



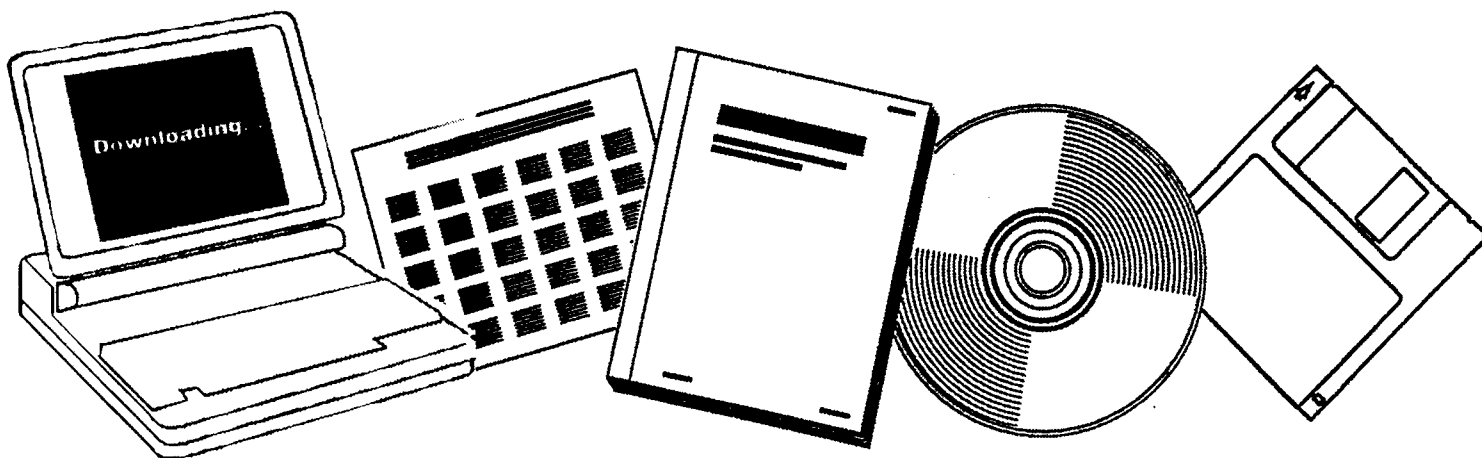
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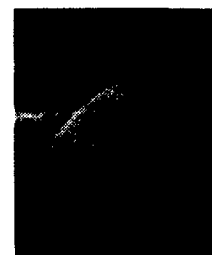
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ANALYTICAL METHODS IN MASS SPECTROMETRY

By A. G. Sharkey, Jr., J. L. Shultz, and R. A. Friedel



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CONTENTS

	Page
Abstract	1
Introduction	1
Experimental procedure	3
Analytical methods	4
Correlation studies	4
Mass spectra of alcohols.....	4
Mass spectra of trimethylsilyl derivatives.....	9
Mass spectra of acetal-type compounds.....	12
Mass spectra of ketones.....	17
Mass spectra of esters: Formation of rearrangement ions.....	19
Type-analysis of paraffin-naphthene mixtures.....	25
Analysis of oils derived from coal.....	29
Methods of analysis.....	29
Application of methods.....	35
Special analytical techniques.....	40
Mass spectrometric determination of the ratio of branched to normal hydrocarbons up to C ₁₅ in Fischer-Tropsch product.....	40
Analysis of butenes and pentenes by hydrochlorination.....	47
Mass spectrometric analysis of mixtures containing nitrogen dioxide.....	48
Mass spectrum of nitric acid.....	56
Determination of H ₂ S and vapor-phase H ₂ O.....	57
Mass spectrum of hydrogen deuteride (HD).....	57
Instrumentation and studies of anomalous peaks.....	60
Conditioning of mass spectrometer filaments: Tungsten carbide formation.....	60
Rhenium filaments for mass spectrometry.....	65
Automatic manometer for constant-pressure gas sampling.....	66
Self-filling micropipet for liquid introduction.....	67
Anomalous negative peaks in mass spectra.....	69
Conclusions	71
References	72

ILLUSTRATIONS

Fig.	Page
1. Parent-minus-15 peak intensities of trimethylsilyl ethers, derivatives of normal alcohols.....	13
2. Rate of decomposition of mass 61 fragment from hemiformal of methanol.....	14
3. Variation with time of several mass peaks in a blend of formaldehyde-methanol-water	15
4. Rate of decomposition of mass 61 fragment from the hemiacetal of methanol.....	16
5. Partial identification of an ester from rearrangement peaks.....	24
6. Fischer-Tropsch oil product, ester distribution from rearrangement peaks.....	24
7. Preliminary separation and mass spectrometric analytical scheme for high-boiling oils from coal	30
8. Typical ionization efficiency curve for molecular ions from hydrocarbons.....	31
9. Partial mass spectrum of naphthalene, normal and reduced ionizing voltages.....	32
10. Low-ionizing-voltage sensitivity data for phenolic types.....	33
11. Low-ionizing-voltage sensitivity data for alkyl-substituted phenols.....	34
12. Variation of sensitivity factor with number of alkyl substituents on the phenol ring.....	34
13. Carbon number distribution of phenols and indanols in a tar-acid fraction.....	35
14. Sensitivities of phenols and their trimethylsilyl ether derivatives at low-ionizing voltage	36
15. Catalytic cracking of phenols from coal-tar distillate as evidenced by low-ionizing-voltage mass spectra.....	37
16. Carbon number distribution of phenols, indans, and benzenes in blended fractions of a coal-hydrogenation oil.....	38
17. Separation and analysis of >170° C fraction of Fischer-Tropsch synthesis product.....	42
18. Sensitivity data for paraffins in Fischer-Tropsch product.....	43
19. Carbon number distribution for paraffins in hydrogenated Fischer-Tropsch products.....	45

	Page
20. Predicted values for carbon number distribution of paraffins in hydrogenated Fischer-Tropsch product	46
21. Variation in proportion of α -isomer with carbon number for paraffins	46
22. Preliminary test for proper conditioning with NO ₂	50
23. Test for proper conditioning with NO ₂ by consecutive runs	50
24. NO ₂ mass spectral patterns at various pressures	51
25. NO ₂ mass spectral sensitivities at various pressures	52
26. Working curve, NO ₂ pressure versus mass 46 peak heights	56
27. Schematic diagram of flow system in mass spectrometer inlet system	58
28. Rate of diffusion curve for determination of H ₂ impurity and relative abundance of D ⁺ from HD	59
29. Change of conductance with carbon content for tungsten at room temperature	61
30. Schematic diagram of a longitudinal section of a well-conditioned filament showing locations of crystalline phases	62
31. Schematic diagram of a longitudinal section of an overconditioned filament showing locations of crystalline phases	63
32. Conductance change with carbon content for a tungsten filament at 2,475° C.	63
33. Current changes observed with the introduction of oxygen or hydrocarbon	64
34. Manometer for obtaining uniform gas pressure during sampling	66
35. Seil-filling 0.001-ml micropipet	68
36. Possible source of negative peaks	69
37. Portion of CO spectrum	69

