

MANUAL ON HYDROCARBON ANALYSIS

PURPOSE OF MANUAL

The purpose of this manual on the analysis of hydrocarbons is to provide a collection of methods and to make them more useful by showing how they fit into a general scheme of analysis. Some historical background is also supplied that will help to explain why some methods are available in ASTM form and some are not. The perspective thus provided may encourage the preparation of additional methods in ASTM form so that this manual may be more complete in the future.

INTRODUCTION

Nature of Short Analysis—Need for Cross-Check Methods

The analysis of hydrocarbon mixtures, particularly from petroleum and coal, can be done in a variety of ways depending on how much information is needed and how thorough an analysis is justified (1-16).¹ An example of an extremely thorough analysis is that performed by the American Petroleum Institute Research Project No. 6, which has been working 40 years, and has spent over 2 million dollars, on the analysis of one sample of crude oil (1,2). Work of this sort provides fundamental information and has developed separation procedures which aid in setting up more rapid methods for general use.

The so-called "short-cut" methods suitable for routine use usually depend on simplifying assumptions that are satisfactory for most samples but may not apply in the case of unusual samples. It is therefore highly desirable to have alternative short methods of analysis which do not involve the same simplifying

ing assumptions. If an analysis for a component, for example, per cent aromatics, is carried out by two independent methods and the results agree, one can be reasonably sure that the answer is correct. If they disagree, more work is indicated to find out why the sample is unusual and what the true composition is.

This does not mean that every analysis must be made by two different methods. An experienced analyst, knowing something about the type of sample, can usually select a reliable procedure for the sample at hand. For unusual samples, however, the use of cross-check procedures is essential. For this reason it has been the practice of Research Division IV of ASTM Committee D-2 on Petroleum Products and Lubricants to put in ASTM form alternative procedures for the determination of the same component. These alternative procedures can be used for cross-check purposes, since they do not depend on the same simplifying assumptions.

Nomenclature

The nomenclature of hydrocarbon types as used in ASTM methods is in

¹ The boldface numbers in parentheses refer to the list of references at the end of this section; see p. 14.

accord with decisions of the Nomenclature Committee of the Division of Petroleum Chemistry of the American Chemical Society, where these are available (17,18). The nomenclature is also in accord with the usage in "Hydrocarbons from Petroleum" by Rossini, Mair, and Streiff (1), with "The Constitution of Mineral Oils" by Van Nes and Van Westen (19), and with ASTM Definitions D 288, Terms Relating to Petroleum.²

The term "aromatic" or "aromatic hydrocarbon" includes all hydrocarbons containing one or more rings of the benzenoid type (18), and the total of such hydrocarbons in a mixture is represented by V_A if the analysis is in terms of volume per cent or W_A if the analysis is in terms of weight per cent. The term "per cent aromatic carbons" is the per cent of carbon atoms in the benzenoid structure of the average molecule. It is generally denoted by % C_A . It also applies to closely related nonhydrocarbons such as benzothiophene (19,20).

This usage of the word "aromatic" is analytically precise and is to be distinguished from the unprecise usage of "aromatic," which is sometimes applied (particularly in Europe) to conjugated or resonant structures showing very little of the chemical stability characteristic of the benzenoid compounds (21). Aromatic compounds containing one or more atoms of sulfur, oxygen, or nitrogen are found in most crude oils. These may be called aromatic nonhydrocarbons or polar aromatics (9,10). Although heterocyclic compounds are plentiful in the nonhydrocarbon fraction, phenols, thiophenols, sulfides, and carboxylic acids may also be present. Many analytical techniques determine the total aromatic material, that is aromatic hydrocarbons and aromatic nonhydrocarbons, as one group. For example, the silica gel sep-

aration of the viscous fractions of petroleum into "saturates" and "aromatics" has been widely used (19,20). Olefin or alkene means any molecule containing a carbon-carbon double bond not in an aromatic nucleus. Styrene and indene are "aromatic olefins" since they contain both an aromatic nucleus and an olefinic double bond.

The per cent of total olefins is usually reported in the analysis of cracked gases, gasolines, and gas oils. The sum of such material may be represented by the symbol V_o if the analysis is on the volume basis or W_o if the analysis is on the weight basis. The symbol % C_o is rarely used, since carbon-type analysis is used primarily for viscous oils, which are usually devoid of olefins.

