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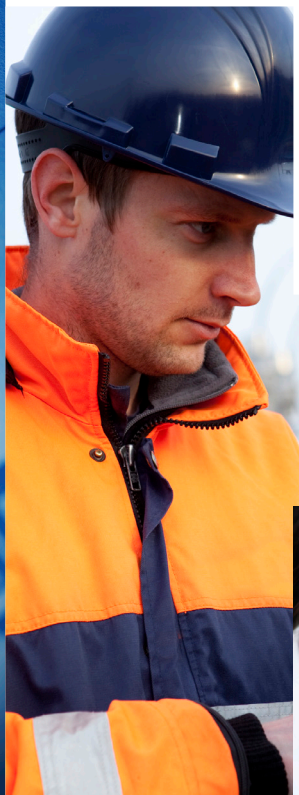
ROUTINE COAL and COKE ANALYSIS:

Collection, Interpretation, and Use of Analytical Data

2nd Edition



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Foreword

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Contents

Introduction

Coal is a very heterogeneous material containing various combinations of organic matter and mineral matter. The principal elements in the organic matter are carbon, hydrogen, nitrogen, sulfur, and oxygen. The mineral matter may contain detectable quantities of as many as 60 elements, which together make up the various minerals found in coal. These minerals include clay minerals, pyrite, marcasite, calcite, silica, and smaller amounts of other minerals. However, the analysis of coal is generally determined from representative samples of the material and not from the individual components. Typical analysis ranges of important analytical parameters (as-received basis) for the principal ranks of coal are given in the table that follows [1]. (In this table and throughout this text all percentages are percent mass fractions unless otherwise noted.) The values for oxygen and hydrogen in this table include the hydrogen and oxygen values for sample moisture. Another common practice is not to report the hydrogen and oxygen in the sample moisture as part of the hydrogen and oxygen values for the coal.

Typical Composition and Physical Property Ranges for Various Ranks of Coal

	Anthracite	Bituminous	Subbituminous	Lignite
Moisture (%)	3–6	2–15	10–25	25–45
Volatile matter (%)	2–12	15–45	28–45	24–32
Fixed carbon (%)	75–85	50–70	30–57	25–30
Ash (%)	4–15	4–15	3–10	3–15
Sulfur (%)	0.5–2.5	0.5–6	0.3–1.5	0.3–2.5
Hydrogen (%)	1.5–3.5	4.5–6	5.5–6.5	6–7.5
Carbon (%)	75–85	65–80	55–70	35–45
Nitrogen (%)	0.5–1	0.5–2.5	0.8–1.5	0.6–1.0
Oxygen (%)	5.5–9	4.5–10	15–30	38–48
Btu/lb	12,000–13,500	12,000–14,500	7500–10,000	6000–7500
Density (g/mL)	1.35–1.70	1.28–1.35	1.35–1.40	1.40–1.45

Source: Reprinted with permission from [1].

Chapter 1 | Classification of Coals by Rank

Because of the worldwide occurrence of coal deposits, the numerous varieties of coal that are available, and its many uses, several national coal classification systems have been developed. These systems often are based on characteristics of domestic coals without reference to the coals of other countries. The terms for describing similar or identical coals are not uniform among these various systems.

Efforts in the United States and worldwide have been made to develop systems for classifying coals that are based on characteristic properties determined by laboratory methods. Attempts have also been made to develop an international system for classifying coals to eliminate confusion in international trade and to facilitate the exchange of technical and scientific information related to coal utilization and research. A discussion of the system used for classifying coals in the United States and the international systems of coal classification follows.

In the ASTM International (previously the American Society for Testing and Materials) Standard D388, Classification of Coals by Rank [**2**], coals are classified according to their degree of metamorphism (i.e., progressive alteration) in the natural series from lignite to anthracite. The basis for the classification is according to fixed carbon and calorific values calculated on the mineral-matter-free basis. Higher-rank coals are classified according to fixed carbon on the dry mineral-matter-free basis. Lower-rank coals are classified according to their calorific values on the moist mineral-matter-free basis. The agglomerating character is also used to differentiate certain classes of coals.

To classify a coal according to this system, the calorific value and a proximate analysis (moisture, ash, volatile matter, and fixed carbon by difference) are needed. To calculate these values on the mineral-matter-free basis, the following Parr formulas are used:

$$\text{Dry, Mm-free FC} = 100\,(\text{FC} - 0.15\text{S})/[100 - (\text{M} + 1.08\text{A} + 0.55\text{S})] \quad (1.1)$$

$$\text{Dry, Mm-free VM} = 100 - \text{Dry, Mm-free FC} \quad (1.2)$$

$$\text{Moist, Mm-free Btu} = 100\ (\text{Btu} - 50S)/[100 - (1.08A + 0.55S)] \qquad (1.3)$$

where:

Mm = percentage of mineral matter,
Btu = gross calorific value, in Btu/lb,
FC = percentage of fixed carbon,
VM = percentage of volatile matter,
M = percentage of moisture,
A = percentage of ash, and
S = percentage of sulfur.

The formulas require all of these parameters to be expressed in the correct basis. In Equations 1.1 and 1.3, the quantities are all on the inherent moisture basis. In all equations, fixed carbon (FC) and ash (A) are adjusted to the sulfur trioxide-free basis. The concept of basis will be discussed in later sections. The moist basis pertains to coal containing its natural inherent (or bed) moisture but not including any surface moisture. The sampling procedures used are to be those that are most likely to preserve the inherent moisture.

Coals are classified by rank according to the information given in **Table 1.1.** Coals with fixed carbon values of 69 % or more, as calculated on the dry, mineral-matter-free basis, are classified according to their fixed carbon values. Coals with calorific values less than 14,000 Btu/lb, as calculated on the moist, mineral-matter-free basis, are classified according to their calorific values on a moist, mineral-matter-free basis, provided that their dry, mineral-matter-free (dmmf) fixed carbon is less than 69 %. The agglomerating character is considered for coals with 86 % or more dmmf fixed carbon and for coals with calorific values between 10,500 and 11,500 Btu/lb, as calculated on the moist, mineral-matter-free basis.

Table 1.1 lists the common ranks of coals. Throughout this work, as in the routine reporting of analytical data, the abbreviations for these ranks will be repeatedly used. **Table 1.2** lists the common ranks of coals and the abbreviations used to designate these ranks.

The ASTM system provides for the classification of all ranks of coal whereas the international classification is based on two systems—one for the hard coals and the other for brown coals and lignites. The borderline between the two systems has been set at 10,260 Btu/lb (5700 kcal/kg or 23.860 MJ/kg) calculated on a moist, ash-free basis. Hard coals are those with British thermal unit values above 10,260 Btu/lb [**3**,**4**].

The term "hard coal," as used in the international system, is based on European usage. The Coal Committee of the Economic Commission for Europe (ECE) first recommended the international classification system in 1956 [**4**]. The importance of brown coal as a fuel and as a raw material for chemical purposes led the ECE Coal Committee in 1957 to recommend a classification system for brown coal that was based on (1) total moisture on an ash-free basis and (2) the tar yield on a dry, ash-free

TABLE 1.1 Classification of Coals by Rank[a]

Class/Group	Fixed Carbon Limits (dmmf basis) %		Volatile Matter Limits (dmmf basis) %		Gross Calorific Value Limits (Moist,[b] Mineral-Matter-Free Basis)				Agglomerating Character
					Btu/lb		MJ/kg[c]		
	Equal or Greater Than	Less Than	Greater Than	Equal or Less Than	Equal or Greater Than	Less Than	Equal or Greater Than	Less Than	
Anthracitic:									
Meta-anthracite	98	...	...	2	...	...	...	...	Nonagglomerating
Anthracite	92	98	2	8	...	...	...	...	
Semianthracite[d]	86	92	8	14	...	...	...	...	
Bituminous:									
Low volatile bituminous coal	78	86	14	22	...	...	...	...	Commonly
Medium volatile bituminous coal	69	78	22	31	...	...	...	...	Agglomerating[e]
High volatile *A* bituminous coal	...	69	31	...	14,000[f]	...	32.557	...	
High volatile *B* bituminous coal	...	...	...	...	13,000[f]	14,000	30.232	32.557	
High volatile *C* bituminous coal	...	...	...	...	11,500	13,000	26.743	30.232	
					10,500	11,500	24.418	26.743	Agglomerating
Subbituminous:									
Subbituminous *A* coal	...	...	...	...	10,500	11,500	24.418	26.743	Nonagglomerating
Subbituminous *B* coal	...	...	...	...	9500	10,500	22.09	24.418	
Subbituminous *C* coal	...	...	...	...	8300	9500	19.30	22.09	

TABLE 1.1 Classification of Coals by Rank (*Continued*)

Class/Group	Fixed Carbon Limits (dmmf basis) %		Volatile Matter Limits (dmmf basis) %		Gross Calorific Value Limits (Moist,[b] Mineral-Matter-Free Basis)				Agglomerating Character
					Btu/lb		MJ/kg[c]		
	Equal or Greater Than	Less Than	Greater Than	Equal or Less Than	Equal or Greater Than	Less Than	Equal or Greater Than	Less Than	
Lignitic:									
Lignite *A*	...	...	...	...	6300[g]	8300	14.65	19.30	
Lignite *B*	...	...	...	...	...	6300	...	14.65	

[a] This classification does not apply to certain coals as discussed in Chapter 1.

[b] Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

[c] Megajoules per kilogram. To convert British thermal units per pound to megajoules per kilogram, multiply by 0.0023255.

[d] If agglomerating, classify in low volatile group of the bituminous class.

[e] It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class and that there are notable exceptions in the high volatile *C* bituminous group.

[f] Coals having ≥69 % fixed carbon on the dmmf basis shall be classified according to fixed carbon, regardless of gross calorific value.

[g] Editorially corrected.

Source: Reprinted with permission from Ref. [**2**].

TABLE 1.2 Abbreviations Used for Various Coal Ranks

Common Coal Rank Names	Abbreviation
Anthracite	an
Low volatile bituminous	ivb
Medium volatile bituminous	mvb
High volatile A bituminous	hvAb
High volatile B bituminous	hvBb
High volatile C bituminous	hvCb
Subbituminous A	subA
Subbituminous B	subB
Subbituminous C	subC
Lignite A	ligA
Lignite B	ligB

basis [**5**]. This document was later adopted, with modifications, as the International Organization for Standardization (ISO) Standard 2950, Brown Coals and Lignites—Classification by Types on the Basis of Total Moisture Content and Tar Yield. These two classification systems, which were based on the analytical parameters of moisture, ash, volatile matter, calorific value, caking properties, and tar yield, were used by the international coal community until 1988, when a modified international classification system was adopted by the ECE.

The International Classification of Hard Coals by Type System is based on the dry, ash-free volatile matter; the calorific value expressed on a moist, ash-free basis; and the coking and caking properties. A coal is given a three-figure code number from a combination of these properties. **Table 1.3** lists the classification parameters and the development of numerical symbols to represent the groups and subgroups [**6**].

Coals are first divided into Classes 1–5, which contain coals with volatile matter (dry, ash-free basis) up to 33 %. Coals with volatile matter greater than 33 % are contained in Classes 6–9 and are separated according to their gross calorific value on a moist, ash-free basis. Although the moist calorific value is the primary parameter for Classes 6–9, the volatile matter does continue to increase with the rising class number.

The classes of coal are subdivided into groups according to their coking properties, as reflected in the behavior of the coals when heated rapidly. A broad correlation exists between the crucible swelling number and the Roga index (ISO methods), and either of these may be used to determine the group number of a coal.

Coals classified by class and group are further subdivided into subgroups that are defined by reference to coking properties. The coking properties are determined by either the Gray-King coke-type assay or the Audibert-Arnu dilatometer test (ISO methods). These tests express the behavior of a coal when heated slowly, as in carbonization.

TABLE 1.3 International Classification of Hard Coal by Type

GROUPS (determined by caking properties)			CODE NUMBERS											SUBGROUPS (determined by caking properties)		
	ALTERNATIVE GROUP PARAMETERS														ALTERNATIVE SUBGROUP PARAMETERS	
GROUP NUMBER	FSI (crucible-swelling no.)	Roga Index	The first figure of the code number indicates the class of the coal, determined by VM content up to 33 % VM and by calorific parameter above 33 % VM. The second figure indicates the group of coal, determined by coking properties. The third figure indicates the subgroup, determined by coking properties.											SUB-GROUP NUMBER	Dilatometer	Gray-King
3	>4	>45						435	535	635				5	>140	$>G_8$
							334	434	534	634				4	>50–140	G_5–G_8
							333	433	533	633	733			3	>0–50	G_1–G_4
							332a | 332 B	432	532	632	732	832		2	=<0	E–G
2	21/2–4	>20–45					323	423	523	623	723	823		3	<0–50	G_1–G_4
							322	422	522	622	722	822		2	=<0	E–G
							321	421	521	621	721	821		1	Contraction only	B–D
1	1–2	>5–20				212	312	412	512	612	712	812		2	=<0	E–G
						211	311	411	511	611	711	811		1	Contraction only	B–D
0	0-1/2	0–5		100		200	300	400	500	600	700	800	900	0	Nonsoftening	A
				A	B											
CLASS NUMBER →			0	1		2	3	4	5	6	7	8	9	As an indication, the following classes have an approximate VM content of:		
CLASS PARAMETERS	Volatile matter (dry ash-free) →		0–3	>3–10		>10–14	>14–20	>20–28	>28–33	>33	>33	>33	>33	Class 633–41 % VM		
				>3–6.5	>6.5–10									Class 733–44 %" "		
														Class 835–50 % " "		
														Class 942–50 % " "		
	Calorific parameter[a] →		—	—	—	—	—	—	>13,950	>13,950	>12,960 – 13,950	>10,980 – 12,960	>10,260 – 10,980			

Source: Reprinted with permission from Ref. [**6**].

In the three-figure code number that describes the properties of a coal, the first digit represents the class number, the second is the group number, and the third is the subgroup number. The international classification accommodates a wide range of coals through the use of the nine classes and various groups and subgroups.

Brown coals and lignites have been arbitrarily defined for classification purposes as those coals having a moist, ash-free calorific value less than 10,260 Btu/lb. These are classified by a code number that is a combination of a class number and a group number. The class number represents the total moisture of the coal as mined, and the group number represents the percentage tar yield from the dry, ash-free coal. **Table 1.3** illustrates this classification system for brown coals and lignites [**6**].

Classes are determined by VM content up to 33 % VM and by calorific value above 33 % VM. The calorific value is the gross calorific value on a moist, ash-free basis (30°C, 96 % relative humidity) in Btu/lb. Where the ash content of coal is too high to allow classification according to the present systems, it must be reduced by laboratory float-and-sink methods or any other appropriate means. The specific gravity selected should allow a maximum yield of coal with 5–10 % of ash. Code 332b coal contains 1–20 % VM.

The International Codification System for Medium and High Rank Coals was published in 1988 and defines the two levels of coal as follows [**7**]:

1. Low-rank coals are those with a gross calorific value (moist, ash-free basis) less than 24 MJ/kg and a mean random vitrinite reflectance (R_r) less than 0.6 %.
2. Medium- and high-rank coals are
   - Those coals with a gross calorific value (moist, ash-free basis) equal to, or greater than, 24 MJ/kg, and
   - Those coals with a gross calorific value (moist, ash-free basis) less than 24 MJ/kg, provided that the mean random vitrinite reflectance is equal to, or greater than, 0.6 %.

In the 1988 international classification system, the nine parameters used to specify coals for different purposes are

1. Random reflectance of the vitrinite,
2. Reflectogram of the vitrinite,
3. Maceral composition,
4. Crucible swelling number,
5. Moisture,
6. Volatile matter,
7. Ash,
8. Total sulfur, and
9. Gross calorific value.

These parameters are used to assign a 14-digit number for classification of the coal. In addition, some "supplementary parameters" are presented in an annex of the

document. This classification system is very complex and more complete than the systems previously discussed.

ISO Standard 11760, Classification of Coals, was published in 2005. This classification system divides coals into three primary categories: low rank, medium rank, and high rank. The parameters used to classify the coals into the primary ranks and subcategories are vitrinite reflectance, vitrinite content, moisture, and ash yield [**8**]. One of the reasons stated for developing this standard was to simplify the international classification system.

Chapter 2 | Microcomponents in Coal

Peat, the material from which coal is formed, consists of loosely consolidated layers of various combinations of plant and mineral matter. Peat accumulates in "peat swamps," "bog lands," and "mires." Over millions of years, burial, compression by overlying sediments, and the effects of heat (from proximity to volcanic sources or depth in the earth) cause peat to very gradually change to coal. Coal is an extremely complex and predominantly organic rock. To be classified as coal, the rock must contain less than 50 % ash-forming mineral matter. In the United States, individual coal beds may be as thin as a few inches or as thick as 200 ft, which is very rare. The bed may cover areas as small as a few square yards or as large as several counties [**9**].

From the time the peat is buried, it goes through a series of chemical and physical changes called "coalification," which leads to coals of various ranks. Coalification is a continuous process involving increases in temperature and pressure resulting from burial under different layers of earth. Higher depths of burial and higher temperatures increase the rate of the coalification process through the elimination of moisture and other volatile elements. In effect, "Coalification is a baking process in the earth, under pressure. As it proceeds, coalification produces coals of increasing hardness and calorific value and results in a reduction of tar, oil and gas" [**10**].

Coal is considered to be composed of two principal parts—an organic part, which is inherited from the remains of plant parts, and an inorganic part. The microcomponents and microstructures that make up the organic part are called "macerals," which are considered to be the building blocks of coal in the same way minerals are the building blocks of rocks. There are three principal types of macerals, which are optically discrete particles of organic material in coal.

1. Inertinite is maceral material derived from the partial carbonization of the coal-forming materials by fire or intensive degradation by microorganisms.
2. Vitrinite is derived from woody tissues and is the most abundant maceral in coal.
3. Liptinite is derived from spores, needles and leaf cuticles, plant resins, and similar materials.

Table 2.1 lists some examples of petrographic values for coals of different ranks. The data in **Table 2.2** illustrate the relative amounts of carbon, hydrogen, and oxygen present in the different types of macerals. The amounts of these three elements illustrate the relative reactivity of the various types of macerals. The percentages of volatile matter (which is a measure of the mass loss of the coal when heated to 950°C in an inert atmosphere) that are listed for the macerals are an indication of the relative reactivity of the various types of macerals. These values show that liptinite macerals are much more reactive than inertinite macerals. The aromaticity of the maceral groups is the ratio of the aromatic hydrocarbon character to the aliphatic

TABLE 2.1 Typical Petrographic Values[a] for Coals of Different Ranks

	SubB	hvCb	hvBb	hvAb	Mvb
Inertinite group					
Fusinite	0.6	1.2	1.6	2.0	2.4
Semifusinite	5.8	4.6	5.2	4.0	7.2
Micrinite	0.4	0.2	0.8	6.0	0.0
Macrinite	0.4	0.4	1.0	1.0	0.4
Vitrinite group	84.8	86.2	81.8	75.4	87.0
Liptinite group					
Sporinite	4.0	2.8	2.0	10.2	1.0
Resinite	0.4	0.0	0.0	0.2	0.0
Cutinite	0.6	0.6	0.2	0.4	0.0
Mineral matter	3.0	4.0	7.4	0.8	2.0
Carbon[b]	59.3	78.9	79.0	81.2	90.5

[a]Petrographic values are given on a percent volume, mineral matter-containing basis.

[b]Carbon is given as percent mass fraction on a dry, ash-free basis.

TABLE 2.2 Comparison of Selected Properties of Macerals

Maceral	Elemental Composition[a]			% Volatile[b]	
Group	% C	% H	% O	Matter	Aromaticity[c]
Inertinite	85.7	3.9	8.0	22.9	0.89
Vitrinite	84.1	5.5	8.0	35.2	0.77
Liptinite	83.9	7.0	6.3	66.7	0.62

[a]Elemental composition values are given as percent mass fraction on a dry, ash-free basis.

[b]Reported on a dry basis.

[c]Fraction of all carbons contained in aromatic units, as determined by nuclear magnetic resonance spectroscopy.

Source: Reprinted with permission from [**11**].

hydrocarbon character in the organic materials. The aromaticities of the maceral groups are also indications of their relative reactivities, with macerals having lower aromaticities being more reactive.

If the elemental composition of the organic components in coal is known, then one could conceivably develop an elemental formula for the coal. However, the elemental composition of the different ranks of coals is quite varied. This variation and the variation in reactivity parameters such as volatile matter and aromaticity preclude the proposal of formulas representing all coal, but general formulas or model formulas can be proposed for different ranks of coals. **Table 2.3** lists the elemental analysis data for coal of different ranks. One can use such data, the degree of aromaticity, and other properties of different ranks of coal to propose formulas, such as the frequently referenced bituminous coal model proposed by Wiser shown in **Fig. 2.1** [**12–16**].

The ranks of coal listed in **Table 2.3** from anthracite (an) to lignite (LigA) represent the most common coals found in the United States. The data in the table illustrate the rank dependency of the elements listed. Carbon, oxygen, and to some degree, hydrogen, are rank-dependent elements.

The highest rank coals have the highest carbon contents and lowest oxygen contents. The mid-rank coals, such as high volatile B bituminous (hvBb) and high

FIG. 2.1 Wiser model for the bituminous coal matrix.

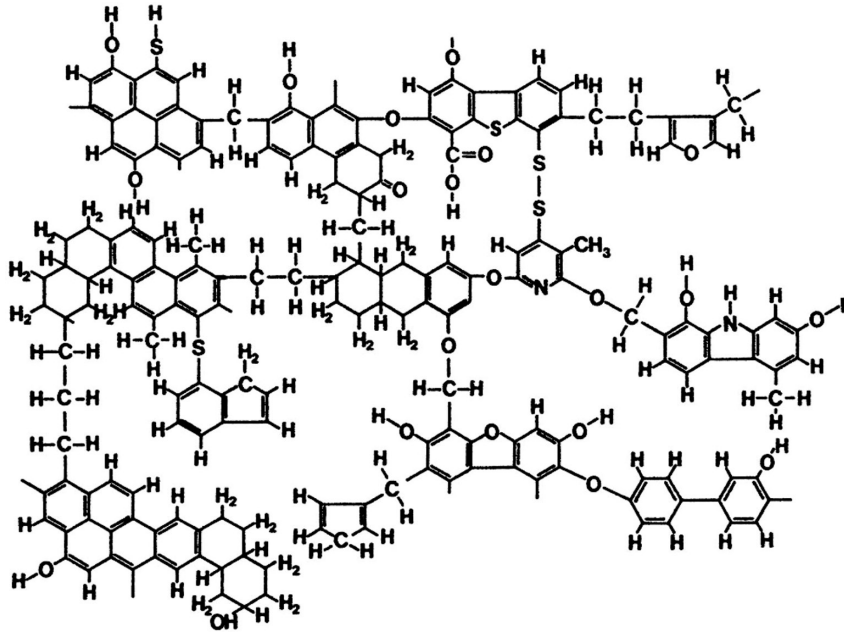


TABLE 2.3 Examples of Elemental Composition of Some Coals of Different Ranks

Coal Rank	% C	% H	% N	% S	% O
an	94.68	2.61	1.24	0.83	0.64
mvb	88.33	5.25	1.63	1.29	3.50
hvAb	83.67	5.46	2.17	1.11	7.58
hvBb	81.70	5.67	1.79	1.37	9.06
hvCb	79.80	5.83	1.67	3.56	9.14
subA	77.33	5.38	1.18	1.22	14.87
subB	74.15	5.34	0.96	0.63	18.93
subC	72.22	5.19	1.03	0.40	21.15
ligA	67.48	4.71	1.26	0.40	26.14

Note: All values are given as percent mass fraction on a dry, ash-free basis.

volatile C bituminous (hvCb), have the highest hydrogen contents, with decreases in hydrogen values as rank increases, and decreases, from these two ranks. Nitrogen, sulfur, and almost all other elements found in coal are not rank dependent.

The inorganic components found in coal are essentially the same types of material that are found in the soils around the coal-bearing seams. These inorganic materials are referred to as coal mineral matter and ash-forming materials and cannot be separated intact from the coal during commercial cleaning operations. However, in efforts to separate very small portions of mineral matter for characterization, geochemists have used low-temperature (oxygen plasma) ashing to burn away the carbon material, leaving most of the mineral matter intact. A discussion of this work is given in Section 8.7. When the coal is combusted or is pyrolyzed as in the formation of coke, the mineral matter is converted to other forms in the residues. **Table 2.4** lists the minerals commonly found in coal.

The principal use for coal is for combustion, primarily for the production of steam to drive steam turbines in electric power-generating facilities. Thus, the term "steam coal" is generally used to describe coal with 2 in. by 0 size consist that is transported all over the world for use in power plants. Some parameters used to describe the quality of coal for commercial transactions are listed in **Table 2.5**, along with examples of the values of these parameters for coals of different ranks. The principal property of coal that establishes its value is its British thermal unit (specific energy) content. Parameters such as moisture and ash detract from the quality of coal because they add weight to the coal, absorb some of the heat produced during combustion, and present disposal problems. Sulfur and ash can also contribute to emissions. Volatile matter is used to estimate the burning rate of coals. Moisture, fixed carbon, volatile matter, and heating value (Btu/lb) are rank dependent, as can be seen from the values listed in **Table 2.5** for the various ranks of coals.

TABLE 2.4 Common Coal Minerals

Major Elements		
Silicates	Kaolinite	$Al_2Si_2O_5(OH)_4$
	Illite	a
	Mixed layer	b
	Chlorite	$(MgFeAl)_6(SiAl)_4O_{10}(OH)_8$
	Quartz	SiO_2
Minor elements		
Carbonates	Calcite	$CaCO_3$
	Dolomite	$CaMg(CO_3)_2$
	Ankerite	$Ca(FeMg)CO_3$
	Siderite	$FeCO_3$
Disulfides	Pyrite	FeS_2 (cubic)
	Marcasite	FeS_2 (orthorhombic)
Sulfates	Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$
	Szmolnokite	$FeSO_4 \cdot H_2O$
	Gypsum	$CaSO_4 \cdot 2H_2O$
	Bassanite	$CaSO_4 \cdot \frac{1}{2}H_2O$
	Anhydrite	$CaSO_4$
	Jarosite	$KFe_3(SO_4)_2(OH)_6$
Feldspars	Plagioclase	$(NaCa)Al(AlSi)Si_2O_8$
	Orthoclase	$KAlSi_3O_8$
Sulfides	Sphalerite	ZnS
	Galena	PbS
	Pyrrhotite	FeS
Trace elements		
Trace minerals		

[a]Illite has a composition similar to muscovite—$KAl_2(Si_3Al)O_{10}(OH)_2$—except for less K^+ and more SiO_2 and H_2O.

[b]Mixed layered clays are usually randomly interstratified mixtures of illitic lattices with montmorillonitic or chloritic lattices or both.

Source: Reprinted with permission from [**17**].

TABLE 2.5 Analytical Parameters Used to Assess the Quality of Coal

Rank	As-Received Moisture (%)	ADL (%)	As-Determined Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)	Btu/lb	Sulfur (%)
an	3.97	0.44	3.55	6.20	82.21	11.59	13 374	0.74
mvb	4.88	3.43	1.50	24.89	68.85	9.26	14 166	1.17
hvAb	4.23	2.15	2.13	33.03	56.94	10.02	13 445	1.00
hvBb	10.02	1.38	8.76	34.25	57.63	8.12	13 428	1.26
hvCb	15.16	3.31	12.26	37.96	55.20	6.84	13 619	1.08
subA	20.96	3.97	17.69	38.42	49.97	11.61	11 896	1.08
subB	27.04	11.20	17.84	44.87	47.39	7.74	11 919	0.58
subC	30.94	14.90	18.85	43.08	50.70	6.21	12 046	0.37
ligA	34.69	19.45	18.92	39.07	45.36	15.57	10 107	0.34

Note: The values given are examples of coals of various ranks. Values for all parameters, except ADL and moisture, are given on a dry basis. ADL, air-dry loss.

Chapter 3 | Sampling and Sample Preparation

Preliminary to any laboratory testing of coal, it is imperative that a representative sample be obtained; otherwise, the most carefully conducted analysis is meaningless. Reliable sampling of a complex mixture such as coal is difficult, and handling and preparation of the sample for analysis presents further problems. Variations in coal handling facilities make it practically impossible to publish a set of rules that would apply to every sampling situation. The proper collection of the sample involves an understanding and consideration of the minimum number and weight of increments, the particle size distribution of the coal, the physical character and variability of the constituents of coal, and the desired precision.

Guidelines for the collection of gross samples of coal are given in ASTM Standard Practice for Collection of a Gross Sample of Coal (**D2234/D2234M**) and in ASTM Standard Practice for Mechanical Sampling of Coal (**D7430**). The newer standard ASTM **D7430** is a combination of several previous sampling standards. Another ASTM Standard Practice for collecting gross samples is Manual Sampling of Stationary Coal from Railroad Cars, Barges, Trucks, or Stockpiles (**D6883**). ASTM **D6609** is a guide for part-stream sampling of coal. Also found in Volume 05.06 of the *Annual Book of ASTM Standards* is a standard practice for the collection and preparation of coke samples (**D346**).

Some specific terms used in coal and coke sampling are "gross sample," "lot," "representative sample," "laboratory sample," and "analysis sample." A gross sample is defined as a sample representing a quantity, or lot, of coal and is composed of several increments on which neither reduction nor division has been performed. A lot is a discrete quantity of coal for which the overall quality to a particular precision needs to be determined. For quantities of coal up to approximately 1000 Mg (1000 tons), it is recommended that one gross sample represent the lot. The number of increments to be taken for the gross sample depends on the type of coal being sampled as shown in **Table 3.1**. The size of each increment depends on the top size of the coal being sampled.

TABLE 3.1 Number and Mass of Increments for General-Purpose Sampling Procedure

Top size	16 mm [5/8 in.]	50 mm [2 in.]	150 mm[a] [6 in.]
MECHANICALLY CLEANED COAL			
Minimum number of increments	15	15	15
Minimum mass of increments, kg [lb]	1 [**2**]	3 [**6**]	7 [**15**]
RAW UNCLEANED COAL			
Minimum number of increments	35	35	35
Minimum mass of increments, kg [lb]	1 [**2**]	3 [**6**]	7 [**15**]

[a]For coals above 150 mm [6 in.] top size, the sampling procedure should be mutually agreed upon in advance by all parties concerned.

Source: Reprinted with permission from [**2**].

For quantities of coal over 1000 Mg [1000 tons], the following alternatives are offered.

- Take one gross sample for the lot and analyze it to represent the quality of the lot. Collect the number of increments, *N*, calculated using the formula

$$N = K\sqrt{\frac{L}{1000}} \tag{3.1}$$

where:

L = number of Mg [tons], and
K = 14.3 [**15**] for mechanically cleaned coal or 33.3 [**35**] for raw coal.

- A second alternative is to divide the lot into sublots and take a separate gross sample from each sublot. Equation 3.1 is used to determine the minimum number of increments in each sublot with *L* being the sublot quantity. Weight average the analyses of the sublot samples to represent the quality of the original lot.

The ASTM general purpose sampling procedures are designed to give a precision such that if gross samples are taken repeatedly from a lot or consignment and one ash determination is made on the analysis sample from each gross sample, 95 of 100 of the determinations of the dry ash results will fall within ± 10% of the average of all dry ash determinations. When other precision limits are required or when other constituents are used to specify precision, some special-purpose sampling procedure is used. These specifications can be found in ASTM **D7430**.

3.1 Preparation of a Sample for Analysis

Once a gross sample has been taken, it is reduced in particle size and quantity to yield a laboratory sample. The particle size distribution, or nominal top size, of the laboratory sample depends on its intended use in the laboratory and the nature of the tests to be run. The minimum allowable weight of the sample at any stage of reduction depends

TABLE 3.2 Preparation of a Laboratory Sample

Crush to Pass at Least 95	Divide to a Minimum Mass or, g	
% through Sieve	Group A	Group B
No. 4 (4.75 mm)	2000	4000
No. 8 (2.36 mm)	500	1000
No. 20 (850 μm)	250	500
No. 60 (250 μm) (100% through)	50	50

Source: Reprinted with permission from [**2**].

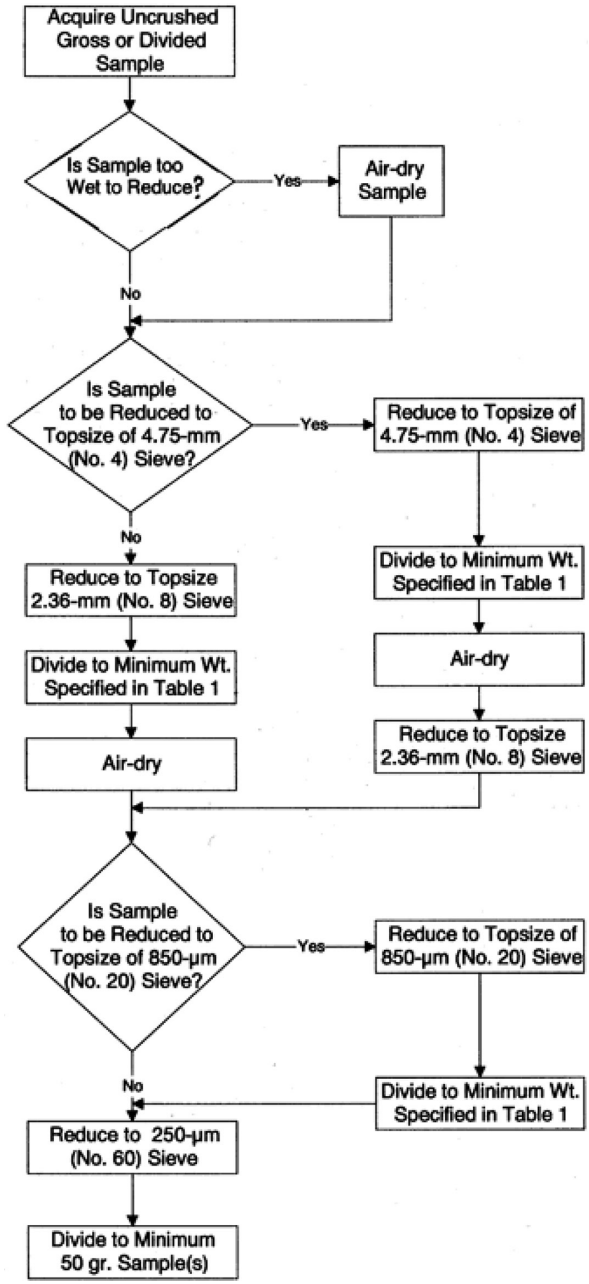
on the size consist, the variability of the constituents sought, and the degree of precision desired. Recommended minimum weights for Group A coals (which have been cleaned in all sizes) and Group B coals (all others, including unknown coals) are listed in **Table 3.2**.

The subsample is reduced through a USA Standard #60 (250-μm) sieve and then divided to not less than 50 g, which is called the *analysis sample* and is required for most ASTM laboratory tests. ASTM **D2013/D2013M** presents standard procedures for preparing coal samples for analysis. The steps followed in preparing an analysis sample from a gross sample are given in **Fig. 3.1**.

