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Manual on Hydrocarbon Analysis

6th Edition

A. W. Drews, editor

Manual on Hydrocarbon Analysis: 6th Edition

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NOTE: This manual does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this manual to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

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Foreword

THIS SIXTH EDITION OF THE *Manual on Hydrocarbon Analysis*, sponsored by ASTM Committee D02 on Petroleum Products and Lubricants, has been expanded even further than the fifth edition. First appearing in 1963 as STP332, this manual was updated by Committee D02 in 1968, 1977, 1987, and 1992. In this 1998 edition, Part 2 has been expanded to include 26 additional ASTM test methods. Furthermore, the number of chapters has been increased from five to seven through the creation of a separate chapter, "Analysis of Kerosine, Diesel and Aviation Turbine Fuels," and a totally new chapter, "Analysis of Waxes." For additional information on the significance of tests, the reader is encouraged to consult the *Manual on Significance of Tests for Petroleum Products, 6th Edition.*

Methodology is changing quickly, requiring revisions to existing methods and the standardization of new ones. The impact of computerization and microprocessors cannot be overemphasized. Modern data-handling capabilities allow highly detailed compositional analyses to be performed that were once only a vision. Some of these resulting methods have been standardized; others will follow rapidly as experience is gained.

Industry and governmental requirements for accurate, more detailed data in a shorter time frame have resulted in substantial method changes. Rapid instrumental techniques, incorporating automatic sampling and on-line instrumentation, are replacing many of the time-honored empirical and, even, wet-chemical procedures. Yet many of the established techniques are still utilized and, thus, they are included in this manual along with the methods that are replacing them. It is exciting to speculate what further changes will occur before issuance of the next edition.

Publication of this manual would not have been possible without the efforts of the ASTM staff, the authors—N. G. Johansen, J. M. McCann, G. Hemighaus, T. M. Warne, A. J. Lubeck, A. D. Barker, C. H. Pfeiffer, the reviewers—S. E. Litka and N. D. Smith, and to L. A. Drews for collating, formatting, and reviewing the texts. I express my appreciation to all those who made this sixth edition a reality.

A. W. Drews, editor
Subcommittee D02.04 on Hydrocarbon Analysis

Purpose of Manual

THE PURPOSE OF THIS MANUAL is two-fold. The seven introductory chapters provide the analyst with a comprehensive overview of current practices and tests relating to the analysis of hydrocarbons. The accompanying collection of ASTM test methods furnishes a convenient reference within a single volume. It is hoped that this combination will provide the reader with a clearer understanding and appreciation of this diversified subject.

Contents

PART 2—ASTM TEST METHODS

The test methods in this section are arranged in alphanumeric sequence. The page numbers apply only to this manual and not to the standard documents as they appear in the annual *ASTM Book of Standards*. See Table 2 for a list of test methods by subject. The following is a list of all test methods included in Part 2. It includes all test methods referenced in the seven chapters except as indicated in the chapters. It does not include all of the test methods cited in Table 2.

Introductory Information

Introduction

THE PETROLEUM ANALYST is a problem solver and, as such, is constantly required to make method choices. In the past, two questions were most frequently associated with the method selection process.

- What properties can be determined to solve a particular production problem?
- What methods are appropriate to determine a specific property?

Now the analyst is faced with additional complications. These include the need to produce results faster, in more detail, at lower concentration levels; to reduce costs (usually in the form of analyst labor); and to provide higher-quality results. In addition, federal and state regulations, particularly on spark-ignition engine fuels, influence method choice. Thus, method choice is now even more difficult.

Fortunately, technology has advanced dramatically. Instrumental techniques have prospered and continue to improve rapidly. Gas chromatography, long a mainstay, is using faster, more efficient columns along with element-specific detectors. Furthermore, hyphenated techniques such as gas chromatography–mass spectrometry (GC/MS) and liquid chromatography–mass spectrometry (LC/MS) are providing separations that were once only a vision. Other spectrometric techniques—near infrared (NIR), Fourier transform infrared (FTIR), and nuclear magnetic resonance (NMR), to name a few, are being utilized on-line virtually unattended to provide real-time data.

