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DER

OVERBURDEN SAMPLING AND TESTING MANUAL

PREPARED UNDER CONTRACT By

EARTHTECH AND GEOCHEMICAL TESTING
DIVISIONS OF ENERGY CENTER INC,

CONTRACT No, ME 86120

Small Operator Assistance Program
Bureau of Mining and Reclamation
Department of Environmental Resources
Room 205 Executive House Apartments
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OVERBURDEN SAMPLING

AND

TESTING MANUAL

BY

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COMMONWEALTH OF PENNSYLVANIA
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FORWARD

The increasing reliance on overburden analyses for the assessment of potential pollutional impacts and the efficient planning of mining operations has led to the development of numerous overburden analysis methods. The various methods do not always produce comparable results because of interferences and sensitivities of the methods used. As a result, the Department of Environmental Resources saw a need for a manual of field and laboratory procedures which could be used by the mining industry and regulatory agencies to select an applicable geochemical testing method for mine overburdens.

This manual provides a step-by-step description of the most commonly used chemical, physical and mineralogic procedures for the analysis of coal overburdens, as well as a discussion of the potential interference and precautions which must be considered for each method. The manual does not recommend or support any specific analytical method, nor does it establish criteria for the interpretation of data resulting from the various methods.

The manual was prepared by the Earthtech and Geochemical Testing Divisions of Energy Center Incorporated in accordance with Contract No. ME 86120 under the sponsorship of the Federal Office of Surface Mining, Reclamation and Enforcement and the Pennsylvania Department of Environmental Resources.

Ernie Giovannitti

Ernest F. Giovannitti, Director
Bureau of Mining and Reclamation

PART 1

COLLECTION AND PREPARATION OF SAMPLES

I. SITE SELECTION FOR OVERBURDEN HOLES OR COLUMNS

A. SCOPE

This section will address the factors that dictate the placement and type of overburden sampling points. The relationship between stratigraphy, structure, hydrogeology, and previous mining development will be examined. Actual requirements for the number of overburden sample holes or columns for a given site are addressed in the Department's Overburden Analysis Manual.

B. PURPOSE

Overburden analyses are performed to satisfy the Department's mining permit requirements as well as to provide useful data to the coal operator as a mining management tool. To maximize the information gained from the laboratory reports, it is necessary to plan the location of the sampling holes or columns, based upon geologic, hydrologic, and previous mining elements that exist on or near the proposed mining site. These elements apply to the Bituminous as well as the Anthracite coal regions of Pennsylvania.

C. PLANNING THE OVERBURDEN SAMPLING PROGRAM

1. LITERATURE/MAP SEARCH

Planning of the sampling program starts with basic research of the existing literature that pertains to the site. This should occur before any drilling is planned. Such research will maximize the results from the initial drilling program, even if the operator decides to test only the quality of the coal seam before proceeding to more thorough exploration and permit-related drilling.

A useful guide is the Atlas of Preliminary Geologic Quadrangle Maps of Pennsylvania, compiled and edited by Thomas M. Berg and Christine M. Dodge, and distributed by the Bureau of Topographic and Geologic Survey, through the State Book Store, as "Map 61". This publication contains a reduced scale (1" = 1 mile) reproduction of most of the 7 1/2 minute quadrangles in Pennsylvania. These maps identify some of the available Formation outcrops and structural geology information produced by government, academic, and industry sources. References to existing publications or open-file reports that cover these quadrangles are listed on the map margins.

Another source of information to consult is "Pennsylvania Geological Publications". This catalogue, prepared by the Bureau of Topographic and Geologic Survey, contains most of the geologic reports written about Pennsylvania. The publications are keyed to 15 minute quadrangles and counties.

The following agencies maintain old and current deep mine maps for many seams in Pennsylvania: U.S. Bureau of Mines in Pittsburgh; Pennsylvania Bureau of Mining and Reclamation, Division of Deep Mine Permitting in McMurray; and Pennsylvania Bureau of Deep Mine Safety in Pottsville. These agencies have map repositories consisting of prints, originals, or micro-film and copies are readily obtained. Included in these archives are the W.P.A. (Works Progress Administration) deep mine maps, generated in the 1930's, covering nearly all the coal fields by 15' quadrangle.

The Pennsylvania Bureau of Mining and Reclamation maintains permit application files, the non-confidential portions of which can be reviewed by any interested party. These files contain geologic and hydrologic data, as well as previous mining information. Specific permit applications may be reviewed at the District Offices at Greensburg, Knox, Hawk Run, Ebensburg, and Pottsville. The central office in Harrisburg maintains a mapping file of most of the mining permit boundaries in the state, plotted on 7 1/2' quadrangles. This office can also be contacted to obtain information on Operation Scarlift reports. These reports, prepared in the late 1960's and early 1970's, contain valuable geologic, hydrologic, and mining history data for major watersheds impacted by mining.

The Bureau also maintains water quality data, derived from mining permit applications as well as numerous other sources. Chapter 93 of Title 25, Rules and Regulations, contains watershed use classifications for every stream and tributary in Pennsylvania.

The Bureau of Topographic and Geologic Survey maintains a state-wide computer file of ground water quality and hydraulic properties for wells and aquifers. This information has been compiled from the required driller's forms, completed when a well is newly developed or renovated. It also includes information from the various hydrologic publications that cover Pennsylvania. The catalogue for this information is entitled "A Guide to DER's Bureau of Topographic and Geologic Survey Well Data System - An Inventory of Water Well Information". Computer print-outs are available by county. Driller's completion forms, too recent to be on the print-out, are on. open-file and may be reviewed in Room 903, Executive House, at 2nd and Chestnut Streets in Harrisburg.

Existing aerial photographs are also a source of geologic and hydrologic data as well as mining history. These are available in a number of different formats from the U.S. Soil Conservation Service and the Pennsylvania Bureau of Topographic and Geologic Survey. Photos can be viewed at any Soil Conservation office or at the Bureau's Pittsburgh or Harrisburg offices. Other agencies, such as the Pennsylvania Department of Transportation, have repositories of aerial photos and photogrammetric mapping.

It is good practice to consult all of the available literature as an integral part of the property evaluation procedure. This information, when interpreted by properly trained professionals, can provide insight into the geologic and hydrologic framework of the site. It also provides an alert to any potential operational or environmental problems that may be incurred. This data will usually save time and money in planning the exploration program for evaluation or permitting purposes because cropline positions and structural, stratigraphic, and hydrologic elements can be anticipated in advance.

2. EXPLORATION PROGRAM DESIGN

It is recommended that projected structure contours for key marker beds, existing mine entries, and other mining or exploration related features be placed on a map (7 1/2' topos are adequate). Previous strip mining and surface features of deep mining activities are evident on existing topographic maps and aerial photos. Using the structure contours and the previous mining or exploration Information, it is possible to project the positions of coal croplines. This is accomplished by determining the average stratigraphic distances between the coal seams and adding or subtracting these distances from the structure contour elevation datum to represent the various seams. This results in structure contour overlays for each seam.

Coal croplines are delineated by mapping the intersection of the structure contour elevations with the corresponding topographic elevations. The same procedure can be followed to project the highwall development heights for each seam. The cropline positions can be checked with the previous mining data by comparing the horizontal and vertical positions of deep mine entry points and abandoned contour strip mine spoil piles with the projected crop-line. The elevations of the spoil piles must be scrutinized to be sure that one is not observing a slide on a steep slope. Careful observation can distinguish features that will indicate the outcrop position and pit bottoms.

A site investigation will provide additional data and will confirm or modify the literature review presumptions. This should maximize the information to be gathered during drilling and/or trenching. Additional benefits include observation of site conditions that will affect the efficiency of the exploration program and the permitting procedure.

Planning of the initial drilling program will be most effective after researching the literature and investigating the site. Sometimes these tasks can be combined, particularly during the field investigation phase. Upon selection of the borehole locations, the Department requires that the Notice of Intent to Explore (ER-MR-30:4/85) be filed with the appropriate District Office. This form must be accompanied by a 7 1/2' topographic map, showing the locations of each test hole, test pit or trenches and the extent of the exploration area. Two copies of this form must be submitted at least seven (7) days in advance of the proposed drilling operation date.

The position of the initial exploration boreholes is dependent upon the goals of the exploration program. The following discussion applies to a comprehensive exploration effort as opposed to a preliminary quality determination project. The exploration borehole positions should be located to maximize information about the structural and stratigraphic framework of the site to obtain data from maximum to minimum cover. Sometimes it is possible to include the sampling of overburden -and coal In the initial exploration effort. However, this is difficult in a steeply dipping, multiple seam area, which can occur in the Bituminous region and almost always does in the Anthracite region.

3. INTERPRETATION OF EXPLORATION PROGRAM

a. MAPPING

Examination of the exploration data is an important step in the planning of overburden sampling sites. This will determine the area to be mined, the position of the deposit, the stratigraphic variability, and also provide some information about the pre and post-mining ground water available to the site. The exploration boreholes and any other field data should be carefully mapped by a survey crew. Accurate measurement of the horizontal position and vertical elevation (keyed to U. S. G. S. mapping) of the boreholes and field data is essential for accurate strata correlation. Once the strata are correlated it is possible to determine the site's' stratigraphic, structural, and hydrologic elements.

b. STRATIGRAPHY

Prior to strata correlation it is sometimes necessary to convert the measured thicknesses to true thicknesses. Failing to adjust the thickness can result in correlation and structural interpretation mistakes, especially where the dip of the strata is variable. The formula to convert to true thickness is (measured thickness) X (cosine of dip angle) = true thickness. This factor is significant for dip angles under 30 degrees, but the true thickness at 40 degrees is 76.5% of the measured thickness. This degenerates to 64% at 50 degrees, 50% at 60 degrees, 34% at 70 degrees, 17% at 80 degrees, and 1.3% at 89 degrees.

The exploration data is correlated by plotting the drilling and/or channel-section logs on forms, such as those provided by the Department for Surface Mining Permit applications (ER-MR-311-13: Rev. 5/86). These forms provide space for written and graphic descriptions of the strata encountered at a consistent scale. Comparison of the lithologic descriptions is accomplished by observing the lithotype characteristics and the vertical distances that separate the marker beds. The graphic log columns can be "cut-and-pasted" to generate either elevation controlled cross-sections or stratigraphic sections that are "hung" on an easily identified marker bed. Isometric fence diagrams or panel diagrams are also useful.

Cross-section type comparison of the graphic logs of drill holes, highwall sections, trench sections or any other columnar representations of the strata in the area illustrates both horizontal and vertical - stratigraphic variations and facies changes. It is important to note the presence and extent of all distinct lithotypes, including coal seams and their carbonaceous remnants, limestones or calcareous deposits, channel type sandstones, unconsolidated deposits (sand, clay, glacial till, mine spoil, mine or tipple refuse), potential water-bearing zones, and potential aquitards or aquicludes. This information can be transferred to the horizontal plane to illustrate the spacial extent of these bodies.

c. STRUCTURE

Correlation of the strata is followed by the structural interpretation. The structural elements of concern are bedding and fault plane orientations (attitudes). According to Marland P. Billings, attitude refers to the three dimensional orientation of a geological feature. The attitude of planar features, such as beds, faults or joints is defined by their strike and dip. The strike of a bedding, fault or joint plane is defined as the direction of a line formed by the intersection of that feature and a horizontal plane. The dip of a geological feature is the angle between its plane and the horizontal plane, measured at a right angle to the strike. The apparent dip is any vertical angle, measured from the horizontal plane, that is not at a right angle to the strike. This angle will be less than the true dip.

The strike and dip of bedding can be physically measured in the field where there is adequate exposure. This will result in an actual compass direction for the strike of the bedding and a vertical angle for the dip. Usually, however, the bedding strike and dip is calculated by using the elevations derived from the drill logs.

The integration of the various strikes and dips that can be measured or calculated for a given bedding plane on a site results in a structure contour map. The structure contour map will illustrate the variations in the strike and dip, facilitating detection of folds and faults. It will also provide the professional with a clearer picture of the relationship between topography and bedding.

The structure contour map can only be accurate if the strata are properly identified (correlated) because it is based upon a comparison of the elevations of a given bedding plane at its points of measurement. It is preferrable to use the elevations of the bottom of the beds, particularly the coal seams, because the top elevations may be inconsistent, due to erosion by stream channels. Additionally, the elevation of the bottom of the coal seams will represent the furthest down-slope development.

The comparison of the bedding elevations results in a combination of slopes that range from 0 degrees (0%) to 90 degrees. The zero degree slope defines the strike of the bedding and the largest value represents the true dip. All vertical angle values in between are apparent dips. The structure contour map for the site can be generated by projecting "straight-line" structure, based on strike and dip, derived through solving a few 3-point problems. However, this method becomes difficult when dealing with a large number of drill-holes in a bed that is folded or faulted, producing variable strikes and dips. For this reason the structure contour map should be constructed by generating equal elevation contour lines, based upon the slope lines between all data points.

4. DEFINING OVERBURDEN SAMPLING ZONES

a. STRATIGRAPHY

Following the generation of the structure contour map, the coal seam or marker bed crop-lines and maximum highwall limits can be plotted. This will help to define the coal extraction area. Reference to the graphic sections or lithotype map will help to define the critical zones to be sampled for overburden analysis. It is important to sample all zones that could contribute to acid and dissolved metals production as well as alkaline zones that may neutralize such products.

To date we know that those strata that contribute to acid and dissolved metals production are coal seams (including pit waste and tipple refuse), carbonaceous mudstones and claystones, and strata immediately in contact with these zones. Channel sandstone deposits can also contribute acids and dissolved metals because they may contain sulfides transported from erosion of coal seams and associated strata. The channel sand depositional environment may also contain ideal conditions for pyrite deposition (i.e., fresh water detrital iron contacting sulfate from marine waters in brackish mixing areas.)

In general, those strata that contribute alkalinity to the aquatic system at the mine sites are limestones, calcareous mudstones and claystones, and some glacial tills. Some sandstones also have calcium carbonate cement.

b. HYDROLOGIC FRAMEWORK

The history of water quality produced by previous mining on the same seam(s) in the permit area and the sensitivity of the watershed will heavily influence the number and spacing of the overburden sampling holes or columns for a site. This is because the importance of the stratigraphic framework will be perceived differently for each situation. For instance, if the seam planned to be mined has been previously mined in the subject watershed and it has been demonstrated that post-mining discharges have been consistently of the quality that present and future watershed use can tolerate, overburden sampling will generally not have to be as thorough as when the opposite is true. Less easily defined situations in sensitive watersheds will usually require rigorous sampling of the strata to be affected, especially if the strata exhibits variability.

