NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

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A METHOD FOR DETERMINATION OF AROMATICS IN 150° TO 300° C FRACTIONS OF CRUDE PETROLEUM BY MEASUREMENT OF ANILINE-POINT RISE

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SUMMARY

A method for determining aromatics in 150° to 300° C fractions of crude petroleum is described. Rise in aniline point resulting from the removal of aromatics from synthetic mixtures by percolation through a particular column of silica gel was found to be an almost linear function of the known aromatic content. A general curve for analysis of cuts of crude petroleum having molal average boiling points near 218° C is presented. Modified curves for more accurate analysis of cuts having average boiling points between 150° and 290° C are also included. Results on nine reblends of aromatics extracted from two cuts of different crude petroleums indicated that aromatics having molal average boiling points near 218° C could be determined with an average error of 0.84 percent by volume based on total sample. Analyses of five cuts of four crude petroleums agreed to within an average of 2 percent with analyses of the same samples by a different method at another laboratory.

INTRODUCTION

Some knowledge of the composition of high-boiling (150° to 300° C) petroleum fractions used in fuels for Diesel and turbojet aircraft engines is essential to the scientific attainment of optimum fuel performance. Aromatics in particular have physical and chemical characteristics that have led to the specification of the maximum aromatic content of fuels for jet-propelled aircraft. Rapid reliable methods for the determination of aromatics in petroleum cuts that boil above the gasoline range are consequently necessary.

Methods suitable for the gasoline boiling range, such as the A.S.T.M. D 875-46 T sulfonation method (reference 1), the picric-acid-solubility method (reference 2), the method based on change in index of refraction (reference 3), and a method based on specific dispersion and bromine number (references 4 and 5) have either not been tested throughout the boiling range considered herein or have been found to be unsuitable. The silica-gel separation methods of references 6 and 7 have been applied successfully in the kerosene and gas-oil boiling range but they are complicated and time consuming. Raman and infrared analyses for individual aromatic components of narrow cuts boiling in the range from 150° to 180° C are reported in references 8 and 9, respectively. Tedious analytical distillations and pure hydrocarbon standards are required by these spectrophotometric methods.

The method of analysis described herein depends on the rise in aniline point that occurs when the aromatic hydrocarbons are removed from a petroleum fraction. This change of aniline point is herein called aniline-point rise. The amount of this aniline-point rise depends on the original aromatic content of the cut and to a much smaller extent on the nature of the aromatics present. The interfering effect of naphthenes in lowering aniline point is evaluated. In reference 10, Carpenter used an aniline-point-rise method in which the aromatic portions of cuts in the 125° to 270° C boiling range were removed by sulfonation. A similar method was used in an investigation of the composition of Russian and American crudes reported in reference 11. Simplicity and speed were desirable characteristics of these aniline-point-rise methods. The unsatisfactory results obtained when the A.S.T.M. D 875-46 T sulfonation method is applied to the higher boiling fractions, however, suggest that sulfonation is not specific for aromatics alone in this range and that possibly some naphthenes and isoparaffins are partly reacted under the conditions used in references 10 and 11. Modification of the aniline-point method by substituting the selective, nonhazardous, convenient, physical process of silica-gel adsorption therefore seemed desirable.

An investigation of an aniline-point-rise method using silica gel as a selective adsorbent for aromatics in cuts of petroleum crudes boiling from 150° to 300° C is described herein. The method was developed from results of investigations conducted at the NACA Cleveland laboratory during the early part of 1947 on 16 synthetic mixtures of various aromatic and naphthene content. Analyses of five cuts from four crudes by this aniline-point-rise method were compared with results on the same samples obtained at another laboratory by a silica-gel adsorption method.

APPARATUS

A conventional aniline-point apparatus and a procedure designated as A.S.T.M. D 611-46 T in reference 12 was used during most of this investigation. As the work proceeded, a photoelectric aniline-point apparatus similar to that described in reference 13 was constructed for use with a smaller quantity, namely 10 milliliters, of aniline-petroleum mixture. The smaller sample container was so insulated that aniline points were within 0.1° C of the values determined by the conventional method. Use of the time-saving, automatic photoelectric apparatus is recommended.

The analytical silica-gel column adopted as standard for this work consisted of a 50-centimeter layer of 20 to 65 mesh silica gel tightly packed above a 10-centimeter layer of 28 to 200 mesh gel. These layers weighed approximately 150 and 40 grams, respectively. A 2.6-centimeter pyrex tube, 100 centimeters long, constricted to an inside diameter of 6 millimeters at the lower end held the gel.

MATERIALS

The silica-gel adsorbent used was supplied by the Davison Chemical Corporation. It was designated as 11-08-05-215 and 14-08-05-215, and was characterized by particle size as 28 to 200 and 20 to 65 mesh, respectively. The gel should be adequately activated when used. Adequate activation may be tested as suggested in reference 6 (p. 159).

Aniline (c.p. grade), dried and freshly distilled as described in reference 12, was used within 1 day of distillation for the aniline-point determinations.

Aromatic hydrocarbons 1 to 13 (table I) were prepared and purified to above 98 percent purity by the Fuel Synthesis Section at the Cleveland laboratory. The other aromatics listed in table I were of technical grade and probably contained only aromatic impurities to the extent of less than 5 percent. These aromatic hydrocarbons were used to prepare the aromatic mixture blended as specified in table I. This mixture parallels the composition of the aromatic fraction of a kerosene as reported in reference 10.

PROCEDURE AND RESULTS

An aromatic-free raffinate was separated from a kerosene by using silica gel, and its aniline point was determined for reference. The aromatic mixture specified in table I was blended with the raffinate at a concentration of about 20 percent. The raffinate and this blend were each percolated through a standard silica-gel column already described in APPARATUS. The aniline points of the first 5 milliliters of the percolates were found to be about 3° C higher than the aniline point of the original raffinate. This difference was seen to affect directly the aniline-point-rise characteristic of the percentage of aromatics removed by the standard column.

