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Analysis of Forms of Sulfur in Coal

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1987

ANALYSIS OF FORMS OF SULFUR IN COAL

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Gary Martin Ruba
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ANALYSIS OF FORMS OF SULFUR IN COAL

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ANALYSIS OF FORMS OF SULFUR IN COAL

Gary Martin Ruba August 1987 60 Pages

Directed by: John T. Riley

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Methods for the determination of sulfur forms are reviewed. Each method is compared to the ASTM D 2492 standard method when data are available. The extraction of pyrites with dilute nitric acid is reviewed in detail because of its relationship to data presented in this thesis.

A new technique for the analysis of organic sulfur was developed in response to a need by the coal community for an accurate and inexpensive method. In this method nitric acid extraction is used to remove the inorganic sulfur forms and the residual coal is then analyzed for organic sulfur. Organic sulfur values obtained by this direct method show good agreement with the sulfur content in "supercleaned" coal which has had almost all mineral matter removed by physical methods. The precision of the direct analysis method is better than that experienced when using ASTM D 2492.

CHAPTER I

INTRODUCTION

In papers as early as 1919, A. W. Powell and S. W. Parr reviewed the determination of sulfur forms in coal.(1) However, it was not until the Clean Air Act in 1981 that the interest in coal beneficiation and the determination of sulfur forms moved to the forefront of coal chemistry. Coal is an important current energy source and will continue to increase in value as crude oil reserves are depleted.

A survey of the existing literature revealed no inexpensive method for the direct determination of organic sulfur. The present American Society for Testing and Materials (ASTM) procedure, D 2492, for determining coal sulfur forms assays the total, sulfate and pyritic sulfur.(2) Organic sulfur is calculated by subtracting the sum of the inorganic forms from the total sulfur. Consequently, the organic sulfur value incorporates errors of all three analyses.

In this report old and new methods for the determination of sulfur forms are reviewed. Each method is compared to the ASTM standard method where data are available. Each analytical procedure includes current modifications. A new method for the direct determination of organic sulfur is also presented.

CHAPTER II

HISTORICAL

In present literature three forms of sulfur in coal are accepted: sulfate, pyritic and organic forms.(3) Although they are less often determined than the total sulfur, these forms are significant in the utilization of coal. Sulfate sulfur occurs mainly as $FeSO_4 \cdot nH_2O$ and is present in coal primarily as a result of oxidation of pyrite. Pyrite and marcasite are two crystalline forms of FeS_2 and are collectively referred to as pyrite.(4) The organic sulfur components were reported in 1919 as being present in two forms: resinic and humus.(1) Current literature does not make this distinction and suggests that the organic sulfur is all the sulfur which is bonded to the organic molecules in coal.(5)

Traces of elemental sulfur have been reported in some coals, but they do not occur to a significant extent. A Mössbauer study of inorganic sulfur forms in coal reported the presence of sphalerite (Zn,Fe)S, jarosite $(Na,K)Fe_3(SO_4)_2(OH)_6$, pentlandite $(Fe,Ni,Co)_9S_8$, pyrrhotite (FeS), galena (PbS), and several others. Nevertheless, the total percentage of all these forms was very low.(6)

Coalification is a process that has been discussed extensively by coal chemists over the years. The two primary stages are diagenesis and metagenesis. The organic material is changed to fossil fuels by reactions which occur at varying temperatures and pressures.(7) The origin of sulfur in coal is obscured by the lack of information about the organic sulfur and pyrite enrichment processes after deposition. Also little is known about sulfur sources in extensive peat beds.(8)

The distribution of sulfur in the two main forms varies widely between coal fields. Pyrite in coal originated from two general pathways which involved bacterial reduction of aqueous sulfate.(9) The amount of hydrogen sulfide produced by the sulfate reducing bacteria is a function of the available organic matter to provide the needed energy and hydrogen.(10)

The mode of pyrite formation determines the size, shape of the crystals formed, and the amount of pyrite liberation during a beneficiation process. For example, pyritic sulfur formed syngenetically with coal in the first stages of coalification is more likely to become encapsulated in the organic matrix of the coal. Pyrite formed after deposition and located between the bedding planes is removed with less difficulty during a mechanical cleaning process.

There are three principal categories of methods for precombustion desulfurization of coal:(11-12)

1) Physical cleaning to remove pyrite
2) Chemical desulfurization
3) Conversion to low sulfur liquid and gaseous fuels.

The degree to which the sulfur can be reduced by the above methods is dependent on the forms of sulfur in the coal. Therefore accurate analytical data is absolutely essential for improvement and evaluation of sulfur reduction technologies.

A. Total Sulfur Determination

The Eschka method for the determination of total sulfur in coal was adopted by the American Chemical Society in 1917.(13) Versions of the method appeared in the Journal of the American Chemical Society as early as 1899. The Eschka method uses a mixture of calcined magnesium oxide and anhydrous sodium carbonate to trap all the sulfur as sulfates upon combustion in air at 800°C. The sulfates formed are subsequently dissolved in hot water and determined gravimetrically. The Eschka method is the standard to which all other total sulfur methods have been compared for nearly one hundred years. Currently ASTM standard method D 3177 includes the Eschka method.(2)

The Eschka method compares favorably to the bomb washing, sodium peroxide fusion, and high temperature combustion methods.(14-16) The bomb washing method makes use of the wash solution from the oxygen bomb used in calorimetric determinations. Iron(III) ions in the wash solution are first precipitated using ammonia and removed by filtration. Barium chloride is added to the filtrate and barium sulfate is determined gravimetrically as in the Eschka method.

A more rapid method for determining total sulfur is the high temperature combustion method using infrared detection. The LECO SC-132/32 Automatic Sulfur Determinators manufactured by the LECO Corporation in St. Joseph, MI, employ this method for sulfur analysis. Sulfur containing materials are combusted in oxygen in a ceramic furnace at 1350°C and the effluent sulfur dioxide is detected by an infrared detector tuned to a stretching frequency of the sulfur dioxide molecule. The method is rapid (2 minutes), precise, and accurate when good sulfur calibration standards are used. It is the most widely used method for sulfur analysis in the U.S. and is included as part of the ASTM standard method D 4239.(2)

Currently there is interest in using fast neutron activation analysis(17) and x-ray fluorescence(18) for determining the total sulfur in coal. The work of Lloyd and Francis using x-ray fluorescence (XRF) for determining total sulfur showed consistent results with the total sulfur determined by ASTM methods in six independent laboratories. The XRF method has the potential of meeting the ASTM standards for precision and accuracy and may someday become a standard method. The XRF method has also been used for pyritic sulfur determination and will be discussed later in the thesis.

B. ASTM Forms of Sulfur Determinations

The ASTM Committee D-5 on Coal and Coke started to investigate methods for determining forms of sulfur in coal in 1957.(3) The study culminated in the current standard method D 2492. The sulfate sulfur in coal is determined by extraction with 4.8 M hydrochloric acid followed by precipitation of the non-pyritic iron with ammonia. Barium chloride is used to precipitate sulfate ions in the filtrate and barium sulfate is determined gravimetrically. The pyritic sulfur is determined by extraction with 2 N nitric acid after the sulfate determination on the same sample. The iron content of the nitric acid extract solution is measured by either titrimetry or atomic absorption spectroscopy and directly correlated to pyritic sulfur content. The inorganic forms are summed and subtracted from the total sulfur to give the organic sulfur content.

The ASTM standard methods suggest maximum tolerances for each of the sulfur form determinations in terms of repeatability and reproducibility(2) as listed in Table 1. If the recommended reproducibility limits for sulfate, pyrite and total sulfur are added together a representative value can be obtained for the organic sulfur reproducibility obtained by the difference method. For example, at the 2% sulfur level a relative value of 32% is acceptable for ASTM reproducibility between two laboratories using samples taken from the same bulk sample. The worst possible ASTM reproducibility is encounted at the 2% sulfur level.