TABLES

1. Comparison of spectrum of primary straight-chain alcohol with corresponding olefin	5
2. Ionization distribution for alcohols among various types of fragmentation peaks	5
3. Comparison of spectrum of primary, β -branched alcohol with corresponding olefin	6
4. Total ionization of aliphatic alcohols	7
5. Groups identifiable in unknown alcohol by mass spectra	8
6. Mass spectral analysis of alcohol synthetic blends	8
7. Mass spectral type-analysis of C ₁ to C ₆ alcohols	9
8. Matrix for type-analysis of C ₁ to C ₆ alcohols	9
9. Fragmentation peaks in mass spectra of normal aliphatic trimethylsilyl ethers	10
10. Rearrangement structures in trimethylsilyl ethers	11
11. Type identification of alcohols by trimethylsilyl ether derivatives	11
12. Evidence of hemiformal in vapor phase of formaldehyde-methanol-water blend	14
13. Evidence of hemiacetal in vapor phase of acetaldehyde-methanol blend	16
14. Acetals formed in alcohol-aldehyde blends	17
15. Correlation of ketone structure with rearrangement peaks	19
16. Identification of ketones from mass spectral characteristics	20
17. Origin of base peaks in mass spectra of esters	20
18. Correlation of rearrangement peaks in mass spectra of esters	21
19. Examples of mass spectral rearrangement ions	22
20. Formation of rearrangement ions	23
21. Mass spectral type-analysis of naphthenes, general calibration peaks	25
22. Outline of type-analysis of naphthene-paraffin blends, C ₁ matrix	26
23. Outline of type-analysis of naphthene-paraffin blends, 5-component C ₁ matrix	27
24. Outline of type-analysis of naphthene-paraffin blends, 7-component C ₁ matrix	27
25. Mass spectral type-analysis of C ₁ and cyclohexane paraffin-naphthene synthetic blends	28
26. Mass spectral type-analysis of C ₁ paraffin-naphthene synthetic blends	28
27. Type-analysis of C ₁ paraffin-naphthene mixtures from coal-hydrogenation product	28
28. Type-analysis of C ₁ paraffin-naphthene mixtures from coal-hydrogenation product	29
29. Approximate ionization potentials	31
30. Low-ionizing-voltage sensitivities of methylindanols	35
31. Low-ionizing-voltage analysis of a synthetic blend of phenols	35
32. Identification of samples analyzed	36
33. Analysis of high-boiling tar acids from Coal Tar Research Association (CTRA), Leeds, England	37
34. Mass spectral analysis of methanol-extract of low-temperature tar from Texas lignite	38
35. Mass spectral analysis of a coal-hydrogenation oil	38
36. Mass spectral analysis of distillable neutral oil from hydrogenation of a high-temperature tar	39
37. Mass spectral analysis of saturated neutral oils produced by hydrogenation of low-temperature tar	39
38. Analysis of 120° to 290° C fraction of neutral oil from carbonization of subbituminous Western coal at 500° C	39

CONTENTS

v

	Page
39. Mass spectral analysis of 120° to 290° C fraction of neutral oil from carbonization of subbituminous Western coal at 500° C.....	39
40. Mass spectral carbon number distribution data for neutral oil from 500° C carbonization of a subbituminous Western coal.....	40
41. Carbon number distribution for paraffins in hydrogenated fractions of Fischer-Tropsch product.....	41
42. Determination of n-paraffins in hydrogenated Fischer-Tropsch synthesis product, bp >170° C.....	42
43. Distribution of normal paraffins in 176° to 323° C fraction of Fischer-Tropsch synthesis product.....	45
44. Mass spectral analysis of synthetic blends of C ₄ and C ₅ hydrocarbons.....	47
45. Mass spectral analysis of a synthetic blend of C ₄ to C ₅ hydrocarbons.....	47
46. Mass spectral patterns of NO ₂ at various pressures.....	52
47. Apparent impurities produced in spectrometer by nitrogen dioxide.....	53
48. NO ₂ patterns at 100 microns obtained with two different mass-spectrometer filaments.....	53
49. NO ₂ mass spectral patterns at ionizing currents of 10 and 50 μa.....	53
50. Mass spectral synthetic blends analysis at 50 μa.....	53
51. Mass spectral patterns of nitric oxide, nitrous oxide, and nitrogen dioxide.....	54
52. Mass spectral analysis of synthetic blends containing NO ₂ and NO.....	54
53. Nonreactivity of NO and O ₂ in micron pressure range.....	55
54. Successive mass spectral patterns of red-fuming nitric acid.....	57
55. Mass spectrometer analysis of synthetic blends of nitric acid and nitrogen dioxide.....	59
56. Mass spectra of H ₂ , HD, and D ₂	59
57. Calculation of equilibrium constants at 500° C for H ₂ + D ₂ ⇌ 2HD from mass spectral analysis.....	60
58. Reproducibility of constant-pressure gas samples, with various introduction methods.....	67
59. Mass spectral test for fractionation through sintered disk.....	67
60. Reproducibility of liquid introduction into mass spectrometer by 0.001-ml self-filling micropipet.....	68
61. Mass spectral analysis of synthetic blend introduced with 0.001-ml self-filling micropipet.....	69
62. Ratio of negative to positive ion peaks.....	70

ANALYTICAL METHODS IN MASS SPECTROMETRY

by

A. G. Sharkey, Jr.,¹ J. L. Shultz,²
and R. A. Friedel³

Abstract

THE PURPOSE of this investigation was to develop methods for analyzing coal derivatives and products from the Fischer-Tropsch synthesis. As part of this investigation it was necessary to study the mass spectral characteristics of many classes of compounds. The mass spectra of alcohols, the trimethylsilyl ether derivatives of alcohols, acetal-type compounds, ketones, esters, and naphthenes were correlated with structure, and analytical methods were formulated. A method was devised to determine the ratio of branched to normal hydrocarbons up to C₁₈ in the Fischer-Tropsch product.