Because of this difference, the effect of the silica gel on the raffinate was further investigated at various aromatic concentrations using four raffinates that varied in naphthene content. These raffinates included the aromatic-free portion of a 175° to 315° C cut of Bradford crude of low naphthene content and the aromatic-free naphthene-enriched raffinate from a 130° to 365° C cut of Hastings crude secured by silica-gel separation.

The naphthene contents of these two raffinates and of two blends from them are characterized in the following table:

Nominal naphthene content	Component raffinates	Naphthene rings (percent by wt.) (a)	Naphthenes (approximate percent by volume)
Low	Bradford[b]	21	40
Medium	Bradford and Hastings	36	70
High	Bradford and Hastings	43	85
Nearly 100 percent	Hastings[b]	51	100

[a] Determined by the method of reference 14.

[b] Data specifying the properties and compositions of these cuts of crude petroleum obtained from the Bureau of Mines, Bartlesville, Oklahoma are given in appendix A.

The percentages by volume of naphthenes were estimated on the basis of molecular weights of 184 and 171 for the Bradford and Hastings raffinates, respectively, assuming single-ring cyclohexanes to be predominant. Molecular weights were cryoscopically determined in benzene.

A 150-milliliter sample of a 20-percent blend of the aromatic mixture with the raffinate of medium naphthene content was percolated through the standard silica-gel column. Aniline points, molecular weights, and percent by weight of naphthene rings in the first seven successive 10-milliliter fractions of the percolate were determined. The results of these measurements, plotted in figure 1 as functions of volume percolated, show, in general, a decrease of aniline point accompanied by an early decrease in the molecular weight and an increase of the naphthene content in successive fractions. Evidently, the raffinate was so fractionated that the naphthene content of the early fractions was below the average for the raffinate.

A series of blends of the aromatic mixture at various concentrations from 0 to 40 percent in the four raffinates was percolated through standard columns of silica gel. The aniline points of the 0-to-5-milliliter, the 20-to-25-milliliter, the 30-to-40-milliliter, and subsequent fractions were measured and are plotted as functions of volume percolated in figure 2. The respective concentrations of the aromatic mixture are indicated by the numbers adjacent to the several curves that resulted. The aniline points of successive small percolate fractions decreased sharply for the first 30 milliliters, partly leveled off and then decreased again at a volume that varied with the aromatic content of the samples. The decrease in aniline points was not attributed to aromatics leaking through to the raffinate because ultraviolet spectrophotometric measurements, which were based on the method of reference 15, of the 70-to-90-milliliter percolate fraction from a blend containing 20-percent aromatics showed less than 0.05-percent aromatics. This decrease in aniline point as the percolation progressed was due to partial fractionation of the percolate. Evidence presented in figure 1 indicates that distribution of molecular weight classes and paraffin-naphthene distribution were affected by this fractionation.

The rise in aniline point of the percolated fractions over that of the unpercolated sample for all cases in figure 2 was plotted (but not shown in this report) as functions of percentages of aromatics for the following percolate fractions: 0-to-5 milliliters, 20-to-25 milliliters, 30-to-40 milliliters, and 40-to-50 milliliters. Scatter of data points with variation of naphthene content was least for the 30-to-40-milliliter percolate fraction; consequently, the plot of the aniline-point rise of the 30-to-40-milliliter percolate fraction was considered most suitable for analytical purposes.

The aniline-point rise of the 30-to-40-milliliter percolate fraction was plotted as a function of aromatic content for 16 aromatic-raffinate mixtures, namely, seven concentrations of the aromatic mixture in the raffinate of low naphthene content, four concentrations of the same aromatics in each of two raffinates of medium and high naphthene content, and one aromatic concentration in the nearly 100-percent-naphthene raffinate. These data were averaged at each aromatic concentration and the 218° C curve of figure 3, which was faired through the average values, was adopted as the most suitable for analysis. This curve is hereinafter called the general curve for analysis. The small deviations from this curve shown in figure 3 and table II indicate the effectiveness of the choice of the 30-to-40-milliliter percolate fraction in reducing interference by naphthenes. These deviations of aniline-point rise are equivalent to an average of 0.2 percent and a maximum of 0.5 percent by volume of aromatics. Between the concentrations of 5 and 30 percent by volume of aromatic mixture, the variation of the aniline-point rise with aromatic content on the 218° C curve is almost linear, a rise of 1° C representing 1.23 percent of aromatic mixture.

In order to determine the effects of some different compositions of the aromatic portion on the reliability of the method, the aromatics from high-boiling cuts of two crudes were separated with silica gel as described in reference 6, and reblended in the low-naphthene raffinate. Deviations of data for these reblends from the general curve for analysis are presented in table III and represent an average of 0.84 percent by volume of aromatics based on total sample. The maximum deviation is 1.6 percent. The values of aniline-point rise for these mixtures plotted against percentage of aromatics by volume are shown with the general curve for analysis in figure 4.

Results of the application of this aniline-point-rise method and the general curve for analysis (218° C) to five high-boiling cuts from four crude petroleums are presented in table IV. Analyses of the same samples by a silica-gel adsorption method are quoted for comparison from data provided by the Bureau of Mines Petroleum Experiment Station and listed in appendix A. The large deviations between the analyses of appendix A and these analyses occur for the cases of cuts that have molal average boiling points considerably above 218° C, for which the present method was established. A family of curves for extending the scope of the method to include cuts having other average boiling points in addition to the curve for 218° C is given in figure 3. The method used to obtain this family of curves is described in appendix B. Results of the application of these modified curves to the five high-boiling cuts are also given in table IV, which shows an average deviation of 1.96 percent.