In reviewing the literature the most often raised question about the ASTM standard method is whether or not 2 N nitric acid extracts all the pyrite from a coal sample.

TABLE 1

ASTM Repeatability and Reproducibility*

Sulfur Form	Repeatability	Reproducibility
Sulfate	0.02	0.04
Pyrite under 2%	0.05	0.30
Pyrite 2% or more	0.10	0.40
Total sulfur under 2%	0.05	0.10
Total sulfur 2% or more	0.10	0.20

* Repeatability -- Duplicate results by the same operator in a given laboratory on consecutive analyses determined within a minimum interval of time shall be considered suspect if they differ by more than limits described above.

* Reproducibility--Duplicate determinations carried out by different laboratories, on representative samples taken from the same bulk sample, after the last stage of reduction, should not differ more than the above described limits.

Since complete extraction is a basic assumption of the method presented in this report it will be investigated in detail. In 1964, A. H. Edwards and co-authors(19) reported the extraction of coal with dilute nitric acid left unattacked pyrite which would result in incorrect pyritic sulfur values. The authors conducted a comparison study of pyrite extraction of -72 British Standard (B.S.) and -300 B.S. mesh coals to demonstrate that grinding coals finer, would allow more pyrite to be extracted. The range of pyritic sulfur differences between the two mesh sizes was between -0.03% and 0.21% with a mean of 0.08% absolute for the 18 coals studied. The worst set of data was obtained on a high rank vitrain type coal. They concluded that particle size effected the extraction efficiency of nitric acid. However in 1964, H. R. Brown and co-authors(20) pointed out that careful attention to agitation of the mixture during extraction of coal with dilute nitric acid has the same effect as grinding the sample to -200 B.S. mesh size.

A 1967 report showed the Bituminous Coal Research (BCR) ashing method yielded higher values for pyritic sulfur than the ASTM standard method.(21) Twelve coals with pyritic sulfur values from 0.2% to 16.0% absolute were used in the study. The average difference between the BCR and the ASTM standard method was reported to be 0.15% for the twelve coals.

In 1975 the Illinois State Geological Survey reported a comparison of x-ray fluorescence, $LiAlH_4$ reduction and the

ASTM standard methods for determining pyritic sulfur in coal.(3) Data from the study showed suitable agreement between total iron values as determined by the ASTM hydrochloric acid and nitric acid extraction procedures and the x-ray fluorescence method. The authors of the report concluded that the total pyritic iron (sulfur) was removed by nitric acid extraction. They also showed no apparent influence of coal particle size on determined pyritic sulfur values. In 1977, J. K. Kuhn, a co-author of the 1975 Illinois Survey Report, concluded that small pyrite particles could be occluded in coal particles or encased in a kaolin lattice which would give rise to small errors of 0.1% to 0.2% absolute.(22) This difference is less than what is normally observed between different samples from the same coal seam or pile.

Additional support for the ASTM standard method came in a report from N. Suhr and Peter H. Given at the Pennsylvania State University.(23) In this study of seven coals, the authors noted that the worst error due to incomplete extraction of pyrite with nitric acid was a lowering of the absolute organic sulfur value from 0.55% to 0.44%. The seven coals were analyzed by first extracting with nitric acid, and then washing, drying, and ashing at 750°C to determine residual iron. Residual iron was extracted from the ash with an $HF/HClO_4$ solution and determined by atomic absorption spectroscopy. The residual iron is a measure of the incomplete extraction of pyrite by the nitric acid which leads to an error in pyritic sulfur and organic sulfur (by difference) determinations. They concluded that the nitric acid extraction of pyrite from coal was essentially complete.

The presence of sulfides, either as sphalerite, chalorphyrite, pyrrhotite, or galena, introduces an additional error into the ASTM standard method for sulfur forms analysis. These minerals may dissolve to form hydrogen sulfide gas during the hydrochloric acid extraction procedure. The sulfur content of these minerals is not measured directly in the ASTM procedure. High values for the organic sulfur are obtained if these minerals are present because of the failure to make the necessary correction to the mineral sulfur.

All non-pyritic iron species may not be soluble in the hydrochloric acid extraction. The presence of sinderite ($FeCO_3$) can make the pyritic sulfur value too high if incomplete hydrochloric acid extraction of this mineral occurs. Material balance work done by R. Miller and P. H. Given has indicated that this is not a major problem.(24) A 1979 report gave a comparison of two hydrochloric acid extraction procedures, a 30 minute boiling extraction and a 40 hour extraction at 60°C. The two extraction procedures showed very good agreement. Siderite, unless completely absent in the coals tested in the study, does not cause a significant problem.

In summary, the ASTM standard D 2492 has been the subject of continued criticism. However, nothing better has passed the ASTM committee process. During the committee process new proposals must be supported by analytical data with acceptable repeatability and reproducibility. Round-robin and double blind studies are used to determine the statistical significance of a method. The current ASTM D 2492 standard is under review and perhaps new methods for the determination of sulfate, pyritic and organic sulfur will be included in the next revision of the standard method.

C. Sulfate Sulfur Determination

The ASTM method D 2492 for sulfate sulfur determination involves a 30 minute extraction with hot 4.8 M hydrochloric acid followed by a gravimetric sulfate determination as described previously under the Eschka method.(2) This procedure is very time consuming and requires good analytical skills. On the other hand, if the method is done correctly the results are quite accurate. Because the sulfate contribution is usually small there has been little work done to improve this determination.

Variations of the basic procedures for sulfate sulfur determination include titrimetry and turbidimetry. Limited success has been achieved using these variations due to interferences from extracted materials which must first be removed before an analysis can be performed. Results of both methods compare favorably to ASTM gravimetric sulfate checks. Another variation of sulfate determination is ion-exchange chromatography which is growing in acceptance.(25)

D. Pyritic Sulfur Determination

1. Mössbauer Spectroscopy

R. L. Mössbauer discovered the Mössbauer effect in 1958 and later received the Nobel prize in physics for his work.(26) The effect has been widely used by researchers in a diversity of disciplines. In the late 1970's the chemical literature contained many articles about the application of Mössbauer spectroscopy in the analysis of coal samples. A description of the Mössbauer spectroscopy effect was reported by F. E. Huggins and G. P. Huffman of which a summary will be presented.(27)

Mössbauer spectroscopy, or nuclear gamma ray spectroscopy, describes the phenomenon of recoilless resonant emission and the absorption of gamma rays. Potassium and iron are the only two elements commonly found in coal which exhibit the effect. Mössbauer spectra are obtained by exciting ^{57}Fe with the radioactive decay of ^{57}Co in a platinum matrix. The subsequent return of the excited ^{57}Fe to the ground state is followed by the emission of 123 KeV and 14.4 KeV photons, which are used to excite the ^{57}Fe in the pyrite. Only the 14.4 KeV photon is used for Mössbauer spectroscopy. The spectrum is observed using a source other than iron for excitation because the electronic charge redistribution takes place much faster than the excited state.(28-29)

Montano reported Mössbauer data for three West Virginia coals.(30) Mössbauer effects on iron in the coals were independent of the size of the crystallites. Evidence of the oxidation of iron, which takes place at the expense of sulfate during low temperature ashing, was presented in this study. Samples examined after low temperature ashing showed new quadruple splitting in the spectra which could be attributed to iron(III) formed on the surfaces of pyrite and iron sulfate. In spite of this apparent oxidation, agreement with the standard method reproducibility for pyrite and sulfate was obtained for two of the three coals.