Low-ionizing-voltage mass spectrometry was combined with type-analyses to analyze tar acids and neutral oils from coal. The necessary sensitivity correlations at low-ionizing voltage were developed, particularly for phenolic compounds.

Special analytical techniques were developed for the mass spectral analyses of specific compounds and compound types including (1) oxides of nitrogen, (2) hydrogen sulfide, (3) isomers of butenes and pentenes, and (4) hydrogen deuteride.

An investigation was made of the effects of various hydrocarbons and oxygenated compounds on tungsten filaments in the mass spectrometer. The operating characteristics of rhenium filaments under similar conditions were studied. Several improved sample handling techniques were developed, including an automatic manometer and a self-filling micropipet. Studies were made of anomalous and negative peaks in the mass spectra of certain gases.

Introduction

Investigations of direct and indirect processes for converting coal to liquid and gaseous fuels and chemicals, and studies of coal structure are carried out at the Pittsburgh Coal Research Center of the Federal Bureau of Mines. The analysis by mass spectrometry of products from these studies has required the development of new methods to interpret mass spectra. Methods were designed to solve specific analytical problems. This report does not represent an exhaustive survey of the analytical techniques used in mass spectrometry.

Analytical schemes developed by petroleum laboratories cannot be applied directly to Fischer-Tropsch synthesis product, because the synthesis

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product contains more oxygenated material and less highly branched hydrocarbons. To assist in developing the required methods of analysis, mass spectral correlation studies were made of several classes of oxygenated compounds contained in Fischer-Tropsch synthesis product. Combined chemical and mass spectrometric techniques to analyze for these compounds were developed.

Coal hydrogenation product contains more aromatic and oxygenated material than petroleum. The gaseous product analyzed by mass spectrometry consists of a high percentage of hydrogen and small amounts of paraffins, naphthenes, and aromatics. The liquid product from the coal hydrogenation process is quite complex, and only a type-analysis is carried out routinely by mass spectrometry on fractions having a limited boiling range. The low-ionizing-voltage technique permits analyses of saturate and aromatic fractions of neutral oils and the tar acids in the coal hydrogenation product.

The mass spectrometer analysis of gaseous hydrocarbon mixtures is described extensively in the literature and will not be included in this report.

The mass spectrometer is an electronic, high-vacuum instrument capable of providing qualitative and/or quantitative analyses of gases, liquids, and, under special conditions, solids. Mass spectrometers at the Pittsburgh Coal Research Center are equipped to obtain spectra of materials having vapor pressures of at least 50 microns at room temperature or at temperatures not exceeding 300° C.

In certain instances it was necessary to adopt procedures to (1) circumvent limitations inherent in the mass spectrometer and (2) simplify mixtures by chemical and physical separations, making it possible to obtain more information.

The three basic types of limitations on the use of the mass spectrometer are: (1) that due to the nature of the material to be analyzed, (2) instrumental limitations, and (3) spectral limitations. As the mass spectrometer involves the production of ions in a high-vacuum system, the compound to be analyzed must be stable under high-vacuum conditions (10^{-6} mm of mercury) and have sufficient vapor pressure of about 50 microns for ion production at the operating temperature of the instrument. This precludes the analysis of any compound that decomposes under high vacuum or reacts with any material in the vacuum system. Traces of samples remaining in the vacuum system can also cause difficulty by producing an undesirable background spectrum or by reacting with succeeding samples. The instrumental limitation primarily involves resolution. Spectral limitations result from similarity in fragmentation patterns and rearrangements producing parent mass peaks of lower members of homologous series.

Chemical and physical methods used in this investigation to make samples amenable to mass spectrometric analysis include (1) reactions to form derivatives, (2) hydrogenation, (3) sulfuric acid treatment, (4) silica gel separations, (5) fluorescent indicator adsorption, (6) distillation, and (7) use of molecular sieves.

After mass spectrometers equipped with elevated-temperature inlet systems became available, making it possible to analyze less volatile liquids and waxes, it soon became evident that the time and expense required to maintain filament stability would be prohibitive. The conditioning of tungsten filaments to produce and maintain operating stability is a technique recommended by the Consolidated Electrodynamics Corp. for all users of analytical mass spectrometers. High-pressure 2-butene is introduced into the ion source to form a tungsten carbide coating on the filament. When the highly aromatic products from the coal hydrogenation process were introduced into the high-temperature mass spectrometer, the tungsten filaments exhibited extreme "gas sensitivity" and deformation after very short periods. The characteristics of carbided tungsten filaments were studied and rhenium, which does not form stable carbides, was recommended as an electron emitter.

EXPERIMENTAL PROCEDURE

The spectra were obtained on two Consolidated Electrodynamics Corp. model 21-103C mass spectrometers,⁴ one with the inlet system operated at room temperature and the other with the inlet at 285° C.

The instrument with the room-temperature inlet was used to analyze gaseous mixtures and mixtures of low-molecular-weight (about 200 or less) liquids using 70-volt electrons, an ionizing current of 10 microamperes and ion source temperature of 250° C, and a mass scan beginning at either mass 12 or mass 17. All spectra used for the correlation studies were started at mass 17. For all liquid samples the spectral data are reported as chart divisions per unit liquid volume. In most instances the unit volume was 0.00068 ml,

⁴ Reference to specific brands, makes, or models of equipment is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

the volume of a self-filling micropipet (32).⁵ For the naphthenes (29) a 0.00036-ml pipet was used. For the acetals (30) peak heights were related to the strongest peak in the spectrum (base peak). The spectra are thus reported as sensitivity coefficients on a liquid-volume basis, and spectral peak heights are directly comparable. The molecular ion peak is frequently referred to as the parent peak.

The mass spectrometer equipped with a heated inlet system operating at 285° C was used for the high-molecular-weight samples (solids and liquids with low vapor pressure). This instrument requires approximately 1 mg of sample. Data were obtained using 70-volt electrons for conventional analyses and 7.0-volt (indicated) electrons for low-ionizing-voltage determinations.

⁵ Italic numbers in parentheses refer to items in the list of references at the end of this report.

ANALYTICAL METHODS

The correlation of mass spectra with molecular structures was studied primarily for oxygenated compounds since there was little information in the literature in this field and since the Fischer-Tropsch synthesis product contains high percentages of alcohols, ketones, and esters. For oxygenated compounds containing more than two or three carbon atoms, serious spectral interference is found. Analysis of oxygenated compounds is difficult because ions that arise from the rearrangement of atoms in the molecule-ion before and/or during fragmentation frequently appear at the parent mass of lower numbers of a homologous series. Interferences among the various classes of oxygenated compounds and hydrocarbons result from similarity of fragmentation processes that occur during ionization by electron impact.