Many problems, such as the loss or gain of moisture, improper mixing of constituents, improper crushing and grinding, contamination of the sample by equipment, and oxidation of coal, may arise during the sampling and sample preparation processes. To minimize the moisture problem, all standard methods include, when necessary, an air-drying stage in the preparation of the analysis sample so that subsequent handling and analysis will be made on a relatively stable laboratory sample with reference to gain or loss of moisture from or to the laboratory atmosphere. In collecting, handling, reducing, and dividing the gross sample, all operations should be done rapidly and in as few steps as possible to minimize moisture loss or gain.

The distribution of mineral matter in coal presents problems for the crushing, grinding, and uniform mixing at each step of the sampling procedure. The various densities of the materials found in coal can easily cause their segregation, especially if there is a wide range of particle sizes. Crushing or grinding coal, or both, from a large particle to a very small particle in one operation tends to produce a wide range of particle sizes and a high concentration of very fine particles. The crushing, grinding, and pulverizing should involve a reasonable number of steps, considering the starting particle size and nature of the coal. At the same time, it should be kept in mind that too many handling steps will increase the exposure of the coal to air and increase the chance of moisture changes and oxidation. Some models of coal sampling and preparation equipment give a wider range of particle sizes than others because of the

FIG. 3.1 Sample preparation flowchart.



Source: Reprinted with permission from [**2**].

manner in which they crush and grind the coal. This should also be taken into consideration when planning routines for sample preparation. In addition to the problems already mentioned that may arise from the crushing and grinding operations, there is the chance that the equipment used may introduce some materials that will contaminate the coal sample.

Coal is susceptible to oxidation at room temperature. Similar to moisture changes, such oxidation has to be considered in sampling, preparing, and storing samples. Comparison of moisture, ash-free (MAF) Btu values is often useful for evaluating suspected oxidation problems. (MAF is the same as DAF, or dry, ash-free). All of these operations should be done rapidly and in as few steps as possible to minimize the oxidation of the coal. The sample containers used should have airtight lids to minimize moisture loss and exposure of the coal to air. Containers should be selected that will hold only the required amount of sample and leave a minimum of air space. Even when such precautions are taken, the samples change very quickly; therefore, the analysis of a sample should be performed as soon as possible after it is received.

Chapter 4 | Coal and Coke Testing

Coal and coke testing may be divided into three categories: proximate analysis, ultimate analysis, and miscellaneous analysis. In the case of coal and coke, proximate analysis is the determination, by prescribed methods, of the contents of moisture, volatile matter, and ash, and the calculation of fixed carbon by difference. ASTM **D3172**—Practice for Proximate Analysis of Coal and Coke, lists the standard test methods and practices used to collect proximate analysis data. As defined in ASTM **D3176**—Practice for Ultimate Analysis of Coal and Coke, ultimate analysis of coal and coke is the determination of carbon, hydrogen, nitrogen, and sulfur in the gaseous products of the complete combustion of the material, the determination of ash content in the material as a whole, and the estimation of oxygen content by difference.

Miscellaneous analysis is a collective category for various types of physical and chemical tests for coal that are commonly requested by coal producers and buyers. Some chemical analyses included in this category are the determination of calorific value, analysis of the forms of sulfur, analysis of the forms of carbon, chlorine analysis, major and minor elements in ash analysis, and trace element analysis. Some other tests included in this category are the determinations of free-swelling index (FSI), grindability, plastic properties of coal, and ash fusibility.

Some of the methods of coal analysis are empirical and require strict adherence to specified conditions, such as particle size, temperature, time and rate of heating, and so on. The establishment of uniform specifications that are recognized as standards and supported by authoritative organizations is essential. The American National Standards Institute (ANSI) represents the United States at the international standards level and is similar to the British Standards Institute (BSI) in the United Kingdom, the Deutsches Institut für Normung (DIN) in Germany, and Australian Standards (SA). However, unlike BSI, DIN and SA, ANSI does not develop standards for coal and coke, but looks to other organizations for such work. Committee D05 on Coal and Coke of ASTM International (formerly the American Society for Testing and Materials) has the responsibility, as granted by ANSI, of developing standard procedures for coal and coke sampling and analysis. This committee consists of approximately 350 members divided among producers, consumers, and those who have a general interest in coal.

4.1 ASTM International Standard Methods

Committee D05 on Coal and Coke is one of 138 technical standards writing committees in ASTM International. Established in 1898, ASTM International is one of the largest standards development and delivery systems in the world. ASTM standards are accepted and used in research and development, product testing, quality systems, and commercial transactions around the globe. ASTM International Committee D05 on Coal and Coke was established in 1904.

Many of the sampling and testing procedures developed by ASTM Committee D05 that are relevant to international trade are also approved by ANSI. The use of ASTM procedures by coal-testing laboratories is optional. However, these standards can have a certain degree of legal status and are used when coal is purchased according to a specification and penalty basis. Also, important criteria that one may use in judging the quality of an individual laboratory is the degree to which the laboratory is able to produce results that agree favorably with the precision limits of ASTM Standard Methods. The discussion of the analysis of coal and coke in this work pertains primarily to the ASTM Standard Methods [**2**].

4.1.1 Standards Development

ASTM standards, whether they are a test method, a practice, or a guide, are consensus standards. This means the ASTM standards development process gives all interested parties an opportunity to provide input and to vote for, or against, a proposed standard method or its revision.

The development of an ASTM Standard Test Method follows a regular sequence of steps. First, a proposal to study a particular problem or evaluate a procedure is made to the membership of an ASTM Subcommittee and Main Committee (i.e., Subcommittee D05.21 on Methods of Analysis and Main Committee D05 on Coal and Coke). If the consensus of the membership is to proceed, a Task Group is formed to conduct the study. The Task Group Chair files a Work Item Request with ASTM, which includes the scope of the project and anticipated completion date. The chair then proceeds to form a Task Group of participants willing to work on the project to develop a standard. ASTM encourages and promotes participation in Task Group studies from all parties, including those that are not ASTM members. In consultation with experts within Committee D05, as well as ASTM, who can provide support services, a work plan is established and ruggedness testing is conducted. These activities are followed by a comprehensive Interlaboratory Study (ILS) to focus on the development of a workable and usable standard. The ILS is organized and conducted according to principles described in ASTM Standard **E691**, "Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method" [**18**]. For coal and coke standards development, an ILS must have at least six participating laboratories and use at least six samples. Normally, D05 ILSs include approximately seven laboratories and use approximately seven samples for each anticipated precision and bias statement.

Data from the ILSs are used to develop suitable precision and bias statements for the proposed standard.

The proposed standard is then written by the Task Group Chair and its members, according to the guidelines in *Form and Style for ASTM Standards* (The "Blue Book") [19]. All proposed standards must contain the sections and elements required by this publication.

The proposed standard method is then subjected to the ASTM balloting process. Balloting begins at the subcommittee level, in which the subcommittee voting members review the standard and submit their vote. Sixty percent of the ballots must be returned and at least two-thirds of the combined affirmative and negative votes cast by voting members must approve. All negative votes must be resolved, either through withdrawal, or by being voted "not persuasive" or "not related" by subcommittee voters at a meeting. With all negative votes resolved, the proposed standard then proceeds to the Main Committee for ballot.

The Main Committee voting members review the proposed standard and submit their votes. Ninety percent of the combined affirmative and negative votes cast by voting members is required, with not less than 60% of the voting members returning ballots. Again, all negative votes must be resolved, either through withdrawal, or by being voted "not persuasive" or "not related" by Main Committee voters at a meeting. Once the balloted document has been approved by the Main Committee D05, it is submitted to the ASTM International Committee on Standards.

All standards processed through ASTM Committee D05 also appear on the ASTM website for society review. All society members have an opportunity to comment on the ballot items.

The Committee on Standards determines whether Committee D05 has exercised due diligence in exercising the procedural requirements of the society. If this committee takes favorable action upon the recommendations from the ASTM Main Committee, then the proposed standard is approved for publication.

4.1.2 Periodic Review of ASTM Standards

All ASTM International standards should be reviewed in their entirety by the responsible subcommittee and balloted for reapproval, revision, or withdrawal within 5 years of their last approval date. The review process serves to keep the standards current. If a standard has not received a new approval date by December 31st of the eighth year since the last approval date, the standard will be withdrawn. The Main Committee chairman and the appropriate subcommittee chairman are notified by ASTM Headquarters in advance of this pending action. If a standard is withdrawn, then it will no longer be published in the *Annual Book of ASTM Standards.* Withdrawn standards are archived by ASTM International and not readily available. The common reason a standard is withdrawn is that its procedures or instrumentation or both become outdated and seldom used. A withdrawn standard is still a viable ASTM International standard.

4.1.3 Precision and Bias Statements

The "heart" of an ASTM International Standard Test Method is the precision and bias statement. This statement serves as a measure of whether a laboratory or instrument is performing as expected. ASTM International Standard Test Methods are developed for use with a 95 % confidence level. Some elements of precision and bias statements are as follows.

- *Repeatability limit* (*r*): The value below which the absolute difference between two results of separate and consecutive test determinations, performed on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogeneous 250 μm (No. 60 USA Standard sieve) material, may be expected to occur with a probability of approximately 95 %.
- *Reproducibility limit* (*R*): The value below which the absolute difference between two test results, performed in different laboratories using samples taken at random from a single quantity of 250 μm (No. 60 USA Standard sieve) material that is as homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

Table 4.1 lists the repeatability and reproducibility limits for some of the more commonly used ASTM International Standard Test Methods. In comparing the results

TABLE 4.1 Repeatability and Reproducibility Intervals for Selected ASTM Standard Test Methods for Coal

	Repeatability Limits	Reproducibility Limits
Moisture (**D3173**)	$I(r) = 0.09 + 0.01\bar{X}$	$I(R) = 0.23 + 0.02\bar{X}$
Ash (**D3174**)	0.22	0.32
ASTM (**D7582**)		
Moisture (drying gas—nitrogen)	0.21	0.69
Moisture (drying gas—air)	0.25	0.79
Ash (dry basis)	0.19	0.31
Volatile matter (dry basis) bituminous	0.36	1.32
Volatile matter (dry basis) subbituminous/lignite	0.84	1.83
Sulfur (**D4239**)—Method A (dry basis)		
Calibrate with coal CRMs	$I(r) = 0.02 + 0.03\bar{X}$	$I(R) = 0.02 + 0.09\bar{X}$
Calibrate with pure substance, BBOT	$I(r) = 0.053 + 0.019\bar{X}$	$I(R) = 0.125 + 0.053\bar{X}$
Carbon (**D5373**)		
Method A (dry basis)	0.45	1.00
Method B (dry basis)	0.55	2.31
Hydrogen (**D5373**)	0.10	0.25
Nitrogen (**D5373**)	0.05	0.15
	(where $\bar{X}$ = average of two replicates)	

Note: All values, except moisture, are compared on a dry basis. CRM, certified reference material; BBOT, 2, 5-di(5-tert-butylbenzoxazol-2-yl)thiophene.

from two consecutive test runs, the analyst has no reason to question the results (at the 95 % confidence level) unless the difference between the results exceeds the repeatability limit. When such a difference is found, there is reason to question both of the test results. Likewise, the reproducibility limit is used for comparing results from different laboratories.

ASTM Committee D05 on Coal and Coke has jurisdiction over approximately 75 standards, all published in the *Annual Book of ASTM Standards*, Volume 05.06. These standards have played, and continue to play, a preeminent role in all aspects important to the effective industrial use of coal, including classification, sampling, preparation, petrography, rheology, analysis, and quality assurance.

Only an outline and a general discussion of each of the ASTM standard methods of coal analysis are given in this work. For precise details of the methods, it is necessary to refer to the latest edition of the *Annual Book of ASTM Standards*, Volume 05.06 [**2**]. In the following chapters, the discussion of each method includes such topics as the nature of the constituents of the coal being analyzed; the chemical reactions that may take place during analysis; and some of the difficulties encountered in the tests and interpretation, uses, and limitations of the data obtained.

Chapter 5 | Proximate Analysis

The proximate analysis of coal was developed as a simple means of determining the distribution of products obtained when the coal sample is heated under specified conditions. As defined by ASTM **D121** [**2**], proximate analysis separates the products into four groups: (1) moisture; (2) volatile matter, consisting of gases and vapors driven off during pyrolysis; (3) fixed carbon, the nonvolatile fraction of coal; and (4) ash, the inorganic residue remaining after combustion. Proximate analysis is the most often used analysis for characterizing coals in connection with their utilization. Differences in the type of information required by coal producers and consumers have led to variations in the kind and number of tests included under the rubric *proximate analysis*. Other terms used in the coal industry are *short prox* and *prox*. Common usage in the field tends to favor short prox, which is the determination of moisture, ash, Btu, and sulfur, whereas prox means the determination of moisture, ash, volatile matter, fixed carbon, Btu, and sulfur. Proximate analysis as defined by ASTM International is the topic of this section.

5.1 Moisture

The most elusive constituent of coal to be measured in the laboratory is moisture. The moisture in coal ranges from 2 to 15 % in bituminous coal up to 50 % in lignite. There are several sources for the water that is found in coal. The vegetation from which coal was formed had a high percentage of water that was physically and chemically bound. Varying amounts of water were still present at different stages of the coalification process. The overall result of coalification was to eliminate much of the water, particularly in the later stages, as is evident from a comparison of the moisture contents of different ranks of coal from lignite to anthracite (see table in the Introduction to this book as well as **Table 2.5**). Water is present in most mines and circulates through most coal seams. After mining, many coals are washed with water during preparation for market and are then subject to rain and snow during transportation and storage. All of these sources contribute to the moisture in coal.

The moisture in coal may be divided into four categories: inherent moisture, surface moisture, decomposition moisture, and water of hydration of mineral matter.

Inherent moisture is also referred to as *bed moisture* or *equilibrium moisture* and is believed to be the water held in the capillaries of varying radii that are found in coal. The vapor pressure of this water is somewhat less than that of the moisture found on the surfaces of coal, which is appropriately called *surface moisture* or *free moisture*. Surface moisture has a vapor pressure equal to that of free water at the same temperature. Decomposition moisture is produced from the thermal decomposition of organic constituents of coal. The water of hydration of mineral matter is incorporated into the crystal lattices of the inorganic and claylike materials found in coal. Air-drying removes the surface moisture and some of the inherent moisture in coal, whereas a temperature of approximately 107 °C is needed to remove the remaining inherent moisture. At temperatures of approximately 200–225°C, moisture from the decomposition of organic materials is driven off, but water of hydration requires a considerable amount of energy for expulsion. For example, the water of hydration in kaolinite is not released until a temperature of approximately 500 °C is reached [**20**]. Decomposition moisture and water of hydration of mineral matter are not commonly dealt with in ordinary coal analysis because the temperatures used for routine moisture testing are well below those needed to remove these two kinds of moisture.

In practice, the various forms of moisture in coal are described according to the manner in which they are measured by some prescribed standard test method. These standard methods will be discussed in the following sections. As described in ASTM **D121**, the moisture forms routinely determined for coals are inherent moisture, total moisture, air-dry loss moisture, residual or air-dried moisture, and as-received moisture [**2**]. Total moisture is defined in ASTM **D121** as "all of the moisture in and on a consignment or sample of coal." Total moisture is determined in ASTM Test Method for Total Moisture in Coal (**D3302**) and ASTM Test Method for Single-Stage Total Moisture Less than 15 % in Coal Reduced to 2.36 mm (No. 8 Sieve) Topsize (**D2961**). Air-dry loss moisture is the loss in mass resulting from the partial drying of coal, and residual moisture is that remaining in the sample after air-drying. Total moisture is the sum of the inherent and free, or surface, moisture in coal and is the sum of the air-dry loss and residual moisture. However, inherent moisture is not the same as residual moisture, nor is free moisture equivalent to air-dry loss moisture. Some relationships may be established between the quantities of inherent moisture and surface moisture because they are determined by standard methods and the presence of these forms of water in coal. However, air-dry loss and residual moisture are determined as steps in an analytical procedure and should not be used as significant values for interpretation. It would simply be a coincidence if inherent moisture had the same value as residual moisture or if free moisture had the same value as air-dry loss moisture for a given coal sample. As-received moisture also is equal to the total moisture.

5.1.1 Determination of Moisture

Many methods have been developed for determining the moisture content of coal. Most of these methods can be included in the following categories: (1) thermal drying

methods, (2) desiccator methods, (3) distillation methods, (4) extraction and solution methods, (5) chemical methods, and (6) electrical methods [**21**]. The most common tests for moisture involve a thermal drying procedure, usually at a temperature a few degrees above the boiling point of water; the moisture released upon heating is measured either directly or indirectly. Thermal drying includes drying in conventional ovens and microwave ovens, where the moisture is lost through vaporization after heating. The direct method involves the gain in weight of a weighing tube packed with desiccant through which the gases evolved from heating a coal sample are passed. This is probably the more accurate method because only water is absorbed by the tube whereas other evolved gases, such as methane, are not. The indirect method is more often used primarily because it is easier to do. The moisture is taken as the mass loss of a coal sample upon heating in various atmospheres. If the coal is susceptible to oxidation, as are some low-rank coals with high moisture contents, then the heating can be done in an inert atmosphere. The drying of most high-rank coals in air is an accepted practice.

Desiccator methods for determining moisture involve the determination of the loss in weight of a coal sample in the presence of a desiccant. Either a normal or reduced pressure (vacuum desiccator) may be used, but the drying is performed at room temperature.

After thermal drying methods, distillation methods are the next most commonly used. In these procedures, coal is heated in a liquid that has a boiling point higher than that of water and is immiscible with it. Xylene, toluene, or a petroleum fraction of a selected boiling range are the liquids normally used. The distilled vapors are condensed in a graduated tube, and the volume of water is measured after the two liquids separate. Distillation methods are considered particularly advantageous for low-rank coals because air is excluded from the coal, which minimizes the error due to oxidation. This is also a direct method of measuring moisture, and consequently there is no error due to the loss of other gases.

A nonthermal method of determining moisture involves the use of an extraction procedure in which the coal is shaken with a solvent that extracts the water from the coal. The degree of change in some physical property of the solvent, such as density, is then used as a measure of the water extracted.

A chemical method used for determining moisture includes the application of the Karl Fischer titration method of determining water content. A second chemical method is the reaction of quicklime with water in coal and the subsequent measurement of the heat generated by the reaction.

Electrical methods of measuring coal moisture involve the determination of the capacitances or the resistances of quantities of coal. Electrical methods have been used by industry, particularly for moving streams of coal.

Magnetic resonance measurements of moisture in coal have been performed over a period of 3 decades. Studies have shown that the total moisture and total hydrogen in −60 mesh (250-μm), −8 mesh (2.36-mm), and −4 mesh (4.75-mm) coal can be

measured in approximately 2 min [22,23]. The method has also been incorporated into an on-line analyzer system [24].

5.1.2 ASTM International Standard Methods of Analysis of Total and Residual Moisture

The ASTM International standard methods of determining the amounts of total and residual moisture in coal are the following:

- *Test Method **D2961**:* Single-Stage Total Moisture Less than 15 % in Coal Reduced to 2.36 mm (No. 8 Sieve) Topsize
- *Test Method **D3173**:* Moisture in the Analysis Sample of Coal and Coke
- *Test Method **D3302**:* Total Moisture in Coal
- *Test Method **D7582**:* Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis

In addition to these, ASTM **D3302** gives directions for air-drying samples. Routine moisture determinations are performed according to specifications in methods **D3173**, **D3302**, **D7582**, and **D2961** depending on the state of preparation or condition of the coal sample or both. The entire procedure for determining the total moisture in coal, after collecting the gross sample, begins with preparing the sample for analysis, as outlined in ASTM **D2013/D2013M**. (see **Fig. 3.1**). In routine work, if the gross sample is dry enough, it is reduced to No. 4, or No. 8, topsize. No. 4 topsize means more than 95 % of the sample passes through a No. 4 sieve. If the sample is too wet to reduce in size, then it is weighed before reduction. Air-drying is performed on a drying floor or in a special drying oven operated at 10–15°C above room temperature. The purpose of air-drying is to reduce the moisture in the sample to approximate equilibrium with the air in the laboratory. This minimizes changes in moisture content when the sample is handled during the crushing and grinding operations or during an analysis. After reduction of the gross sample to No. 4 or No. 8 topsize, it is divided and a laboratory sample is taken. The laboratory sample is then air-dried and reduced to No. 8 topsize, if necessary. If the total moisture is to be determined as in ASTM **D3302**, then No. 8 topsize coal is used, and residual moisture is determined by heating at 104–110°C for 1.5 h. If a full analysis of the coal (proximate or ultimate analysis) is desired, then the laboratory sample must be reduced to No. 60 (250 μm) size and divided and an analysis sample must be taken. Using the analysis sample, residual moisture is determined according to ASTM **D3173** or **D7582** by heating for 1 h (**D3173** and **D7582**), or to a constant weight (**D7582**), at 104–110°C.

The drying gas for determining residual moisture in ASTM **D3173** is dry air, whereas ASTM **D7582** normally uses dry nitrogen, an inert atmosphere, which reduces the chance for oxidation of the sample. Using a macro-thermogravimetric analysis (TGA) system (to be discussed later in Section 5.2) that complies with ASTM **D7582** also allows for drying the sample to a constant mass, which can reduce the drying time.

The moisture values obtained from the various drying procedures are expressed as percentage mass fraction of the sample used in the particular test. Consequently, a correction factor must be used to make the various moisture values additive so that total moisture values can be obtained. The air-dry loss moisture and total moisture values can be calculated using the following formulas (with all values expressed as percentage mass fraction):

$$ADL = A' \times (100 - A)/100 + A \tag{5.1}$$

$$M = R \times (100 - ADL)/100 + ADL \tag{5.2}$$

where:

M = total moisture,
ADL = complete air-dry loss moisture,
A' = air-dry loss of laboratory sample,
A = air-dry loss of gross sample, and
R = residual moisture.

ASTM **D2961** is a single-stage procedure for determining total moisture less than 15 % in coal reduced to 2.36 mm (No. 8 USA Standard sieve) topsize. Moisture in the 2.36-mm topsize sample is determined by heating the test portion (minimum of 125 g) evenly dispersed (1 in. maximum depth) in a shallow pan at 104–110°C for 1.5 h. After weighing, the sample is reheated and reweighed at half-hour intervals until the mass loss is less than 0.05 % of the original sample mass per half-hour period. This method was formally referred to as a *limited purpose* method or an *industrial* method. Use of the method requires prior agreement of all of the parties involved. The materials subjected to the test shall not be used in the determination of other test parameters because the conditions for the test can increase the potential for significant oxidation effects on some coals. This test method is not to be construed as a substitute for the referee standard test method for total moisture, which is ASTM **D3302**.

In routine moisture determinations, sample handling should be kept at a minimum because loss or gain of moisture may occur during prolonged handling. If too long of a period is used in completing the analysis of a coal sample, moisture may evaporate from the coal in a container and condense on container surfaces. It is almost impossible to uniformly redistribute this moisture once this has occurred. Changes in the moisture content may also occur during reduction of the gross sample. Heat generated by the crushing and grinding operations may be sufficient to cause moisture loss. The relative humidity of the sample preparation and laboratory rooms is likely to be different from the atmosphere where the gross sampling was done. The relative humidity in the laboratory rooms also may change while a complete analysis is being performed. Air-drying steps in the analysis and efficient sample handling help minimize the effects of relative humidity changes.

Exposure of the coal sample to the atmosphere for extended periods of time increases the opportunity for oxidation, which would result in a mass change of the coal sample that would give moisture results that are misleading. In the determination of moisture by a mass loss method, it is necessary to attain a constant mass, which requires alternating heating and cooling of samples. Prolonged heating or an excessive number of alternating heating and cooling steps should be avoided to minimize the chances of oxidation.

5.1.3 Equilibrium Moisture

The ASTM standard method of determining the equilibrium moisture in coal is ASTM **D1412**—Equilibrium Moisture of Coal at 96 to 97 Percent Relative Humidity and 30°C. Equilibrium moisture is the best estimate of the inherent moisture. In this method, a sample is brought into equilibrium in a partially evacuated desiccator with an atmosphere of 96–97 % relative humidity at 30°C. The amount of moisture in the coal under these conditions is determined by mass loss upon heating. As in all methods of determining moisture, there are problems associated with this equilibrium moisture method, and precautions must be taken to obtain reliable results. Overdried or oxidized coals, or both, result in low moisture values. To prevent overdrying, the sample should be kept wet before this test is run. Nothing can be done for samples that are oxidized before testing. During the test itself, it is important to observe the specified temperature and time limits for equilibration and restoring the pressure in the desiccator to atmospheric conditions. A sudden lowering of the temperature or a sudden surge of air into the desiccator after equilibration can cause condensation of moisture on the coal. Mechanical losses of the coal sample caused by sudden surges of air into the evacuated desiccator when atmospheric pressure is restored will void the results of the test.

The primary reason for using a high relative humidity in the determination of equilibrium moisture is to approximate 100 % relative humidity. However, because of physical limitations, equilibrium moisture determinations are made at 96–97 % relative humidity and used as inherent moisture values. It has been found that equilibrium moisture determined at 96.7 % relative humidity and 30°C averages approximately 96 % of the 100 % value. These values were based on data for the three ranks of high-volatile A, B, and C bituminous coal found in Illinois [**25**]. Although equilibrium moisture provides a fairly accurate estimate of the inherent moisture in high-rank coals, the same is not true for low-rank coals where the equilibrium moisture is usually less than the inherent moisture. The chemical and physical nature of the low-rank coals, as compared with higher-rank coals, and differences in pore size distribution and resulting capillary action are just some of the factors affecting the measured equilibrium moisture in low-rank coals. Although longer equilibration times are used for low-rank coals, equilibrium moisture values are still often less than the inherent moisture.

The banded constituents—vitrain, clarain, durain, and fusain—that occur in coal vary considerably in the amount of moisture they hold at various relative humidities.

One constituent, fusain, holds relatively little moisture below 90 % relative humidity. This is another reason for using a high relative humidity in the determination of the equilibrium moisture of coal.

5.1.4 Interpretation and Uses of Moisture Data

Moisture values are very important because of the influence they have on other measured and calculated values used in coal analysis and, ultimately, because of the part they play in the buying and selling of coal. The various forms of moisture in coal and the methods by which moisture values are obtained have been discussed in the preceding sections. The interpretation of moisture data and the uses and limitations of these data are of primary concern to the analyst.

The first moisture value to be obtained on a coal sample is usually the air-dry loss moisture. This moisture loss occurs during an attempt to bring the coal sample into equilibrium with the atmosphere in the sample preparation room. Temperatures used for air-drying vary over a wide range. The ASTM specifications call for air-drying on a drying floor at room temperature or in a drying oven at temperatures 10–15°C above room temperature, with a maximum of 40°C. The practice of using temperatures above room temperature may accelerate oxidation, but it shortens the time needed for air-drying, which reduces total exposure of the coal and decreases the chances of oxidation. The shorter exposure time should compensate for the use of the elevated temperature. In very warm climates or on very warm days in moderate climates, it may not be possible to conduct air-drying experiments without exceeding the recommended maximum temperature. Temperatures above 40–45°C should not be used for air-drying.

The air-dry loss moisture as a percentage of the total moisture in coal is variable. It may vary from 25 to 90 % of the total moisture for different samples and may vary widely for coals of the same rank. It has been used incorrectly in some instances as a measure of the surface or free moisture. The use of the air-dry loss moisture value by itself has no real significance in the characterization of coals. A laboratory's air-dry moisture value for a particular coal is unique and not comparable to some other laboratory's air-dry moisture value for the coal.

Residual moisture, or as-determined moisture, is used to calculate other measured analytical values to the dry basis. Residual moisture alone has no significance in the characterization of coals.

The sum of residual moisture and air-dry loss moisture is equal to the total moisture. As measured in ASTM **D3302**, total moisture in coal is that which exists at the site, at the time, and under the conditions it is sampled. It applies to coals as mined, processed, shipped, or used in normal commercial operations. Coal-water slurries, sludges, or pulverized products under 0.5-mm diameter sieve size are exceptions. Total moisture applies to coals of all ranks.

Total moisture is used for calculating other measured quantities to the as-received and dry basis. In the buying and selling of coal, as-received calorific values are often

used as the basis for contracts. To obtain as-received calorific values, the dry calorific values are converted to the as-received basis using total moisture values. When thousands of tons of coal are involved in a contract, an error that may seem insignificant in a normal laboratory situation may be serious from a monetary standpoint.

Total moisture is important in assessing and controlling the commercial processing of coals. It is used to determine the amount of drying that is needed to reach a given moisture requirement and to determine the amount of dust-proofing and freeze-proofing agents to add. In coking processes, coals with high moisture contents require more heat for vaporization of the moisture, which leads to longer coking cycles and decreased production. The total moisture of the coal used must be accurately known to allow for proper charging of the coke ovens and overall control of the coking process.

Inherent or equilibrium moisture is used for calculating moist mineral-matter-free calorific values for the rank classification of high-volatile bituminous coals. It is also used for estimating free or surface moisture because total moisture is equal to the sum of the inherent moisture and the free moisture. The inherent moisture value is also referred to as *bed moisture* because it is considered to be the moisture of the coal as it occurs in the unexposed seam, where the relative humidity is 100 %. As mentioned above, equilibrium moisture provides a fairly accurate estimate of the inherent moisture in high-rank coals but the same is not true for low-rank coals where the equilibrium moisture is often less than the inherent moisture. Appendix X1 in ASTM **D1412** provides a method for validating the equilibrium moisture/inherent moisture relationship.

Surface moisture values are really estimates [**26**]. These are obtained by subtracting equilibrium moisture from total moisture. However, there is no sharp dividing line between inherent moisture and surface moisture. The measurement of inherent moisture depends on the fact that its vapor pressure is less than that of surface moisture. It is commonly thought that inherent moisture is contained in the pores and capillaries of coal. However, these pores and capillaries may vary in diameter and size to such an extent that the water in the larger capillaries has a vapor pressure approaching that of surface moisture. Thus, moisture in the larger pores behaves like surface moisture and is "lost" during the equilibrium moisture test. Because pore size increases as rank decreases, low-rank coals are more problematic regarding equilibrium moisture [**26**].

Drying, pulverizing, dust-proofing, and the general handling of coal all depend on surface moisture data. Too much surface moisture is particularly troublesome in pulverizing and handling operations. A wet coal is very difficult, and in some instances almost impossible to pulverize. The presence of only 0.5 % surface moisture is enough to cause coal to stick in a chute.

There is no simple and reliable method of determining the water of hydration of mineral matter. The average value of 8 % of the ash is used as the value for water of hydration of mineral matter in coals in the United States. This value is acceptable, although it is an average of values that range from 2 to 3 % up to 15–30 %. Water of

hydration values are used to correct ash to the form of hydrated minerals in mineral matter calculations.

5.2 Ash

Coal ash is the residue remaining after the combustion of coal under specified conditions. It does not occur as such in the coal but is formed as the result of chemical changes that take place in the mineral matter during the ashing process. The quantity of ash can be more than, equal to, or less than the quantity of mineral matter in coal, depending on the nature of the mineral matter and the chemical changes that take place in ashing.

There are two types of ash-forming materials in coal: extraneous mineral matter and inherent mineral matter. The extraneous mineral matter consists of materials such as calcium, magnesium, and ferrous carbonates; pyrite; marcasite; clays; shales; sand; and gypsum. Inherent mineral matter represents the inorganic elements combined with organic components of coal. The origin of such materials is probably the plant materials from which the coal was formed. Ash from the inherent mineral matter is usually a minor component of the total quantity of ash [**27**].

The composition of coal ash varies widely, depending on the mineral matter associated with the coal. Typical limits of the composition of ash of bituminous coals are given in **Table 5.1**.

Some of the chemical changes that take place during ashing include the loss of water of hydration from clay-like material, the loss of carbon dioxide from mineral carbonates, and the conversion of pyrite to Fe_2O_3 and oxides of sulfur. The organically combined inorganic elements are also converted to oxides. Some recombination reactions do occur depending on the conditions and composition of materials in the coal sample. Under certain conditions, sulfur dioxide is oxidized to sulfur trioxide (SO_3),

TABLE 5.1 Typical Limits of Ash Composition (%) in Bituminous Coals

Constituent	United States	England	Germany
SiO_2	20–60	25–50	25–45
Al_2O_3	10–35	20–40	15–21
Fe_2O_3	5–35	0–30	20–45
CaO	1–20	1–10	2–4
MgO	0.3–4	0.5–5	0.5–1
TiO_2	0.5–2.5	0–3	…
$Na_2O + K_2O$	1–4	1–6	…
SO_3	0.1–12	1–12	4–10

Source: Reprinted with permission from [**28**].

which reacts with metal oxides, particularly alkali and alkaline earth metal oxides, to form stable sulfates, which remain in the ash.

5.2.1 Determination of Ash Content

The procedures for the determination of ash content in coal are outlined in ASTM Test Method for Ash in the Analysis Sample of Coal and Coke from Coal (**D3174**) and ASTM **D7582**. In ASTM **D3174**, 1 g of coal is weighed and placed in the preweighed porcelain crucible. The coal used may be from the analysis sample or the dried coal sample from the moisture determination, ASTM **D3173**. The crucible is then placed in a muffle furnace, which is at ambient temperature, and the temperature is raised at such a rate that it reaches 500°C at the end of 1 h. Heating is continued so that the temperature rises from 500°C to 750°C at the end of 1 h. Heating at the 750°C temperature is continued until the test specimen reaches a constant mass or for an additional 2 h. During the ashing procedure, an adequate supply of air must be supplied to the furnace.

Coals with unusually high amounts of calcite $\left(CaCO_3\right)$ and pyrite may retain varying amounts of sulfate sulfur upon ashing. Coals are ashed by the two-step heating rate in an attempt to minimize this retention. Pyrites are oxidized to sulfur oxides and iron oxides at temperatures of approximately 450°C. Calcite and other carbonate minerals decompose to the metal oxides and carbon dioxide at temperatures of approximately 600°C and above. Oxidizing pyrites at the lower temperatures rids the sample of sulfur that may be converted to sulfur oxides and retained by the metal oxides formed at the higher temperatures.

ASTM **D3174** was revised in 2012 to remove the use of temperature ranges for the determination of ash in coals and cokes. This practice of using temperature ranges was initiated in a 1982 revision to **D3174**. The apparent purpose of the revision was to substitute an alternative procedure in **D3174** for the primary procedure because it worked for troublesome coals. If it worked for troublesome coals, then it would likely work for all coals. The original language for the alternative procedure was as follows: "Place the capsules containing the dried coal from the moisture determination in a cold muffle furnace and heat gradually so the temperature reaches 500°C in 1 h, and 750°C in 2 h" [**29**]. However, the 1982 revision inserted the temperature ranges, 450–500°C and 700–750°C for the two heating stages. It is speculated that because some of the ashing furnaces used in the 1970s and 1980s did not have temperature controllers that the temperature ranges were chosen as a compromise [**30**].

In 2011, an ASTM Task Group that had reviewed the use of the temperature ranges for the determination of ash in the analysis samples of coal and coke decided the temperature ranges were not acceptable. Data from a 1982 Interlaboratory Study and data from a 2011 study using a macro-TGA showed a significant bias between the ash determined using 450°C for the first-stage temperature and the ash determined using 500°C as the first-stage temperature. **D3174** was subsequently revised and successfully balloted to use the fixed temperatures of 500°C and 750°C instead of the temperature ranges [**31**].