DISCUSSION OF RESULTS

If there were no hydrocarbon fractionation in the aromatic-free portion of the silica-gel percolate, this raffinate would have a constant aniline point throughout and any portion that did not contain aromatics could be used for the determination of aniline-point rise. Removal of aromatics blended in crude-petroleum raffinates by fractionation in a silica-gel column, however, produces an initial percolate having an aniline point higher than that of the original raffinate.

Within a given class of hydrocarbons the aniline point increases with increase in molecular weight and, at constant molecular weight, paraffins have higher aniline points than naphthenes according to data in reference 16. The general shape of the curves in figure 2 can be explained in all cases on the basis of preferential adsorption of lower-aniline-point compounds, particularly naphthenes, by the gel. If this is the case, the fact that aniline points of the 30-to-40-milliliter percolate fractions average about 1° C higher than those of corresponding whole raffinates taken prior to blending (see values listed in fig. 2) indicates that lower-aniline-point compounds are slightly deficient even in the 30-to-40-milliliter percolate fractions. Similarly, the rapid decrease of aniline point at about 90 milliliters of percolate for the 20-percent aromatic blends and at about 60 milliliters of percolate for the 30-percent aromatic blends can be attributed to the efflux of the excess of hydrocarbons having low aniline points that have been temporarily withheld from the earlier percolate by the gel. The greatest decrease in aniline point for the first 30 milliliters of percolate is found for samples with the highest naphthene content.

The extent to which the effect of varying naphthene content has been reduced by choosing the 30-to-40-milliliter percolate fraction is indicated in figure 3 and table II. The three raffinates used include the approximate extremes and a medium value of naphthene content found in crude petroleums. A single curve (218° C) adequately represents the data. The deviations from the curve average only 0.15° C. The intercept of the general curve for analysis at 0-percent aromatics represents the limit of an effect of silica-gel adsorption on aniline-point rise as aromatic content approaches 0. The finite positive value of this intercept (aniline-point rise at 0-percent aromatics) probably results from the extraction of some naphthenes as the aromatic content becomes small. This intercept is satisfactorily constant for raffinates containing high, medium, and low concentrations of naphthenes.

In the investigation of the concentrations of individual aromatics and other hydrocarbons for the 102° to 180° C boiling range in seven representative American crude petroleums (reference 17), uniformity rather than diversity of composition of the aromatic portion of different crude petroleums was found. The statement is also made (p. 143) that, ". . . the alkylbenzenes in the C_9 fraction of petroleum are present in relative amounts which are of the same magnitude for different crude petroleums. . . . This follows similar relations previously reported for the lower alkylbenzenes and for certain other groups of hydrocarbons in different crudes." These findings suggest that variations in the relative amounts of individual aromatics in the 150° to 300° C boiling range are also limited. Hence, anomalous effects on aniline-point rise due to abnormal relative concentrations of some polyalkylbenzenes that have high aniline points are probably definitely limited.

The extent to which the different compositions of the aromatic portions of two cuts of crude petroleum, Bradford from Pennsylvania and Hastings from Texas, influence analytical results is shown in figure 4 and table III. A maximum deviation of 1.6 percent by volume and an average deviation of 0.84 percent by volume from the known aromatic contents were found in the case of these nine reblends of crude-petroleum aromatics in a low-naphthene raffinate.

The improvement in accuracy obtainable by the use of the modified general curves for analysis, which are shown in figure 3, for cuts having average boiling points different from 218° C is shown in table IV. These differences may include errors of the silica-gel adsorption method. The sample of Midway 3B crude petroleum used in this investigation yielded nonuniform results when several methods were applied in two laboratories and may not be the unadulterated cut that the boiling range indicates.

ANALYTICAL METHOD

The following method was used for the determination of the total aromatic content of cuts of crudes that distill in the boiling range from 150° to 300° C and have average boiling points near 218° C:

The aniline point of the dry sample is determined. A 150-milliliter sample is poured into the standard silica-gel column and allowed to enter the gel completely; 150 milliliters of isopropyl alcohol is then added at the top of the column. The aniline point of the 30-to-40-milliliter fraction of the percolate is determined. Subtraction of the aniline point of the original sample from that of the 30-to-40-milliliter fraction gives the aniline-point rise. The percent by volume of aromatics corresponding to this rise can be obtained directly from the general curve for analysis (218° C) of figure 3 for the cuts of crudes specified. For cuts having other molal average boiling points, use of the other curves of figure 3 gives more accurate results.

SUMMARY OF RESULTS

A method for determining the percentage aromatics in 150° to 300° C fractions of crude petroleum has been developed and evaluated.

1. Rise in aniline point resulting from the removal of aromatics by percolation through a particular column of silica gel was found to be an almost linear function of aromatic content of the sample.

2. Nine reblends of aromatics from two crude petroleums having molal average boiling points near 218° C were analyzed for aromatics to within 0.84 percent by volume based on total sample.

3. Modified curves for analysis of cuts having molal average boiling points between 150° and 290° C are presented and on the basis of these curves analyses of five cuts of four crude petroleums agreed to within an average of 2 percent with analyses of the same samples by a different method at another laboratory.

Flight Propulsion Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, March 24, 1948.

APPENDIX A

PHYSICAL AND CHEMICAL PROPERTIES OF CRUDE-PETROLEUM CUTS

The following data specifying the properties and compositions of five cuts from four crude petroleums were furnished by the Petroleum Experiment Station, Bureau of Mines, Bartlesville, Oklahoma.