Levinson and co-authors(31-32) used Mössbauer spectroscopy to study the iron forms present after hydrochloric acid and nitric acid extractions of coal. They concluded that a decrease in the spectral intensity of treated versus untreated coal was unequivocal evidence that hydrochloric acid treatment removes some pyrite. Also, the remaining spectrum after nitric acid extraction showed about 5% iron absorbance. They made no attempt to quantify their findings reported in this paper by studying a large library of coals.

In a method developed by Huffman and Huggins(6) mixtures of pyrite and coconut charcoal were used to determine the Mössbauer mass-absorption thickness for pyrite. The determined mass-absorption coefficient was then used to calculate the percentage of pyritic sulfur in the coal. The data reported on seven coals was within the reproducibility limits of the ASTM standard method. However, there were no observable trends when comparing the pyritic sulfur values to those determined by the ASTM standard method. If the values for pyrite sulfur were all higher than the ASTM standard method one could invoke the incomplete extraction argument. For example, pyritic sulfur data obtained by Mössbauer were 1.04% and 0.02% on two different coals while determinations with the ASTM standard method yielded 0.90% and 0.21%, respectively. The authors concluded that the direct, non-destructive measurement of pyrite using Mössbauer spectroscopy was more accurate than the ASTM standard method.

An article on the construction of a simple Mössbauer pyritemeter was published in 1979 by Jaggi and Rao.(33) They proposed using a stationary sample and measuring the incident gamma-radiation at an angle equal to the gamma cosine of theta. The angle setting method eliminates the need for sophisticated drives and multichannel analyzers, and it also shortens the computational time. The main flaw with the design is that the sulfate sulfur would contribute to the pyrite absorption. This method could be applied to freshly mined samples as a rough check of the pyrite concentration.

Neto and co-authors reported successful application of Mossbauer to Brazilian coals containing about 30% ash.(34) The constant acceleration mode was used for a ^{57}Co:Rh radiation source. The recoilless fractions were determined on standards of FeS_2 and $FeSO_4 \cdot 7H_2O$. The results of pyrite determinations on coal samples before pretreatment with hydrochloric acid were higher than the values determined by the ASTM standard method. The contention is supported that hydrochloric acid removes some of the pyritic iron which is lost in the ASTM standard method for pyritic sulfur determination.

In summary, Mössbauer spectroscopy shows promise for the direct determination of pyrite. Differences in Mossbauer parameters of chemically treated coals indicate differences with those matrices and thus may be an important tool in future characterizations of coals. Further work is needed to study this method in comparison to other methods currently available. Mössbauer results generally report values for the pyritic sulfur which are higher than those obtained by the ASTM standard method.

2. Low Temperature Ashing

Low temperature ashing (LTA) of coal using an oxygen plasma was reported by Gluskoter in 1968.(35) The investigation used a high energy electromagnetic field to generate a plasma started by an electrodeless discharge ring. The purpose was to ash a coal at low enough temperatures so as not to change the chemical state of the inorganic matter and selectively remove the organic matrices. The procedure required 80-90 hours, with periodic stirrings to expose a fresh surface. Chemical analysis showed a portion of the total sulfur had been lost.

Hamersma and Kraft(25) presented data that indicated acceptable agreement between plasma ashing and ASTM atomic absorption measurements for pyrite in coal. However the sulfate sulfur values were 30% higher on the average than the ASTM standard method. A tailings coal sample showed a 22-fold increase from 0.02% to 0.44% in sulfate sulfur after low temperature ashing. The authors concluded that this was due to very fine occlusions which were difficult to extract by the standard method. It would seem more likely that the tailings sample contained finely divided pyrite which was easily oxidized to sulfate by the low temperature ashing procedure.

Another study compared five variations of low temperature ashing with a modified standard method.(36) Iron concentrations were determined by inductively coupled plasma spectroscopy. The atomic ratios of sulfur to iron were reported to vary according to sample origin and not proportionately with sulfur content. The validity of the assumption that pyrite occurs mainly in the formula FeS_2 and that iron can be correlated to pyritic sulfur concentrations is questioned. Each LTA method used in the study showed differing recoveries ranging from 57% to 85% in pyritic sulfur. The authors made no attempt to optimize recoveries or suggest reasons for the poor recoveries. It appeared that in two cases the ashing procedures were designed to give poor results.

Comparison of microwave ashing and LTA of coal was done using chemical methods and Mossbauer spectroscopy to determine sulfur forms.(37) The results suggested effective ashing without the oxidation of pyrite by either method. However, in both methods the iron sulfate mineral rozenite is altered from $FeSO_4 \cdot 4H_2O$ to an unidentified iron(II) bearing compound and at least two iron(III) bearing compounds. Other sulfates were also reported to dehydrate and sometimes decompose.

In summary, the LTA method for the determination of pyritic sulfur needs to be improved before it can become an acceptable standard method since the sulfate sulfur value is affected. Some authors report no apparent changes in sulfate sulfur after ashing when their data clearly indicated a 30% relative increase. On the other hand, others reported significant losses in sulfate while using the identical method. Consequently, the user is left to decide if low temperature ashing is worth the 80 hours required to ensure complete ashing when the data can only be considered to be qualitative.

3. X-Ray Fluorescence

X-Ray Fluorescence determination of sulfur and inorganics in coal was reported by Sweatmen and co-authors(38) and L. T. Kiss.(39) The adverse effects of particle size were avoided by grinding the marcasite to about 0.2 microns. Elements must be uniformly distributed on the atomic scale to avoid losses in fluorescence radiation.(40) The judicious selection of standard compounds seems to be the key for accurate analytical results. The precision of x-ray fluorescence is dependent on the time and count-rate of the analysis. Newer computers have made dramatic improvements in this area possible.

In support of the Meyers desulfurization process, coal was pelletized and analyzed for pyrite content by x-ray fluorescence using the iron K-alpha line.(41) The major problem encountered was the preparation of standards to calibrate the pyrite concentration of a treated coal. When compared to the ASTM standard method, reasonably accurate data within ASTM reproducibility was obtained for all the coals. Above 3% pyrite accuracy and precision of the determination suffered from matrix effects.

4. X-Ray Diffraction

In x-ray diffraction experiments, atomic planes within the crystal reflect electromagnetic radiation in lines as defined by Braggs relationship. Thus the determination of pyrite depends on its cubic structure, which produces measurable x-ray diffraction lines. The method has not been extensively published because Greer and others have demonstrated that pyrite can occur in large framboidal assemblies as well as single crystals.(42) The random diffraction patterns produced by the framboidal pyrite limits the sensitivity of the method to those coal samples with over 5% pyritic sulfur. High mineral matter can also give rise to background interference.(43-44)

5. Oxidation

Oxidation has long been used as a method for the determination of total sulfur. In a paper by Finkelman, pyritic sulfur was determined by using 15% hydrogen peroxide to convert pyrite to sulfate sulfur.(45) The sulfate was determined colorimetrically using a Hach DR #100 portable colorimeter. The advantage of this method is the analysis time of one hour. The problems are that water insoluble sulfate may be measured as pyrite. Also, the recovery was less than 100% on a pure sample of known pyrite concentration and was therefore calibrated 6% higher mathematically. Finally the results presented were effected tremendously by particle size. The author assumes the extraction with 15% hydrogen peroxide to be more effective than the ASTM 2 N nitric acid extraction for pyrite removal and makes another empirical correction to calibrate the data to the correct result. However, it could be possible that a peroxide solution in such a high concentration, oxidizes organic sulfur linkages known to be present in coal.

