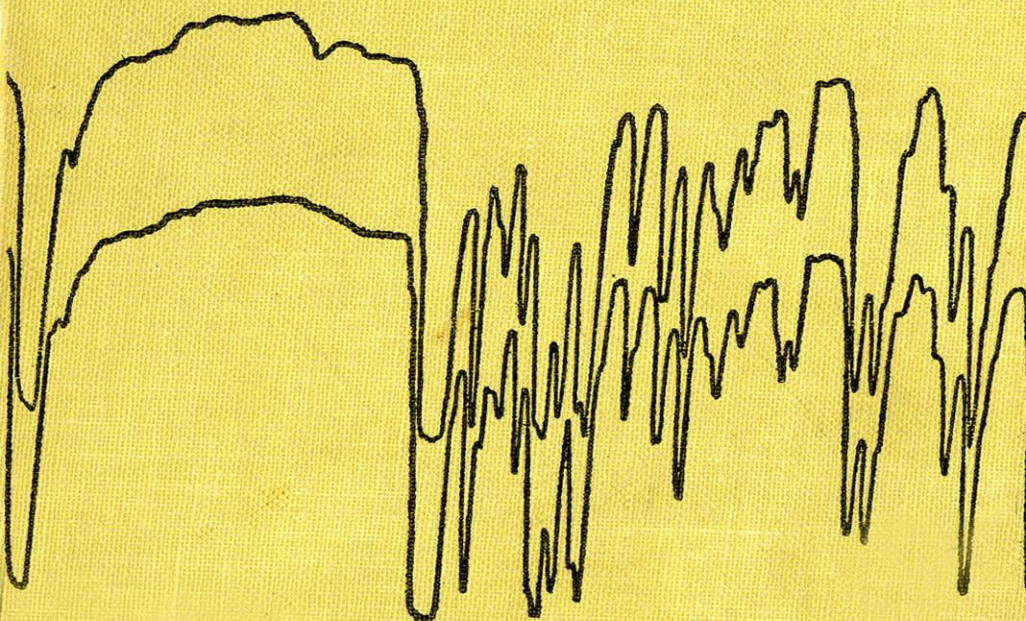




**HYDROCARBON
ANALYSIS**

ASTM STP 389



Hydrocarbon Analysis

A Symposium

Presented at the

Meeting of Committee D-2 on Petroleum Products and Lubricants of the
AMERICAN SOCIETY FOR TESTING AND MATERIALS
Houston, Tex., Jan. 22-23, 1965



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RELATED ASTM PUBLICATIONS

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- Physical Constants of Hydrocarbons C₁ to C₁₀,
DS 4 (1963), \$3.00
 - Knocking Characteristics of Pure Hydrocarbons,
STP 225 (1957), \$6.00
 - Manual on Hydrocarbon Analysis, STP 332 (1962),
\$14.00

PREFACE

By J. F. Hickerson¹

The papers in this publication discuss the various techniques for hydrocarbon analysis that are potentially available and their application, both alone and combined. Some of the presentations relate to the analyses for hydrocarbon and non-hydrocarbon impurities in petroleum. Together these contributions cover the entire complicated field of petroleum products, and vary in degree of technical intensity from the work of those laboratories doing pure research to those doing applied work on final products with practical implications.

The question might well be asked, "What is Research Division IV's role in this dynamic field?" To answer that question let's look back to what happened in the past in Research Division IV, let's review the current situation and then let's see if our crystal ball will tell us anything.

Before proceeding we need to understand the two objectives of ASTM. One is standardization of tests and specifications of products. The second is the promotion of knowledge of materials of engineering. While the first objective is well known, the second one, promotion of knowledge, is sometimes forgotten. It is for this reason that only recently the name was changed to "The American Society for Testing and Materials". It is not just a testing society, and Research Division IV represents a forum where new techniques can be presented and translated into practical everyday application.

Research Division IV was formed in 1943 for the main purpose of writing a manual on the hydrocarbon analysis of petroleum products. It was not until 1963, however, that the manual, STP 332, became a reality. This slow progress was not due to a lack of informed, enthusiastic leadership. Stewart Kurtz, Sun Oil Company, was the first chairman of the division and the first editor of the manual. I took a course at the University of Houston during the War Years in petroleum chemistry, and the authorities most quoted in "PONA" analysis were Kurtz and Headington. The first chairman of Research Division IV was certainly a recognized authority in the field of hydrocarbon analysis.

¹ Humble Oil and Refining Co., Baytown, Tex.

Stewart served as chairman until 1954 when he stepped down and Wes Scovill, SOHIO, the faithful secretary of the division since its inception, became the new leader. Under Wes's wise guidance the division was reorganized along its present lines, and he introduced many of the ways it is presently conducting its business.