"Naphthene" or "naphthenic hydrocarbon" is synonymous with "saturated cyclic hydrocarbon" or "cycloalkane." These materials may consist of ring structures only or may have in addition noncyclic side chains. When the saturated cyclic hydrocarbons can be determined as a group, the total of such hydrocarbons in a mixture is represented by V_N , if the analysis is in terms of volume per cent, or W_N if the analysis is in terms of weight per cent. The term "per cent naphthenic carbon atoms" refers to the per cent of carbon atoms in the naphthenic structures of the average molecule and is generally designated by % C_N .

Naphthenic ring structures are also found in molecules containing aromatic rings. The term "cyclanoaromatics" is often used to designate such a class of hydrocarbon.

"Paraffinic hydrocarbon" includes all noncyclic saturated hydrocarbons, that is, both normal alkanes and branched alkanes. When these compounds can be determined as a group, either by separation or calculation, the total of such hydrocarbons in a mixture is represented by V_P if the analysis is on the volume per

² 1968 Book of ASTM Standards, Part 17.

cent basis or W_P if the analysis is on a weight per cent basis. Normal paraffin hydrocarbons and compounds with long normal paraffin side chains may be determined as a group by clathrating agents such as urea (20). The symbol P_N can be used to distinguish the normal paraffinic molecules from total paraffinic molecules P .

Paraffin chains may exist as separate molecules or attached to aromatic or naphthenic rings. The term "per cent paraffinic carbon atoms" refers to the per cent of such carbon atoms in the average molecule, and is generally denoted by $\% C_P$.

"Saturates" is a term often used for the sum of the naphthenic fraction and the paraffinic fraction. Therefore, $V_S = V_N + V_P$ or $W_S = W_N + W_P$.

Nonhydrocarbons occur in all crude oils and range from a minor constituent category to being major components of certain fractions from some crude oils. The nonaromatic nonhydrocarbons such as mercaptans and disulfides are easily removed in refining and are usually not a problem in analysis. Naphthenic acids are also usually removed in refining. The aromatic nonhydrocarbons, predominantly molecules containing one atom of sulfur, oxygen, or nitrogen, are less easily removed and may occur in substantial amounts in certain viscous fractions (23). The available methods for separating this fraction are not scientifically precise in terms of the structure of the material separated but give adequate relative numbers for the purpose of comparison. Ease of adsorption is the traditional basis for separating the neutral or basis nonhydrocarbons (23). This fraction has been called "resin," "polar aromatic," "polar fraction," "nonhydrocarbon fraction," "heterocyclic fraction," and even "basic nitrogen." Since there is much evidence (23) that the nonhydrocarbon fraction which

is separated by adsorbents contains at least one aromatic ring per molecule, and since the method of separation (namely, selective adsorption) determines that it must be relatively polar, it is not unreasonable to call such a fraction by the term "polar aromatic." This nomenclature is reasonably descriptive, even though not as precise as may be desired.

Composition of Petroleum and Available Methods

The practical problems involved in hydrocarbon analysis, the methods to be used, the type of data that can be gotten, and the method of reporting vary greatly depending on the boiling range (or molecular weight range) of the sample being analyzed.

Table 1 presents a summary of the hydrocarbon types normally found in petroleum fractions, and Table 2 the range of carbon number and boiling points (for the normal paraffins) for several of the more common petroleum products of commerce. ASTM methods of analysis for many of these hydrocarbon types, and specific compounds as well, are shown in Table 3. These tables are intended only as an over-all condensed picture of the complex field of hydrocarbon analysis. Additional details on these analytical methods, as well as techniques and procedures under development, are discussed in the following chapters.