6. Reduction

J. K. Kuhn and co-authors reported the results of the determination of sulfur forms for nine coals using reduction with lithium aluminum hydride and the ASTM standard method extraction procedures.(46) In the reduction method the sulfate sulfur is first removed by hydrochloric acid extraction. The remaining coal is then reacted with lithium aluminum hydride to reduce pyrite and produce hydrogen sulfide. The hydrogen sulfide gas is subsequently trapped in a cadmium sulfate solution by the formation of cadmium sulfide which is then analyzed to determine pyritic sulfur. The reduction method compares very favorably with the ASTM standard method for sulfur forms in coal. This work supports the ASTM extraction with 2 N nitric acid because no particle size effect was seen between -60 and -400 mesh. Mass balance was not obtained when the sum of all three forms was compared to the total sulfur. They concluded that hydrogen sulfide could be lost during the hydrochloric acid extraction step.

An Australian laboratory showed that careful control of the reduction temperature using tin powder and orthophosphoric acid could yield sulfide sulfur separate from pyrite and sulfate.(47) The reaction of sulfide sulfur occurs between 60-120°C which was too close to the reduction temperatures of pyrite and sulfate sulfur forms for the simultaneous determination. The method has the advantage of accounting for sulfide sulfur separately so that it will not be calculated as organic sulfur. Agreement with the ASTM standard method was well within reproducibility limits for the coals studied. However, the amounts of sulfate and pyritic sulfur were well below those commonly found in American coals. It was concluded that the non-pyritic sulfide sulfur found in the coals examined by the procedure had values predominantly less than 0.01% with only a few ranging from 0.05 to 0.1% absolute. The method could yield important sulfur information about the possibility of a fourth sulfur form currently not considered as significant in coal chemistry.

A recently developed method for the determination of hydrogen sulfide gravimetrically by precipitation with copper may be of significance in pyrite determinations using the reduction method.(48) Elemental copper suspended in acetonitrile or benzene solvents reacts with hydrogen sulfide spontaneously to form a black copper sulfide ($Cu_{1.8}S$) which can be determined by weight. The authors report a nonstoichiometric sulfide which does follow the reaction equation previously reported in the literature(49) $2Cu + H_2S \rightarrow Cu_2S + H_2$. They also observed no hydrogen evolution as suggested by the preceeding equation. Perhaps future work will reveal a better stoichiometry with less carcinogenic solvents.

In summary, the reduction methods for sulfur forms can be used as a check of the ASTM standard extraction/oxidation methods. The selection of the reducing agent determines if a prior extraction is needed for sulfate sulfur. The lack of enthusiasm about these methods could be caused by the unique rotten egg odor and the poisonous nature of the hydrogen sulfide gas.

7. Thermomagnetogravimetry

Thermomagnetogravimetry is a combination of thermogravimetry and thermomagnetic analysis.(50) The principle of operation uses a Cahn RG electrobalance with a sample suspended in a controlled atmosphere between the poles of a permanent magnet. Another essential component is a heater with thermocouple control. Using the weight loss curve and variations in the magnetic field (apparent weight losses or gains measurements) the proximate analysis and pyrite sulfur content of coal can be determined. Errors in the pyrite determination can occur if variations in the iron species not associated with the sulfur in the coal cause interferences. Also the sulfate sulfur would be measured as pyritic sulfur. The authors showed disagreement with the ASTM standard method when they stated that the hydrochloric acid extraction procedure removes sulfate sulfur which should be analyzed as pyrite.

E. Organic Sulfur Determination

The determination of organic sulfur by the current ASTM standard method incorporates the errors of sulfate, pyritic and total sulfur determinations. To avoid these problems, several alternative procedures have been proposed in the literature for the direct determination of the organic sulfur. Most of these methods are not widely used and hence the need still remains for a simple and inexpensive method.

1. Soft X-Ray

In the soft x-ray method (SXR) one measures the ratio of the sulfur K-Beta/K-Beta' peaks and a suitable background intensity.(51) The calibration standards were solids of high purity which were obtained commercially. SXR uses a two angle setting which reduces analysis times of all sulfur forms to 1 1/2 hours. The reported precision of the method is approximately 2% relative for total sulfur and 5% for the sulfur forms. Problems with the method are that it requires a specially modified apparatus and the measured intensities are of the order of 1 - 2 eV and therefore resolution problems occur when large amounts of several sulfur forms are present. Organic sulfur determination on a large library of coals would demonstrate if the method is as accurate and precise as reported.

2. Microprobe Analysis

Sutherland first used an electron microprobe to determine the organic sulfur in coal.(52) The microprobe method makes use of a finely focused electron beam which strikes a carefully selected area in the coal to produce x-rays characteristic of the elements present. Pretreatment with hydrochloric acid to remove iron and sulfate sulfur and a 1.2 specific gravity float/sink separation was required before an analysis could be performed. His work reported results on only two coals, which were 15% (relative) higher in organic sulfur than the values obtained by the ASTM difference method.

Raymond described the use of a new standard for determining organic sulfur in coal, which was composed of carbon beads containing four percent sulfur.(53) Statistics performed on vitrinite grains suggested that only 10 minutes were required for 2% reproducibility. Vitrinite grains contain an organic sulfur content approximately equivalent to the mean of all the coal macerals. Good agreement was shown between the ASTM difference method and the electron microprobe method on the 29 coals reported. A potential problem with the method is that incorrect petrographic identification could result in errors. The operator would have to first become a skilled petrographer to ensure meaningful results. Additionally, no mention was made of the possibility of high pyrite concentrations causing interferences.

The possible lithotype identification problems can be solved by using a scanning electron microscope (SEM) in conjunction with energy dispersive x-ray spectrometer (EDX). Sutherland coined the name of microprobe analysis which was dropped for the acronym SEM-EDX. Discrepancies observed in several of the samples analyzed by both SED-EDX and the ASTM standard method were attributed to incomplete extraction of the nitric acid.(54) Another study using SED-EDX showed no discrepancies in the two method in the coals reported.(55) Dutch researchers used the incomplete extraction with nitric acid to explain the difference of 2.71% absolute between the ASTM difference method for organic sulfur and SED-EDX organic sulfur.(56) Finally, C. P. Clark and co-authors reported EDX spectroscopy capable of measuring micro and bulk levels of organic sulfur in coal. They also showed agreement with the ASTM standard methods for pyrite and total sulfur.(57)

In summary, the SEM-EDX data seems to have good agreement with ASTM standard data most of the time. Using the SEM combination makes identification of lithotypes more accurate. The calibration standard developed by Raymond appeared to be adequate in several of the studies. Total analysis times were not reported for the SEM-EDX procedures in any of the papers reviewed. The shortage of the SED-EDX instrumentation in current analytical laboratories could be responsible for its lack of application.

3. Low Temperature Ashing

Low temperature ashing (LTA) was previously discussed as it related to inorganic sulfur determination. The basic assumption of this technique is that mineral sulfur does not undergo oxidation and that the organic sulfur is selectively removed during the low temperature ashing. It was found that pyrite oxidation increased directly with ashing temperature and inversely with particle size.(58) The sulfur dioxide generated by the oxidation of organic sulfur was trapped as a solid at -196°C and then converted to sulfate by hydrogen peroxide upon warming. The sulfate was determined using a Pioneer Model 10 Ion Chromatograph.

Problems associated with the above LTA method are that the trapping system is complicated and that leaks in the system can cause losses. Sulfur dioxide can also deposit on the walls of the glass trap and reduce repeatability.

Finally, due to the small sample size of 25 mg, any coal sample inhomogeneity can cause error in the analysis.