The history of water quality produced by previous mining can be determined by sampling discharges from mined areas on the same seam(s) on or near the permit area. The quality of receiving streams at points upstream and downstream of any mined areas should also be determined. Additionally, one can gauge the effects of previous mining by sampling private or public water supply sites that are down-gradient from the mine sites.

Another useful tool is sampling of water that enters the exploration boreholes. This is particlarly true if the boreholes are developed in spoil, generated from mining of the seam of interest, or in unconsolidated deposits, such as glacial till or alluvial gravels. Boreholes developed in such unconsolidated deposits, if developed down-gradient of mining that produced or affected the deposit, may intercept ground water flow from these areas.

Watershed sensitivity refers to the influence that the quality or use of the receiving streams and/or down-gradient aquifers exert on determining the details of the overburden sampling program. All the streams in Pennsylvania have been classified according to variations in water quality and water use. These classifications are published in 25 Pa. Code Chapter 93 of the Department's Rules and Regulations. Additionally, some streams have been informally classified as "high quality" or "sensitive" by the Pennsylvania Fish Commission and others. The proximity of the proposed mining site to water supplies also contributes to the sensitivity of the watershed.

The sensitivity of the watershed area may also be influenced by the total amount of acreage affected by mining. This factor is most important when the proposed mining is located in the headwaters of a receiving stream and will change as mining progresses in a watershed and as the uses for the watershed change.

D. PROPOSAL TO CONDUCT OVERBURDEN SAMPLING AND TESTING

Before collecting the overburden samples it is advisable to contact the appropriate District Office in person or in writing to propose the sampling program. The Department's Hydrogeologists will review the proposal and will provide the applicant with input regarding the adequacy of the plan to address the factors described above. If the proposal is supported by sufficient research, the value of the Department's input is increased because of the positive effect upon the efficiency of the sample collection ' program.

The proposal should include the following information:

1. U.S.G.S. based topographic mapping (preferably a Module 6.2 map) showing, at a minimum, surface contours and features, property lines, exploration hole locations, crop lines, proposed coal extraction areas, and proposed overburden hole locations.
2. Correlated logs of all exploratory logs (keyed to Module 6.2).
3. A narrative explaining the depth of the proposed overburden holes and the coal seams to be encountered.

4. A description of the sampling methods.

5. A description of the analytical techniques to be employed; and

6. Name of the consultant and laboratory who will perform the overburden analysis.

It is also advisable to include information about the structure of the site and water quality associated with previously mined coal seams.

Part 1, Section 2 of this manual addresses methods of sample collection, collection devices, sampling techniques, identification of gross mineralogy, and logging methods. Part 1, Section 4 addresses the compositing of the samples according to lithology and mineralogy and the actual crushing, riffling and pulverizing of air rotary chips and cores. Please refer to these sections for discussions of sample collection method(s), sampling technique(s), and sample compositing and their applicability to the stratigraphic conditions, previous mining effects (spoil, underlying deep mines, etc.), and watershed sensitivity conditions.

PART I

COLLECTION AND PREPARATION OF SAMPLES

2. SAMPLE COLLECTION

A. SCOPE

This section addresses the most common methods of overburden sample collection. Included in this section will be collection equipment, collection devices, sampling techniques, logging methods, and methods of identification of selected gross lithology and mineralogy.

B. SAMPLE COLLECTION

The importance of representative (unbiased) sampling cannot be overemphasized. The following methods of sample collection are those commonly used in Pennsylvania today. However, it is advisable to consult the "Applicability" section to understand the limitations with respect to representative sampling.

1. DRILLING

a. AIR ROTARY - STANDARD CIRCULATION

(1) EQUIPMENT AND SAMPLING DEVICES

Standard-circulation air rotary is the most common method of collecting overburden samples employed in Pennsylvania. It is generally the least expensive drilling option available and can usually deliver samples to the surface very quickly.

The essential equipment consists of a drilling rig, hollow drill stems, a hollow bit, and an air compressor. The air compressor is usually mounted on the rig truck and the air is forced down the hollow drill stem and through the bottom of the cutting bit. The cutting bits used for this type of sampling range from approximately four to eight inches in diameter. The bit extracts the samples through a rotary cutting or percussive motion and the air forces the cuttings up to the surface via the hole annulus.

The size of the cuttings that are delivered to the surface are approximately 1/2 inch maximum diameter and are delivered at a rate relative to the pressure of the compressed air, the moisture and competency of the material being drilled, and the degree of fracturing of the rock.

(2) SAMPLING TECHNIQUES

Prior to sampling the underside and aprons of the drill table must be cleaned to prevent caking of the air-blown material and contamination of the sample. During sampling, care must be taken to insure that any build-up of this material is scraped off. The pile of cuttings that build up around the hole entrance must be shoveled away from the hole to prevent further contamination of the sample. This latter type of contamination can be minimized by installing a short length of casing into .the top of the hole so that the cuttings exit through the top of the casing, preventing contact with the cuttings pile.

The samples are generally caught on a shovel after they ricochet off of the underside of the drill table. Separate samples should be collected for every one-foot interval or lithology break, if shorter. The bit advance should be halted for each sampling and the hole should be blown clean before subsequent drilling. (The drive chain or drill stem can be marked to facilitate measurement.) Each one-foot increment should be separately containerized (see Part 1, Section 3) for subsequent compositing (see Part 1, Section 4). The cooperation of the driller is essential to proper sampling. Since many air-rotary drillers are unaccustomed to stopping and blowing out the hole every foot, advance warning of this requirement should be given before entering the site.

For damp or wet holes it is advisable to use a perforated screen device to collect the cuttings because the water will flow through the screen, leaving the cuttings intact and, usually, much cleaner than if collected on a shovel or in a bag.

(3) APPLICABILITY

The standard-circulation air rotary drilling method has inherent limitations with respect to representative sampling. These are listed below.

1. The air does not deliver a representative sample to the surface in highly fractured rocks. This may occur over a deep mine, near an active or abandoned highwall, or in a naturally fractured or faulted zone.

2. The air does not generally deliver a representative sample to the surface if the material is unconsolidated, especially if it is moist. In this category are mine spoil, tipple refuse, glacial till, alluvial sands or gravels, and lacustrine clays.

3. Sampling of discrete, critical zones is sometimes difficult, due to the inability to anticipate exactly when the evidence of a lithology break will exit through the top of the hole. This can result in contamination of the sample by potentially acidic or alkaline material present in strata adjacent to the sample zone. This problem is especially common in the strata within one to two feet above and below coal seams and the strata below calcareous zones. This can sometimes be minimized by drilling a pilot hole first or by drilling the overburden sample hole very close to an exploration hole for which an accurate log has been kept.

b. AiR ROTARY - REVERSE CIRCULATION

(1) EQUIPMENT AND SAMPLING DEVICES

Reverse-circulation air rotary drilling equipment is similar to standard-circulation air rotary, except that it utilizes double-walled drill stems to isolate the sample stream from the perimeter of the hole. The compressed air is driven down the opening between the drill stems and forces the cuttings to the surface via the inside of the inner tube.

The drilling rig may or may not be equipped with an automatic sampling device. Ingersoll Rand has developed an automatic, continuous bagging mechanism that collects the samples in plastic tube bags. Usually, however, the samples are caught in a hand held sampling bag or on a shovel.

(2) SAMPLING TECHNIQUES

Unless the drill rig is equipped with a continuous sampling device, separate samples should be collected for every one-foot interval or lithology break, if shorter. The bit advance should be halted for each sampling and the hole bottom blown clean before subsequent drilling. Each one-foot increment should be separately containerized (see Part 1, Section 3) for subsequent compositing (see Part 1, Section 4).

(3) APPLICABILITY

This type of air rotary drilling generally does not lose the compressed air to' voids in the rock and is, therefore, more suitable than standard-circulation for extracting representative samples above deep mine subsidence zones, near active or abandoned highwalls or in a normally fractured or cavernous rock zone.

This method is especially well suited for delivering representative samples of unconsolidated deposits to the surface, even if they are moist. This is possible because the outer casing holds the hole open and the cuttings flow to the surface, unimpeded by unconsolidated material squeezing against the drill stems. It has been used extensively for sampling glacial tills, mine spoil, and tipple refuse.

Except when an automatic, continuous sampling device is used, representative sampling of discrete, critical zones is sometimes difficult. This is due to the inability to anticipate exactly when the evidence of a lithology break will exit through the top of the hole. This can result in contamination of the sample by potentially acidic or alkaline material present in strata adjacent to the sample zone. This problem is especially common in the strata within one to two feet above and below coal seams and the strata below calcareous zones. Contamination can be minimized by drilling a pilot hole first or by drilling the overburden sample hole very close to an exploration hole for which an accurate log has been kept.

c. AIR ROTARY AUGMENTED WITH CORING

(1) EQUIPMENT AND SAMPLING DEVICES

This method is applicable to standard and reverse circulation air rotary drilling and involves the use of a continuous core barrel to extract relatively undisturbed samples for critical zones. It is the method normally used to determine coal quality in surface mine exploration.

The equipment used is considered auxiliary to an air rotary drilling outfit. It consists of a hollow steel barrel, usually eight to ten feet long, threaded at one end to attach to the end of the drill stem string and similarly fixtured at the other end to receive a doughnut-shaped, diamond-studded bit.

(2) SAMPLING TECHNIQUES

The air rotary drill bit advancement is stopped one to two feet short of a critical zone, such as a coal seam, and the drill stem string is pulled up to the surface and the bit is removed. The core barrel and bit are then attached to the end of the drill stem that will access the bottom of the hole and the remaining drill stems are attached and fed down the hole until there is a continuous string from the hole bottom to the drive mechanism on the drill rig.

The bit advancement mechanism is again activated and the zone of concern is cored for the effective sampling length of the barrel, which is usually at least 80% of the total length. For a coal seam five feet thick, this technique should obtain the coal seam, plus one to two feet of the strata that immediately overlays and underlies the coal seam. The sample is hoisted to the surface and is extracted from the core barrel as a solid column of rock, approximately three inches in diameter. The sample is then containerized (see Part 1, Section 3) for subsequent breakdown (see Part 1, Section 4).

(3) APPLICABILITY

This method is especially useful for representative sampling of critical zones, such as coal seams and adjacent strata. It provides a very clear picture of the rock that will be encountered at that spot and precludes sample contamination if correctly handled. It is also valuable to the operator as an additional coal quality determinant.

d. CONTINUOUS CORING

(1) EQUIPMENT AND SAMPLING DEVICES

This method utilizes a drilling rig that advances a doughnut shaped, diamond-studded bit through the entire column of rock to be sampled. The sample is collected as a continuous cylinder five to fifteen foot increments, depending upon the length of the core barrel. As the bit is advanced by a rotary motion water is injected down the hole to cool and lubricate the bit. The water is pumped to the site or can be transported by tanker.

This method is much slower than the air rotary methods, due to the frequent core barrel sample extractions and set-up time, but it generally delivers a more representative sample.

(2) SAMPLING TECHNIQUES

Sampling is continuous from the surface to the bottom of the hole, although the initial soil/regolith horizon may be augered to the point where less weathered rock is encountered. Each time the core barrel is filled it is hoisted to the surface. The sample is extracted from the core barrel as a solid column of rock, normally ranging from two to four inches in diameter. The sample is then containerized (see Part 1, Section 3) for transport and laboratory preparation (see Part 1, Section 4).

(3) APPLICABILITY

This method of sampling will generally deliver the most complete sample of the entire column of strata to be affected and is the best method to use when evaluating a site in a sensitive watershed. It will produce a sample that will facilitate detailed macro or micro-descriptions of lithology and mineralogy. This increases the ability to test discrete zones and insures that compositing does not misrepresent the potential of the sample to produce acidity or alkalinity.

Continuous coring does not necessarily guarantee a continuous sample in all situations. Unconsolidated or highly fractured or friable zones can create sampling gaps. This may be due to the barrel's inability to either smoothly progress through the zone or retain the sample during ascension. A faulty barrel may also cause sample loss. Field personnel should check this by comparing the measured length of the sample column with the total depth of the hole. Nuclear logging techniques are also useful for determining sample recovery.

Continuous coring machines can also be adjusted to drill at steep angles. This is a valuable asset for sampling steeply dipping strata that is common in the Anthracite region and can sometimes occur in the Bituminous region (Broadtop). The ability to drill more or less perpendicular to bedding will insure that the strata to be affected is adequately sampled. Adequate sampling of the strata to be affected in steeply dipping areas can be accomplished by drilling a series of vertical holes, but this is time consuming and expensive.

2. HIGHWALL SAMPLING

(1) EQUIPMENT AND SAMPLING DEVICES

Highwall sampling is usually accomplished with a hammer, pick, chisel or other hard, sharp object. The samples can also be dislodged using air or gasoline-powered "jack-hammers" and percussion-type attachments on heavy equipment, such as "Gradalls".

(2) SAMPLING TECHNIQUES

The face of the highwall must be cleaned of all debris, down to the lowest strata to be sampled. Talus piles must be removed in the sampling area to insure that sloughing of this material will not contaminate the samples being extracted near the bottom of the column. The face must then be prepared by removing weathered rock to the maximum depth possible. Upon developing a channel of less weathered rock, actual sampling for analysis purposes can begin.

The samples should be dislodged carefully and in a manner that will discourage excessive propulsion. Normally, the samples are caught in a bag, on a shovel, or on a ground cloth. The samples should be containerized (see Part 1, Section 3) in one-foot increments to insure that there is no mixing or cross-contamination. Subsequent compositing can take place in the field or at the preparation facility as Per Part 1, Section 4.

(3) APPLICABILITY

Highwall sampling should only be employed to supplement existing data or for mine development sampling on a fresh, unweathered face. Generally it is very difficult to extract an unweathered sample from an abandoned highwall or highway cut. Therefore, the analysis of the sample could be meaningless. Relatively unweathered samples can be obtained from newly developed highwalls. This is frequently done to satisfy the special handling requirements of permits.

The sampler(s) must exercise great caution in sampling abandoned highwalls, fresh highwalls, and highway cuts because the danger of injury is great.

C. SAMPLE LOGGING

Documentation of the physical characteristics of the overburden samples is accomplished by logging the information on forms that address the following items:

- Sampling date
- Site identification (Location and sample site number)
- Container identification number
- Laboratory identification number
- Depth range
- Thickness
- Lithotype (see Part 1, Section 2, Item D.1. - Gross Lithology)
  - lithology
  - color
  - streak
  - grain size
  - moisture
  - weathering
  - effervescence in dilute acid (10% HCL)
  - mineral inclusions (see Sect. 2, Item D.2.- Gross Mineralogy)
- Structural features (fractures, faults)
- Bedding characteristics (fissility, attitude)
- Fossils (marine or freshwater, invertebrates or plants)

The three basic types of samples extracted by the sampling methods discussed in Section B are air-rotary chips, cores, and highwall rock fragments. Because of the consistency of these samples some of the items addressed in logging one type of sample may not apply to the others.