The ashing of different types of coals in the same furnace can lead to increased retention of sulfur oxide by the more alkaline ashes. **Table 5.2** lists the oxide composition of two dissimilar coal ashes and the resulting SO_3 contents in the ashes when various combinations of the coals were thoroughly mixed and ashed [**32**]. The SO_3 retention in the ash of the 75 % ligA and 25 % hvBb coals is nearly double that in the ligA coal alone and over 20 times that in the hvBb coal alone. It should be strongly emphasized that the retention of sulfate in this blend is due to the dissimilar coals being thoroughly mixed. The capture of sulfur oxides by the unblended coals in separate vessels heated in the same furnace would never be this efficient, but the analyst should be aware that some sulfur oxide transposition is likely.

ASTM **D7582**—Proximate Analysis of Coal and Coke by Macro-Analysis—was first approved in 2010. It replaced the earlier Instrumental Proximate Analysis Standard, **D5142**, which was withdrawn from publication. Using the macro-TGA, samples of approximately 1-g size are loaded into ceramic crucibles on a multisample carousel and repeatedly weighed with an internal balance as they are heated in a carefully controlled atmosphere inside of the furnace. The heating rate used is the same as that for other ashing methods (ambient to 500 °C at the end of 1 h and from 500 °C to 750 °C at the end of 1 h). A fixed ashing period can be used, but with the macro-TGA, the mode that allows weighing to a constant mass is commonly used because the samples are repeatedly weighed over time periods of 3 min or less.

ASTM **D7582** allows for the sequential determination of moisture, volatile matter, and ash on a single sample. With the macro-TGA system, the first step in the sequence is the determination of moisture at 104–110 °C in an uncovered crucible using nitrogen as the drying gas. The crucible is then covered and heated rapidly to 950 °C in

TABLE 5.2 Sulfate Retention (%) by Blends of Two Coals with Dissimilar Ashes

Oxide	100 % ligA	100 % hvBb	25 % LigA 75 % hvBb	50 % ligA 50 % hvBb	75 % ligA 25 % hvBb
SiO_2	41.1	45.5			
Al_2O_3	23.2	19.2			
Fe_2O_3	4.20	24.1			
CaO	13.2	0.55			
MgO	1.40	1.07			
Na_2O	0.92	0.51			
K_2O	1.60	2.63			
TiO_2	0.82	1.00			
SO_3	7.84	0.72	3.0	8.0	15.5
P_2O_5	0.63	0.20			

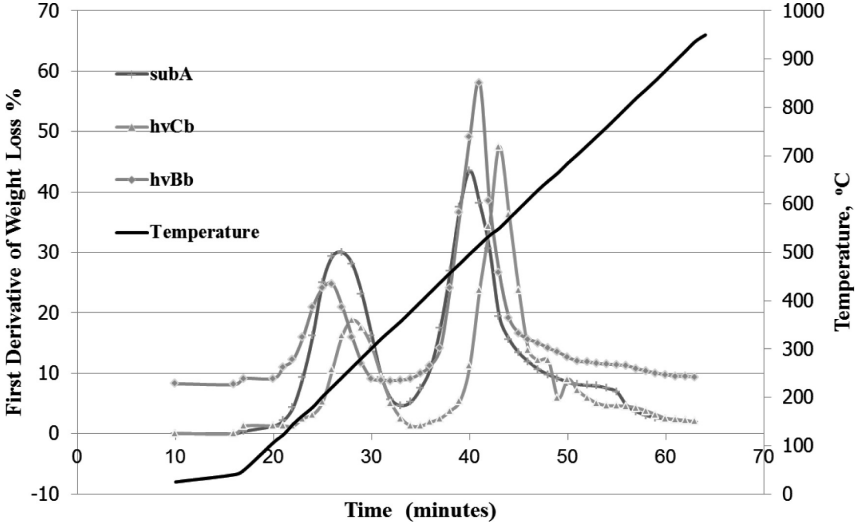
nitrogen and then weighed to determine volatile matter. This is followed by cooling the furnace and crucibles to 600°C, the crucible covers are removed, oxygen is admitted, and the furnace heated to 750°C. Ash is determined by heating and weighing until the samples reach a constant mass.

The instrumentation used in the macro-TGA method normally has a rotating carousel with positions for 20 crucibles, which allow for the analysis of 19 samples because 1 crucible is used for a reference. All crucibles are weighed every 3 min, which is the normal time for one complete revolution of the carousel. Mass change plots as a function of time or temperature or both allow the operator to observe the rate of mass loss from the various samples. A first derivative of the mass loss plotted as a function of the time or temperature or both yields a "mass loss profile" that coincides with the rate of the reactions taking place in the furnace. **Figure 5.1** shows differential thermogravimetric plots of the rate of mass loss versus time and temperature for the volatile matter determination of three coals. Other coal types give different plots. This useful information allows the operator to observe differences in the reactivity of fuel samples.

5.2.2 Preparation of Ash for Various Analyses

A considerable number of ASTM Standard Test Methods require prepared ash for analyses. Test methods for the determination of major and minor elements, for ash fusion analysis, and for many of the trace elements in coal and coke need prepared ash for the tests. In most cases, the development of these test methods included the

FIG. 5.1 Differential thermogravimetric plots of two bituminous and a subbituminous coal showing areas of maximum mass losses during heating in nitrogen.



adoption of a procedure for the preparation of ash to be used in the method. As a result, these individual ash preparation procedures were not the same, although they were similar to each other. It should be obvious that analytical procedures (e.g., atomic absorption spectroscopy, inductively coupled plasma–atomic emission spectroscopy, and X-ray fluorescence spectroscopy [all to be discussed later]) that are used to determine the elemental composition of ash should all use ash prepared in the same way. In 2011, ASTM Committee D05 formed a joint Task Group between Subcommittee D05.21—Methods of Analysis—and Subcommittee D05.29—Major and Minor Elements in Coal and Coke and Trace Elements in Coal—to develop a common procedure for the determination of ash in coal and coke samples. The Task Group also was charged with the responsibility of developing a common procedure for the preparation of ash for elemental analysis and other uses. The development of a common language for the determination of ash in coal and coke and for the preparation of coal and coke ash for elemental analysis has been completed.

5.2.3 Interpretation and Uses of Ash Data

The value obtained for the ash content is not a true indication of the noncombustible material occurring in coal. The indefinite amount of sulfur that may be retained in the ash and the high-temperature interaction of the various ash-forming components to produce new compounds make it impossible to give an exact interpretation of the relationship between the composition of the ash and clinkering or fusing of ash particles, boiler tube slagging, and other problems associated with ash formation. Although the ash value is an empirical quantity, it is quite useful for many practical applications.

The ash value is the analytical value most commonly used for evaluating sampling procedures and is one of the values almost always specified in coal contracts. In combustion, high ash content is an indicator of reduced heat obtainable from a given quantity of coal. High ash content can indicate the potential for problems with handling and disposing of larger amounts of ash residues produced during combustion. The composition of coal ash is considered in the amount of clinkering and boiler tube slagging that may occur in a boiler. The design of most boilers is such that only coals with a specified range of ash content may be used in the efficient operation of the boiler. The amount of ash in coal used in a coking process is an indication of the amount of ash that will remain in the coke that is made. Coke with a high ash content that is used in a blast furnace requires more fluxing limestone to compensate for the ash, and a greater volume of coke to obtain the required amount of usable carbon.

Coal can be cleaned by various processes to reduce the ash-forming minerals and sulfur content. The ash content of raw coal is often used to select the best cleaning method, and the ash content of the cleaned coal is used to measure the effectiveness of the cleaning process. In the commercial pulverization of coals, the amount and nature of ash is carefully considered before selecting pulverizing equipment or setting up the process.

Finally, in the ASTM system of classifying coals by rank, it is necessary that some of the parameters that are used be calculated to a mineral-matter-free basis. An

estimate of mineral matter needed for these calculations can be derived from the ash value.

5.3 Volatile Matter

The loss of mass, corrected for moisture, that results when coal is heated in specified equipment under prescribed conditions is referred to as *volatile matter*. The matter lost is composed of materials that form upon the thermal decomposition of the various components of coal. Some of the constituents of coal volatile matter are hydrogen, carbon monoxide, methane and other hydrocarbons, tar vapors, ammonia, some organic sulfur- and oxygen-containing compounds, and some incombustible gases (e.g., carbon dioxide and water vapor), all of which come from the decomposition of organic materials in coal. Inorganic materials in coal contribute the water of hydration of mineral matter, carbon dioxide from carbonates, and hydrogen chloride from inorganic chlorides to the volatile matter. Volatile matter does not include the residual moisture, as determined in ASTM **D3173** or **D7582**.

5.3.1 Determination of Volatile Matter Content

Volatile matter is determined by establishing the loss in mass resulting from heating a coal sample under rigidly controlled conditions. The ASTM procedures for determining volatile matter are outlined in ASTM Test Method for Volatile Matter in the Analysis Sample of Coal and Coke (**D3175**) and Proximate Analysis of Coal and Coke by Macro-Thermogravimetric Analysis (**D7582**). Because the methods are empirical, they require close adherence to detailed specifications.

In ASTM **D3175**, the type of heating equipment (electric Fieldner-type tube furnace) and the size and shape of the sample holders, as well as the material from which they are made (platinum crucibles recommended and nickel-chromium allowed), all influence the rate of heating of the sample and the range of temperatures to which it is exposed. The crucibles used are 10- to 20-mL capacity of specified size with close-fitting lids. There are two procedures. The regular method is used for nonsparking coal and coke. The modified method is used for fuels that do not yield a coherent cake as residue in the determination and evolve gaseous products at a rate sufficient to carry solid particles out of the crucible when heated at the standard rate. Such fuels are referred to as sparking fuels and normally include all low-rank noncaking coals and lignite, but they may also include other coals.

In the regular procedure, 1 g of the analysis sample of coal is weighed in a preweighed crucible (10-to 20-mL capacity, 25–35 mm in diameter, and 30–35 mm in height) with a close-fitting cover. The crucible is then suspended at a specified height in the furnace chamber. The temperature of the region in the furnace where the crucible is suspended must be maintained at 950 °C ± 20 °C. After the more rapid discharge of volatile matter, as evidenced by the disappearance of the luminous flame, the cover of the crucible should be tapped to ensure that the lid is still properly seated to guard against the admission of air. After heating for exactly 7 min, the crucible is removed from the furnace and cooled. The crucible should be weighed as soon as it has reached

ambient temperature. The percentage loss of mass minus the percentage moisture equals the volatile matter.

In the modified procedure for all sparking fuels, the sample is suspended and heated in a cooler zone of the furnace such that the temperature inside of the crucible reaches 600 °C ± 50 °C in 6 min. After the preliminary heating, the crucible is lowered into the hot zone (950 °C ± 20 °C) of the furnace and held there for 6 min. The crucible is then removed from the furnace and set on a metal block to cool before weighing. The cooling period should be kept constant and should not exceed 15 min to ensure uniformity of results. The volatile matter is calculated in the same manner as in the regular method.

The furnace used for the volatile matter determination must be checked frequently because any variance from proper standardization produces erratic results. The thermocouple in the furnace chamber may break or change over a period of time. Probably no two furnaces have the same heating characteristics. Therefore, it is necessary to check them regularly and certainly after any repairs.

The rate of heating of the sample influences volatile matter values and makes it necessary to calibrate equipment to achieve a satisfactory and reproducible heating rate. This calibration can be accomplished by using either a manual or an automatic mechanical device that lowers the sample crucible at a reproducible rate into the electrically heated furnace.

Sparking is caused by incandescent particles of coal that are carried out of the crucible by the rapid release of moisture or volatile matter. The loss of these particles results in volatile matter values that are too high. Sparking may intensify with an increase in the amount of very fine particles in the analysis sample. The concentration of such fine particles can be avoided to some degree by proper reduction of coal particles during the preparation of the analysis sample.

The crucibles and covers must be properly shaped to ensure a proper fit. Oxidation is not a serious problem in volatile matter determinations because the rapid release of large amounts of gases during the test does prevent the entry of air into the crucible, thereby reducing the chance of oxidation. Addition of a few drops of a volatile material, such as toluene, may also help prevent oxidation. However, a loose-fitting cover allows air to come in contact with the hot coal sample, with subsequent formation of oxidized gaseous products that result in a high volatile matter value.

In the determination of volatile matter content, the modified ASTM method, using a slower heating rate, is applicable to a wider variety of coals. However, the values obtained are sometimes lower (1–3 % absolute) than those obtained from the regular method. This illustrates the empirical nature of this test and the importance of strict adherence to detailed specifications. The complexity of the constituents of coal that undergo decomposition during this test explains the wide tolerances for repeatability and reproducibility observed for the different procedures.

The mass loss recorded in the ASTM procedures for determining the volatile matter in coal includes the residual moisture and the water of hydration of mineral matter.

The residual moisture value is subtracted from the mass loss to obtain the determined volatile matter. However, the water of hydration of mineral matter is included in the volatile matter because there is no satisfactory method of determining it.

The volatile matter values obtained by the ASTM procedure using dried coal samples are lower than those obtained using the analysis sample. Studies of bituminous coals in which the volatile matter values were determined using dried samples from the residual moisture determination (ASTM **D3173**) yielded values that were an average of 0.94 % (absolute) lower than the corresponding ASTM values [**33**]. The coals studied had residual moisture values ranging from 1.71 % to over 10 %. There was a moderate correlation between the residual moisture content of the coals and the difference between the volatile matter values. This observation indicates that partial gasification of the coal occurs in the presence of residual moisture [**33**].

In ASTM Test Method **D7582**, volatile matter is determined by rapidly heating the samples at approximately 40°C/min from 107 °C (after the moisture determination) in a covered crucible in an inert atmosphere to 950 °C and holding at this temperature for 7 min. The mass of the samples taken after the 7-min holding period are used to calculate the volatile matter. The volatile matter values determined in ASTM **D7582** are quite often different from those determined by the classical method ASTM **D3175**. ASTM **D3175** is considered to be the reference method and the volatile matter values determined in **D7582** are referenced to **D3175** values using certified reference materials. Reference coals with volatile matter values certified to **D3175** are available for calibrating the macro-TGA system instruments used in **D7582**.

A combination of Fieldner furnaces, a macro-TGA, and micro-TGA systems were used in a study to determine the reason for the differences between volatile matter values as a function of heating rate [**34**]. Nineteen coals of various ranks and heating rates of 10, 20, 30, 40, 50, 60, 100, 200, and 400 °C/min were used in the study. A macro-TGA system was used for the 10, 20, 30, and 40 °C/min rates and micro-TGA systems were used for the 50, 60, 100, and 200 °C/min rates. The Fieldner furnaces operated at a 400 °C/min heating rate. The study showed that for heating rates of 100 °C/min and higher there was no significant difference in the volatile matter values obtained with the micro-TGA and the Fieldner furnaces. If the heating rates were 40–50 °C, then there were some significant differences between the volatile matter values obtained with the TGA systems and the Fieldner furnaces. The relative percentage differences were as follows:

- *Anthracites:* TGA volatile matter values were approximately 27 % higher.
- *Low and medium volatile coals:* Fieldner furnace volatile matter values were approximately 6 % higher.
- *High volatile bituminous coals:* Fieldner furnace volatile matter values were approximately 7 % higher.
- *Subbituminous and lignitic coals:* Fieldner furnace volatile matter values were approximately 0.5 % higher.

ASTM **D3175** uses a Fieldner-type furnace, whereas ASTM **D7582** uses a macro-TGA system. In the Fieldner furnace preheated to 950 °C, when the test sample is lowered into the furnace, the heating rate for the sample is approximately 400 °C / min. At this heating rate, bituminous coals melt when the temperature approaches 330 °C because all bituminous coals have some plastic properties. The hot molten mass in the crucible attacks the solid coal matrix over the 30–60 s it is in the molten state. As the temperature of the sample approaches 600 °C, the volatile matter (much of which is the molten material) escapes and a coke button forms. The entire process converts some of the naturally occurring solid matrix of the coal to molten material and eventually to volatile matter. The macro-TGA system heats the coal sample at a much slower rate $\left(40-45\,^{\circ}\mathrm{C}/\mathrm{min}\right)$, allowing volatile components to escape before the sample reaches the plastic state. There is less molten material formed in the process, and less solid matrix converted to volatile matter, as in the case with the Fieldner furnace. For this reason, the bituminous coals yield higher volatile matter values in ASTM **D3175** than in **D7582**.

Data collected in three separate studies, including two ASTM Interlaboratory Studies, were used to show the relationship between ASTM **D3175** volatile matter values and those from ASTM Standard Test Method **D7582** [**35**]. The data were collected over a period of 23 years. The first data were collected in an ASTM Interlaboratory Study conducted in the mid-1980s that led to the development of the "automated procedure" in ASTM Method **D5142** [**36**]. The second study was part of the M.S. thesis work of E. Yanes in the mid-1990s [**37**]. The third set of data was collected in an ASTM Interlaboratory Study conducted in 2008 that led to the development of ASTM **D7542** [**38**]. **Figure 5.2** is a scatterplot of data from the three studies comparing the volatile matter yields for the ASTM **D3175** and macro-TGA (**D5142** and **D7582**) standard methods. This plot shows that the data from the three different studies line up very well with each other.

Figure 5.3 has the same data as **Figure 5.2** with trend lines and equations added for bituminous coals, subbituminous coals, and lignites and cokes. The R^2 value of 0.99 for the bituminous coals indicates the best fit for this rank of coals. The cokes give the next best R^2 of 0.978, whereas the R^2 value of 0.906 for subbituminous coals shows a less favorable, but good fit, for the wide range of data used. The equations associated with the trend lines are very useful for predicting the relationship between the two methods for the different groups of coals and cokes.

5.3.2 Interpretation and Uses of Volatile Matter Values

Volatile matter values are useful in choosing the best match between a specific type of coal-burning equipment and the coal to use with the equipment. Such values are valuable to combustion engineers in setting up and maintaining proper burning rates. Volatile matter values are used as an indication of the amount of smoke that may be emitted from furnaces or other types of coal-burning equipment. Limits may be set on the volatile matter content of the coal used in certain coal-burning facilities to control smoke emissions.

FIG. 5.2 Plot of dry volatile matter values determined by two ASTM methods in three separate studies [35].

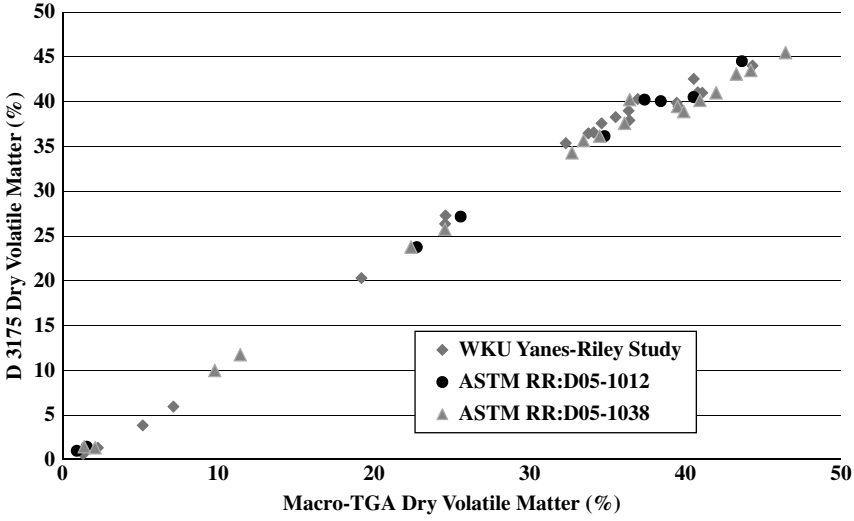
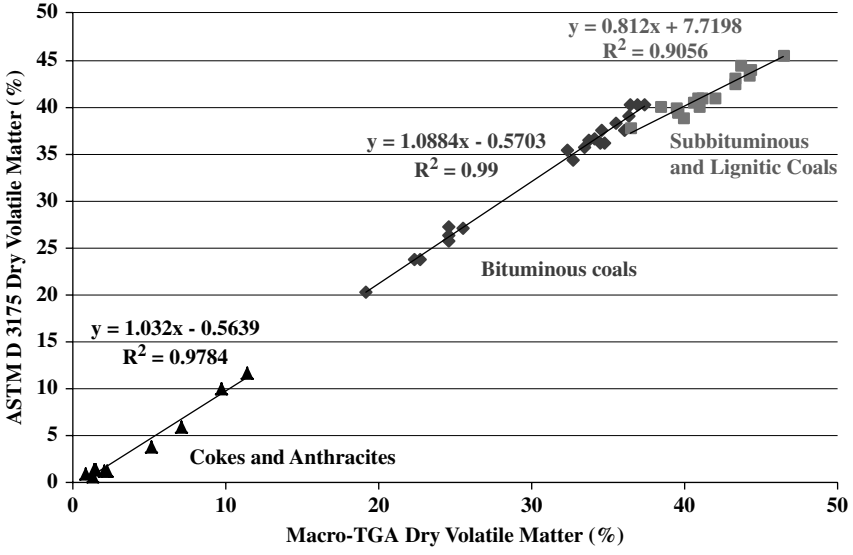


FIG. 5.3 Plot of dry volatile matter values determined by two ASTM methods with trend lines and equations [35].



Volatile matter values are also important in the selection of coals and in determining the blending proportions of coal for coking. The volatile matter value of coke is used as a means of evaluating the extent of coking, depending on the intended use of the coke.

5.4 Fixed Carbon

The fixed carbon value is obtained by subtracting the sum of the percentages of moisture, ash, and volatile matter from 100. This value is considered to be the amount of carbon residue that remains after the volatile matter test. The residue is the product of the thermal decomposition of the coal.

5.4.1 Interpretation and Uses of Fixed Carbon Data

The fixed carbon value is one of the values used in determining the efficiency of coal-burning equipment. It is a measure of the solid combustible material that remains after the volatile matter in coal has been removed. For this reason it is also used as an indication of the yield of coke in a coking process. Fixed carbon plus ash essentially represents the yield of coke. Fixed carbon values, corrected to a dry, mineral-matter-free basis, are used as parameters in the ASTM coal classification system.

Chapter 6 | Ultimate Analysis

Ultimate analysis of coal and coke is defined in ASTM **D3176** as the determination of the carbon, hydrogen, nitrogen, and sulfur in the material, as found in the gaseous products of its complete combustion, the determination ash in the material as a whole, and the estimation of oxygen by difference. The carbon determination includes that present in the organic coal substance and any carbon originally present as mineral carbonate. The hydrogen determination includes that in the organic materials in coal and in all water associated with the coal. All nitrogen determined is assumed to be part of the organic materials in coal. For practical reasons, sulfur is assumed to occur in three forms in coal: as organic sulfur compounds; as inorganic sulfides, which are mostly the iron sulfides pyrite and marcasite; and as inorganic sulfates. The total sulfur value is used for ultimate analysis.

Moisture is not by definition a part of the ultimate analysis of coal but must be determined so that the analytical values obtained can be converted to bases other than that of the analysis sample. In other words, analytical values may need to be converted to an as-received or a dry basis. When suitable corrections are made for the carbon, hydrogen, and sulfur derived from the inorganic material, and for conversion of ash to mineral matter, the ultimate analysis represents the elemental composition of the organic material in coal in terms of carbon, hydrogen, nitrogen, sulfur, and oxygen.

The current practice in most coal and fuel laboratories is to determine carbon, hydrogen, nitrogen, and sulfur using instrumental methods. The classical methods for determining these elements have been withdrawn from publication because of the lack of use. Several of the instrumental methods that are now used were developed using chemical information and procedures found in the classical methods. In the following sections the chemical processes used in the classical ASTM methods will be discussed to gain a better understanding of the current test methods.

6.1 Carbon and Hydrogen

Almost all of the carbon and hydrogen in coal occurs in the combined form. Both of these elements are present in the very complex organic compounds found in coal.

Carbon also occurs in the mineral carbonates, with calcite being the principal component. Hydrogen is also present in the various forms of moisture found in coal.

6.1.1 Determination of Carbon and Hydrogen Content

All methods of determining the carbon and hydrogen content of coal are very similar in that a weighed sample is burned in oxygen in a closed system under carefully controlled conditions. The carbon is converted to carbon dioxide and the hydrogen to water. A general equation for coal combustion is

$$C_zH_yN_xS_wCl_vO_u + \text{excess } O_2 \rightarrow zCO_2 + (y - v) / 2H_2O + xNO_2 + wSO_2 + vHCl \quad (6.1)$$

In the classical ASTM Test Method for Carbon and Hydrogen in the Analysis Sample of Coal and Coke (**D3178**), the coal sample is burned in a tube furnace at 850–900°C, the combustion products are completely converted to gases over a copper oxide catalyst heated to 850°C, and the combustion gases are stripped of acid gases using silver gauze or potassium chromate heated to 500°C and passed through an absorption train to capture water and carbon dioxide. The amount of carbon and hydrogen is calculated from the mass gained by the reagents in the absorption train.

Some problems that may arise with the use of the equipment described are the incomplete combustion or conversion of carbon to carbon dioxide and of hydrogen to water. Several things can cause these problems to occur. If the unit used for burning the sample is heated too rapidly, then volatile matter may be released at such a rate that some of it may pass through the entire system and not be completely converted to carbon dioxide and water and absorbed. To prevent this from happening, the temperature of the combustion unit must be at the proper level, and enough time must be allowed for complete combustion. In addition, a sufficient flow of oxygen must be maintained through the system, and all connections in the apparatus must be made gas tight. Whenever a combustion tube is put into use after standing idle for some time, it is necessary that the tube be reconditioned for several hours before making any determinations. To condition the system, the combustion train is tested under normal operating conditions until stable results are obtained.

In this method, all organic carbon is burned to carbon dioxide. Inorganic carbonates are also decomposed under the conditions used, and the CO_2 produced is absorbed in the absorption train. For coals that have a high carbonate content, it may be necessary to determine the carbonate carbon content and subtract it from the total carbon content to obtain a more accurate value of the combustible carbon content. The formation of oxides of nitrogen during the combustion process may lead to slightly higher results for carbon and hydrogen because the oxides are acidic in nature and would be absorbed in the absorption train. For more precise results, such as in certain research applications, these oxides of nitrogen can be removed by absorption on manganese dioxide, or in some cases lead dioxide, before absorption of the water and carbon dioxide [**39**].

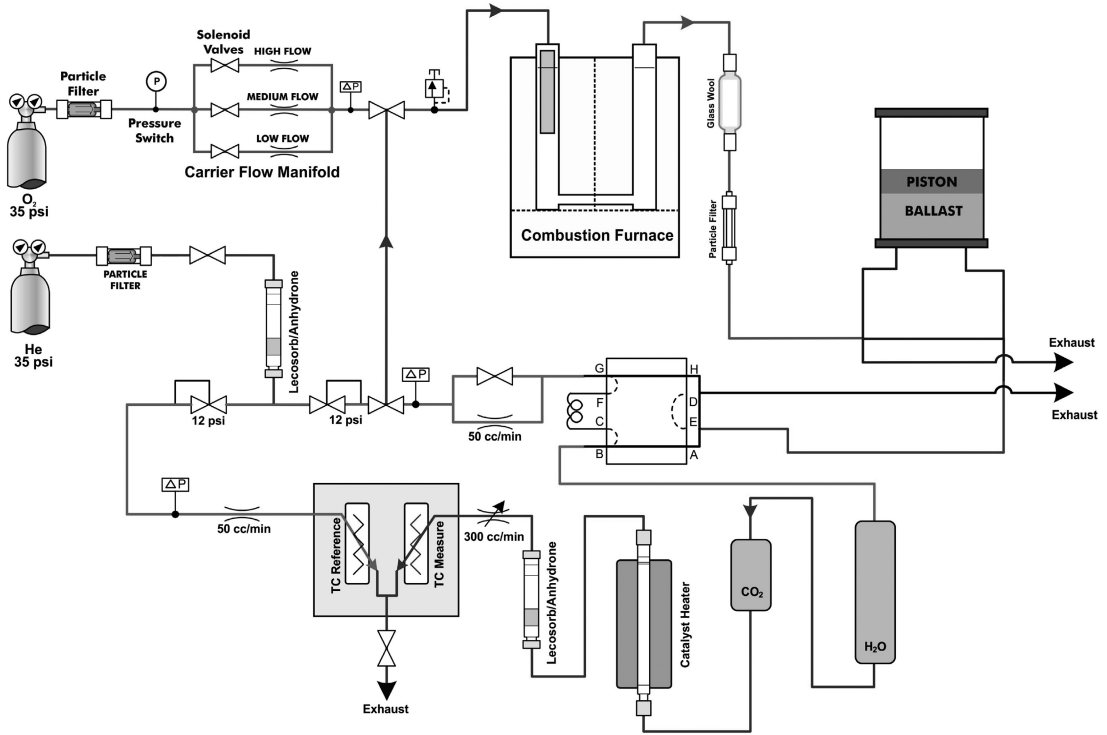
ASTM Standard Test Methods for the Determination of Carbon, Hydrogen, and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke (**D5373**) allows the use of computer-controlled instrumentation for the simultaneous determination of carbon, hydrogen, and nitrogen in coal and coke samples. Some basic requirements for the instruments are that they provide for the complete conversion of the carbon, hydrogen, and nitrogen in coal to carbon dioxide, water vapor, and elemental nitrogen, and for the quantitative determination of these gases in an appropriate gas stream. Just like the classical method for determining carbon and hydrogen, most analyzers must remove halides and sulfur oxides from the combustion gas stream. Carbon dioxide and water vapor are most often determined by infrared (IR) detection using precise wavelength windows so that the measured absorbance is due only to these gases. Most analyzers must also remove residual oxygen and reduce all nitrogen oxides to nitrogen before their detection by a thermal conductivity detector. **Figure 6.1** is a schematic diagram of a system used for the determination of carbon, hydrogen, and nitrogen by IR and thermoconductivity detection. Some analyzers use thermal conductivity detectors for the determination of all three gases.

A disadvantage of some of the instrumental methods for determining carbon, hydrogen, and nitrogen is the small sample size used in the analysis. A typical sample size for some instruments is 1–10 mg because of the detection systems used and the requirements for scrubbing the gas streams. Some analyzers use a ballast tank for collecting the combustion gases. Aliquots of the combustion gases are then taken for analysis. This type of system allows for the use of much larger samples, typically 100 mg. The larger sample size reduces the probability that sample inhomogeneity could affect the reliability of the results.

ASTM Standard Test Method **D5373** for coal and coke was initially approved in 1993. The precision and bias statement for the standard was developed using a coal standard reference material (SRM) from the National Institute for Science and Technology (NIST) to calibrate the instruments used in the Interlaboratory Study (ILS). Problems with the stability of the carbon in this SRM coal later prompted NIST to withdraw certification of the carbon value for the coal. An international ILS was conducted to develop a new precision and bias statement for **D5373**. The revision was approved in 2008. The very extensive ILS concentrated on the use of pure substances for the calibration of carbon, hydrogen, and nitrogen (CHN) analyzers. However, the ILS did not use any coke samples in its study, and coke was left out of this **D5373** revision.

Another ILS was conducted in 2012 to examine the analysis of carbon in coal and coke samples using analyzers operating at 1350°C. The higher temperature, as compared with the 950°C temperature normally used for CHN analyzers, promotes a more efficient combustion of coke samples. The carbon analyzers were calibrated with graphite, a pure substance. This ILS led to a new precision and bias statement that was added as Method B to **D5373**.

FIG. 6.1 Schematic diagram of an analytical instrument for the determination of carbon, hydrogen, and nitrogen.



Source: LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI.

6.1.2 Interpretation and Uses of Carbon and Hydrogen Data

As mentioned in the previous section, inorganic carbonates contribute to the carbon value in coal as it is normally determined. Hydrogen values also are usually high because of the inclusion of the various forms of moisture that are present in coal. All of these factors limit the reliability of carbon and hydrogen data for predicting the amount of combustible carbon and hydrogen in coal.

A reasonable correction to the hydrogen value for the moisture in coal can be made by subtracting one-ninth of the determined moisture from the determined hydrogen. A correction to the hydrogen value for the water of hydration of mineral matter is more difficult. The water of hydration of mineral matter for coals in the United States has been estimated to be 8 % of the ash value. Thus, a correction to the hydrogen value for the water of hydration can be estimated by multiplying the ash value by 0.08, and one-ninth of this figure will give the correction to be subtracted from the determined hydrogen. Upon making these corrections for the forms of moisture, the value for the hydrogen in the organic portion of coal is given by

$$H_{coal} = H_{as\text{-}determined} - 2.02/18.02[M_{as\text{-}determined} + 8/100\ A_{as\text{-}determined}] \qquad (6.2)$$

The results of the carbon and hydrogen analysis may be reported on any number of basis, differing from each other in the manner by which moisture values are treated. However, hydrogen values on the dry coal basis are commonly corrected for the hydrogen of moisture. No corrections are normally made to the determined hydrogen value for the water of hydration of mineral matter because of the uncertainty of the estimate of its value. Examples of the calculations involved and equations used in the treatment of ordinary laboratory data are given in Chapter 7—Calculating Coal Analyses from As-Determined Values to Different Basis.

Hydrogen values are used in the conversion of as-determined gross calorific values to net calorific values, as required in many coal contracts, especially international contracts. Carbon and hydrogen values are used to determine the amount of oxygen (air) required in combustion processes and for the calculations of the efficiency of the combustion. The use of carbon and hydrogen data is fundamental for basic coal research directed at the development of alternative coal utilization technologies, such as coal gasification and coal liquefaction, both of which may become critical to the security of the energy supply.

Developing issues involving emissions of carbon dioxide and carbon monoxide have focused attention on carbon analysis. More power plants are requiring carbon analysis as part of the suite of requested routine analyses.

6.2 Nitrogen

Nitrogen occurs almost exclusively in the organic matter of coal. Very little information is available concerning the nitrogen-containing compounds present in coal, but they do appear to be stable and are thought to be primarily heterocyclic. The

original source of nitrogen in coal may have been plant and animal protein. Plant alkaloids, chlorophyll, and other porphyrins contain nitrogen in cyclic structures stable enough to have withstood changes during the coalification process and thus to have contributed to the nitrogen content of coal.

6.2.1 Determination of Nitrogen

The instrumental determination of nitrogen is covered in ASTM **D5373**, which was discussed in the previous section. The classical methods for determining nitrogen in solid fuels involve its liberation in measurable form from the organic material in which it occurs. The methods are based on quantitative chemical reactions and involve converting the nitrogen into ammonia or oxidizing it to the elemental state.