4. Pyrolysis

In a pyrolysis method for determining organic sulfur, coal samples were heated in a nonoxidizing atmosphere to evolve the pyrolysis products.(59) The sulfur content of these products was then determined by their oxidation products. The pyrolysis temperature used was 500 - 600°C and the heating rate could be programmed. No data was presented in the above patent application. However, a study of several Nova Scotian coals indicates that this method could have some major problems.(60) For example, the reaction of pyrite to pyrrhotite could cause the emission of hydrogen sulfide gas. Also, a substantial amount of the released sulfur could become trapped in the carbon matrix as organic sulfur. Consequently, the pyrolysis method could only be applied to coal which had been previously extracted for pyrite and not as a one-step method as reported.

CHAPTER III

EXPERIMENTAL

A. Instrumentation

Total sulfur in all coal samples was determined using a LECO SC-132 Sulfur Determinator. Calibration standards used were National Bureau of Standards material 1632B and LECO ultimate analysis coal standards. The standard reference materials used had sulfur values as close as possible to those of the analysis sample to reduce the possibility of calibration error.

The moisture, ash, fixed carbon and volatile matter values were determined using a LECO MAC-400 Proximate Analyzer, a single furnace unit. This instrument meets and usually exceeds ASTM requirements for repeatability and reproducibility. The MAC-400 is currently under review to be accepted as a standard method by an ASTM committee on proximate analysis in coals.

The drying oven used was a Fisher Isotemp model 287 vacuum oven with a gas circulating pump attached. The temperature was maintained at 100 $\pm 5^{\circ}C$ for two hours of drying under a circulating atmosphere of nitrogen. Drying was greatly facilitated by passing the circulating gas over a vertical water cooled condenser packed with 1 mm glass beads. The condensate water was collected in a round bottom flask and discarded.

Optimized milling conditions for stirred ball slurry attritor mills were used for coal particle size reduction below two microns.(61) Coal slurries of 20% solid W/W in water were milled for 2 minutes using either 3/16 or 1/4 inch stainless steel media in either a Union Process Mill 1-S or Yoon Mill.

The centrifuge used was an International, model K, run at 1700 r.p.m. for 45 minutes to achieve float-sink separation. The size two cups could hold approximately 150 ml of slurried coal.

Weighings were done on a Sartorius Electronic Analytical Balance. The calibration was checked with a type S weight set and found to be constant. All analysis samples were weighed to a tenth of a milligram.

The raw coals used were from the Western Kentucky University Coal Characterization Library. Splits of -4 mesh coal stored under argon at -5°C were pulverized to -60 mesh, split, and analysis samples (50 - 100 g) prepared from the splits. To help prevent the possible oxidation of pyrite by air, a layer of nitrogen and heavy sealing tape was applied to each bottle before storage in a freezer. ASTM procedures for obtaining a representative analysis sample were followed.

The float-sink separations were accomplished in an apparatus which follows the recommendations of ASTM D 4371.

Aqueous solutions of $ZnCl_2$ were used as the separation medium. The apparatus consisted of a 2 liter Erlenmeyer flask with a ground-glass joint opening which could be connected to a funnel with similar capacity. After a float-sink separation was achieved a rubber stopper was inserted into the bottom of the funnel to separate the float slurry in the funnel from the sink slurry in the flask. The funnel was then separated from the flask and the float slurry was filtered with a Büchner funnel under vacuum. The float was then dried for 2 - 3 hours under nitrogen in the drying oven. Optimized milling conditions were used as described earlier on the float coal portion.

Extraction work was done in 250 ml round bottom flasks in heating mantles mounted over magnetic stirrers to allow for variable stirring and heating controls. The apparatus for trapping H_2S and SO_2 used two flasks filled with 5 N $CdSO_4$ and 10% H_2O_2, respectively. Titration with 0.1 N NaOH was used to measure the H_2SO_4 produced in the solution.(5)

B. Reagents

Reagents 1 - 7 were prepared according to ASTM D 2492 and D 3177 standard recommendation.(2)

1. Ammonium Hydroxide Solution -- mix 1 part aqueous ammonia and 10 parts of distilled water to make a 1.3 N solution.
2. Barium Chloride Solution -- dissolve 100 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 liter.

3. 12 N Hydrochloric acid -- (specific gravity 1.19) reagent grade concentrated aqueous HCl.
4. 4.8 N Hydrochloric acid -- mix 2 volumes of solution 3 above with 3 volumes of water.
5. Hydrogen peroxide was used at 30% and 10% concentrations.
6. Methyl Orange Indicator Solution -- dissolve 0.02 g of methyl orange in 100 ml of hot water.
7. 2 N Nitric Acid Extraction Solution -- mix 1 volume of concentrated aqueous HNO_3 with 7 volumes of water.
8. 1.3 N Cadmium Sulfate Solution -- dissolve 128.0 g ($3CdSO_4 \cdot 8H_2O$) in water and dilute to 1 liter.
9. Zinc Chloride Solution -- 1.30 specific gravity is made by dissolving $ZnCl_2$ in water until the correct density is achieved as measured by a hydrometer.

C. Procedures

1. Nitric Acid Extraction

a) Weigh 6 ±0.1 grams of coal to the nearest 0.1 mg and place into a 250 ml round bottom flask.

b) Add 120 ml of 2 N nitric acid solution and mix with a magnetic stirrer until all the coal appears to be wet. This requires 5 - 10 minutes depending on the coal. If wetting of the coal cannot be achieved in 15 minutes the addition of 5 ml of ethanol will aid in wetting.

c) Effective stirring has been reported to improve extraction. Therefore continuous stirring through out the entire procedure is required.

d) Start timing the reflux for 30 minutes when the solution commences boiling. Heating was controlled by using a 180 watt mantle connected to a 120 volt variable transformer set at 50 - 60% of full scale.

e) Periodically wash the walls of the reaction flask with a few milliliters of dilute HNO_3 so that no coal is left unreacted on the sides of the flask.

f) Filter the coal and HNO_3 slurry while hot using a 5.5 cm Büchner funnel and two layers of Whatman #1 or #2 filter paper under vacuum. If an aspirator vacuum is used make sure a trap is installed to prevent contamination of the filtrate by backwash into the flask.

g) Wash the coal with small portions of hot distilled water to ensure the removal of all the HNO_3 extracts. Wash with about 500 ml of water in small portions. If the filtrate is still colored as it leaves the funnel, this indicates extracted organic material.

h) Transfer the filtrate into a 1000 ml beaker using four rinses of distilled water to ensure complete transfer of the extract solution.

i) Add 5 ml of 30% H_2O_2 and boil for 10 minutes. This ensures conversion of all sulfur forms to sulfate ions and iron(II) to iron(III).

j) Precipitate the iron by slowly adding concentrated NH_4OH until a slight excess is present, as measured by pH indicator paper.

k) Add 5 ml excess NH_4OH with constant stirring to coagulate the $Fe(OH)_3$.

l) Boil the mixture for five minutes, remove the heat and allow the solution to cool until warm.

m) The solution should be clear after the $Fe(OH)_3$ has settled to the bottom. If not, there may be unprecipitated iron or extracted organic material. Check for the complete iron precipitation by the addition of several drops of aqueous NH_4OH.

n) Filter by gravity using Whatman #1 filter paper and collect the filtrate in a 1000 ml beaker.

o) Wash the filter paper with several washings of hot 1.3 N NH_4OH solution to help remove any trapped sulfate ions.

p) Discard the $Fe(OH)_3$ and follow procedure two for the determination of sulfate sulfur.

