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Decomposition of coal with periodic acid plus perchloric acid for the isolation of spores and for the determination of minor components

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DECOMPOSITION OF COAL WITH PERIODIC ACID PLUS PERCHLORIC ACID
FOR THE ISOLATION OF SPORES AND FOR THE DETERMINATION
OF MINOR COMPONENTS

by

Gerald I. Spielholtz

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PERCHLORIC ACID

Perchloric acid dihydrate, $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$, is the perchloric acid of commerce and is the only form of the acid commonly found in the laboratory. It is referred to commonly as "perchloric acid", such designation having been a grievous source of confusion. Three forms of perchloric acid exist and it is essential that they be distinguished:

1. Anhydrous perchloric acid, HClO_4
2. Oxonium perchlorate, $\text{HClO}_4 \cdot \text{H}_2\text{O}$
3. Perchloric acid dihydrate, $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.

Commercial perchloric acid, i.e., perchloric acid dihydrate, having a composition of approximately 72 per cent perchloric acid is a perfectly stable compound. It is a strong acid and when hot and concentrated is a powerful oxidizing and dehydrating agent; cold and dilute it has neither oxidizing nor dehydrating properties. When knowledge and care are exercised in its use, as should be the case with any chemical, no hazard is involved.

Perchloric acid is extensively used for the oxidation of organic matter; such use has also been regarded in some quarters with apprehension. At room temperature perchloric acid dihydrate may be mixed with organic matter safely, but at higher temperatures precautions are indeed necessary. Alcohol and similar hydroxylic solvents must not be heated with

perchloric acid; perchlorate esters are formed which are shock sensitive explosives. In all other instances the oxidation of organic matter is safe but in general oxidations of organic matter should be started with a mixture of nitric acid and perchloric acid. The nitric acid serves to oxidize the easily oxidizable organic matter. As the temperature rises the nitric acid is expelled and the perchloric acid concentration increases. In this fashion the oxidizing power of the perchloric acid is brought to bear gradually and a smooth, hazard-free oxidation is effected. The perchloric acid is used in effect as the final agent, to oxidize only the most difficultly oxidizable portion of the organic material.

Perchloric acid dihydrate is prepared by the distillation of dilute aqueous solutions of the acid. The dihydrate boils at 203° at a pressure of 760 mm., distilling as a constant boiling mixture or azeotrope. Because distillation at 760 mm. pressure is accompanied by appreciable decomposition to give chlorine and oxides of chlorine the distillation is performed under reduced pressure. Decomposition is thus prevented. A composition greater in perchloric acid than the dihydrate is never obtained no matter how low the pressure.

Anhydrous perchloric acid can be prepared by vacuum distillation from a mixture of fuming sulfuric acid and the commercially available, 72 per cent perchloric acid. In great

contrast to the dihydrate, it is unstable and can be stored safely only at liquid air temperatures. On continued storage decomposition products accumulate which ultimately explode. It is only the anhydrous acid which will cause explosions upon contact with most organic substances.

The monohydrate, oxonium perchlorate, is prepared by mixing equimolar quantities of the anhydrous acid and the dihydrate. It is a white crystalline solid, melting at 50°. It may be stored for any period of time with no hazard.

Commercial perchloric acid is a strong acid as useful in the chemical laboratory as any other commonly found acid. However, perchloric acid possesses unique properties, second to none, that enable it to effect certain reactions in which other strong acids fail. When hot and concentrated, it is a powerful oxidizing agent. The reduction potential is approximately 2.0 volts and the hot, concentrated acid is thus comparable to ozone in oxidizing power. Cold, dilute or concentrated perchloric acid is not an oxidizing agent. Hot, dilute perchloric acid is not an oxidizing agent. The oxidizing action of the boiling acid begins at concentrations about 50 per cent in perchloric acid, boiling at 150°, and becomes greater as the concentration is increased.

Hot, concentrated perchloric acid is an efficient dehydrating agent, particularly useful in the determination of silica in iron and steel, and in cement and other silicate

materials.

Hot, concentrated perchloric acid is a remarkably efficient solvent for metals and alloys, ores and minerals. The perchlorates of all the metals are soluble in water; the perchlorates of the alkali metals are anomolous being the least soluble of all.

The properties of hot, concentrated perchloric acid dihydrate make the acid ideally suited to the wet oxidation of coal preparatory to the determination of its inorganic components. The rapid and efficient oxidizing property and the efficient dehydrating power along with the remarkable solubility of the metal perchlorates make perchloric acid the choice reagent. The organic matter is completely destroyed; the inorganic constituents are instantly soluble; all that is left behind is a residue of dehydrated silica. The problems come in applying it with safety and speed in laboratory practice.

WET OXIDATION OF COAL FOR THE ISOLATION OF SPORES

Introduction

It is obvious that in an undisturbed sequence of sedimentary rocks, occurring as relatively thin layers over wide areas of the earth that the lower layer was laid down first. To the geologist this is the fundamental law of superposition. Each layer represents an interval of time, recorded in orderly succession from bottom to top in any ordinary stratigraphic arrangement. Such a relationship is referred to as a conformable sequence. However, if the succession of parallel rock layers has been interrupted by erosion or non-deposition a hiatus results.

An unconformity is a buried erosion surface representing a period of erosion or non-deposition corresponding to a hiatus or existence of a missing part of the deposition record. Three types of unconformities exist. If the unconformity is a break between two series of rock layers such that the rocks of the lower series contact rocks of the upper series at an angle there exists an angular unconformity. If the older and younger sets of beds are parallel but separated by a surface of erosion, the break is a disconformity. If the beds below the break are of igneous origin or have lost their bedding through metamorphism, the break is called a non-conformity.

These all represent gaps in the stratigraphic record. Nowhere does one find a continuous record of time in the form of a series of continuous deposits. The picture is a series of rocks conformable only over small local sections.

If there is a break in materials of the earth's crust on which there have been movements parallel with the surface along which the break occurs there exists a fault. A fault occurs when rocks are strained past the breaking point and yield along a fracture or series of fractures so that the corresponding points on the two sides are offset. Either side may rise, fall or move laterally with respect to the other.

Materials may be eroded away during the formation of an unconformity and deposited in some adjoining basin. The event of the destroying of the record will thus be recorded in another area. The most important principle used to work out these rock relationships over a wide area is "correlation" which is a process of determining the age equivalence of rock layers.

There are two types of correlation. The first aims at determining whether specific rock samples were once part of a single, physically continuous unit; the second entails matching rocks that were never physically continuous and are equivalent only in time of formation.

Owing to the effects of faulting and existence of unconformities it may be readily understood why any simple

correlation of strata with time may be incorrect.

Correlation is widely used in aerial studies, working out the geological history of an area. The principle is used to supply information to link broken and undisturbed areas where faulting occurs. It is of importance to all problems of applied geology involving minerals such as coal, clay, oil, petroleum and salt deposits.

Broader correlations between widely separated portions of the earth's crust are of less practical value but are essential in building up an integrated picture of geological history. By combining many local correlations, more accurate regional or world wide correlations can be achieved.

A most significant development in the field of applied micropaleontology is the use of spores in stratigraphic correlation and in the interpretation of ancient sedimentary environments.

The term spore may be defined in a broad sense as a reproductive organ or body formed by a plant. A spore is one of the most common of the remains of plants; it may be properly considered a micro fossil. Spores are found in abundance in near shore-marine sediments and in pelagic sediments.

The use of spores in applied micropaleontology include the following:

1. Widespread correlation of marine sediments later than Silurian in age.
2. Location of ancient shorelines of marine depositional

units by means of the number and the variation of spores in the marine sediments. Their widespread use in correlation is made possible by their extremely small size which prevents their destruction by normal drilling and coring operations. In addition, the fact that spores are transported great distances by the wind frees them from the usual environmental restrictions of most organisms. It makes possible the correlation of marine and non-marine sediments of contemporaneous deposition. The rapidity of their dispersal over wide areas by the wind, together with the wide variety of genera and species, make spores ideal as guide or index fossils.

Coal is formed from plant remains deposited in a reducing environment, and progressively altered from their original state by increasing pressure, temperature and the passage of time. Coal quite naturally becomes a rich source of plant spores. Spores preserved in coal show some striking differences from zone to zone and therefore become well suited for correlation. It is even possible that a characteristic succession of different spore zones within a single coal bed may aid in its identification throughout considerable areas.

Spores vary greatly in character. Some 130 different species have been identified from Illinois coal beds alone. A goodly number are described by Kosanke (30) who tabulated the generic characteristics for all of the small spore genera observed in Illinois coal beds. Kosanke presents numerous plates

illustrating species to serve as a guide for identification. His investigation into the distribution of spores in Illinois coal beds leaves no doubt as to the value of spores for the positive identification and correlation of coal beds.

Several chemical procedures have been used for the oxidation of coal for the isolation of spores, a review of the subject being given by Staplin, Pocock et al. (45). A combination of 10 per cent nitric acid plus 10 per cent chromic anhydride has proved useful in isolating cells of lignified tissues (49). Staplin mentions the effectiveness of a solution of potassium permanganate in sulfuric acid. This choice is indeed startling for such a mixture yields permanganic acid which in the presence of sulfuric acid gives manganese heptoxide, Mn_2O_7 , a violently explosive compound.

One of the most important contributions to the study of isolated plant remains found in coal was made by Franz Schulze in 1855. He discovered that coal could be macerated with chemicals without harm to the botanical ingredients. Of the methods reviewed by Staplin, some modification of the procedure utilizing Schulz's reagent remains the most popular. Schulz's reagent is a solution prepared by mixing 30 g. of potassium chlorate, 300 ml. of water and 600 ml. of nitric acid. The Raistrick, or dry Schulz's method, has long been used in England (37, 38). Two grams of coal and two grams of potassium chlorate are mixed with sufficient water to

dampen the mixture and 10 ml. of nitric acid are added very slowly. The former method has been found to be time consuming while an element of hazard is inherent in the latter dry modification because chloric acid at concentrations above 30 per cent explodes spontaneously.

It is obvious that a rapid and safe method for the isolation of spores would be of value. The most likely procedure to apply is that based on the work of Smith and Diehl (43), who employ a mixture of periodic acid plus perchloric acid for the total destruction of organic matter. The advantages attained by this method are the low temperature requirements, and the noteworthy reactivity of periodic acid in downgrading heavy, complex organic molecules to fragments more readily soluble in the perchloric acid. These fragments may be oxidized by the perchloric acid; the reactions involved are hazard free.

It has been found that oxidation of coal can be effected quickly, cleanly, and safely by heating the sample with a mixture of periodic acid and 50 per cent perchloric acid. The low concentration of perchloric acid used is sufficient to liberate the spores present in coal. The oxidation is effected primarily by the periodic acid used, as hot perchloric acid of 50 per cent concentration has little oxidizing power. Provision is made for complete reflux; but, even hot, concentrated perchloric acid works on coal slowly.

Experimental Work

Reagents

Periodic acid (Para, H_5IO_6). Reagent grade material; available from the G. Frederick Smith Chemical Company, Columbus, Ohio.

Perchloric acid, 50 per cent $HClO_4$. Dilute 10.0 ml. of reagent grade, vacuum distilled, 70 per cent perchloric acid with 5.0 ml. of water. Check the concentration of this acid by determining its boiling point in the apparatus described below. The temperature should reach a steady value between 130° and 133° .

Vanadium Pentoxide. Reagent or technical grade; available commercially. Ammonium vanadate may be used in place of the oxide.

Apparatus

A 250 ml.-flask with thermometer-well and reflux condenser with a ground glass joint. Seal a thermometer-well into the side of a 250 ml. conical pyrex flask with 24/40 standard taper joint at the neck so that it reaches within 2 mm. of the bottom of the flask. This thermometer-well should accommodate a 250° thermometer, and is conveniently made from a pyrex test tube. Place a water-cooled condenser with a male 24/40 joint on the flask. The flask and condenser are commercial items.

