Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications

Mark F. Vitha, Series Editor

Handbook of Coal Analysis

SECOND EDITION



JAMES G. SPEIGHT

WILEY

HANDBOOK OF COAL ANALYSIS

SECOND EDITION

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CHEMICAL ANALYSIS

A SERIES OF MONOGRAPHS ON ANALYTICAL CHEMISTRY AND ITS APPLICATIONS

Series Editor
MARK F. VITHA

Volume 182

A complete list of the titles in this series appears at the end of this volume.

PREFACE

The success of the first edition of this text has been the primary factor in the decision to publish a second edition.

Coal analysis is an essential task in determining the use of coal. Analytical methods help determine whether or not coal meets the needs of a specific application, or to characterize the general quality of the coal for future reference. For example, if the coal has high organic sulfur content, then it may have to be mixed or blended with a coal of lower sulfur content in order to meet sulfur emissions standards, or the sulfur may have to be cleaned out of the flue gas by flue-gas desulfurization (FGD), which is an expensive procedure. Similarly, analysis may determine whether a trace element, such as arsenic or mercury, may be eliminated from a coal by washing or whether it must be removed during flue gas cleaning. Finally, in extreme cases, analysis may determine that the coal cannot be used.

Furthermore, coal is again being seriously considered as an alternate fuel source to petroleum, not so much for the production of liquids but more for the generation of power and as a source of chemicals. The reaffirmation by the United States to a clean environment through the passages of the various environmental laws as well as serious consideration to the effects of combustion products (carbon dioxide) on the atmosphere are all given consideration in this new text.

In addition, the demand for coal products, particularly liquid fuels (gasoline and diesel fuel) and chemical feedstocks (such as aromatics and olefins), is increasing throughout the world. Traditional markets such as North America and Europe are experiencing a steady increase in demand whereas emerging Asian markets, such as India and China, are witnessing a rapid surge in demand for liquid fuels. This has resulted in a tendency for existing refineries to seek fresh refining approaches to optimize efficiency and throughput. In addition, the increasing use of the heavier

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feedstocks by refineries is forcing technology suppliers/licensors to revamp their refining technologies in an effort to cater to the growing customer base.

As in the previous Edition, this Edition has references cited throughout the text, which will allow the reader to such citations for more detail. However, it should be noted that only selected references could be employed lest the reference lists outweigh the actual text. It would have been impossible to include all of the relevant references. Thus, where possible, references such as review articles, other books, and those technical articles with substantial introductory material have been used in order to pass on the most information to the reader.

In addition, chapters have been added to give the reader an introduction to the formation of coal, which will help understands the complexity of the organic portion of coal as well as the complex nature of the inorganic portion of coal (the mineral matter). Overall, the book will provide the reader with a detailed overview of the chemistry and technology of coal analysis as is required in the 21st century. Moreover, the text will prove useful for those scientists and engineers already engaged in the coal industry who wish to gain a general overview or update of the science of coal and the various analytical test methods.

The book will also provide the reader with the necessary information about testing and analyzing coal. Moreover, it will explain the meaning of test results and how these results can predict coal behavior and its corresponding environmental impact during use and include:

- Coverage of nomenclature, terminology, sampling, and accuracy and precision of analysis.
- Explanation of coal behavior relative to its usage alongside the corresponding environmental issues.
- · Presentation of necessary standard tests and procedures.
- Step-by-step test method protocols for proximate analysis, ultimate analysis, mineral matter, physical and electrical properties, thermal properties, mechanical properties, spectroscopic properties, and solvent properties.
- Emphasis on relevant American Society for Testing and Materials (ASTM) standards and test methods

To assist readers in understanding the material, a comprehensive Glossary is provided in which each item is defined in straightforward language that will enable readers to better understand the terminology related to coal. References at the end of each chapter lead readers to more in-depth discussions of specialized topics.

This book will be an essential reference for analytical chemists, process chemists, and engineers in the coal industry as well as other professionals and researchers who are looking to coal as a means to decrease dependence on foreign oil sources and devise more efficient, cleaner methods of energy production from coal.

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HISTORY AND TERMINOLOGY

1.1 INTRODUCTION

Coal is an organic sedimentary rock that contains varying amounts of carbon, hydrogen, nitrogen, oxygen, and sulfur as well as trace amounts of other elements, including mineral matter, as well as methane which is found within the pore systems of the coal (ASTM D121; Speight, 2013a). It is a solid, brittle, combustible, carbonaceous rock formed by the decomposition and alteration of vegetation by compaction, temperature, and pressure and varies in color from brown to black and is usually stratified as a *coal seam*. The source of the vegetative precursors to coal is a variety of ancient plant forms as well as ancient woody precursors. The plant precursors that eventually formed coal were deposited as dead and decaying carbonaceous materials that were compacted, hardened, chemically altered, and metamorphosed by the pressure (in some cases accompanied by heat) of overlying sediments over geologic time (Table 1.1). When the plants died, the biomass was deposited in anaerobic, aquatic environments where the low oxygen level prevented the reduction of the biomass and release of carbon dioxide.¹

¹The standard method (ASTM D121) forms the basis for coal standards in which the technical terms used in the standards for coal and coke are defined. In addition, the standards includes terms related to the sampling of coal and coke under conditions required for most commercial and technical purposes related to coal and coke as well as the bias and related statistical testing terms. Also included are (1) the description of coal, both visually in the field and microscopically in the laboratory, and (2) the chemical and physical analyses of coal and coke involved in the classification of coal.