2. <u>Precipitation of Sulfate ions using $BaCl_2$</u>

a) Add 2 or 3 drops of methyl orange solution and neutralize the filtrate of procedure 1, step n, by cautiously adding concentrated HCl until the solution just turns pink. Then add 1 ml HCl in excess.

b) Bring the solution to a boil and slowly add 10 ml of $BaCl_2$ solution from a pipet, in a dropwise manner with continues stirring.

c) The $BaCl_2$ solution must be in excess. Continue boiling gently for 10 to 15 minutes and allow to stand warm for at least 2 hours. In this work the solutions were left overnight with a watch glass as a covering to reduce evaporation.

d) Filter while warm through fine ashless Whatman #42 paper and wash with hot water until 1 drop of $AgNO_3$ solution (about 5% concentration) produces no more than a slight opalescence when added to 8 to 10 ml of the filtrate.

e) Place the wet filter paper containing the precipitate of $BaSO_4$ in a porcelain crucible which has been dried to constant weight. Generally, after 4 hours of heating at 850°C constant weight has been achieved.

f) Place the sample crucible in a cold muffle furnace with an air flow of 2 - 4 volume changes per minute and gradually allow the temperature to rise to nearly 500°C until most of the paper has been smoked off. At no time should the sample be allowed to ignite.

g) Once the paper is removed gradually raise the temperature to 800 ±50°C and heat to constant weight.

h) Weigh the $BaSO_4$ to the nearest 0.1 mg.

i) Results in percent sulfate are calculated by the formula:

$$\frac{(\text{Weight of precipitate - weight of blank})\ (13.735)}{\text{Weight of raw coal}}$$

j) The blank is determined by conducting the procedures with all the reagents and no coal sample. Nominal values for the blank are between 1 and 2 mg. The 13.735 multiplier is a combination of constants used to convert $BaSO_4$ to a sulfur value.

3. Determination of Sulfide Sulfur

a) This procedure was used for samples expected to contain sulfide minerals. The samples were extracted with HCl or HNO_3.

b) Figure 1 illustrates the set up of the apparatus used for trapping the H_2S or SO_2 gases.

c) Potential gases were carried from the reaction vessel to the traps by 50 ml/min of nitrogen gas flow. The traps were fitted with fritted discs to bubble the gases.

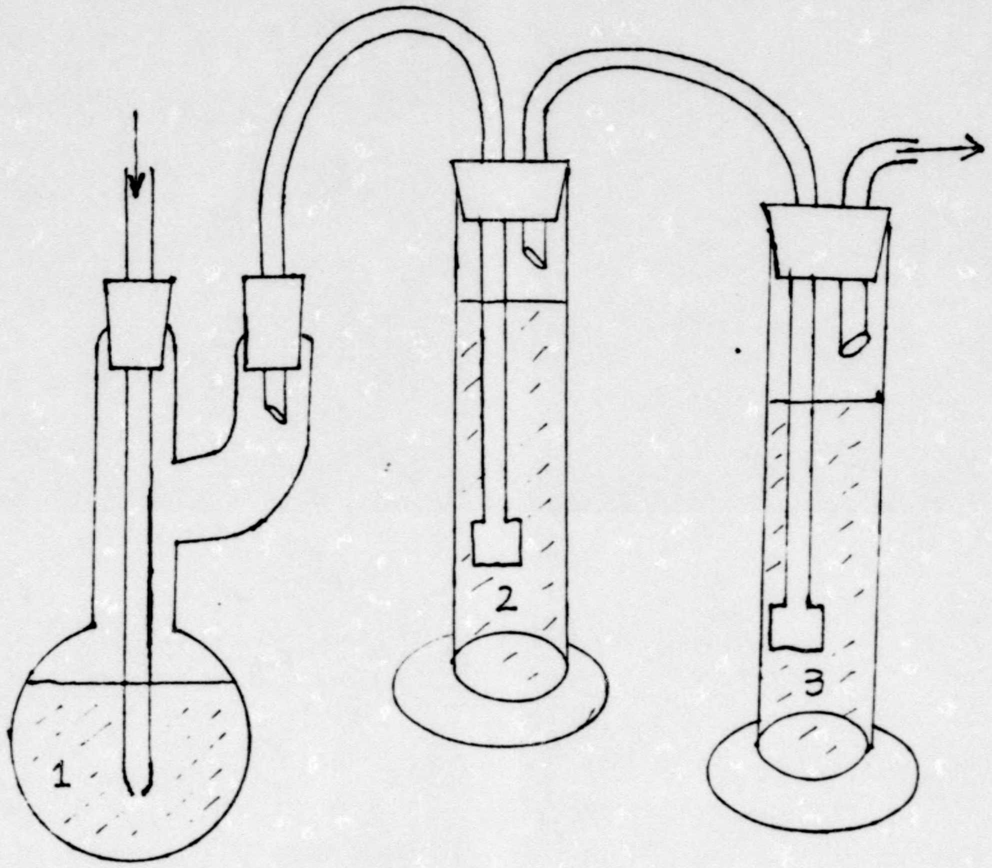

Figure 1: Apparatus for trapping of H_2S or SO_2 gases.

Solution 1: the extract acid being used

Solution 2: 10% H_2O_2 solution

Solution 3: 1.3 M $CdSO_4$ solution

d) The following reaction chemistry is believed to occur in the traps.

$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$

$$H_2S + CdSO_4 \longrightarrow H_2SO_4 + \underset{\text{yellow precipitate.}}{CdS}$$

e) Based on the above reaction one can titrate the H_2SO_4 formed with 1 N NaOH to an end point pH of 5.25 as measured with a meter.

f) A blank was run to correct for the possibility of HCl or HNO_3 vapor which could have been trapped.

g) Sulfur concentrations were calculated by the equivalents of NaOH used.

4. <u>Supercleaning of Coals by Float/Sink Separation</u>

a) Weigh 500 g of -60 mesh coal.

b) Mix the coal with 1.30 specific gravity $ZnCl_2$ solution in a 1.5 - 2.0 liter container with a sealable lid. Stir continuously while adding small amounts of the $ZnCl_2$. During the addition a paste is obtained which turns to a slurry as more $ZnCl_2$ solution is added.

c) Shake the coal slurry until complete wetting has been achieved. It may be necessary to add a few milliliters of ethanol.

d) Let the coal slurry set overnight, or longer, in the float-sink apparatus. The $ZnCl_2$ solution should be clear between the layers of float and sink portions.

e) Separate the float container from the sink container by inserting a rubber stopper between the sections. Filter the float coal through two layers of Whatman #1 paper using a Buchner funnel and vacuum. Wash with small amounts of water to remove the majority of the $ZnCl_2$ from the coal. The $ZnCl_2$ solution can be reused. Then change the filter flasks and wash with 1000 ml of water.

f) Discard the sink portion of coal.

g) Dry the float portion for 3 hours at 110°C in a recirculating atmosphere oven.

h) Mill 50 g of dry coal in water with 20% solids loading at 290 r.p.m. for 2 minutes using 1/4" media in a Union Process Mill or Yoon Mill.

i) Filter and dry the coal as described previously.

j) Slurry 20 g of dried milled coal in 150 ml of 1.30 or 1.40 specific gravity $ZnCl_2$ solution.

k) Centrifuge for 45 minutes at 1700 r.p.m.

l) Filter the slurry as described in (e) and dry as described in (g) of this procedure.

m) Analyze for sulfur, ash, moisture and volatile matter using LECO instrumentation.