The Kjeldahl-Gunning method for determining nitrogen was the basis of the ASTM Test Method for Nitrogen in the Analysis Sample of Coal and Coke (**D3179**). The test method offered procedures for macro (gram size) and semimicro (0.1-g size) determinations. In this method, any nitrogen present in the sample is converted into ammonium salts by the destructive digestion of the sample by a hot mixture of concentrated sulfuric acid and potassium sulfate. After the digestion mixture has been made alkaline with sodium or potassium hydroxide, ammonia is expelled by distillation, condensed, and absorbed in an excess of boric acid. The ammonia in the boric acid solution is then titrated with a standard acid solution. Proper precautions should be taken in performing this procedure, especially the digesting and distillation steps. In addition to the possibility of losing nitrogen-containing species if the proper heating rate is not observed, there is the problem of working with hot concentrated sulfuric acid and caustic solutions. In ASTM **D3179**, the first step is digestion of the sample in concentrated sulfuric acid.

$$2C_zH_yN_xS_wCl_vO_u + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2C_zH_{y-3}S_wCl_vO_u \quad (6.3)$$

In the analysis of the ammonium salts produced, the following reactions take place:

$$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2H_2O \text{ (distillation)} \quad (6.4)$$

$$NH_3 + H_3BO_3 \rightarrow (NH_4)H_2BO_3 \ (NH_3 \text{ capture}) \quad (6.5)$$

$$(NH_4)H_2BO_3 + HCl \rightarrow NH_4Cl + H_3BO_3 \text{ (titration)} \quad (6.6)$$

A catalyst is used in the Kjeldahl-Gunning method to increase the rate of digestion of the nitrogen-containing sample and shorten the digestion period. The total digestion time for most bituminous and low-rank coal samples is well over 6 h, even with the aid of a catalyst, whereas anthracite and coke samples may require as much as 12–16 h. The catalyst used in this method may be one of the

following: elemental mercury, mercuric sulfate ($HgSO_4$) and selenium, mercuric selenite ($HgSeO_3$) , or cupric selenite dihydrate ($CuSeO_3 \cdot 2H_2O$). Whenever mercury or a mercury-containing catalyst is used, the addition of potassium or sodium sulfide to the digestion mixture is necessary. The sulfide ions precipitate any mercuric ions as mercuric sulfide and prevent them from forming a stable complex ion with the ammonia produced in the digestion.

The Kjeldahl-Gunning semimicro method can be completed in much less time than the macro method [**40**]. The primary differences between the semimicro method and the macro method are that in the semimicro method smaller-sized equipment is used, smaller samples are analyzed, and after the digestion mixture is made alkaline ammonia is separated by steam distillation.

The most serious analytical problem associated with the use of the Kjeldahl-Gunning method is the incomplete conversion of nitrogen in the nitrogenous compounds to ammonia. This may be due to several reasons. In the decomposition of the nitrogenous compounds, the nitrogen is converted or reduced to ammonia, and organic materials are oxidized to various products. The digestion rate can be increased by the addition of stronger oxidizing agents, which more readily oxidize the organic matter. However, this cannot be done under normal conditions because the nitrogen would also be oxidized to nitrogen oxides and be lost from the analysis. The reaction mixture is not capable of reducing nitrogen oxides or nitro compounds. The decomposition must be performed within a very narrow oxidation-reduction range. In addition, pyridine carboxylic acids may be formed that are resistant to decomposition. Potassium sulfate is added to the sulfuric acid digestion mixture to raise its boiling point. At no time in the digestion process should the composition of the digestion mixture approach that of potassium acid sulfate or ammonia will be lost. Because of the somewhat limited oxidation and digestion conditions, and the possible formation of unwanted but stable byproducts, a lengthy digestion period is required.

In the analysis of a coal sample, the heterogeneous digestion mixture may become a clear, straw-colored solution. To ensure complete conversion of the nitrogen to ammonia, the digestion must be continued for an additional 1.5–2 h beyond the straw-colored stage. Finer grinding of the more resistant coals may shorten the digestion time. The addition of chromium (III) oxide (Cr_2O_3) to the digestion mixture increases the rate of digestion of coke.

The Kjeldahl-Gunning method for nitrogen determination has many analytical problems, especially with coal and coke samples. Even with these shortcomings the method was still accepted as an ASTM Standard Test Method for decades. The only viable alternative was the instrumental determination of carbon, hydrogen, and nitrogen (**D5373**). Standard Test Method **D3179** was withdrawn from publication in 2008. The reason for its withdrawal was its use of mercury catalysts and all test methods calling for the use of a mercury reagent have been dropped by ASTM.

6.2.2 Interpretation and Uses of Nitrogen Data

Historically, nitrogen data are primarily used in research and for the comparison of coals. These values are needed so that the oxygen content of a coal can be estimated by difference. During combustion, the nitrogen in coal can be converted to ammonia, elemental nitrogen, or nitrogen oxides, depending on the conditions of burning and the nature of the coal used. Nitrogen values could possibly be used to estimate the amount of nitrogen oxides that would be emitted upon burning of certain coals. For this reason, some regions of the country require the analysis of nitrogen in coal in addition to the analyses normally requested for steam coal. Coal nitrogen values are also useful in predicting the amount of nitrogen in the products of coal liquefaction and gasification processes.

6.3 Total Sulfur

For practical reasons sulfur is considered to occur in three forms in coal: as part of the organic matter; as inorganic sulfides, primarily pyrite and marcasite; and as inorganic sulfates. Elemental sulfur as such does not occur in coal to any significant extent [**41**]. The amount of the sulfur-containing materials in coal varies considerably, especially for coals from different seams. This variation is not as great for coals from a given field. On the average, coals from the Illinois Basin contain approximately equal amounts of organic and inorganic sulfur, although the relative amounts of these two sulfur forms may make up as much as 20–80 % of the total sulfur in individual coals. Most of the sulfur-containing organic compounds in coal are heterocyclic in nature and are likely to be uniformly distributed throughout the coal matrix. Pyrite and marcasite are two different crystal forms of FeS_2. For this reason, they are usually referred to simply as *pyrite*. Pyrite is not uniformly distributed in coal. It can occur as layers or slabs or it may be disseminated throughout the organic material as very fine crystals of 0.5- to 40-μm size. The content of sulfates, mainly gypsum ($CaSO_4 \cdot 7H_2O$) and ferrous sulfate ($FeSO_4 \cdot 7H_2O$), rarely exceeds a few hundredths of a percent, except in highly weathered or oxidized coals.

6.3.1 Determination of Total Sulfur

The sulfur content is an important value to consider in the utilization of coal and coke for most purposes. A considerable amount of work has been done in improving the accuracy and precision of sulfur determinations and in reducing the time for the analysis.

There are two ASTM methods of determining the total sulfur in coal and coke, with alternative procedures in each method. The classical ASTM Test Method for Total Sulfur in the Analysis Sample of Coal and Coke (**D3177**) has two alternative procedures referred to as the *Eschka* and the *combustion vessel washing methods*. ASTM Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Methods (**D4239**) has two alternative procedures with the basic difference being the combustion temperature used for decomposing the sample and production of sulfur dioxide (SO_2). Method A uses a

combustion temperature of 1350°C and Method B uses a combustion temperature of 1150°C and combustion aids to produce SO_2.

In the classical Eschka method, 1 g of the analysis sample is thoroughly mixed with 3 g of Eschka mixture, which is a combination of two parts by weight of light calcined magnesium oxide with one part of anhydrous sodium carbonate. The combination of sample and Eschka mixture is placed in a porcelain crucible (30 mL) and covered with another gram of Eschka mixture. The crucible is placed in a muffle furnace, heated to a temperature of 800°C ± 25°C, and held at this temperature until oxidation of the sample is complete. The sulfur compounds evolved during combustion react with the magnesium oxide and sodium carbonate, and under oxidizing conditions they are retained as magnesium sulfate and sodium sulfate. The sulfate in the residue is extracted with hot water and treated with a barium chloride ($BaCl_2$) solution to form insoluble barium sulfate ($BaSO_4$), which is determined gravimetrically.

In the combustion vessel washing method, sulfur is determined in the washings from the oxygen combustion vessel calorimeter after the calorific value determination. After opening, the inside of the vessel is washed carefully, and the washings are collected. After titration with standard base solution to determine the acid correction for the heating value, the solution is heated and treated with ammonium hydroxide to precipitate iron ions as iron (III) hydroxide. After filtering and heating, the sulfate is precipitated with $BaCl_2$ and determined gravimetrically.

ASTM **D4239**—Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Methods—was first approved in 1983. As originally developed, the test method used sulfur analyzers operating at 1350°C and offered three different procedures for detection of SO_2 gas. One procedure determined SO_2 using an acid-base titration after absorption of the gas in hydrogen peroxide solutions. A second procedure used an iodimetric titration to determine the SO_2 dissolved in a methanol-water-pyridine solution. The third procedure used IR absorption to detect the SO_2 in the combustion gases. The iodimetric titration procedure was dropped from ASTM **D4239** in 2002 because of its declining use and the fact that noxious chemicals were required. The acid base titration procedure was dropped from **D4239** in 2011 because of the decline in its use and the need to update its precision and bias statement.

In 2012, a new procedure (Method B) was approved for **D4239**. In this procedure the sulfur analyzer combustion tube is operated at 1150°C and combustion aids (tungsten trioxide and a tin boat) are used. The method also uses IR absorption for the detection of SO_2.

An ILS to examine the analysis of sulfur in coal and coke samples using sulfur analyzers operating at a temperature of 1350°C and calibrated with the pure substance, BBOT, was conducted in 2012. BBOT (2,5-di(5-tert-butylbenzoxazol-2-yl) thiophene ($C_{26}H_{26}N_2O_2S$)) has a sulfur value of 7.47 %. The precision and bias statement generated from this study was added to **D4239**'s Method A, giving the method

two precision and bias statements. The original precision and bias statement was developed using analyzers operating at 1350°C and calibrated with certified reference coals.

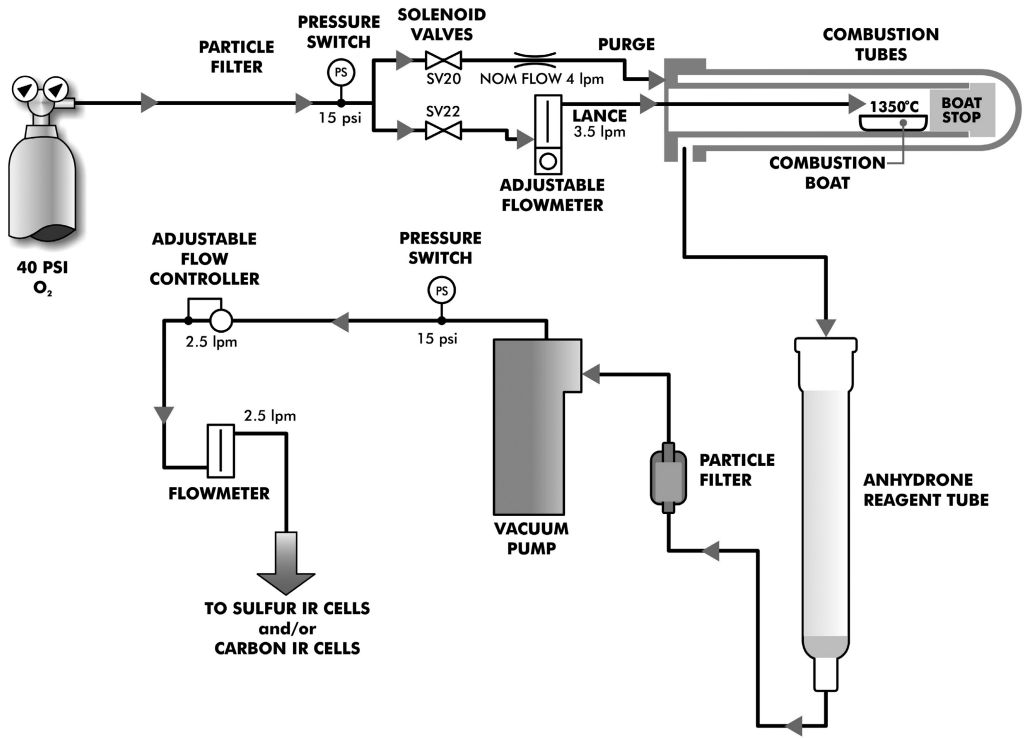
In the high-temperature combustion methods, a weighed sample is burned in a tube furnace in a stream of oxygen to ensure the complete oxidation of sulfur-containing components in the sample. Method A uses an operating temperature of 1350°C whereas Method B uses an operating temperature of 1150°C and combustion aids. Under these conditions, sulfur-containing materials in the coal or coke sample are reproducibly converted to SO_2. Moisture and particulates are first removed from the combustion gas stream by traps filled with anhydrous magnesium perchlorate. The gas stream is then passed through an IR absorption cell tuned to a frequency of radiation absorbed by SO_2. The IR radiation absorbed during combustion of the sample is proportional to the SO_2 in the combustion gases and therefore to the sulfur in the sample. Certified reference materials with sulfur percentages in the range of the samples to be analyzed are used to calibrate the instrument before use. A diagram of the type of apparatus used in Method A is given in **Fig. 6.2**.

Some general problems associated with the determination of sulfur in coal are nonuniform distribution of pyrite particles, failure to recover all of the sulfur as sulfate, and loss of sulfur as SO_2 during the analysis. The nonuniform distribution of pyrite necessitates the collection of many sample increments to ensure that the gross sample is representative of the lot of coal in question. Pyrite particles are hard, heavy, and have a tendency to segregate during the preparation and handling of samples. Because the particles are harder, they are more difficult to crush and pulverize and tend to concentrate in the last portion of material that remains from these processes. The sample preparation procedure is done to ensure that, at the time it is taken, the analysis sample is representative of the gross sample. However, because the heavy pyrite particles do segregate themselves in the sample bottle, uniform mixing of the analysis sample is necessary before test portions are taken for analysis.

Failure to recover all of the sulfur present in a sample as sulfate in the Eschka and combustion vessel-washing methods results in low total sulfur values. Because the methods depend on the combustion of the sample, it is important that the combustion products are completely oxidized. The temperature used must be high enough, the rate of burning must not be too fast, and sufficient time must be allowed to complete the conversion.

In each of the methods discussed, sulfur is oxidized to SO_2 during the analysis. Some SO_2 may be lost unless the necessary precautions are taken. In the Eschka method, a generous layer of Eschka mixture covering the fusion mixture helps prevent the loss of sulfur as SO_2. The mixture must be heated gradually to guard against the production of SO_2 at a rate that is too high for it to be absorbed by the Eschka mixture. In the combustion vessel-washing method, the pressure of the combustion vessel

FIG. 6.2 Schematic diagram for an apparatus for the determination of sulfur by the IR detection method.



Source: LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI.

should be released slowly after the sample is burned in oxygen so that sulfur oxides will not be carried out of the combustion vessel. In the high-temperature combustion methods, it is essential that the flow of oxygen is sufficient and that the rate of heating is not too high. A high rate of heating will lead to the evolution of combustion products, including SO_2, at a rate that is too rapid for complete absorption in the solutions or for detection by the IR cell.

The gravimetric determination of sulfate can be and is most often used to finish the Eschka and combustion vessel-washing methods. The most serious problem that arises concerns the $BaSO_4$ precipitate. It may be extremely fine and difficult to filter. One way to obtain a $BaSO_4$ precipitate that is easily filtered is to add the $BaCl_2$ precipitant rapidly to the hot solution and stir the mixture vigorously. Heating and digestion for a lengthy period improve the filterability of the precipitate. Addition of a slurry of filter paper, prepared by digesting small pieces of paper in hot water, acts as a filter aid. After filtering, the precipitate must be washed several times with hot water to remove adsorbed materials that will cause the results to be too high. $BaSO_4$ is a rather strong adsorbing agent and readily adsorbs iron during the precipitation. Whenever the iron content of the coal sample is high, the iron should be removed through precipitation and filtering before the sulfate is precipitated.

In the high-temperature combustion methods, the determination of sulfur depends on the detection of SO_2 in the combustion gas. The following equation represents the SO_2/sulfur trioxide (SO_3) equilibrium.

$$SO_2 + 0.5\ O_2 \leftrightarrow SO_3 \quad \Delta H = -99.0\ \text{kJ/mol} \tag{6.7}$$

This is the principal reaction in the "Contact Process" for the manufacture of sulfuric acid. The maximum amount of SO_3 is produced when a vanadium pentoxide catalyst is used at a temperature of 400-450°C. The reaction is exothermic, and the equilibrium shifts to the left, producing more SO_2 as the temperature is raised. The maximum amount of SO_2, and minimum SO_3, occurs at temperatures of approximately 1350°C. The SO_2/SO_3 ratio decreases as the temperature is lowered. Stable operating temperatures are needed for better precision.

6.3.2 Interpretation and Uses of Total Sulfur Data

Total sulfur data are necessary for the effective control of the emissions of oxides of sulfur whenever coal is used as a fuel. The emission of sulfur oxides can lead to the corrosion of equipment and slagging of combustion or boiler equipment as well as contribute to atmospheric emissions. Therefore, sulfur data are necessary for the evaluation of coal to be used for combustion purposes.

Most coal conversion and cleaning processes require two sets of sulfur values: the sulfur content of the coal before it is used and the sulfur content of the products formed. In the coking of coal, some of the sulfur is removed in the coking process, which makes it necessary to obtain the before and after values. The commercial uses of coke, as in metallurgical processes, require low sulfur contents

and necessitate an accurate sulfur value for the coke. In coal gasification and liquefaction processes, the sulfur in the coal is sometimes carried through to the products. Therefore, it is necessary to determine the amount of sulfur in each of the products before it is used. One of the primary reasons for cleaning coal is to reduce the sulfur content. It is necessary to know the sulfur content before and after cleaning to evaluate the cleaning process.

Total sulfur values alone are not adequate in accessing a cleaning process for reducing the sulfur content of coal. Only pyritic sulfur can be removed by specific gravity separations, and its removal depends on the way the pyrite is distributed throughout the coal. If pyrite occurs as very small crystals widely dispersed in the coal, then it is almost impossible to remove by these methods. When pyrite occurs in large pieces, it can be successfully removed by specific gravity methods. Organic sulfur is usually uniformly dispersed throughout the organic material in coal and can only be reduced through chemical reactions that convert the sulfur-containing species to a material that can be physically separated from the coal.

6.4 Oxygen

Oxygen occurs in the organic and inorganic portions of coal. In the organic portion, oxygen is present in ether, hydroxyl, carboxyl, methoxyl, and carbonyl groups. In low-rank coals, the hydroxyl oxygen averages approximately 6–9 % of the coal whereas high-rank coals contain less than 1 %. The percentages of oxygen in ether, carbonyl, methoxyl, and carboxyl groups average from a few percent in low-rank and brown coals to almost no measurable value in high-rank coals [**42**].

The inorganic materials in coal that contain oxygen are the various forms of moisture, silicates, carbonates, oxides, and sulfates. The silicates are primarily aluminum silicates found in the shale-like portions. Most of the carbonate is calcium carbonate, the oxides are mainly iron oxides, and the sulfates are calcium and iron sulfates.

6.4.1 Determination of Oxygen Content

Currently, there is no direct ASTM method of determining oxygen content in coal. In an ultimate analysis, it is calculated by subtracting the sum of the percentages of C, H, N, S, and ash from 100. All values must be on the same basis. This estimated value is affected by errors incurred in the determinations of the values for the other elements and by changes in the mass of the ash-forming constituents on ignition. The oxygen value calculated as a percentage mass fraction of the analysis sample according to this procedure does not include the oxygen in the ash but it does include the oxygen in the moisture associated with the analysis sample. The oxygen and hydrogen values can then be recalculated so as not to include the hydrogen and oxygen in the sample moisture, which is a common practice in the coal industry.

The most widely used direct method of determining oxygen in coal is known as the Schütze-Unterzaucher method, with modifications by various workers and instruments [**43–45**]. The method has been developed into a standard test method

by the International Organization for Standardization (ISO). In ISO Test Method 1994, the general procedure is to pyrolyze the coal in a stream of dry nitrogen. The volatilized products are passed over carbon at 1100°C (900°C using a platinum-carbon catalyst), which converts the oxygen in the volatile products to carbon monoxide. The carbon monoxide is then oxidized to carbon dioxide, usually with iodine pentoxide, which releases free iodine. The iodine released can be determined titrimetrically or the carbon dioxide produced can be absorbed and determined gravimetrically to calculate the amount of oxygen in the original samples.

The basic principles involved in the Schütze-Unterzaucher method of determining the oxygen content of coal may lead one to believe it is relatively simple. However, the method is a complicated one, is time-consuming, requires special equipment and reagents, and has many other problems associated with its use. The varied sources of oxygen in coal—such as the oxygen in the moisture and water of hydration of mineral matter, the oxygen in carbonates, and the oxygen in silicates and other inorganic compounds in addition to the oxygen in the organic matter—all offer difficulties. The original procedure has been modified in several ways to reduce the contribution made by some of these oxygen sources to the determined oxygen value. Thorough drying in a nitrogen atmosphere before the pyrolysis of the sample minimizes the effect of moisture, and much of the mineral matter is removed by a specific gravity separation or chemical treatment with hydrochloric and hydrofluoric acid. The reduction of mineral matter minimizes the contribution that the water of hydration and the inorganic compounds (e.g., carbonates, silicates, oxides, and sulfates) make to the determined oxygen value. The oxygen value obtained by this method, after all of the pretreatment steps are taken to remove moisture and mineral matter, is essentially a measure of the oxygen contained in the organic matter in coal.

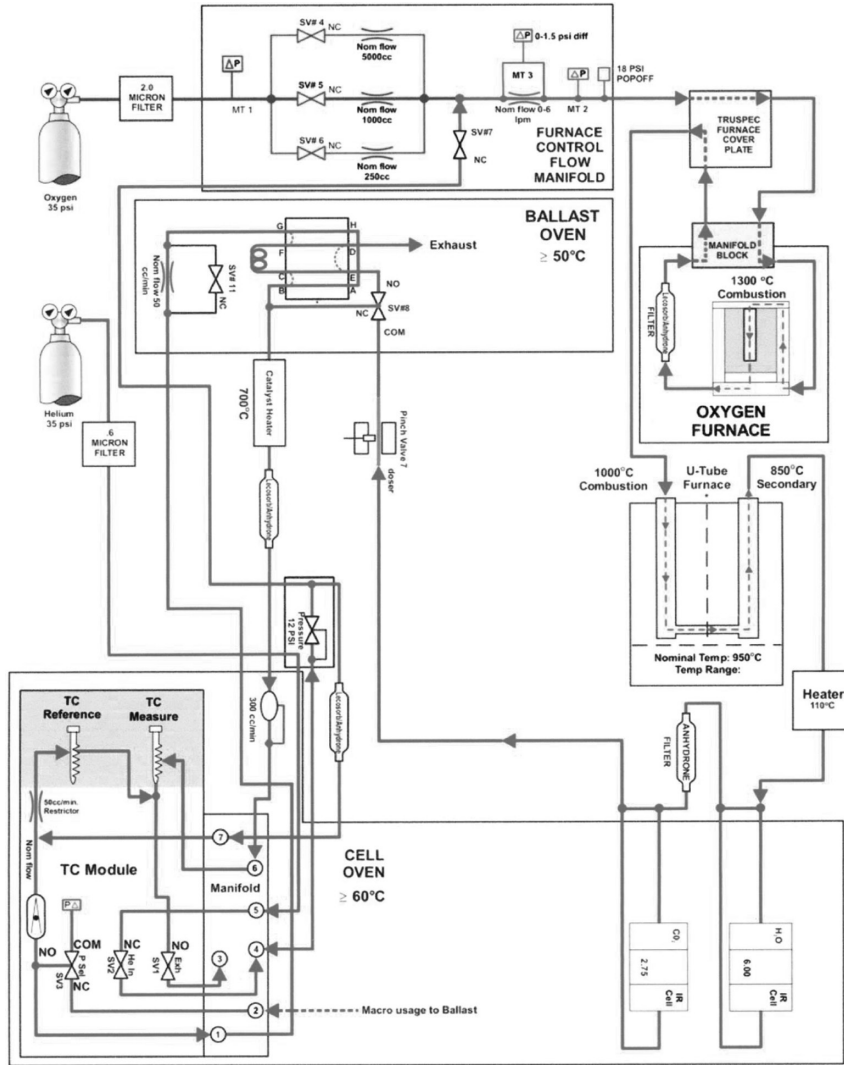
The precision and accuracy obtained in using the direct method of determining oxygen content is not as reliable as that obtained in other analytical methods used in coal analysis. However, the direct method does allow one to obtain a more precise value of the oxygen content of coal than can be obtained in the estimation of oxygen content by the difference method.

Figure 6.3 is a schematic diagram of an analytical instrument used to determine oxygen in coal, coke, and many other materials. The instrument uses a modification of the Schütze-Unterzaucher procedure in that it uses the pyrolysis over a carbon catalyst and release of oxygen-containing materials in helium, converting the oxygen-containing materials first to carbon monoxide in the pyrolysis furnace (1300°C) and then to carbon dioxide in the second furnace at a temperature of 1000°C. The oxygen is then determined by measuring the carbon dioxide produced with an IR absorption cell.

6.4.2 Interpretation and Uses of Oxygen Data

When the oxygen value is estimated by subtracting the determined percentages of all other constituents from 100, the errors in the determined values are reflected in

FIG. 6.3 Schematic diagram of an analytical instrument for the determination of oxygen.



Source: LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI.

the estimated oxygen value. These errors may be partially compensating or they may be additive. It is important that accurate determinations are made and appropriate corrections for overlapping values, especially hydrogen, be calculated.

The following is an expression for calculating the percentage oxygen according to the ASTM definition:

$$O_x = 100 - [C + H + N + S + \text{ash}] \tag{6.8}$$

where:

C = the total carbon,
H = the total hydrogen,
N = the total nitrogen,
S = the total sulfur, and
ash is the high-temperature ash.

All parameters in **Eq. 6.8** are determined by one of the previously discussed ASTM test methods and all must be reported on the same basis (to be discussed later). All of these values above pertain to those obtained from the analysis sample, and the simplest calculations are performed with the as-determined values. The total carbon represents the organic and the carbonate carbon. The total hydrogen represents the organic hydrogen, the hydrogen in the residual moisture, and the hydrogen in the water of hydration of mineral matter. The total sulfur value in coal represents that which is contained in the organic matter, pyrites, and sulfates. Ash is mostly metal and silicon oxides. Therefore, the estimated value of the oxygen includes the oxygen contained in the organic matter, in the moisture, and in the mineral matter, except that which is combined with metals in coal ash.

A rough estimate of the oxygen contained in the organic matter in coal can be obtained by correcting the oxygen value obtained by **Eq. 6.8** for the oxygen in residual moisture and water of hydration of mineral matter. Adding this correction to the sum subtracted from 100 gives the following expression:

$$O_x = 100 - [C + H + N + S + \text{ash} + 8/9\ (H_2O + H_2O \text{ of hydration})] \tag{6.9}$$

where:

H_2O = as-determined residual moisture and
H_2O of hydration = 8.0% of ash.

Several improvements in the estimation of organic oxygen can be made when the analytical data are available. Values for chlorine, carbon dioxide, pyritic sulfur, and sulfur in coal ash are helpful in improving the estimation. Failure to include the chlorine value in the sum subtracted from 100 according to **Eq. 6.8** leads to a high value for the organic oxygen. This oxygen value should also be reduced for the oxygen present in the carbon dioxide that is associated with the mineral matter. The inclusion of total sulfur and ash in the sum that is subtracted from 100 % in

estimating the oxygen content of coal lowers the oxygen value because part of the sulfur may be retained in the ash. Therefore, the sulfur that is retained is counted twice in the sum for subtraction. Correcting the coal ash for the SO_3 present compensates for this error. Likewise, the coal ash should be corrected for any Fe_2O_3 that results from the heating of pyrite (FeS_2) in air, as is done in the ashing process. In the ashing process, three oxygen atoms replace four sulfur atoms, as is illustrated by the equation

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \tag{6.10}$$

On a mass basis, 48 parts of oxygen replace 128 parts of sulfur. This oxygen is from an external source and not from the coal itself. Because this oxygen contributes to the mass of the ash, a correction of 3/8 of the pyritic sulfur value is necessary. The pyritic sulfur that is replaced is accounted for in the total sulfur value. When the values are available to make these corrections, a good estimate of the percentage of oxygen in the organic or combustible portion of coal can be made, according to the following formula:

$$\begin{aligned} O_x = 100 - [&C + H + N + S + Cl + (\text{ash} - 3/8S_p - SO_3 \text{ in ash}) \\ &+ 8/9(H_2O + H_2O \text{ of hydration}) + 32/44\ CO_2] \end{aligned} \tag{6.11}$$

where:

Cl = chlorine,
S_p = pyritic sulfur,
SO_3 in ash = sulfur trioxide in ash, and
CO_2 = carbon dioxide in coal.

All other terms are as given in the previous formulas, and all values are expressed as mass percentages.

In the uses and applications of oxygen data, the most important value is the oxygen content of the organic matter in coal. This can be estimated by one of the above formulas, depending on the information available. If the oxygen is determined directly, using one of the methods previously discussed, then the oxygen value in this case represents the total oxygen and includes the organic and inorganic oxygen. In calculating heat balances for boiler efficiency studies, it is important that an accurate value of the combustible material in coal be obtained. Thus, a correction for the oxygen content of the organic matter of coal should be made. Of course, corrections to the carbon and hydrogen values for the amount of these elements found in the moisture and inorganic constituents of coal should also be made. Oxygen data are used for determining the suitability of coals for coking, liquefaction, or gasification processes. In general, coals with high oxygen contents are unsuitable for coking but may be more reactive and thus easier to gasify or liquefy.

Chapter 7 | Calculating Coal Analyses from As-Determined Values to Different Bases

The results of a coal analysis may be reported on any of several bases, differing from each other in the manner by which moisture and ash are treated. Except for data reported on a dry basis, it is essential that an appropriate moisture content be given in the data report. This would avoid ambiguity and provide a means for conversion of data to other bases. These bases are defined in ASTM **D121** [**2**] and include the following:

- *As-determined basis (ad):* The basis for analytical data obtained from an analysis sample of coal or coke after conditioning and preparation to USA Standard No. 60 (250 μm) sieve in accordance with ASTM **D2013**. As-determined data represent the numerical values obtained at the particular moisture level in the analysis sample at the time of the analysis.
- *As-received basis (ar):* The basis for analytical data calculated to the moisture condition of the sample as it arrived at the laboratory and before any processing or conditioning. If the sample has been maintained in a sealed state so there has been no gain or loss, then the as-received basis is equivalent to the moisture basis as sampled.
- *Dry basis (d):* The basis for analytical data calculated to a theoretical basis of no moisture associated with the sample. The numerical value as established in ASTM **D3173** or **D7582** is used for converting the as-determined data to a dry basis.
- *Dry, ash-free basis (daf):* The basis for data calculated to a theoretical basis of no moisture or ash associated with the sample. Numerical values as established by ASTM **D3173** and **D3174**, or **D7582**, are used for converting the as-determined data to a moisture- and ash-free basis.
- *Equilibrium moisture basis*: The basis for data calculated to the moisture level established as the equilibrium moisture. Numerical values as established by ASTM **D1412** are used for the calculation to an equilibrium moisture basis.

It should be noted that if a coal sample is analyzed over a period of time, or in different laboratories with different temperature and humidity conditions, there will

be more than one as-determined moisture value. Ideally, a split for moisture should be weighed at the same time and under the same conditions for each separate analysis. Also, it should be noted that samples previously processed, including grinding and air-drying, are not as-received samples even if they arrived at the laboratory in that condition. They are as-determined samples and a new moisture value should be determined.

7.1 Formulas for Converting Data

In converting from the as-determined *(ad)* basis to the as-received *(ar)* basis, the following formulas are used (all values are expressed in percentage mass fraction).

For moisture *(M)*,

$$M_{ar} = M_{ad} \times (100 - ADL)/100 + ADL \tag{7.1}$$

where ADL = air-dry loss in percentage mass fraction of as-received sample (see Eqs. 5.1 and 5.2).

For hydrogen (H) and oxygen (O), including the hydrogen and oxygen in the moisture associated with the sample,

$$\mathrm{H}_{ar} = (\mathrm{H}_{ad} - 0.1119\, M_{ad}) \times (100 - ADL)/100 + 0.1119\, M_{ar} \tag{7.2}$$

$$\mathrm{O}_{ar} = (\mathrm{O}_{ad} - 0.8881\, M_{ad}) \times (100 - ADL)/100 + 0.8881\, M_{ar} \tag{7.3}$$

For hydrogen and oxygen not including the hydrogen and oxygen in the moisture associated with the sample,

$$\mathrm{H}_{ar} = (\mathrm{H}_{ad} - 0.1119\, M_{ad}) \times (100 - ADL)/100 \tag{7.4}$$

$$\mathrm{O}_{ar} = (\mathrm{O}_{ad} - 0.8881\, M_{ad}) \times (100 - ADL)/100 \tag{7.5}$$

In converting from the as-determined to the dry *(d)* basis, the following formulas apply to hydrogen and oxygen:

$$\mathrm{H}_{d} = (\mathrm{H}_{ad} - 0.1119\, M_{ad}) \times 100/(100 - M_{ad}) \tag{7.6}$$

$$\mathrm{O}_{d} = (\mathrm{O}_{ad} - 0.881\, M_{ad}) \times 100/(100 - M_{ad}) \tag{7.7}$$

In converting all other parameters from one basis to another, the following general formula applies when using the appropriate conversion factor from **Table 7.1**:

$$\mathrm{P}_{\text{wanted}} = \mathrm{P}_{\text{given}} \times \text{conversion factor} \tag{7.8}$$

TABLE 7.1 Conversion Factor Chart

Given	Wanted			
	As-Determined (*ad*)	As-Received (*ar*)	Dry (*d*)	Dry, Ash-Free (*daf*)
As-determined (*ad*)	…	$\frac{100 - ADL}{100}$	$\frac{100}{100 - M_{ad}}$	$\frac{100}{100 - M_{ad} - A_{ad}}$
As-received (*ar*)	$\frac{100}{100 - ADL}$	…	$\frac{100}{100 - M_{ar}}$	$\frac{100}{100 - M_{ar} - A_{ar}}$
Dry (*d*)	$\frac{100 - M_{ad}}{100}$	$\frac{100 - M_{ar}}{100}$	…	$\frac{100}{100 - A_{d}}$
Dry, ash-free (*daf*)	$\frac{100 - M_{ad} - A_{ad}}{100}$	$\frac{100 - M_{ar} - A_{ar}}{100}$	$\frac{100 - A_{d}}{100}$	…

The parameters to which Eq. 7.8 and **Table 7.1** apply are the following:

Ash (A)	Fixed carbon
Calorific value (gross)	Nitrogen
Carbon	Sulfur
Chlorine	Sulfur forms (pyritic, sulfate, and organic)
Carbon Dioxide	Volatile matter

The parameters must be expressed as percentage mass fraction, except for gross calorific value, which is expressed as British thermal units per pound. An example of ultimate analysis data that has been calculated to various bases is given in **Table 7.2**. Additional information and formulas for converting data to other bases can be found in ASTM Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases (**D3180**).

The diagram shown in **Fig. 7.1** can be used to illustrate the formulas given in **Table 7.1**. When converting a fuel parameter from one base to one of the other three bases, the conversion factor (as shown in **Table 7.1**) contains the term, or terms, shown on the curve linking the two bases.