NACA fuel number	45-659	45-626	45-623	45-669	45-670
Bureau of Mines designation	Tomball 1B	Bradford 2B	Midway 3B	Hastings 5B	Hastings 5C
Distillation temperature, °F					
A.S.T.M. method D 86-40					
Initial boiling point	357	324	287	278	374
Percentage evaporated					
5	420	353	425	301	433
10	432	366	445	308	451
30	464	410	475	327	483
50	486	441	506	343	511
70	507	470	543	361	546
90	540	506	594	388	624
95	568	524	621	402	682
End point	584	540	625	420	690
Specific gravity, 60/60° F	0.8513	0.7983	0.8794	0.8101	0.8606
Gravity, °A.P.I.[a]	34.7	45.7	29.4	43.2	32.9
Density at 20° C	0.8468	0.7945	0.8746	0.8060	0.8580
Refractive index at 20° C					
n_D[b]	1.47559	1.44387	1.48375	1.44685	1.47525
n_g[c]	1.49038	1.45477	1.49785	1.45830	1.48844
n_e[d]	1.47837	1.44599	1.48645	1.44904	1.47782
Viscosity, centistokes					
100° F (37.8° C)	2.313	1.701	3.218	1.051	3.408
-40° F (-40° C)	Frozen	Frozen	114.81	5.098	125.15
Aniline point, A.S.T.M. D611-41T					
°F	138.0	160.0	124.4	117.0	146.8
°C	59.0	71.0	51.2	47.0	63.9
Freezing point, °F	-17	-29	Below-76	Below-76	-63
Sulfur, percent by weight	0.08	0.14	0.45	0.03	0.13
Bromine number, A.S.T.M. ES-45a	3.36	6.63	6.65	Negative	2.62
Flash point, °F	180	137	149	89	184
Molecular weight	192	183	197	138	204
Molecular volume	227	230	225	171	238
Aniline function	122	126	119	99	128
Specific dispersion	174.7	137.0	161.2	142.1	153.7
Refractivity intercept	1.0522	1.0466	1.0465	1.0439	1.0463

[a] $°\text{A.P.I.} = \frac{141.5}{G}$ where G is specific gravity at 60/60° F.

[b] n_D = refractive index for the sodium D line.

[c] n_g = refractive index for the mercury g line.

[d] n_e = refractive index for the mercury e line.

NACA fuel number	45-659	45-626	45-623	45-669	45-670
Bureau of Mines designation	Tomball 1B	Bradford 2B	Midway 3B	Hastings 5B	Hastings 5C
A.S.T.M. ES-45a hydrocarbon analysis					
Extract (aromatic), percent by volume	29.9	17.1	29.4	18.5	20.2
Density at 20° C	0.9428	0.8532	0.9422	0.8692	0.9257
n_D	1.54585	1.48906	1.53742	1.49530	1.53836
n_g	1.57197	1.50573	1.55993	1.51459	1.58198
Monocyclic aromatics, percent by volume	100	100	-------	100	60
Dicyclic aromatics, percent by volume	0	0	-------	0	40
Raffinate, percent by volume	70.1	82.9	70.6	81.5	79.8
Density at 20° C	0.8059	0.7824	0.8465	0.7916	0.8408
n_D	1.44562	1.43455	1.46140	1.43585	1.45928
n_g	1.45558	1.44426	1.47200	1.44552	1.46477
Naphthene rings, percent by weight	29.8	18.2	59.4	47.8	53.5
Paraffin and paraffin side chains, percent by weight	70.2	81.8	40.6	52.2	46.5
Silica-gel hydrocarbon analysis					
Extract (aromatic), percent by volume	32.25	12.45	33.23	16.82	25.17
Density at 20° C	-------	--------	0.9431	0.8799	0.9363
n_D	-------	1.51573	1.53277	1.50524	1.53353
n_g	-------	1.53639	1.55408	1.50904	1.55619
n_e	-------	1.51950	1.53647	1.52551	1.53771
Monocyclic aromatics, percent by volume	64.3	--------	99.4	88.7	90.9
Dicyclic aromatics, percent by volume	35.7	--------	0.6	11.3	9.1
Raffinate, percent by volume	67.75	87.55	66.77	83.18	74.83
Density at 20° C	0.7930	0.7788	0.8405	0.7915	0.8311
n_D	1.44119	1.43408	1.45964	1.43577	1.45639
n_g	1.45091	1.44359	1.46980	1.44546	1.46654
n_e	1.44305	1.43586	1.46146	1.43761	1.45832
Naphthene rings, percent by weight	19.7	15.3	54.9	47.7	45.1
Paraffin and paraffin side chains, percent by weight	80.3	84.7	45.1	52.3	54.9
Estimated best analysis of total sample					
Paraffin, percent by volume	31.85	54.25	0	4.98	0
Naphthenes, percent by volume	35.90	33.30	66.77	78.20	74.83
Monocyclic aromatics, percent by volume	20.75	12.45	33.03	14.92	22.87
Dicyclic aromatics, percent by volume	11.50	0	0.20	1.90	2.30
Naphthene rings, percent by weight	12.5	13.1	35.2	39.0	32.7
Paraffin and paraffin side chains, percent by weight	51.0	72.7	28.9	42.7	39.8

APPENDIX B

MODIFICATION OF THE GENERAL CURVE FOR ANALYSIS FOR CUTS HAVING OTHER AVERAGE BOILING POINTS

The progressive decrease of the difference between critical solution temperatures of saturates and aromatics, evident in figure 1 of reference 17, indicates that analyses of cuts having average boiling points other than 218° C would be more accurate if suitable modified general curves for analysis were used. These curves are developed herein from functions reported in references 15 and 18.