CHAPTER IV

RESULTS

The bituminous coals used in this study have been characterized for the Western Kentucky University Coal Characterization Library. Each coal has been assigned an identification number that will be used throughout the results and discussion sections. All eight of the coals are part of a current Department of Energy study. Four of the coals originated from Muhlenberg County, Kentucky, while the remaining four were from out-of-state. Table 2 lists the proximate and ultimate analysis, apparent rank, Hardgrove index, F.S.I. and forms of sulfur data.(62)

Table 3 represents the mean values for eight coal samples obtained from quadruplicate determinations using the nitric acid extraction method. The data is presented on an as determined basis. The moistures were determined after two hours of drying in a circulating nitrogen atmosphere oven. Coal 86039 was determined without drying and was allowed to come to equilibrium with room atmosphere. Table 4 shows the changes in the ash content after nitric acid extraction as compared to untreated coal. The changes in moisture and ash content necessitate the comparison of coals on a dry, ash-free basis. The average ash values were decreased by 32% ±13% at one standard deviation.

TABLE 2

Characterization of Coals

Coal No.*	85098	85099	86024	86025
Seam	WKY #11	WKY #12	WKY #10	WKY #9
County	Muhlenberg	Muhlenberg	Muhlenberg	Muhlenberg
Mine	Sinclair	Sinclair	Gibraltar	Gibraltar
<u>Proximate</u>				
Moisture**	4.31%	5.62%	4.76%	4.07%
Ash	18.96	15.91	22.97	15.50
Volatile matter	34.7	32.8	31.6	35.3
Fixed Carbon	46.3	51.3	45.4	49.2
<u>Ultimate</u>				
Carbon	63.22	66.34	60.25	66.74
Hydrogen	4.35	4.39	4.20	4.59
Nitrogen	1.28	1.46	1.39	1.42
Sulfur	5.96	4.02	4.45	4.55
Oxygen(by Diff.)	6.19	7.85	6.71	7.17
<u>Miscellaneous Analysis</u>				
Btu/lb	11,830	12,050	11,012	12,350
Apparent rank***	hvAb	hvBb	hvBb	hvAb
Hardgrove index	62	54	84	66
F.S.I.	3.00	3.00	3.00	4.00
<u>Forms of Sulfur</u>				
Pyritic	2.85	1.62	2.43	1.73
Sulfate	0.55	0.51	0.04	0.51
Organic	2.60	1.93	2.05	2.40

* Accession number, Center for Coal Science.

** Moisture is as determined; all other analyses are reported on a dry basis.

*** Using as determined moisture.

TABLE 2 (Continued)

Characterization of Coals

Coal No.*	86038	86039	8640	86041
Seam	ETNA	Wyodak	Upper Kittanning	Lower Kittanning
County	Marion	Campbell	Clearfield	Cambria
State	TN	WY	PA	PA
Mine	Sand Mtn.	Jacobs Ranch	Penn #4	Dean #1
Proximate				
Moisture**	1.50%	22.51%	1.25%	1.80%
Ash	9.25	9.26	10.21	11.31
Volatile Matter	24.90	43.54	20.96	24.84
Fixed carbon	65.84	47.20	68.83	63.85
Ultimate				
Carbon	80.15	53.78	81.26	75.90
Hydrogen	4.76	4.59	4.56	4.73
Nitrogen	1.48	1.01	1.60	1.40
Sulfur	1.16	0.76	0.65	2.29
Oxygen(by diff.)	3.17	30.57	1.59	4.35
Miscellaneous Analysis				
Btu/lb	14,166	11,568	13,848	13,254
Apparent rank***	mvb	sub	mvb	mvb
Hardgrove Index	112	70	98	89
F.S.I	8.50	0.00	5.00	7.50
Forms of Sulfur				
Pyritic	0.67	0.16	0.11	0.81
Sulfate	0.05	0.07	0.02	0.36
Organic	0.44	0.53	0.52	1.12

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* Accession number, Center for Coal Science.

** Moisture is as-determined; all other analyses are reported on a dry basis.

*** Using as-determined moisture.

Table 3

Analytical Results for Coals Extracted with 2 N Nitric Acid

Coal No.	Moisture	Volatile Matter$_{ad}$*	Ash$_{ad}$	Sulfur$_{ad}$
85098	1.48	34.28	11.61	2.10
85099	1.18	34.55	9.95	1.25
86024	0.92	35.94	14.16	0.93
86025	1.06	35.47	8.79	1.66
86038	0.78	25.38	6.80	0.46
86039	19.32	52.37	3.53	0.31
86040	0.84	23.50	9.25	0.48
86041	0.72	25.30	9.09	0.74

* as determined basis

TABLE 4

Ash Comparison of Extracted Coal vs. Untreated Coal on a Dry Basis

Coal No.	Untreated Coal (Uc)	Extracted Coal (Ec)	Ec-Uc	Difference*
85098	18.04	11.78	-6.26	-34.7
85099	15.71	10.07	-5.64	-35.9
86024	21.64	14.30	-7.34	-33.9
86025	15.33	8.88	-6.45	-42.0
86038	9.42	6.86	-2.56	-27.2
86039	9.26	4.38	-4.88	-52.7
86040	10.36	9.33	-1.03	-9.9
86041	11.67	9.15	-2.52	-21.6

$$* \ \frac{\text{Extracted Coal - Untreated Coal}}{\text{Untreated Coal}} \times 100$$

Data were collected on the sink portion of four coals to study the effects of the volume of nitric acid used in the extraction procedure. The runs were done under identical conditions except for the changes in the volume of nitric acid. A ratio of 20 ml of 2 N nitric acid per gram of coal was used for all subsequent analysis to ensure complete extraction. The ASTM recommended volume of acid is 10 ml/g depending on the grams of coal used in the analysis. Table 5 provides a data summary of extracted sink samples.

The recovery is only 10 - 20% on the float/sink separation; therefore one could propose that segregation of the sample occurs in this process. The sulfur values for the sink portion in Table 5 are in good agreement with the analysis of nitric acid extracted float coal in Table 3. This agreement suggests that organic sulfur particles contained in the coal are not segregated by the float/sink separation.

Table 6 contains data from an unpublished round-robin study using ASTM method D 2492 for the the determination of pyritic sulfur.(63) The high and low values in each coal sample are significantly different from the mean value. New methods for pyritic sulfur determination may have difficulty in coinciding because the data clearly illustrate a problem with the precision and accuracy of the ASTM standard method.

TABLE 5

Dry, Ash-Free Sulfur Values of Sink Samples Extracted with Different Volumes of Nitric Acid*

Coal No.	6.6 ml/g	10 ml/g	13.2 ml/g	30 ml/g
85098	4.45	3.35	2.23	2.09
85099	2.19	1.97	1.32	1.26
86024	3.33	1.97	1.22	1.14
86025	2.55	2.31	1.80	1.73

* All values are the average of duplicate runs.

TABLE 6

Pyritic Sulfur Repeatability Data of ASTM Task Group

Lab No.	Sample Numbers								
	1	2	3	4	5	6	7	8	9
1	0.15	0.27	0.96	2.02	2.08	2.43	4.26	6.62	10.01
2	0.16	0.30	0.91	1.92	1.93	2.22	4.49	5.96	9.28
3	0.09	0.23	0.87	1.98	1.97	2.53	4.13	6.65	9.90
4	0.12	0.25	0.88	2.03	2.01	2.58	4.41	6.81	10.31
5	0.18	0.44	1.35	1.53	1.54	1.90	3.54	5.77	8.00
6	0.08	0.22	0.74	1.68	1.71	2.13	3.47	5.86	10.72
7	0.01	0.21	0.73	1.69	1.75	2.14	3.81	7.27	8.51
*	0.11	0.27	0.92	1.83	1.85	2.27	4.00	6.42	9.53
**	0.03	0.02	0.04	0.11	0.08	0.12	0.22	0.15	0.37
***	27.3	7.4	3.3	6.0	4.3	5.3	5.5	2.3	3.8

* Mean value.