A few comments on Table 1 are in order. As the number of carbon atoms increase the possible complexity of petroleum mixtures increases rapidly (see Table 4—nature may have selection rules that eliminate many of the theoretically possible paraffin isomers in the high molecular weight range; even if this is true there is little hope of identifying, as individual compounds, the more complex naturally occurring isomeric hydrocarbons). Up to and

TABLE 1—SUMMARY OF HYDROCARBON TYPES IN PETROLEUM FRACTIONS

Number of Carbon Atoms..... Boiling Point of Normal at 760 mm(deg C deg F	C ₁ -161 -259	C ₂ -89 -127	C ₃ -42 -44	C ₄ -0.5 +31	C ₅ +36 97	C ₆ 69 156	C ₇ 98 209	C ₈ 126 258	C ₉ 151 303	C ₁₀ 174 345	C ₁₁ 196 384	C ₁₂ 216 421	C ₁₃ 235 456	C ₁₄ 253 488	C ₁₅ 270 519	C ₁₆ 287 548	C ₁₇ 302 575	C ₁₈ 316 601	C ₁₉ 329 625	C ₂₀ 343 649	>C ₂₀ >355 >671
Normal alkanes.....	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Branched alkanes.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cycloalkanes, mono.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cycloalkanes, di.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cycloalkanes, poly.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Noncyclic alkenes.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cycloalkenes.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Alkylaromatics, mononuclear.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Alkylaromatics, dinuclear.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Alkylaromatics, polynuclear.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cyclanoaromatics, mononuclear.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cyclanoaromatics, dinuclear.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cyclanoaromatics, polynuclear.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Acetylenes.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Heterocyclics.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

P = Present in major amount.

M = Present in minor amount.

PC = Present in cracked products only.

P^a = Acetylenes are found only in gases and liquids subjected to high temperature.M^b = Thiophene is usually found in the C₆ fraction.

TABLE 3 -- SUMMARY OF ASTM METHODS

Number of Carbon Atoms	C ₁ -C ₂	C ₃ -C ₅	C ₆ -C ₁₀	C ₁₁ -C ₁₅	C ₁₆ -C ₂₀	>C ₂₀
Boiling Point of Normal at 760 mm, deg C	-161 to -89	-42 to +36	69 to 174	196 to 270	287 to 343	>355
PHYSICAL PROPERTIES						
D 941, D 1217, Density of low vis. liquids			X	X	X	X
D 1480, D 1481, Density of high vis. liquids			X	X	X	X
D 287 ^a , API Gravity			X	X	X	X
D 1070 ^a , Specific gravity of gaseous fuels	X	X	X	X	X	X
D 1298 ^a , Specific gravity of liquids						
D 1657, Specific Gravity of light hydrocarbons		X				
E 12 ^a , Terms relating to density & sp. gr.						
D 87 ^a , D 127 ^a , Melting point of wax			X		X	X
D 852 ^a , Solidification point of benzene			X			
D 1015, Freezing point of pure hydrocarbons		X	X	X	X	
D 1016, Purity from freezing point		X	X			
D 1493 ^a , Solidification organic chemicals			X			
D 2421, Interconversion of C ₅ & lighter			X			
D 1218, Refractive index & dispersion	X	X	X	X	X	X
D 1747, Refractive index of viscous material						
D 1807 ^a , Refractive index of insulating oils				X	X	X
IP 60 ^a , ^b , Specific refractivity					X	X
D 2503, Molecular Weight			X		X	X
D 445, Kinematic Viscosity				X	X	X

<p>SOLVENCY TESTS</p> <p>D 611, D 1012^a, Aniline point D 1133^a, Kauri-Butanol value</p>														
<p>CORRELATIVE METHODS</p> <p>D 875, Olefins & Aromatics in distillates D 2140, Carbon types in insulating oils D 2159, Naphthenes by refractivity intercept D 2501, Viscosity-gravity constant of oils D 2502, Molecular weight of oils</p>														
<p>LIQUID CHROMATOGRAPHIC METHODS</p> <p>D 936, In olefin-free gasoline D 1319, Hydrocarbon types by FIA D 2002, D 2003, Isolation of saturates D 2007, Rubber extender & processing oils D 2549, Aromatics & non-aromatics in Distillates Aromatics & Non-Aromatics in Diesel Fuels (ASTM Stds. on Pet. Prods., Nov.1950, p.672)</p>														
<p>GAS CHROMATOGRAPHIC METHODS</p> <p>D 1717, Butane-butene mixtures D 1945, Natural gas D 1946, Analysis of reformed gas D 2163, LPG & propylene concentrates D 2267, Aromatics in naphtha & reformates D 2268, High-purity heptane & isooctane</p>														

TABLE 3 -- SUMMARY OF ASTM METHODS
(Continued)