Symbols

A	molal average boiling point, °K
A_x	molal average boiling point of sample x, °K
A_y	molal average boiling point of sample y, °K
b_a	aniline-function intercept constant for aromatic hydrocarbons
b_s	aniline-function intercept constant for saturated hydrocarbons
M	molecular weight
M_x	molecular weight of sample x
M_y	molecular weight of sample y
m	aniline-function slope constant
T_a	aniline point of aromatic hydrocarbons, °K
T_c	critical solution temperature, °K
T_s	aniline point of saturated hydrocarbons, °K
ΔT	aniline-point rise, °C
ΔT_x	aniline-point rise of sample x, °C
ΔT_y	aniline-point rise of sample y, °C

When aniline function, which is the product of the molecular weight and the ratio of the absolute critical solution temperature to the absolute boiling point, is plotted against the molecular weight (reference 15, fig. 2), lines of nearly equal and constant slope and of different intercept for each hydrocarbon class result. These lines may be characterized mathematically as follows:

$$\frac{T_c M}{A} = mM + b_s \tag{1}$$

and

$$\frac{T_c M}{A} = mM + b_a \tag{2}$$

If it is assumed that these expressions are valid and that, in the boiling range considered,

(a) the critical solution temperature equals the aniline point

(b) the molal average boiling point is the same for each hydrocarbon class in a given sample

(c) the molecular weight is the same for each hydrocarbon class in any given sample

(d) the aniline point is an additive function

the following derivation is possible.

If aniline point is substituted for critical solution temperature and equations (1) and (2) are multiplied by boiling point, versions of the these equations may be written to characterize saturates or aromatics:

$$T_s M = AmM + Ab_s \tag{3}$$

$$T_a M = AmM + Ab_a \tag{4}$$

The maximum aniline-point rise possible for the theoretical limiting case of 100-percent aromatics is $T_s - T_a$. Subtraction of equation (4) from equation (3) and factoring gives the following equation:

$$\Delta T_{max} = T_s - T_a = \frac{A(b_s - b_a)}{M} \qquad (5)$$

The ratio of the maximum aniline-point rise of sample x to that for sample y is found to be a function of only the molecular weights and the boiling points of the two samples. Division of equation (5) by a similar equation representing a cut having a different average boiling point and then factoring gives:

$$\frac{\Delta T_x}{\Delta T_y} = \frac{A_x M_y}{A_y M_x} \qquad (6)$$

Knowledge of the functional relation between the boiling point and the molecular weight, and use of equation (6) would allow calculation of ratios for modifying the general curve for analysis established for one average boiling point (such as fig. 3 at 218° C) to secure other such curves suitable for cuts having other average boiling points. This relation is available in figure 2 of reference 18 where molecular weight is plotted as a function of boiling point averaged on the basis of moles distilled (molal average boiling point) at various values of the parameter characterization factor (the cube root of the molal average boiling point in °R divided by the specific gravity, 60°/60° F). The characterization factor is a measure of the paraffin content of the crude and was found to average 11.5 for the five cuts analyzed at the NACA Cleveland laboratory. Aniline-point-rise ratios were calculated using this value as typical according to equation (6) to yield the desired modification ratios. Choice of characterization factor has only an insignificant effect on analytical results. Resulting modified curves for a range of molal average boiling points are given in figure 3.

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TABLE I - COMPOSITION OF AROMATIC MIXTURE USED FOR PREPARATION OF AROMATIC RAFFINATE BLENDS

Hydrocarbon		Approximate boiling point (°C)	Percent by weight	Approximate percent by volume
1	Ethylbenzene	135	0.957	1.0
2	Cumene	153	5.993	6.0
3	1,3,5-Trimethylbenzene	164	4.303	4.5
4	tert-Butylbenzene	167	.955	1.0
5	1,2,4-Trimethylbenzene	169.5	4.138	4.5
6	1,2,3-Trimethylbenzene	175	2.464	2.5
7	*p*-Cymene	175	3.790	4.0
8	Isobutylbenzene	180	.941	1.0
9	Diethylbenzene	182	3.850	4.0
10	*n*-Butylbenzene	183	.940	1.0
11	Triethylbenzene	217	3.828	4.0
12	Triisopropylbenzene	237	11.351	12.0
13	α-Isopropylnaphthalene	270	13.752	12.5
14	Xylenes	140	3.810	4.0
15	Monoamylbenzene	193	1.901	2.0
16	Diisopropylbenzene	203	3.878	4.0
17	Naphthalene	218	1.712	1.5
18	Methylnaphthalenes	241	6.187	5.5
19	Diamylbenzene	265	7.551	8.0
20	Hexaethylbenzene	298	7.584	7.5
21	Monoamylnaphthalene	305	10.117	9.5

TABLE II - DEVIATIONS FROM GENERAL CURVE FOR ANALYSIS WITH VARYING NAPHTHENE CONTENT

Aromatic mixture (percent by volume)	Naphthene content in raffinate					
	Low		Medium		High	
	Deviation of aniline-point rise (°C)	Deviation from known aromatic content (percent by volume)	Deviation of aniline-point rise (°C)	Deviation from known aromatic content (percent by volume)	Deviation of aniline-point rise (°C)	Deviation from known aromatic content (percent by volume)
0	0.1	0.12	0.3	0.4	-0.3	-0.4
5	0	0	.4	.5	-.1	-.12
10	0	0	----------	------------	----------	------------
15	.1	.12	----------	------------	----------	------------
20	0	0	-.1	-.12	-.1	-.12
30	0	0	-.3	-.36	-.3	-.36

Average deviation of aniline-point rise, 0.15° C.

Average deviation of determined aromatic content from the known aromatic content, 0.19 percent.

TABLE III - DEVIATIONS FROM GENERAL CURVE FOR ANALYSIS OF AROMATIC FRACTIONS OF CRUDE PETROLEUM REBLENDED IN BRADFORD RAFFINATE

Reblended aromatic fraction (percent by volume)	Source and boiling range of aromatic fraction			
	Bradford, 175-315° C		Hastings, 130-365° C	
	Deviation of aniline-point rise (°C)	Deviation from known aromatic content (percent by volume)	Deviation of aniline-point rise (°C)	Deviation from known aromatic content (percent by volume)
5	0.3	0.4	0.7	0.9
10	0	0	.6	.7
20	-1.4	-1.6	.6	.7
30	-1.1	-1.4	.4	1.6
40	.2	-.25	-----------	--------------

Average deviation of aniline point, 0.60° C.

