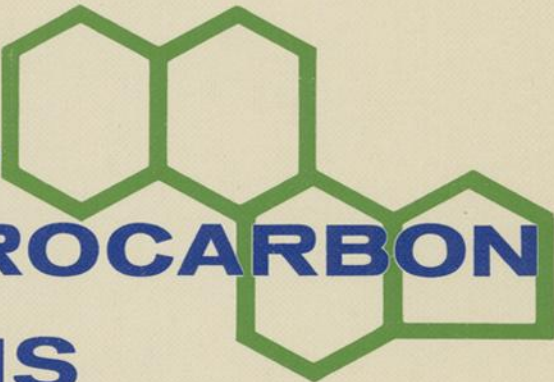


# MANUAL ON HYDROCARBON ANALYSIS



American Society for Testing and Materials



STP 332 A

# ASTM

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# MANUAL ON HYDROCARBON ANALYSIS

SECOND EDITION—1968

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ON  
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## FOREWORD TO FIRST EDITION

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The history of analysis for hydrocarbons in petroleum and its products started a long time ago. The records indicate that de LaRue and Miller in 1856 identified several aromatic hydrocarbons in Burma petroleum by the formation of the barium salts of benzenesulfonic acids followed by fractional crystallization. The father of American petroleum chemistry, Benjamin Silliman, made a distillation of petroleum in the early 1870's. The development of analytical hydrocarbon chemistry is excellently covered in an interesting résumé by Beveridge J. Mair in a chapter on the composition of petroleum and petroleum products in the book, "Chemical Technology of Petroleum" by Gruse and Stevens.

The American Society for Testing and Materials became active in developing standard tests for lubricants in 1904 with the formation of Technical Committee N. In 1920, this committee became Technical Committee D-2 on Petroleum Products and Lubricants, as it still is today, with a scope that included almost all petroleum products. However, during the first 38 years of committee work on petroleum, there were only four methods standardized that even approached hydrocarbon analyses—typified by methods such as the determination of oil in wax or acid heat of gasoline. In contrast, in the past 21 years since 1942, between 40 and 70 methods, depending upon whether or not ancillary methods such as refractive index are considered, have been issued as standard or tentative methods and about 10 proposed methods have been published as information.

This large increase is, of course, made necessary by the greater attention to and need for reliable information concerning the composition of petroleum products. This information is increasingly requested in terms of individual hydrocarbons or certainly as a minimum in terms of type such as paraffinic, naphthenic, aromatic, olefinic, or combinations of these. However, the demand for these data could not have been met without real advance in the art and science of separating hydrocarbons and hydrocarbon types and concurrent development of instrumental methods for determining physical, optical, and spectral properties with great accuracy and precision. These developments, taken together with the fruits of the American Petroleum Inst Research Projects Nos. 6, 42, 44, and 45 in making available both data on and samples of pure hydrocarbons for calibration purposes, have in effect marked the culmination of an era for analyses dependent primarily on fractionation, a few physical properties such as boiling point and density, and chemical reactions. Today in the fifty-ninth year of committee activity on petroleum and the twenty-first year of organized ASTM activity on hydrocarbon analysis, hydrocarbon analysis has come of age.

Research Division IV on Hydrocarbon Analysis of Committee D-2 recognizes that the manual is incomplete in several respects and does not represent

the advanced analytical methods currently used in many laboratories. This must always be so in developing standard methods because much research must precede the final adoption of standard procedures. The manual is weak in the diesel fuel, gas oil, and lubricating oil areas. However, with the coming of the age of high-resolution mass spectrometry, gas-liquid chromatography—not to mention nuclear magnetic resonance—and physical property correlations, Research Division IV feels that progress will be such that revision of the manual will be necessary every few years and confidently expects many of the present omissions to be filled. Present methods under study by Research Division IV in the fields of mass spectrometry and chromatography bear out this thought.

I am pleased that as chairman of ASTM Committee D-2 it is my privilege to congratulate the leadership and members of Research Division IV on their foresight through the years that has enabled them to be ready for problems as they arise and on the excellent work that has resulted in this present compilation.

I am sure that even greater progress is in prospect for the future.

H. M. SMITH  
*Chairman*  
ASTM Committee D-2

February, 1963.

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## FOREWORD TO SECOND EDITION

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Since the First Edition of the Hydrocarbon Analysis Manual was published in 1963, there has been a large increase in the number of analytical methods considered by ASTM Technical Committees. A review of the list of new methods included in this edition gives a good indication as to where the emphasis on hydrocarbon analysis is being placed. Of the 28 new methods included 15 are gas chromatography and 7 are mass spectrometry. Because of the increased number of chromatographic instruments in laboratories throughout the country and the relative simplicity of the methods, this analytical tool is being used more frequently for hydrocarbon analysis than any other.

Due to the large increase in the number of new methods, the Editorial Committee, Section G, decided to include in this edition only methods used directly for determination of composition or by correlation. The committee excluded obsolete methods of hydrocarbon analysis; methods for other classes of compounds, such as sulfur; and methods that give a rough indication of composition, such as distillation and gravity.

The American Society for Testing and Materials has as its purpose “the

promotion of knowledge of materials of engineering and the standardization of specifications and the methods of testing." Consistent with the promotion of knowledge, Research Division IV has taken as its goal the complete hydrocarbon analysis of petroleum and petroleum products, limited only by the availability of methods and the willingness of laboratories to participate in the work. The Division never expects to achieve its goal completely since petroleum is such a complex mixture of thousands of hydrocarbon compounds. In view of the ever increasing needs of the industry for more information on the composition of petroleum, this effort on the part of Research Division IV becomes increasingly more significant. Although not complete, this Second Edition is a big step forward and represents a tremendous effort on the part of many people. E. T. Scafe, J. Herman, and the Editorial Committee are to be commended for their diligence and work in producing this very useful volume.

J. F. HICKERSON  
*Chairman*  
Research Division IV,  
ASTM Committee D-2

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J. F. HICKERSON—Chapter I  
R. A. KLETT—Chapter II  
R. W. KING—Chapter III

January, 1968.

## STATEMENT OF ORIGIN

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This manual has been prepared by members of Section G on Hydrocarbon Type Analysis Manual of Research Division IV on Hydrocarbon Analysis of ASTM Committee D-2 to give some guidance in the analysis of hydrocarbon mixtures, particularly by ASTM methods. The methods reproduced in full are only those which have been published in one form or another by the American Society for Testing and Materials. Most of these have been published by Committee D-2, but useful methods from other committees, specifically Committees D-3 on Gaseous Fuels, D-11 on Rubber and Rubber-Like Materials, D-16 on Industrial Aromatic Hydrocarbons and Related Materials, D-27 on Electrical Insulating Liquids and Gases, and E-1 on Methods of Testing have also been included. Since there is rapid change in this area of analysis, this manual will require periodic revision. The members of the committee sincerely hope that this manual will be found useful.

The membership of the committee wishes to acknowledge the assistance of many individuals in ASTM who have helped to make this manual possible.

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February, 1963.



**This Manual is Dedicated to**

***Stewart S. Kurtz, Jr.***

*By vote of Research Division IV, June 28, 1962, in grateful acknowledgment of his leadership, tireless efforts, and inspiration as chairman of Section G and member of Research Division IV, the Hydrocarbon Analysis Committee of ASTM Committee D-2.*

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<sup>c</sup> 1968 *Book of ASTM Standards*, Part 18.

<sup>d</sup> Available from Institute of Petroleum, London, England.

<sup>e</sup> Compilation of ASTM Standards on Petroleum Products and Lubricants, Vol. I, October, 1961.