Recommended Procedure

Place 1.0 g. of finely crushed coal in the flask and add 15 ml. of 50 per cent perchloric acid, 1.5 g. of periodic acid, and 1 or 2 mg. of vanadium pentoxide. Insert the condenser and thermometer, and heat the mixture on a hot plate or over a micro burner until a constant temperature is attained and the acid is refluxing gently down the walls of the flask. This will normally take from ten to twenty minutes, depending on the rate of heating. Iodine crystallizes in the condenser during this operation. Cool the mixture, dilute to 50 ml. with water, and then neutralize the solution with 10 per cent sodium hydroxide until the solution turns dark brown. Centrifuge the solution, decant away the supernatant liquid and wash the residual material with water. The residue may be dried, and the spores then isolated.

A method of isolation is described by Kosanke (30). The residue is divided into two fractions by screening with a standard 65-mesh Tyler screen. The filtrate contains the small spores and may be selected by examination under a microscope. The spores vary in colors from light yellow to dark brown. Staining is advised to obtain good photo micrographs and to study the minute structural details of the spore coat and appendages. A concentrated aqueous solution of Safranin Y or equivalent may be employed. The spores may then be washed with water and mounted.

Discussion

The concentration of perchloric acid specified in the procedure, 50 per cent, appears to be optimum; at greater concentration, some spores are destroyed; at lower concentration, the oxidation is slower and less effective. The oxidation of the carbonaceous material is usually completed in the time required to reach a constant boiling temperature, about 20 minutes for either coal or carbonaceous shale. The vanadium acts as a catalyst for the oxidation.

The oxidation may be stopped at any time by simply cooling the mixture, or by diluting with water.

ANALYSIS OF COAL FOR SULFUR AND OTHER MINOR COMPONENTS

Introduction

The major cause of reduced efficiency of coal as a boiler fuel is the fusion or cementation of the burning mass. The passage of air and gases through the mass is blocked and the combustion rendered incomplete.

The organic matter of some coals exhibits a tendency to fuse but the greatest problem arises from the tendency of the inorganic matter in the coal to form a clinker. Clinker formation is the result of a fusion of the inorganic or ash constituents of the coal into a plastic mass. Clinkers interfere with the access of air to the burning mass. Under normal conditions, from 10-25 per cent of the total combustible matter is discharged into the combustion chamber for burning above the fuel bed. The formation of clinker and the resulting shortage of oxygen promotes the formation of carbon monoxide and increases the amount of unburned material which leaves the burning mass as smoke or ash.

The formation of clinker tends to produce more clinker. As a case in point, pyrite (FeS_2), a substantial constituent of many coals, melts at 1171° , decomposing to ferrous sulfide, which has a melting point at about the same temperature, 1197° . Ferrous sulfide is stable. If nothing occurs to change its composition and if present in sufficient quantity it may flow

down upon and through the grates as a viscous mass. When the grates are covered the cooling effect of the air is lost and the grates rapidly burn out. Further, reducing conditions which prevail may in instances even produce the free, or metallic iron, adding again to the initial clinker. If the conditions of combustion are retained, all the sulfur is burned and the iron is oxidized to ferric oxide which has a fusion point of 1548°. The possibility of clinker formation is eliminated once complete oxidation is assured.

The formation of clinker is not the only problem presented by the inorganic constituents of coal. Deposits found on boiler heat-exchange surfaces have their origin in the metallic components of the coal. These deposits reduce the efficiency of the exchanger. A substantial sulfur content in coal leads not only to stack deposits but also to air pollution. Coals rich in arsenic also present an atmospheric pollution problem. Phosphorus is of special importance, for low-phosphorus blast furnace coke is essential in the manufacture of pig iron for manufacture of steel. It is apparent, then, that means for the rapid and accurate determination of the various constituents of coal would be of value.

Procedures for the destruction of organic matter in coal and coke preparatory to the determination of its inorganic constituents appear in the most recent book of ASTM Standards (1, pp. 1227-1358). All employ a dry ashing method of one

form or another. The Book of ASTM Standards carries no methods for determining the metallic constituents which reduce the efficiency of coal as a boiler fuel. Methods are given for the determination of moisture, ash, volatile matter, fixed carbon, carbon and hydrogen, and the non-metals, sulfur, phosphorus, and nitrogen. No satisfactory method is known for the determination of oxygen and it is suggested that it be calculated by subtracting from 100 the sum of the values for hydrogen, carbon, nitrogen, sulfur, moisture, and ash content.

For the determination of the ash in coal according to the ASTM procedure either a gas or electric muffle furnace may be used, good air circulation should be provided, and provision should be made for temperature regulation between 700 and 750°. For the determination of the ash of coke either a gas or electric muffle or Meker burner may be employed. The muffle should also have good air circulation and be provided with temperature regulation up to 950°. In each case ignition must be made to constant weight.

That difficulty may be experienced in securing satisfactory check determinations of ash in the same or different laboratories for coals unusually high in calcite and pyrite is pointed out by the ASTM. This difficulty is caused by variation in the amount of sulfur retained in the ash as sulfate. For such samples, a modified procedure is recommended in which the sample is placed in a cold muffle and heated gradually so that the temperature reaches 500° in one hour and 750° in two

hours; the heating is continued at 750° until constant weight is obtained. In this fashion pyritic sulfur is oxidized and expelled before calcite is decomposed.

Three methods are described in the Book of ASTM Standards for the determination of sulfur. These are the Eschka method, the bomb washing method, and the sodium peroxide fusion method. The Eschka method involves mixing thoroughly one gram of coal and three grams of Eschka mixture. The Eschka mixture is prepared by mixing by weight two parts of magnesium oxide to one part of sodium carbonate. The four grams are placed in a crucible and covered with an additional one gram of Eschka mixture. The crucible is heated to 800°, the contents are digested with hot water, filtered and washed. The filtrate is treated with bromine water, made acid and boiled to expel the excess bromine. The pH is adjusted and the sulfate is precipitated with barium chloride. The residue of magnesium oxide is dissolved in hydrochloric acid and tested for sulfur. If an appreciable amount of sulfur is present it must be determined and combined with that found originally. The ASTM points out that the amount of sulfur retained is by no means a negligible quantity.

The bomb washing method allows the sulfur to be determined in the washings from the oxygen-bomb calorimeter following the calorimetric determination.

In each method the silica of the coal is probably not

completely dehydrated and removed by filtration. In the Eschka method volatilization of sulfur during the ignition may occur. In the bomb washing technique directions are given to open the bomb after reaction and examine inside for traces of unburned or sooty deposit. If these are found, the determinations should be discarded.

The conclusion to be drawn from the above discussion is that considerable uncertainty exists, as to the recovery of the sulfur and as to the efficiency of the combustion in the bomb washing method. None of the methods is as satisfactory with respect to the time required and the accuracy obtained as the wet oxidation method to be described.

A major disadvantage of the dry combustion technique is the loss by volatilization of metals present. Gorsuch (12), Klumpp (29), Farrar (8) and Pijck, Hoste and Gillis (33) present substantial proof of this. Recently Kelleher and Johnson (26) have reported the loss of selenium upon allowing a solution containing this element to be taken to dryness. Particularly with trace amounts of inorganic constituents, any loss during ashing would be of grave consequence. In addition the dry ashing leaves a solid residue after ignition which may be difficult to take into solution for the subsequent analysis. Such residues may require treatment with acids, or mixtures of acids, or even a fusion with some basic or acidic flux. Silicates containing a relatively high per-

centage of alkali or alkaline earth metals, the so called basic silicates, may be dissolved by treatment with mineral acids other than hydrofluoric acid, hydrated silica and the salts of the metals being formed. Those silicates not dissolved by acids must be treated with a basic material, generally sodium carbonate, and fused. This process renders them soluble in acids. When a determination of silica is not desired, hydrofluoric acid may be used to decompose the silicate. In the wet oxidation method to be described, the problem of dissolving solid residues does not appear.

The general trend in the oxidation of organic materials has been to replace the dry combustion with a wet ashing procedure. This procedure offers the chemist both speed and efficiency. It does not suffer from the need of large samples and multiplicity of equipment such as muffle, platinum or porcelain crucibles. Lower reaction temperatures are used and loss due to volatilization is non-existent.

An obviously tedious and time consuming requirement is the ignition of the ash to constant weight as prescribed in the dry ashing method. Wet combustion with perchloric acid eliminates this. The wet oxidation of coal followed by the analysis for inorganic constituents requires about the same time as does the determination of ash content by the dry combustion.

The dissolution of samples of organic matter by wet com-

bustion using perchloric acid in preparation for the determination of either metallic or non-metallic components has been aptly designated "the liquid fire reaction". The dissolution of the sample and quantitative destruction of the organic matter requires a short period of time. The excess oxidant need not be removed; simple cooling and dilution is all that is required. Wet oxidation with its numerous advantages is highly recommended for the rapid and accurate determination of the inorganic constituents of coal.

A scheme for the determination of the ten major constituents in coal was reported by Pringle (36). The organic matter in the sample is destroyed by an initial attack with a mixture of sulfuric and nitric acids, then repeating the attack with nitric acid alone until a specific volume of the acid has been added. The oxidation is continued by the addition of 72 per cent perchloric acid and the solution is boiled until white fumes of sulfuric acid appear. Pringle states that the perchloric acid digestion is essential. It insures the removal of nitric acid and prevents the formation of nitrites which lead to high results in the titanium determination. After the organic matter is destroyed by the wet oxidation, the silica is filtered off and determined gravimetrically. Aluminum, iron, titanium, phosphorus, and manganese are then determined on the solution by photometric procedures. On another aliquot of solution and after removal of inter-

ferences such as iron and aluminum, calcium, magnesium, potassium and sodium are separated and subsequently determined by photometric methods.

A later paper by Archer, Flint and Jordan (2) describes the methods used by The British Coal Utilization Research Association for the rapid, complete analysis of inorganic residues from coal. Instructions for determining the individual constituents are reportedly based on extensive investigations involving more than 1,000 determinations. The results reported agree well with those obtained by the classical procedures. Two solutions are prepared for analysis, one from a fusion of the sample with sodium hydroxide for the determination of silica and aluminum, the other from a digestion of the sample with hydrofluoric acid and sulfuric acid for the determination of all other constituents than sulfur. Colorimetric procedures are used for silica, aluminum, iron, titanium, manganese, and phosphorus. Calcium and magnesium are determined by titration with EDTA, using calcein as indicator for calcium only and screened o-cresolphthalein complexone for calcium plus magnesium. Sodium and potassium are determined by flame photometry. Sulfur is determined gravimetrically on a separate sample.

The work to be described employs the wet oxidation procedure of Smith and Diehl (43). This method has been adopted to destroy all organic matter in coal and subsequently bring

into solution all ions of analytical interest. The silica is dehydrated and is then the only constituent left insoluble and is therefore available for immediate determination.

The procedure is faster and far less subject to error by loss of inorganic content than any method employing dry combustion. It is more rapid and efficient than the methods of Pringle or Archer, Flint and Jordan.

The use of periodic acid in preference to nitric acid along with perchloric acid has marked advantages. Not only does the periodic acid serve as an oxidant, but also it contributes to the ready fragmentation of large molecular species by degradation, to smaller organic entities. The latter are more soluble in perchloric acid and are more easily oxidized by 66-69 or 70 per cent perchloric acid (43). The periodic acid plus perchloric acid attack is direct and there is no reason for any dry ashing.

The absence of nitric acid precludes any interference which can arise in the colorimetric determination of titanium by Tiron (1,2-dihydroxybenzene-3,5-disulfonic acid) as reported by Pringle.

Using a new iron reagent, 1,10-phenanthroline-5-sulfonic acid (5) the determination of iron can be carried out in a perchlorate solution; this was not possible previously owing to the insolubility of ferrous tris(1,10-phenanthroline) perchlorate. 1,10-Phenanthroline-5-sulfonic acid has essen-

tially the same spectrophotometric characteristics of the parent compound.