The lack of progress during these years, therefore, was not due to a lack of leadership but to a lack of practical techniques. During this time, we saw the birth and growth of the petrochemical industry with its demands for hydrocarbon analysis. Initially, there were practically no standard methods available. At the present time, we are beginning to catch up on meeting these demands and the demands of the petroleum industry in general.

This is a dynamic and rapidly changing field, and it is difficult for us to keep abreast. The manual, then, represents the consensus of methods that are being used in the petroleum industry at the time it is published. It is planned to bring this up-to-date every three years.

Last year Research Division IV restated its objective in the following manner: The division will endeavor to develop and cooperatively test methods of analysis for the complete composition of petroleum and petroleum products, limited only by the lack of methods and cooperators. In order for methods to be considered they usually have the following characteristics: (1) are relatively short, not requiring more than about one day's time; (2) have economic significance, that is, they must give information which can be used profitably by some segment of the industry; (3) have sufficient precision for the purpose intended; and (4) are of interest to the cooperating laboratories to such an extent that they will perform the work with the equipment they have or be willing to purchase the apparatus needed.

Figure 1 is a summary of the status of methods at the present time. The true status is not as sharply defined as shown in the chart, but the chart does convey a general impression of where we are today. Methods have been published for determining individual compounds for paraffins through C_5 , mono-olefins, diolefins, acetylenes through C_4 , and aromatics through C_8 . Work is in progress for individual paraffins and cycloparaffins through C_8 , C_5 mono-olefins, C_{16} reference fuels, and normal paraffins in wax. Methods are probably available for the determination of, normal paraffins from C_9 through C_{20} , of the individual isoparaffins through C_9 , individual mono-olefins through C_7 , diolefins through C_5 , acetylenes through C_5 and aromatics through C_{10} .

Methods for individual compounds could of course be used for determining the types of compounds by carbon number or the total amount of a given type. In considering measuring types by carbon number, we see that

methods are in progress for measuring olefins in the C_9 to C_{15} range and alkylbenzenes in the C_{13} to C_{40} range. Methods are probably available for measuring both cycloparaffins and non-cyclic-paraffins by carbon number through the gasoline boiling range and olefins and aromatic types through C_{20} compounds.

Methods have been published for total hydrocarbons by type through the gasoline boiling range with the exception of acetylenes and diolefins. In addition, methods are in the ASTM books for total hydrocarbon types for total paraffins, olefins, alkylbenzenes, naphthalenes and other aromatics through the gas oil range. Methods are probably available for the measurement of total paraffins, cycloparaffins and aromatics through the C_{40} range.

Backing off and looking at the chart, we see that there is a lot to be done in the way of analytical development. We see, however, that there is still considerable work to be done in the immediate future in completing the work in progress and in developing the methods probably available.

You may see in this chart an area in which you think work could be done. You may also see areas in which you believe others may be interested. The field is wide open, limited only by participation and cooperation.

Research Division IV is in a challenging position. We must survey the needs of industry and have methods available when they are needed. It is our plan to develop methods of analysis, publish them for information, and place them in the Hydrocarbon Analysis Manual as it is revised.

This symposium presents two challenges for us to meet. The first one is to extend the field of analysis and the scope of knowledge, reduce the developments to practical application. Mr. L. C. Dawson, in his paper, touches on this major factor that is lacking in our field of methods, the translation of information into performance. Unless we are able to do this, the information presented will not have the use that it should and will not have full meaning to our industry.

The second challenge is to recognize current practices and incorporate them into methods that can be used for commercial purposes. One of the trends is the use of plant analyzers for which there are no ASTM methods.

This symposium presents an overall view of methods and techniques currently available that should stimulate our ambition to put them together and meet these challenges.