TABLE 1.1 The Geologic Timescale

Era	Period	Epoch	Approximate Duration (Millions of Years)	Approximate Number of Years Ago (Millions of Years)
Cenozoic	Quaternary	Holocene	10,000 years	
		Pleistocene	ago to the present	0.01
	TP			
	Tertiary	Pliocene	11	2
		Miocene	12	13
		Oligocene	11	25
		Eocene	22	36
		Paleocene	71	58
Mesozoic	Cretaceous		71	65
	Jurassic		54 .	136
	Triassic		35	190
Paleozoic	Permian		55	225
	Carboniferous		65	280
	Devonian		60	345
	Silurian		20	405
	Ordovician		75	425
	Cambrian		100	500
Precambrian			3380	600

Evidence of the types of plants that contributed to carboniferous deposits can occasionally be found in the coal as fossil imprints as well as in the shale and sandstone sediments that overlie coal deposits.

Coal sediments (coal beds, coal seams) can range from fractions of an inch to hundreds of feet in thickness and are found in all geologic periods from Silurian through Quaternary, but the earliest commercially important coals are found in rocks of Mississippian age (Carboniferous in Europe). Coal is generally formed in either a fluvial environment or in a basin that is open to marine incursions and consists of more than 50% w/w (typically more than 70% v/v) carbonaceous material (organic material containing carbon, hydrogen, and other elements as well as inherent moisture, which is a moisture that occurs within the coal).

1.2 DEFINITIONS AND TERMINOLOGY

Simply and by definition, coal is an organic rock. In addition, coal is also defined as a black or dark-brown combustible mineral substance consisting of carbonized vegetable matter, used as a fuel.

It is customary (especially through this text) to use the word *coal* in the singular form but the word is, in reality, applicable to materials having a rather wide range of properties – this is similar to the use of the word *petroleum* (or *crude oil*), which encompassed a variety of materials from low-boiling (light) conventional crude oil to

the thicker viscous high-boiling heavy oil (Speight, 2014). In terms of coal, one sample might be a wet, easily crumbling brown material looking like partially decayed wood (Lignite) while another would be a very hard, glossy black, lustrous material (anthracite). In addition, the heating value (Chapter 8) of these samples would range from about 5000 to about 15,000 BTU/lb. Thus, the use of the word *coal* in this text implies either a single family member of a uniquely defined material as well as a family of natural-occurring family of organic rocks having both similarities and differences within the members of that family.

The name *coal* is thought to be derived from the Old English *col* that was a type of charcoal at the time. Generally, coal was not mined to any large extent during the early Middle Ages (prior to 1000 AD) but there are written records of coal being mined after 1000 AD. Moreover, coal is, in some areas, referred to as *sea-coal* as it is occasionally found washed up on beaches, especially those in the north east area of England. However, the rapidly expanding use of coal throughout the nineteenth century and the early part of the twentieth century has seen a phenomenal increase in coal use. This increased popularity has made it necessary to devise acceptable methods for coal analysis with the goal of correlating fuel composition and properties with behavior (Vorres, 1993; Speight, 2013a).

In the modern system of terminology, coal is subdivided into various types that are the result of geological processes pressure to the dead precursors over time and under suitable conditions (which are difficult to define), it is transformed successively into: (1) lignite, (2) sub-bituminous coal, (3) bituminous coal, and (4) anthracite (Speight, 2013a,b).

Lignite (sometimes referred to as brown coal) is the lowest rank of coal and used almost exclusively as fuel for electric power generation. Sub-bituminous coal, which has properties that range from similar properties of lignite to those of bituminous coal, is used primarily as fuel for steam-electric power generation (Speight, 2013b) and is an important source (through pyrolytic decomposition) of low-boiling aromatic hydrocarbons for the chemicals industry (Speight, 2013a). Bituminous coal is a dense black sedimentary rock that often has well-defined bands of bright and dull material; it is used primarily as fuel in steam-electric power generation, with substantial quantities used for heat and power applications in manufacturing and to make coke. Anthracite (black coal, hard coal, stone coal, blind coal, black diamond, and crow coal) is a hard, glossy black coal and is the most metamorphosed type of coal (the highest rank of the coal series) in which the carbon content is between 92.1% and 98%. Anthracite does not emit tar or other hydrocarbonaceous vapor when heated below the point of ignition - it ignites with difficulty and burns with a short, blue, and smokeless flame. Finally, although not an official definition in the sense of the four previous definitions, steam coal is the name given to a grade of coal that has properties between those of bituminous coal and anthracite and which was once widely used as a fuel for steam locomotives. With respect to this specialized use, it is sometimes known as sea coal in the United States.