1. AIR ROTARY CHIPS

Air rotary chips generally have a mean diameter of 1/2 inch to 200 mesh. For a one foot increment it is possible to have as little as a few teaspoons of material to enough to nearly fill a one-gallon zip-lock bag.

The chips must be broken to obtain a fresh face for the lithologic description because the chips are usually coated with dust that masks the true color and, sometimes, the lithology of the sample. Because of the small size of the particles it is difficult to detect mineral inclusions and impossible to determine structural features. Care must be exercised during the application of diluted HCL to observe if the effervescence is confined to the fresh face or the dust that usually covers the chips.

2. CORES

Cores are usually two to four inches in diameter and of varying lengths, depending upon the core barrel dimensions and the number of continuous core samples extracted. They must also be broken to obtain a fresh face for the lithologic description because there is often an outer coating of silt or mud, generated by the water used as the drilling fluid.

Certain types of structural features can be distinguished in core samples. Fracturing is usually obvious and brecciated areas are many times the evidence of a fault zone. Bedding characteristics, such as fissility, are easily observed as are bedding plane inclinations and fossils. The latter two can be useful tools for correlation and structural interpretation, particularly when an anomalous incline is observed. The presence of cross-bedding in sandstones may also be an indicator of a channel-sandstone deposit.

3. HIGHWALL SAMPLES

All of the logging requirements discussed above can be met with highwall sampling because the structural and bedding plane features can be identified beyond the actual sample extracted. Usually a far greater exposure of highwall is available for observation than the sample channel and these observations should be noted on the log form.

D. SAMPLE IDENTIFICATION

1. GROSS LITHOLOGY

The following lithotypes are common in Pennsylvania and these macro-descriptions should be consulted when determining gross lithology:

a. SANDSTONE

Sandstone contains more than 50% sand-size (less than 2 mm and greater than 1/16 mm median diameter) particles. The particles are predominately quartz and may be cemented with silica, iron oxide, carbonates, or clays. Qualitative modifiers, such as calcareous (noticeable fizz), argillaceous (mud inclusions), micaceous, and pyritic, for example, may be added to the description when they provide useful information.

b. MUDROCK (MUDSTONE, SILTSTONE, AND SHALE)

Mudrock is a broad term for a sedimentary rock dominated by silt-size (1/256 mm to 1/16 mm mean diameter) and/or clay-size (< 1/256 mm) particles. The term is used when a rock cannot be definitely distinguished as either a mudstone or a shale. Mudrock may contain as much as 50% sand-size particles if properties are Judged to be dominated by silt and/or clay (sandy mudstone or shale). Mudrocks may contain any proportion of carbonates or carbonaceous material, provided the properties are dominantly silt and/or clay when rubbed in water.

Mudstones are mudrocks that do not exhibit fissility. Shales are mudrocks that do exhibit fissility.

Claystone is a mudrock that is dominated by clay-size particles. It can contain up to 50% sand-size particles if the properties are Judged to be dominated by clay. It can also contain any proportion of carbonates or carbonaceous matter if the same criteria are met. Claystones can be competent if they contain a high enough proportion of sand or silt particles and are sufficiently indurated or incompetent (plastic) when dominated by clay size particles and not highly indurated. This is the lithology that is most often associated with the common term "underclay".

c. LIMESTONE

Limestone is a sedimentary rock primarily consisting of calcium carbonate, although it can have fairly high proportions of clay, mud, or sand-size particles, depending upon the depositional environment. When dominated by high proportions of calcium carbonate, limestone will have a distinctly crystalline appearance and will fizz vigorously when contacted by 10% HCL. The calcium can be easily replaced by other minerals, such as magnesium or iron, which noticeably affects the rock's ability to fizz in acid.

d. COAL

Coal is a black, or brownish-black, solid, combustible mineral substance that is formed by the partial decomposition of vegetable matter without free access of air, under the influence of moisture, and in many cases, increased temperature and pressure.

Coal is classified according to rank by the amount of organic and volatile matter present. The lowest rank is lignite, which contains the lowest amount of organic material, and the highest is anthracite, which contains the highest amount of organic material. Coal can contain varying amounts of non-organic impurities (ash) and moisture, but organic content should be at least 50% of the total of all constituents.

e. CARBOLITH

Carbolith is a name that has been coined (Smith et al., 1974) to cover dark colored sedimentary rocks that will make a black or very dark (Munsell color value of 3 or less) streak or powder. Rocks under this name include coal not scheduled for mining, impure waste coal, bone coal, high-carbon mudrock, and high-carbon claystones. In general, such rocks will contain at least 25% carbonaceous matter.

Any carbonaceous lithotype can be termed a carbolith if it meets the criteria stated above.

f. INTERCALATE

intercalate is a term coined by Sobek et al. to describe rocks which contain at least two different rock types that are so intimately interlayered or "intercalated" that they cannot conveniently be sampled separately. Intercalates have at least three or more layers within a 5 inch measured section. This rock type can be defined in greater detail by listing in order of abundance some or all of the kinds of rocks included. (e.g. Intercalate - sandstone/mudstone).

g. GLACIAL TILL

Till is unconsolidated, unstratified, poorly sorted drift, deposited directly by glacial ice. Till consists of clay, silt, sand, gravel, and boulder-size particles of varied rock types which can be intermixed in any proportion.

Pennsylvania tills have been classified according to glaciation period and have varying properties with respect to overburden acidity or neutralization potential.

h. GLACIAL OUTWASH

Glacial outwash was deposited by melt-water streams fed by the active glacial ice. In contrast to till, outwash is stratified and well-sorted.

In addition to the identification of the lithotype the following descriptions should be noted.

a. COLOR

Color is most accurately determined by applying the Munsell System. This system uses sample chips of predetermined color classifications to compare with freshly broken surfaces of the rock to be identified. It is very accurate because it eliminates the variance in color perception among loggers, due to habit, lighting conditions, and color differentiation problems.

References that may be purchased are "The-Rock Color Chart", distributed by the Geological Society of America; and "Munsell Soil Color Charts", published and distributed by the Munsell Color Company.

b. GRAIN SIZE

Grain sizes are expressed by the following ranges measured in millimeters. Claystone, mudstone, and limestone are composed of grains < 1/256 mm median diameter. Silt is composed of grains ranging in median diameter from 1/256 mm to 1/16 mm. Very fine sand ranges from 1/16 mm to 1 /8 mm, fine sand from 1/8 mm to 1/4 mm, medium sand from 1/4 mm to 1/2 mm, coarse sand from 1/2 mm to 1 mm, and very coarse sand from 1 to 2 mm.

Unconsolidated deposits also can be differentiated by grain sizes. Those found in the Pennsylvania coal fields can range from clay (1/256 mm) to boulder size (> 256 mm) but, except for some mine spoil, till, and landslide deposits, rarely exceed 256 mm (1 inch).

Grain sizes can give an indication of the water-bearing potential for the strata sampled. Generally, the larger and better sorted the grain sizes are, the more suitable the rock or unconsolidated deposit will be as an aquifer.

c. MOISTURE

The moisture content of the sample will indicate the presence of saturated or non-saturated zones. It also can indicate the degree of weathering.

d. WEATHERING

The degree of sample weathering is an indicator of numerous types of processes that may be operating on the strata. The disintegration of a sandstone, for instance, is a good indicator that the cement has been dissolved by aqueous solutions.

A highly weathered sample will generally be soft and crumbly while less weathered samples will merely exhibit some staining or efflorescence, due to oxidation of iron or other metals. Weathered rock will almost always contain less calcareous material and sulfides than the same rock in an unweathered state.

Weathering is often the reason for misidentification of lithotypes, particularly by loggers with little or no professional training. It is not uncommon to see logs that have identified a weathered sandstone as "shale", simply because the sandstone had decomposed to the point that it had become soft. Weathered calcareous mudstones are often misclassified as "shale".

e. EFFERVESCENCE (FIZZ) IN 10% HYDROCHLORIC ACID (HCL)

Certain minerals will react with varying intensity when contacted with acid. A solution of one part HCL and nine parts water works well as a qualitative identification of carbonate based rocks. The test must be performed on a freshly broken face of the sample.

Pure limestone (> 99% calcium carbonate) will fizz strongly when exposed to this solution. Calcareous rocks with less calcium carbonate will fizz less vigorously. Certain carbonate minerals that are created through replacement of the calcium by other elements will fizz only when the face of the sample is scraped to produce a powder. Such minerals are dolomite, in which magnesium replaces some of the calcium, and siderite, in which iron replaces the calcium. Either of these minerals can fizz weakly without powdering if the degree of calcium replacement is low.

f. STREAK

Streak is noted by scraping a freshly broken face of the sample on a white surface such as porcelain. The scraping action will produce a powder and the color of this powder is recorded. Streak plates can be purchased, but any surface that is light and is hard enough to powder the sample face when scraped will suffice.

Streak is a widely used diagnostic tool for rock and mineral identification. In overburden sample identification it is primarily used to determine if a sample is carbonaceous. A carbonaceous black shale will leave a sooty, black streak, whereas a non-carbonaceous black shale will leave a gray streak.

2. GROSS MINERALOGY

It is important to identify and describe certain minerals when they are observed. Usually this is only possible with core or highwall samples, but careful scrutiny of air rotary chip samples can result in some discoveries. The most significant minerals that should be noted are the iron sulfides (pyrite and marcasite), carbonates (calcite, and siderite), iron sulfates, and limonite.

The following brief descriptions provide a guide to identification of these minerals, but there are many excellent reference works that provide in-depth diagnostic tools. Among these are Dana's Manual of Mineralogy and The Audubon Society Field Guide to North American Rocks and Minerals. The latter provides many excellent photographs of "museum-quality" specimens, but these can be useful for describing less perfect crystals.

a. PYRITE

Pyrite is iron sulfide that often crystallizes in isometric forms, ranging from cubic to octahedral. It will also occur in nodules and massive forms, sometimes described as framboidal. It is colored pale to brass-yellow and is often tarnished with a brown film of iron oxide.

Pyrite is very common in the coal deposits and will occur on bedding planes, Joint planes, and cleats of the coal seam and associated strata as distinct crystals, nodules, or framboids. These same morphologies abound when the pyrite is disseminated throughout the sediments. Although framboidal pyrite is suspected to be the most significant contributor to acid production, determination of this form without a microscope is difficult. Notation of visible pyrite and a hand-lens description of the morphology is acceptable.

b. MARCASITE

Marcasite is also iron sulfide that crystallizes in a different symmetry classified as orthorhombic. It will not produce cubic crystals like pyrite and can also be differentiated from pyrite by the fact that it is generally much whiter. Marcasite is also known to be a significant contributor to acid production.

c. HYDROUS IRON SULFATES

Hydrous iron sulfates. can be significant acid producers. Melanterite, Jarosite, and alunite are very similar in appearance and are produced as a white efflorescence from oxidation of iron sulfides. The evidence of this mineralization is especially noticeable in black shales, carboliths, and coals.

d. CALCITE

Calcite is calcium carbonate. Although it is the primary constituent of limestone, it can occur in any type of sediment, including coal seams. Calcito effervesces strongly in 10% HCL. It forms hexagonal crystals, but frequently in rhombohedral and tabular form. The color is usually white, although it can be translucent or fairly dark, depending upon the amount of impurities. Calcite is a significant producer of alkalinity.

e. SIDERITE

Siderite is iron carbonate In which iron has replaced calcium. It is very common in sedimentary rocks and can be distinguished from calcite by its brown color, its resistance to fizzing in 10% HCL, and the fact that it becomes strongly magnetized when heated.

Because of the replacement of calcium with iron, siderite's role as a producer of alkalinity is tempered by the degree of replacement which can be more or less empirically determined by the fizz test.

f. LIMONITE

Limonite is a mixture of hydrous iron oxides of indefinite composition. It is yellow to brown, forming as an amorphous earthy or fibrous substance. Limonite is the result of alteration of iron-bearing minerals, especially sulfides such as pyrite and marcasite. It is often- responsible for the characteristic rusty brown color on the weathered surfaces of rocks.

3. SAMPLE STORAGE AND CHAIN OF CUSTODY

A. SCOPE

This section addresses methods of containing and labeling the overburden samples for storage and for transportation to the laboratory and/or preparation facility.

B. CONTAINERIZATION

1. CORES

Cores are the most fragile types of samples extracted in terms of their ability to remain intact after transport and during storage. The containers must be designed with this in mind. The personnel packing cores into the containers must also take care to protect the samples.

Cores are usually extracted when detailed logging and critical sampling are desired. The intact core samples are generally transported from the site because detailed logging is much more convenient in a protected location. For those situations in which the logger records the information and extracts the analysis samples in the field, containerization will be no different than for air-rotary or highwall samples.

There are two different types .of containers for cores that are commonly used in Pennsylvania and both serve to protect the samples well if care is used.

a. SEGMENTED CONTAINERS

These are divided boxes made of wood, plastic, or laminated cardboard that hold approximately 10 feet of two inch diameter core. These boxes are approximately two to three feet long and hold four to five lengths of core in separate channels, each length separated by a partition.

To secure those core samples not long enough to snugly fill a channel, the core must be rigidly blocked with a piece of wood or similarly inflexible material. It is also a good idea to line the channels with paper or rags if they are too wide for a snug fit. The top of the box is either nailed down or secured with hinges and a clasp.

b. SINGLE CHANNEL BOXES

Single channel boxes are usually used for cores obtained with an air rotary drilling rig, although they can be used for continuous core samples. The core sample is pushed out of the core barrel directly into the box, which is generally long enough to hold the entire length of core. This results in an unbroken sample, if extracted properly.

As in segmented boxes, if the core does not fit snugly against one of the box ends, it must be blocked with rigid material. Paper or rags should be used to pack the sides and top of the core sample. The lid is usually nailed down because these containers are often assembled by the driller in the field.

2. CHIP OR HIGHWALL SECTION SAMPLES

Overburden samples extracted by air rotary drill or highwall sampling are usually stored in various types of bags, ranging from plastic to burlap or cloth. One-gallon zip-lock bags are best for short and long term storage of the one-foot sample increments extracted by air-rotary drilling. They are durable, easily labeled, and hold moisture well for long term storage. Because of their clearness these containers also make sample recognition and organization very easy. Larger samples can be stored in plastic coal sampling bags or common rock and soil sample bags made of cloth or burlap. The plastic bags hold the moisture longer, however.

C. LABELING

1. CORES

This discussion pertains to transportation and storage of core samples in the containers addressed in Part 1, Section 3, Item B. Cores placed in bags will be treated the same as air-rotary and highwall samples.