Assume that a coal, coke, or other fuel sample is delivered to a laboratory for analysis. Unless noted otherwise in the papers delivered with the sample, the sample's condition upon delivery would be considered to be "as-received." Once the sample is dried, using one of the ASTM standard methods, the sample is altered by removing part of the original material—the moisture. This means the percentage of the other components in the sample increases because the base has changed. Thus, when the amount of a component in the original sample is multiplied by the appropriate conversion factor, its percentage increases. Likewise, when the amount of a particular parameter is calculated back to an as-received base, the percentage of the parameter decreases

TABLE 7.2 Ultimate Analysis Data Calculated to Different Bases

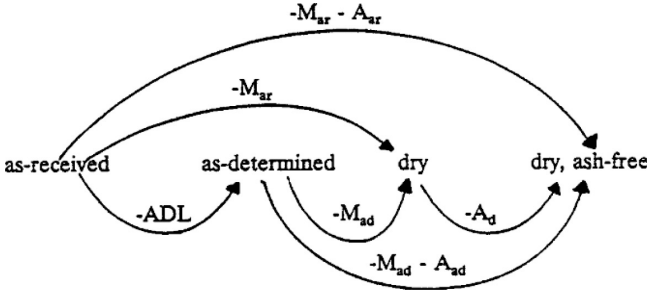
Parameter[a]	As-Determined	As-Received[b]	As-Received[c]	Dry	Dry Ash-Free
Carbon	68.30	64.48	64.48	73.21	79.24
Hydrogen	5.49	5.81	4.48	5.08	5.50
Nitrogen	1.19	1.12	1.12	1.28	1.38
Sulfur	2.60	2.45	2.45	2.79	3.02
Ash	7.11	6.71	6.71	7.62	
Oxygen	15.31	19.43	8.84	10.02	10.86
Total percent	100.0	100.0	88.08	100.00	100.00
Moisture					
Air-dry loss moisture	5.60				
Moisture (analysis sample)	6.70				
Total moisture			11.92		
Total percent			100.00		

[a]All values are given in percent mass fraction.

[b]Hydrogen and oxygen include H and O in the sample moisture (M_{ar}).

[c]Hydrogen and oxygen do not include H and O in the sample moisture (M_{ar}).

FIG. 7.1 Base conversion diagram.



because the base has changed, or calculated back to its original state. **Table 7.1** gives examples of data calculated to different bases.

7.1.1 Comparison of Intralaboratory and Interlaboratory Data

The various bases are used to compare analytical data within a laboratory (intralaboratory) and between laboratories (interlaboratory). Most parameters are compared on

a dry or as-received basis. Dry basis values factor out the moisture in the sample. Checking the repeatability interval is done using values calculated to a dry basis. Any changes in the moisture during the analysis period due to loss (or gain) of moisture upon sitting for days in the laboratory can be tracked by measuring the moisture content again. A suggested practice is to measure the moisture content of a sample within 48 h of an analytical measurement.

Comparing the dry, ash-free values for samples from the same source (seam and maybe a mine) is quite helpful. The dry, ash-free Btu values for coals from the same source should agree within approximately 100 Btu. Differences greater than 100 Btu lead one to quickly check three parameters: moisture, ash, and calorific value. The most common error is a recording error.

Dry basis is the only acceptable way for comparing interlaboratory results for a coal or coke sample. Dry basis values are used for checking reproducibility values. The dry, ash-free basis is also very useful for comparing between-laboratory values.

Chapter 8 | Miscellaneous Analysis

The category of miscellaneous analysis encompasses element-related analyses—such as chlorine, forms of sulfur, forms of carbon, carbon dioxide (CO_2), major and minor elements in ash analysis, and trace elements in coal—as well as special tests—such as the determination of the calorific value, fusibility of coal and coke ash, free-swelling index, grindability, and plastic properties of coal. Other tests can be included in this category, but those listed are discussed here.

8.1 Chlorine

The chlorine content of coal is normally low, usually only a few tenths of a percent or less. It occurs predominantly as sodium, potassium, and calcium chlorides, with magnesium and iron chlorides present in some coals. There is some evidence that chlorine may also be combined with the organic matter in coal [**46**], but exhaustive studies over the past 20 years have all but ruled out the existence of compounds in coal in which chlorine is directly bonded to carbon.

8.1.1 Determination of Chlorine Content

Methods of converting the chlorine in coal into a form suitable for its determination involve combusting the sample, with or without a combustion aid. There are three ASTM standard methods of determining chlorine in coal:

1. *ASTM **D2361**:* Chlorine in Coal
2. *ASTM **D4208**:* Total Chlorine in Coal by the Oxygen Bomb Combustion/ Ion-Selective Electrode Method
3. *ASTM **D6721**:* Determination of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry

The classical ASTM **D2361** Test Method for Chlorine offers a choice of two procedures for combusting the coal sample. In the combustion vessel procedure, the oxygen combustion vessel used is the same as, or very similar to, that used in the determination of the calorific value of coal and coke. In the determination, 1 g of the analysis sample of coal is placed in a crucible inside of an oxygen combustion vessel. An ammonium carbonate solution is added to the vessel to trap the chloride-containing species

produced in the combustion. After charging with oxygen to 25 atm, the vessel is fired and allowed to stand in the calorimeter water for at least 10 min. The pressure on the vessel is then released slowly, the vessel is disassembled, and all parts of the vessel interior are washed with water. The washings are collected in a beaker and acidified with nitric acid (HNO_3). The amount of chloride in the solution is then determined by a potentiometric titration with silver nitrate solution.

In the second procedure of ASTM **D2361**, 1 g of the coal analysis sample is mixed with 3 g of Eschka mixture in a suitable crucible. The Eschka mixture is a combination of two parts by weight of magnesium oxide and one part of anhydrous sodium carbonate. The coal mixture is covered with an additional 2 g of Eschka mixture to ensure that no chlorine is lost during combustion. The mixture is then ignited gradually in a muffle furnace by raising the temperature to 675°C ± 25°C within 1 h. This temperature is maintained for 1.5 h before cooling. The incinerated mixture is washed with hot water into a beaker. The contents of the beaker are acidified with HNO_3, and the chloride is determined as in the previously described procedure.

ASTM **D2361** was withdrawn from publication in 2008. The method was not applicable to coals with less than 300 ppm chlorine; therefore, its use as a standard test method was limited.

In ASTM **D4208**, 1 g of the analysis sample of coal is placed in a crucible inside of an oxygen combustion vessel used in determining the calorific value of coal. A sodium carbonate solution is added to the vessel to trap the chloride-containing species produced. After charging with oxygen to 25 atm, the vessel is fired and allowed to stand in the calorimeter water for at least 15 min. After the pressure is slowly released, the vessel is disassembled, and all parts of the combustion vessel interior are washed with water. The washings are collected, an ionic strength adjuster (sodium nitrate [$NaNO_3$]) is added, and the chloride is determined with an ion-selective electrode by the standard addition method.

In both methods described above, it is possible to lose some of the chlorine during combustion unless necessary precautions are taken. Thoroughly mixing the coal sample with Eschka mixture and carefully covering this with additional Eschka mixture will minimize the loss of chlorine. In the combustion vessel methods, the ammonium and sodium carbonate solutions in the vessel are used to absorb the chlorine as it is released in the combustion. The 10- and 15-min waiting periods and the slow release of the pressure on the combustion vessel also help to prevent the loss of chlorine.

In ASTM **D6721**, the newest standard test method for chlorine, the coal sample is combusted in humidified oxygen at 900°C. A tungsten accelerator helps in the combustion and release of chlorine, which is converted to hydrogen chloride during the moist oxygen combustion. The hydrogen chloride is captured in a titration cell and determined by microcoulometry.

In an Interlaboratory Study (ILS) comparing various methods for chlorine determination, ASTM **D2361** and **D4208** gave an unacceptable performance for the determination of chlorine in coal at levels below 200 ppm [**47**]. The instrumental

method, ASTM **D6721**, was shown to give the best performance for determining low levels of chlorine in coal, as is illustrated in the precision and bias statement of **D6721**.

One of the reasons for the very good performance of ASTM **D6721** for determining chlorine is the excellent recovery of chlorine as hydrogen chloride during the combustion process. This recovery is due to the "Deacon reaction" [**48**], which is illustrated by the equation

$$2Cl_2 + 2\,H_2O \leftrightarrow 4HCl + O_2 \tag{8.1}$$

During the high-temperature combustion of organic materials containing chlorides, atomic chlorine and molecular chlorine are formed, both of which are extremely reactive. Molecular chlorine and atomic chlorine react with almost all materials at slightly elevated temperatures. As the molecular chlorine and atomic chlorine exit the combustion zone and start to cool, they will likely react with most materials, inorganic and organic, and are lost from the exit stream. If the chlorine is converted to gaseous hydrogen chloride, via the Deacon reaction, then the chlorine is less likely to be lost in the exit stream. Using moist (humidified) oxygen as the combustion gas ensures that there is always an excess of water to drive the Deacon reaction (Eq. 8.1) to the right, converting the chlorine to gaseous hydrogen chloride.

8.1.2 Interpretation and Uses of Chlorine Data

The chlorine in coal and in the products derived from coal is known to contribute significantly to the corrosion of the coal handling and processing equipment. Because the corrosion of this equipment is the result of several causes, one being the chlorine content of coal, it is difficult to predict the degree of corrosion within a given time frame. It is equally as difficult to predict the degree to which the chlorine content contributes to the corrosion, other than the general prediction that the higher the chlorine content, the greater the chances for corrosion of the equipment. As a general rule, coals with high chlorine contents are less desirable.

Chlorine data are used in ultimate analysis to improve the estimate of oxygen by difference. The chlorine value is included in the sum of the items determined, which, when subtracted from 100, gives an estimate of the oxygen content of coal.

Recent studies of mercury emissions from power plants have shown that coal chlorine content plays a prominent role in the formation of oxidized mercury in flue gas. Higher concentrations of oxidized mercury are found in utility flue gases when the coal chlorine is high, or approximately 0.1–0.3 % by weight [**49, 50**]. Chlorine promotes the oxidation of mercury in flue gas. Oxidized mercury is more easily absorbed on fly ash and removed by ash collection and scrubber systems [**51–53**]. Sulfur was also shown to promote the oxidation of mercury in the flue gas, but high sulfur dioxide (SO_2) concentrations interfere with the absorption of oxidized mercury species on fly ash and subsequent removal [**52,53**].

8.2 Forms of Sulfur

Sulfur occurs in coal as inorganic sulfates, as pyrites (disulfides), as sulfides (small amounts of galena, pyrhotite, etc.), and in combination with the organic matter. Organic sulfur and pyrites are the predominant forms of sulfur in most coals. Sulfate sulfur is usually less than 0.1 %, except in weathered coal containing an appreciable amount of pyrites or coals high in alkaline sulfates. The pyritic sulfur content varies considerably more than does the organic sulfur content and is of more interest because it is the form that can be most easily removed from coal by current preparation practices.

8.2.1 Determination of the Content of the Forms of Sulfur

The procedures for determining the forms of sulfur in coal are described in ASTM Test Method for Forms of Sulfur in Coal (**D2492**). In this method, the sulfate sulfur is determined directly, the pyritic sulfur is determined as the amount of pyritic iron, and the organic sulfur is taken as the difference between the total sulfur and the sum of the sulfate and pyritic sulfur.

In the determination of sulfate, 2–5 g of the analysis sample are mixed with hydrochloric acid (HCl; two volumes concentrated HCl + three volumes of water) and the mixture is gently boiled for 30 min. After filtering and washing, the undissolved coal may be retained for the determination of pyritic sulfur, or it may be discarded and a fresh sample used for pyritic sulfur. Saturated bromine water is added to the filtrate to oxidize all sulfur forms to sulfate ions and ferrous ions to ferric ions. After boiling to remove excess bromine, the iron is precipitated with excess ammonia and filtered. This precipitate must be retained for the determination of nonpyritic iron if a fresh sample of coal was used for the determination of the pyritic iron. The sulfate is then precipitated with barium chloride ($BaCl_2$), and the barium sulfate ($BaSO_4$) is determined gravimetrically.

The residue from the sulfate determination is used for the determination of pyritic sulfur content. Two procedures are allowed, one by extracting the pyrite from the sample with dilute HNO_3 (Referee Method) and the other by extracting the iron from the ash produced by the combustion of the residue (Alternative Method). In the Referee Method, the sample is added to dilute HNO_3 and the mixture boiled gently for 30 min or allowed to stand overnight. This treatment oxidizes iron species to iron (III) and inorganic sulfur compounds to sulfate. The mixture is then filtered, and the filtrate is saved for the determination of iron by atomic absorption spectrometry (AAS) or by a titration procedure. If iron is to be determined by the atomic absorption method, no further work is done on the filtrate other than to dilute it to an appropriate volume before the determination. If a titration method is to be used for the determination of iron, then the filtrate is treated with 30 % hydrogen peroxide (H_2O_2) to destroy any coloration arising from the coal. The iron is then precipitated, filtered, and washed. The precipitate is then dissolved in HCl, and the iron is determined by titration with either potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).

In the Alternative Method, the iron originally present as pyrite is extracted from the incinerated ash of the residue. The iron is then determined by AAS or by titration.

If a new sample was used for the determination of the pyritic iron, then the iron determined by these procedures represents the combination of the pyritic and nonpyritic iron. The amount of nonpyritic iron must then be determined separately and subtracted from the amount determined by the methods described here. If the residue from the sulfate determination was used, then the iron determined by the above procedures represents the pyritic iron. Once the correct value for the pyritic iron is determined, the pyritic sulfur is calculated using the following expression:

$$\% \text{ Pyritic sulfur} = \% \text{ Pyritic iron} \times 2 \times 32.06/55.85 \tag{8.2}$$

where $2 \times 32.06 / 55.85$ is the ratio of sulfur to iron in pyrite.

Some difficulties encountered in determining the amounts of the various forms of sulfur in coal are adsorption of other materials on $BaSO_4$ when it is precipitated, inability to extract all of the pyritic sulfur from the coal during the extraction process, and possible oxidation of pyritic sulfur to sulfate in the pulverization and storage of the coal sample. The adsorption of other materials on $BaSO_4$ and the oxidation of pyritic sulfur lead to high values for the sulfate sulfur. Iron ions are readily adsorbed on $BaSO_4$, which could be particularly objectionable for coals containing large amounts of nonpyritic iron. Removal of the iron by precipitation and filtration before the precipitation of $BaSO_4$ minimizes the adsorption of the iron. Inadequate pulverization and mixing of the sample appear to be the major causes of the incomplete extraction of pyritic sulfur from coal. A very small amount of organic sulfur may also be extracted with the pyritic sulfur. For this reason, the amount of pyritic iron extracted is used as a measure of the pyritic sulfur. To control the oxidation of pyritic sulfur to sulfates, exposure of the coal sample to the atmosphere at elevated temperatures should be avoided and the sample should be analyzed as soon as possible. A discussion of other problems associated with the determination of sulfur forms, as well as efforts to develop new methods of analysis, has been given by Kuhn [**54**].

On the basis of matched pair comparison at the 95 % confidence level, the Alternative Method for the determination of pyritic sulfur was found to have a high relative bias with respect to the Referee Method. The minimum detectable bias for the coals tested was 0.06 % (absolute) [**55**]. This information is consistent with the information for extraction procedures in the Kuhn report previously mentioned [**56**].

Other reported procedures for sulfur forms analysis include the Lithium Aluminum Hydride Method, in which sulfate sulfur and nonpyritic iron are removed with HCl, pyrite is extracted with lithium aluminum hydride ($LiAlH_4$) in tetrahydrofuran, and organic sulfur is determined in the extracted residue. The determined organic sulfur values are 0.2–0.3 % lower than the calculated ASTM organic sulfur values [**56**]. Scanning electron microscopy-energy dispersive X-ray spectrometry

(SEM-EDX; or scanning electron microscopy-energy dispersive X-ray microanalysis [SEM-XRMA]) has been successfully used to determine organic sulfur [**57**]. Good agreement with ASTM **D2492** was obtained. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies have also been used to examine the sulfur compounds in coal [**58-60**].

In one reported study, coals of different ranks were reduced to a very small particle size and physically cleaned to reduce their mineral matter to 2–3 %. The dry, ash-free (*daf*) sulfur values for these deep-cleaned coals showed very good agreement with the *daf* sulfur values of the coals that had been extracted with 2 M HNO_3. Because the physical cleaning of the coals removes almost all of the sulfate, pyritic, and other mineral sulfur, it is assumed that only the organic sulfur remained in the deep-cleaned coals. Likewise, extraction of the coal with 2 M HNO_3 removes all sulfate, pyritic, and other mineral sulfur and some other minerals. Calculating the extracted residues to a *daf* basis allows the comparison of the organic sulfur values of the two types of materials. The *daf* organic sulfur values calculated by ASTM **D2492** for the coals used in the study were an average of 26 % higher than the *daf* sulfur values in the HNO_3-extracted and deep-cleaned samples [**61**].

An ASTM Task Group is currently working on an ILS to develop new procedures for the determination of forms of sulfur in coal. The proposed method involves the extraction of sulfate sulfur from coal with dilute HCl. The coal sample from this extraction is then extracted with dilute HNO_3 to dissolve the pyritic sulfur. The sample is then filtered, washed with deionized water, and then washed with HCl to ensure complete extraction of the pyritic iron. These extractions are essentially the same as those in the current method. The proposed procedures call for the determination of sulfate sulfur and pyritic iron using inductively coupled plasma-atomic emission spectrometry (ICP-AES), which is different from the current method. Organic sulfur is then calculated as the difference between the total sulfur and the sum of the sulfate and pyritic sulfur [**62**].

8.2.2 Interpretation and Uses of Forms of Sulfur Data

The principal use of forms of sulfur data is in connection with the cleaning of coal. Within certain limits, pyritic sulfur can be removed from coal by gravity separation methods whereas organic sulfur cannot. Therefore, pyritic sulfur content can be used to predict how much sulfur can be removed from the coal and to evaluate cleaning processes. If the pyritic sulfur occurs in layers, then it usually can be removed efficiently. If it occurs as fine crystals dispersed throughout the coal, then its removal is very difficult.

Other uses of forms of sulfur data are the inclusion of the pyritic sulfur value in the formula for the estimation of oxygen by difference and as a possible means of predicting the extent of weathering of coal. The sulfate concentration increases upon weathering, so the sulfate sulfur value could be used as an indication of the extent of weathering of coal.

8.3 CO_2 in Coal

Most coals contain small amounts of mineral carbonates made up primarily of calcium carbonate and to a lesser extent ferrous and other metal carbonates. Some coals contain a comparatively large amount of the inorganic carbonates, and the determination of CO_2 content is required in estimating the mineral matter content of these high-carbonate coals.

8.3.1 Determination of CO_2 Content

In summary, the determination of the CO_2 content of coal is made by decomposing, in a closed system, a weighed sample of coal with HCl, which liberates the CO_2. This is absorbed in a CO_2 absorbent, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) on an inert carrier. The increase in mass of the absorbent is a measure of the CO_2 released by the coal sample, which can be used to calculate the amount of mineral carbonates in the coal.

Because of the small amount of CO_2 in coal and the difficulty of accurately measuring the CO_2 that is liberated, some strict requirements have been set for the construction and design of the apparatus to be used. These requirements are given in detail in ASTM Test Method for Determination as Carbon Dioxide of Carbonate Carbon in Coal (**D1756**). The apparatus must contain an air flow meter and purifying train, a reaction unit fitted with a separatory funnel and water-cooled condenser, a unit for removing interfering gases, and an absorber. The air-purifying train removes all CO_2 and the water-cooled condenser removes moisture before it can enter the absorption train. Acid-forming gases, such as SO_2, hydrogen sulfide (H_2S), and halogen acids are produced in the reaction and must be removed before entering the CO_2 absorber. Otherwise, they will be weighed as absorbed and measured as CO_2. Anhydrous copper sulfate on pumice or granular silver sulfate is positioned in the absorption train to remove these interfering gases from the air stream before it enters the CO_2 absorber. The entire system must be gas-tight to prevent error, and a time schedule is specified to ensure repeatability and reproducibility.

8.3.2 Interpretation and Uses of CO_2 Data

The CO_2 value is used primarily in the estimation of the mineral matter of high-carbonate coals. When the CO_2 value is high, it is also used to correct volatile matter values. A high value indicates a large amount of calcium carbonate, which can retain sulfur oxides as sulfate quite readily during combustion. Consequently, this also gives a high ash value.

8.4 Calorific Value of Coal

The calorific value of a coal is primarily the combined heats of combustion of the carbon, hydrogen, nitrogen, and sulfur in the organic matter and of the sulfur in pyrite. The energy released upon combustion is of primary interest to coal producers and users. The calorific value, on a specified basis, is one of the more important parameters used in the classification of coals.

8.4.1 Determination of the Gross Calorific Value of Coal

The common method of determining the gross calorific value of coal is with either an adiabatic or an isoperibol calorimeter. The procedures for using these calorimeters are specified in ASTM Test Method for the Gross Calorific Value of Coal and Coke (**D5865**). In these procedures, a weighed sample is burned in an oxygen combustion vessel immersed in water in a container surrounded by a jacket. In an adiabatic calorimeter system, the jacket temperature is adjusted during the measurement so that it is essentially the same as the calorimeter water temperature. In an isoperibol calorimeter system, the temperature rise of the calorimeter water is corrected for the heat lost to or gained from the surrounding jacket during measurement. In both systems, the corrected temperature rise times the energy equivalent of the calorimeter gives the total amount of heat produced from burning the sample. The energy equivalent (also called the *water equivalent* or *heat capacity*) of the calorimeter is determined by burning standard samples of benzoic acid.

ASTM **D5865** allows for determining or calculating the acid corrections needed to determine the gross calorific value of the solid fuel. In the determination of the acid correction, the contents of the combustion vessel after firing are washed into a beaker and titrated with standard sodium carbonate solution to determine the amount of acid (HNO_3 and H_2SO_4) produced in the combustion. In the calculated acid correction, the amount of acid (HNO_3) produced during the test firing of benzoic acid is calculated (per gram of benzoic acid). An additional correction for the H_2SO_4 produced (from sulfur in the sample) is also calculated. Corrections for the amount of acid, the amount of fuse wire or cotton thread used in firing, and the sulfur content of the sample are made to the total heat produced in the calorimeter (energy equivalent times corrected temperature rise) to determine the gross calorific value of the solid fuel.

Perhaps the greatest potential for error in this method is in temperature measurement. If mercury in glass thermometers is used, then they must be properly calibrated and consistent readings must be made. Modern calorimeters are equipped with digital thermometers or with thermocouple or thermistor probes and microprocessors to control the firing and record the temperatures at prescribed intervals. This alleviates most of the human error in recording the temperature changes.

Igniting the coal sample in the oxygen combustion vessel can be difficult. The sample may be blown out of the crucible by introducing the oxygen too quickly. Pressing the coal sample into a pellet may prevent the sample from blowing out. Coals with a high mineral content are hard to ignite, and mixing the sample with a measured amount of standard benzoic acid and pelleting may be helpful.

After firing, restoring the combustion vessel pressure to atmospheric pressure too rapidly may result in the loss of oxides of sulfur and nitrogen. A correction must be made to the gross calorific value for the amounts of these acid-forming oxides produced in the combustion vessel. Their loss results in a high calorific value. The pressure of the combustion vessel must be restored very slowly to prevent this.

The equipment used must be checked periodically for any changes in the energy equivalent of the calorimeter; any corrosion or damage to the calorimeter bucket; any damage (however slight it may be) to the oxygen combustion vessel; and any malfunction of the stirrers, electrical system, or other parts of the calorimeter. Any of these changes or malfunctions may change the energy equivalent of the calorimeter or introduce extra heat, which would lead to errors in the measured calorific value.

8.4.2 Predicting the Calorific Value from Elemental Analysis

For many years, the calorific values for pure organic compounds have been estimated from their elemental composition. This relationship has allowed chemists to calculate the standard heats of formation of pure organic compounds. Estimating the calorific values of coals from elemental composition has become a very desirable practice because such formulas can be used with on-line elemental analyzers. **Table 8.1** lists the coefficients of a general equation used to estimate the calorific value from elemental analysis data [**63–65**]. In the table, the two Francis-Lloyd equations represent attempts to estimate the calorific value from the enthalpies of combustion of pure compounds (Table Eq. 2) and from the calorific values of various coals (Table Eq. 1). Both equations were derived by multiple linear regression analysis. In the derivation of Table Eq. 2, there was a systematic offset of approximately 419 Btu/lb, which appears as the intercept in the correlation equation.

Table 8.2 lists the relative accuracies of predicting the calorific values of various groups of coals using the formulas. The average errors are comparatively small considering the multiplicity of errors possible in measuring the percentages of the various elements. In the *Journal of Coal Quality* article, the value of ±0.5 kJ/g was used for comparison. The 0.5-kJ/g value is equivalent to 215 Btu/lb [**63**].

TABLE 8.1 Coefficients of the Equation for Estimating Calorific Values from the Elemental Composition of Materials[A]

Author	a	b	c	d	e	f	I
Dulong[B]	145.5	620.3	...	40.5	77.5	...	...
Mott-Spooner[C]	144.6	610.2	...	40.5	62.4	...	...
Boie[B]	151.2	499.8	27.0	45.0	47.7	...	...
Lloyd-Francis (1)[B]	148.7	530.6	...	26.76	55.41	...	...
Lloyd-Francis (2)[B]	153.9	488.6	25.6	48.14	36.35	...	419
Neavel[D]	145.9	569.9	...	43.08	−53.89	−6.30	...

[A] Calorific Values = a [%C] + b [%H] + c [%N] + d [%S] − e[%O] − f [%Ash] − I.

[B] [**63**].

[C] [**64**].

[D] [**65**].

TABLE 8.2 Accuracies of Several Methods for Estimating Calorific Values

	38 Low-Rank Coals	125 hvb Coals	33 High-Rank Coals	All 196 Coals
Average *daf* Btu/lb	12,560	14,580	15,400	14,540
Regressions				
Dulong				
Average error, Btu/lb	224	168	159	176
% within ±215 Btu/1b	53 %	69 %	76 %	67 %
Mott and Spooner				
Average error, Btu/lb	163	159	129	155
% within ±215 Btu/1b	66 %	73 %	73 %	71 %
Boie				
Average error, Btu/lb	250	219	219	224
% within ±215 Btu/1b	45 %	52 %	58 %	52 %
Lloyd and Francis (1)				
Average error, Btu/lb	133	112	103	116
% within ±215 Btu/1b	79 %	89 %	88 %	87 %
Lloyd and Francis (2)				
Average error, Btu/lb	151	108	103	112
% within ±215 Btu/1b	84 %	88 %	88 %	87 %

Source: Reprinted with permission from [**63**].

8.4.3 Interpretation and Uses of Calorific Data

The calorific value is normally the basic item specified in contracts for coal used in steam plants. It is the most important value determined for coal used for heating purposes. In coal contracts, the calorific value is usually specified on the as-received basis. Any error in the moisture value is reflected in the as-received calorific value.

The laboratory-determined calorific value is called the *gross calorific value*, which is normally reported in the coal industry. It may be defined as the heat produced by combustion of a unit quantity of coal at constant volume in an oxygen combustion vessel calorimeter under specified conditions such that the end products of the combustion are in the form of ash, gaseous CO_2, SO_2, nitrogen, nitrogen oxides, and liquid water. Burning coal as a fuel does not produce as much heat per unit quantity. Corrections are made to the gross calorific values for this difference between the laboratory and coal-burning facility. The corrected value is referred to as the *net calorific value*. This is defined as the heat produced by combustion of a unit quantity of coal at constant atmospheric pressure under conditions such that all water in the products remains in the form of vapor. The net calorific value is lower than the gross calorific value.

In the ASTM system of classifying coals by rank, the calorific value is used as one of the main parameters for the classification of bituminous, subbituminous, and lignitic coals. Coal calorific values are also used in estimating resources.

8.5 Fusibility of Coal Ash

Coal ash is the noncombustible residue that remains after all of the combustible material has been burned. It is a complex mixture that results from chemical changes that take place in the components of the coal mineral matter during the ashing process. The composition of coal ash varies extensively just as the composition of coal mineral matter varies.

The ash fusibility determination is an empirical test designed to simulate as closely as possible the behavior of coal ash when it is heated in contact with either a reducing or an oxidizing atmosphere. The test is intended to provide information on the fusion characteristics of the ash. It gives an approximation of the temperatures at which the ash remaining after the combustion of coal will sinter, melt, and flow. Sintering is the process by which the solid ash particles weld together without melting. The temperature points are measured by observation of the behavior of triangular pyramids (cones) prepared from coal ash when heated at a specified rate in a controlled atmosphere. The critical temperature points are as follows:

Initial deformation temperature (IT): Temperature at which the first rounding of the apex of the cone occurs.

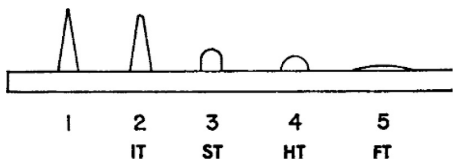
Softening temperature (ST): Temperature at which the cone has fused down to a spherical lump in which the height is equal to the width of the base.

Hemispherical temperature (HT): Temperature at which the cone has fused down to a hemispherical lump at which point the height is one half of the width of the base.

Fluid temperature (FT): Temperature at which the fused mass has spread out in a nearly flat layer with a maximum height of 1/16 in.

In determining the initial deformation temperature, shrinkage or warping of the cone is ignored if the tip remains sharp. **Figure 8.1** illustrates the appearance of the cone before heating and at the above temperatures.

FIG. 8.1 Critical temperature points as defined in ASTM **D1857**.



Source: Reprinted with permission from [**2**].

8.5.1 Determination of the Fusibility of Coal Ash

The standard test method for the fusibility of coal and coke ash is ASTM Test Method for Fusibility of Coal and Coke Ash (**D1857**) [**2**]. Ash for the test is prepared from the analysis sample of coal or coke, which is pulverized to pass a 250 μm (No. 60) sieve in accordance with Practice **D2013/D2013M** or Practice **D346**. The coal or coke is spread approximately 0.25 in. thick in a fireclay or porcelain roasting dish, which is then placed in a muffle furnace at ambient temperature. The temperature is raised at such a rate that it reaches 500°C at the end of 1 h. Heating is continued so that the temperature rises from 500°C to 750°C at the end of 1 h. Heating at the 750°C temperature is continued for an additional 2 h. During the ashing procedure, an adequate supply of air or oxygen must be supplied to the furnace.

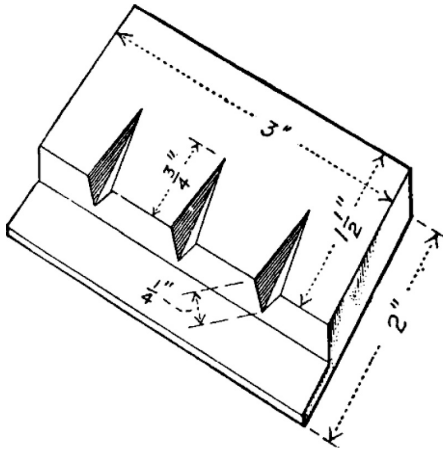
The ash is ground in an agate mortar to pass a No. 200 (75 μm) sieve, spread on a suitable dish, and heated in air or oxygen for 1.5 h at 750°C. Enough coal is used to produce 3–5 g of ash.

In preparing ash for the fusibility test, it is important that the coal be spread out in a thin layer and that adequate circulation of air be maintained during burning. All iron must be converted to the ferric state, and all combustible matter must be removed. A low initial heating temperature and a slow heating rate tend to minimize the retention of sulfur as sulfates in the ash. After the initial ashing steps, pulverizing the ash and reigniting it will help ensure complete conversion of iron to the ferric state and that all combustible material is burned.

The ash is mixed thoroughly and moistened with a few drops of dextrin binder and worked into a stiff plastic mass. The mass is then formed into a cone using a cone mold such as that illustrated in **Fig. 8.2**. The cones are dried and mounted on a refractory base. If dextrin or other carbon-containing binders are used to make the cones and if the cones are to be used in the reducing atmosphere test, then they should be heated at 750°C for 1 h to remove all carbon from the cones. If the cones are to be used in the oxidizing atmosphere test, then there is no need to reheat the cones before the test.

The mounted cones are heated at a specified rate in a gas-fired or electrically heated furnace under either oxidizing or reducing conditions. In gas-fired furnaces, the atmosphere is controlled by regulating the ratio of air to combustible gas. For reducing conditions, an excess of gas over air is maintained, and for oxidizing conditions an excess of air over gas is maintained. Hydrogen, hydrocarbons, and carbon monoxide produce a reducing atmosphere whereas oxygen, CO_2, and water vapor are considered to be oxidizing gases. Nitrogen is inert. For a mildly reducing atmosphere, the ratio by volume of reducing gases to oxidizing gases must be maintained between the limits of 20–80 and 80–20 on a nitrogen-free basis. That is, in a reducing atmosphere test the amount of reducing gases must be between the limits of 20 % and 80 % of the volume on a nitrogen-free basis. In a gas-fired furnace, this ratio may be difficult to achieve at high temperatures while maintaining the required temperature rise. For an oxidizing atmosphere, the volume of reducing gases present must not exceed 10 %.

FIG. 8.2 Brass cone mold.



Source: Reprinted with permission from [**2**].

In electrically heated furnaces, a mixture of 60 % (by volume) carbon monoxide and 40 ± 5 % CO_2 produces a reducing atmosphere in the furnace. A regulated stream of air produces an oxidizing atmosphere. The gas stream is regulated to provide a measured flow of 1.3–1.5 furnace volumes per minute.

The ASTM ash fusion test method is empirical, and strict observance of the requirements and conditions is necessary to obtain reproducible results. Proper control of the atmosphere surrounding the test specimen is potentially the greatest problem encountered in determining ash fusibility, particularly when a reducing atmosphere is used. A mildly reducing atmosphere is specified because it is believed that this more closely approximates conditions existing in fire beds when coal is burned in several types of combustion equipment. Lower softening temperature values are obtained with a mildly reducing atmosphere than in either strongly reducing or oxidizing atmospheres. With a mildly reducing atmosphere the iron in the ash is present predominantly in the ferrous state, whereas in a strong reducing atmosphere some of the iron may be in the metallic state. In an oxidizing atmosphere the iron is in the ferric state. Ferric and metallic iron increase the refractory quality of the ash, resulting in higher fusion temperatures. Softening temperature values may vary as much as 150–200°C depending on the atmosphere in which the test is made.

Temperature measurements are made either with an optical pyrometer or a platinum and platinum-rhodium thermocouple with a high-resistance millivoltmeter. The millivoltmeter or potentiometer should be accurate and readable to 5.5°C (10°F) over the range of 1000–1600°C. The temperature-measuring equipment must be properly calibrated by a reliable means. At least once during each week of operation the

temperature-measuring equipment should be checked for accuracy by observation of the behavior of small pieces of gold or nickel wire, or both, with known melting points under routine test conditions. Pure gold (melting point 1063°C) can be used to calibrate the temperature-measuring equipment in both an oxidizing and a reducing atmosphere. Pure nickel (melting point 1452°C) can be used only in a reducing atmosphere because it is susceptible to oxidation. This property can be used to advantage in determining whether a furnace that has been set up to operate with a reducing atmosphere is performing properly. Provided the temperature-measuring equipment is calibrated properly, an erratic reading for the melting point of nickel would indicate something other than a reducing atmosphere in the furnace.

8.5.2 Ash Fusion Instrumentation

Over the past 3 decades, there have been several improvements in the instrumentation used for ash fusion determination, most of which have not been added to the standard method. One type of ash fusion furnace system uses a rotating pedestal inside of the furnace to present the ash cones to the measurement window of a diode array, once each 6 s. As each cone is scanned, the diode array effectively draws a digital photograph of the cone. Each subsequent scan is compared with the previous scan, and temperatures are automatically recorded when the height of each melting cone reaches a preset level.