Number of Carbon Atoms	C ₁ -C ₂	C ₃ -C ₅	C ₆ -C ₁₀	C ₁₁ -C ₁₅	C ₁₆ -C ₂₀	>C ₂₀
Boiling Point of Normal at 760 mm, deg C	-161 to -89	42 to +36	69 to 174	196 to 270	287 to 343	>355
GAS CHROMATOGRAPHIC METHODS (Cont'd)						
D 2306, Xylene isomers in xylene			X			
D 2360, Non-aromatics in BTEX			X			
D 2426, Butadiene dimer & styrene			X			
D 2427, C ₂ -C ₅ in gasoline	X	X				
D 2504, Non-condensibles in C ₃ & lighter	X					
D 2505, Analysis high-purity ethylene	X					
D 2593, Butadiene purity and hydrocar. impurities		X				
D 2597, Natural gas-liquid mixtures	X	X	X			
D 2600, Aromatic traces in saturates		X	X			
Analysis of isoprene (ASTM Stds. on Pet. Prod., Dec. 1962, Vol. I, p. 1231)						
E 260, Recommended practices for GC						
IP 184 ^a , C ₂ -C ₅ paraffins in crude oils	X	X				
Analysis of propylene (1965 ASTM Standards, Part 18, p. 817)	X	X				
SPECTROSCOPIC METHODS						
D 1017, Benzene & toluene in light distillates			X			
D 1095 ^a , 60 octane no. isooctane/n-heptane			X			
D 1096, 1,3-Butadiene in C ₄ fractions		X				
D 1137 ^a , Analysis of natural gases	X	X				

SPECTROSCOPIC METHODS (Cont'd)	X	X	X	X	X
D 1302 ^a , Carbureted water gas					
D 1658, Carbon No. distribution of aromatics					
D 1840, Naphthalenes in aviation turb. fuels					
D 2008, UV abs. of petroleum products					
D 2144 ^a , Examm. of electrical insulating oils					
D 2269 ^a , Evaluation of white mineral oils					
D 2424 ⁱ , Hydrocarbon types in C ₃ polymers					
D 2425, Hydrocarbon types in distillates					
D 2498, Isomer distr. of detergent alkylate					
D 2567, Mol. Distr. mono-n-alkylbenzenes					
D 2601, Carbon No. distr. propylene tetramer					
D 2650, Chemical composition of gases					
Carbon No. distr. of sats. and aromatics in wax (1968 ASTM Stds., Part 18, p. 907)					
E 131 ^a , Terms relating to absorption spec.					
E 137, Evaluation of mass spectrometers					
E 168, Techniques of infrared spectroscopy					
E 169, Techniques of ultraviolet spectroscopy					
E 204 ^a , ASTM-Kuentzel card index					
Analysis of C ₄ fractions by infrared (ASTM Stds. on Pet. Prod. Nov. 1954, p. 860)					
Benzene, Toluene and C ₈ Aromatics by Infrared (ASTM Stds. on Pet. Prod., Nov. 1955, p. 925)					
Aromatics in xylenes by infrared (ASTM Stds. on Benzene, Toluene, Xylene, Solvent Naphtha, Oct. 1962, p. 202)					
Hydrocarbon types in gasoline (ASTM Stds. on Pet. Prod., Oct. 1961, Vol. I, pp. 1120-1127; pp. 1128-1141) ^a					

TABLE 3 -- SUMMARY OF ASTM METHODS
(Continued)

Number of Carbon Atoms	C ₁ -C ₂	C ₃ -C ₅	C ₆ -C ₁₀	C ₁₁ -C ₁₅	C ₁₆ -C ₂₀	>C ₂₀
Boiling Point of Normal at 760 mm, deg C	-161 to -89	-42 to +36	69 to 174	196 to 270	287 to 343	>355
CHEMICAL METHODS						
D 483 ^a , Unsulfonated residue of spray oils				X	X	X
D 973, Butadiene content		X				
D 1019, Olefins plus aromatics		X	X		X	
D 1020, Acetylenes Acetylenes in C ₄ fractions						
D 1024, Butadiene dimer & styrene			X			
D 1136, Analysis of natural gases	X					
D 1158, Bromine number by color-indicator titn.		(X)	X	X	X	
D 1159, Bromine number by electrometric titn.		(X)	X	X	X	
D 1268, Unsaturated hydrocarbons in gases	X	X				
D 1491, D 1492, Bromine index of aromatics			X	X	X	
D 2006, Rubber extender & processing oils	X					X
Acetylene in ethylene (ASTM Stds. on Pet. Prod., Dec. 1962, Vol. I, p. 1224)						
MISCELLANEOUS METHODS						
D 86 ^a , Distillation of petroleum products		X	X	X	X	X
D 848 ^a , Acid wash color of industrial aromatics			X			
D 1023, Sepn. residue from butadiene		X				