Both types of core boxes discussed above should be labeled following the same conventions. Each box should be labeled on the outside with permanent marker to identify the site and the hole number. This is the same designation that should appear in that slot on the logging form described in Part 1, Section 2, Item C and later referenced in Part 1, Section 4, Item A. The depth limits of the samples should also be indicated on the outside of the box.

The inside of the box should be also labeled with permanent marker to indicate the positions of the top and bottom of the core as well as the depths the core represents in each channel. There should also be indicators to represent section of the rock column not recovered by the core.

2. CHIP OR HIGHWALL SECTION SAMPLES

Each bag used for storage of a given sample increment must be clearly and permanently labeled directly by permanent marker or by attaching a tag marked with permanent marker or indelible ink. It is also good practice to place a folded piece of paper, indicating the sample identification, inside the bag.

The identification labeled on each bag should include at least a coded designation for the hole number and depth range. This can be keyed to a log book kept by the geologist. The identification on or in the bags should match that used on the log form discussed above. The log form should also reflect any sampling gaps due to poor recovery.

PART I

COLLECTION. AND PREPARATION OF SAMPLES

4. PREPARATION OF SAMPLES

A. ANALYSIS SAMPLE SELECTION/COMPOSITING

Overburden analysis samples are selected or composited, based upon the following criteria:

1. Lithology
2. Identifiable mineralogy
3. Stratigraphic variability
4. History of same seam(s) mining near the site being tested
5. Watershed sensitivity
6. Advance knowledge of potential acid/metals production
7. Advance knowledge of potential alkalinity production

It is critical that 100% of the sample volume be included for single sample or compositing purposes. Splitting of samples should be performed, with riffles at the preparation facility. (See Part 1, Section B, Item 4.)

The compositing procedure for non-core type samples is designed to minimize the number of samples tested while not sacrificing accuracy in determining the potential of the strata to produce acidity or alkalinity. This procedure reduces the number of samples in a 75 feet deep hole from a theoretical maximum of 75 to 80 samples (based upon sampling in one-foot increments) to approximately 25 to 30 samples.

The following table lists the Department's required maximum thicknesses to be tested for certain lithotypes. Lithotypes are not to be combined.

LITHOTYPE	MAXIMUM COLUMN THICKNESS (FT)
Sandstone *	3
Limestone or calcareous deposits	3
Mudstone or claystone	3
Coal **	3
Mine spoil	5
Tipple refuse	5
Glacial till or outwash	5
Unspecified unconsolidated deposits	5

* Channel sandstones with coal inclusions should be tested separately.
** Strata within 1 foot above and below coal should be tested separately.

The notes for compositing should be indicated on the logging form, discussed under Part 1, Section 2, Item C (Sample Logging). The laboratory sample number column can be utilized for this purpose because brackets or vertical arrows can be inserted to mark the sample increments to be composited and the laboratory number, when assigned, can be entered in that segment of the form.

The physical act of combining the sample increment bags into analysis samples can be handled by the logger or by personnel at the preparation facility. In the case of core sample selection, this work should be performed by the logger. If core sample selection or sample bag compositing is performed by the logger, the following procedure is to be used:

1. The core section or the contents of the individual sample bags are to be put into a container that will hold the contents of the analysis sample. In the case of bagged sample increments the individual samples may be kept in their original containers (one reason may be for individual splitting before compositing) or they may be dumped out of their original containers and mixed together in the container used for the analysis sample.

2. Each container used to hold an analysis sample should be labeled, preferably with a laboratory identification card. Instructions for preparation and analysis of the sample should be written on the card.

3. A copy of the complete log form should accompany the group of analysis samples so that the preparation supervisor understands the full scope of the task assigned.

If the sample bag compositing Is assigned to personnel at the preparation facility the following procedure should be used:

1. The individual sample increment bags are to be well labeled as per the discussion under Part 1, Section 3 - Sample Storage and Chain-of-Custody.

2. A copy of the complete log form should accompany the group of individual sample increment bags so that the preparation supervisor understands the full scope of the task assigned.

3. The preparation supervisor will fill out sample identification cards for each analysis sample indicated by the complete log form.

B. LABORATORY PREPARATION METHODS FOR OVERBURDEN SAMPLES

1. SCOPE

1.1 The purpose of overburden sample preparation is to provide the laboratory with an analytical sample that accurately represents the chemical composition of the overburden sample. The preparation facility may receive overburden samples that range in size from rock dust to solid core borings at the other end of the range. The weight of the samples may range from less than a few hundred grams to more than 50 pounds. The laboratory sample will be pulverized to a maximum particle size of 60M (mesh) or 0.25 millimeters.

1.2 The preparation methods discussed here are designed to address processes of reducing (crushing) and dividing (splitting) the overburden sample to generate the final analysis sample.

1.3 It is not in the scope of this procedure to address the health and safety or regulatory aspects that may apply. These aspects must be considered by those performing the tasks inherent in this procedure.

2. APPARATUS AND MATERIALS

2.1 The apparatus listed here is not the exclusive set of apparatus required for overburden sample preparation. Reference to a particular product does not imply an endorsement of that product. Apparatus designed to accomplish similar results are also acceptable.

2.2 Jaw Crusher (Marcy 4 inch X 6inch): Capable of reducing the sample to a 4M (mesh) top size as defined by the Tyler system.

2.3 Riffle (splitter) (Humbolt 3962): Capable of dividing 4M material in a representative manner. Chute openings should be 3/8" to 3/4" wide.

2.4 Air-Dry Oven (Blue-M EM166F): Capable of maintaining an inside temperature of 40 Deg. C. and air flow rate of 2 oven volumes per minute.

2.5 Balance (Mettler PC24): Capable of weighing up to 20,000 grams to the nearest gram.

2.6 Pulverizer (Holmes 500): Capable of reducing 4M material to a size passing a 60M screen.

2.7 Screen (Gilson 4M, 8" round): Capable of determining the amount of 4M material in a sample.

2.8 Containers: Capable of maintaining an air-tight seal around a sample. One quart freezer bags are recommended for most samples.

3. IDENTIFICATION

3.1 Before any reduction or division is performed on any overburden sample, it must identified by supervisory personnel as a discrete sample. This may involve any or all of the following steps:

3.1.1 Verifying that the sample to be processed is an overburden sample.

3.1.2 Checking the sample card identification against a drill hole log, if available.

3.1.3 Labelling the sample with a unique identification system. This is usually accomplished by assigning a "Lab Number" to the sample. It is recommended practice to implement a labelling system that causes the identifying label to be physically associated with the sample throughout the preparation procedure.

3.1.4 A determination of the size consist of -the sample is to be made so that the proper processing techniques are applied to the sample.

3.1.5 The weight of the overburden sample is determined and recorded.

3.1.6 Any unusual characteristics inherent in the sample are to be noted and documented (sample very wet, etc.).

4. PROCEDURE

4.1 For overburden samples that are too wet to be processed through the first applicable stage of preparation, a gross sample air-drying procedure must be performed on the sample to lower the level of surface moisture in the sample. Depending upon the size of the sample, the procedure described in 4.5 below may be suitable for this purpose. For larger samples, it may be necessary to spread the sample on a clean surface (a tarp is recommended) and allow the sample to air dry. Air drying is accomplished by allowing the sample to reside in the ambient conditions of a room for a period sufficient to lower the surface moisture content to acceptable levels. (Overnight or 12-16 hours is adequate for most samples.)

4.2 For overburden samples that have a "top-size" (95% or more passing) that is greater than 4M (4.75 mm), the entire sample will be reduced to a 4M or smaller top size. A "jaw" crusher or other suitable device will be used for this purpose. Care must be exercised in this process to avoid loss of material. The crushing device is to be thoroughly cleaned with brushes and/or compressed air between usage on different samples.

4.3 Samples that are received with a 4M or smaller top size or that have been reduced to 4M are to be divided in a riffle or other suitable dividing device to a weight of not less that 500 grams. (Some overburden samples may have an initial weight of 500 grams or less - these samples are not to be divided unless leachate testing is anticipated.) The dividing device must be thoroughly cleaned between the processing of different samples. The 500 gram portion of 4M overburden Is now the subsample that, after further processing, will be used to generate the laboratory 60M sample.

4.4 For samples that have a weight of more than 500 grams, the material that is not used for the 500 gram subsample will be saved for archiving. Because of storage considerations the archived sample may be limited to 2000 grams by division (splitting). Samples that have an initial weight of 500 grams or less will not have an archived 4M subsample, unless leachate testing is anticipated (See 4.3 above). Archived samples will be properly identified and sealed in air-tight containers to retard degradation.

4.5 Many of the 500 gram subsamples will require air-drying prior to further reduction (grinding or pulverizing). Excessive surface moisture may cause caking and plugging of reduction equipment. For subsamples that may contain excessive surface moisture, an air-drying procedure is implemented. For this purpose, an oven with the capability to maintain a temperature of 40 Degrees C and the capability to effect 2 oven volume air changes per minute is recommended, but not required. The air-drying procedure may be also accomplished_ by spreading the sample in a pan or other suitable container until it has dried sufficiently.

4.6 The 4M sample should now be ready for further size reduction to 60M via the pulverization process. In cases when samples are very hard (e.g. sandstone) reduction to sub-4M sizes may be necessary, prior to pulverization. Most 500 gram subsamples may be directly reduced to 60M. Until the entire subsample is reduced to 60M, however, no division (splitting) is permitted. A pulverizer or other suitable device is used to reduce the entire 500 gram subsample to 60M. This reduction device must be thoroughly cleaned between usage on different samples.

4.7 The 60M subsample is then divided in a riffle or other suitable device to a weight of approximately 125 grams. The remainder of the 500 gram 60M material may be discarded. The 125 gram lab sample is to be placed into an air-tight container where it will remain during testing and storage. This container should have a capacity such that the lab sample occupies no more than 3/4 of the volume of the container.

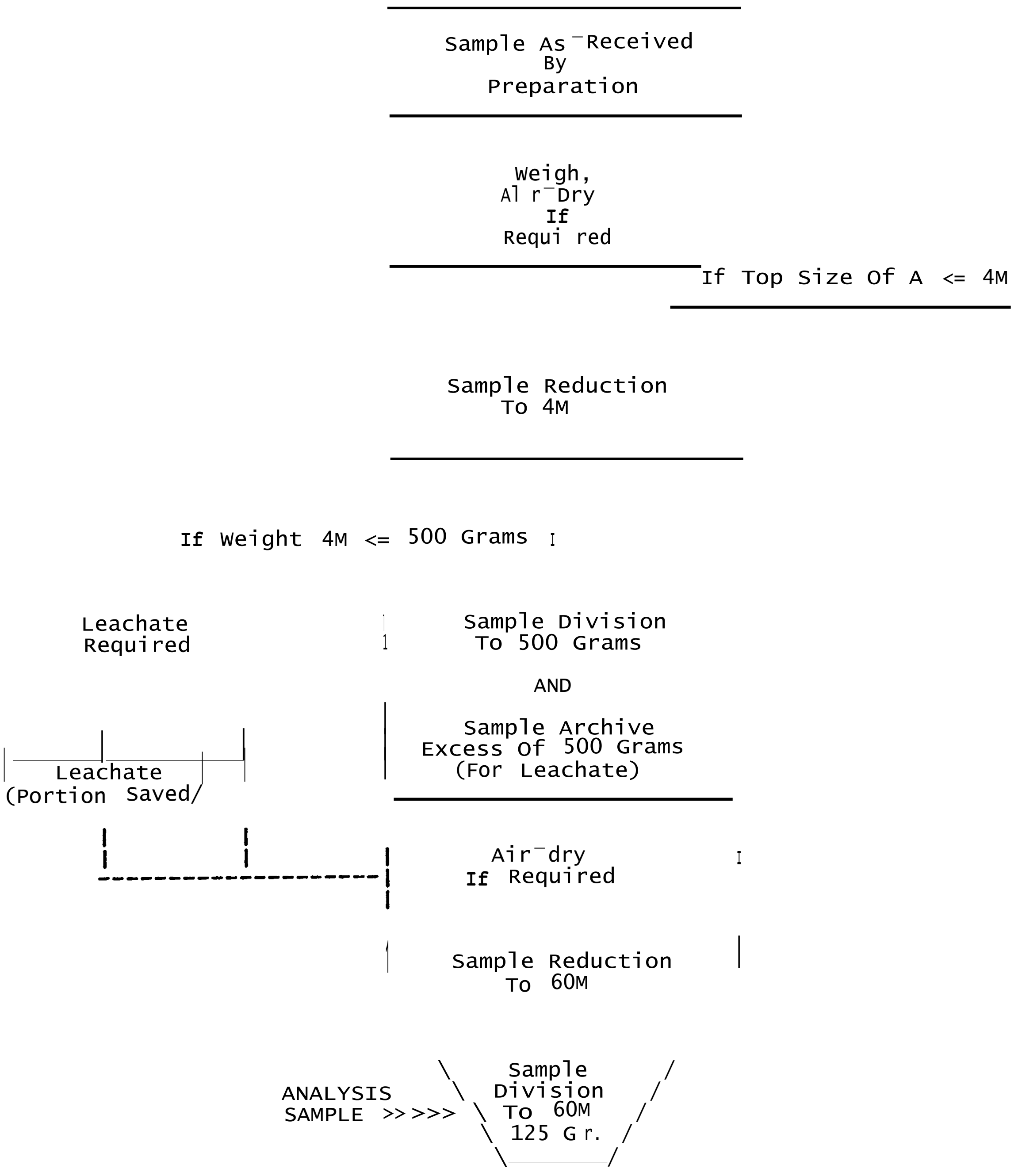
4.8 The 60M sample is to be thoroughly mixed on a mechanical mixing device (e.g., mixing wheel) or by a manual method designed to thoroughly mix the sample. This procedure is to be performed prior to any analytical testing and is to be repeated if a significant time period has elapsed between analytical testing on any given sample.

4.9 The 125 gram subsample is delivered to the analytical lab for the required testing. All pertinent information, such as drill logs, is also delivered to the lab with the analytical sample.

FIGURE 1

OVERBURDEN SAMPLE PREPARATION

FLOW CHART



PART 2

ANALYTICAL PROCEDURES

These procedures are modification of standard methods which have been adapted for the analysis of Pennsylvanian overburden. The procedures are presented in a step-by-step manner and include lists of needed equipment and reagents. The essentials for a Quality Assurance plan are given along with quality control measures which are required so that data submitted to the state will be of a consistent quality.

A complete list of references which were used in the preparation of this manual is given In the appendix.

