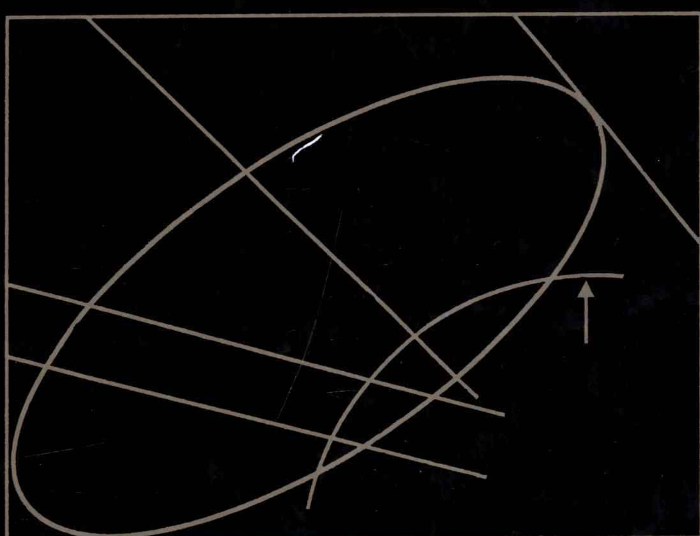
Handbook of Petroleum Product Analysis



JAMES G. SPEIGHT

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PREFACE

This book complements the book *Handbook of Petroleum Analysis* (J.G. Speight, John Wiley & Sons, 2001), and it is the purpose of these books to make available, in two handy volumes the essential elements of all analytical tests used to characterize petroleum and petroleum products.

It is, of course, critical for testing laboratory personnel to be fully familiar with all the details of the tests they are performing. But it is also important for nonlaboratory personnel to know at least the significance, advantages, and limitations of particular tests used to characterize product quality. Both the suppliers and the customers need to agree on the appropriate product quality specifications, and this can be achieved by understanding the intricacies of the respective test methods.

Product specifications not based on realistic testing capabilities can only lead to quality complaints and unhappiness on the part of both suppliers and customers. Therefore, we expect that this book will prove useful not only to laboratory personnel but also to product specification writers, process engineers, process scientists, researchers, and marketing staff in understanding the importance of these tests as well as their limitations, so that sound conclusions can be reached regarding the quality and performance of a particular product.

Organizations such as the American Society for Testing and Materials (ASTM) in the United States, the Institute of Petroleum (IP, London, U.K.), the Association Française de Normalisation (AFNOR, Paris, France), the Deutsche Institut für Normung (DIN, Germany), the Japan Industrial Standards (JIS, Tokyo, Japan), and the International Organization for Standardization (ISO, Geneva, Switzerland) have made significant contributions in developing standard test methods for the analyses of petroleum products. Although it is not possible to include all of the test methods of these organizations, cross-reference is made of the standard methods of analysis of the ASTM to those that are known for the IP.

In addition, the ASTM has discontinued several of the tests cited in the text for testing and materials, but they are included here because of their continued use by analytical laboratories. Several tests may even have been modified for internal company use, and there is no way of authenticating such use. Indeed, many tests should be adopted for internal company use instead of existing in-house testing protocols. For example, one might read in the published literature of the use of modified naphtha to precipitate an asphaltene fraction. Such a statement is meaningless without precise definition of the chemical composition of the modified naphtha. Naphtha is a complex petroleum product that can vary depending on the method of production. So, without any qualification or chemical description of the modified naphtha, a comparison of the precipitate with a pentane-asphaltene or heptane-asphaltene will be futile. Indeed, cross-comparisons within the in-house laboratories may be difficult if not impossible. The moral of this tale is that testing protocols *should* be standardized!

It is not intented that this book should replace the *Annual Book of ASTM Standards*. This book is intended to be a complementary volume that contains explanations of the *raison d'être* of the various test methods.

Each chapter is written as a stand-alone unit, which has necessitated some repetition. This repetition is considered necessary for the reader to have all of the relevant information at hand, especially where there are tests that can be applied to several products. Where this is not possible, cross-references to the pertinent chapter(s) are included. Several general references are listed for the reader to consult for a more detailed description of petroleum products. No attempt has been made to be exhaustive in the citations of such works. Thereafter, the focus is to cite the relevant test methods that are applied to petroleum products.