Mass spectral correlation studies have been carried out for several classes of hydrocarbons (11-12, 29, 69, 93), sulfur compounds (50), and amines (17). The mass spectra of various oxygen-containing compounds have been investigated, including aliphatic acids by Happ and Stewart (43), high-molecular-weight primary straight-chain alcohols by Brown (14), ethers by McLafferty (61), and aldehydes by Gilpen and McLafferty (39). At the Pittsburgh Coal Research Center, correlation studies have been carried out for alcohols (34), ketones (81), acetals (30), trimethylsilyl ether derivatives of alcohols (76), esters (80), and naphthenes (29).

Correlation studies have led to the development of type-analyses where classes of compounds are determined as a sum rather than specific compounds identified. As part of the present investigation, a type-analysis for C_6 to C_8 paraffin-naphthene mixtures was developed. The general technique is to use the summation of intensities for peaks characteristic of various compound types. Analyses of complex mixtures can be obtained in this manner. A type-analysis for alcohols has also been developed (34).

CORRELATION STUDIES

Mass Spectra of Alcohols

The mass spectra of 69 alcohols from C_1 through C_{11} were studied and the correlation of molecular structure with mass spectral fragmentation patterns was investigated.

Alcohols are usually considered to be of three major types—primary, secondary, and

tertiary. Mass spectra make subclassifications desirable. Thus, the primary group contains two classes: (1) normal straight-chain and γ -branched (γ , δ , etc., branched) and (2) β -branched. Secondary alcohols may be classified as 2-, 3-, 4-, etc., types. Tertiary alcohols have also been subclassified into partly symmetrical types (dimethyl, diethyl, etc.) and the completely unsymmetrical types (methyl, ethyl, methyl propyl, etc.). Complete mass spectra for the 69 alcohols investigated have been published (34).

Primary Alcohols

Normal and γ -Branched.—Thirteen normal and γ -branched primary alcohols were investigated. In the spectra of alcohols above C_3 , one of the highest mass peaks is attributable to loss of water. This peak is always appreciable. As one proceeds to lower masses the second important peak corresponds to the loss of mass 33, either water and a methyl group or $-\text{CH}_2\text{OH}$ plus two hydrogens. The third important peak represents loss of mass 46, which may signify a split between the β - and γ -carbon atoms plus transfer of one hydrogen, or a split between the α - and β -carbon atoms plus loss of a methyl group. For the C_2 to C_8 alcohols in this group, the parent molecule minus mass 46 produces an olefin-type peak that is either the base peak or at least 40 percent of the base. When it is not the base peak, the 41 peak is the base. The base peak for all but one of the primary alcohols above 1-butanol is an olefin-type peak (41, 42, 56). 3,4-Dimethyl-1-pentanol has its base peak at 43, presumably because of splitting between the third and fourth carbon atoms. Normal alcohols below 1-pentanol all have the base peak at mass 31. The parent peaks in all cases, except 1-propanol and below, are small.

The mass spectra of primary alcohols may be considered to consist of fragment ions from two different molecular species arising from the molecule-ion. One species arises from primary dissociation of the alcohol molecule-ion to produce a set of alcohol-type (31, 45, 59, etc.) and a set of alkane-type (29, 43, 57, etc.) fragments. The other species derived from the molecule-ion may be considered an olefinic ion, fragmentation of which produces olefin-type (41, 42, 55, 56, etc.) and alkane-type peaks. Rate of effusion measurements (24, 31) and appearance potentials show that an olefin does not actually form in the ionization region before

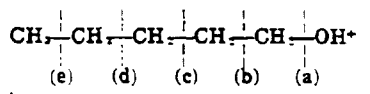
ionization occurs. However, many of the major peaks in the alcohol spectrum have intensities similar to the peaks at the same masses in the spectrum of the corresponding olefin. This similarity is shown for 1-pentanol and 1-pentene in table 1.

TABLE 1.—Comparison of spectrum of primary, straight-chain alcohol with corresponding olefin

m/e	Olefin-type peaks, relative abundance	
	1-Pentanol	1-Pentene
70.....	45.0	31.7
69.....	5.3	1.7
56.....	15.4	2.6
55.....	64.1	57.9
42.....	100	100
41.....	67.4	45.0
39.....	27.3	34.6
28.....	20.9	4.9
27.....	53.2	32.3
Base peak intensity, divisions per μ mole.....	156	179

The relative abundance figures for pairs of fragments in diagram A indicate the relative probabilities for charge distribution between the fragments; however, the actual ionization and dissociation processes are not implied in the fragmentation presented. The numbers in parentheses indicate relative abundance of ions; arrows indicate increasing abundances.

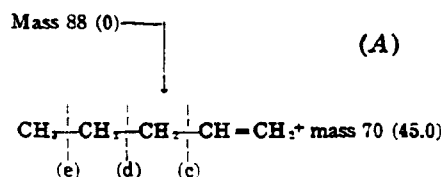
The probability that the alkane-type fragment carries the positive charge increases with decreasing mass; the same occurs for the alcohol-type fragments. The average percentage of total ionization observed as mass peaks of types such as olefinic, paraffinic, and alcoholic is given for each class of alcohols in table 2. The spectra of secondary and tertiary alcohols are not comparable with the corresponding olefins.



β -Branched.—The six β -branched primary alcohols exhibit patterns similar to those of the other primary alcohols. The first major peak in the high mass region of the spectrum is represented by the parent molecule minus mass 18, except for 2,2-dimethyl-1-propanol, which has no hydrogens on the β -carbon atom. In contrast to the normal primary alcohols, fragmentation in the β -branched compounds is prominent between the α - and β -carbons, the latter being a tertiary carbon. In the three alcohols of lower molecular weight, this fragmentation produces a base peak of the alkane type resulting from loss of mass 31. In the three alcohols of higher molecular weight, the base peak may be represented by loss of mass 31 plus a number of CH_2 groups. The alkane-type base peaks (29, 43, 57, 71) are more intense than the base peaks of other primary alcohols. Loss of mass 33 produces a peak of moderate intensity in β -branched alcohols. A mass 33 fragment ion in the spectrum of 2-methyl-1-propanol is very intense. The parent-minus-32 peaks are also intense.