This manual may contain procedures that involve hazardous materials, operations, and equipment. This manual does not purport to address all of the safety problems associated with their use. It is the responsibility of whoever uses this manual to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

I. MAXIMUM POTENTIAL ACIDITY

Sulfur occurs in three basic forms in the coal bearing strata of Pennsylvania; sulfate sulfur, sulfide sulfur, and organic sulfur. Sulfate sulfur is usually only found in minor quantities and is frequently the result of recent oxidation of sulfide sulfur. Sulfide sulfur is the predominate sulfur species in the majority of overburden samples and is the species of greatest concern. The breakdown of pyrite, either chemically or biologically, is the primary cause of acid mine drainage. Following common convention, sulfide sulfur will be referred to as pyrite. Organic sulfur is only found in appreciable quantities in coal seams and in other carbonaceous rock strata.

Maximum Potential Acidity is the amount of acid that overburden could produce from the oxidation of the sulfide sulfur that it contains. In many cases, the total sulfur determination is an adequate estimation of the sulfide sulfur content and Is a easier test to perform. Organically bound sulfur is the only major form of sulfur which is generally considered not to produce any acid.

1. TOTAL SULFUR

This section will cover In detail the instrumental and wet chemical procedures that are most prevalent. Included are the Eschka Method, Bomb Washing Method, and high temperature combustion methods that use Infrared absorption, iodimetric and acid base titration sulfur detection systems.

A. ESCHKA METHOD (ASTM D3177)

1. SCOPE AND APPLICATION

The Eschka Method is a gravimetric procedure that is appropriate for the determination of total sulfur in all coals and overburden.

2. SUMMARY OF METHOD

A portion of the laboratory sample is heated with eschka mixture to convert all sulfur to the sulfate form. The sulfate sulfur is then leached with hot water and precipitated as barium sulfate. The total sulfur content is calculated from the weight of barium sulfate.

3. INTERFERENCES AND PRECAUTIONS

3.1 Furnaces that have been used for ashing coal or any material that would evolve large amounts of sulfur shall not be used for the initial heating of the sample and eschka mixture. Sulfur is absorbed during one heating cycle and will desorb readily, from furnace elements and insulation during the next. Eschka mixture can absorb this sulfur, thereby causing high results. For this reason, a separate furnace shall be used for the initial eschka sulfur burnoff.

3.2 The major reason for errors is poor analytical technique. Specific areas of concern would be, 1) Improper mixing of the sample with the eschka mixture and using an insufficient amount of eschka mixture to cover the sample. 2) Poor transfer technique which results in the physical loss of sample.

4. APPARATUS AND MATERIALS

4.1 MUFFLE FURNACE: Capable of maintaining 800°C. (refer to 3.1)

4.2 CRUCIBLES: 30 ml platinum or porcelain for igniting the sample and 15 ml platinum, porcelain, or silica for igniting the barium sulfate.

4.3 HOTPLATE: Size is dependent on sample quantity.

4.4 GLASSWARE: 200 and 400 ml beakers

4.5 FILTER PAPER: #40 and #42 Whatman or equivalent.

4.6 FILTER RACK AND FUNNELS

5. REAGENTS

5.1 All chemicals should be reagent grade and the water should be Type Ill reagent water. (ASTM D1193)

5.2 BARIUM CHLORIDE SOLUTION: Dissolve 100 grams of BaCl2.2H20 in water and dilute to a final volume of 1 liter.

5.3 ESCHKA MIXTURE: This is available commercially or can be made by mixing 100 g. of anhydrous sodium carbonate with 200 g. of calcined magnesium oxide.

5.4 HYDROCHLORIC ACID (1:3): Dilute one volume of concentrated hydrochloric acid in 3 volumes of water.

5.5 METHYL ORANGE INDICATING SOLUTION: Dilute 5 ml of saturated methyl orange solution in 500 ml of water.

6. SAMPLE CONSIDERATIONS

6.1 This procedure does not require any special sample handling considerations. The normal -60m sample is all that is required.

7. PROCEDURE

7.1 Weigh approximately 1 gram of sample to the nearest .1 mg. Mix this thoroughly with approximately 3 grams of eschka mixture. (refer to 3.2)

7.2 Settle this mixture into a clean 30 ml crucible and cover completely with approximately 2 gram of eschka mixture.

7.3 Heat the crucible in a muffle furnace (refer to 3.1) to a temperature of 500° C and hold for 1/2 hour. Increase the temperature to 800° C and maintain for 2 hours. (Total time is approximately 3 hours)

7.4 Transfer the contents to a 200 ml beaker and add 100 ml of hot water. Rinse any remaining sample from the crucible into the beaker with a stream of hot water. Periodically stir the sample until it has been leached for 1/2 hour. (refer to 3.2)

7.5 Filter the supernatant, by decanting thru #40 Whatman, into a 400 ml beaker.

7.6 Wash the residue in the beaker with hot water and decant as in 7.5. Repeat this procedure a total of three times.

7.7 Wash the residue out of the beaker onto the filter paper, rinse the beaker twice and then wash the filter paper and residue an additional three times with hot water.

7.8 Adjust the volume of filtrate to approximately 250 ml and make the solution slightly acidic with 1:3 HCI using the methyl orange solution as the indicator, then add an additional 1 ml of 1:3 HCI.

7.9 Place the beakers on the hotplate and heat to boiling. Note: The samples will evolve CO_2 gas prior to coming to a boil.

7.10 Slowly add 10 ml of barium chloride solution and continue to boil for 15 minutes. Cover the samples with a watch glass and let them remain standing for several hours at a temperature just below boiling. This will facilitate quantitative filtration of the $BaSO_4$ due to the formation of larger crystals.

7.11 After cooling, filter the precipitate using #42 Whatman filter paper. Wash the beaker twice after triturating with a policeman and then wash the filter paper and precipitate an additional 8 times.

7.12 Transfer the filter paper, lightly folded, to a 15 ml crucible and place in a cool muffle furnace.

7.13 Smoke off the filter paper b, heating to 500° C. After 1/2 hour raise the temperature to 800 C and maintain for 1/2 hour.

7.14 Weigh the residue after the crucible has cooled.

8. CALCULATIONS

8.1 % SULFUR = (A-B) * 13.738 / C

A = weight of BaSO4 precipitate
B = weight of blank residue
C = weight of sample

9. QUALITY CONTROL

9.1 A blank determination shall be made with every set of samples.

9.2 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required and 1 in 10 is considered optimum. Acceptable precision is as follows:

% Sulfur less than 2	+/- .05%
% Sulfur of 2 or more	+/- .10%

9.3 Accuracy shall be checked by the monthly running of a SRM, such as the NBS Sulfur in Coal Standards. Each standard specifies an acceptable range of values that can be used to judge an analyst's performance.

B. BOMB WASHING METHOD (ASTM D3177)

1. SCOPE AND APPLICATION

The Bomb Washing method of determining total sulfur is applicable to all coals without modifications and to all overburden if a combustion aid is used.

2. SUMMARY OF METHOD

A portion of the laboratory sample is combusted in an oxygen bomb, the contents of the bomb are washed into a beaker, neutralized and filtered. The sulfur in the filtrate is precipitated as $BaSO_4$, filtered, ashed and the $BaSO_4$ residue weighed to determine the amount of sulfur in the sample. Most overburden samples will not sustain combustion so a combustion aid must be used to quantitatively determine the sulfur content.

3. INTERFERENCES AND PRECAUTIONS

3.1 This procedure is dependent on good analytical technique for accurate and precise results. Specific areas of concern are: releasing the bomb pressure too rapidly and incomplete washing of the bomb interior and valves. Both of these errors will result in an underestimation of the total sulfur content.

4. APPARATUS AND MATERIALS

4.1 COMBUSTION BOMB: Parr #1108 or equivalent

4.2 CRUCIBLES: 15 ml platinum, porcelain, or silica for igniting the barium sulfate.

4.3 HOTPLATE: Size is dependent on sample quantity.

4.4 GLASSWARE: 200 and 400 ml beakers

4.5 FILTER PAPER: #40 and #42 Whatman or equivalent.

4.6 FILTER RACK AND FUNNELS

4.7 COMBUSTION CRUCIBLE: Parr #43AS or equivalent

5. REAGENTS

5.1 All chemicals should be reagent grade and the water should be Type Ill reagent water.

5.2 BARIUM CHLORIDE SOLUTION: Dissolve 100 grams of $BaCl_2.2H_2O$ in water and dilute to a final volume of 1 liter.

5.3 HYDROCHLORIC ACID (1:3): Dilute one volume of concentrated hydrochloric acid in 3 volumes of water.

5.4 METHYL ORANGE INDICATING SOLUTION: Dilute 1 ml of saturated solution in 500 ml of water.

5.5 COMBUSTION AID: mineral oil

5.6 NaOH SOLUTION: Dissolve 20 grams of NaOH in 1 liter of water.

6. SAMPLE CONSIDERATIONS

6.1 This procedure does not require any special sample handling considerations. The normal -60m sample is all that is required.

7. PROCEDURE

7.1 Weigh approximately 1 gram of sample, to the nearest .1 mg., into a clean combustion capsule.

a. For samples that will not sustain combustion, reduce the weight of the sample to .75 gram and add .75 gram of mineral oil. After the oil has soaked into the sample continue with 7.2. The sample weight may need to be decreased further if the sample does not completely react when the oil burns.

7.2 Thoroughly wash the bomb, including through the valves, with water.

7.3 Follow the manufacturers recommended procedure for loading the bomb and charging with oxygen.

7.4 Immerse the bomb in water, connect the firing circuit and fire the bomb. Wait a minimum of five minutes before removing the bomb from the water.

7.5 Rinse the bomb head with water and dry with a clean towel.

7.6 Release the pressure in the bomb at a very slow and even rate.(1 minute minimum) A loss of sulfur will result if the pressure is released to rapidly.

7.7 Wash the contents of the bomb into a 400 ml beaker using methyl orange solution. Rinse the capsule and all bomb parts. Be especially careful to completely wash through all valves. The methyl orange solution will stay yellow in the bomb when it is completely washed. Transfer all washings to the beaker.

7.8 Neutralize the washings with dilute NaOH to the methyl orange endpoint. Heat to boiling and then filter thru #40 Whatman filter paper into a 400 ml beaker. Wash the beaker twice and the filter paper an additional four times.

7.9 Adjust the volume of filtrate to approximately 250 ml and make the solution slightly acidic with 1:3 HCI using the methyl orange solution as the indicator, then add an additional 1 ml. of 1:3 HCI.

7.10 Place the beakers on the hotplate and heat to boiling.

7.11 Slowly add 10 ml of barium chloride solution and continue to boil for 15 minutes. Cover the samples with a watch glass and let them remain standing for several hours at a temperature just below boiling. This will facilitate quantitative filtration of the $BaSO_4$ due to the formation of larger crystals.

7 12 After cooling, filter the precipitate using #42 Whatman filter paper. Wash the beaker twice after triturating with a policeman and then wash the filter paper and precipitate an additional 8 times.

7.13 Transfer the filter paper, lightly folded, to a 15 ml crucible and place in a cool muffle furnace.

7.14 Smoke off the filter pager by heating to 500° C. After 1/2 hour raise the temperature to 800 C and maintain for 1/2 hour. If any carbon remains, retrn the crucible to the furnace for an additional 1/2 hour at 800' C.

7.15 Weigh the residue after the crucible has cooled.

7.16 A blank determination is made by using the above procedure on .75 gram of mineral oil.

8. CALCULATIONS

8.1 % SULFUR = (A-B) * 13.738 / C

A = weight of BaSO4 precipitate
B = weight of blank residue
C = weight of sample

9. QUALITY CONTROL

9.1 A blank determination shall be made with every set of samples.

9.2 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required and 1 in 10 is considered optimum. Acceptable precision is as follows:

% Sulfur less than 2 +/- .05%
% Sulfur of 2 or more +/- .10%

9.3 Accuracy shall be checked by the monthly running of a SRM, such as the IBS Sulfur in Coal Standards. Each standard specifies an acceptable range of values that can be used to judge an analyst's performance.

C. HIGH TEMPERATURE COMBUSTION, INFRARED ABSORPTION (ASTM D 4239)

1. SCOPE AND APPLICATION

The high temperature instrumental technique of total sulfur analysis is applicable to all coal samples and, if prescribed measures are followed, to overburden samples.

2. SUMMARY OF METHOD

A portion of the laboratory sample is combusted in a stream of oxygen at a temperature of approximately 1350 °C. The resultant SO_2 gas is detected by infrared absorption and compared to a standard calibration.

3. INTERFERENCES AND PRECAUTIONS

3.1 Samples of limestones and highly calcareous strata can absorb SO_2 gas being evolved during combustion and thereby cause low results. Operationally this problem can be minimized with the use of an accelerator such as vanadium pentoxide.

3.2 Comparative techniques such as this are only as good as the standards that are being used to calibrate the instrument so it is essential that only the highest quality standards be used.

3.3 Preventive maintenance is essential for the proper operation of this instrument.

4. APPARATUS AND MATERIALS -

4.1 LECO SC¯32 or equivalent

4.2 SAMPLE BOATS

4.3 GLASS WOOL

5. REAGENTS

5.1 VANADIUM PENTOXIDE: reagent grade

5.2 OXYGEN: 99.999% purity

5.3 MAGNESIUM PERCHLORATE: reagent grade, 10m x 20m.

5.4 PRIMARY STANDARDS: NBS 1932b, 1935, 2682, 2683, 2684, 2685, 2692

5.5 SECONDARY STANDARDS: Those standards that are purchased or prepared and which have been validated with Primary Standards.

a. VALIDATION PROCEDURE FOR PURCHASED SECONDARY STANDARDS

I. Use the manufacturer's recommended procedure to calibrate the instrument with an NBS primary standard of approximately 3.00% sulfur. This calibration should be confirmed by analyzing the 3.00% sulfur standard to make sure that its determined value falls within its certified range of values. If the determined value is outside the certified range, repeat the process. After acceptable calibration, make two determinations for the secondary standard. The secondary standard is acceptable if both of the obtained values are within the certified range as stated for that standard. If the values are not within that range, that secondary standard is not suitable for use with this procedure.

b. IN-HOUSE PREPARATION OF SECONDARY STANDARDS

i. Twenty sulfur determinations shall be performed using any one of the proposed methodologies: eschka, bomb washing, or high temperature combustion. These twenty determinations shall consist of ten determinations for the proposed secondary standard and ten determinations of a primary standard of comparable sulfur content. If one of the high temperature combustion techniques is used, instrument calibration shall be performed as described in 5.5.a.i. Also, if a high temperature combustion procedure is used, the running of samples shall be alternated, primary then secondary, until the required number of determinations has been made. The corresponding averages and standard deviations shall be computed for the ten (10) primary determinations and the ten (10) proposed secondary determinations.

ii. Data validation of primary standard determinations - All ten values as determined for the primary standard shall fall within the certified range of the standard. If any of the values fail to be within the certified range, step 5.5.b.i must be repeated.

iii. Data validation of proposed secondary standard determinations- The ten values as determined for the proposed secondary standard shall meet the following criterion: two standard deviations shall be equal to or less than one-half the repeatability interval for the given methodology (i.e. 2 S.D. < I(r)/2). The repeatability interval shall be defined based on the average value (x) of the 10 proposed secondary standard determinations as follows:

Methodology	Repeatability interval I(r).
Eschka	$x < 2.00\%$ sulfur; $I(r) = .05$ x 2 2.00% sulfur; $I(r) = .10$
Bomb Washing	$x < 2.00\%$ sulfur; $I(r) = .05$ x 2 2.00% sulfur; $I(r) = .10$
Infrared	$I(r) = 0.03 + 0.04\,x$
Iodimetric Titration	$I(r) = 0.08\,x$
Acid Base Titration	$I(r) = 0.06 + .03\,x$

If the proposed secondary standard data set fails to meet this criterion (2 S.D. _< I(r)/2) then step 5.5.b.i must be repeated.

iv. Certified range of the proposed secondary standard- Assuming both the primary and secondary data sets satisfy the required validation criteria, the certified value of the proposed secondary standard shall be calculated as follows:

$c = x + (p - px)$ where

c = certified value of secondary standard
x = computed average of the ten secondary standard determinations
p = certified average of primary standard
px = computed average of the ten primary standard determinations

The certified range of the secondary standard shall be computed as follows:

$cr = c \pm I(r)/2$ where

cr = certified range of secondary standard
c = certified value of secondary standard
I(r) = repeatability interval as defined in 5.5.b.iii

6. SAMPLE CONSIDERATIONS

6.1 This procedure does not require any special sample handling considerations. The normal -60m sample is all that is required.