[illegible]

TABLE 3 -- SUMMARY OF ASTM METHODS
(Continued)

Number of Carbon Atoms	C ₁ -C ₂	C ₃ -C ₅	C ₆ -C ₁₀	C ₁₁ -C ₁₅	C ₁₆ -C ₂₀	>C ₂₀
Boiling Point of Normal at 760 mm, deg C	-161 to -89	-42 to +36	69 to 174	196 to 270	287 to 343	>355
NON-HYDROCARBON CONSTITUENTS ^a (Cont'd)						
D 1551, Sulfur by quartz-tube method						
D 1552, Sulfur by high-temperature method				X	X	X
D 2385, Hydrogen sulfide & mercaptans in natural gas	X			X	X	X
D 2420, Hydrogen sulfide in LPG		X				
D 2622, Sulfur by X-ray method			X	X	X	X
E 258, Total nitrogen by Kjeldahl method				X	X	X
E 191, Apparatus for micro C + H				X	X	X

^a Not reprinted in this compilation.^b IP = Institute of Petroleum, London.^c Thiophene is usually found in the C₆ fraction.

including eight carbon atoms, the number of possible paraffins and naphthenes is small enough so that the determination of the individual compounds is not too difficult. However, olefin mixtures beyond the C_6 range are so complex that accurate analyses are not possible for all of the isomers. Aromatics having not more than ten carbon atoms can be identified and determined in a straightforward fashion but the naphthenes are limited to about eight carbon atoms. Individual compounds having molecular weights higher than those mentioned can be determined but with varying degrees of completeness.

TABLE 4—NUMBER OF ISOMERIC HYDROCARBONS OF METHANE SERIES AS CALCULATED BY HENZE AND BLAIR (22)

Carbon Atoms	Number of Isomers
1.....	1
2.....	1
3.....	1
4.....	2
5.....	3
6.....	5
7.....	9
8.....	18
9.....	35
10.....	75
15.....	4 347
20.....	366 319
25.....	36 797 588
30.....	4 111 846 763
40.....	62 491 178 805 831

Hydrocarbon-type analysis, in contrast with the determination of the specific compounds making up a hydrocarbon mixture, is applicable to a much broader range of molecular weight. But even here restrictions are imposed, particularly by the very low- and high-boiling materials. Molecular-type analysis for total paraffins, naphthenes, olefins, and aromatics is satisfactory for gasolines and most aviation turbine fuels. For higher-boiling products, pro-

cedures are available for separation of representative aromatic and nonaromatic fractions by elution chromatography. For such materials, analysis in terms of percentages of C_A , C_N , and C_P is also valuable as well as mass spectrometric data on the separated fractions obtained by elution chromatography.

Olefins as a class are essentially absent in petroleum fractions that have not been subjected to cracking. This materially simplifies hydrocarbon type analysis of such materials. However, with cracked distillates boiling above the gasoline fraction the determination of "total olefins" becomes difficult. This comes about not only because both nonaromatic and aromatic olefins are present, but because di- or even tri-olefinic types coexist.

Two points must be kept in mind in all type analysis work:

(1) With molecules of mixed hydrocarbon types, for example, aromatic olefins, it is possible to classify them as aromatics or as olefins depending upon the approach utilized. For this reason, it is important that the method of analysis be known when comparing data from another source on a common sample.

(2) Carbon-type analysis is distinctly different than group-type analysis both with respect to the approach and utilization of the data. In carbon-type analysis, the ambiguity just pointed out in connection with hydrocarbon-type analysis is avoided. Again taking the example of an aromatic olefin, the weight per cent of aromatic carbons is that fraction of carbons in the aromatic structure to the total number of carbons in the molecule. Carbon-type data (19) are usually derived from correlations of properties easily measured to eliminate time-consuming and tedious analyses of composition.