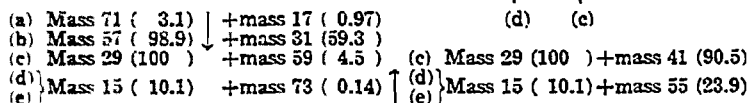
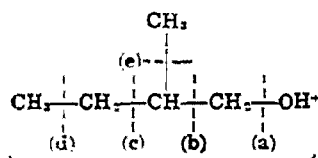
TABLE 2.—Ionization distribution for alcohols among various types of fragmentation peaks

Alcohol group	Fragmentation peaks, percent		
	Olefinic (41, 42, 55, 56...)	Alcoholic (31, 45, 59...)	Paraffinic (29, 43, 57...)
Primary:			
Normal.....	55.9	11.4	20.5
γ -Branched....	50.6	9.8	25.0
β -Branched....	40.3	9.9	35.2
Secondary:			
2-Type.....	28.5	42.6	18.7
3-Type.....	32.9	34.6	18.6
Other.....	42.2	23.7	20.6
Tertiary:			
Dimethyl-type..	21.3	49.0	17.4
Diethyl-type...	24.1	44.1	21.3
Other.....	25.2	43.3	20.0



- | | | |
|--------------------|-----------------|------------------------------------|
| (a) Mass 71 (3.2) | +mass 17 (6.94) | |
| (b) Mass 57 (23.9) | +mass 31 (77.6) | |
| (c) Mass 43 (29.9) | +mass 45 (6.3) | (c) Mass 43 (29.9) +mass 27 (53.2) |
| (d) Mass 29 (72.0) | +mass 59 (0.93) | (d) Mass 29 (72.0) +mass 41 (67.4) |
| (e) Mass 15 (9.4) | +mass 73 (0.08) | (e) Mass 15 (9.4) +mass 55 (64.1) |

The fragmentation of a β -branched primary alcohol, 2-methyl-1-butanol, is given in diagram B, and its spectrum is compared in table 3 with that of the corresponding olefin, 2-methyl-1-butene. The presented fragmentation is not, however, representative of the actual ionization and dissociation processes. The numbers in parentheses indicate relative abundance of ions; arrows indicate increasing abundances. Paraffinic-type peaks from 2-methyl-1-butanol are quite intense, so that the alcohol is not as closely related to the olefin as 1-pentanol is to 1-pentene.



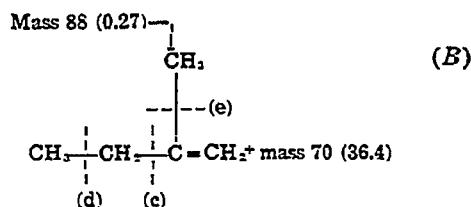
Secondary Alcohols

The secondary alcohols were subclassified on the basis of location of the hydroxyl group on the 2-, 3-, 4-, etc., carbon atom. In contrast to the data obtained from primary alcohols, fragmentation patterns indicate that the first and second intense peaks below the parent peak result, respectively, from the loss of a hydrocarbon group and from the loss of water plus the hydrocarbon group. Base peaks for 2- and 3-type secondary alcohols are alcohol-type peaks and can be attributed to the loss of the larger alkyl group from the parent mass. For the 2-type alcohols investigated, the base is mass 45 ($\text{CH}_3\text{CHOH}-$) and for 3-type, mass 59 ($\text{CH}_3\text{CH}_2\text{CHOH}-$). The 4- and 5-types investigated show olefin-type base peaks, masses 55 and 69. The intensity of parent peaks for all secondary alcohols is less than 2 percent of the base peak intensity.

Mass spectra of four naphthenic alcohols were also studied. Loss of mass 18 and of mass 33 produces large peaks, but loss of mass 31 is insignificant. The base peak may be represented by loss of 29 plus a number of CH_2 groups. In this respect, these alcohols behave like secondary alcohols, as expected.

TABLE 3.—Comparison of spectrum of primary, β -branched alcohol with corresponding olefin

m/e	Olefin-type peaks, relative abundance	
	2-Methyl-1-butanol	2-Methyl-1-butene
70.....	36.4	31.0
69.....	1.3	2.9
56.....	85.5	4.4
55.....	23.9	100
42.....	16.1	32.6
41.....	90.5	27.4
39.....	29.2	33.9
28.....	12.7	4.7
Base peak sensitivity, divisions per μ mole....	185	149



Molecular ion intensities are greater than those found in any other group of alcohols.

Tertiary Alcohols

The tertiary alcohols investigated included the partly symmetrical types (dimethyl alkyl, diethyl alkyl, etc.—for example, dimethyl propyl carbinol) and the completely unsymmetrical types (methyl ethyl alkyl, methyl propyl alkyl, etc.—for example, methyl ethyl butyl carbinol). Base peaks are of the alcohol type. For the dimethyl type and for the completely unsymmetrical types the base peak results from the loss of the largest of the three alkyl groups. For the dialkyl-type tertiary alcohols above the dimethyls, the base peak results from loss of one of the two identical alkyl groups—for example, a diethyl type loses an ethyl group. Dimethyl tertiary alcohols give the most intense base peaks of all of the types studied. Tertiary alcohols, other than the dimethyl type, have a base peak and also one or more other alcohol-type peaks of about the same intensity. Parent peaks are all insignificant. Fragmentation of tertiary alcohols does not produce intense olefin-type peaks (table 2).

Total Ionization

Total ionization, expressed as divisions per micromole (table 4), was calculated by

TABLE 4.—Total ionization of aliphatic alcohols, in divisions per micromole

(Variation with carbon number shows stepwise character)

	Number of isomers	Average total ionization above mass 17
C ₁	1	280
CC ₂	1	525
CCC ₃	2	603±27
CCCC ₄	4	843±70
CCCCC ₅	7	1,006±35
CCCCCC ₆	11	1,264±59
CCCCC ₇	11	1,300±76
CCCCCC ₈	16	1,475±106
C ₉	6	1,533±171

addition of all sensitivity coefficients above mass 17. Total ionization increases continuously from C₁ through C₉, then it appears to start leveling off. These data agree with the findings of Mohler, Williamson, and Dean for hydrocarbons, total ionization of which increased up to C₁₀ and then remained constant (65). Because the total ion current should increase with increasing molecular weight, the constancy observed above C₁₀ can be the result of several factors, including poor vaporization or changes in ion-collection efficiency with mass distribution. Observed total ion currents of alcohol versus molecular weight exhibits discontinuities between the following pairs of carbon numbers: C₂ and C₃, C₄ and C₅, C₆ and C₇, and C₈ and C₉. Mohler's data showed a break only between C₂ and C₃ for naphthenes, olefins, and paraffins.