Hot concentrated 72 per cent perchloric acid, being not only a powerful oxidizing agent but also an excellent dehydrating agent, is well suited for the determination of silica. The boiling acid rapidly takes the water away from any silicic acid, leaving behind anhydrous silica.

Literature Review on Methods of Determining Sulfur and Various Metals

Survey

Silica One of the earliest applications of perchloric acid in analytical chemistry was to the determination of silica. This is the classical work of Willard and Cake (51) which takes advantage of the dehydrating power of boiling concentrated perchloric acid. The gravimetric determination is simple and yields excellent results; alternative methods seem hardly worth the effort. An indirect, and empirical volumetric method based on the precipitation of the 8-hydroxyquinoline derivative of molybdisilicic acid has been used (52). A colorimetric method based on the blue color formed on reducing molybdisilicic acid is useful for trace amounts of silica but is not useful for the relatively large amounts of silica in coal.

Sulfur Methods for the determination of sulfur in organic compounds starting with wet oxidation with perchloric

acid go back to the 1920's. One of the earliest of these is that of Kahane (15, 16), further studied by Wolessenky (53) and by MacKay (31), for the determination of sulfur in rubber. The nitric acid-perchloric acid mixture was used to destroy the rubber, and following this smooth oxidation of the organic matter, the sulfur was precipitated as barium sulfate.

Loss of sulfur by volatilization during the oxidation was generally ignored, see for example, Toepfer and Boutwell (47) who used the method for sulfur in foods and biological materials. Proof that all sulfur was retained as sulfuric acid was not offered. Kahane, however, began to have serious doubts as to recovery and in 1934 published four papers on the determination of sulfur, in rubber (18), in organic substances (23, 24), and in medicinals (17), in which he reported that the sulfur is not all oxidized to sulfate. Indeed hydrogen sulfide and sulfur dioxide are liberated in the course of the nitric acid attack. This loss of sulfur leads to low results. The loss is dependent on the amount and concentration of the acids used and on the temperature and rate of heating.

Kahane attempted to rectify the situation by the use of fuming nitric acid; the results were no better and the violence of the reaction of fuming nitric acid with organic matter (fire is sometimes produced) warned against its use. Nor did the addition of bromine, of iodine, or of hydrogen perox-

ide help. By proceeding very slowly it was sometimes possible to get satisfactory results with a bromine-nitric acid-perchloric acid mixture but this was tedious and uncertain. In the end Kahane found it necessary to trap the gases evolved and return them to the solution. This operation was effected in a scrubber containing a solution of iodic acid which served to trap the hydrogen sulfide, sulfur dioxide and other sulfur-bearing gases, which were later returned to the solution.

The fact that sulfur bearing gases escape during wet combustion with nitric acid and perchloric acid was further confirmed by Bethge (4) in a study of a method for the determination of sulfur in wood. Bethge concluded that the escaping gas was probably sulfur dioxide as no hydrogen sulfide could be detected, although he mentions the possibility that the gas could be carbonyl sulfide, COS. The latter was observed by Staudinger and Niessen (46) to be the product of the nitric acid oxidation of trimethylthiourea. Using a specially devised apparatus Bethge (3) was able to recover sulfur quantitatively; the iodic acid recommended by Kahane was omitted. Presumably the contact between the gases evolved during the combustion is better and the nitric oxide formed fills the reflux receiver and remains there during the whole operation. All the sulfur dioxide coming from the reaction flask is oxidized by the nitrogen dioxide to sulfuric acid, condenses and is returned to the flask. The top most part

of the Bethge apparatus, the scrubber, is filled with either a few milliliters of water or with 3 per cent hydrogen peroxide solution.

The conventional way of determining sulfate is the gravimetric barium sulfate method. In spite of the numerous, well known errors to which this method is subject, it is still the most widely used of all methods.

That free perchloric acid in small amounts or large amounts of neutral, sodium perchlorate do not interfere in the gravimetric barium sulfate method was shown by Kahane (19) and confirmed by Wolesenky (53).

Smith and Deem (42), applying the wet oxidation procedure to the determination of sulfur in coal first noted that volatile compounds of sulfur, oxygen and chlorine were formed, appreciating the fact that perchloric acid alone does not convert all sulfur to sulfuric acid. Nitric acid or potassium nitrate or a mixture of the two were used to bring about the complete oxidation of the sulfur to sulfuric acid. Low results were obtained by Smith and Deem and several reasons for this were postulated. One was that the earlier results on their samples were high because of a silica contamination in the barium sulfate resulting from incomplete dehydration. The efficient dehydration of silica during the wet oxidation with perchloric acid and the subsequent complete removal of silica made for a purer barium sulfate and lower results.

The second explanation was that because of a high concentration of perchloric acid at the time of precipitation of barium sulfate an efficient precipitation did not result. Coprecipitation does occur in highly acid media. In any case standard samples were (and are yet) not available and in view of the work by Kahane and by Bethge it is probable that the results of Smith and Deem were low.

Iron No loss of iron by volatilization during wet oxidation occurs. Studies on the recovery of iron added to urine were made by Collins and Diehl (7), who wet ashed samples with a mixture of nitric acid and perchloric acid. Gorsuch (12) who performed radioactive tracer studies found no loss of iron by wet oxidation. Smith (41) investigated the loss of iron by possible volatilization by distillation with perchloric acid and several non-oxidizing acids at 200 to 220° and obtained 100 per cent recoveries in every case.

Of the numerous methods available for the spectrophotometric determination of iron, the 1,10-phenanthroline method is superior in reliability, sensitivity and convenience. Unfortunately, the perchlorate of the iron(II) 1,10-phenanthroline cation is insoluble and perchlorate must be removed before the determination can be made. This difficulty has been overcome by the sulfonation of 1,10-phenanthroline (5); the sulfonated material, 1,10-phenanthroline-5-sulfonic acid, possesses the characteristics of the parent compound but the

iron derivative is soluble in solutions containing perchlorate.

More sensitive reagents are available for the determination of smaller amounts of iron than can be determined by the 1,10-phenanthroline method. Bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) and TPTZ (2,4,6-tripyridyl-s-triazine) are the most satisfactory and are widely used for the less than p.p.m. concentrations of iron (7).

Calcium and magnesium No loss of calcium and magnesium during wet oxidation occurs. The wet oxidation of plant material with nitric acid plus perchloric acid was reported simultaneously by Gerritz (10), for the determination of calcium, and by Giesecking, Snider and Getz (11), for the determination of calcium and magnesium. Giesecking, Snider and Getz added known amounts of calcium and magnesium to the plant material before the analysis and obtained excellent recoveries.

Smith (41) investigated the loss of calcium and magnesium by possible volatilization on distillation at 200-220° with perchloric acid and several non-oxidizing acids. Smith obtained 100 per cent recoveries in every case.

Traditionally calcium has been determined by precipitation as the oxalate. The calcium determination may be performed by igniting the oxalate to the carbonate at 500° to 525° or to the oxide at 800°, or titrimetrically by dissolving the oxalate in sulfuric acid and titrating with permanganate

or perchlorato ceric acid.

Magnesium has been determined by precipitation as the double ammonium phosphate or as the 8-hydroxyquinoline salt. The determination is completed by igniting the magnesium ammonium phosphate to the pyrophosphate in a muffle furnace; the 8-hydroxyquinoline compound is dried and weighed. An alternative procedure is to dissolve the magnesium 8-hydroxyquinoline compound in acid, brominate the compound with a standard bromate-bromide solution and determine the excess bromate-bromide, thus indirectly measuring the magnesium.

In the past fifteen years two other methods have been introduced for the determination of calcium and magnesium, the ethylenediamine-tetraacetic acid (EDTA) titrimetric method and the flame photometer method. The titrimetric method employing EDTA is a direct method for calcium plus magnesium or calcium only depending on the pH chosen, suitable indicators for each titration being available.

Aluminum The investigation by Smith (41) of the volatilization of numerous elements from solutions of perchloric acid plus a number of non-oxidizing acids showed that aluminum is not distilled at temperatures of 200 to 220°. Recovery in each case is 100 per cent.

Several colorimetric methods are available for the determination of small amounts of aluminum. One of the oldest methods is that using aluminon, the ammonium salt of aurin

tricarboxylic acid. Aluminon gives a red color with aluminum at a suitable pH; the coloration is not caused by a definite compound but by an adsorption compound or lake as it is sometimes called. Recent work by Owen and Price (32) has eliminated many of the shortcomings of this method. The addition of isopropyl alcohol to the aluminon reagent improves its stability remarkably, the reagent remains clear indefinitely and the aluminum content is reproducible for a month.

A colorimetric method using aluminum oxinate is widely used, however the selectivity is very low. The oxinate is usually extracted into an organic solvent, chloroform, carbon tetrachloride or benzene being employed. There is considerable absorption in the ultra-violet. The oxinate is a definite compound. Preliminary separations are usually necessary; numerous colored oxinates are extracted at the same time as the aluminum.

A fluorometric method (50) with Chrome Blue has been suggested. The fluorescence is practically specific, only gallium also gives a fluorescence. The method is not very accurate.

Vanadium The investigation by Smith (41) of the volatilization of numerous elements from solutions of perchloric acid plus a number of non-oxidizing acids showed that titanium in all cases except two is not distilled. In the hydrochloric acid plus perchloric acid procedure the approxi-

mate loss was 0.5 per cent and 2 per cent in the hydrobromic acid plus perchloric acid procedure. When extremely small amounts of vanadium are present the loss in the hydrochloric acid plus perchloric acid procedure is negligible. However, Pijck, Hoste and Gillis (33) using radioactive vanadium, the isotope⁴⁸V, obtained 100 per cent recoveries during wet ashing with nitric acid plus perchloric acid plus sulfuric acid.

Three important colorimetric methods exist for determining small amounts of vanadium. Hydrogen peroxide reacts to give an orange complex but should not be used for small traces; the method is not very sensitive. The presence of titanium will interfere.

The phosphovanadotungstate complex is an accurate and sensitive method (54). In the simultaneous presence of phosphoric, vanadic and tungstic acids a yellow compound is formed. The acidity of the medium has little effect.

Recently, 3,3'-diaminobenzidine tetrahydrochloride was studied for its use in the determination for vanadium (6). The procedure developed has been found to be simple, rapid and highly selective for determining small amounts of vanadium. The method is based on the oxidation of diaminobenzidine with vanadate ion. A thorough interference study has been made by Hoste (14).

Titanium The investigation by Smith (41) of the volatilization of numerous elements from solutions of perchlo-

ric acid plus a number of non-oxidizing acids showed that titanium is not distilled at temperatures of 200 to 220°. Recovery in each case is 100 per cent.

An extremely sensitive colorimetric method for titanium is that employing Tiron, 1,2-dihydroxybenzene-3,5-disulfonate (55). A well known method for the determination is that using the complex formed by titanium with hydrogen peroxide. It is not a very sensitive method.

Titanium also gives a color with Thymol in concentrated sulfuric acid. The reaction is practically specific and the lower limit of detection is 0.1 p.p.m. Unfortunately, many sulfates are of low solubility in concentrated sulfuric acid and make the solution cloudy and the method is not much used.

Phosphorus In the determination of phosphorus in organic material, the loss by volatilization is reported to be non-existent during wet ashing with perchloric acid. Kahane (19) investigated this in his studies on perchloric acid ashing and found experimentally that no phosphorus is lost during wet ashing with the nitric acid-perchloric acid or the nitric acid-perchloric acid-sulfuric acid mixture even in the digestion of compounds in which phosphorus is in the lower oxidation states such as in sodium hypophosphite, triphenylphosphine and diphenylphosphite.

King (27) determined phosphorus in biological materials and organic compounds using digestion with perchloric acid

alone or sometimes with the dropwise addition of a little nitric acid. The results on various organic phosphates were excellent. King experienced no trouble in the digestion with perchloric acid alone.

From the studies of Kahane and especially King there leaves no doubt that phosphorus is also retained in the perchloric acid plus periodic acid wet oxidation procedure. The concentration of perchloric acid called for in the perchloric acid plus periodic acid procedure is greater by at least 10 per cent than in the procedures reported by Kahane and King. Phosphorus in hot concentrated perchloric acid solution will be rapidly and efficiently oxidized to phosphate with no loss.