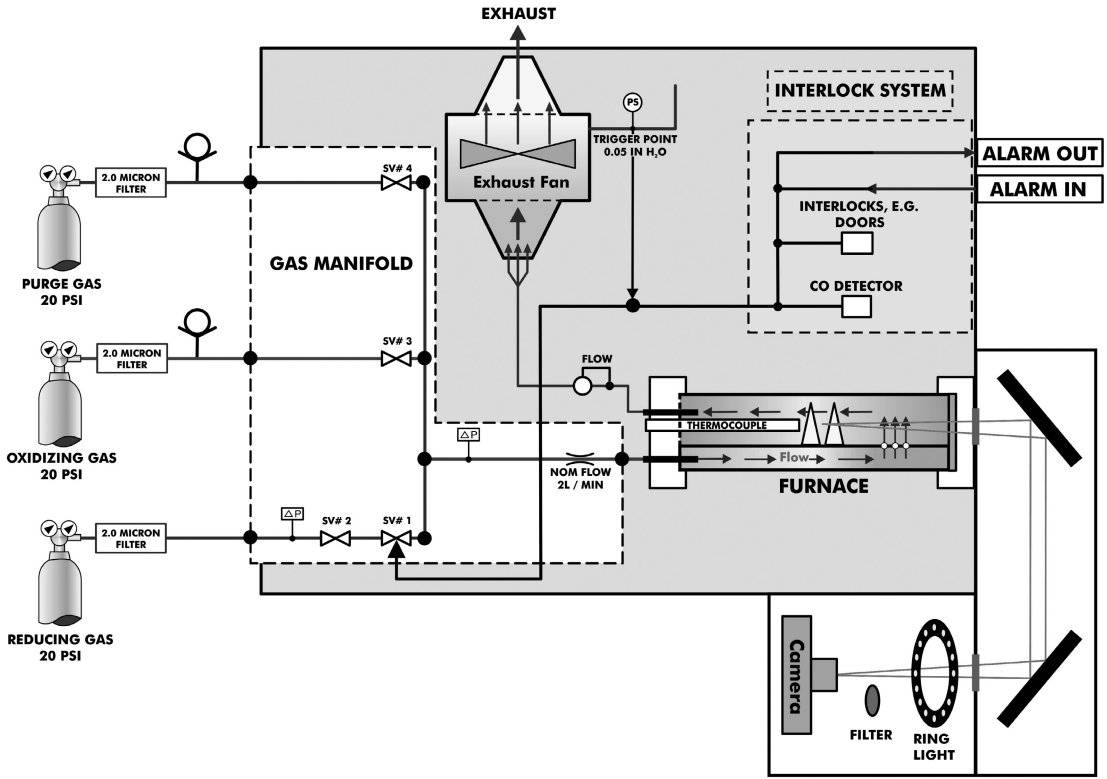
Some ash fusion systems currently use a high-resolution television camera, a monitor, and a videotape recorder to record the melting of ash cones in a stationary furnace. The operator can then view the videotape to record the ash fusion temperatures. A common problem with these types of instruments is the heat generated by the furnace and its effects on the camera components. One type of instrument that reduces the effects of the furnace heat uses an offset camera and reflective mirrors, as shown in Fig. 8.3. The system also uses image analysis software to interpret the data recorded by the digital camera. The user can look at the actual recordings of cone behavior or use the software to identify the critical temperature points or both.

The ash fusion test method is empirical, and manually reading the critical temperature points is subjective. The use of video cameras and image analysis software presents better opportunities for the analyst to improve the accuracy of the reading of the critical temperature points.

8.5.3 Interpretation and Uses of Ash Fusibility Data

Ash fusibility values are often specified in coal contracts because they are believed to be a measure of the tendency of coal ash to form clinkers. Softening temperatures probably are used most often for this purpose. For example, if it is desirable to have the ash fuse into a large clinker that could be easily removed, then coal with a softening temperature low enough to allow the ash to fuse would be chosen. However, the ash should not soften at too low of a temperature because it may become fluid enough to run through the fire bed and solidify below it, making the ash harder to remove. Coals with high softening temperatures produce ash with relatively small particle size rather

FIG. 8.3 Schematic diagram for an ash fusion system with offset camera.



Source: LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI.

than fused masses. Initial deformation and fluid temperatures may also be useful, depending on the type of combustion equipment to be used for burning coal and the manner in which the ash is to be removed.

In practice, types of burning equipment, rate of burning, temperature and thickness of the fire bed, distribution of ash-forming minerals in the coal, and viscosity of the molten ash may influence ash behavior more than do the laboratory-determined ash fusibility characteristics. The correlation of the laboratory test with the actual utilization of coal is only approximate because of the relative homogeneity of the laboratory test sample compared with the heterogeneous mixture of ash that occurs when coal is burned. Conditions that exist during the combustion of coal are so complex that they are impossible to duplicate completely in a small-scale laboratory test. Because the test is empirical, the data should be used as a gross indicator for screening of coals.

8.5.4 Estimating Ash Fusion Temperatures from the Elemental Composition of Ashes

With the introduction of on-line elemental analyzers, it was just a matter of time before the development of equations to estimate the fusion temperatures of ashes from their elemental composition. Several studies have been conducted on developing predictive equations of this type [**32, 66–69**]. Most of these studies used multiple regression analysis of a large set of ash fusion temperatures to develop the equations. However, several of the major and minor oxides in coal and coke ashes show a high level of collinearity when used in multiple regression analysis, a condition leading to high standard errors of estimates and equations with very little predictive power. In one study using 70 prepared ashes from 7 source coals, ranging in classification from medium-volatile bituminous down to lignite, the fusion temperatures and the 10 predominant oxide compositions were subjected to a multiple regression analysis [**68**]. In this scheme, a series of limitations were imposed on regression terms possessing excessive collinearity. From the many possibilities, the "best" set of ten-term equations for predicting ash fusion temperatures was used to estimate the ash fusion temperatures. The average errors for the predicted 4 temperatures for the set of 70 ashes are listed in **Table 8.3**. These are well below the repeatability and reproducibility intervals for ashes.

TABLE 8.3 Average Errors for Estimating Fusion Temperatures from the Elemental Composition of the Ashes [**68**]

Temperature	Average Error for 70 Ashes (°F)
Initial deformation (IT)	32.6
Softening (ST)	28.1
Hemispherical (HT)	26.6
Fluid (FT)	29.7

The average errors listed in **Table 8.3** look encouraging as a way for the estimation of fusion temperatures from elemental analysis. However, the results were derived from a relatively small group of source coals (seven) and a total of 70 ashes. When the equations from this study were applied to a wide variety of ashes, the errors were sometimes unexpectedly large. The study obviously did not cover all of the factors that may affect the fusion temperatures of ashes.

When mixtures of metal oxide and nonmetallic oxide solids are heated to the molten state, the high temperatures and reactivity of the solid materials cause some of the materials to react with each other. Probably the best approach to explain this behavior is through the use of phase diagrams. **Figure 8.4** is an example of a phase diagram illustrating the behavior of mixtures of two solid materials when heated above their melting points. Quite often these mixtures form a eutectic system, in which the melting point of the mixture is much lower than the melting point of each component. In a eutectic system, two solid+liquid mixtures combine to form a single molten mixture. Examples of eutectic systems will be shown later (**Table 8.7**). **Figure 8.5** shows the iron-carbon phase diagram with its associated eutectic and peritectic systems. A peritectic transformation is one in which a liquid and solid phase of fixed proportions react at a fixed temperature to yield a single solid phase. Such a transformation exists in the iron-carbon system, as seen near the upper-left corner of the figure. It resembles an inverted eutectic, with the δ phase combining with the liquid to produce pure austenite at 1495°C and 0.17 mass % carbon. The presence of these metal oxide-nonmetallic oxide interactions make it almost impossible to estimate ash fusion temperatures from elemental composition.

8.6 Composition of Coal Ash

When coal is burned, the mineral constituents form an ash residue composed chiefly of compounds of silicon, aluminum, iron, and calcium, with smaller quantities of

FIG. 8.4 Phase diagram for a eutectic system.

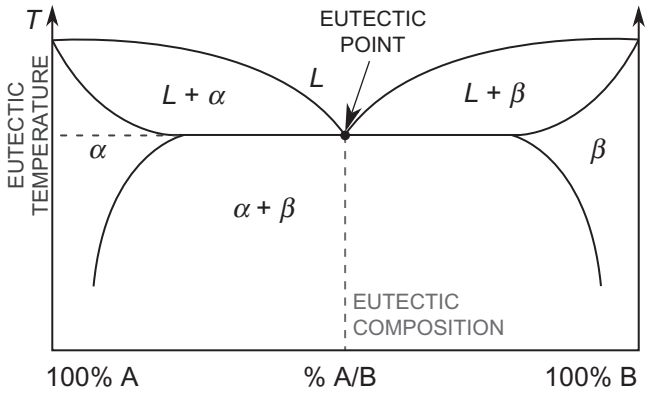
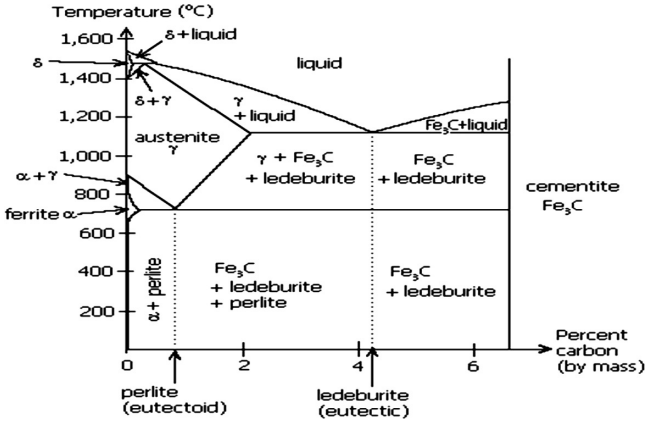


FIG. 8.5 The iron-carbon phase diagram, showing eutectic, eutectoid, and peritectic transformations.



compounds of magnesium, titanium, sodium, and potassium. Although the constituents are reported as oxides, they occur in the ash primarily as a mixture of silicates, oxides, and sulfates. The silicates originate in the shale, clay minerals, silts, and sands. The principal source of iron oxide is pyrite, which burns to form ferric oxide and sulfur oxides. Calcium and magnesium oxides result from the decomposition of carbonate minerals whereas the sulfates are formed from interaction among carbonates, pyrite, and oxygen. Examples of the minerals found in coals were given in **Table 2.4**, and typical limits of the ash composition of bituminous coals (reported as oxides) were given in **Table 5.1**.

8.6.1 Determination of the Composition of Coal Ash

The following are ASTM Standard Test Methods that pertain to the determination of the composition of coal ash:

- *ASTM **D3682**:* Major and Minor Elements in Combustion Residues from Coal Utilization Processes (AAS)
- *ASTM **D3683**:* Trace Elements in Coal and Coke Ash by Atomic Absorption Spectrometry (AAS)
- *ASTM **D4326**:* Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence (XRF)
- *ASTM **D6349**:* Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)
- *ASTM **D6357**:* Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by Inductively Coupled

Plasma-Atomic Emission Spectrometry, Inductively Coupled Plasma-Mass Spectrometry, and Graphite Furnace Atomic Absorption Spectrometry (ICP-AES, ICP-MS, GFAAS)

- *ASTM **D1757**:* Test Method for Sulfate Sulfur in Ash from Coal and Coke
- *ASTM **D5016**:* Test Method for Total Sulfur in Coal and Coke Combustion Residues Using a High-Temperature Tube Furnace Method with Infrared Absorption
- *ASTM **D6316**:* Determination of Total, Combustible, and Carbonate Carbon in Solid Residues from Coal and Coke

The following are tables listing the elements determined in ash and combustion residues and the various analytical methods used to determine these elements. **Table 8.4** lists the major and minor elements, which are generally elements occurring in concentrations greater than 0.1 %. These elements are generally reported as oxides. **Table 8.5** lists various trace elements determined in coal, coke, and coal combustion

TABLE 8.4 ASTM Methods of Analysis for Major and Minor Elemental Oxides in Coal, Coke, and Coal Combustion Residues

Oxide	Analytical Methods
SiO_2	AAS, XRF, ICP-AES
Al_2O_3	AAS, XRF, ICP-AES
Fe_2O_3	AAS, XRF, ICP-AES
CaO	AAS, XRF, ICP-AES
MgO	AAS, XRF, ICP-AES
Na_2O	AAS, XRF, ICP-AES
K_2O	AAS, XRF, ICP-AES
TiO_2	AAS, XRF, ICP-AES
MnO_2	XRF, ICP-AES
SO_3	XRF, ICP-AES
P_2O_5	XRF, ICP-AES

TABLE 8.5 ASTM Methods Used for the Analysis of Trace Elements in Coal, Coke, and Coal Utilization Residues

Elements	Methods
Be, Cd, Cr, Cu, Mn, Ni, Pb, V, Zn	**D3683** (AAS)
As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V, Zn	**D6357** (ICP-AES, ICP-MS, and GF-AAS)
Hg	**D3684**, **D6414**, and **D6722** (CVAAS)
As, Se	**D4606** (Hydride-AAS)

residues. These elements generally occur at concentrations less than 0.1 % and are normally reported as elements and not oxides.

8.6.1.1 *ASTM Methods for Major and Minor Element Analysis*

The preparation of ash from coal or coke for major and minor element analysis is the same in ASTM Methods **D3682**, **D4326**, and **D6349**. The analysis sample of coal or coke is pulverized to pass a 250 μm (No. 60) sieve in accordance with Practice **D2013/D2013M** or Practice **D346**. The coal or coke is spread approximately 0.25 in. thick in a fireclay or porcelain roasting dish, which is then placed in a muffle furnace at ambient temperature. The temperature is raised at such a rate that it reaches 500°C at the end of 1 h. Heating is continued so that the temperature rises from 500°C to 750°C at the end of 1 h. Heating at the 750°C temperature is continued for an additional 2 h. During the ashing procedure, an adequate supply of air must be supplied to the furnace. The ash is ground in an agate mortar to pass a 200 mesh, 75 μm sieve and reignited at 750°C for 1 h.

In the preparation of ash samples for analysis, the slow burning of the coal samples is necessary to prevent the retention of sulfur as sulfate in the ash. Pyrites are oxidized to sulfur oxides and iron oxides at temperatures around 450°C. Calcite and other carbonate minerals decompose to the metal oxides and CO_2 at temperatures near 600°C and at lower temperatures in rapidly combusting materials. Oxidizing pyrites at the lower temperatures rids the sample of sulfur that can be converted to sulfur oxides and retained by metal oxides formed during rapid combustion. If the rate of burning is too rapid, then some of the sulfur oxides produced from burning pyrite can react with metal oxides to form stable sulfates. The result is that indefinite amounts of sulfur are retained, which introduces an error into all of the analytical results unless all other oxides are corrected to the sulfur trioxide (SO_3)-free basis.

The preparation of ash to be used for major and minor element analysis from combustion residues uses a heating procedure essentially the same as that used for **D3682**, **D4326**, and **D6349**. ASTM Test Method **D7348**—Loss on Ignition (LOI) of Solid Combustion Residues – serves two purposes. Loss on ignition (LOI) is a test sometimes required in the analysis of combustion residues. The ignition of the sample in the determination of LOI prepares the sample for major and minor element analysis. **D7348** has two procedures for determining LOI at two different temperatures. One procedure uses an oven and muffle furnace for moisture and ash determination, and the second procedure uses a macro-thermogravimetric analysis (TGA) system. Determining the LOI at 750°C produces ash for major and minor element analysis. Determining the LOI at 950°C produces an ash that is not acceptable for major and minor element analysis because some elements (e.g., Na and K) are often lost at this high temperature. LOI values determined at 950°C are needed by the cement industry.

In recent years, the increase in instrumental methods of analysis as the basis for ASTM Standard Test Methods has prompted ASTM Committee D05 on Coal and Coke to include generic statements for set up and calibration of the instruments. Standard reference materials (SRMs) from the National Institute of Science and Technology (NIST) or certified reference materials (CRMs), or both, from reputable organizations are always recommended for calibration and calibration verification of the various instruments. Generic statements such as "Calibration of the spectrometer shall be done according to the manufacturer's instructions" have replaced statements with the specific details for preparing the analysis equipment used in older standards. This is necessary because many of the older standards were written for a specific measurement with equipment provided by a limited number of, or sometimes a unique, supplier.

In ASTM **D3682**—Major and Minor Elements in Combustion Residues from Coal Utilization Processes—the ash is mixed with lithium tetraborate ($Li_2B_4O_7$) in a platinum dish and heated to 1000°C for 15 min. The fused mixture is then dissolved in dilute HCl or HNO_3 (50 mL of concentrated acid diluted to 1000 mL) and appropriate dilutions made for AAS analysis. Proper AAS procedures, including background correction and analysis of SRMs or CRMs, are essential parts of the procedures. A combination of air-acetylene and nitrous oxide-acetylene flames are used for the analysis of the eight elements listed in the standard test method.

For ASTM **D4326**, the ash is mixed with $Li_2B_4O_7$ or other fluxing agents that produce a uniform homogeneous test sample in a platinum or graphite crucible and heated to 1000°C. The fused mixture is poured into a platinum/gold dish to form a glass pellet to be analyzed by XRF. The pellet is irradiated with a high energy X-ray beam, and the X radiation that is emitted, or fluoresces, from the sample is characteristic of the elements in the sample. The X radiation from the sample is dispersed, and the intensities are measured at selected wavelengths. These intensities are related to the concentrations of the elements in the prepared ash sample as determined by comparison to calibration curves for reference materials analyzed under the same conditions.

Two types of XRF spectrometers may be used for the analysis: an energy-dispersive system and a wavelength-dispersive system. Wavelength-dispersive systems are more versatile than the less expensive energy-dispersive type. Both systems require a robust and accurate set of six to ten standards, prepared in the exact same manner as the samples being analyzed.

For ASTM **D6349**, a choice of methods for dissolving the ash is given, either by heating the prepared ash mixed with a fluxing agent ($Li_2B_4O_7$) or anhydrous lithium metaborate ($LiBO_3$) to 1000°C and dissolving in 5 % HNO_3, or by dissolving the ash in a mixed acid solution of HCl/HF/HNO_3. The solutions are then analyzed by ICP-AES. Matrix and spectral interferences are tracked and minimized using internal standards and SRMs or CRMs.

Table 8.6 lists the major and minor element concentrations in various ranks of coals [**68**]. The coals were collected from across the United States, and the concentrations of

TABLE 8.6 Ash Composition of Coals of Various Ranks [**68**]

Elemental Oxide	LigA	SubC	SubB	hvBb	hvAb	mvb
			Acidic Oxides			
SiO_2	41.1	33.1	35.5	45.5	50.4	38.6
Al_2O_3	23.2	14.7	16.7	19.2	24.5	24.7
TiO_2	0.82	1.25	1.12	1.00	1.66	1.18
			Basic Oxides			
Fe_2O_3	4.20	5.57	6.25	24.1	5.32	12.3
CaO	13.2	26.9	18.5	0.55	2.71	9.26
MgO	1.40	4.59	3.27	1.07	1.06	1.61
Na_2O	0.92	1.04	1.20	0.51	0.63	0.79
K_2O	1.60	0.16	0.48	2.63	1.91	1.34
			Other Oxides			
SO_3	7.84	9.26	10.5	0.72	1.08	7.99
P_2O_5	0.63	1.50	1.31	0.20	2.36	0.01
MnO_2	0.06	0.03	0.05	0.07	0.02	0.05

the elemental oxides are typical of those found in coal ashes. It should be noted that the ashes with the highest concentrations of alkaline earth (calcium oxide [CaO] and magnesium oxide [MgO]) and alkali metal (sodium oxide [Na_2O]) and potassium oxide [K_2O]) oxides have the highest concentrations of SO_3. This occurs although other coals listed in **Table 8.6** have much higher concentrations of sulfur, as indicated by their higher than normal concentrations of iron (III) oxide (Fe_2O_3).

8.6.2 Sulfur and Carbon in Ash and Combustion Residues

Two nonmetallic elements that are almost always found in combustion residues are sulfur and carbon. The sulfur present usually exists as sulfates, which may be from the mineral matter originally present in the coal or were formed when sulfur oxides were trapped by metal oxides formed during combustion. The amount of sulfate (expressed as SO_3) can range from a few tenths of a percent to well over 10 %. The amount of SO_3 in the ash or combustion residue must be known for mass balance calculations.

There are two ASTM standard methods for the determination of sulfur in ash or combustion residues or both. In the classical method, ASTM **D1757**, there are two options for determining sulfur in the sample. The first option is to digest a portion of the sample in boiling dilute HCl with bromine water to convert any sulfite to sulfate, neutralize the solution with ammonium hydroxide, and then filter to remove iron hydroxides. The sulfate in the filtrate is then determined gravimetrically as $BaSO_4$ after precipitation with $BaCl_2$ solution. The second option is to ignite in air a portion of the

sample with a mixture of solid sodium carbonate and MgO (Eschka's mixture). After treating the residue with hot water and filtering, the sulfate in the filtrate is determined gravimetrically as $BaSO_4$ after precipitation with $BaCl_2$ solution. Although **D1757** is a viable method for determining sulfate in ash, it was withdrawn from publication in 2009 because of the unavailability of Eschka's mixture and lack of use.

The second method for determining sulfur in combustion residues, ASTM **D5016**, is an instrumental method (see **Fig. 6.2**). The sample is ignited with a promoting agent at 1350-1450°C in a stream of oxygen. Sulfur in the sample is released as SO_2 into the combustion stream. The combustion stream is dried by passing it through a magnesium perchlorate trap and then filtered. The filtered combustion stream is passed through an infrared (IR) absorption cell where it is illuminated with IR radiation. The cell contains a detector tuned to monitor the wavelengths of IR radiation absorbed by SO_2. The amount of IR radiation absorbed during the test is a measure of the amount of SO_2 produced. The method requires careful calibration of the sulfur analyzer with CRMs.

ASTM **D6316** involves a combination of methods for the determination of total, combustible, and carbonate carbon in solid residues. The relationship among the three carbon values is given by the equation

$$\text{Total carbon} = \text{carbonate carbon} + \text{combustible carbon} \tag{8.3}$$

Thus, only two of the carbon values need to be determined because the third can be calculated from Eq. 8.3.

Total carbon is determined by the oxidative thermal decomposition of a weighed quantity of sample in a closed system. After filtering unwanted materials from the combustion gas stream, the CO_2 produced is determined by procedures outlined in ASTM **D5373**.

Carbonate carbon is determined by decomposing a weighed quantity of the sample with dilute mineral acid and, after purification of the evolved gases, quantitatively measuring the amount of CO_2 produced. Three methods of determining the CO_2 are available. In the absorptive determination of carbonate carbon, the evolved CO_2 is passed through an absorptive train and the amount of CO_2 is measured gravimetrically as described in ASTM Test Method **D1756** (see Section 8.3). In the coulometric determination of carbonate carbon the CO_2 is collected in an absorption cell, where it is coulometrically titrated. In the instrumental determination of carbonate carbon, the CO_2 liberated upon acidification of the sample is quantitatively determined by the IR absorption cell in automated carbon, hydrogen, and nitrogen (CHN) analyzers (ASTM **D5373**). The CHN analyzer has to be adapted for determining CO_2 by replacing the sample combustion section with a provision for acidification of the sample.

Combustible carbon is determined directly by first acidifying a weighed quantity of the sample and heating it to dryness. All carbonate carbon is evolved as CO_2. The dried sample is then analyzed for total carbon content as described above.

8.6.2.1 *ASTM Methods for Trace Element Analysis*

To prepare ash for trace element analysis methods **D3683** and **D6357**, a -60 mesh (250 μm) coal sample is gradually heated to reach a temperature of 300°C at the end of 1 h and heated to 500°C at the end of a second hour. The 500°C temperature is maintained for at least 2 more hours with occasional stirring. The ash is ground to pass a 150 μm (No. 100 U.S.A.) standard sieve and reignited at 500°C for an additional hour. When coal ash is prepared according to this method, it is believed that all of the elements listed in **Table 8.5**, except Hg, As, and Se, are quantitatively retained in the ash and are representative of concentrations in the whole coal.

In the determination of trace elements in coal or coke ash by atomic absorption according to method **D3683**, the coal ash is dissolved in aqua regia and hydrofluoric acid (HF). A boric acid solution (H_3BO_3) is added to aid in the dissolution. The elements in the solution are then determined by conventional atomic absorption procedures using background correction. Nitrous oxide-acetylene flames are used for the determination of Be, V, and Cr, whereas air-acetylene flames are used for the determination of Cd, Cu, Mn, Ni, Pb, and Zn.

For the analysis of trace elements by ASTM **D6357**, the sample is digested in a mixture of aqua regia and HF in a polytetrafluoroethylene beaker. The mixture is heated to dryness and the residue finally dissolved in 1 % HNO_3. The solutions are then analyzed by ICP-AES or inductively coupled plasma-mass spectrometry (ICP-MS) or graphite furnace atomic absorption spectrometry (GFAAS). GFAAS may be used for selected elements that occur at concentrations below the detection limits of ICP-AES. The analysis of 13 elements (Sb, As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Zn, and V) are included in the procedure.

8.6.2.2 *Mercury in Coal and Coal Combustion Residues*

Environmental concerns for some trace elements, particularly trace elements with potential high toxicity, have encouraged ASTM Committee D05 on Coal and Coke to develop special test methods for their determination. The chemical and physical properties of mercury make it one of the most active metals we have. It is a liquid at ambient temperatures with a relatively high vapor pressure, which allows it to be easily dispersed into the atmosphere. It readily forms amalgams with many metals, which increases opportunities for its dispersal into the environment. Mercury's unique and extensive chemical and electrochemical properties lead to extensive interactions between mercury and other elements and potentially wide dispersal into the environment.

There are three ASTM standard methods of analysis for mercury resulting from gradual developments over a couple of decades of new and more reliable methods of analysis. All three methods cover the analysis of mercury in coal and in coal combustion residues. The ASTM methods are:

- *ASTM **D3684**:* Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method

- *ASTM **D6414**:* Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption
- *ASTM **D6722**:* Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis

The oldest of the three standard methods (ASTM **D3684**) involves the decomposition of the sample in a pressurized oxygen combustion vessel and determination of mercury in the vessel digestate using cold vapor atomic absorption spectrometry (CVAAS). A newer standard (ASTM **D6414**) uses an acid digestion (aqua regia) or wet oxidation (HNO_3 and H_2SO_4 with vanadium pentaoxide) to dissolve mercury before analysis by CVAAS. Another newer ASTM standard (**D6722**) involves the thermal decomposition of the sample in oxygen, passing over an acid gas-scavenging catalyst before passing over a gold amalgam to trap the mercury vapor. The gold amalgam is then heated rapidly to release the mercury that is determined by CVAAS.

In an ILS using the above three methods for mercury determination in a suite of coals and combustion residues, the direct combustion method (ASTM **D6722**) performed better than the other two methods with regard to multiple laboratory precision and lower quantitative limits [**47**]. The data from this study were used to prepare the precision and bias statements for the three mercury standards.

The U.S. Environmental Protection Agency (EPA) in 2005 issued a federal rule to permanently cap and reduce mercury emissions from coal-fired power plans. To comply with the EPA mercury emission standard, the power industry is required to determine the amount of mercury emitted from their power plants. One approach for this purpose is the use of continuous emission monitors, an approach that will require high capital expenditure. Another approach (Appendix K) allows for sampling of the stack effluent and off-line analysis of mercury retained by sorbent tubes.

In a study conducted by the Electric Power Research Institute (EPRI), four methods proposed for the analysis of the mercury sorbent tubes were evaluated in an ILS. Two of the methods, Draft EPA Method 324 and a method similar to ASTM **D6414**, involved the extraction of mercury from the iodide-treated activated carbon in the sorbent tubes with concentrated acid solutions. After extraction, filtering, and dilution (20–100 times) to minimize the chemical interference from iodine, mercury was determined by cold vapor atomic fluorescence spectroscopy (CVAFS) or CVAAS. Molecular iodine produced by the concentrated HNO_3 in the solutions reacts with the stannous chloride used to reduce the mercury in the CVAFS and CVAAS techniques. The other two methods were a thermal desorption method with CVAAS detection and a thermal decomposition method with CVAAS (ASTM **D6722**). A part of the study demonstrated that the heterogeneous activated carbon with adsorbed mercury in the sorbent tubes could be homogenized and split, allowing the analysis of small (100 mg) samples as used in ASTM **D6722** [**70**]. The procedure developed for the homogenation of the activated carbon in the sorbent tubes was incorporated into ASTM **D6722** (Appendix A2) in 2011.

The ILS conducted during the EPRI project demonstrated that acceptable accurate measurements of mercury captured on iodide-treated activated carbon sorbent material can be obtained by any one of the four analytical methods evaluated. For each of these methods, at least one laboratory achieved better than 95 % recovery of mercury from spiked sorbent tubes at spike levels between 250 and 40,000 ng of mercury. These results indicate that meeting Appendix K criteria for spike recovery will be possible with any of the methods. The progression of work during the project indicated that there are several factors to consider and conditions that must be met to ensure accurate laboratory measurements of mercury in iodide-treated activated carbon tubes. One of these factors is the exceptional laboratory technique each laboratory needs to establish that their chosen method of analysis and analytical instrumentation is capable of achieving acceptable accuracy at the target levels of mercury loading. Another factor is better calibration of the mercury CVAAS/CVAFS systems that can be done to improve precision and accuracy at low mercury levels. Because of the ILS design, most laboratories calibrated their instruments over a wide range of concentrations, which means that measurements at the outer ranges of the calibration had larger measurement errors. Normally, laboratories will generally know in advance the approximate mercury loading on a sample tube and can calibrate their instrument over an appropriate, narrower range of concentrations [**70**].

8.6.2.3 *Other Methods for Major, Minor, and Trace Element Analysis*

In addition to the AAS, GFAAS, CVAAS, ICP-AES, ICP-MS, and XRF analytical techniques discussed as part of ASTM standard methods in previous sections, there are several other instrumental analytical techniques that have been used to determine major, minor, and trace elements in coal as well as in ash and coal-derived materials. These methods include spark-source mass spectrometry (SSMS), instrumental neutron activation analysis, and direct current spectrographic analysis.

SSMS has been used in the determination of trace elements in coal. Whole coal samples, as well as ash residues, fly ash, respirable coal dust, and lung tissue, have been analyzed using this technique. Sharkey et al. [**71**] analyzed trace elements in 13 coals from 10 coal seams located in Pennsylvania, West Virginia, Virginia, Colorado, and Utah using SSMS. Sixty-four elements ranging in concentration from 0.01 to 41,000 ppm were determined. Kelly and Moore [**72**] compared results from SSMS determination of Mn, Ni, Cr, V, Cu, and Zn with atomic absorption values for the same samples. The relative standard deviations ranged from 6 to 15 % for SSMS and 2–3 % for atomic absorption.

XRF analysis spectroscopy is a rapid, simple, and accurate method of determining the concentration of major and minor elements in ashed materials (see Section 8.6.1). The coal ashing procedure removes most of the combustible and volatile components (C, H, O, N, S, Cl, Hg, Pb, As, Sb, etc.). XRF analysis of whole coal is more challenging. The major elements in whole coal (C, H, O, and N) cannot be analyzed by XRF. However, most other elements at levels greater than a few parts per million (ppm)

are readily determined, depending on the availability of suitable standards. Successful analyses of whole coal by XRF spectrometric techniques were reported by Kuhn et al. [**73**] and Johnson et al. [**74**].

The concentrations of 25 major, minor, and trace elements in 8 Argonne Premium Coal Samples were determined using XRF spectrometry [**75**]. Trace element (Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce) determinations on the whole coal by energy-dispersive XRF (EDXRF) generally show close agreement (±10 %) between replicate samples. However, a wide variance was noted when the whole coal trace element results were compared with the results obtained on the coal ash. The authors believed further work on evaluating the accuracy of the matrix correction methods for whole coals was needed.

Neutron activation analysis techniques have been used for trace element analyses of whole coal and coal-related materials. As many as 61 elements have been examined using instrumental neutron activation analysis (INAA) [**76**]. Precision of the method is 25 % on the basis of all elements reported in coal and other sample matrices. Overall accuracy is estimated at 50 % [**77**]. In a later study INAA was used for the determination of 29 elements in 8 Argonne Premium Coal Samples [**78**]. Results obtained for the 29 elements compare favorably with those from the other analytical techniques used in this project. Errors reported were generally less than 10 %, except when the element's concentration was near the detection limit. Using INAA, elements can be determined on the whole coal without dissolution, eliminating errors of recovery and volatility. Its major drawbacks are that several of the major elements, especially silicon, are not detected; high costs; and long analysis times for analysis of full element suites.

Emission spectroscopic methods of analysis have been used to determine up to 25 elements present in coal ash. Dreher and Schleicher [**79**] developed methods of analyzing 16 trace elements in high-temperature coal ash. Concentration ranges were from less than 0.3 to 249 ppm, with detection limits of 2.2–5 ppm, for the 16 elements studied. Skeen and coworkers used an automated semiquantitative direct-current arc atomic emission spectrograph to determine the concentrations of 62 elements in 8 Argonne Premium Coal Ash Samples [**80**]. The precision of the method for most elements was generally ±10%. The accuracy of this method was assumed to be limited to +50% or -33% because of the nature of the standard curves for each of the elements.

A disadvantage in using AAS, as well as most of the other instrumental techniques, is the time required for preparation of the sample. O'Reilly and Hale developed a procedure for the direct atomic absorption or emission AAS analysis of powdered whole coal slurries, thereby eliminating time-consuming ashing and sample-digestion procedures. Preliminary results indicate that the method is applicable to the estimation of minor-level and trace-level constituents [**81,82**].

There have been several studies of the ICP-AES analysis of slurries of coals, ashes, and other solids. Ebdon and Wilkinson injected aqueous slurries of coal into an

ICP-AES spectrometer using a high-solids nebulizer and a conventional torch. Determination of major and minor elements was reported with an average precision of approximately 12 % [**83,84**]. A similar study involving the injection of aqueous slurries of coal (0.25 %) using a high-solids nebulizer and a conventional torch produced precision of approximately 10 % for most major and minor elements analyzed [**85**]. The study showed there was a relationship between analysis errors and ranks of the 14 coals used. In a study with 16 samples, including fly ashes, burnt refractories, slags, and soil ashes, aqueous slurries of 0.1 % solids were injected into an ICP-AES spectrometer using a high-solids nebulizer and a conventional torch [**86**]. The best results were obtained with solids having a 2 to 5 μm particle size. The average percentage relative error for most major and minor elements was generally less than 5 % for the solids studied.

Finally, a compilation of the results from multitechnique determinations of 51 elements in Argonne Premium Coal Samples was reported by Palmer and Klizas [**87**]. Each of the 51 elements was determined by two or more of the following techniques: energy and wavelength-dispersive XRF spectrometry, INAA, ICP-AES, AAS, ICP-MS, and direct current arc spectrographic analysis. This is one of the most thorough studies of major, minor, and trace element analysis of coal reported in the literature.

8.6.2.4 *Interpretation and Uses of Ash Composition Data*

A compositional analysis of the ash in coal can be useful in the total description of the quality of the coal. Knowledge of the composition of ash is useful in predicting the behavior of ashes and slags in combustion chambers. The amount and composition of ash is important in determining the most effective cleaning methods for coals, in selecting coals to be used in the production of coke, and in selecting pulverizing equipment to be used in commercial pulverizing operations. Utilization of the ash byproducts of coal combustion often depends on the chemical composition of the ash.