Identification of Alcohols

Correlations lead to the following information, which is helpful for identification of an unknown alcohol.

Primary Alcohols**General characteristics:**

1. At least 6 percent of the total ion current is observed at masses corresponding to alcohol-type peaks (mostly mass 31).
2. Base-peak intensity is only slightly greater than intensities of other strong peaks.

Specific characteristics:

1. Straight-chain and γ -branched. Base peak for C₄ and below is mass 31; base peak for C₅ and above is generally an olefin-type peak.

2. β -branched. Base peaks are alkane-type peaks.

Secondary Alcohols**General characteristics:**

1. At least 15 percent of the total ion current is observed at masses corresponding to alcohol-type peaks.
2. Base peak is usually alcohol-type.
3. Parent-peak intensity is less than 2 percent of the base peak intensity.

Specific characteristics:

1. Symmetrical $\left(\begin{array}{c} R_1 - CH - R_1 \\ | \\ OH \end{array} \right)$. One

intense alcohol-type peak; mass of R is identified by subtracting 30 (CHOH) from the mass of this peak.

2. Unsymmetrical $\left(\begin{array}{c} R_1 - CH - R_2 \\ | \\ OH \end{array} \right)$.

Two intense alcohol-type peaks; mass of R₂ is identified by subtracting 30 (CHOH) from highest mass alcohol-type peak.

Mass of R₁ is identified by subtracting 30 (CHOH) from next highest mass alcohol-type peak.

- (a) 2-type $\left(\begin{array}{c} CH_2 - CH - R_2 \\ | \\ OH \end{array} \right)$. Base peak is at mass 45; base-peak intensity is at least four times that of any other peak; mass

45 and 19 peaks are more intense than for other alcohols; mass 31 peak is less intense than for other types of secondary alcohols.

- (b) 3-type $\left(\begin{array}{c} CH_2CH_2 - CH - R_2 \\ | \\ OH \end{array} \right)$. Base peak is at mass 59; base-peak intensity is at least 1.5 times that of any

other peak; mass 31 is 30 percent or more of the base peak.

- (c) 4- and 5-type. Base peak is olefin-type peak (mass 55 or 69, for example); base-peak intensity is at least three times that of any other peak; mass 31 is 30 percent more of the base peak.

Tertiary Alcohols**General characteristics:**

1. Base peak is of the alcohol type.
2. At least 30 percent of the total ion current is found at alcohol-type peaks.

Specific characteristics:

1. Partially symmetrical: $\begin{array}{c} R_3 \\ | \\ R_1 - C - R_2 \\ | \\ OH \end{array}$

(a) Dimethyl (R₁ = R₂ = methyl group). Base peak is at least twice as intense as any other peak; base peak results from loss of larger alkyl group (R₃).

(b) Diethyl (R₁ = R₂ = ethyl group). Base peak results from loss of ethyl group (R₃); there are two or more intense alcohol-type peaks.

(c) Dipropyl (R₁ = R₂ = propyl group). Base peak results from loss of propyl group (R₃); there are two or more intense alcohol-type peaks.

2. Completely unsymmetrical (methyl ethyl and methyl propyl types): $R_1 \neq R_2 \neq R_3$. Base peak results from loss of largest alkyl group (R_1); there are three or more intense alcohol-type peaks.

Table 5 is a summary of groups identifiable in an unknown alcohol by mass spectra. These findings may be compared with results obtained for alcohols by infrared spectrometry. In infrared analysis all primary alco-

TABLE 5.—Groups identifiable in unknown alcohol by mass spectra

Alcohol group	Structure
Primary:	
Normal	—CCCC—OH
β -branched	—CCC—OH C
Secondary:	
2-type	—CCCC OH
3-type	—CCCC OH
4-type	—CCCC OH
Tertiary	—CCC C OH

¹ Masses of both groups on carbinol are identifiable.

hols show a band near 9.5 microns, secondary alcohols near 9.0, and tertiary alcohols near 8.5 microns. But infrared assignments are not mutually exclusive; thus, a primary alcohol also may have a band at 9.0, a secondary alcohol a band at 9.5, etc. Infrared analysis can be used more easily than mass spectrometry to identify a substance as an alcohol. However, infrared usually cannot identify alkyl substituents on the carbinol group; these substituents can be identified in the

mass spectrum. Hence, the combination of both methods is much more powerful than the application of either method independently.

Quantitative Analysis of Alcohols

Pressure Measurement Errors.—Sensitivity values based on micromanometer pressure (instead of unit volume introductions) were not reliable for all alcohols; difficulties were encountered with hexanols and higher alcohols. Determinations of 1-octanol in synthetic blends were about 30 to 35 percent low when based on pressure sensitivities. Micromanometer measurements of known microvolumes of liquid indicated that calculated molecular weights of 1-octanol were high by about 30 to 35 percent. In contrast, sensitivities based on liquid volume produced accurate determinations of 1-octanol in blends (table 6). These mass spectral (MS) analyses were made with the micromanometer in the system; therefore, the volume measurements were not adversely affected by any sorption which may occur in the micromanometer. Micromanometer measurements on alcohols up to the hexanols were quite reliable, and operation at elevated temperatures should raise this limit.

Type-Analyses.—The two types of primary alcohols and secondary plus tertiary alcohols can be determined (in mixtures containing only these alcohols) by a type-analysis method (12, 19). Table 2 gives data on total ionization for various groups of mass peaks in the various types of alcohols. Appropriate groups of peaks for type-analyses were selected on the basis of these data, and results of a type-analysis are given in table 7. The matrix given in table 8 includes all alcohols above C_1 . Furthermore, the 2-type secondary alcohols can be analyzed by means of mass peaks 45 and 19.

A simple means has been found for estimating C_6 to C_8 primary alcohols in products from synthetic fuel processes. The 31 and 27 mass peaks of these compounds are of nearly

TABLE 6.—Mass spectral analyses of alcohol synthetic blends

	Alcohol, volume-percent				
	1-Butanol	1-Pentanol	1-Hexanol	1-Heptanol	1-Octanol
Synthetic blend A.....	31.3				68.7
MS analysis 1	30.4				69.6
MS analysis 2	31.8				68.2
Synthetic blend B.....	71.7				28.3
MS analysis 1	71.7				28.3
MS analysis 2	71.0				29.0
Synthetic blend C.....	85.0				12.0
MS analysis 1	89.7				10.3
MS analysis 2	87.9				12.1
Synthetic blend D.....		40.6	30.0	19.7	9.7
MS analysis		39.2	30.3	19.6	10.9

equal intensity; also the 27 peaks of paraffins and olefins in the same fractions are approximately the same as the 27 peaks of these three alcohols. Therefore, the alcohol content can be estimated from the ratio of the 31 peak to the 27 peak. This determination checks the infrared type-analysis for total alcohols.