The phosphovanadomolybdate method is the most specific method so far developed for the colorimetric determination of phosphorus. The possible interference of 60 different ions is discussed by Kitson and Mellon (28).

Arsenic Dry ashing of organic matter is of no value for the determination of arsenic. This had been generally appreciated for some time but was made quite evident by the work of Pijck, Hoste and Gillis (33) using radioactive arsenic, the isotope ^{76}As , as a tracer. Only 23 per cent of the arsenic was retained on dry ashing at the lower temperature of 400° and none at all at 500° and higher.

Pijck, Hoste and Gillis found losses as great as 8 per cent of arsenic during wet ashing with nitric acid plus per-

chloric acid plus sulfuric acid although 100 per cent recovery was obtained if digestion was carried out under reflux. The loss of arsenic during digestion with nitric-perchloric and nitric-perchloric-sulfuric acid mixtures was investigated in detail by Kahane (20, 21, 22, 25) who showed by the absence of arsenic in the escaping gases that no arsenic was lost and this was confirmed by the successful analysis of organic arsenic compounds. The disparity between these workers may well be the matter of reflux; Kahane used a long necked Kjeldahl flask, the upper walls of which remain cool and act as a trap for spray.

In general because of interference of phosphate and other elements, arsenic must be separated before it can be determined. The separation is usually based on a distillation of either arsine or arsenic trichloride.

The evolution of arsine, AsH_3 is quite an old method, known as the Gutzeit method. The arsenic is reduced to arsine either with zinc in acid solution or by electrolysis. The arsine passes through a paper impregnated with mercuric bromide. A yellow to brown stain is produced, which is deeper and wider the larger the quantity of arsenic present. This is an extremely sensitive method but obtaining reproducible spots and their quantitative measurement is difficult. Colorimetric methods are preferred to complete the determination.

A most popular colorimetric method has been the molybdenum

blue method based on the color formed when a solution containing molybdic acid and arsenic acid is treated with a reducing agent. Hydrazine sulfate appears to be the best of the reducing agents and is now the only one used.

The silver diethyldithiocarbamate method for arsenic is a recent development, by Vasak and Sedivec (48). This method is based on the red color formed by the direct interaction of arsine with a pyridine solution of silver diethyldithiocarbamate. The method is highly sensitive to arsenic, the working range being 0 to 18 μg . of arsenic in a volume of 3 ml. of pyridine. Because the operation involves arsine directly there are fewer operations than in the molybdenum blue method.

Experimental Work

Reagents

Aluminon reagent for aluminum: obtained from Fisher Scientific Co., Fairlawn, New Jersey.

Aluminum: Alcoa aluminum round wire alloy and temper 1199-H19; assay 99.99 per cent aluminum. Obtained from the Aluminum Company of America.

Calcium Carbonate: Ultra-Pure Mallinckrodt reagent.

Calmagite: Indicator for the titration of calcium plus magnesium. Obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio.

3,3'-Diaminobenzidine tetrahydrochloride: The reagent is snow white in color and obtained from the G. Frederick Smith

Chemical Co., Columbus, Ohio.

EDTA, (Ethylenedinitrolo) tetraacetic Acid Disodium Salt: Eastman white label. It is necessary to filter before use.

Electrolytic iron: Ignited in moist hydrogen, obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio.

Perchloric acid: Reagent grade, vacuum distilled with assay of 70 per cent. Obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio.

Periodic acid (Para, H_5IO_6): Reagent grade material; obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio.

1,10-Phenanthroline-5-sulfonic acid: obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio.

Phenylthiourea: Eastman white label.

Triton X-100, wetting agent. Obtained from Rohm and Haas, Philadelphia, Pa.

All other chemicals were of reagent grade.

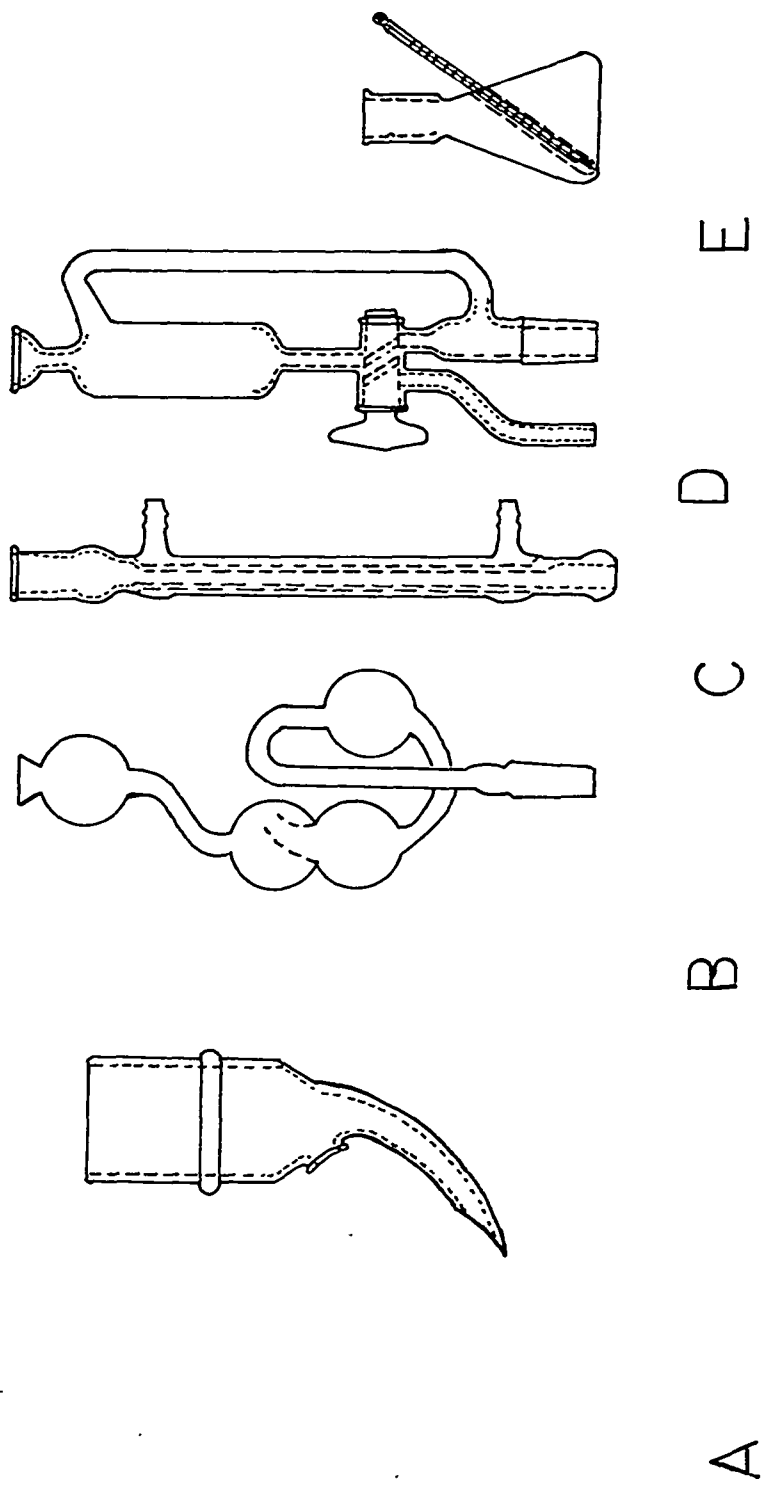
Apparatus

In most cases digestions with the periodic acid-perchloric acid combination were carried out in a conical flask utilizing a condenser head (44), in the neck of the flask; Figure 1, A.

The apparatus employed for the determination of sulfur was that designed by Bethge (3); Figure 1, B-E. The Bethge apparatus consists of four parts:

Figure 1. Apparatus for wet combustion

- A. Condenser head
- B.-E. Bethge apparatus
 - B. Scrubber
 - C. Condenser
 - D. Reflux reservoir
 - E. Reaction flask with thermometer well.



1. Reaction flask with or without a thermometer well.
2. Middle part or retaining reflux reservoir. Reflux may be withdrawn or returned to the reaction flask thereby controlling the perchloric acid concentration.

3. Condenser.

4. Top most part or scrubber for retaining volatile sulfur compounds. A 250 ml. conical flask with a 40/50 standard tapered neck was used. A lip was formed on the flask for ease in transferring liquids while the abnormally wide mouth made for easy access to the inner walls. The reflux reservoir was fitted with a three way teflon stopcock.

Spectrophotometric data were secured on a Beckman Model DU spectrophotometer using 1-cm. matched cells.

All water used was distilled water further purified by passage through a monobed ion exchange unit.

Coal samples

1. A series of samples were obtained from the Illinois Geological Survey, courtesy of Dr. Orin W. Reese. Values for sulfur, ash, and BTU were supplied.

2. Approximately 20 pounds of coal were obtained from the Iowa State University power plant. The coal had been piled and exposed to the weather for a period of 36 days. This coal came from the Wilkerson Coal Co., Pershing mine located south east of Des Moines, Iowa. The coal was a sub-bituminous, typical low-grade, Iowa coal. Several pounds were ground

in a ball mill to pass a no. 60 mesh sieve and enough sample to fill a gallon metal capped jug was mixed in a blender for a period of twelve hours. This is hereafter referred to as the Pershing Mine coal.

3. Approximately one pound of coal was obtained from the Iowa State University geology department, the original source being the Scandia Coal Co., mine at Madrid, Iowa. Several grams were ground with a mortar and pestle to yield a homogenous lot.

Recommended Procedures

The procedures described below for determining the major inorganic components of coal are the best found during the course of the experimental work. They provide the optimum in speed, accuracy, reproducibility and selectivity.

Wet oxidation of coal with perchloric acid plus periodic acid

Transfer an accurately weighed sample of about 1 g. of the coal to the 250 ml.-flask of the Bethge apparatus. Add 50 ml. of 68-70 per cent (no greater) perchloric acid and 1.5 g. of paraperiodic acid. Place several ml. of 3 per cent hydrogen peroxide in the scrubber. No catalyst is necessary. Assemble the Bethge apparatus. Heat the mixture using a microburner. Approximately thirty minutes is necessary. The acid concentration is unaltered throughout the major part of the reaction period. However, flocks of carbonaceous matter

cling to the upper walls of the flask if foaming occurs. In this case, after the principal reaction is over (at essentially the initial concentration of the perchloric acid) cut off the reflux return to the reaction flask and allow the acid to concentrate to the composition of the azeotrope, 72.5 per cent perchloric acid. At this concentration the destruction of the carbon flocks takes place rapidly.

After complete oxidation remove the scrubber, wash down the condenser with water and remove the reaction flask. Place a condenser head in the neck of the flask and evaporate to a volume of about 50 ml. The special condenser head prevents loss of material by spattering and reduces the escape of perchloric acid into the atmosphere. As soon as the volume of solution is low enough to insure no loss add slowly 30 per cent hydrogen peroxide. Continue this addition until no more iodine is evolved from the mixture. Boil the solution for a further five minutes. Add 100 ml. of water, cool and filter into a 600 ml. beaker. Wash with 1 per cent perchloric acid solution.

If sulfur is not to be determined filter instead into a 500-ml. volumetric flask and set aside. The solution in the flask is hereafter referred to as the test solution.

If sulfur is not to be determined use of the Bethge apparatus is not necessary. Simply place the special condenser head in the neck of a 250 ml.-flask and proceed as above. For

such digestions however, a stone hood is advised. Hoods and ducts for perchloric acid vapor should be made of chemically inert materials.

Two solutions need be prepared for analysis, both from the wet oxidation with perchloric acid plus periodic acid. Silica may be determined on either, sulfur is precipitated as the barium sulfate from one solution, and the other minor components, iron, aluminum, vanadium, phosphorus, titanium, arsenic, and calcium plus magnesium are determined in the second solution.