Peat is considered by some observers/scientists/engineers to be a precursor of coal and to be a type of coal but the lack of any obvious resemblance to any other four coal types presented earlier tends to negate such inclusion into the coal sequence.

It was during the Industrial Revolution in the eighteenth and nineteenth century the demand for coal surged. The great improvement of the steam engine by James Watt, patented in 1769, was largely responsible for the growth in coal use. The history of coal mining and use is inextricably linked with that of the Industrial Revolution – iron and steel production, rail transportation, and steamships. Coal was also used to produce gas for gas lights in many cities, which was called *town gas*. This process of coal gasification witnessed the growth in gas lights across metropolitan areas at the beginning of the nineteenth century, particularly in London. The use of coal gas in street lighting was eventually replaced with the emergence of the modern electric era. With the development of electric power in the nineteenth century, the future of coal use became closely tied to electricity generation. The first practical coal-fired electric generating station, developed by Thomas Edison, went into operation in New York City in 1882, supplying electricity for household lights.

Steam coal, also known as thermal coal, is used in power stations to generate electricity (Speight, 2013a, 2013b). The earliest conventional coal-fired power stations used lump coal, which was burnt on a grate in boilers to raise steam. Currently, the coal is first milled to a fine powder, which increases the surface area and allows it to burn more quickly. In these pulverized coal (PC) combustion systems, the powdered coal is blown into the combustion chamber of a boiler where it is burnt at high temperature. The hot gases and heat energy produced converts water – in tubes lining the boiler – into steam.

As a result of the surge in coal use during the decades of the nineteenth and twentieth century, the use of coal increased and it was during this time that coal properties were not consistent and that certain types of coal were available – the adage *coal was not coal was not coal* gained wide acceptance and several types of coal existed. Thus, coal is now classified as various types and each type has distinctly different properties from the other types. In fact, each country has a varied system of nomenclature to describe the various types of coal and it is only through measurement of the analytical properties that any relationship can be made between the various names (Table 1.2). However, the terminology is not always standard and whether or not a standard terminology will ever be accepted remains to be seen. But understanding the analytical chemistry and analytical properties of coal is an essential aspect in international trade.

1.3 PRECURSORS OF COAL

Coal formation began during the Carboniferous Period, which is known as the *first coal age* and major coal deposits were formed in every geological period since the Upper Carboniferous Period, 270–350 million years ago (Table 1.1).

Layers of plant debris – such as lignin, were deposited in wet or swampy regions under conditions of limited exposure to air and complete decay as the debris accumulated, thereby resulting in the formation of peat. As the peat became buried by sediment, it was subjected to higher temperatures and pressures resulting in chemical and physical changes that, over time, formed coal. Cycles of plant debris accumulation and deposition were followed by diagenetic

TABLE 1.2 Variations in the English and German Systems of Coal Nomenclature

German Classification ^a	English (UK) Designation	Volatiles (% w/w)	Carbon (% w/w)	Hydrogen (% w/w)	Oxygen (% w/w)	Sulfur (% w/w)	Heat Content (Btu/lb) ^b
Braunkohle	Lignite (brown coal)	45-65	60-75	6.0-5.8	34-17	0.5-3.0	<12,250
Flammkohle	Flame coal	40-45	75-82	6.0 - 5.8	>9.8	ca. 1.0	<14,150
Gasflammkohle	Gas flame coal	35-40	82-85	5.8-5.6	9.8-7.3	ca. 1.0	<14,600
Gaskohle	Gas coal	28-35	85-87.5	5.6-5.0	7.3-4.5	ca. 1.0	<15,030
Fettkohle	Fat coal	19-28	87.5-89.5	5.0-4.5	4.5-3.2	ca. 1.0	<15,200
Esskohle	Forge coal	14-19	89.5-90.5	4.5-4.0	3.2-2.8	ca. 1.0	<15,200
Magerkohle	Non-baking coal	10-14	90.5-91.5	4.0 - 3.75	2.8-3.5	ca. 1.0	15,200
Anthrazit (Steinkohle)	Anthracite	7-12	>91.5	<3.75	<2.5	ca. 1.0	<15.175

Esskohle, and Magerkohle) represent a step-by-step transition from sub-bituminous coal to bituminous coal (US classification, ASTM D388) while the last class ^aWhile Braunkohle (brown coal) has the approximate properties of US lignite, the next six grades in the table (Flammkohle, Gasflammkohle, Gaskohle, Fettkohle, (Anthrazit) is approximately equivalent to anthracite, but more inclusive (US anthracite has < 6% volatiles). ^bRounded to the nearest 10 units; 1 kJ/kg = 0.4299 Btu/lb.