** Average standard deviation.

*** Average percent relative standard deviation.

Table 7 reports the determined organic sulfur of coals that have been float/sink cleaned to reduce the amount of ash present. The cleaning was conducted in a manner to get a fraction that closely resembled the organic portion of coal and not to maximize recovery, as is characteristically done in float/sink separation. A 1.30 specific gravity solution of zinc chloride was used on all the coals except for 86039 in which a 1.40 specific gravity was employed. The differences between the total sulfur and the sum of the three sulfur forms are very small. The consistency of the method is shown by the mass balance results. The float/sink separations were not as effective on the medium volatile bituminous coals as compared to high volatile A & B bituminous coals.

Table 8 reports the results of mass balance accounting for all the sulfur following an extraction of coal samples with 2 N nitric acid. The filtrate from the extraction was neutralized and treated with barium chloride to determine the total concentration of sulfate ions. This value was equated to the total of pyritic and sulfate sulfur present in the coal. Organic sulfur values were determined for the coal residue after the extraction. It is possible and very likely that the nitric acid also oxidizes the sulfide sulfur to sulfate during the extraction.

TABLE 7

Supercleaned Float/Sink Coals

Coal No.	Moisture_{ad}	Volatile Matter_{ad}	Ash_{ad}	S_{ad}	S_{daf}*
85098	2.08	39.66	1.47	2.09	2.17
85099	1.23	35.42	1.78	1.36	1.40
86024	5.38	38.08	2.32	1.06	1.14
86025	3.06	39.57	1.16	1.81	1.89
86038	0.46	n/a	2.34	0.56	0.58
86039	0.15	48.70	6.78	0.53	0.56
86040	0.63	n/a	5.54	0.56	0.60
86041	0.55	n/a	6.17	0.93	1.00

* Dry, ash-free basis.

TABLE 8

Mass Balance of Sulfur Forms of DAF Basis

Coal No.	Total Sulfur	Pyritic & Sulfate Sulfur	Organic Sulfur	Difference*
85098	6.96	4.59	2.42	-0.05
85099	4.36	2.92	1.40	0.04
86024	4.77	3.67	1.10	0.00
86025	5.17	3.36	1.84	-0.03
86038	1.32	0.75	0.50	0.07
86039	0.75	0.33	0.41	0.01
86040	0.67	0.11	0.54	0.02
86041	2.41	1.53	0.82	0.06

* Pyritic, sulfate and organic sulfur subtracted from the total sulfur.

The summary of research results for this thesis is given in Table 9. All values are means of quadruplicate runs (duplicate analysis on separate days) and are calculated on a dry, ash-free basis. The difference between the ASTM D 2492 and the extraction method is greatest for the high sulfur coals. The low sulfur coal 86038 showed no difference between the two methods. The supercleaned coal data is a mechanically achieved value in which nearly all of the mineral matter has been removed. The extraction data were also illustrated in Table 3 on an as determined basis.

TABLE 9

Summary of Organic Sulfur Data

Coal No.	ASTM D 2492 Organic Sulfur by Difference	Direct Extraction Method (DEM)	Supercleaned Coal Method	ASTM D 2492 Minus DEM
85098	3.19	2.19	2.17	1.00
85099	2.28	1.40	1.40	0.88
86024	2.66	1.10	1.14	1.56
86025	2.84	1.84	1.89	1.00
86038	0.50	0.50	0.58	0.00
86039	0.59	0.41	0.56	0.18
86040	0.58	0.54	0.60	0.04
86041	1.26	0.82	1.00	0.44

CHAPTER V

DISCUSSION

The basic assumption of the direct method for the determination of organic sulfur in coal by nitric acid extraction is that almost 100% of the pyritic and sulfate sulfur is removed by the procedure. After an extensive review of the literature it does seem likely that some pyrite could remain unextracted. The small amount of pyrite remaining in the extracted coal would be measured as organic sulfur by the direct method. However, the intent of this thesis has not been to evaluate the magnitude of the extraction, but to demonstrate that extraction can be used as a better estimate of organic sulfur than the ASTM difference method.

To accomplish this task it was first determined that comparisons could be made only on a dry, ash-free basis because of changes in the ash and moisture contents. Coal desulfurization processes are commonly calculated on a moist mineral matter free basis for the same reasons. The MAC-400 was used for proximate analysis because of the accuracy of the data and ease of operation.

Throughout the historical section of this thesis the ASTM standard method was used for comparison purposes. It is generally accepted that the sulfate sulfur determined directly by the precipitation of barium sulfate is a good value and the sulfate contribution to the total sulfur is usually very small in coal. Consequently, there are relatively few improvements to the ASTM standard method for sulfate determination.

There is excellent conformity between the organic sulfur determined by extraction in the float portions and the sink portions of coal after a float/sink separation. The data of Table 3 and Table 5 demonstrate that segregation of the coal does not occur during the float/sink process. If large differences were experienced one could possibly investigate the volume of nitric acid used in the extraction. Perhaps more nitric acid would be necessary on coals with higher ash contents.

Table 6 illustrates the variations that occur when using the D 2492 procedure for pyritic sulfur determinations. The reproducibility of the method is much poorer than the standard indicates. If data were obtained on a new pyritic sulfur method the conclusions could be influenced significantly by comparison to data obtained with the ASTM standard method. To ensure accurate data for comparison in this study the ASTM standard method was performed in quadruplicate on all samples. On many samples a second person repeated the quadruplicates as an independent check.

The direct measure of all sulfur (as sulfate ions) in the nitric acid extract solutions gave a good value for the total sulfur in pyritic, sulfate and other forms. The nitric acid extraction method does not distinguish between different inorganic sulfur forms during the oxidation. Only the organic sulfur is believed to be left unreacted by the extraction. This is why the mass balance experiments worked successfully as illustrated in Table 8.

There is still room for error in the ASTM D 2492 standard method, if sulfur exists as metal sulfides other than iron sulfide. The hydrochloric acid extraction could yield many undesirable possibilities. For example, the metal sulfide could form hydrogen sulfide which is undetected in the ASTM standard method. Also, the presence of free sulfur or soluble sulfides in strongly acid solutions could introduce uncertainty. These soluble sulfides would be removed during washing of the residue.

The main objection to the ASTM standard method for determining pyritic sulfur is that it is an indirect method. Pyritic sulfur is determined indirectly by measuring the iron(III) in a nitric acid extract solution. The assumption used as a basis for the ASTM standard method that iron can be related to pyritic sulfur is questioned by data from Mössbauer and inductively coupled plasma studies. Studies using Mössbauer have discovered several sulfur species in coal which do not contain pyritic or sulfate sulfur. Inductively coupled plasma studies showed iron-to-sulfur ratios to be dependent on the sample origin. These discoveries point out areas where errors could be introduced into the ASTM standard method.

Using adequate nitric acid to extract the coals explains the good repeatability for the direct method of organic sulfur determination. Following the ASTM procedure for calculating repeatability, a value of 0.05% was achieved for the direct organic sulfur method at the 2% level, thereby is representing a marked improvement over the ASTM difference method for organic sulfur measurement. The implication of these improvements could be felt in desulfurization studies in the near future.

CHAPTER VI

SUMMARY

Based on the needs of the coal community for an inexpensive method with accurate results for the determination of organic sulfur the direct nitric acid extraction method was studied. The direct method for organic sulfur determination meets these requirements. Most analytical coal labs have all the instrumentation needed to determine total sulfur, ash and moisture which is required for the direct organic sulfur method.

Organic sulfur values obtained by nitric acid extraction show good agreement with the sulfur content in "supercleaned" coal from which almost all the mineral matter has been removed by float/sink cleaning. The repeatability and reproducibility of the direct organic sulfur method are better than those experienced by the ASTM difference method.

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