Spectrophotometric procedures are used for iron (1,10-phenanthroline-5-sulfonic acid), aluminum (aluminon dissolved in isopropyl alcohol), vanadium (phosphovanadotungstic acid), phosphorus (phosphovanadomolybdate complex), titanium (Tiron), and arsenic (silver diethyldithiocarbamate). The calcium plus magnesium is determined titrimetrically using EDTA with Calmagite as the indicator. The determination for silica is made by the usual gravimetric method and sulfur is determined by the barium sulfate gravimetric method.

Determination of constituents

Silica To the solution after the oxidation and subsequent dehydration add 100 ml. of water. Immediately cool and filter using a hard ashless paper. Wash the silica with a 1 per cent perchloric acid solution, and then with water. Any black material is not unreacted coal but mineral in

character and will be subsequently decomposed by the hydrofluoric acid used in correcting the silica determination. After the last washing moisten the paper with a few drops of 2 per cent ammonia and transfer the filter to a previously ignited and weighed platinum crucible. Burn away the paper and ignite to constant weight.

Add about 5 ml. of hydrofluoric acid to the residue in the platinum crucible. Evaporate to dryness, add several drops of perchloric acid and again evaporate to dryness. Cool and weigh. The loss in weight represents the silica (corrected) in the coal sample.

If a residue remains in the crucible proceed as follows: fuse the residue with one gram of a 1:1 mixture of sodium carbonate-sodium borate flux and heat over the flame of a Meker burner. Take up the solid melt with hot 1:1 hydrochloric acid. Transfer the solution to the volumetric flask containing the original filtrate and dilute to the mark.

Sulfur Adjust the filtrate in the 600-ml. beaker to a volume of about 200 ml. Dissolve 0.5 moles or 20 g. of sodium hydroxide in a small amount of water. Add the sodium hydroxide slowly with stirring to the sulfate solution. Stop the addition short of the point where hydrous oxides begin to precipitate. At this point the pH of the solution should be about one. Heat the solution almost to boiling. Add, all at once, 50 ml. of 0.1 M barium chloride solution. Heat

for 5-10 minutes just below boiling with frequent stirring. Then allow the solution to digest one hour or longer on a steam bath. When the precipitate has settled, add one drop of barium chloride to test for completeness of precipitation. After the digestion and subsequent cooling, filter by suction through a previously weighed porcelain, porous bottom crucible. Wash with water until a negative test for chloride is obtained on a small portion of the filtrate.

Heat the crucible plus precipitate in a 110° oven for five or ten minutes and then bring to constant weight in a muffle furnace at 650° .

Calcium plus magnesium

Reagents Dissolve 3.7 g. of disodium dihydrogen ethylenediaminetetraacetate dihydrate in one liter of water. Weigh 0.100 g. of magnesium chloride hexahydrate, and add this to the above solution and mix well. This solution will be about 0.01 M in EDTA.

Dissolve 1.000 g. of calcium carbonate in a little dilute hydrochloric acid. Dilute exactly to one liter and mix well; 1.00 ml. of this solution is equivalent to 1.00 mg. of calcium carbonate.

Calcium carbonate meeting the A.C.S. specifications is not satisfactory, as the tolerance for magnesium plus alkali metals is too high, 0.5 per cent. A more highly purified grade is required and available commercially.

Prepare a 10 per cent solution of sodium cyanide by dissolving 10 g. of the salt in 100 ml. of water.

Prepare a 10 per cent solution of hydroxylammonium chloride by dissolving 10 g. of the salt in 100 ml. of water.

Prepare a quantity of buffer solution by mixing 6.75 g. of ammonium chloride with 57.0 ml. of concentrated ammonium hydroxide and dilute to 100 ml. The pH of this mixture is just above 10.

Prepare a solution of the indicator by dissolving 0.05 g. of Calmagite (1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid) in 100 ml. of water.

Procedure Pipet 25.0 ml. of the standard calcium chloride solution, add 10.0 ml. of the buffer solution, 5.0 ml. of sodium cyanide, 5.0 ml. of hydroxylammonium chloride solution and three drops of Calmagite indicator. Titrate with the EDTA solution as described below for the determination of calcium plus magnesium in the coal. The EDTA prepared as described above should be equivalent to about 1.0 mg. of calcium carbonate per ml.

Adjust the pH of a 25 ml.-aliquot of the test solution to about five or six with sodium hydroxide. Add 10 ml. of buffer solution, 5 ml. of hydroxylammonium chloride and 5 ml. of sodium cyanide; mix well and add three drops of Calmagite. Titrate with the 0.01 M EDTA solution. At the endpoint the color will change from wine red to pure blue.

If the coal contains an appreciable amount of iron alter the procedure as follows: adjust the pH of the test solution to between one and two with sodium hydroxide. Add 5 ml. of triethanolamine. This will bring the pH to a value around 5.0. Add in succession and with stirring 5.0 ml. of 5 per cent sodium cyanide and 10.0 ml. of buffer solution. To the yellow solution now add 10-20 mg. of sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), and boil till colorless and then for a further two minutes. Add an additional 5-10 ml. of buffer solution, cool and proceed with the titration as above. If the Calmagite rapidly decomposes to colorless this indicates insufficient boiling with incomplete destruction of excess sodium hydrosulfite.

Iron

Reagents Sodium 1,10-phenanthroline-5-sulfonate; 0.005 M. Dissolve 1.4 g. of solid 1,10-phenanthroline-5-sulfonic acid in water, add two or three pellets of sodium hydroxide and as soon as the solid has dissolved dilute to one liter with water.

Hydroxylammonium chloride solution: Dissolve 100 g. of hydroxylammonium chloride in one liter of water.

Sodium acetate-acetic acid buffer: Dissolve 83 g. of sodium acetate in water, add 57.5 ml. of glacial acetic acid and dilute to one liter. The pH of this solution will be about 4.7.

Standard iron solution: Dissolve a quantity of about

0.14 g. of electrolytic iron in 20 ml. of hydrochloric acid, transfer the solution to a one liter volumetric flask, dilute to the mark with water and mix thoroughly. Pipet 100 ml. of this solution into a one liter volumetric flask, add 5 ml. of hydrochloric acid, dilute exactly to one liter and mix thoroughly. From the initial weight of the iron, calculate the iron content of this solution which will be about 14.7 $\mu\text{g./ml.}$

Procedure Pipet that volume of test solution which will yield a transmittance between 20 and 80 per cent into a 100 ml. volumetric flask. Add one or two ml. of hydroxylammonium chloride solution and one or two pellets of sodium hydroxide. Shake well until the pellets dissolve and the solution is colorless. Add 10 ml. of buffer solution and 10 ml. of sodium 1,10-phenanthroline-5-sulfonate. Dilute to the mark with water and mix well. Measure the transmittance of the solution at 512 $m\mu$ against a reagent blank.

Preparation of calibration curve Pipet various volumes ranging from 0-50 ml. of standard iron solution into 100-ml.-volumetric flasks. Add one or two ml. of hydroxylammonium chloride solution, 10 ml. of buffer solution and 10 ml. of phenanthroline reagent. Dilute to the mark, mix well and measure the transmittance of the solution in the identical fashion as above.

Aluminum

Reagents Modified aluminon reagent prepared according to the directions of Owen and Price (32). Dissolve 500 g. of ammonium acetate in water, filter and dilute the filtrate to one liter pouring the water through the filter paper. Add 80 ml. of glacial acetic acid, 1 g. of aluminon dissolved in 100 ml. of water and then 2 g. of benzoic acid dissolved in 300 ml. of reagent grade isopropyl alcohol. Add 450 ml. of isopropyl alcohol and dilute to two liters with water.

Dissolve 10 g. of gelatin in 250 ml. of hot water, dilute with 500 ml. of cold water and filter. Make up to one liter, transfer to a three liter beaker, and gradually add the two liters of aluminon solution, with constant stirring. The final solution should be clear and remain so when set aside and cooled; store in a polyethylene container and in the dark.

Cupferron: Prepare a 6 per cent solution by dissolving 6 g. in 100 ml. of water. Keep the solution cold. Dispose of the solution when it is no longer clear.

Standard aluminum solution: Dissolve a quantity of 0.16 g. of pure aluminum in 20 ml. of dilute hydrochloric acid, transfer the solution to a one-liter volumetric flask, dilute to the mark with water and mix thoroughly. Pipet 10 ml. of this solution into a one liter volumetric flask,

dilute exactly to one liter and mix thoroughly. From the initial weight of the aluminum, calculate the aluminum content of this solution which will be about 1.6 $\mu\text{g./ml.}$

Procedure Pipet an aliquot of the test solution which will ultimately give a transmittance reading between 20 and 80 per cent into a 125-ml. separatory funnel. Dilute with cold water to 50-75 ml. Add 3 ml. of concentrated perchloric acid and then drop by drop a cold 6 per cent solution of cupferron. Stop the dropwise addition when the first formation of a white precipitate is noticed. This is the excess reagent precipitating out of solution. Extract three or four times with ten ml. portions of cold chloroform. The last extract should be clear. The aluminum is to be found in the aqueous layer.

Transfer the aqueous layer to a beaker and evaporate to near dryness. Take up the remainder with water and transfer to a 100 ml. volumetric flask. Adjust the solution to the pale pink color of m-cresol purple or thymol blue. Add 1 ml. of 0.1 per cent solution of Triton X-100, 6 ml. of isopropyl alcohol and then 15 ml. of aluminon reagent solution. Mix by swirling and heat in a boiling water bath for two minutes. Add 20 ml. of cold water ($20^{\circ} \pm 1^{\circ}$), mix by gentle swirling, and heat in the boiling water bath for a further three minutes. Remove the flask and its contents from the bath, set aside for five minutes and cool to about 30° in

a beaker of cold water. This last step requires about five minutes. Add 10 ml. of isopropyl alcohol, and keep the mixture at 20° for twenty minutes. Dilute to 100 ml. with water, mix well and set aside for five minutes. Determine the transmittance of the solution at 540 m μ against a reagent blank.

Preparation of calibration curve Pipet various volumes ranging from 0-25 ml. of standard solution into 100-ml. volumetric flasks. From here treat the solutions in the identical fashion as above.

Vanadium

Reagents Sodium tungstate, Na₂WO₄·2H₂O; 0.5 M.
Dissolve 41 g. of the solid in 250 ml. of water.

Phosphoric acid, ortho, 85 per cent.

Cation exchange resin: Dowex-50W.X8 analyzed reagent resin, 100 to 200 mesh. Use ion exchange columns 1.2 cm. in diameter adding a slurry of resin until a bed of about 6 cm. is reached. Wash the resin with 10 per cent ammonium citrate, 3 M hydrochloric acid and finally with water.

Eluting solution: 0.01 M perchloric acid in 0.7-1.0 per cent hydrogen peroxide. Mix 0.85 ml. of concentrated perchloric acid and 23 ml. of 30 per cent hydrogen peroxide. Dilute to one liter with water.

Standard vanadium solution: Dissolve a quantity of about 0.117 g. of ammonium metavanadate in water; add 30 ml.

of perchloric acid, dilute exactly to one liter with water and mix thoroughly. The vanadium content of this solution will be about 50 $\mu\text{g./ml.}$

Preparation of calibration curve Pipet various volumes ranging from 5 to 25 ml. of standard vanadium solution into 50 ml. volumetric flasks. Add 2.5 ml. of 0.5 M tungstate and 2 ml. of phosphoric acid. Boil the solution, cool to room temperature and dilute the solution to exactly 50 ml. with water and mix well. Measure the transmittance of the solution at 400 $\text{m}\mu$ against a reagent blank.

Procedure Pipet into a beaker that volume of test solution which will yield a transmittance between 20 and 80 per cent. Evaporate to near dryness. Take up the residue in a minimum of 0.1 M perchloric acid and transfer to the resin. The vanadium will pass through the column. Elute with 50-75 ml. of 0.01 M perchloric acid in hydrogen peroxide as prepared. This will elute the vanadium quantitatively. Evaporate the eluate to near dryness, take up in water and transfer to a 50 ml. volumetric flask. Treat the solution in the identical fashion as above and determine the transmittance against a reagent blank at 400 $\text{m}\mu$.