Average deviation of determined aromatic content from the known aromatic content, 0.84 percent.

TABLE IV - DIFFERENCES BETWEEN ANALYSES OF FIVE CUTS OF CRUDE PETROLEUM

BY SILICA-GEL ADSORPTION METHOD AND BY ANILINE-POINT-RISE METHOD

Crude petroleum	NACA fuel number	Boiling range (°C)	Molal average boiling point (°C)	Aromatics (percent by volume)			Differences	
				Aniline-point rise		Silica-gel adsorption[a]	Using 218° C curve (4-6)	Using modified curves (5-6)
				Using 218° C curve	Using modified curves			
	1	2	3	4	5	6	7	8
Tomball 1B	45-659	185-295	248	28.6	30.7	32.25	-3.65	-1.55
Bradford 2B	45-626	175-315	220	12.2	12.0	12.45	-.25	-.45
Midway 3B	45-623	205-330	260	26.3	28.7	33.23	-6.93	-4.53
Hastings 5B	45-669	130-225	170	17.6	15.5	16.82	.78	-1.32
Hastings 5C	45-670	195-365	265	20.6	23.2	25.17	-4.57	-1.97
Average difference							3.24	1.96

[a] Data furnished by the Petroleum Experiment Station, Bureau of Mines, Bartlesville, Oklahoma.

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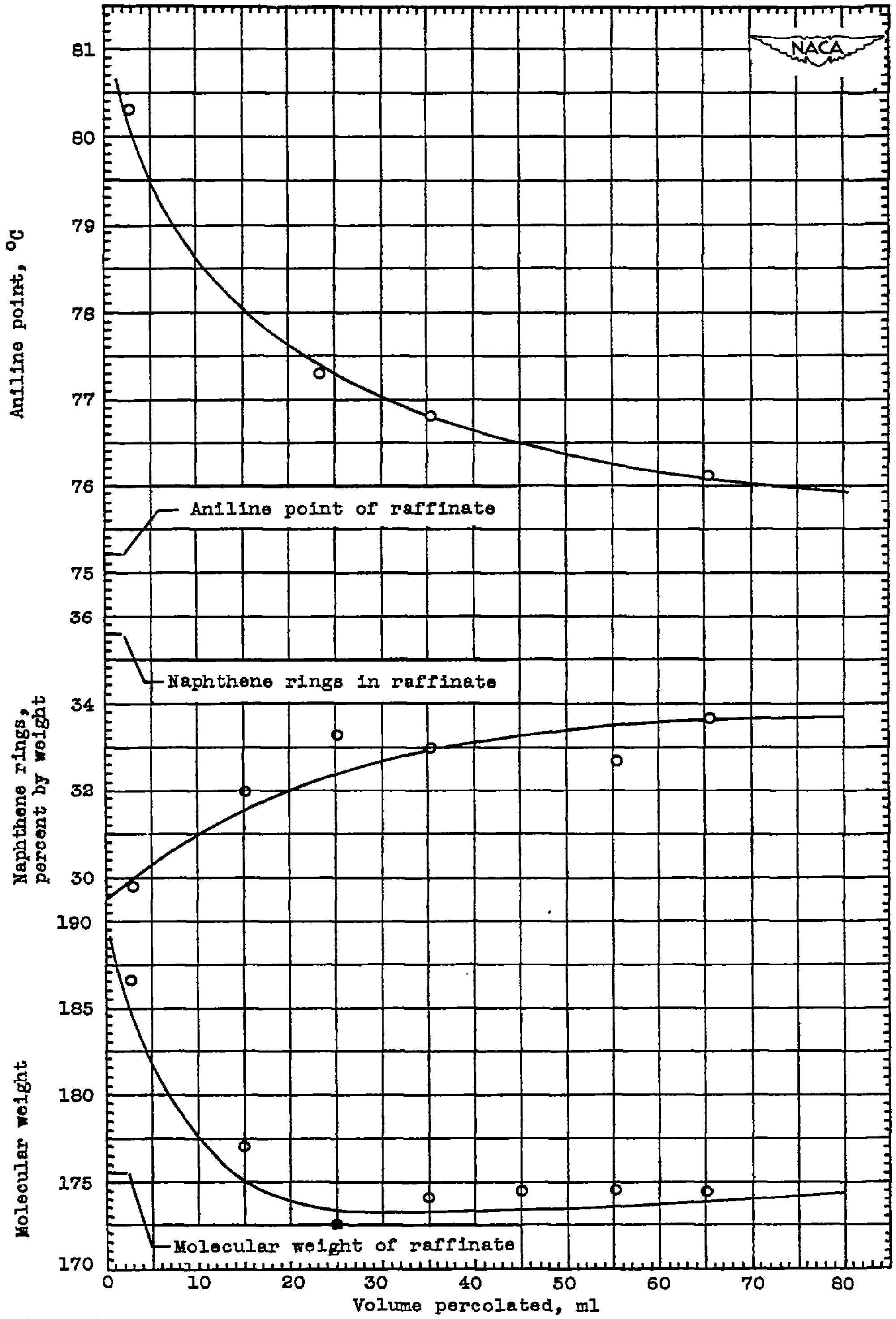

Figure 1. - Variation of aniline point, percent by weight of naphthene rings, and molecular weight as functions of volume percolated for a 20-percent blend of aromatic mixture with medium naphthene raffinate.