Nevertheless, the method of choice will still depend on the boiling range (or carbon number) of the sample to be analyzed, and, following this, the resources available to the analyst. Therefore, in this manual, the hydrocarbons, along with their associated methods, are discussed according to boiling range. The first five chapters of this manual are arranged beginning with "Analysis of C_5 and Lighter Hydrocarbons," followed by "Analysis of Gasoline and Other Light Distillate Fuels," "Analysis of Kerosine, Diesel, and Aviation Turbine Fuel," "Analysis of Viscous Oils," and "Analysis of Waxes." Chapter 6, "Analysis of Crude Oils," deals with the total span of compounds, from gases to non-distillables. Chapter 7, "Analysis of Aromatics Hydrocarbons," is a special case that discusses a particular class of compounds that has increasingly gained importance in octane enhancing and, particularly, in petrochemicals.

Table 1 shows the carbon number range and boiling points (of normal paraffins) for some of the more common petroleum products of commerce. ASTM methods that may be applied to these boiling ranges are shown in Table 2. These tables are provided as an overview of the complex hydrocarbon analysis field; they do not show all of the methods that might be applicable. Details on many of these analytical methods, as well as techniques and procedures under development, are discussed in the appropriate chapters.

Crude petroleum and fractions (or products) obtained from it contain a complex variety of compounds. It is interesting to note that as the number of carbon atoms increases, the possible complexity of petroleum mixtures also rapidly increases (see Table 3). Consequently, detailed analysis of the higher boiling fractions becomes increasingly difficult. Instrumental techniques have improved this situation, and the data being obtained provide extremely valuable input for the design, control, and evaluation of petroleum processes.

Traditionally, however, these techniques were not available. It was necessary (and in many cases, satisfactory) to empirically determine specific physical properties that could be related to product quality and process control. Although the number of these tests is diminishing, many of them are still in common use. Some appear in this text because product specifications reference them and some referee methods still utilize the more basic testing procedures.

Additionally, "classes" or types of hydrocarbons were and still are determined based on the capability to isolate them by separation techniques. The four types usually sought are paraffins, olefins, naphthenes, and aromatics. Paraffinic hydrocarbons include both normal and branched alkanes. 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 of the petroleum industry that refers to the saturated cyclic hydrocarbons or "cycloalkanes." Finally, aromatics include all hydrocarbons containing one or more rings of the benzenoid structure. These general hydrocarbon classifications are complicated by many combinations of the above types, for example, olefinic aromatics (styrene) or alkylbenzenes (cumene). Table 4 presents a summary of the hydrocarbon types usually found in specific petroleum fractions.

Table 1—Summary of Product Types Produced from Petroleum

Number of Carbon Atoms	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	$>C_{20}$
Boiling Point of Normal Paraffin at 760 mm Hg																					
°C	−161	−89	−42	−0.5	+36	69	98	126	151	174	196	216	235	253	270	287	302	316	329	343	
°F	−259	−127	−44	+31	97	156	209	258	303	345	384	421	456	488	519	548	575	601	625	649	
Refinery off gas	◄	─	─	►																	
Liquefied petroleum gas		◄	─	►																	
Butanes/butylenes			◄	►																	
Solvents						◄	─	─	─	─	─	─	─	─	─	─	►				
Mineral spirits								◄	─	─	─	►									
Cracking naphtha						◄	─	─	─	─	─	►									
Reformate					◄	─	─	─	─	─	─	►									
Gasoline				◄	─	─	─	─	─	─	─	►									
Kerosine, diesel fuel									◄	─	─	─	─	─	─	─	►				
Aviation turbine fuel									◄	─	─	─	─	─	─	►					
Gas oil, fuel oil												◄	─	─	─	─	─	─	─	►	
Transformer oil															◄	─	─	─	─	►	
FCC & hydrocracker feed																				►	
Lubricating oil																				►	
Asphalt, pitch																				►	
Wax																		◄	─	─	►
Residuums & asphalt																				C_{44+}	►