Techniques and methods that are currently being used for research purposes in hydrocarbon analysis do not properly fall within the scope of this compilation. These developments are significant, however, in the development of new and improved ASTM methods of test. Considerable information along this line has been made available by ASTM Committee D-2 (24).

Precision of Methods

Experience has shown that in hydrocarbon analysis in general, and carbon-type analysis in particular, it is extremely difficult to achieve repeatability of better than 0.5 per cent standard deviation in any one laboratory, or reproducibility limits between laboratories of better than 1.0 per cent standard deviations. In terms of 95 per cent confidence limits, these standard deviations correspond approximately to 1.5 per cent repeatability and 3.0 per cent reproducibility (25).

In setting up control methods that may be used in connection with Government purchases as, for example, per cent aromatics in fuels, the procurement agencies want analytical procedures having the highest practical precision. Part of the difficulty in obtaining acceptance of methods for hydrocarbon analysis is the thought that 1 per cent standard deviation for repeatability and 3 per cent for reproducibility is not good enough.

If serious consideration is given to the possible effect of a 1 per cent change in composition it will probably be concluded that a change of 1 per cent is not really

important. Future work may lead to some improvement in the precision of carbon-type analysis, but it will probably be a good many years before the standard deviation for repeatability in such methods will be much better than 0.5 per cent; it certainly will be some time before standard deviation reproducibility within 1 per cent will be achieved.

About the same conclusion is to be drawn from cooperative data on hydrocarbon-group analysis methods. Repeatability of the order of 1 per cent and reproducibility of the order of 3 per cent are reasonable at present. With every new method that is proposed there is hope that better reproducibility will be achieved, but so far these hopes have not been verified by ASTM cooperative study.

Methods Published for Information

A comment on the ASTM practice of Publication for Information appears in order for the benefit of individuals not familiar with this practice. This procedure is used to cover two situations: (1) methods are sometimes evaluated that are not adopted as standards (for various reasons) but nonetheless represent information potentially useful in studies related to the material covered, and (2) comments on the utility or shortcomings of such methods from a wider cross section of industry are possible than if the information were restricted to a Technical Committee. Such methods have no official ASTM status; they are, as their name implies, published for the purpose of disseminating information.

REFERENCES

- (1) F. D. Rossini, B. J. Mair, and A. J. Streiff, *Hydrocarbons from Petroleum*, Reinhold Publishing Corp., New York, N. Y. (1953).
- (2) B. J. Mair and F. D. Rossini, "Summary

of Work of the API Research Project 6 on Hydrocarbons in the C₁₃ to C₂₈ Fraction of Petroleum," *Symposium on Composition of Petroleum Oils, Determination and Evalua-*