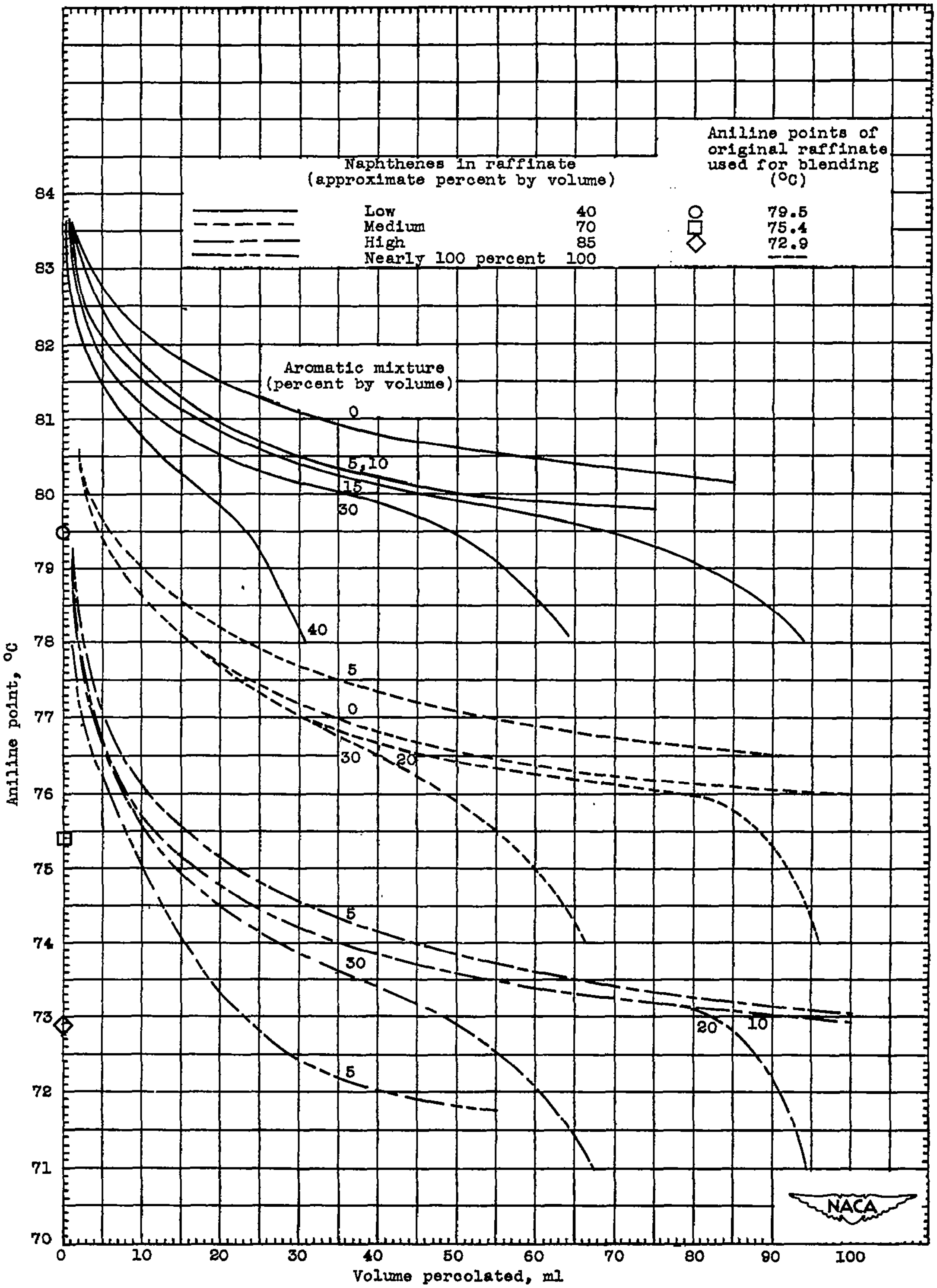

Figure 2. - Variation of aniline point as a function of volume percolated for various concentrations of aromatic mixture blended with raffinates containing low, medium, high, and nearly 100-percent naphthenes.