Finally, in this book, no preference is given to any particular tests. All lists of tests are alphabetical.

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CHAPTER

1

PETROLEUM ANALYSIS

1.1. INTRODUCTION

Petroleum, meaning literally "rock oil," is the term used to describe a myriad of hydrocarbon-rich fluids that have accumulated in subterranean reservoirs. Petroleum (also called *crude oil*) varies dramatically in color, odor, and flow properties that reflect the diversity of its origin (Table 1.1).

Petroleum products are any petroleum-based products that can be obtained by refining (Chapter 2) and comprise refinery gas, ethane, liquefied petroleum gas (LPG), naphtha, gasoline, aviation fuel, marine fuel, kerosene, diesel fuel, distillate fuel oil, residual fuel oil, gas oil, lubricants, white oil, grease, wax, asphalt, as well as coke. Petrochemical products (Speight, 1999a) are not included here.

Petroleum products are highly complex chemicals, and considerable effort is required to characterize their chemical and physical properties with a high degree of precision and accuracy. Indeed, the analysis of petroleum products is necessary to determine the properties that can assist in resolving a process problem as well as the properties that indicate the function and performance of the product in service.

Crude petroleum and the products obtained therefrom contain a variety of compounds, usually but not always hydrocarbons. As the number of carbon atoms in, for example, the paraffin series increases, the complexity of petroleum mixtures also rapidly increases. Consequently, detailed analysis of the individual constituents of the higher boiling fractions becomes increasingly difficult, if not impossible.

Additionally, *classes* (or *types*) of hydrocarbons were, and still are, determined based on the capability to isolate them by separation techniques. The four fractional types into which petroleum is subdivided are paraffins, olefins, naphthenes, and aromatics (PONA). Paraffinic hydrocarbons include both normal and branched alkanes, whereas olefins refer to normal and branched alkenes that contain one or more double or triple carbon-carbon bonds. *Naphthene* (not to be confused with *naphthalene*) is a term specific to the petroleum industry that refers to the *saturated cyclic hydrocarbons* (*cycloalkanes*). Finally, the term *aromatics* includes all hydrocarbons containing one or more rings of the benzenoid structure.

Table 1.1. Illustration of the Variation in Composition (Residuum Content) and Properties (Specific Gravity and API Gravity) of Petroleum

Crude Oil	Specific Gravity	API Gravity	Residuum > 1000°F
U.S. Domestic			
California	0.858	33.4	23.0
Oklahoma	0.816	41.9	20.0
Pennsylvania	0.800	45.4	2.0
Texas	0.827	39.6	15.0
Texas	0.864	32.3	27.9
Foreign			
Bahrain	0.861	32.8	26.4
Iran	0.836	37.8	20.8
Iraq	0.844	36.2	23.8
Kuwait	0.860	33.0	31.9
Saudi Arabia	0.840	37.0	27.5
Venezuela	0.950	17.4	33.6

These general definitions of the different fractions are subject to the many combinations of the hydrocarbon types (Speight, 1999a; Speight, 2001) and the action of the adsorbent or the solvent used in the separation procedure. For example, a compound containing one benzenoid ring (six aromatic carbon atoms) that has 12 nonaromatic carbons in alkyl side chains can be separated as an aromatic compound depending on the adsorbent employed.

Although not directly derived from composition, the terms *light* and *heavy* or *sweet* and *sour* provide convenient terms for use in descriptions. For example, *light petroleum* (often referred to as *conventional petroleum*) is usually rich in low-boiling constituents and waxy molecules whereas *heavy petroleum* contains greater proportions of higher-boiling, more aromatic, and heteroatom-containing (N-, O-, S-, and metal containing) constituents. *Heavy oil* is more viscous than conventional petroleum and requires enhanced methods for recovery. *Bitumen* is *near solid* or *solid* and cannot be recovered by enhanced oil recovery methods.

Conventional (light) petroleum is composed of hydrocarbons together with smaller amounts of organic compounds of nitrogen, oxygen, and sulfur and still smaller amounts of compounds containing metallic constituents, particularly vanadium, nickel, iron, and copper. The processes by which petroleum was formed dictate that petroleum composition will vary and be *site specific*, thus leading to a wide variety of compositional differences. The term *site specific* is intended to convey that petroleum composition will be dependent on regional and local variations in the proportion of the various precursors that went into the formation of the *protopetroleum* as well as