7. PROCEDURE

7.1 Insure that the instrument is functioning properly. (Refer to section # 9 on Quality Control)

7.2 Calibrate the instrument at the 3.0 % +/- 0.5% sulfur level using the manufacturer's recommended procedure.

7.3 Verify that the instrument is properly calibrated by running a secondary standard with a nominal value of 1 or 2 % sulfur. Compare the obtained value to the certified range for that standard.

7.4 For each sample, tare a sample boat and then weigh between 0.300 and 0.400 grams of sample.

a. If the sample has a Fizz rating of 2 or 3, (refer to section II, Neutralization Potential), the sample has to be covered with vanadium pentoxide to insure that all sulfur is released from the sample and not trapped by the calcium carbonate present in the sample.

7.5 Verify that the instrument is properly calibrated by running a secondary standard after each group of samples.

a. Maximum group = 20 samples

b. Optimum group = 10 samples

c. If the standard is outside the certified limits repeat steps 7.2 and 7.3. If the standard is still outside the certified limits the instrument will have to be recalibrated. Reanalyze the previous group of samples after the conditions of 7.3 have been met.

d. If the standard is within the certified range continue with the next group of samples.

7.6 Replace the first moisture trap after every 75 runs or whenever the top 1/3 of the trap is saturated.

8. CALCULATIONS

8.1 % Sulfur is calculated directly with a properly calibrated instrument.

9. QUALITY CONTROL

9.1 Prepare the instrument for analysis by performing the recommended weekly maintenance.

a. Perform an oxygen system leak test

b. Clean the main fan filter

c. Replace the liner and boat stops after every 1000 runs.

d. Verify the calibration with a primary standard.

e. Inspect the dust traps and replace if necessary.

9.2 Prepare the instrument for analysis by performing the recommended daily maintenance.

a. Clean the collection tube, boat stop and delivery tube

b. Replace the first moisture trap.

c. Inspect the second moisture trap and replace if necessary.

d. Check the lance tube for proper operation.

e. Check the gas pressures and flow rates and adjust to specifications if necessary.

f. Verify that all system constants are correct.

9.3 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision is as follows:

a. 0.03 + 0.04 * X where X = the average of the two results.

9.4 Accuracy shall be checked by the weekly running of a standard reference material such as the NBS Sulfur in Coal Standards. Each standard specifies an acceptable range of values that can be used to judge the acceptability of secondary standards as well as an analyst's performance.

D. HIGH TEMPERATURE COMBUSTION, IODIMETRIC TITRATION (ASTM D 4329)

1. SCOPE AND APPLICATION

The high temperature instrumental technique of total sulfur analysis is applicable to all coal samples and, if prescribed measures are followed, to overburden samples.

2. SUMMARY OF METHOD

A portion of the laboratory sample is combusted in a stream of oxygen at a temperature of approximately 1350 °C. The resultant SO2 gas is scrubbed from the gas stream and titrated with iodine solution. The percent sulfur is calculated from a standard calibration.

3. INTERFERENCES AND PRECAUTIONS

3.1 Refer to section 3 of Infrared Absorption.

3.2 Chlorine and iron concentrations in the samples that are dissimilar to those in the standards used for the instrument calibration can cause errors.

4. APPARATUS AND MATERIALS

4.1 FISHER SULFUR ANALYZER or equivalent

4.2 COMBUSTION BOATS

5. REAGENTS

5.1 VANADIUM PENTOXIDE: reagent grade

5.2 OXYGEN: 99.999% purity

5.3 TITRANT: Fisher # So-S-10 or equivalent

5.4 DILUENT: Fisher # So-S-11 or equivalent

5.4 PRIMARY STANDARDS: NBS 1932b, 1935, 2682, 2683, 2684, 2685, 2962.

5.5 SECONDARY STANDARDS: Those standards that are purchased or prepared and which have been validated with Primary Standards. Refer to this section C.1. 5:5.

6. SAMPLE CONSIDERATIONS

6.1 This procedure does not require any special sample handling considerations. The normal -60m sample is all that is required.

7. PROCEDURE

7.1 Insure that the instrument is functioning properly by performing preventive maintenance as recommended by the manufacturer.

7.2 Calibrate the instrument at the 3.0 % +/- 0.5 sulfur level using the manufacturer's recommended procedure.

7.3 Verify that the instrument is properly calibrated by running a secondary standard with a nominal value of 1 or 2 % sulfur. Compare the obtained value to the certified range for that standard.

7.4 For each sample, tare a sample boat, then weigh approximately 0.150 grams and proceed with the analysis.

a. If the sample has a Fizz rating of 2 or 3, (refer to section II, Neutralization Potential), the sample has to be covered with vanadium pentoxide to insure that all sulfur is released from the sample and not trapped by the calcium carbonate present in the sample.

7.5 Verify that the instrument is maintaining calibration by running a secondary standard after each group of samples.

a. Maximum group = 20 samples

b. Optimum group = 10 samples

c. If the standard is outside the certified limits repeat steps 7.1. If the standard is still outside the certified limits the instrument will have to be recalibrated. Reanalyze the previous group of samples after the conditions of 7.3 have been met.

d. If the standard is within the certified range continue with the next group of samples.

8. CALCULATIONS

8.1 % Sulfur is calculated directly with a properly calibrated instrument.

9. QUALITY CONTROL

9.1 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision is as follows:

a. 0.08 * X where X = the average of the two results.

9.2 Accuracy shall be checked by the weekly running of a standard reference material such as the PBS Sulfur in Coal Standards. Each standard specifies an acceptable range of values that can be used to judge the acceptability of secondary standards as well as an analyst's performance.

E. HIGH TEMPERATURE COMBUSTION, ACID BASE TITRATION (ASTM D 4239)

1. SCOPE AND APPLICATION

The high temperature instrumental technique of total sulfur analysis is applicable to all coal samples and, if prescribed measures are followed, to overburden samples.

2. SUMMARY OF METHOD

A portion of the laboratory sample is combusted in a stream of oxygen at a temperature of approximately 1350 C. The resultant gas is absorbed in a solution of H_2O_2 and forms dilute. solutions of H_2SO_4 and HCI which is titrated with dilute NaOH to determine the amount of sulfur present in the sample.

3. INTERFERENCES AND PRECAUTIONS

3.1 Refer to section 3 of lodimetric Titration

4. APPARATUS AND MATERIALS

4.1 ACID-BASE SULFUR ANALYZER

4.2 COMBUSTION BOATS

5. REAGENTS

5.1 VANADIUM PENTOXIDE: reagent grade

5.2 OXYGEN: 99.999% purity

5.3 TITRANT: 0.05N NaOH

5.4 DILUENT: 1.0% H_2O_2

5.5 PRIMARY STANDARDS: NBS 1932b, 1935, 2682, 2683, 2684, 2685, 2962.

5.6 SECONDARY STANDARDS: Those standards that are purchased or prepared and which have been validated with Primary Standards. Refer to this section B.1. 5.5.

6. SAMPLE CONSIDERATIONS

6.1 This procedure does not require any special sample handling considerations. The normal -60m sample is all that is required.

7. PROCEDURE

7.1 Insure that the instrument is functioning properly by performing preventive maintenance as recommended by the manufacturer.

7.2 Verify that the instrument is properly calibrated by running a secondary standard with a nominal value of 1 or 2 % sulfur. Compare the obtained value to the certified range for that standard.

7.3 For each sample, tare a sample boat, then weigh approximately 0.400 grams and proceed with the analysis.

a. If the sample has a Fizz rating of 2 or 3, (refer to section II, Neutralization Potential), the sample has to be covered with vanadium pentoxide to Insure that all sulfur is released from the sample and not trapped by the calcium carbonate present in the sample.

7.4 Verify that the instrument is maintaining calibration by running a secondary standard after each group of samples.

a. Maximum group = 20 samples

b. Optimum group = 10 samples

c. If the standard is outside the certified limits repeat steps 7.1. If the standard is still outside the certified limits the instrument will have to be recalibrated. Reanalyze the previous group of samples after the conditions of 7.2 have been met.

d. If the standard is within the certified range continue with the next group of samples.

8. CALCULATIONS

8.1 % Sulfur is calculated directly when an exact weight is used for all standards and samples.

8.2 The % Sulfur needs to be corrected for %CI if optimum accuracy is to be obtained.

a. Corrected % SULFUR = Determined % SULFUR - .45 * (% CI)/ sample weight

9. QUALITY CONTROL

9.1 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision is as follows:

a. 0.06 + 0.03 * X where X = the average of the two results.

9.2 Accuracy shall be checked by the weekly running of a standard reference material such as the IBS Sulfur in Coal Standards. Each standard specifies an acceptable range of values that can be used to judge the acceptability of secondary standards as well as an analyst's performance.

2. FORMS OF SULFUR

This section covers in detail the procedures which are used to quantify the amount of sulfate, sulfide and organic sulfur in coal and overburden. The ASTM procedure that is presented is applicable for coal but it is not always appropriate for overburden. The EPA procedure is adequate for coal and overburden but is not as precise as the combination procedure which uses the best features of the ASTM and EPA methods.

A. ASTM STANDARD METHOD D2492

1. SCOPE AND APPLICATION

The ASTM Method D2492 is appropriate for the determination of the forms of sulfur in all coals but was not intended to be used with any other sample matrix. Mineralogies can exist in overburden that can cause an over estimation of the pyritic content of some samples. This is possible since the ASTM procedure assumes that all iron extracted with nitric acid, after the sample has been leached with hydrochloric acid, is of pyritic origin.

2. SUMMARY OF METHOD

A portion of the laboratory sample is heated with a dilute solution of HCI to remove sulfate sulfur and to remove Iron that would interfere with the pyritic iron determination.The sulfate sulfur content is calculated from the weight of barium sulfate which is precipitated from the HCI extraction filtrate. Pyritic and organic sulfur remain in the sample residue since neither are soluble in hydrochloric acid. The sample residue from the HCI extraction is then extracted with dilute nitric acid to dissolve the pyrite in the sample. The iron in this extract is quantified by titration or by atomic absorption spectrophotometry. This value is used to calculate the amount of pyritic sulfur in the sample. Organic sulfur is calculated from the difference between the total sulfur determination and the sum of the sulfate and pyritic sulfurs.

3. INTERFERENCES AND PRECAUTIONS

3.1 This procedure was developed solely for the analysis of coal and may not be appropriate for the analysis of some overburden samples.

3.2 Low results may be obtained on the determination of pyritic iron due to the incomplete dissolution of the pyrite if a large sample size is used with a sample of high pyritic sulfur content. This problem can easily be overcome by choosing reasonable sample weights and by further size reduction of samples with exceptionally high pyritic sulfur contents.

4. APPARATUS AND MATERIALS

4.1 MUFFLE FURNACE : Capable of maintaining 800°C.

4.2 CRUCIBLES: 15 ml platinum, porcelain, or silica for igniting the barium sulfate.

4.3 HOTPLATE: Size is dependent on sample quantity.

4.4 GLASSWARE: 150 and 400 ml beakers

4.5 FILTER PAPER: #4, #40 and #42 Whatman or equivalent.

4.6 FILTER RACKS AND FUNNELS:

4.7 ATOMIC ABSORPTION SPECTROPHOTOMETER:

4.8 Refer to the total sulfur technique that will be used to analyze the subsamples.

5. REAGENTS

5.1 All chemicals should be reagent grade and the water should be Type III reagent water.

5.2 BARIUM CHLORIDE SOLUTION: Dissolve 100 grams of BaCl2.2H2O in water and dilute to a final volume of 1 liter.

5.3 HYDROCHLORIC ACID (40%) : Dilute two volumes of concentrated hydrochloric acid in 3 volumes of water.

5.4 METHYL ORANGE INDICATING SOLUTION: Dilute 5 ml of saturated solution in 500 ml of water.

5.5 AMMONIA HYDROXIDE SOLUTION (1:1): Dilute one volume of concentrated NH4OH with one volume of water.

5.6 BROMINE WATER: saturate water with liquid bromine and store in a dark bottle under a hood.

5.7 METHANOL (25%): Dilute one volume of methanol in three volumes of water.

5.8 NITRIC ACID(12.5%): Dilute 1 volume of concentrated nitric acid in seven volumes of water.

5.9 LANTHANUM SOLUTION: Dissolve 175 grams of $LaCl_3$ or 265 grams of $LaCl_3.7H_2O$ in water and dilute to 1 liter.

5.10 Refer to the total sulfur technique that will be used to analyze the subsamples.

6. SAMPLE CONSIDERATIONS

6.1 This procedure does require special sample handling considerations. The normal -60m sample is not adequate for samples with high sulfur contents. Samples that contain more than 8% sulfur need to be ground to pass a 200m screen in order to insure a complete extraction of the pyritic iron.