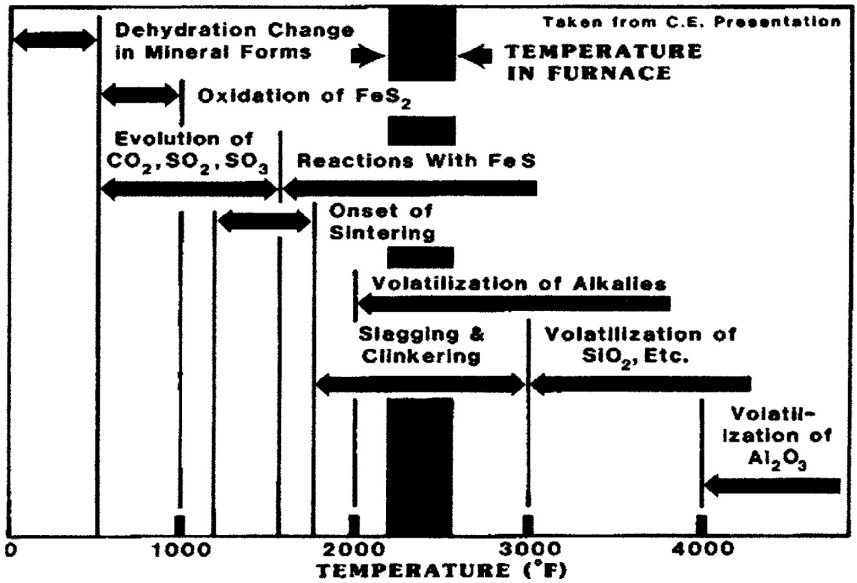
Table 8.7 lists melting temperatures of some of the major oxides present in coal ashes along with the melting temperatures of compounds formed from some of these

TABLE 8.7 Fusion Characteristics of Ash Components

Element	Chemical Property	Oxide	Melting Temperature (°F)	Compound	Melting Temperature (°F)
Si	Acidic	SiO_2	3120	Na_2SiO_3	1610
Al	Acidic	Al_2O_3	3710	K_2SiO_3	1790
Ti	Acidic	TiO_2	3340	$Al_2O_3 \cdot Na_2O \cdot 6SiO_2$	2010
Fe	Basic	Fe_2O_3	2850	$Al_2O_3 \cdot K_2O \cdot 6SiO_2$	2010
Ca	Basic	CaO	4570	$FeSiO_3$	2090
Mg	Basic	MgO	5070	$CaO \cdot Fe_2O_3$	2280

Source: Reprinted with permission from [**88**].

FIG. 8.6 Diagram of chemical changes in coal ash as a function of temperature.



Source: Reprinted with permission from [**88**].

oxides. It is apparent from the differences between the melting temperatures of the oxides and the compounds formed from these oxides that there is likely to be a wide variation in fusion temperatures of the ashes, depending on their composition. As previously discussed in Section 8.5, there has been some success in predicting the fusion temperatures of the ashes from their elemental composition, but the interactions between the individual oxides must be considered. **Figure 8.6** illustrates some of the interactions that take place among these elements at elevated temperatures when combinations of these materials, as found in various coals, are heated to the elevated temperatures typical of those found in coal-fired boilers.

The amounts of various elements in ashes can be used to estimate the performance of electrostatic precipitators. **Table 8.8** lists some of the indices used to make such predictions. It is obvious from the formulas and relationships shown in the table that the alkali and alkaline earth metals play prominent roles in the performance of these devices.

Table 8.9 lists some fouling indices for convective passes. In this scheme, the alkali metals (sodium and potassium) play prominent roles, as does the chlorine content.

Table 8.10 lists several furnace slagging indices. As shown from these indices, the basic oxides (Fe_2O_3, CaO, MgO, Na_2O, and K_2O) and high base-acid ratios are major contributors to furnace slagging.

TABLE 8.8 Electrostatic Precipitator Indices

Index	Factors	Collection Performance		
		Good	Medium	Poor
Base %	$Fe_2O_3 + CaO + MgO + Na_2O + K_2O$	<15	15–40	>40
Base/sodium	Base % /Na_2O %	<20	20–30	>30
Potassium %	K_2O	<1		
Calcium-magnesium	CaO + MgO			>20

Source: Reprinted with permission from [**88**].

TABLE 8.9 Convective Passes Fouling Indices

Index	Factors	Type of Ash	Fouling Tendency			
			Low	Medium	High	Severe
Fouling factor (R_f)	(Base/acid)/Na_2O	Eastern Bit.	<0.2	0.2–0.5	0.5–1.0	>1.0
Fouling factor (R'_f)	(Base/acid)(water-soluble Na_2O)	Eastern Bit.	<0.1	0.10–0.25	0.25–0.70	>0.70
Alkalies in coal	(% ash) (Na_2O + 0.0659 K_2O)/100	Eastern Bit.	<0.3	0.30–0.45	0.45–0.60	>0.60
Sodium in ash	Na_2O%	Eastern Bit.	<0.5	0.50–1.0	1.0–2.5	>2.5
Sodium in ash	Na_2O%	Western Bit.	<3.0	3.0–5.0		>5.0
Ash sintering strength	psi at 1700° F		1000	1000–5000	5000–16 000	>16000
Chlorine in coal	Cl %		<0.2	0.2–0.3	0.3–0.5	>0.5

Bit, bituminous. *Source*: Reprinted with permission from [**88**].

A wide range of trace elements occurs in coal, primarily as a part of the mineral matter. The potential release of certain trace elements into the environment as combustion products or in the disposal of ash can be a concern for coal-burning facilities. The determination of certain trace elements in coal and coal ash is an increasingly important part of coal analysis.

The chemical composition of laboratory-prepared coal ash may not be exactly representative of the composition of fly ash, power plant, ash or industrial process ash resulting from the commercial burning of coal. The composition of ash does not give an exact representation of the noncombustible material, or mineral matter, occurring in coal, but it is useful for practical applications.

8.7 Mineral Matter in Coal

Coals are complex mixtures of organic and inorganic species. The term *mineral matter* refers to the inorganic constituents of coal and is considered to be the sum of all elements that are not part of the organic coal substance (containing carbon, hydrogen,

TABLE 8.10 Furnace Fouling Indices.

			Slagging Tendency			
Index	**Factors**	**Ash[A]**	**Low**	**Medium**	**High**	**Severe**
Slagging Factor	(Base/Acid)(S_{dry})	E	<0.6	0.6–20	2.0–2.6	>2.6
Silica Percentage	(100 × SiO_2)/(SiO_2 + Fe_2O_3 + CaO + MgO)	E	30 ←	30 to 82	→	82
Base - Acid Ratio	Base % / Acid %	E/DB E/WB	<0.5 >0.27			
Ash Fusion Temp	Initial Def. – Fluid	E	High ←			Low
Slagging Factor	(Max Hem T + 4 × Min Def T)/5	W	>2450°	2250 – 2450°	2100 – 2250°	<2100°
Base – Acid Ratio	Base % / Acid %	W	0.25 or >0.8 ←		0.25 to 0.80	→
Iron – Calcium Ratio	Fe_2O_3 % / CaO %	W/DB	<0.31 or >3.0 ←		0.31 to 3.00	→
Silica – Alumina Ratio	SiO_2 % / Al_2O_3%	W	Low	→		High
T_{250} Temperature (°F)	Temperature to attain 250 poise	DB	>2325°	2100–2550°	2050–2275°	<2200°
		WB	<2600			
Critical Viscosity T	T_{CV} (Poise)	WB	10–100			

[A] E = Eastern Bituminous Ash; W = Western Lignitic Ash; WB = Wet Bottom Boilers, DB = Dry Bottom

Source: Reprinted with permission from [**88**].

nitrogen, oxygen, and sulfur). The mineral matter includes the minerals associated with coal and the chemically bound elements in the organic portion of coal (other than C, H, N, O, and S). The mineral matter is the principal source of the elements that make up the ash when the coal is burned in air or oxygen.

There are several sources of mineral matter in coal. Inherent mineral matter generally arises from the plant material from which the coal was formed. This type of mineral matter cannot be easily removed by physical methods because it is intimately associated with the organic fraction of coal. Extraneous mineral matter is composed primarily of quartz, clays, inorganic sulfides, carbonates, and sulfates. This type of mineral matter can usually be separated from the coal during cleaning and washing operations. A partial list of the minerals that have been reported as being associated with coals was given in **Table 2.4**.

Mineral matter content generally represents a significant proportion of a coal's composition. The amount varies from seam to seam, and values up to 50 % have been reported for coals mined in North America. A reasonable value for the "average" amount of mineral matter found in North American coals has been estimated to be 15 % [**89**].

In general, mineral matter is considered undesirable and detrimental in coal utilization. Its presence affects almost every aspect of mining, preparation,

transportation, and utilization. Coal preparation is aimed at reducing the quantity of mineral matter and the efficient use of the methods chosen depends on its concentration and composition. However, no matter how effective the coal preparation technique, there is always some amount of residual mineral matter.

The quality of coke is related to its ash and sulfur content, which are both dependent on the mineral composition of the feed coal. It is thought that the inorganic constituents of coking coals may have a marked effect on the yield of carbonization products and the structure, strength, and reactivity of the resulting coke. The presence of inorganic species can be advantageous because some act as catalysts and thus increase the reactivity of the coke.

When coal is burned in a combustion unit, mineral matter undergoes major changes that can lead to problems of clinker formation, ash, slagging, and boiler tube corrosion. The efficiency of a combustion unit is related to the amount of ash produced because it is a diluent. Disposal of the ash can result in large capital expenditures. On the positive side, ash has been used as a construction material and is a source of refractories. The composition of the ash must be known before it can be used in this way.

The interest in coal gasification and liquefaction has produced a need for a better understanding of the behavior of minerals in these processes. The possible poisoning of catalysts and the removal of insolubles such as minerals, unreacted coal, char, and insoluble products from the liquefaction product stream are some of the major problems that are encountered. Because of their mineral matter content, the use of certain coals in liquefaction streams and in coal slurries also leads to greater abrasion of valves and pumps.

8.7.1 Determination of the Mineral Matter Content of Coal

The mineral matter content of coal cannot be determined qualitatively or quantitatively from the ash that is formed when coal is oxidized. The combustion of coal at 750°C, as designated by ASTM ashing methods, causes a series of reactions involving the minerals in coal. For example, pyrite is oxidized to ferric oxide and SO_2, carbonates form oxides, and clays lose all water. Quartz is about the only mineral that remains unaltered.

A reliable method of measuring the mineral matter content of a coal is an acid demineralization procedure [**90,91**]. The method depends on the loss of mass of a sample when treated with 40 % HF at 50–60°C. Treatment of the sample with HCl before and after the HF treatment helps prevent the retention of insoluble calcium fluoride (CaF_2) in the coal. Pyrite is not dissolved in the treatment. Consequently, this compound, along with a small amount of residual ash and a small amount of retained chloride (as HCl), must be determined separately. Because two thirds of the mass of the pyrite (FeS_2) is accounted for by the presence of Fe_2O_3 in the residual ash, the mineral matter content is then given by the formula:

$$MM = \text{weight loss} + HCl + 1/3\ (FeS_2) + \text{residual ash} \tag{8.4}$$

This method has been used with coals of all ranks and requires no assumptions about the nature of the mineral matter. The key limitation of this method is that it is slow and tedious and gives only data on the total amount of mineral matter and not its composition.

For analytical purposes, it is desirable to separate the minerals from the coal in an unaltered form. In early studies, density separation methods were used, which were unsatisfactory because of the enrichment of certain minerals in the process. A low-temperature ashing, or plasma ashing, technique was developed that is more reliable and faster than density separations [**92**]. In this method, low-pressure oxygen is activated by a radio-frequency (rf) discharge. The excited oxygen and other oxygen-containing species oxidize the carbonaceous material at low temperatures (approximately 150°C). The effects of low-temperature ashing and of the oxidizing gas stream on the minerals in coal are minimal. Some pyrite can be oxidized, and to some extent organic sulfur can be fixed as sulfates. The rates of these reactions are functions of operating conditions, such as rf power level and oxygen flow rate.

Factors that affect the rate of low-temperature ashing other than rf power and oxygen flow rate mentioned above are the coal particle size and depth of sample bed. Typical conditions for ashing are a particle size of less than 80 mesh, a sample layer density of 30 mg/cm^2, an oxygen flow rate of 100 cm^3/min, chamber pressure of approximately 2 torr, and a 50-W net rf power. The total time required is 30–72 h, and specified conditions must be met during the procedure to obtain reproducible results.

8.7.1.1 *Mineralogical Analysis of the Mineral Matter in Coal*

Once the low-temperature ashing procedure has been performed and the mineral matter residue has been obtained, the minerals can be identified and their concentrations can be determined by various instrumental techniques. It can generally be said that no single method yields a complete analysis of the mineral matter in coal. It is often necessary to use a combination of methods.

One of the more reliable methods used thus far for distinguishing minerals in low-temperature (plasma) ashing (LTA) is X-ray diffraction analysis. However, its application can be limited because of orientation effects, and a reliable method of sample preparation is necessary to prevent these from occurring. X-ray diffraction profiles are determined by using a conventional diffractometer system with monochromatic X radiation. For qualitative analysis, the specimen is scanned over a wide angular range to ensure all of the major diffraction peaks of the component minerals are recorded. Diffraction spacings are then calculated from the peak positions, and the elements present in the sample are determined by using standard tables of diffraction spacings.

X-ray diffraction procedures were used for quantitative analysis of pyrite, calcite, and quartz in LTA residues [**93,94**]. Thoroughly mixed calibration mixtures of known proportions of calcite, pyrite, quartz, clay, and an internal standard of CaF_2 were used.

Spinning of the sample to remove orientation effects, slow scan rates, and a stabilized X-ray generator and counter are required. The best precision for this type of analysis is only approximately 10 % because of problems in obtaining uniform mixing of the sample and standards, orientation problems, and difficulty in obtaining representative standards.

Before the development of low-temperature (plasma) ashing techniques, the IR analysis of minerals in coals was severely limited because the broad bands of the organic portion of coal overlapped those of the mineral constituents. Since the development of LTA for the removal of the organic fraction of coal, it has been demonstrated that several minerals in coal can be identified and analyzed using IR spectroscopy [**95**]. The spectra are obtained using potassium bromide (KBr) or cesium iodide (CsI) pellets containing the finely divided mineral matter. Conventional IR techniques have been used for successful quantitative measurements of kaolinite and gypsum in mineral matter.

Fourier transform infrared (FTIR) spectroscopy can be successfully applied to the characterization of coals, coal-derived materials, and mineral matter [**96,97**]. It is somewhat limited for identification purposes, but it can be used for quantitative analysis.

SEM-EDX has been used to identify the composition and nature of minerals in coals and to determine the associations of minerals with each other. Examinations can be made on samples resulting from LTA techniques on or whole coal. With this technique, it is possible to identify the elemental components and deduce the mineral types present in coal samples. Computerized systems to evaluate scanning electron microscopy images have been developed and are useful in characterizing the minerals in coal mine dusts, coals, and coal liquefaction residues [**94,98**]. In this system, mineral grains are located, and their elemental compositions are determined by monitoring seven X-ray channels (Al, Si, S, Ca, Fe, K, and Ti). From the various combinations of these elements, it is possible to characterize most of the commonly occurring minerals in coals. Quantitative measurements can be obtained only if the mineral grains are larger than approximately 1 μm in diameter because of the limited resolution of the X-ray system.

Optical microscopy is another method that has been used to determine the distribution of minerals in coal. This method is based on the detailed microscopic examination of polished or thin sections of coal in transmitted or reflected light or both. In principal, identification of a mineral type is made by observing several of its optical properties, such as morphology, reflectance, refractive index, and anisotropy. These methods are widely used by petrographers.

8.7.1.2 *Calculation of Mineral Matter Content of Coal*

Determination of a good value for the percent of mineral matter content (% MM) is a very important component of coal analysis. If this quantity cannot be determined directly by the acid demineralization or LTA procedures discussed previously, or by

other suitable methods, then it is possible to calculate a reasonable value for the mineral matter in coal provided that the necessary data are available.

Several formulas have been proposed for calculating mineral matter in coal, but the two most used formulas are the formula of Parr [**99**] and that of King et al. [**100**]. The Parr formula is the one most often used in the United States and requires only ash and sulfur values as determined in routine analysis:

$$\% \text{ MM} = 1.08\text{A} + 0.55\text{S} \tag{8.5}$$

where:

A = percentage of ash and

S = percentage of sulfur.

The first term in this formula, 1.08A, is a correction for the loss in weight due to the elimination of water in the decomposition of clay minerals at high temperatures. As mentioned in Chapter 5, the water of hydration of mineral matter has been estimated to be 8 % of the ash value. The second term in the formula is a correction for the loss in weight when pyrite burns to Fe_2O_3. The Parr formula treats all sulfur as pyritic and makes no allowance for the decomposition of carbonates or fixation of sulfur in the ash.

The formula of King et al. is a more elaborate formula that allows for several effects:

$$\% \text{ MM} = 1.09\text{A} + 0.5\text{S}_{\text{pyr}} + 0.8\text{CO}_2 - 1.1\text{SO}_{3\text{ash}} + \text{SO}_{3\text{coal}} + 0.5\text{Cl} \tag{8.6}$$

where:

$$\begin{aligned}
\text{A} &= \text{percentage of ash,} \\
\text{S}_{pyr} &= \text{percentage of pyritic sulfur,} \\
\text{Co}_{2,}\ \text{So}_{3\text{ash,}} \text{ and } \text{So}_{3\text{coal}} &= \text{percentage of mineral carbon dioxide,} \\
\text{So}_{3\text{ash}} &= \text{percentage of So}_3 \text{ in ash,} \\
\text{So}_{3\text{coal}} &= \text{the total sulfur appearing as sulfates in coal, and} \\
\text{Cl} &= \text{percentage of chlorine.}
\end{aligned}$$

In this formula, the various numbers represent correction factors for the loss in mass due to the elimination of water in the decomposition of clay minerals (1.09), for the oxidation of pyrite to Fe_2O_3 and SO_2 (0.5), for the loss of CO_2 from mineral carbonates (0.8), and for the fixation of sulfur in the ash (1.1). The addition of the value representing the sulfate content of the coal sample and one half of the chlorine (assuming one half of the chlorine in coal is found in the mineral matter) completes the formula.

The formula of King et al. has been revised by the British National Coal Board, and the final formula is as follows [**46**]:

$$\% \text{ MM} = 1.13\ \text{A} + 0.5\text{S}_{\text{pyr}} + 0.8\text{CO}_2 - 2.8\text{S}_{\text{ash}} + 2.8\text{S}_{\text{coal}} + 0.5\text{Cl} \tag{8.7}$$

With this formula, a reasonably accurate value of the mineral matter can be calculated, but many parameters need to be determined to perform the computation.

8.7.1.3 *Interpretation and Uses of Mineral Matter Data*

An ultimate analysis that can claim to represent the composition of the organic substance of a coal is said to be on the dry, mineral-matter-free (dmmf) basis. The dmmf basis is a hypothetical condition corresponding to the concept of a pure coal substance.

The ASTM method of classifying coals depends on the calculation of the volatile matter yield and fixed carbon values on the dmmf basis. Calorific values are calculated on the moist, mineral-matter-free basis. The Parr formula is used in the ASTM system to calculate the mineral matter from ash and sulfur data.

8.8 Hardgrove Grindability Index of Coal

Grindability is an indication of the relative ease with which a coal may be pulverized in comparison with coals chosen as standards. The Hardgrove method has been accepted as the standard, and the ASTM Test Method for Grindability of Coal by the Hardgrove Machine Method (**D409**) is the standard method of grindability of coal. Recognizing the inherent quality and robustness of **D409**, the International Organization for Standardization (ISO) approved ASTM **D409** as the recommended grindability standard for its member organizations.

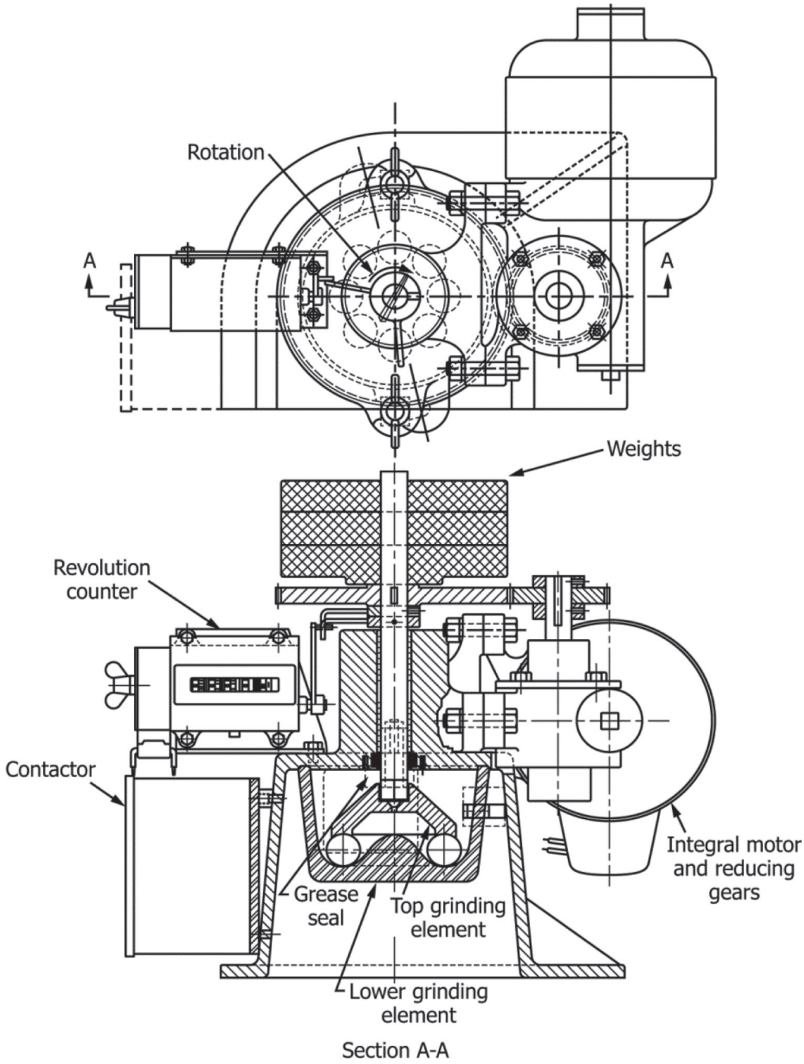
Each Hardgrove machine is calibrated by use of standard reference samples of coal with grindability indexes of approximately 40, 60, 80, and 110. These numbers are based on an original soft coal chosen as a standard coal, the grindability index of which was set at 100: the harder the coal, the lower the index number.

8.8.1 Determination of the Grindability of Coal by the Hardgrove Machine Method

In the Hardgrove machine method, a prepared sample receives a specified amount of grinding energy in a miniature pulverizer, and the change in size consist is determined by sieving. Equipment and materials needed to perform the test include a Hardgrove grindability machine (**Fig. 8.7**); USA Standard sieves with 16.0, 4.75, 2.36, 1.18, 0.60, and 0.07 mm openings; a mechanical sieve shaker; and standard reference samples for calibrating the grindability machine (indexes of approximately 40, 60, 80, and 110).

Before the test is run, a sample of coal is collected in accordance with ASTM Practice **D2234/D2234M**, **D6883**, or **D7430** and prepared according to Practice ASTM **D2013/D2013M**, except that the sample is not reduced beyond No. 4 (4.75 mm) sieve size. A 1000 g portion of this coal is air-dried for 12–48 h and stage-crushed to pass a No. 16 (1.18 mm) sieve with the production of a minimum of material passing a No. 30 (0.60 mm) sieve. A 50 g ± 0.01 g portion of the 16 × 30 material is evenly distributed in the grinding bowl of the Hardgrove grindability machine. The bowl is fastened into position, and the load is fully applied to the driving spindle.

FIG. 8.7 Hardgrove grindability machine.



Item	Mass, kg	Mass, lb
Lead	25.9	57.0
Shaft and Gear	2.0†	4.5
Top Ring	1.1	2.5
Total	29.0 ± 0.2	64.0 ± 0.5

† Editorially corrected in February 2012.

Source: Reprinted with permission from [**2**].

The machine is turned on and allowed to make 60 ± 0.25 revolutions. The grinding bowl is removed from the machine, and all of the coal particles are brushed onto a No. 200 (75 μm) sieve with a close-fitting receiving pan. The sieve is covered and shaken mechanically for exactly 10 min, and the underside of the sieve is brushed carefully into the receiver pan. This shaking and cleaning is repeated for two 5-min periods. The two portions of coal (i.e., that remaining on the sieve and that passing the sieve) are weighed separately to the nearest 0.01 g. The grindability index is then determined using a calibration chart obtained by processing the four standard samples. The calibration chart is constructed by plotting, on linear scale coordinates, the calculated weight of material passing a No. 200 sieve (50 g ± 0.01 g minus the weight remaining on the No. 200 sieve) versus the Hardgrove grindability index of the standard samples (see **Fig. 8.8**).

Failure to obtain duplicate results that fall within the tolerance levels allowed for intra- and interlaboratory comparisons may be due to several factors. The sample moisture may not have been in equilibrium with the laboratory atmosphere, the sample may have been over or under air-dried, excessive dust loss may have occurred during screening due to a loose-fitting pan and cover on the sieve, or the sample may not have had an even distribution of particles. The sample should be crushed with a plate mill to obtain an optimal distribution of particles that will pass a No. 16 sieve but not a No. 30 sieve.

8.8.2 Interpretation and Uses of Hardgrove Grindability Data

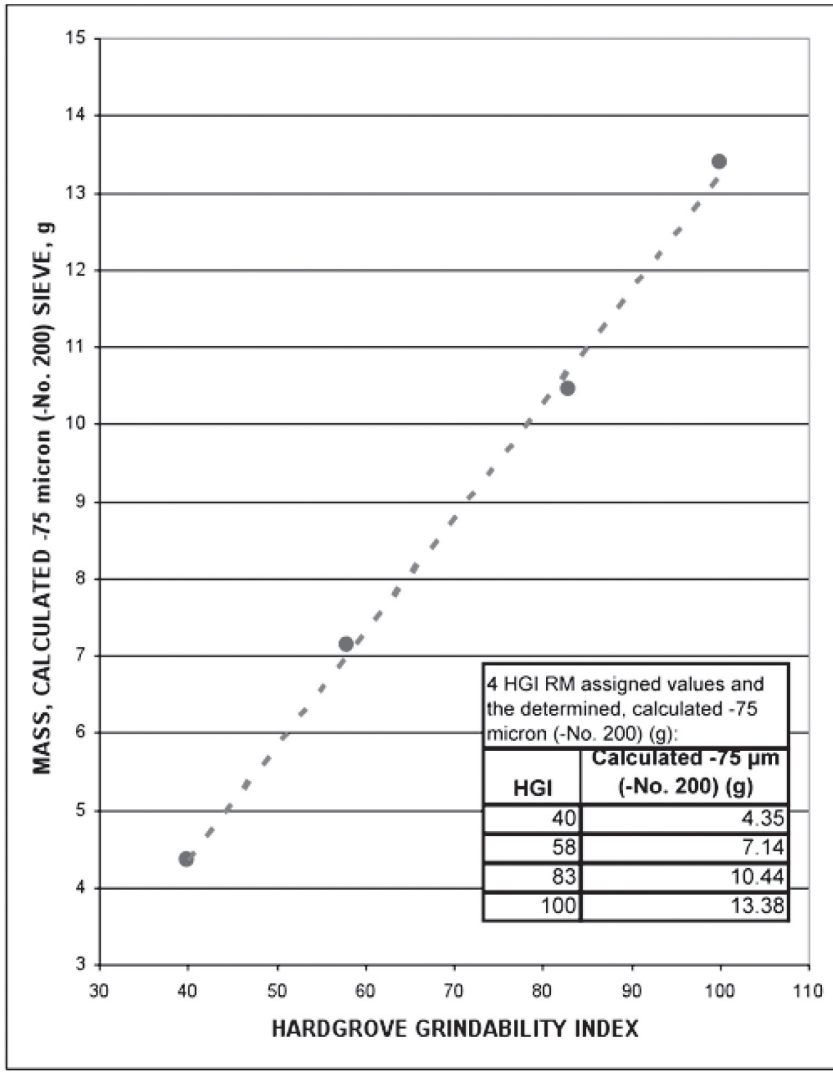
Generally, Hardgrove grindability index values follow the trend illustrated in **Fig. 8.9** [**101**]. However, the results of grindability measurements with the Hardgrove machine are affected by several factors, including ash content, moisture content, and temperature. The grindability index of coal varies from seam to seam and within the same seam. Grindability data are of utmost economic importance to the users of commercial grinding equipment and are used to predict how well coal can be ground for use in various types of combustion equipment.

8.9 Plastic Properties of Coals

All bituminous coals exhibit some degree of plasticity. Most of them are agglomerating, which is one of the parameters used to classify coals by ASTM **D388**. This means that these coals exhibit plastic properties ranging from becoming "sticky" to melting and becoming fluid when heated to temperatures above 300°C. ASTM standards used to assess the plastic properties of coals are as follows:

- ***D720:*** Test Method for Free Swelling Index of Coal
- ***D2014:*** Test Method for Expansion or Contraction of Coal by the Sole-Heated Oven
- ***D2639:*** Test Method for Plastic Properties of Coal by the Constant-Torque Gieseler Plastometer
- ***D5515:*** Test Method for Determination of the Swelling Properties of Bituminous Coal Using a Dilatometer

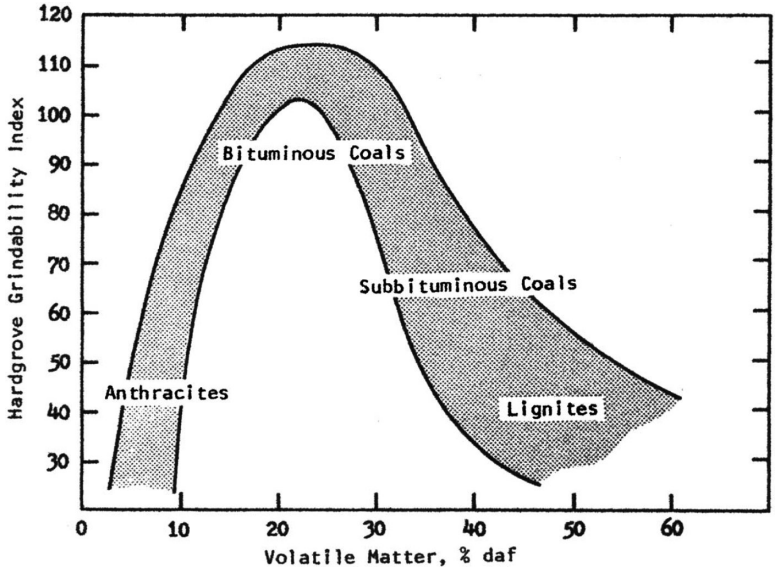
FIG. 8.8 Example of Hardgrove grindability calibration chart.



NOTE 1—Example: Use certified HGI RM and develop a similar calibration chart(s) for each HGI apparatus, or sieve sets, or both.

Source: Reprinted with permission from [**2**].

FIG. 8.9 Variation of Hardgrove grindability for different various coal ranks.



Source: Reprinted with permission from [**101**].

8.9.1 Free-Swelling Index of Coal

The free-swelling index (FSI) is a measure of the increase in volume of coal when heated under specified conditions. The results from a test may also be used as an indication of the caking characteristics of the coal when it is burned as a fuel. The volume increase can be associated with the plastic properties of coal; coals that do not exhibit any plastic properties when heated do not show free swelling. Gases formed by thermal decomposition while the coal is in a plastic or semifluid condition are responsible for the swelling. The amount of swelling depends on the fluidity of the plastic coal, the thickness of bubble walls formed by the gas, and interfacial tension between the fluid and solid particles in the coal. When these factors cause more gas to be trapped, greater swelling of the coal occurs.

The FSI of bituminous coals generally increases with an increase in rank, as is illustrated by the data given in **Table 8.11** [**102**]. Values for individual coals within a rank may vary considerably. The values for the lower-rank coals are normally less than those for bituminous coals, whereas anthracitic coals do not fuse and show no swelling value.

8.9.1.1 Determination of the FSI of Coal

The detailed procedures for determining the FSI of coal are found in ASTM **D720**. In this method, 1 g of the analysis sample is placed in a translucent silica crucible with a prescribed size and shape, and the sample is leveled in the crucible by light tapping

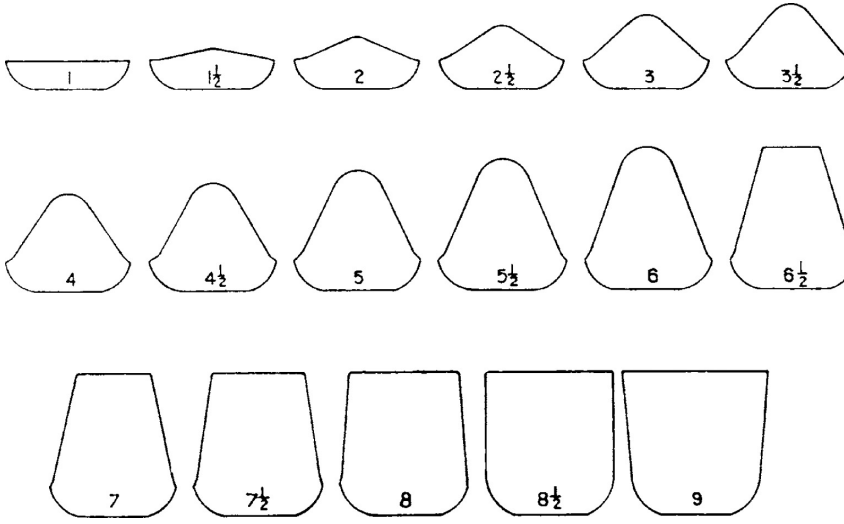
TABLE 8.11 Average FSI Values for Illinois and Eastern Bituminous Coals

Increasing Rank	Coals	FSI
High volatile C	Illinois Number 6	3.5
High volatile B	Illinois Number 6	4.5
High volatile B	Illinois Number 5	5.0
High volatile A	Illinois Number 5	5.5
High volatile A	Eastern	6.0–7.5
Medium volatile	Eastern	8.5
Low volatile	Eastern	8.5–9.0

Source: Reprinted with permission from [**102**].

(12 times with rotation) on a hard surface. The cold crucible is then lowered into a special furnace and heated to 800°C ± 5°C in 2.5 min. The test can be made with either gas or electric heating. The button formed in the crucible is then compared to a chart of standard profiles and corresponding swelling index numbers as shown in **Fig. 8.10.** Three to five buttons are made for each sample, and the average of the profile numbers is taken as the FSI.

FIG. 8.10 Profiles and corresponding swelling index numbers—not presented at full scale.



Source: Reprinted with permission from [**2**].

Some problems associated with the FSI measurement method are the proper heating rate, oxidation or weathering of the coal sample, and an excess of fine coal in the analysis sample. Failure to achieve the proper temperature in the furnace or, more importantly, the proper heating rate for the sample in the crucible leads to unreliable results. Uneven heat distribution along the walls of the crucible may also cause erratic results. Therefore, careful standardization of the equipment used is essential.