- tion *ASTM STP 224*, Am. Soc. Testing Mats., (1958) pp. 9-48.
- (3) W. Murphy, J. S. Ball, and H. M. Thorne, "Determination of Aromatics in Light Petroleum Distillate," *Industrial and Engineering Chemistry*, Analytical Edition, Vol. 17, p. 481 (1945). (Specific dispersion.)
 - (4) J. S. Ball, G. U. Dinneen, J. R. Smith, C. W. Bailey, and R. Van Meter, "Composition of Colorado Shale-Oil Naphtha," *Industrial and Engineering Chemistry*, Vol. 41, p. 581 (1949). (Paraffin-naphthene by refractive index versus boiling points.)
 - (5) G. U. Dinneen, J. R. Smith, and J. S. Ball, "Olefins in Naphthas," *Petroleum Refiner*, May, 1950. (Comparison of olefin determination by bromine number, nitrogen tetroxide, and silica gel.)
 - (6) John S. Ball, "Aniline Points of Hydrocarbons" *Report of Investigation 3721*, U. S. Dept. of Interior, Bureau of Mines (1943).
 - (7) H. M. Smith, A. J. Kraemer, and H. M. Thorne, "Aviation Gasoline and Its Component Hydrocarbons: Wartime Research (1942-1945)," *Bulletin 497*, U. S. Dept. of Interior, Bureau of Mines. (Analyses of straight run naphthas for paraffins, naphthenes, and aromatics.)
 - (8) N. G. Adams and D. M. Richardson, "Aromatic Hydrocarbons in Some Diesel Fuel Fractions," *Analytical Chemistry*, Vol. 23, p. 129 (1951). (Fractionation and ultraviolet spectra.)
 - (9) C. C. War, F. G. Schwartz, and N. G. Adams, "Composition of Fischer-Tropsch Diesel Fuel," *Industrial and Engineering Chemistry*, Vol. 43, p. 1117 (1951). (Fractionation and physical properties.)
 - (10) N. G. Adams and D. M. Richardson, "Isolation and Identification of Biphenyls from West Edmond Crude Oil," *Analytical Chemistry*, Vol. 25, p. 1073 (1953). (Fractionation, silica gel, infrared.)
 - (11) C. M. McKinney and R. L. Hopkins, "Alumina-Adsorption Analysis of Petroleum Aromatics in 420 to 600 F Range," *Analytical Chemistry*, Vol. 26, p. 1460 (1954). (Adsorption, density, refractive index, refractivity intercept.)
 - (12) H. M. Smith, "Composition of United States Crude Oils," *Industrial and Engineering Chemistry*, Vol. 44, p. 2577 (1952). (Correlation index in conjunction with Sun method for naphthene rings and paraffins.)
 - (13) G. U. Dinneen, R. A. Van Meter, J. R. Smith, C. W. Bailey, G. L. Cook, C. S. Allbright, and J. S. Ball, "Composition of Shale-Oil Naphtha," *Bulletin 593*, U. S. Dept. of Interior, Bureau of Mines (1961). (Adsorption, bromine number, nitrogen tetroxide.)
 - (14) L. Mikkelsen, R. L. Hopkins, and D. Y. Yee, "Mass Spectrometer-Type Analyses for Olefins in Gasoline," *Analytical Chemistry*, Vol. 30, p. 317 (1958).
 - (15) R. W. Hurn, J. O. Chase, and K. J. Hughes, "A Multistage Analyzer for Exhaust Gas Analyses," *Annals*, New York Academy of Sciences, Vol. 72, p. 675 (1959). (Gas-liquid chromatography.)
 - (16) W. C. Holliman, H. M. Smith, C. M. McKinney, and C. R. Sponsler, "Composition of Petroleum: Properties of Distillates to 600 F," *Technical Paper 722*, U. S. Dept. of Interior, Bureau of Mines (1950). (Application of silica gel, acid adsorption, physical and optical properties to analysis of distillates.)
 - (17) A. M. Paterson, "The prefix-*n*-(normal)," Report of Nomenclature Committee of the Division of Petroleum Chemistry, *Chemical and Engineering News*, Vol. 32, p. 4884 (1954).
 - (18) Anon., "Naming Hydrocarbon: Nomenclature Approved by ACS Division," *Chemical and Engineering News*, Vol. 35, p. 72, Feb. 25, 1957.
 - (19) K. Van Nes and H. A. Van Westen, *Constitution of Mineral Oils*, Elsevier, New York, N. Y. (1951).
 - (20) W. J. Stout, R. W. King, M. E. Peterkin, and S. S. Kurtz, Jr., "Adsorption and Physical Property Methods," *Symposium on Composition of Petroleum Oils, Determination and Evaluation, ASTM STP 224*, Am. Soc. Testing Mats., (1958), pp. 230-247.
 - (21) D. Ginsburg, *Non-Benzenoid Aromatic Compounds*, Interscience Publishers, Inc., New York, N. Y. (1959).
 - (22) H. R. Henze and C. M. Blair, "Number of Isomeric Hydrocarbons of Methane Series," *Journal*, Am. Chemical Soc., Vol. 53, pp. 3077-3085 (1931).
 - (23) A. N. Sachanen, "Chemical Constitution of Petroleum," Reinhold Publishing Corp., New York, N. Y. p. 386 (1945).
 - (24) *Hydrocarbon Analysis, ASTM STP 389*, Am. Soc. Testing Mats. (1965).
 - (25) Proposed Recommended Practice for Application of Precision Data to Methods of Test and Specifications for Petroleum Products and Lubricants, *1968 Book of ASTM Standards*, Part 18.