7. PROCEDURE

7.1 Sample weights are based on the following:

% Total Sulfur	Weight of analysis sample
< 2.0 %	1.0 gram
2.0 to 4.0 %	0.5 gram
4.0 to 8.0 %	0.3 gram
> 8.0 %	0.15 gram

7.2 Analyze the sample for sulfate sulfur.

a. Weigh an amount of sample based on the chart in 7.1, record the weight to the nearest .1 mg.

b. Transfer the sample to a 150 ml beaker, wet with 25% methanol and add 50 ml of 40% HCI.

c. Boil gently for 30 minutes and remove from the hotplate.

d. Filter thru #40 Whatman filter paper into a 400 ml beaker. Rinse the beaker twice and the residue six times with cold water. Save the residue and filter paper for the pyritic iron determination. (refer to 7.3)

e. Add approximately 5 ml of bromine water to the filtrate and boil for 5 minutes. This step insures that all iron present in the filtrate will be oxidized to the ferric form for subsequent removal as ferric hydroxide. Heat for a few minutes to insure a complete reaction.

f. Stir in 25 ml of 1:1 NH_4OH to precipitate any iron and manganese in the filtrate.

g. Filter into a 400 ml beaker using #4 Whatman filter paper. Rinse the beaker twice and the residue six times with hot water. Discard the filter paper and residue.

NOTE: If a large amount of manganese was dissolved with the iron, as evidenced by a fine textured brown precipitate instead of an orange colloidal precipitate, #42 Whatman filter paper will have to be used to effectively remove the metals. Some samples have such a high concentration of iron and manganese that steps (e) thru (g) have to be repeated in order that a clear filtrate will be obtained.

h. Adjust the volume of filtrate to approximately 250 ml and make the solution slightly acidic with 40% HCI using the methyl orange solution as the indicator, then add an additional 1 ml of 40% HCI.

i. Place the beakers on the hotplate and heat to boiling.

j. Slowly add 10 ml of hot barium chloride solution and continue to boil for 15 minutes. Cover the samples with a watch glass and let the samples remain standing for several hours at a temperature just below boiling. This will facilitate quantitative filtration of the $BaSO_4$ due to the formation of larger crystals.

k. After cooling, filter the precipitate using #42 Whatman filter paper. Rinse the beaker twice with water after triturating with a rubber policeman. Rinse the filter paper and precipitate an additional 8 times.

I.Transfer the filter paper, lightly folded, to a 15 ml crucible and place in a cool muffle furnace.

m. Smoke off the filter paper by heating to 500° C After 1/2 hour raise the temperature to 800° C and maintain for 1/2 hour. If any carbon remains, return the crucible to the furnace for an additional 1/2 hour at 800° C.

n. Weigh the barium sulfate after the crucible has cooled.

7.3 Analyze the residue from 7.2d for pyritic iron.

a. Return the filter paper and residue from 7.2d to the 150 ml beaker that was used for the HCI extraction.

b. Add 50 ml of 12.5% nitric acid to the beaker and stir thoroughly until the filter paper has disintegrated. Cover the beaker with a watch glass and either boil gently for 1/2 hour (fume hood required.) or let the sample stand overnight at room temperature.

c. Filter the sample into a 100 ml volumetric flask, washing the beaker twice and the filter paper plus residue an additional six times.

I. If an air/acetylene flame is going to be used, add 10 ml lanthanum solution before diluting to volume. The lanthanum solution is added to minimize interferences that can occur in the relatively cool air/acetylene flame. An easier alternative is to simply use the hotter nitrous oxide/acetylene flame for the elimination of interferences.

d. Prepare standards that have the same acid concentration as the samples and which have iron concentrations that bracket the samples. Add 10 ml of lanthanum solution per 100 ml of standard if the air /acetylene flame is to be used.

e. Set the atomic absorption spectrophotmeter operating conditions according to the manufacturers recommendations. Let the light source and the flame reach equilibrium prior to running any samples. (approx. 15 min.)

f. Determine the concentration of iron in the samples to the nearest 0.1 mg/I.

g. Refer to ASTM volume 05.05, Gaseous Fuels; Coal and Coke, D2492 Forms of sulfur in Coal if the titration technique for the iron determination is used.

7.4 Analyze the sample for total sulfur using one of the procedures that are explained in this manual.

8. CALCULATIONS

8.1 % SULFATE SULFUR = (A-B) * 13.738 / C

A = weight of $BaSO_4$ precipitate
B = weight of blank residue
C = weight of sample

8.2 % PYRITIC SULFUR = A * B * .01148 / C

A = ppm of iron as determined by AAS
B = dilution factor
C = weight of sample

8.3 % ORGANIC **SULFUR** = A - (B + C)

A = % TOTAL SULFUR
B = % SULFATE SULFUR
C = % PYRITIC SULFUR

9. QUALITY CONTROL

9.1 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision is as follows:

	% S < 2.0 %	% S > 2.0 %
Sulfate sulfur	+/- 0.02 %	+/- 0.02 %
Pyritic sulfur	+/- 0.05 %	+/- 0.10 %
Organic sulfur	+/- 0.10 %	+/- 0.20 %

9.2 Currently accuracy can not be determined since there are no NBS certified standards available.

B. MODIFIED EPA METHOD

1. SCOPE AND APPLICATION

This procedure is applicable to all coals and overburden with the following qualifications: 1) The precision of the sulfate sulfur determination is limited to twice the total sulfur precision which means that the possible error could be an order of magnitude greater than the actual sulfate sulfur content. 2) The organic sulfur content could be over estimated since any unreacted pyrite will be determined as organic sulfur. Modifications must be made to the procedure to ensure complete dissolution of the pyritic sulfur. Both of these errors would in most cases cause an underestimation of the pyritic sulfur content and therefore would underestimate the maximum potential acidity.

2. SUMMARY OF METHOD

In this procedure three portions of the laboratory sample are analyzed for sulfur. One portion is analyzed without any pretreatment to determine the total sulfur content of the sample. A second portion is analyzed for pyritic plus organic sulfur after the sample has been leached with dilute hydrochloric acid. The third portion is analyzed for organic sulfur after the sample has been leached with dilute nitric acid. The concentrations of the forms of sulfur are then calculated from the three results.

3. INTERFERENCES AND PRECAUTIONS

3.1 Low results may be obtained for the calculated pyritic sulfur if a large sample size is used with a sample of high pyritic content, due to possible positive errors in the determinations of sulfate and organic sulfur.

4. APPARATUS AND MATERIALS

4.1 FUNNEL RACK:

4.2 BEAKERS: 100 ml pyrex

4.3 FILTER PAPER: glass fiber or cellulose, depending on which total sulfur procedure is chosen.

4.4 Refer to the total sulfur technique that will be used to analyze the subsamples.

5. REAGENTS

5.1 All chemicals should be reagent grade and the water should be Type III reagent water.

5.2 HYDROCHLORIC ACID (40%): Dilute 2 parts of concentrated HCI in 3 parts of water.

5.3 NITRIC ACID (12.5%): Dilute 1 part of concentrated HNO_3 in 7 parts of water.

5.4 Nessler's Reagent

5.5 Silver Nitrate Solution (10%)

5.6 Refer to the total sulfur technique that will be used to analyze the subsamples.

6. SAMPLE CONSIDERATIONS

6.1 This procedure requires special sample handling considerations. The normal -60m sample is not adequate for samples with high sulfur contents. Samples containing more than 8% sulfur shall be ground to pass a 200m screen in order to insure a complete extraction of the pyritic iron.

7. PROCEDURE

7.1 Analyze the sample for total sulfur using one of the procedures in this manual.

7.2 Analyze the sample for pyritic plus organic sulfur.

a. Weigh approximately 0.5 gram of sample,to the nearest 0.1 mg, into a clean 100 ml beaker.

b. Add 50 ml of 40% HCI to the beaker, cover with a watch glass and boil gently for 1/2 hour.

c. Filter the sample, washing the beaker twice and the residue an additional six times. Discard the filtrate.

I. Use # 40 Whatman if you use the Eschka method for analyzing the residue. Use glass fiber filters if you use any of the high temperature combustion methods to analyze the residue.

ii. If the iodimetric or the acid base titration techniques are to be used then the filtrate will have to be tested for the presence of chlorides with 10% $AgNO_3$ solution. If chlorides are detected, wash the residue until the filtrate does not produce a white precipitate. upon the addition of $AgNO_3$.

d. Dry the sample and determine the sulfur content using one of the total sulfur methods. The bomb washing method would be cumbersome due to the mass of the filter paper.

7.3 Analyze the sample for organic sulfur.

a. Weigh approximately 0.5 gram of sample,to the nearest 0.1 mg, into a clean 100 ml beaker.

b. Add 50 ml of 12.5% nitric acid to the beaker and stir thoroughly until the filter paper has disintegrated. Cover the beaker with a watch glass and either boil gently for 1/2 hour (fume hood required) or let the sample stand overnight at room temperature.

c. Filter the sample, washing the beaker twice and the residue an additional six times.

i. Use # 40 Whatman if you use the Eschka method for analyzing the residue. Use glass fiber filters if you use any of the high temperature combustion methods to analyze the residue.

ii. If the iodimetric or the acid base titration total sulfur method is to be used to analyze the residue then the filtrate will have to be tested for the presence of nitrates with Nessler's reagent. If nitrates are detected, wash the residue until the filtrate does not turn yellow upon the addition of Nessler's reagent. (Allow one minute for the reaction.)

d. Dry the sample and determine the sulfur content using one of the total sulfur techniques. The initial sample weight from 7.3a must be used in all calculations. The bomb washing method would be cumbersome due to the mass of the filter paper.

8. CALCULATIONS

8.1 Calculate the forms of sulfur from the results of the three determinations from section 7 as follows:

TOTAL SULFUR = (7.1)
SULFATE SULFUR = (7.1) - (7.2)
PYRITIC SULFUR = (7.2) - (7.3)
ORGANIC SULFUR = (7.3)

9. QUALITY CONTROL

9.1 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision is as follows:'

	% S < 2.0 %	% S > 2.0 %
Sulfate sulfur	+/- 0.05 %	+/- 0.10 %
Pyritic sulfur	+/- 0.15 %	+/- 0.25 %
Organic sulfur	+/- 0.05 %	+/- 0.05 %

9.2 Currently accuracy can not be determined since there are no NBS certified standards available.

C. ASTM/EPA COMBINATION METHOD

1. SCOPE AND APPLICATION

This procedure is applicable to all coals and overburden samples common to Pennsylvania.

2. SUMMARY OF METHOD

The sulfate sulfur content is accurately determined using a gravimetric procedure that is essentially ASTM method D2492. The organic sulfur content is determined on a subsample that has been leached with nitric acid using a procedure that is close to the EPA procedure. The sulfide sulfur content of the sample is calculated from the difference of the total sulfur and the sum of the sulfate and organic sulfurs.

3. INTERFERENCES AND PRECAUTIONS

The modifications of the ASTM and EPA methods contained in this procedure minimize the errors that were possible with those procedures.

4. APPARATUS AND MATERIALS

4.1 MUFFLE FURNACE : Capable of maintaining 800°C.

4.2 CRUCIBLES: 15 ml platinum, porcelain, or silica for igniting the barium sulfate.

4.3 HOTPLATE: Size is dependent on sample quantity.

4.4 GLASSWARE: 150 and 400 ml beakers.

4.5 FILTER PAPER: Glass fiber #4, #40 and #42 Whatman or equivalent.

4.6 FILTER RACK AND FUNNELS:

4.7 Refer to the total sulfur technique that will be used to analyze the subsample for organic sulfur.

5. REAGENTS

5.1 All chemicals should be reagent grade and the water should be Type Ill reagent water.

5.2 BARIUM CHLORIDE SOLUTION: Dissolve 100 grams of $BaCl_2.2H_2O$ in water and dilute to a final volume of 1 liter.

5.3 HYDROCHLORIC ACID (40%): Dilute two volumes of concentrated hydrochloric acid in 3 volumes of water.

5.4 METHYL ORANGE INDICATING SOLUTION: Dilute 5 ml of saturated solution in 500 ml of water.

5.5 AMMONIA HYDROXIDE SOLUTION (1:1): Dilute one volume of concentrated NH_4OH with one volume of water.

5.6 BROMINE WATER: saturate water with liquid bromine and store in a dark bottle under a hood.

5.7 METHANOL (25%): Dilute one volume of methanol *in* three volumes of water.

5.8 NITRIC ACID(12.5%): Dilute 1 volume of concentrated nitric acid in seven volumes of water.

5.9 Refer to the total sulfur technique that will be used to analyze the subsample for organic sulfur.

6. SAMPLE CONSIDERATIONS

6.1 This procedure does require special sample handling considerations. The' normal -60m sample is not adequate for samples with high sulfur contents. Samples that contain more than 8% sulfur shall be ground to pass a 200m screen in order to insure a complete extraction of the pyritic iron.

7. PROCEDURE

7.1 Analyze the sample for total sulfur using one of the procedures that are explained in this manual.

7.2 Analyze the sample for sulfate sulfur.

a. Weigh approximately 2 grams of sample and record the weight to the nearest .1 mg.

b. Transfer the sample to a 150 ml beaker, wet with 25% methanol and add 50 ml of 40% HCI.

c. Boil gently for 30 minutes and remove from the hotplate.

d. Filter through #40 Whatman filter paper into a 400 ml beaker. Rinse the beaker twice and the residue six times with cold water. Discard the filter paper and residue.

e. Add approximately 5 ml of bromine water to the filtrate and boil for 5 minutes. This step insures that all Iron present in the filtrate will be oxidized to the ferric form for subsequent removal as ferric hydroxide.

f. Stir in 25 ml of 1:1 NH_4OH to precipitate any iron and manganese in the filtrate.

g. Filter into a 400 ml beaker using #4 Whatman filter paper. Rinse the beaker twice and the residue six times with hot water. Discard the filter paper and residue.

NOTE: If a large amount of manganese was dissolved with the iron as evidenced by a fine textured brown precipitate instead of an orange colloidal precipitate, #42 Whatman filter paper will have to be used to effectively remove the metals. Some samples have such a high concentration of iron and manganese that steps (e) thru (g) will have to be repeated in order that a clear filtrate is obtained.

h. Adjust the volume of filtrate to approximately 250 ml and make the solution slightly acidic with 40% HCI using the methyl orange solution as the indicator, then add an additional 1 ml of 40% HCI.

I. Place the beakers on the hotplate and heat to boiling.

j. Slowly add 10 ml of barium chloride solution and boil for 15 minutes. Let the samples remain standing for several hours, preferably overnight. This will facilitate quantitative filtration of the $BaSO_4$ because of the formation of larger crystals.

k. Filter the precipitate using #42 Whatman filter paper. Rinse the beaker twice with water after triturating with a policeman. Rinse the filter paper and precipitate an additional 8 times.