Titanium

Reagents Standard titanium solution: Weigh accurately a quantity of about 1.018 g. of NBS no. 154 TiO_2 . This material should be dried and taken into solution as described by the circular provided with the standard sample.

Dilute the solution to mark in a one liter volumetric flask and mix well. Pipet 25 ml. of this solution into a one liter volumetric flask. Dilute exactly to one liter and mix thoroughly. From the initial weight of sample calculate the titanium content of this solution, which will be about 15 $\mu\text{g./ml.}$

Cation exchange resin: Prepare the same as in the determination of vanadium.

Eluting solution: 1 M perchloric acid in 0.7-1.0% hydrogen peroxide. Mix 85 ml. of concentrated perchloric acid and 23 ml. of 30 per cent hydrogen peroxide to one liter with water.

Sodium acetate-acetic acid buffer: Dissolve 82 g. of sodium acetate in water, add 57.5 ml. of glacial acetic acid and dilute to one liter.

Tiron: Dissolve 4 g. of disodium-1,2-dihydroxybenzene-3,5-disulfonate monohydrate in 100 ml. of water.

Preparation of calibration curve Pipet into 100-ml. volumetric flasks various volumes ranging from 5 to 25 ml. of standard solution. Add 10 ml. of buffer solution, 10 ml. of Tiron and dilute to the mark and mix well. Measure the transmittance of the solution at 400 $\text{m}\mu$. against a reagent blank.

Procedure Pipet into a beaker that volume of test solution which will yield a transmittance between 20 and

80 per cent. The volume taken initially for the vanadium determination may suffice, both elements being determined in the same aliquot. Follow the procedure as given under vanadium, first eluting it from the column and then eluting the titanium with 100-125 ml. of 1 M perchloric acid in 0.7 per cent hydrogen peroxide. Evaporate to dryness, take up in water and transfer to a 100-ml. volumetric flask. Add two pellets of sodium hydroxide to offset the acidity, 20 ml. of buffer solution and 10 ml. of Tiron reagent. Dilute exactly to 100 ml. and mix thoroughly. Measure the transmittance as directed above.

Phosphorus

Reagents Standard phosphorus solution: Weigh accurately a quantity of about 0.447 g. of disodium hydrogen phosphate and dilute to one liter with water and mix well. From the initial weight of this salt calculate the phosphorus content of this solution which will be about 0.1 mg./ml.

Ammonium molybdate: Prepare a 5 per cent solution by dissolving 5 g. of the salt in 100 ml. of water.

Ammonium vanadate: Dissolve 2.5 g. in 500 ml. of warm water, cool, add 20 ml. of nitric acid and dilute to one liter.

Nitric acid, 6 M: Dilute 100 ml. of concentrated nitric acid to 250 ml. with water.

Procedure Pipet that volume of test solution which will yield a transmittance between 20 and 80 per cent

into a 50-ml. volumetric flask. Add 10 ml. of 6 M nitric acid, 10 ml. of vanadate solution and 10 ml. of molybdate solution in that order. Dilute with water to 50 ml. and mix well. Allow to stand for thirty minutes. Measure the transmittance of the solution at 460 m μ against a reagent blank.

Preparation of calibration curve Pipet various volumes of standard phosphorus solution ranging from 1-20 ml. into 100-ml. volumetric flasks. Treat the solution in the identical fashion as above measuring the transmittance at 460 m μ against a reagent blank.

Arsenic

Reagents Standard arsenic solution: Weigh accurately a quantity 0.073 g. of arsenic trioxide. Dissolve the salt in a small amount of water with several pellets of sodium hydroxide. Add 25 ml. of perchloric acid and dilute to one liter with water and mix well. Pipet 10.00 ml. of this solution into a one liter volumetric flask, dilute exactly to one liter with water and mix thoroughly. From the initial weight of the arsenic trioxide, calculate the arsenic content of this solution which will be 0.6 μ g./ml.

Silver diethyldithiocarbamate: Prepared according to the directions of Powers et al. (35). Slowly add a 0.1 M aqueous solution of silver nitrate to an equal volume of a vigorously stirred 0.1 M aqueous solution of sodium diethyldithiocarbamate trihydrate. Water is removed with a beaker

filter, and the precipitate is washed three times with water. The solutions and rinses are chilled to below 8° before mixing, and the precipitate is kept below 8° until the last rinse has been completed. The precipitate is finally dried under vacuum at room temperature. The silver diethyldithiocarbamate solution is prepared by dissolving 1 g. of the dry salt in 200 ml. of pyridine, which has been percolated over activated alumina and then silica gel.

Impregnated cotton: Prepare by soaking cotton in a filtered, saturated, aqueous solution of lead acetate. The cotton is compressed to remove as much liquid as possible and then dried under vacuum until just dry to the touch.

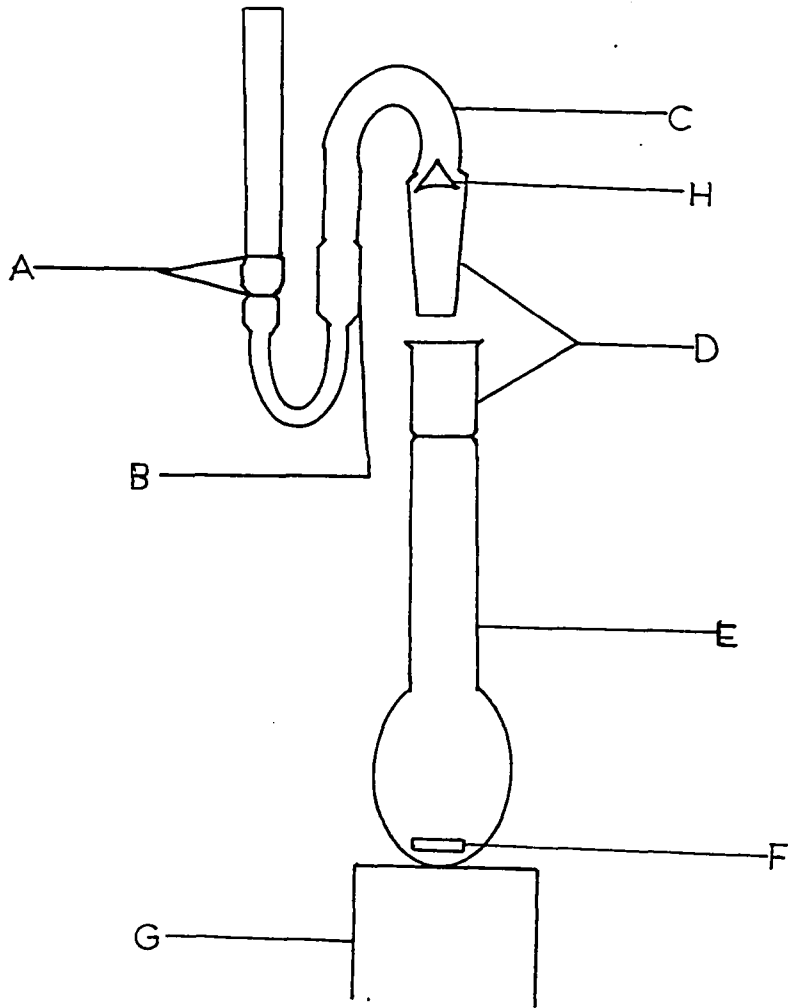
Stannous chloride solution: Dissolve 20 g. of stannous chloride in 50 ml. of concentrated hydrochloric acid.

Sodium iodide solution: Prepare a 15 per cent solution by dissolving 15 g. of sodium iodide in 100 ml. of water.

Procedure Pipet an aliquot of the test solution which will give a transmittance reading between 20 and 80 per cent into the 100 ml. digestion flask. See Figure 2 for the description of apparatus. Add 20 ml. of water, 4 ml. of perchloric acid, 2 ml. of 15 per cent sodium iodide and stir the mixture using a Teflon stirring bar and magnetic stirrer. Place the flask in an ice bath for five minutes. Remove, stir the contents and add 12 drops of stannous chloride solution. Allow the mixture to stand in the ice bath for 15 minutes.

Figure 2. Flask and arsine absorber

- A. Coarse-porosity fritted glass
- B. 3-ml. reservoir
- C. 2-mm. capillary
- D. 19/38 standard taper
- E. 100 ml. Kjeldahl flask
- F. Teflon stirring bar
- G. Magnetic stirrer
- H. Impregnated cotton



Pack a small wad of the impregnated cotton firmly inside the joint of the arsine absorber. Grease the joint with a non-silica stopcock grease. Pipet 3.00 ml. of silver diethyldithiocarbamate into the dry absorber.

Remove the flask from the ice bath and stir the contents moderately. Add 6 g. of zinc, 20 mesh, and quickly connect the arsine absorber to the flask. Stir for a period of twenty to thirty minutes. Disconnect the absorber and inspect the impregnated cotton. If most of it is blackened, discard the analysis because hydrogen sulfide may have reached the absorber.

Draw the liquid in the absorber back and forth through the fritted-glass disks until it is uniform in color, and then force it out of the absorber into an absorption cell. Determine the transmittance of the solution at 540 m μ with silver diethyldithiocarbamate solution in the reference cell.

Determine a blank by running through the entire procedure. Subtract any absorbance obtained in the blank from that of each sample, both standard and unknown.

Preparation of calibration curve Pipet various volumes of standard arsenic solution ranging from 5-20 ml. into the digestion flask. From here treat the solution in the identical fashion as above. Measure the transmittance at 540 m μ against a silver diethyldithiocarbamate blank.

Results and Discussion

It has been found that the wet oxidation of coal using perchloric acid plus periodic acid is complete and sufficiently rapid without the addition of a catalyst as suggested by Smith and Diehl (43) in their application of this acid mixture to organic matter in general. Any addition of metal content is not advisable because of the interference the metal may cause later in the analysis. Vanadium, an excellent catalyst, for example, causes fleeting endpoints in the determination of calcium plus magnesium by the EDTA titration method. The presence of vanadium increases the error due to coprecipitation in the determination of sulfur as barium sulfate. Further, such addition is especially inadvisable if the element added is the one being determined.

The oxidation of coal with the periodic acid-perchloric acid mixture progresses smoothly if the starting acid is 68-69 per cent perchloric acid. By using either a condenser head in a conical flask or the more elaborate Bethge apparatus, the acid concentration can be increased gradually and a stepwise increase in oxidation power exercised. The more concentrated the perchloric acid at the start, the shorter is the time required for a complete oxidation.

Coals obtained from the Illinois Geological Survey and the Scandia Mine at Madrid, Iowa were oxidized smoothly with the formation of very little foam.

Some coals were found which produce considerable foam and with these coals it was necessary to limit the concentration of perchloric acid used at the start to 68 per cent. Explosions resulted from heating coals which foamed badly with perchloric acid of greater than 70 per cent. The explosions apparently resulted from a vapor phase reaction of some component of the foam with perchloric acid vapor. Thus, when a 2 g. sample of the Pershing Mine coal was mixed with 3 g. of periodic acid plus 75 ml. of 71.3 per cent perchloric acid in a 250-ml. conical flask, foam formed which reached the condenser head immediately preceding the explosion. When 1 g. samples were treated in the same fashion explosions also occurred. In any case coals which foam excessively should be treated with caution, at least initially.

Preliminary experiments with small quantities, say a 10 mg. sample, should be made first on a coal which has not been previously wet ashed. If the oxidation proceeds smoothly, the sample may be increased to 100 mg., then to 500 mg., and finally to one gram or larger. In a stepwise fashion the per-

chloric acid concentration may also be increased starting from a composition of about 68 per cent. This is not so much an admission that a violent reaction will always occur as a sensible approach to the problem of reducing the time required for the analysis of a given type of coal on a routine basis. For most coals initial concentrations of 70 per cent perchloric acid is hazard free and for all 68 per cent perchloric acid at the start is safe.