Component Analyses.—Table 6 illustrates the analyses of three different blends of 1-butanol and 1-octanol, and the analysis of a four-component C_3 to C_8 alcohol blend. Such analyses are straightforward when no unknown interfering compounds are present.

TABLE 7.—Mass spectral type-analyses of C_3 to C_8 alcohols

Alcohol group	Blend 1			Blend 2		
	No. of alcohols in blend	Synthetic, volume-percent	MS analysis, volume-percent	No. of alcohols in blend	Synthetic, volume-percent	MS analysis, volume-percent
Primary (normal and γ -branched)	5	64.2	65.0	5	72.4	75.4
Primary (β -branched)	1	21.7	18.6	2	27.6	22.4
Secondary	1	14.1	16.4	0	0	2.2
Tertiary	3			0		

TABLE 8.—Matrix for type-analysis of C_3 to C_8 alcohol fractions

Mass peaks ¹	Primary alcohols		Secondary and tertiary alcohols
	Normal and γ -branched	β -branched	
$\Sigma 42 + 56 + 70 +$	1,379	897	218
$\Sigma 43 + 57 + 71 +$	918	1,848	856
$\Sigma 45 + 59 + 75 +$	102	173	2,270

¹ Data include all alcohols above C_8 .

Mass Spectra of Trimethylsilyl Derivatives

Although mass spectrometric methods have been used to analyze mixtures of alcohols as previously described (14, 34), determination of individual C_3 to C_{10} primary alcohols in the presence of hydrocarbons requires preliminary separation before chemical or spectroscopic methods can be applied. A method, utilizing the trimethylsilyl ether derivatives of alcohols, has been developed for rapid, direct analysis of individual alcohols in hydrocarbon solutions (54–55, 77). The trimethylsilyl ether derivatives of alcohols, $(CH_3)_3SiOR$, are readily prepared (53) and produce distinct mass spectra free of interference by hydrocarbons.

The mass spectra of 26 aliphatic trimethylsilyl ethers and 8 related silicon compounds were obtained. Trimethylsilyl ethers have higher volatility than hydrocarbons and oxygenated compounds containing fewer carbon atoms. For example, the mass spectrum of a C_{10} alcohol from a conventional room-temperature mass spectrometer is not usable, but the spectrum of a trimethylsilyl ether prepared from a C_{10} alcohol can be obtained without difficulty.

Trimethylsilyl ethers show several intense rearrangement peaks in addition to the expected fragmentation peaks. Numerous other

instances of intense rearrangement peaks in mass spectra, mainly of oxygen-containing compounds, have been reported (43, 52, 81, 87). Earlier work by Dibeler on a similar silicon compound, hexamethyldisiloxane, $(CH_3)_6Si_2O$, also showed many rearrangement peaks (22). The complete mass spectra of the 26 trimethylsilyl ethers have been published (76).

Fragment Ions

Primary Straight-Chain Trimethylsilyl Ethers.—A characteristic mode of fragmentation was found for all the normal (C_3 to C_{10}) aliphatic trimethylsilyl ethers: Parent mass peaks are weak, but a very intense peak resulting from the loss of one of the four methyl groups appears 15 mass units below the parent mass. Peaks at masses 73, 89, and 103 also are characteristic of this series, and these peaks have been correlated with the trimethylsilyl ether structure. The spectrum of the 1-hexyl ether is given as an example in table 9. Mass 43, which is an important peak in the mass spectra of many compounds, is a major peak for the trimethylsilyl ethers.

Patterns of the C_3 to C_{10} normal aliphatic trimethylsilyl ethers are similar for normal fragmentation masses 103, 89, 73, 43, and 29, and for rearrangement masses 75, 61, and 45. The methyl, ethyl, branched, and secondary

trimethylsilyl ethers do not show this pattern similarity. The intensity of mass 89, $(\text{CH}_3)_3\text{SiO}^+$, is different for the C_1 , C_2 , and C_3 normal aliphatic compounds. For the methyl derivative, mass 89 is the parent-minus-15 ion and is therefore very strong; for the ethyl and propyl trimethylsilyl ethers, mass 89 is much less intense than for any of the C_4 to C_{10} normal alcohol derivatives. Thus, the ion $(\text{CH}_3)_3\text{SiO}^+$ is unimportant unless the hydrocarbon chain consists of four or more carbon atoms.

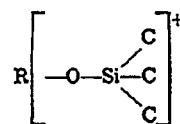
TABLE 9.—Fragmentation peaks in mass spectra of normal aliphatic trimethylsilyl ethers
Example: 1-hexyl derivative

<i>m/e</i>	Structure	Relative intensity
43	$\begin{array}{c} \text{CH}_3 \\ \\ \text{—Si—(or—C}_5\text{H}_{11}) \\ \end{array}$	17
73	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—Si—} \\ \\ \text{CH}_3 \end{array}$	45
89	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—Si—O—} \\ \\ \text{CH}_3 \end{array}$	16
103	$\begin{array}{c} \text{CH}_3 \qquad \text{H} \\ \qquad \quad \\ \text{CH}_3\text{—Si—O—C—} \\ \qquad \quad \\ \text{CH}_3 \qquad \quad \text{H} \end{array}$	25
Parent minus 15	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—Si—O—CH}_2\text{—CH}_2 \\ \qquad \quad \qquad \quad \\ \text{CH}_3 \qquad \quad \text{or} \qquad \quad \uparrow \end{array}$	100
Parent	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—Si—O—CH}_2\text{—CH}_2 \\ \\ \text{CH}_3 \end{array}$.9

The most intense (base) peak is the parent-minus-15 ion for the derivatives of the normal alcohols C_1 , C_2 , and C_3 to C_{10} . Mass 75, a rearrangement ion, is the base peak for the C_3 , C_4 , and C_5 normal alcohol derivatives, although the parent-minus-15 peaks are almost equally intense.