I. Transfer the filter paper, lightly folded, to a 15 ml crucible and place in a cool muffle furnace.

m. Smoke off the filter paper by heating to 500° C. After 1/2 hour raise the temperature to 800 ^{0} C and maintain for 1 /2 hour.

n. Weigh the residue after the crucible has cooled.

7.3 Analyze the sample for organic sulfur.

a. Weigh approximately 0.5 gram of sample, to the nearest 0.1 mg, into a clean 100 ml beaker.

b. Add 50 ml of 12.5% nitric acid to the beaker and stir thoroughly until the filter paper has disintegrated. Cover the beaker with a watch glass and either boil gently for 1/2 hour (fume hood required) or let the sample stand overnight at room temperature.

c. Filter the sample, washing the beaker twice and the residue an additional six times.

I. Use #40 Whatman if you use the Eschka method for analyzing the residue. Use glass fiber filters if you use any of the high temperature combustion methods to analyze the residue.

ii. If the iodimetric or the acid base titration techniques are to be used then the filtrate will have to be tested for the presence of nitrates with Nessler's reagent. If nitrates are detected, wash the residue until the filtrate does not turn yellow upon the addition of the Nessler's reagent. (Allow one minute for the reaction.)

d. Dry the sample and determine the sulfur content using one of the total sulfur techniques. The bomb washing method would be cumbersome due to the mass of the filter paper.

8. CALCULATIONS

8.1 % SULFATE SULFUR = (A-B) * 13.738 / C

A = weight of BaSO4 precipitate
B   weight of blank residue
C = weight of sample

8.2 % ORGANIC SULFUR = VALUE FROM 7.3d

8.3 % PYRITIC SULFUR = % TOTAL SULFUR - (% SULFATE SULFUR + % ORGANIC SULFUR)

9. QUALITY CONTROL

9.1 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision is as follows:

	S < 2.0 %	% S > 2.0 %
Sulfate sulfur	+/- 0.02 %	+/- 0.02 %
Pyritic sulfur	+/- 0.10 %	+/- 0.15 %
Organic sulfur	+/- 0.05 %	+/- 0.05 %

9.2 Currently accuracy can not be determined since there are no ' BS certified standards available.

II. NEUTRALIZATION POTENTIAL

1. SCOPE AND APPLICATION

The neutralization potential test procedure quantifies the neutralizing compounds in coal and overburden. Of the many types of basic compounds present, carbonates are the only basic compounds that occur in sufficient quantity to be considered as effective deterrents to the production of acid mine drainage. As always there are exceptions, siderite ($FeCO_3$) which is a carbonate, is not a desirable neutralizer since it will produce an alkaline discharge that can contain a significant amount of iron.

2. SUMMARY OF METHOD

A portion of the laboratory sample is qualitatively ranked as to its carbonate concentration by means of the fizz rating. A quantity of dilute hydrochloric acid, based on the fizz rating, is added to another portion of the laboratory sample which is then heated to insure complete reaction with the sample. After the sample has cooled, it is back titrated with a dilute solution of sodium hydroxide to determine the quantity of HCI that was neutralized by the sample. This value is then used to calculate the neutralization potential of the sample and is expressed as $CaCO_3$.

The procedure that is presented is a slight modification of the procedure Sobek et.al. offered in Field and Laboratory Methods Applicable to Overburdens and Minesoil. The changes are in the acid digestion procedure which has been simplified by eliminating unnecessary steps. These changes-do not alter the results obtained by the Sobek procedure.

3. INTERFERENCES AND PRECAUTIONS

3.1 Many interactions take place in the course of this test that effect the precision which can be obtained but they do not effect the usefulness of the results.

I. Certain iron complexes which can be dissolved in the HCI digestion, consume NaOH in the back titration with the formation of iron hydroxide. This tends to lower the calculated neutralization potential and also causes a very uncertain endpoint due to the slow hydrolysis process below a pH of 7. This is why siderite containing strata does not show .an appreciable amount of neutralization potential even though they show a fizz rating of 1 or even a 2.

ii. Pyrite will not dissolve appreciably under the conditions of this test.

4. APPARATUS AND MATERIALS

4.1 pH METER and ELECTRODE: Automated systems will improve the precision of the test as well as remove the tedium of the titration, but manual systems are adequate.

4.2 BURET: automatic or standard

4.3 HOTPLATE:

4.4 BEAKERS or ERLENMYER FLASKS:

4.5 BALANCE:

4.6 WATCHGLASSES:

5. REAGENTS

5.1 All chemicals shall be reagent grade and the water shall be Type Ill reagent water or better.

5.2 HYDROCHLORIC ACID (0.1N):Dilute 8.3 ml of concentrated HCI in 1 liter of water, mix well. Standardize as follows:(refer to ASTM E 200)

a. Dry 2 g of anhydrous sodium carbonate at 250 C for 4 hours. Cool in a desiccator.

b. Weigh .22 g of Na_2CO_3 to the nearest 0.1 mg. Dilute with 50 ml of water.

c. Titrate with the .1N HCI solution to the methyl red endpoint, or potentiometricly to a pH of 4.5.

d. Calculate the normality:

$$A = B/(.053*C)$$

A = normality of the HCI solution
B = grams of Na_2CO_3 used
C = milliliters of HCI solution used in the titration

e. Use the average of three standardizations for all subsequent calculations.

5.3 HYDROCHLORIC ACID (0.5N):Dilute 41.5 ml of concentrated HCI in 1 liter of water, mix well. Standardize as follows: (refer to ASTM E 200)

a. Dry 5 g of anhydrous sodium carbonate at 250 C for 4 hours. Cool in a desiccator.

b. Weigh 1.10 g of Na_2CO_3 and record the weight to the nearest .1 mg. Dilute with 50 ml of water.

c. Titrate with the .5N HCI solution to the methyl red endpoint, or potentiometricly to a pH of-4.5.

d. Calculate the normality:

$$A = B/(.053*C)$$

A = normality of the HCI solution
B = grams of Na2CO3 used
C = milliliters of HCI solution used in the titration

e. Use the average of three standardizations for all subsequent calculations.

5.4 HYDROCHLORIC ACID (25%): Dilute one volume of concentrated HCI in three volumes of water.

5.5 SODIUM HYDROXIDE (0.1N): Dilute 5.45 ml 50 % NaOH to 1 liter with water. Mix well. The concentration will not be determined but is a part of the blank data.

5.6 SODIUM HYDROXIDE (0.5N): Dilute 27.25 ml of 50 % NaOH to 1 liter with water. Mix well. The exact concentration will not be determined but is a part of the blank data.

5.7 SODIUM CARBONATE (anhydrous):

5.8 ASCARITE:

5.9 CALCIUM CARBONATE:

6. SAMPLE CONSIDERATIONS

This procedure does not require any special sample handling considerations. The normal -60m sample is all that is required.

7. PROCEDURE

7.1 Determine the fizz rating of the samples as follows:

a. Place a small amount of sample on a watchglass and make a depression in the center. Add one or two drops of 25% HCL to the depression. Determine the fizz rating based on the following criteria:

0 FIZZ (NONE): No reaction or an occasional bubble caused by trapped air.

1 FIZZ (SLIGHT): Minimal reaction, the reaction ranges from a few bubbles per second to many fine bubbles that cover the entire sample/acid interface.

2 FIZZ (MODERATE): Active bubbling with only a small amount of splashing.

3 FIZZ (STRONG): Very active bubbling that includes substantial splashing of the acid.

Proper identification of the fizz rating will minimize the number of neutralization potential determinations that will have to be rerun due to insufficient addition of acid and will serve as a qualitative check of the neutralization potential.

7.2 Determine the neutralization potential (NP).

a. Weigh 2.000 gram of sample and transfer to an appropriate size beaker or flask.

b. Add the quantity of dilute HCI to the sample that is indicated in the following Table according to the fizz rating that was determined in the preceding step.

FIZZ RATING	VOLUME OF HCI	NORMALITY OF HCI
NONE	20 ml	0.1N
SLIGHT	40 ml	0.1N
MODERATE	40 ml	0.5N
STRONG	80 ml	0.5N

c. Add water to make the volume approximately 100 ml.

d. Cover with a watchglass and boil gently for 5 minutes.

e. Cool and then titrate to pH 7.0 with the corresponding normality of NaOH.

f. Determine reagent blank titration values by following the NP procedure, 7.2 (b. thru e.), for each fizz rating. Boileasers may be necessary to avoid the loss of acid during the boiling stage of the procedure.

8. CALCULATIONS

8.1 $A = (B - (C * (D / E))) * 25 * N$

A = Tons of $CaCO_3$ equivalent per 1000 tons of material

B = ml of acid added to the sample

C = ml of base used to titrate the sample

D = ml of acid added to the blank

E = ml of base used to titrate the blank

N = normality of the acid

9. QUALITY CONTROL

9.1 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision, categorized by fizz rating, is as follows:

	ACCEPTABLE PRECISION (tons / 1000 tons of material)
Neutralization Potential 0 to 30	± 5.0
Neutralization Potential 30 to 100	± 10.0
Neutralization Potential 100 to 500	± 25.0
Neutralization Potential 500 +	± 50.0

9.2 Accuracy shall be based on the analysis of reagent grade calcium carbonate which has been dried for 4 hours at 250 C.

The CaCO3 standards shall be run at least once per month and whenever new 0.1 and 0.5 N NaoH or HCI solutions are prepared. Standards shall be run as follows:

	Weight of CaCO3 (grams)	Allowable Range (tons / 1000 tons of material)
FIZZ = 1	0.100	50.0 +/- 2.5
FIZZ = 2	1.000	500.0 +/- 25.0
FIZZ = 3	2.000	1000.0 +/- 50.0

III. PASTE pH

1. SCOPE AND APPLICATION

The paste pH is a qualitative test which only indicates the hydrogen ion activity under the particular test conditions that are used. The paste pH can not quantify the amount of acidic or alkaline material in the sample. For these reasons the paste pH is of limited usefulness in the assessment of overburden quality.

2. SUMMARY OF METHOD

A portion of the laboratory sample is mixed in a two to one ratio with deionized water. The pH is measured electrometricly after one hour.

3. INTERFERENCES AND PRECAUTIONS

The paste pH is subject to many variables such as; sample to water ratio, the partial pressure of CO2, the quantity of soluble salts and the condition of the pH electrode.

4. APPARATUS AND MATERIALS

4.1 pH METER AND ELECTRODE:

4.2 BALANCE:

4.3 CUPS: approximately 50 ml

5. REAGENTS

5.1 All chemicals shall be reagent grade and the water shall be Type Ill reagent water or better.

5.2 STANDARD BUFFER SOLUTIONS: pH 4.00, 7.00, 10.00

6. SAMPLE CONSIDERATIONS

6.1 This procedure does not require any special sample handling considerations.The normal -60m sample is all that is required.

7. PROCEDURE

7.1 Weigh 10.0 g of sample and place in the measuring cup.

7.2 Add 5.0 ml of water and let soak for 1 hour.

7.3 Standardize the pH electrode according to the manufacturers recommendations using the 4.00 and 7.00 pH buffers.

7.4 Check the standardization with the 10.00 pH buffer.

7.5 Thoroughly mix the sample

7.6 Read the pH of the sample after making sure that the electrode is making good contact with the sample and that the reading has stabilized (a minimum of 1 minute).

7.7 Rinse the electrode thoroughly before proceeding to the next sample.

7.8 Verify that the electrode calibration is still valid after every 12 samples by reading the 4 and 7 pH buffers.

8. CALCULATIONS

No calculations are required for this procedure.

9. QUALITY CONTROL

9.1 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision is +/- 0.3 pH units.

IV. LEACHING TESTS

1. SCOPE AND APPLICATION

Leaching tests have been utilized in an attempt to simulate what occurs in nature after mining is completed. The ASTM test D3987 "Shake extraction with water" is a short term test that only measures readily soluble components of the sample. The Weathering Cell Method, which has several variations, is a longer term, usually 8 weeks, multiple extraction technique that add the dimensions of time and some oxidation to the test as well as the option of seeding with bacteria. Column leaching is a weathering cell that adds the interaction of several strata. Soxhlet extractions are elevated temperature tests that reduce the time needed to estimate leachate quality. There are several other tests that may be applicable to overburden, such as the EPA tests for E.P. Toxicity and the T.C.L.P. (Toxicity Characteristic Leaching Procedure).

V. QUALITY ASSURANCE / QUALITY CONTROL

1. INTRODUCTION

According to the USEPA, Quality assurance (QA) is a system for ensuring that all information, data, and resulting decisions compiled under a specific task are technically sound, statistically valid and properly documented. Quality control is the mechanism through which quality assurance achieves its goals.

Quality control programs define the frequency and methods of checks, audits, and reviews necessary to identify problems and dictate corrective action, thus verifying product quality.

2. MINIMUM QA/QC REQUIREMENTS

Every lab is required to have a written Quality Assurance Manual which addresses the following areas.

2.1 SAMPLE PREPARATION

a. All samples shall be clearly identified throughout the entire preparation procedure.

b. All preparation equipment shall be inspected before use for proper operation and condition. If any problems are found, corrective action is taken before the equipment is used for samples.

c. One sample of pulverizer product from each group or every 50th sample, whichever is greater, will be screened on a 60m sieve. If the +60m sieve fraction represents more than 5% of the pulverizer product, the pulverizer screen must be replaced.

2.2 ANALYTICAL PROCEDURES

a. The laboratory shall have maintenance plans for all major pieces of equipment that will include periodic inspection, preventive maintenance and provisions for service.

b. Balances - minimum requirements

i. Monthly calibration checks with class S weights.

ii. Yearly inspection and calibration by a qualified balance service.

c. Calibrations standards shall be traceable to NBS standards.

d. A minimum of 5% of the samples must be run in duplicate as a check on precision.

e. Participation in interlaboratory comparison studies and use of primary standards are imperative if a lab is to evaluate the accuracy of its results.

f. Records must be maintained that include all Quality Control activities and analytical data.

2.3 DATA HANDLING

a. All manual data transfers and calculations must be verified by a second person. The use of computers and instruments that are directly linked greatly reduce the chance of transfer and calculation errors and increase laboratory productivity.

b. Reporting shall be in format that is acceptable to Pa. DER and shall include the following information.

I. The analytical techniques which were used and any deviations from stated procedures.

ii. Sample type; core, rotary chips, etc.

c. Precision and accuracy data shall be maintained on file.

d. All final data shall be reviewed for completeness and correctness.

2.4 PROGRAM COORDINATION

A person knowledgeable in quality assurance is to be assigned the responsibility of ensuring that the laboratories Quality Assurance program is followed and that corrective actions are taken when needed.

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