A 1.0 g. sample of coal requires 1.5 g. of periodic acid. Lower forms of iodine are oxidized by boiling concentrated perchloric acid to iodic acid so that all of the iodine present is converted to iodic acid. It is best to remove this iodic acid before proceeding with the determinations of sulfur and arsenic. Hydrogen peroxide is used to reduce the iodic acid formed. The decomposition of the iodate removes any error caused by precipitation of barium iodate in the gravimetric determination of sulfur as barium sulfate and in the arsenic determination the error which results from iodine evolved along with the arsine.

The perchloric acid plus periodic acid procedure serves admirably for the oxidation of coal preparatory to the analysis of silica, sulfur, arsenic, phosphorus and the metals. The method has several advantages over the other existing wet oxidation methods. The periodic acid brings about the initial oxidation of organic matter at more moderate temperatures and

with controlled intensity. Complete oxidation with the mixture requires only a short period of time. The volatile combustible matter is oxidized rather than volatilized. The presence of periodic acid as well as its reduction products, iodic acid, and iodine perchlorate, ensures more favorable conditions for retention of arsenic (43).

Determination of constituents of coals

Silica One dehydration is sufficient for the determination of silica. Evidence for this is given in the work of Willard and Cake (51) who report: "the removal of silica is remarkably complete considering the amount present, and in all but the most accurate work the amount remaining in solution can be disregarded". Because of the high solubility of metal perchlorates the residue of metal perchlorates dissolves rapidly when water is added following the dehydration.

There is present in many coals a large amount of iron and experience indicated that considerable iron was carried by the silica in the periodic acid-perchloric acid attack. That a significant residue remains after the removal of silica as volatile silicon tetrafluoride is shown in Table 1. This residue was far too much to be neglected and was taken into solution and added to the original filtrate. A major part of this residue is probably baked iron oxide. A blistery, reddish brown solid was present in some samples which, once dissolved, gave a confirmatory test for iron with 1,10-

Table 1. Silica in Pershing Mine coal; periodic acid-perchloric acid ashing; gravimetric determination

Pershing Mine Coal g.	Impure silica g.	Pure silica g.	Silica Per cent
1.0050	0.0381	0.0312	3.11
1.0168	0.0391	0.0321	3.16
1.0096	0.0554	0.0316	3.14
1.0084	0.0385	0.0323	3.20
1.0022	0.0374	0.0316	3.14
1.0015	0.0350	0.0310	3.09

phenanthroline.

A first attempt was made to take up the residue in hot concentrated hydrochloric acid. This was not successful. A creamy white precipitate remained resistant to solution. On the premise that this solid was silica, it was filtered, ignited and treated with hydrofluoric acid. No difference in weight was observed before and after this last step. It was concluded that all silica was accounted for initially. A second and successful attempt was made to fuse the residue remaining with a flux of one to one sodium carbonate-sodium borate. The melt was taken up in a one to one hot hydrochloric acid solution and then added to the test solution. Before this addition it was necessary to reduce the volume of

the solution containing the melt by evaporation.

The results on a number of determinations of silica in the Pershing Mine coal are shown in Table 1.

Sulfur It was found that perchloric acid plus periodic acid oxidation of phenylthiourea, and various coal samples yields quantitative recovery of sulfur. Sulfur bearing gases were evolved in this oxidation procedure but were retained in the Bethge apparatus by use of the scrubber containing a 3 per cent hydrogen peroxide solution.

Unsuccessful attempts were made to determine sulfur under the following conditions: without the use of a scrubber, with a scrubber filled only with water, scrubber filled with a 3 per cent solution of hydrogen peroxide. In each case the solution in the scrubber was mixed with that in the reaction flask and the sulfate was precipitated as the barium salt. In all three cases results were found to be low. Escaping gases were absorbed in the 3 per cent hydrogen peroxide solution but were not oxidized to sulfate. Total conversion only came about by combining the solution in the scrubber with that in the reaction flask and boiling to fumes of perchloric acid.

In order to check the procedure, analyses were made on phenylthiourea. Owing to the high concentration of sodium ions present resulting from the neutralization with sodium hydroxide the method of reverse precipitation (34) was used.

As can be seen from the results given in Table 2, the values obtained were somewhat higher than the theoretical sulfur content. This is to be expected because the method favors the coprecipitation of chloride ion and introduces a positive error.

If a slight excess of barium chloride is added quickly to the solution of the sulfate, the precipitate grows in a solution where the concentration of barium ions is only slightly greater than that of the sulfate ion. Thus, neither the positive error due to coprecipitation of chloride ion nor the negative error due to coprecipitation of sodium ion is great. The negative and positive errors of coprecipitation tend to cancel. This is the method of Hintz and Weber (13). This method is accurate and convenient, particularly for samples that contain a large amount of sodium chloride. An investigation into the accuracy of several methods for the determination of sulfur in the presence of sodium chloride was made by Rieman and Hagen (39). An excellent short summary appears in Rieman, Neuss and Naiman (40).

Values for per cent sulfur in phenylthiourea by the method of Hintz and Weber after the periodic acid-perchloric acid oxidation were obtained, see Table 2.

A further check on the method was made. Samples of DPS 5695-60 coal, supplied by the Illinois Geological Survey, were also analyzed by the method of Hintz and Weber after the

Table 2. Sulfur in various samples; periodic acid-perchloric acid ashing

Sample	Method of precipitation	Weight sample g.	Sulfur theoretical per cent	Sulfur found per cent	
Phenyl-thiourea	Reverse	0.5049	21.07	21.20	
		0.5017	21.07	21.28	
		0.5111	21.07	21.22	
		0.5013	21.07	21.25	
		0.5093	21.07	21.26	
	Hintz and Weber	0.5027	21.07	21.11	
		0.5075	21.07	21.05	
		0.5027	21.07	21.17	
	DPS 5695-60	Hintz and Weber	1.0303	6.39	6.39
			1.0124	6.39	6.35
0.5017			6.39	6.38	
1.0095			6.39	6.20	
Pershing Mine coal	Hintz and Weber	1.0015	-	3.67	
		1.0018	-	3.72	
		1.0036	-	3.76	
		1.0065	-	3.71	

periodic acid-perchloric acid oxidation. The results are given in Table 2.

The results of the analysis of Pershing Mine coal for sulfur content are also given in Table 2. The periodic acid-perchloric acid oxidation was applied and the sulfur determined by the method of Hintz and Weber.

Iron The results obtained in the determination for iron in Pershing Mine coal using 1,10-phenanthroline-5-sulfonic acid are shown in Table 3. Four ml. aliquots were taken in order to obtain transmittance values in a favorable region of transmittance.

Table 3. Iron in Pershing Mine coal; periodic acid-perchloric acid ashing; 1,10-phenanthroline-5-sulfonic acid colorimetric method

Weight of sample g.	Transmittance per cent	Absorbance	Iron per cent
1.0045	38.2	0.418	2.41
1.0040	38.2	0.418	2.42
1.0018	38.7	0.412	2.38
1.0065	38.3	0.417	2.41

Data obtained for iron content without fusing the residue after the volatilization of silica with hydrofluoric acid gave an average value of 2.19 per cent iron. The fusion of the residue with a sodium carbonate-sodium borate flux is

indeed necessary. If not for this step an error of about 10 per cent would be immediately introduced into the iron determination. For the most part this residue probably consisted of oxides of aluminum and iron, probably present originally in the coal as silicates.

Vanadium and titanium Initially, attempts were made to determine vanadium in coals after the oxidation with perchloric acid plus periodic acid using the 3,3'-diaminobenzidine tetrahydrochloride method. Cheng (6) reported favorably on the speed and high selectivity of the 3,3'-diaminobenzidine method for determining small amounts of vanadium. However, selenium(IV) and 3,3'-diaminobenzidine react to form a colored solution and even form a flocculent yellow precipitate if sufficient selenium be present. Hot, concentrated perchloric acid does not oxidize selenium to the hexavalent state, which does not react with 3,3'-diaminobenzidine. Selenium is present in many coals and attempts were made to circumvent this interference in the determination of vanadium.

Fritz (9) reported a scheme for the separation of vanadium from a number of metal ions by elution from a cation exchange with dilute acid containing 1 per cent or less hydrogen peroxide. Vanadium is quantitatively removed as a vanadium(V)-hydrogen peroxide complex; other metal ions such as iron and titanium are eluted later with stronger acid. Fritz reported that vanadium does not remain on the resin as the VO_2^+ cation

when eluted with dilute acid but that any vanadium(IV) present as the VO^{++} cation is not eluted. The hydrogen peroxide serves to oxidize vanadium(IV) to vanadium(V) and complex the latter which is then eluted.

Several attempts were made to separate vanadium from selenium prior to its determination. One attempt involved the Fritz ion exchange procedure with slight modification. It appeared likely that the more highly charged VO^{++} cation would remain on the cation exchange column and be selectively eluted by the 0.01 M perchloric acid-1 per cent hydrogen peroxide solution. Selenium, existing as an anion, should pass directly through a cation exchange column. Work was done with standard vanadium solutions. Vanadium(V) was reduced to vanadium(IV) with sodium bisulfite but a selective separation was not achieved. A mixture of vanadium(IV), titanium(IV), selenate and iron(III) was placed on the resin from a dilute perchloric acid in order to check the separation procedure. The mixture contained about 200 ug. each of selenium and vanadium, and 250 ug. each of titanium and iron. The resin was washed with 50 ml. of water to carry through the anion and then eluted with 50-75 ml. of 0.01 M perchloric acid in 0.7 per cent hydrogen peroxide. Incomplete recoveries of vanadium were consistently obtained.

After the 3,3'-diaminobenzidine method was shown to be unsatisfactory, the phosphovanadotungstate method (54) was

employed for the determination of vanadium. Selenium does not interfere in this method for vanadium. The vanadium(V) was placed on Dowex 50W-X8 cation exchange resin and eluted with 0.01 M perchloric acid in 1 per cent hydrogen peroxide solution. Interferences such as cobalt, copper, nickel, manganese and uranium are not eluted. Excellent recoveries of vanadium were obtained.

Titanium may be determined along with vanadium. Once titanium has been placed on the cation exchange resin it may be eluted after the vanadium by increasing the strength of eluant to 1 M perchloric acid in 1 per cent hydrogen peroxide. Titanium was determined with Tiron (1,2-dihydroxybenzene-3,5-disulfonic acid). Tiron is selective and extremely sensitive; it is a superior reagent for the determination of titanium and coupled with the described ion exchange procedure is highly specific; interfering metals such as molybdenum, uranium, nickel, iron, and chromium are not eluted by 1 M perchloric acid in hydrogen peroxide solution.

Standard solutions of vanadium(V), titanium(IV) and iron(III) were placed on the cation exchange column. Vanadium and titanium were separated by the method described in the section on the experimental procedure for titanium. Quantities of 0.241 mg. of titanium were placed on the column, eluted and analyzed by the recommended procedure; the following recoveries were obtained: 0.247, 0.267, 0.188,

0.250, 0.252, 0.230, average: 0.247 mg. Again, 1.02 mg. of titanium taken; 0.99, 0.99 mg. found.

The vanadium in the Pershing Mine coal is below the limit of detection of the reagent employed. Aliquots of 100 ml. gave colorless solutions.

In Table 4 are given the titanium analyses obtained on the Pershing Mine coal. Aliquots of 100 ml. were taken in order to obtain transmittance values in a favorable region of transmittance.

Table 4. Titanium in Pershing Mine coal; periodic acid-perchloric acid ashing; tiron colorimetric method

Weight of sample g.	Transmittance per cent	Absorbance	Titanium per cent
1.0045	69.0	0.261	0.059
1.0040	84.1	0.075	0.066
1.0018	69.5	0.258	0.058
1.0065	88.0	0.055	0.050

Calcium plus magnesium The ethylenediaminetetraacetate (EDTA) titration of calcium plus magnesium is now well known and is adequately described in the text books on quantitative analysis. The titration is generally performed with solutions 0.01 M in EDTA at pH 10, the end-point being marked by the change from red to blue of either Eriochrome Black T

or Calmagite. The end-point is better with 0.01 M solutions of EDTA than with more dilute solutions.