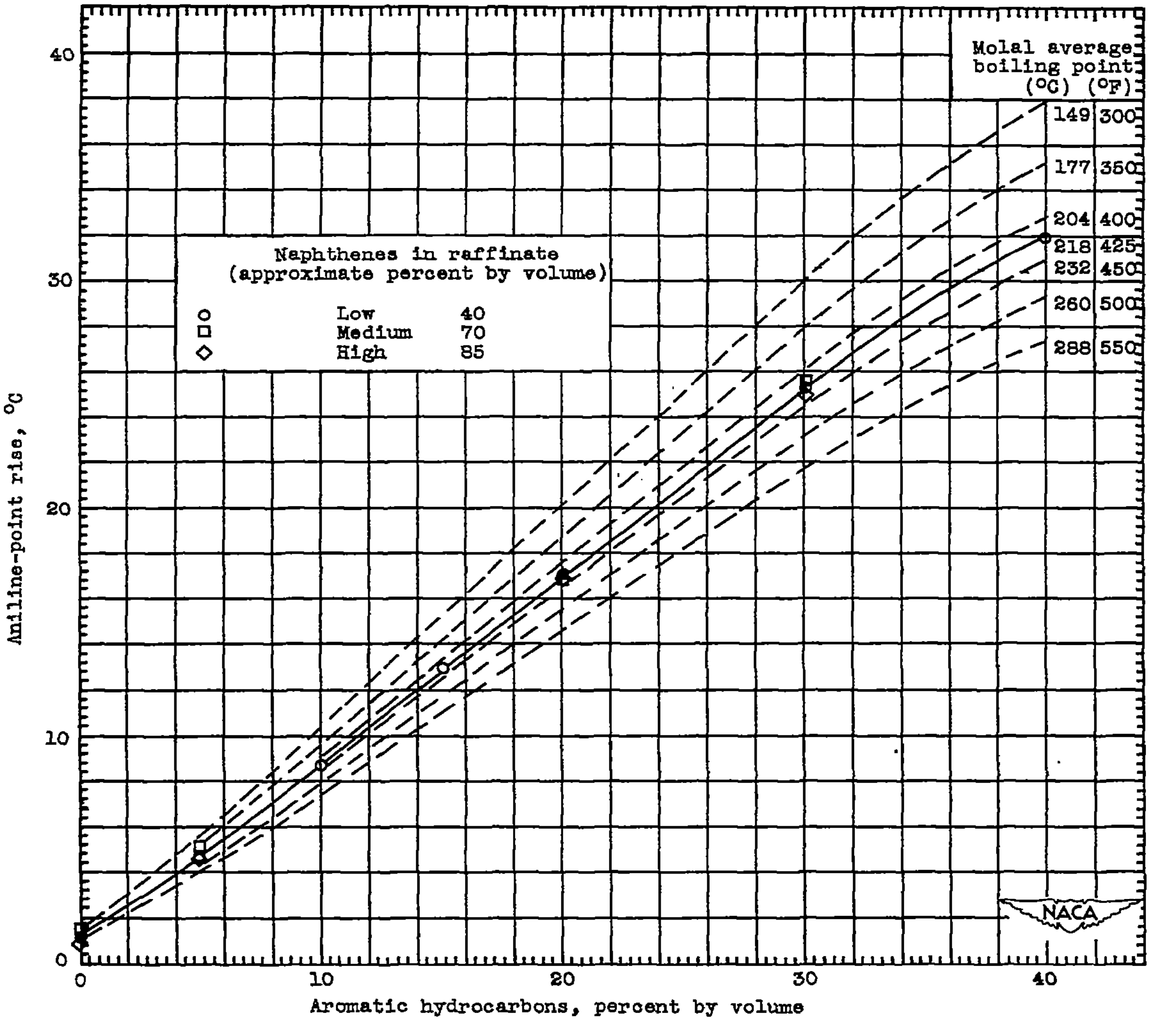

Figure 3. - Variations of expected aniline-point rise with aromatic content for application to narrow cuts of petroleum having molal average boiling points as indicated.

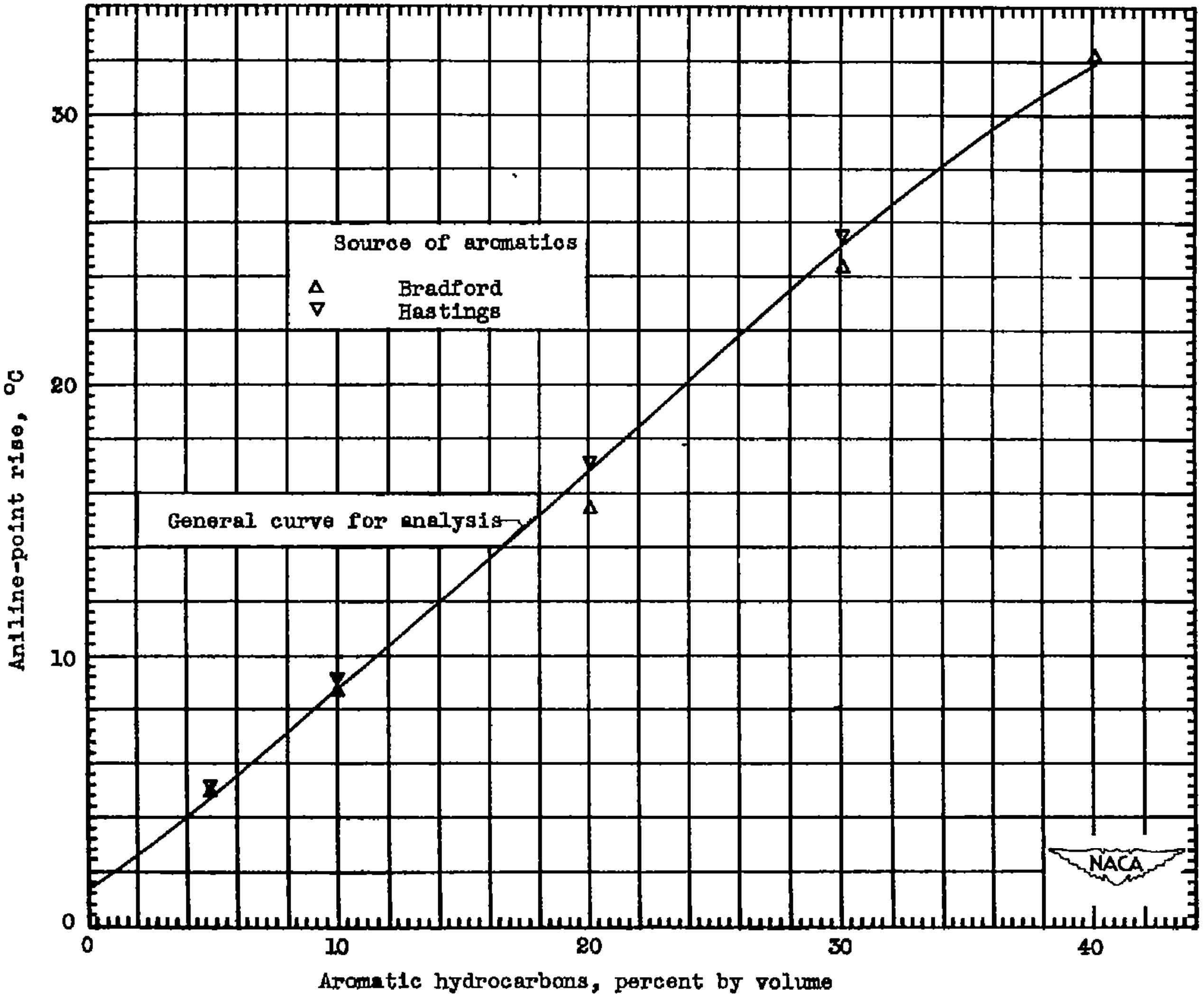

Figure 4. - Comparison of aniline-point rise for blends containing various percents by volume of aromatics from Bradford and Hastings crude petroleums with the general curve for analysis of figure 3. Raffinate from Bradford crude was of low naphthene content.