Oxidation or weathering of the coal sample leads to a low FSI. To minimize oxidation and the effects on the FSI, samples should be tested as soon as possible (within 24 h suggested) after they are collected and prepared. If oxidation of the coal is suspected, the test should be repeated on a known fresh sample of the same coal.

The size consist of the analysis sample may influence the FSI values of some coals. There is evidence that, for many coals, an excess of fine coal (-100 to -200 mesh) can cause FSI values to be as much as two index numbers high [**102**]. The amount of fine coal in the analysis sample should be kept at a minimum for this test (and others). Reducing the coal from a large particle size to a small particle size in one step tends to produce a high concentration of fine coal. The reduction of coal samples should be done in an appropriate number of steps to avoid this.

8.9.1.2 *Interpretation and Uses of FSI Values*

The test for the FSI is an empirical one, and FSI values can be used to indicate the coking characteristics of coal when burned as a fuel. However, these values are not reliable enough for use as parameters in a classification system. FSI values have been considered useful as an indication of the tendency of coals to form objectionable "coke trees" when burned in certain types of equipment, particularly equipment with underfeed stokers. The decline in the use of underfeed stokers in coal burning equipment, along with adjustments of combustion conditions, have minimized the problems due to coke tree formation. The use of FSI test data for help in solving this problem has also declined.

FSI values can be used as an indication of the extent of oxidation or weathering of coals. However, these are not as sensitive to weathering as calorific values or Gieseler plasticity values.

8.9.2 Plastic Properties of Coal by the Gieseler Plastometer

Testing with a Gieseler plastometer gives a semiquantitative measurement of the plastic property, or apparent melting of coal, when heated under prescribed conditions in the absence of air. The chemical nature of the constituents that account for a coal's plastic properties is not known. The material thought to be responsible for the plastic properties of coal has been successfully removed from coal by solvent extraction, leaving a nonplastic residue [**103**]. Such residue has been rendered plastic by returning to it the extracts obtained by the solvent extraction. No definite relationship has been established between the amount of extract and the plastic properties of the coal.

The plastic properties of coal are of practical importance in the coking industry. Therefore, the test for plasticity is useful in studying coals and blends used in carbonization.

8.9.2.1 *Determination of the Plastic Properties of Coal*

The Gieseler plastometer is one of the most often used instruments to measure the plastic properties of coal. It consists of a sample holder, a stirrer with four small rabble arms attached at its lower end, a means of applying a known torque to the stirrer, a means of measuring the rate of turning of the stirrer, and a way to heat the sample including provisions for controlling the temperature and rate of temperature rise. A schematic of the Gieseler retort assembly is shown in **Fig. 8.11** and the furnace assembly is illustrated in **Fig. 8.12**.

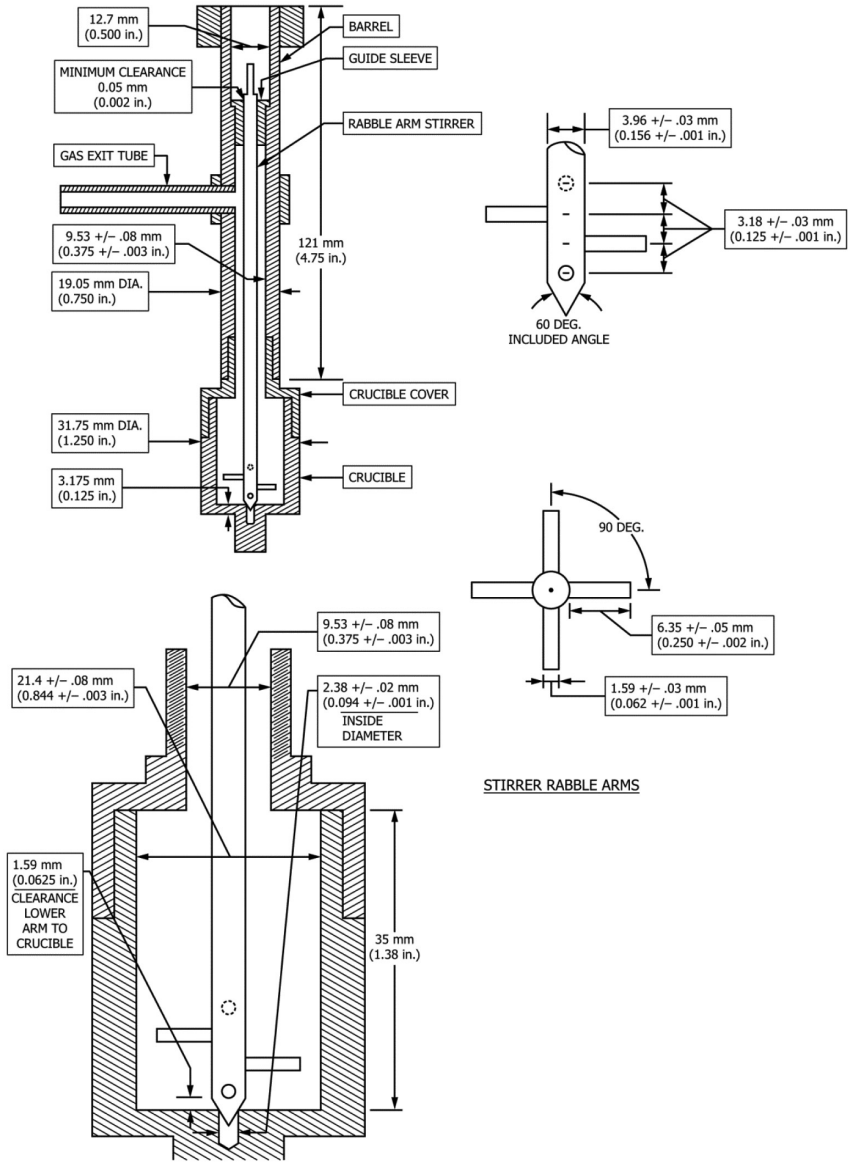
The procedure for measuring the plastic properties of coal is found in ASTM **D2639**. In this procedure, 5.0 g of coal passing a No. 40 sieve (425 μm) is placed in the sample holder with the stirrer in place. The coal is packed in and around the stirrer by rotating the stirrer to fill any voids and then applying a weight (10 kg) for 15 min to compress coal around the stirrer. The apparatus is then assembled and immersed in the heating bath, and a known torque is applied constantly and automatically to the stirrer by a magnetic brake system. No movement of the stirrer occurs at first, but as the heating continues, the stirrer begins to turn and its speed increases as the temperature rises. The movement of the stirrer is measured by a magnetic counter actuated by an electric eye or other suitable method. The temperature and rate of movement of the stirrer are observed and recorded throughout the test. The measured values are reported in dial divisions per minute (ddpm). The values normally determined with the Gieseler plastometer are the following:

- *Initial softening temperature:* Temperature at which the dial movement reached 1.0 ddpm (100 dial divisions = 1 complete revolution of the stirrer); may be characterized by other rates, but if so, then rate must be reported.
- *Maximum fluid temperature:* Temperature at which the dial pointer movement (stirrer revolutions) reaches the maximum rate.
- *Solidification temperature:* Temperature at which the dial pointer movement stops.
- *Maximum fluidity:* Maximum rate of dial pointer movement in dial divisions per minute.

The sample used in this test should be prepared by air-drying a laboratory sample (4 kg crushed to pass a No. 4 [4.75 mm] sieve) and then crushed in stages to pass a No. 40 (425 μm) sieve. The test should be run immediately after preparing the sample.

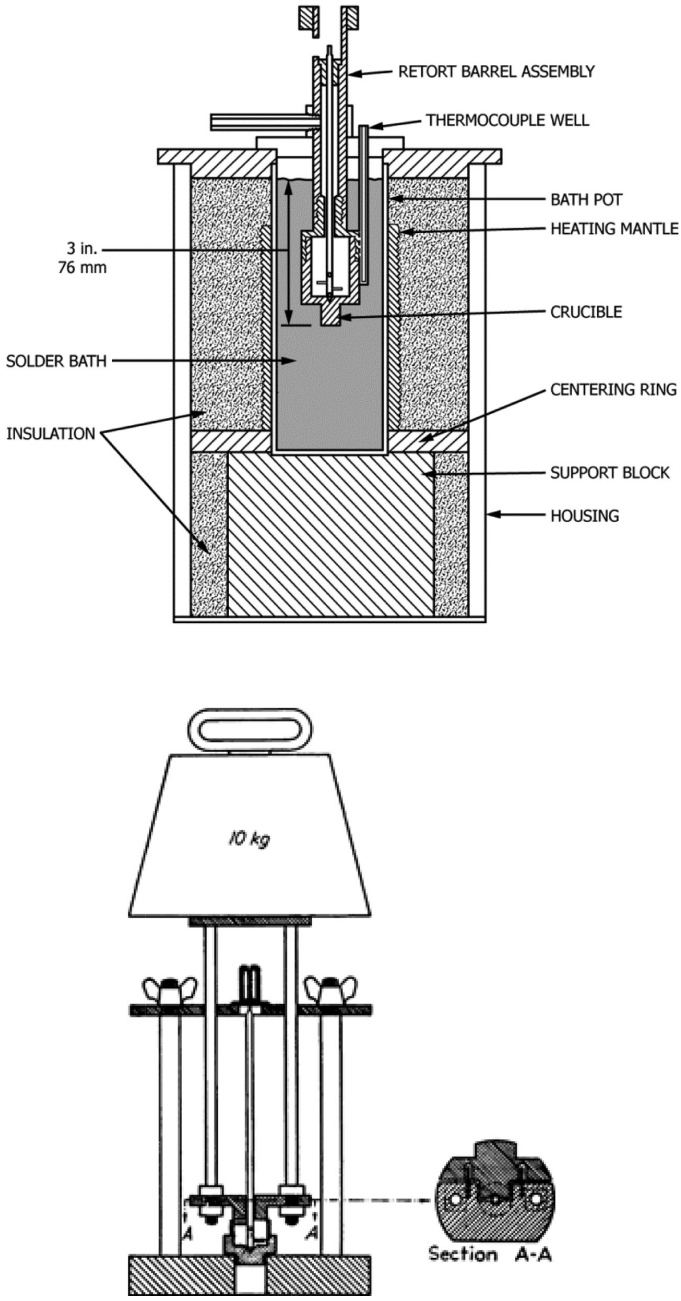
The method of measuring the plastic properties of coal is empirical, and strict observance of the requirements and conditions is necessary to obtain repeatable and reproducible values. Many problems are associated with the method, some of which are due to the nature of the coal itself and others to the equipment used. Some problems that arise because of the nature of the coal used are oxidation, packing in the sample holder, and swelling.

FIG. 8.11 Gieseler retort assembly.



Source: Reprinted with permission from [**2**].

FIG. 8.12 Gieseler loading device and furnace assembly.



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Plastic properties are sensitive to the oxidation of weathering of coals. Maximum fluidity is lessened, and extensive oxidation may completely destroy the fluidity of coal. Samples should be tested as soon as possible after they are collected and should be stored under water or in a nonoxidizing atmosphere if there is to be a delay before they are tested.

Proper packing around the stirrer in the plastometer is an important step in the measurement of plastic properties. Some coals may not pack easily because of their weathered condition or the size consist of the sample. An excess of very fine coal makes the test sample hard to pack.

Some coals swell considerably when heated and may extrude from the sample cup into the barrel of the plastometer. This swelling applies extra resistance to the stirrer, leading to lower plasticity values. A well-fitted washer on top of the coal sample may help control the swelling.

Some problems associated with the equipment used are the rate of heating, surface area of the rabble arms on the stirrer, and the manner in which torque is applied. The standard rate of heating influences values obtained in the test, with maximum fluidity being influenced the most. Heating rates higher than the standard lead to higher fluidity values, and lower rates of heating produce lower fluidity values. The plastometer must be thoroughly cleaned after each test. Frequent use and cleaning wear away the stirrer and the rabble arms, gradually decreasing their surface area. As a result, higher maximum fluidity values will be obtained. When new, the rabble arms have a total surface area of 136 mm^2. When the surface area decreases to 116 mm^2 (usually after 30–40 tests), the rabble arms should be discarded.

8.9.3 Dilatometer Test

Another ASTM test method for measuring the swelling properties of bituminous coals is the ASTM Test Method for Determination of the Swelling Properties of Bituminous Coal Using a Dilatometer (**D5515**). This test method involves preparing a coal pencil and determining the changes of the coal pencil height in a retort tube during a prescribed heating cycle. The principle of this test method is that the final volume of char obtained at the conclusion of the test is dependent on the mass of coal in the coal pencil and on the radius of the retort tube.

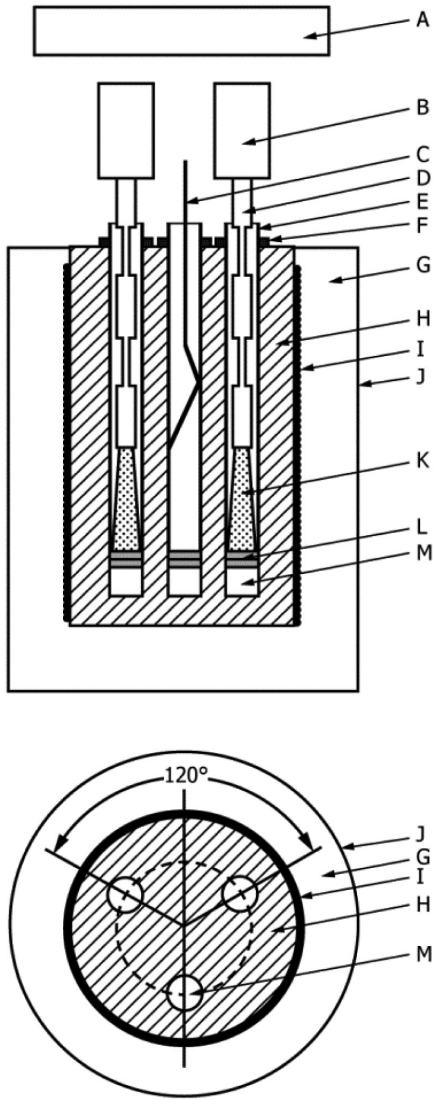
In ASTM **D5515**, a coal pencil is prepared from a mixture of air-dried 250-μm (No. 60 sieve) coal and distilled water (<11% by weight). The pencil is trimmed to 60 mm, placed in a retort tube, and a piston inserted (see **Fig. 8.13**). The mass of the pencil is recorded, as is the amount of coal and water used to prepare it. The retort tube is placed into the heating apparatus and heated from 315°C at 3 ± 0.1°C /min to as high as 520°C. The test is terminated when there is no movement of the piston. The movement of the piston in the retort is recorded with the appropriate apparatus, and the following information is reported:

- *Maximum contraction temperature, T2:* The temperature at which the coal pencil starts swelling, expressed in degrees Celsius. For coals that exhibit contraction

only, T2 is the temperature at which the coal pencil reaches its minimum (see **Fig. 8.14**).

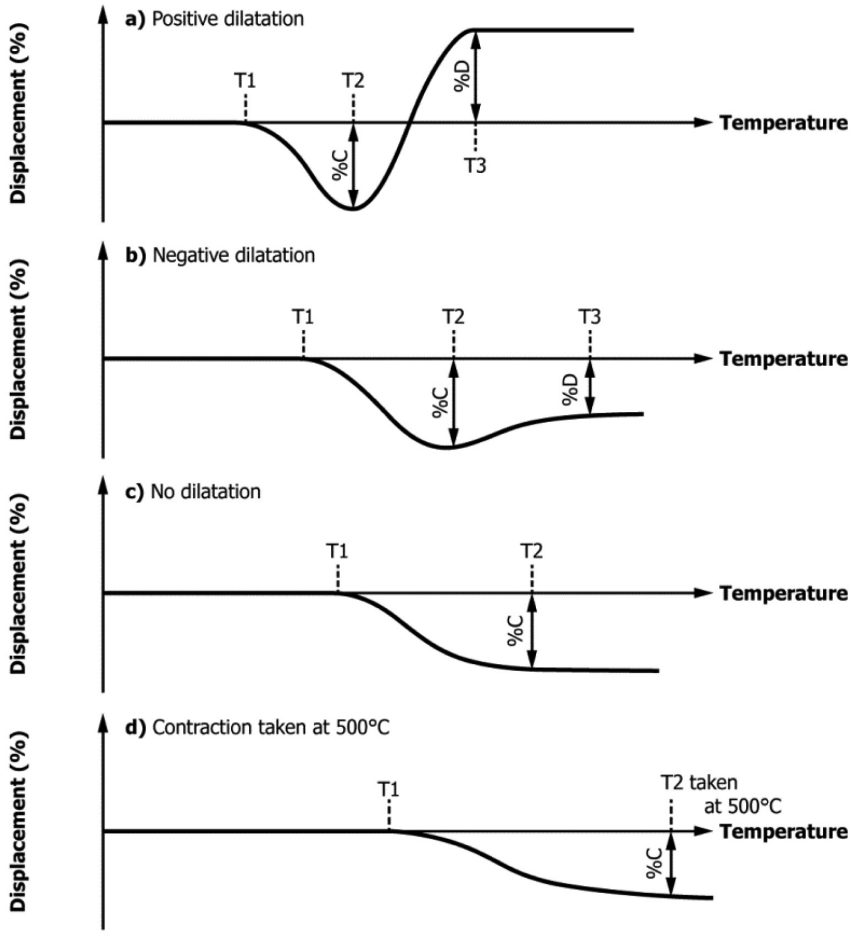
- *Maximum dilation temperature, T3:* The temperature at which the coal pencil first reaches a maximum height after swelling, expressed in degrees Celsius.

FIG. 8.13 Typical dilatometer apparatus.



Source: Reprinted with permission from [**2**].

FIG. 8.14 Types of dilation curves.



Source: Reprinted with permission from [**2**].

- *Percent contraction, % C:* The minimum recorded height of char expressed as a percentage and based on an initial coal pencil height of 60 mm.
- *Percent dilation, % D:* The maximum recorded height of char expressed as a percentage and based on an initial coal pencil height of 60 mm.
- *Softening temperature, T1:* The temperature at which the height of the coal pencil contracts 1.0 % (0.6 mm) from the highest recorded initial pencil height, expressed in degrees Celsius.
- *Equivalent percent dilation for* 2.50 g *air-dried coal, %* $D_{2.50}$*:* The calculated percent expansion for a 2.50 g, unmoistened, 60 mm long, coal pencil corrected for average tube radii, expressed as a percentage.

Other dilatometer test methods used to measure the swelling properties of coal are the Ruhr (ISO Method 8264) and the Audibert-Arnu (ISO Method 349) methods, neither of which agree very well with ASTM **D5515** test results or with each other. The primary reason for the differences in the methods is the manner in which the coal pencil used for the tests is trimmed (different ends).

8.9.3.1 *Interpretation and Uses of Plasticity Data*

The primary use of plastic property data is for assessing the coking properties of coals. Maximum fluidity values are most often used in this respect, but the plastic range of coals has also been used as a guide for blending coals for carbonization. The plastic range is the temperature between the softening and the solidification temperature. Plastic property data should not be interpreted too closely. These data are probably more useful when applied to low-fluid, less strongly coking coals than in assessing differences in the coking characteristics of high-fluid, more strongly coking coals.

Chapter 9 | Developments in Instrumentation for Routine Coal and Coke Analysis

Over the past three decades there have been several new ASTM Standard Test Methods developed that introduced new analytical instrumentation into the area of routine coal and coke analysis. Instrumentation examples include X-ray fluorescence spectrometry (XRF); inductively coupled plasma-atomic emission spectroscopy (ICP-AES); inductively coupled plasma-mass spectroscopy (ICP-MS); graphite furnace atomic absorption spectrometry (GFAAS); macro-thermogravimetric analyzer (macro-TGA); and automated elemental analyzers for carbon, hydrogen, and nitrogen, mercury, arsenic, selenium, and chlorine. In addition, there have been computer-based automatic controllers and recorders developed for several types of instrumentation. Examples include calorimeters, plastometers, and dilatometers.

Starting in the 1980s and continuing through to the present, perhaps the most significant development in analytical instrumentation has been the implementation of computer control of instruments. The interfacing of a computer, even as primitive as it was in the 1980s, with an analytical instrument completely changed the manner in which laboratory measurement data were acquired. At first, the fact that measurements could be made rapidly and repeatedly with computer-controlled instrumentation allowed the use of less precise instruments to acquire many data that could be massaged and summarized to yield precise results. The observation that "the precision of a mean value is inversely proportional to the square root of the number of measurements that yield the value" holds true for this measurement concept. This is the principle of operation of Fourier-transform and signal averaging techniques in analytical instrumentation.

The development of computer-controlled instrumentation, sometimes using less precise hardware to deliver precise measurements through repetitive measurements and signal averaging techniques, reduced the cost of analytical instrumentation. This led to more instrumentation and subsequently to many more improvements in the instrumentation. The very successful introduction of computer-controlled instrumentation changed the course of data gathering in most coal and fuel laboratories. Instruments that could deliver repetitive measurements coupled with autosampling attachments allowed even more unassisted data collection.

Gradually, this computer-controlled instrumentation has been included in the development and refinement of ASTM International standard methods.

The introduction of microcomputers and their interfacing with analytical instrumentation has revolutionized laboratories everywhere over this time period. Coal analysis laboratories have also benefited greatly from these developments. Most of the time the new analytical instrumentation performs tests and analyses in a fraction of the time needed for classical methods of analysis. Several ASTM Standard Test Methods have been revised to include computer-controlled instrumentation for data gathering, interpretation, and reporting. At the same time, there are many analytical instruments being used for coal analysis and characterization that have not been developed into standard test methods.

The development of an ASTM Standard Test Method involves a sometimes lengthy process of ruggedness testing of proposed methods, approval of the ruggedness test results by the ASTM Task Group planning an Interlaboratory Study (ILS; round robin), and then balloting through the ASTM International subcommittee and main committee. The standard development process was discussed in Chapter 4 on coal testing. Quite often the entire process requires several years to complete.

All ASTM standards are reviewed every 5 years. All parts of a standard may be reviewed and revisions recommended. Editorial changes can be automatically accepted, but any recommended change in the standard that is deemed a noneditorial change must be balloted at the subcommittee and main committee levels. If a proposed revision of a standard is deemed to be a substantial change, such as a change in procedure or a change in type of instrumentation, there may be a need for an evaluation of the precision and bias statement. A Task Group is often formed to make such an evaluation. Sometimes the evaluation leads to the organization of an ILS to revise the precision and bias statement. Of course, these revisions take time and are always balloted at the subcommittee and main committee levels before publication. This entire process helps keep the ASTM International standards up to date by introducing new and updated instrumentation and equipment through the revisions.

The review of ASTM Standard Test Methods is an effort to upgrade the standards to keep up with developments in the areas of testing and characterization of coals and coal products. The rapid expansion of different types of computer-controlled analytical instrumentation over the last three decades has made good, inexpensive, and advanced instrumentation available for use in coal analysis laboratories. Committee D05 on Coal and Coke has made commendable efforts to incorporate this new instrumentation into the standard test methods. However, there is a lot more that can be done.

9.1 Reference Materials and Calibration

Coal is a very heterogeneous material, any sample of which contains 50–60 elements detectable by today's analytical methods. Although a few elements (e.g., C, H, and O)

are rank dependent, the concentrations of most elements vary from coal to coal and location to location. Many of the routine tests to determine the quality of coal (moisture, ash, volatile matter, ash fusion, plasticity, etc.) involve a combination of physical and chemical tests. Some of these tests are highly empirical.

In the world of coal and coke testing, emphasis is placed on a laboratory's ability to generate results comparable to those obtained by most other laboratories when performing the same test (reproducibility). ASTM Standard Test Methods all have precision and bias statements to help laboratories compare their results to other laboratories. Because many of the routine test methods used for coal and coke are empirical, the laboratories must closely adhere to specified test conditions to get comparable results. Sometimes it is necessary to use "correction factors" generated through extensive studies to obtain comparable results.

One pathway to generate results that show good agreement among laboratories is to use certified reference materials (CRMs) for calibrating instruments or "correcting" results to those obtained by a "referee" method. NIST standard reference materials (SRMs) are available for calibrating instruments that yield comparable results in elemental analysis. Sulfur, chlorine, mercury, major and minor elements, etc., are examples. For empirical tests such as moisture, ash, and volatile matter, CRMs are available. These CRMs allow laboratories to calibrate equipment for the classical methods (**D3173**, **D3174**, and **D3175**) and the macro-TGA methods (**D7582**). This practice for proximate analysis needs to grow. CRMs are also available for the Hardgrove Grindability Test Method (**D409**). However, CRMs are not available for other empirical tests such as the ash fusion and plasticity test methods. Work is needed in this area.

As mentioned previously, NIST SRMs are generally available for the different types of elemental analysis commonly used for coal and coke. High-quality CRMs are also readily available for most of the elements of interest to laboratories that analyze coal and coke. These reference materials are used for calibration of the various elemental analyzers. Until recently, most coal chemists believed that only coals, cokes, or coal and coke ashes were acceptable for calibrating instruments for coal and coke analysis. This perceived requirement has held up the development of some standard test methods, especially those using analytical instrumentation. The following comments are offered about calibrating materials.

Every test method has two basic parts: (1) sample preparation and decomposition and (2) detection of analyte. In classical gravimetric methods, such as the determination of sulfur in coal by the Eschka method or calorimeter combustion vessel washing method, the detection of the analyte is done by weighing the ignited barium sulfate ($BaSO_4$) precipitate. Moisture in coal is determined as the mass lost after drying the sample. This mass loss is measured in a final weighing. Ash and volatile matter are also determined by the final weighings of residues after heating. In classical volumetric titration methods, the endpoint in the titration determines the amount of analyte. There are many preparation and decomposition steps in the various methods before the analyst can get to the final weighing in classical gravimetric methods or the final

endpoint in classical volumetric methods. Most of the work in performing these tests involves the sample preparation and decomposition (if needed) and the presentation of the sample for measurement in the "cleanest" form possible. The measurement or detection of the sample should not be hindered by any material or species considered an interferent in the measurement.

In instrumental test methods, especially spectroscopic methods, the need to present a "clean" analyte for a final measurement is extremely important. For example, in the atomic absorption spectrometric analysis of major, minor, and trace elements, the instrument is calibrated with the purest materials available in very dilute solutions with just enough acid to keep the elements in solution. The same is true for ICP-AES procedures and is especially true for ICP-MS or GFAAS procedures. In the workup and preparation of solutions containing the analytes, every effort is made to reduce the amount of extra material (through filtration or dilution) that is presented to the flame, torch, etc., for analysis. A blank with all reagents prepared and analyzed in the same manner as the sample allows the analyst to subtract absorbances contributed by materials other than the analyte.

In the case of instrumental analysis of solid substances such as coal and coke, the most common method of preparing and decomposing the sample is combustion in oxygen. After combustion, the gaseous products are filtered to remove dust. Sometimes some acid gases are scrubbed using special reagents. The resultant analyte gas, whether it is carbon dioxide (CO_2), water vapor, nitrogen (N_2), sulfur dioxide (SO_2), or mercury (Hg), is fairly clean when it is measured by absorption of infrared or ultraviolet (UV) radiation or with a thermoconductivity detector.

For best results, the instrumental detection system should be calibrated with the cleanest calibrant available. Recent revisions have been made to some ASTM Standard Test Methods to incorporate the use of CRMs that are pure substances to calibrate elemental analyzers. These standards include **D5373** (carbon, hydrogen, and nitrogen in coal and carbon in coke) and **D4239** (sulfur in coal and coke). Standards that use AAS, ICP-AES, and ICP-MS instruments have always required solutions of pure elements for calibration. The calibration of calorimeters has always been done with pure substances.

9.2 New Standard Test Method Development

One of the most accurate and most reliable methods for determining the presence and concentration of common anions, including F^-, Cl^-, Br^-, SO_4^{2-}, and PO_4^{3-}, is ion chromatography (IC). After years of work and several "almost finished" studies, there is still no standard test method using this powerful tool for the analysis of common anions in coal and products from coal. Many laboratories are using some form of IC for anion analysis, and these procedures need to be included in standard test methods for coal and coal products.

As research uncovers new methods for characterizing coal and materials derived from coal, there is an increase in the interest in developing the procedures and

methods for the routine analysis of coal and coal products. Quite often these specialized methods are restricted for use in a single laboratory, in a small group of related laboratories, or by a single operator or small group of operators. To be eligible for development into an ASTM Standard Test Method, a procedure must be rugged enough that at least six different laboratories can use the same procedure and same type of instrumentation and produce results that are statistically similar at the 95 % confidence level. This is a tall order for analyses that require very expensive instrumentation and highly trained technicians.

There are currently no standard test methods under the jurisdiction of ASTM International Committee D05 on Coal and Coke that are "performance based." The development of this type of standard test method relies on the ability of the participating laboratories to convincingly demonstrate a high degree of accuracy and acceptable precision in the analysis of a particular type of material. The laboratory can use any analytical method they choose within the guidelines of the ILS. The success of these methods relies on the availability of SRMs or high-quality CRMs, or both, which laboratories can use to check their performance.

The ASTM D05 Standard Test Method that comes closest to a performance-based standard is Method **D6357**—Trace Elements in Coal, Coke, and Combustion Residues by Inductively Coupled Plasma-Atomic Emission Spectrometry Inductively Coupled Plasma-Mass Spectrometry and Graphite Furnace Atomic Absorption Spectrometry (ICP-AES, ICP-MS, GFAAS). This test method uses a combination of three types of analytical instrumentation to determine a suite of 13 trace elements. None of the 3 instruments is the "best" for determining each of the 13 trace elements, but each of the 3 is the "best" instrument for a few of the elements. Therefore, the ILS used to develop the conditions and procedures for determining the 13 elements involved the use of all three instruments. It is highly unlikely that more than one or two laboratories participating in the study had the capability to use all three types of analytical instrumentation for their analysis. The combination of laboratories participating in the study did have the collection of instrumentation needed to analyze enough samples (at least six) to satisfy the requirements for preparing the precision and bias statement needed for the standard test method. In the ILS, the laboratories were not asked to achieve a specified level of competence in analyzing all of the elements, as would be the case in the development of a true "performance-based" study. Instead, the laboratories were requested to submit data for the elements they believed they could analyze with one or more of the three instruments listed above.

There are currently several active ASTM D05 Task Groups working on the development of new standard test methods. Some of these are:

- A test method using oxidative hydrolysis with IC detection for determining chlorine and fluorine in coal and coal combustion residues.
- A test method for the determination of chlorine in whole coal using XRF spectroscopy.

- An improved method for the determination of moisture in coke.
- A method for determining the air dry loss moisture in coal using microwave drying.
- An improved method for determining the forms of sulfur in coal. The proposed procedures call for the determination of sulfate sulfur and pyritic iron using ICP-AES, which is a different procedure than that in the current method.
- Development of a common ash preparation procedure for the standard test methods for major, minor, and trace elements in coal and coke and their combustion residues.
- An improved method for determining the equilibrium moisture in coal.

Discussions of biomass, refuse-derived fuels (RDFs), municipal solid waste (MSW), and blended fuels are very common at all ASTM D05 meetings. Currently, many of the test methods used for the testing and characterization of coal and coke are being used for the analysis of these new fuels. Future developments in the uses of these fuels will mandate that new testing and characterization standards be developed or that the current test methods used for coal and coke be modified to more adequately address the needs of this new and developing industry.

Petroleum coke has chemical and thermal properties much like those of coal-derived coke. Many of the Committee D05 standard tests for coal and coke are well suited for use with petroleum coke. Several recent interlaboratory studies used petroleum coke samples in the suite of samples chosen for the study. Some studies have often led to separate precision and bias statements for coke, whereas previous versions of the standard had a single coal and coke precision and bias statement. The use of a combination of petroleum coke and coal-derived coke for the development or revision of standard test methods will continue.

9.3 Historical Coal and Coke Data

One of the major concerns about the development of new standard test methods is a possible bias that may exist between the values obtained by two or more test methods. When a new standard test method is under development, it is a common practice to conduct an ILS to compare values obtained by the new test method with the values obtained by the older (classical) method. The existing test method is considered the "referee method." An example of such a comparison was reported in the development of the macro-TGA test methods for proximate analysis [**35,36**]. These studies also showed that preserved splits of some coals yield essentially the same dry ash and dry volatile matter values when tested by different instruments 20 or more years later. As was shown in **Figs. 5.2** and **5.3**, there is a consistent relationship between the volatile matter values determined by the classical method (**D3175**) and the newer macro-TGA method (**D7582**). This relationship allows laboratories to predict values of one method from the measured values of the other method. This is the same principle that allows a laboratory to use CRMs to calibrate their instruments and report the expected values

of the "referee" method. The important aspect of these comments is that it shows the consistency of proximate analysis values over time.

Instrument manufacturers offer new versions of an analytical instrument when they think the market wants or needs it. A company will generally offer a new version of a popular analytical instrument every 7–10 years. Instrument manufacturers have offered four to six models of calorimeters; sulfur analyzers; macro-TGA systems; and carbon, hydrogen, and nitrogen analyzers over the last 3 decades. The critical test for these new models is that they must yield values comparable to the older version of the instrument and to the values from similar instruments. If they do not meet this requirement, then they lose their place in the market. More importantly, almost all of these new instruments can produce results as good, or better, than the equipment and instruments used to develop the original precision and bias statements in ASTM International Standard Test Methods.

For some highly empirical test methods such as Hardgrove grindability and volatile matter determination, the use of CRMs maintains a reasonably good agreement between values obtained recently with historical data. For some highly empirical test methods such as free-swelling index, Gieseler plasticity, and dilatometry, no reference materials are available to verify the consistency of values. These standard tests are fortunately robust enough that they can "stand on their own" with the only requirement being that agreement of values is reached among laboratories associated with a particular commercial transaction.

In summary, there are many problems associated with the analysis of coal. Some of these problems are due to the heterogeneous nature of coal, some are due to the tendency of coal to gain or lose moisture and to undergo oxidation when exposed to the atmosphere, and some are due to the many tests and analyses required to adequately characterize a coal.

ASTM International, with the cooperation of representatives from all areas of the coal industry, has developed standard methods of analysis for coal. Many of these tests are empirical in nature, and strict adherence to the procedural guidelines is necessary to obtain repeatable and reproducible results. The type of analysis normally requested in the coal industry may be a proximate analysis (moisture, ash, volatile matter, and fixed carbon) or an ultimate analysis (carbon, hydrogen, sulfur, nitrogen, oxygen, and ash). Quite often, a variation of a proximate analysis or an ultimate analysis is requested, along with one or more of the miscellaneous analyses or tests discussed in this chapter.

Restrictions that have been placed on the coal used in coal-fired power plants and other coal-burning facilities have created a need for more coal analyses as well as a need for more accurate and faster methods of analysis. This trend will continue, and more testing will be required.

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Dr. John T. Riley, professor emeritus of Western Kentucky University, has served as secretary, vice chair, and chair of ASTM International Committee D05 on Coal and Coke. He has also been chair of Subcommittee D05.29 and several D05 task groups in addition to serving as secretary of others. He has served as chair of task groups leading to the development of six standard test methods advancing instrumental coal analysis, and has written papers promoting the use of ASTM standards both domestically and internationally.

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