Iron if present, is precipitated as hydrated ferric oxide upon addition of sodium hydroxide during neutralization of the acidic solution prior to the titration. Precipitation is usually prevented by prior reduction of iron(III) and addition of cyanide which converts the iron to colorless ferrocyanide. A high iron concentration, as is present in many coals will result in formation of an intense yellow color at this point. This yellow color is disturbing in the determination of the end-point in the subsequent titration. To obviate this problem two procedures are available. The pH of the solution may be adjusted to five and the ferric hydroxide precipitate removed by filtration. Alternatively the pH of the solution may be adjusted to between one and two with sodium hydroxide, hydroxylammonium chloride and triethanolamine added, and then in succession cyanide, buffer to pH 10 and sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$); the solution is then boiled until colorless, cooled and titrated.

The precipitation method was performed on the coal from the Scandia Mine at Madrid, Iowa, while the reduction procedure was applied to the Pershing Mine coal. In each case the results were quite good but the reduction procedure is recommended. The method of sodium hydrosulfite reduction is faster and not subject to the error of coprecipitation.

Two samples of Madrid, Iowa coal, each weighing 1.000 g. were oxidized by the recommended wet ashing procedure. One sample was spiked with 0.1000 g. of calcium carbonate to investigate the possible loss of calcium during oxidation. To the second sample no calcium was added. The final solutions were filtered and diluted to 250 ml. in volumetric flasks. The results obtained are shown in Tables 5 and 6.

Table 5. Calcium plus magnesium in Madrid, Iowa coal; periodic acid-perchloric acid ashing; EDTA titration

Weight of sample g.	Calcium carbonate added g.	Aliquot ml.	0.009835 M EDTA ml.	Calcium plus magnesium per cent calcium
1.0000	0.1000	25	10.90	4.29
1.0000	0.1000	25	10.90	4.29
1.0000	none	25	0.90	0.28
1.0000	none	25	0.90	0.28

Table 6. Calcium plus magnesium in Pershing Mine coal; periodic acid-perchloric acid ashing; EDTA titration

Weight of sample g.	Aliquot ml.	0.009500 M EDTA ml.	Calcium plus magnesium per cent calcium
1.0045	25/500	1.89	1.43
1.0040	25/500	1.92	1.48
1.0018	25/500	1.91	1.45
1.0065	25/500	1.91	1.45

Aluminum Iron, copper, and titanium interfere in the determination of aluminum by the spectrophotometric procedure using aluminon in isopropyl alcohol. These elements were separated by precipitation with cupferron from an acid solution. At a pH of about one, a separation of all commonly interfering metals from aluminum can be made rapidly and effectively by extracting the cupferrates of the interfering metals into chloroform.

In the present study employing aluminon, the intensity of the color was found to be non-reproducible and unstable. Over a period of five to ten minutes the transmittance value was observed to drift as much as 10 per cent. This difficulty was eliminated by controlling the temperature of the solution

during the spectrophotometric measurements; this was accomplished by circulating cold water through "thermospacers" in the Beckman DU spectrophotometer.

In Table 7 are given the results for aluminum obtained on the Pershing Mine coal. It was necessary to reduce the aliquot to 3.00 ml. out of a volume of 500 ml. to obtain transmittance values in a favorable region of transmittance.

Table 7. Aluminum in Pershing Mine coal; periodic acid-perchloric acid ashing; aluminon colorimetric method

Weight of sample g.	Transmittance per cent	Absorbance	Aluminum per cent
1.0045	43.2	0.364	-
1.0040	56.2	0.250	0.59
1.0018	55.8	0.253	0.60
1.0065	53.8	0.269	0.64

A solution containing 40.0 μg . of aluminum was carried through the identical procedure as for the determination of aluminum in the coal sample. The amount recovered was 38.8 μg .

Phosphorus Because of the small amounts of metals in coal, interferences in the phosphovanadomolybdate method are negligible. The tolerance limits for this method were established by Kitson and Mellon (28).

Interference was expected from titanium, the phosphate of which is insoluble but this proved to be negligible. As much as 2 mg. of phosphorus as phosphate was mixed with sufficient titanium(IV) and 10 ml. of 6 M nitric acid in 50 ml. of solution but no precipitate resulted and the correct result for phosphorus was obtained.

Results for the phosphorus content in the Pershing Mine coal are shown in Table 8.

Table 8. Phosphorus in Pershing Mine coal; periodic acid-perchloric acid ashing; phosphovanadomolybdate colorimetric method

Weight of sample g.	Aliquot ml.	Transmittance per cent	Absorbance	Phosphorus per cent
1.0040	50/500 ^a	95.0	0.022	0.090
1.0065	50/500 ^a	95.3	0.021	0.089
1.0045	100/500 ^b	82.8	0.082	0.086
1.0040	100/500 ^b	83.3	0.079	0.083
1.0065	100/500 ^b	83.5	0.078	0.083

^a50 ml. aliquots worked up and taken to mark in 100 ml. volumetric flasks

^b100 ml. aliquots evaporated to ca. 20 ml., worked up and taken to mark in 50 ml. volumetric flasks

Arsenic Quantitative recoveries of arsenic were obtained by the perchloric acid plus periodic acid oxidation

procedure. Samples of arsenic trioxide were placed in 500 ml. conical flasks, and dissolved in water with several pellets of sodium hydroxide. Fifty milliliters of concentrated perchloric acid plus 0.5-1.0 g. of periodic acid were added. Condenser heads were placed in the neck of the flasks and the solutions were boiled for 20 to 30 minutes. The iodate was decomposed with 30 per cent hydrogen peroxide; the solutions were cooled and purged with nitrogen for 15 to 20 minutes in order to drive out any chlorine. The solutions were diluted with water, an excess of 20 per cent sodium iodide was added and the solutions were titrated with standard sodium thiosulfate using the disappearance of the starch iodine complex as the end point. The results are shown in Table 9.

Table 9. Recovery of arsenic trioxide after oxidation with perchloric acid-periodic acid

Arsenous oxide taken g.	Arsenous oxide found g.	Recovery per cent
0.2399	0.2402	100.3
0.2454	0.2405	98.0
0.2340	0.2340	100.0
0.2331	0.2332	100.0
0.2378	0.2382	100.2
0.2499	0.2504	100.2
0.2337	0.2315	99.1

The method adopted to determine arsenic in coal after wet oxidation with perchloric acid plus periodic acid is that of Powers et al. (35) who employed the silver diethyldithiocarbamate method for arsenic in naphtha. Powers et al. report that this method is simpler to use than the molybdenum blue method and is equally sensitive.

The procedure of Powers et al. was modified and the time required for an analysis has been decreased significantly. The arsenic need not be concentrated by adsorption onto silica gel impregnated with sulfuric acid as in the naphtha determination and because silica gel is absent during the arsine evolution the time required is cut in half. The determination of arsenic in coal can be completed in forty minutes.

The results for the arsenic content of the Pershing Mine coal are shown in Table 10. Coal samples were oxidized by the recommended procedure, silica was filtered off and each filtrate was diluted with water to 250 ml. in volumetric flasks. A 25 ml. aliquot was taken for each determination.

Table 10. Arsenic in Pershing Mine coal; periodic acid-perchloric acid ashing; silver diethyldithiocarbamate colorimetric method

Weight of sample g.	Absorbance	Arsenic per cent
2.0110	0.274	0.0022
2.0075	0.249	0.0027
2.0083	0.253	0.0020
1.0065	0.173 ^a	0.0028
2.0080	0.335	0.0027
2.0006	0.281	0.0022
2.0075	0.286	0.0023

^a50 ml. aliquot taken for the determination

SUMMARY

A method has been developed for the isolation of spores present in coal. The method involves a differential, wet oxidation procedure employing periodic acid plus perchloric acid by which most of the carbonaceous material is burned away leaving the spores untouched. Perchloric acid of 50 per cent concentration is best for this purpose. Some spores are destroyed at greater concentrations of perchloric acid; at lower concentration, the oxidation is slower and less effective. The method is fast and efficient; the time required for reaction is about twenty minutes. This method is hazard free in contrast to earlier methods involving chlorates.

Complete destruction of coal results from the attack by periodic acid plus perchloric acid of final concentration about 70 per cent. A catalyst is not necessary. The attack proceeds smoothly if begun with acid of 68 per cent concentration. With certain coals that produce foam, explosions may result if the attack is begun with acid of 71 per cent concentration. This method of wet oxidation is an excellent way of preparing a sample of coal for a determination of the minor constituents present. This method has several advantages over the other existing wet oxidation methods. The periodic acid brings about the initial oxidation of organic matter at moderate temperatures and with controlled intensity.

The complete oxidation requires only a short period of time. The volatile-combustible matter is oxidized rather than volatilized. The presence of periodic acid as well as its reduction products, iodic acid and iodine perchlorate, ensures the retention of arsenic.

A knowledge of the content of the minor elements, sulfur, arsenic, phosphorus, and various metals, is of interest to those employing coal as a boiler fuel for these components are closely related to the problems of clinker formation and air pollution.

On the basis of earlier investigations no loss of metal was expected during the wet oxidation of coal by the periodic acid-perchloric acid mixture. With the non-metals, especially sulfur, loss by volatilization is a serious problem. A technique was developed to obviate the loss of sulfur.

The periodic acid-perchloric acid destruction of the organic matter leaves the residue in excellent chemical form for subsequent determination, although it is best to remove the iodic acid produced in the attack by addition of 30 per cent hydrogen peroxide. Iodine is produced and is removed by boiling the solution.

In the residue from the oxidation, silica was determined first, the silica being already dehydrated by the boiling perchloric acid (the classical Willard and Cake procedure).

The various metallic elements were then determined on aliquots of the filtrate by spectrophotometric methods of recent origin: iron by the 1,10-phenanthroline-5-sulfonic acid method; aluminum by aluminon in isopropyl alcohol; vanadium as phosphovanadotungstic acid; titanium by Tiron and calcium plus magnesium by EDTA titration using Calmagite indicator.

In the determination of aluminum by the aluminon in isopropyl alcohol method the intensity of the color was found to be non-reproducible and unstable with time. This problem was eliminated by controlling the temperature of the cell compartment of the spectrophotometer.

An appreciable iron concentration obscures the end-point in the titrimetric determination of calcium plus magnesium using EDTA. Some ferrocyanide is formed having an intense yellow color. This difficulty can be circumvented by either precipitating the hydrous ferric oxide and filtering or by reducing the yellow species by boiling with sodium hydrosulfite.

It was found that sulfur was evolved during the periodic acid-perchloric acid attack and that it was not retained in the so-called Bethge apparatus in which there is placed on the reaction flask a condenser and a collecting sump from which the condensate can be either returned to the reaction mass or withdrawn. A scrubbing tube containing a three per cent hydrogen peroxide solution placed at the top of the condenser of the Bethge apparatus proved effective. By combining

this solution with the main portion in the reaction flask and boiling to fumes of perchloric acid a quantitative conversion to sulfuric acid was obtained. The procedure was checked on phenylthiourea and on the few analyzed coals available from the Illinois Geological Survey.

Retention of arsenic was complete without the additional scrubbing operation required for sulfur. In the new silver diethyldithiocarbamate method, in which the arsenic is reduced with zinc in acid solution, the arsine evolved is absorbed in a three milliliter pyridine solution of silver diethyldithiocarbamate and the arsenic determined spectrophotometrically. This method is rapid, reproducible and highly sensitive. For maximum accuracy, the sample should contain between three and eleven micrograms of arsenic. In conjunction with periodic acid-perchloric acid ashing this proved an excellent method for arsenic in coal.

With phosphorus too, no loss was experienced in the periodic acid-perchloric acid ashing. The phosphovanadomolybdate method proved best for the spectrophotometric determination of phosphorus.

The complete analysis devised was applied to a bituminous coal of Iowa origin.

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