfur, pyritic sulfur, and organic sulfur respectively. Although the means (as well as their standard deviations) are small and indicate good agreement, examination of all of the data shows notable exceptions for some high sulfur samples. In one coal, percent differences between analyzed and calculated values for total sulfur, pyritic sulfur, and organic sulfur were -0.56, -0.49, and -0.10, respectively. Careful resampling and analysis has shown that differences of this magnitude are not due to poor sampling or analytical techniques, but rather to small errors in the analysis of high sulfur materials using the ASTM method of determining forms of sulfur. Such errors may be magnified by factors of 10 or 20 in making the calculations.

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* For the reduction method, it was shown by Kuhn et al. (26) that pyritic sulfur can be determined in the presence of sulfate sulfur.

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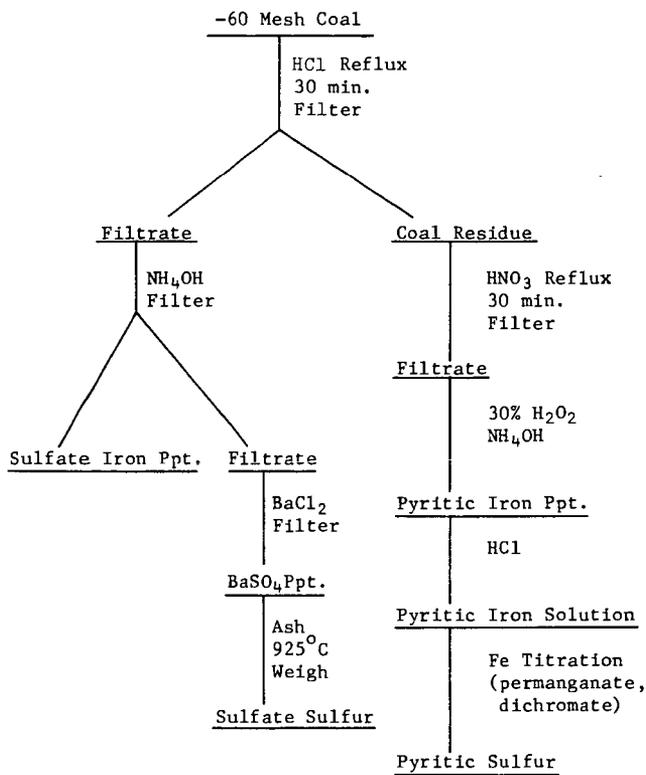


Figure 1. Flow diagram for ASTM determination of forms of sulfur in coal.