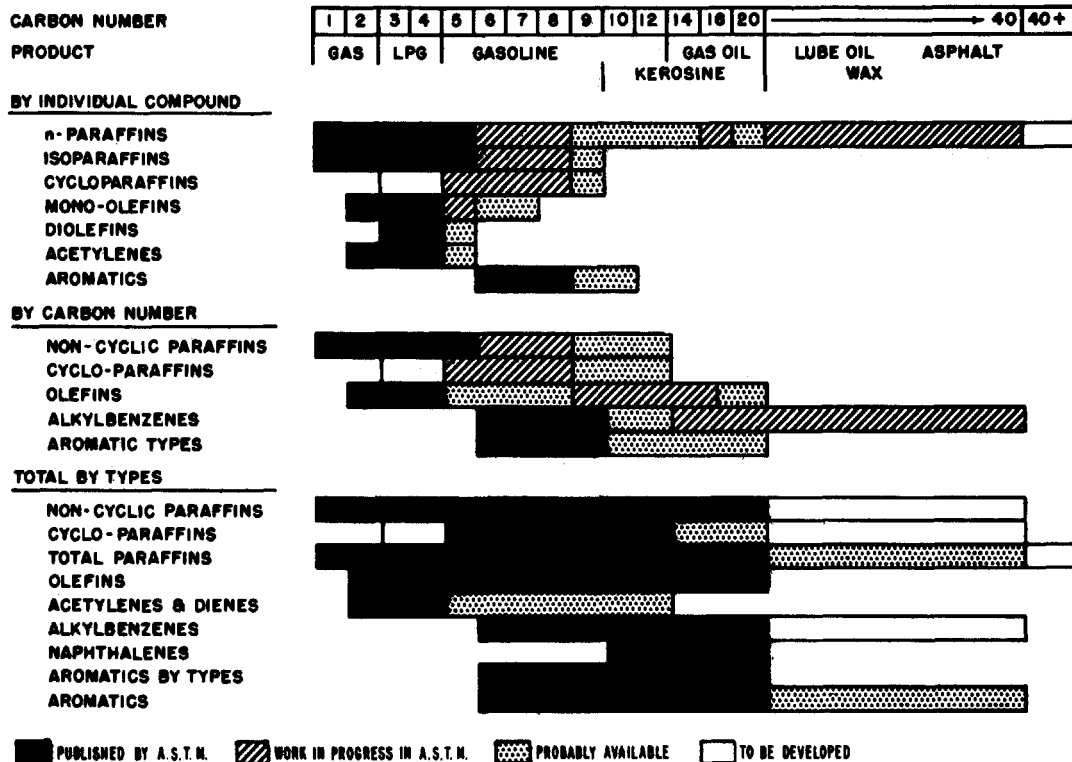


Figure 1— Status of Methods for Hydrocarbon Analysis

INTRODUCTORY REMARKS

By H. M. Smith¹

I welcome you to this symposium on Hydrocarbon Analysis which has been sponsored by Research Division IV on Hydrocarbon Analysis of ASTM Committee D-2 on Petroleum Products and Lubricants. You might ask "Why have such a symposium?" There are a number of reasons, but primarily because Research Division IV realizes that its Manual on Hydrocarbon Analysis must be revised fairly frequently to present up-to-date methods, and especially important are the recent developments in instrumental methods of analysis. There has been much progress in the last decade and probably much more will be reported in the next, and RD IV wants to direct its efforts towards the most promising developments. One of the best ways to determine the direction of progress is to review where we seem to be going in the field of hydrocarbon analysis. This, then, essentially, is the plan of the symposium.

There are really five parts:

"Where We Are", and a little of "How We Got Here", plus something about "Future Applications of Hydrocarbon Analysis", are covered by two papers under the chairmanship of W. E. Scovill, Standard Oil Co. of Ohio.

Second, we have arranged to hear what the experts say concerning the potentialities of the various instruments and instrumental methods that are considered to offer the most promising development during the next decade. These ideas will be presented in a group of four papers under the chairmanship of R. W. King, Sun Oil Co.

Next, the use of isolated individual methods is being largely supplanted by the application of several methods used consecutively and carefully integrated. How can these be applied to give more accurate results

¹ U. S. Bureau of Mines, Bartlesville, Okla.
Chairman, ASTM Committee D-2 on
Petroleum Products and Lubricants

more quickly for petroleum products such as gasoline, gas oil, high boiling oils and asphalts? Some of the answers will be found in a group of papers under the chairmanship of Jack Herman, Socony Mobil Oil Co.

Today, impurities in hydrocarbons are important both in processing and in utilization, and new analytical methods are constantly being developed for their determination. Also, it is often necessary to know the identity of the kinds of compounds composing these impurities. A group of papers dealing with this subject will discuss the problems of hydrocarbons as impurities and of sulfur and nitrogen compounds in petroleum and petroleum products. The speakers will describe successful analytical methods for these purposes, show how they are applied, and suggest potential developments. These presentations are under the chairmanship of John S. Ball, Bureau of Mines.

To sum up, the chairman of Research Division IV, J. F. Hickerson, Humble Oil and Refining Co., will present a discussion of the place of Research Division IV and its leadership in this general field and most importantly, present challenges to analytical chemists in the petroleum field and particularly to RD IV. These remarks will constitute the preface of the publication of this symposium.

Finally, my thanks to R. W. (Dick) King, R. A. (Roy) Klett and Jack Herman, the members of the symposium committee, for their very fine cooperation — that really made the symposium possible.