Table 2—Summary of ASTM Test Methods

Number of Carbon Atoms Boiling Range of Normal Paraffins at 760 mm Hg, °C	C_1-C_2 -161 to -89	C_3-C_5 -42 to +36	C_6-C_{10} 69 to 174	C_{11}-C_{15} 196 to 270	C_{16}-C_{20} 287 to 343	>C_{20} >355
Physical Methods						
D5, Penetration of bituminous materials						X
D36, Ring and ball softening point						X
D56, Flash by tag closed cup tester			X			
D86, Distillation of petroleum products			X	X	X	
D87, Melting point of wax					X	X
D92, Flash and fire Cleveland open cup						X
D93, Flash and fire by Pensky-Martens closed cup				X	X	
D97, Pour point				X	X	X
D127, Melting point of wax					X	X
D189, Conradson carbon residue					X	X
D287, API gravity by hydrometer			X	X	X	
D323, Vapor pressure (Reid method)			X			
D445, Kinematic viscosity			X	X	X	
D447, Distillation of plant spray oils				X	X	
D473, Sediment by extraction			X	X	X	X
D482, Ash from petroleum products					X	X
D524, Ramsbottom carbon residue					X	X
D611, Aniline point			X	X		
D721, Oil content of petroleum waxes					X	X
D850, Distillation of industrial aromatics			X			
D852, Solidification point of benzene			X			
D972, Evaporation losses of greases & oils					X	X
D1015, Purity from freezing point			X			
D1016, Purity from freezing point			X			
D1078, Distillation of volatile organic liquids			X	X	X	
D1142, Water vapor of gaseous fuels	X	X				
D1160, Distillation at reduced pressure					X	X
D1218, Refractive index & dispersion			X	X		
D1267, Vapor pressure of LP gases		X				
D1298, Relative density of liquids			X	X	X	
D1322, Smoke point of aviation turbine fuels				X	X	
D1493, Solidification point of organic chemicals			X			
D1657, Relative density of light hydrocarbons		X				
D1747, Refractive index of viscous materials					X	X
D1807, Refractive index of insulating oils					X	X
D1837, Volatility of LP gases		X				
D2158, Residue in LP gases		X				
D2171, Viscosity of asphalts						X
D2386, Freezing point of aviation fuels			X	X		
D2500, Cloud point of petroleum oils				X	X	

Table 2 - continued

Number of Carbon Atoms Boiling Range of Normal Paraffins at 760 mm Hg, °C	C_1-C_2 -161 to -89	C_3-C_5 -42 to +36	C_6-C_{10} 69 to 174	C_{11}-C_{15} 196 to 270	C_{16}-C_{20} 287 to 343	>C_{20} >355
D2503, Molecular weight					X	X
D2533, Vapor-liquid ratio of gasoline			X			
D2892, Distillation of crude oil			X	X	X	X
D3205, Viscosity of asphalt (cone & plate)						X
D3279, *n*-Heptane insolubles					X	X
D3828, Flash point by Seta flash closed tester			X	X	X	X
D4052, Density by digital density meter			X	X	X	
D4206, Sustained burning test by Seta flash			X	X	X	X
D4207, Sustained burning test by wick method			X	X		
D4530, Micro carbon residue					X	X
D4809, Precise heat of combustion			X	X	X	
D4953, Vapor pressure of gasoline oxygenate blends			X			
D5002, Density of crude oil						X
D5190, Vapor pressure (automatic method)			X			
D5191, Vapor pressure (mini method)			X			
D5236, Distillation of heavy oils						X
D5482, Vapor pressure of petroleum products			X	X	X	
D5853, Pour point of crude oils		X	X	X	X	X
Correlative Methods						
D341, Viscosity-temperature charts for hydrocarbons			X	X	X	X
D976, Calculation of cetane index of distillate fuels				X	X	
D1250, Petroleum measurement tables		X	X	X	X	
D2270, Calculation of viscosity index					X	
D2501, Viscosity-gravity constant of oils					X	X
D2502, Molecular weight of oils					X	X
D2598, Physical properties of LP gases	X	X				
D2889, Calculation of true vapor pressure			X	X	X	
D3238, Carbon distribution & structure analysis, n-d-M				X	X	X
D3338, Estimation of heat of combustion of aviation fuels			X	X		
D3343, Hydrogen content of aviation gasoline			X			
D4529, Estimation of heat of combustion of aviation fuels			X	X		
D4737, Calculated cetane index			X			
Liquid Chromatographic Methods						
D1319, Hydrocarbon types by FIA			X	X	X	
D2007, Rubber extender & processing oils					X	X
D2549, Aromatics & nonaromatics in distillates					X	X
D5186, Aromatics in diesel fuel by SFC					X	
Gas Chromatographic Methods						
D1945, Analysis of natural gas	X	X				
D1946, Analysis of reformed gas	X	X				
D2163, LP gases & propylene concentrates	X	X				
D2268, High-purity heptane & *iso*octane			X			
D2306, Xylene isomers in xylene			X			