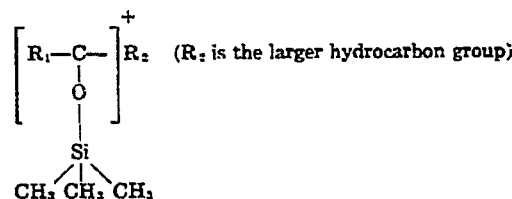
Primary Branched Trimethylsilyl Ethers.—Below mass 103 the same major peaks appear in the spectra of the primary branched- and straight-chain alcohol derivatives.

However, the pattern variation is larger for the branched than for the normal derivatives. Derivatives for two γ -branched alcohols, 3-methyl-1-butanol and 3-methyl-1-pentanol, produce more mass 89 positive ions than other branched- or straight-chain derivatives.



A strong peak, corresponding in mass to the alkyl radical minus two hydrogen atoms, is also in the spectra of the γ -branched derivatives.

Secondary Trimethylsilyl Ethers.—The five ethers derived from straight-chain secondary alcohols show intense peaks resulting from a break at the functional carbon.



This fragmentation produces the base peak at mass 117 for 2-pentyl and 2-hexyl trimethylsilyl ethers and a strong peak at mass 131 for 3-type trimethylsilyl ethers. The branched-chain secondary alcohol derivative (3-methyl-2-butanol) behaves similarly by losing the larger alkyl group and producing the second most intense peak in the spectrum at mass 117. Mass 73 is more intense for the straight-chain secondary than for the corresponding primary alcohol derivative and is the base peak for 2-butyl and 3-heptyl trimethylsilyl ethers. Parent-minus-15 mass peaks are less intense for the derivatives of the secondary alcohols.

Tertiary Trimethylsilyl Ethers.—The mass spectra of the two tertiary alcohol trimethylsilyl ethers are similar. The parent-minus-15 ion for the tertiary butyl and parent-minus-29 ion for the tertiary amyl produce intense peaks at mass 131 in both spectra. All other peaks down to mass 75 are weak.

Rearrangement Ions

Several intense rearrangement peaks appear in the mass spectra of all the normal alcohol derivatives with the exception of methyl. Mass 75 is the most prominent rearrangement peak and always one of the three largest peaks in the spectrum. Rate of effusion determinations (24, 31) made on

mass 75 rule out the possibility of an impurity. With *n*-butyl trimethylsilyl ether, identical effusion rates were obtained for masses 131, 75, and 73, indicating that the mass 75 fragment is derived from the parent mass 146.

Two series of rearrangement peaks were found in the mass spectra of derivatives of normal aliphatic alcohols (table 10). The first series is that found by Dibeler in hexamethyldisiloxane, $(\text{CH}_3)_6\text{Si}_2\text{O}$, and includes masses 59, 45, and 31 (22). These same mass ions were also found by Zemany and Price in the mass spectrum of tetramethylsilane, $(\text{CH}_3)_4\text{Si}$ (101). These authors concluded that the rearrangement fragments contain Si—H bonds. The second series also has peaks differing by 14 mass units and includes masses 75, 61, and 47. This series is also explained by rearrangement structures similar to those proposed by Dibeler, with the addition of an oxygen atom (22).

Derivatives of the branched primary, secondary, and tertiary alcohols investigated show the same two series of rearrangement peaks as the normal compounds. Mass 75 is the base peak in the spectra of all the derivatives of β -branched primary alcohols investigated.

Isotope determinations indicate that this is the correct assignment. Rearrangement peaks in the mass spectrum of hexamethyldisilazane, $(\text{CH}_3)_6\text{Si}_2\text{NH}$, parallel those in the spectrum of hexamethyldisiloxane.

Analyses of Alcohol by Trimethylsilyl Ethers

Because of their high volatility, normal aliphatic trimethylsilyl ether derivatives of C_6 to C_{10} alcohols can be analyzed by the mass spectrometer without difficulty. Relative intensities of the parent-minus-15 peak, useful in such analyses, are given in figure 1. These peaks are not fragmentation peaks in the spectra of hydrocarbons and oxygenated compounds normally analyzed by the mass spectrometer. With derivatives of normal C_6 to C_{10} alcohols, the total contribution of the characteristic parent-minus-15 peak of a compound by its homologs is less than 5 percent of the peak intensity. This slight interference can be corrected on the basis of the

spectra of the pure compounds. Considerably less than 1 percent of any of the normal aliphatic trimethylsilyl ethers should be detectable in the presence of hydrocarbons. Mass 75 is of uniform intensity for the C_6 to C_{10} normal alcohol derivatives and therefore serves as a convenient check on the total alcohol content.

TABLE 10.—Rearrangement structures in trimethylsilyl ethers

Rearrangement series		Apparent structure
r_1	r_2 ¹	
<i>m/e</i> 59	<i>m/e</i> 75	$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{Si}-\text{CH}_3 \\ \\ \text{H} \end{array} \right]^+$
<i>m/e</i> 45	<i>m/e</i> 61	$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{Si}-\text{H} \\ \\ \text{H} \end{array} \right]^+$
<i>m/e</i> 31	<i>m/e</i> 47	$\left[\begin{array}{c} \text{H} \\ \\ -\text{O}-\text{Si}-\text{H} \\ \\ \text{H} \end{array} \right]^+$

¹ $r_1 + \text{oxygen} = r_2$.

Individual alcohol derivatives can be identified as to type by means of the mass spectral correlations described previously. These can be summarized as follows.

Only secondary and tertiary alcohol derivatives have strong peaks (other than the usual parent-minus-15 peak) above mass 103.

The intensity ratio of mass 75 to 73 is different for primary, primary-branched, and secondary alcohol derivatives according to class. The ratios are given in table 11.

Mass 89 is useful in determining the position of branching. Of the primary alcohols, only those having γ -branching show intense peaks at mass 89.

Secondary and tertiary alcohols can be identified as to type from the original alcohol spectrum (34).

The trimethylsilyl derivative of propylene

TABLE 11.—Type identification of alcohols by trimethylsilyl ether derivatives, chart divisions

Alcohol type (trimethylsilyl derivatives)	Ratio, $\frac{\text{mass } 75}{\text{mass } 73}$		Mass 73 ¹	
	Average	Spread	Average	Spread
Primary, straight-chain 1-butyl to 1-decyl	2.0	0.1	513	38
Primary, single-branched butyl to octyl, including methyl and ethyl branching	1.3	.2	665	210
Secondary (2-type only), 2-butyl to 2-hexyl	1.3	.04	1,013	40

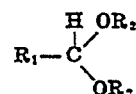
¹ *n*-Heptane mass 27 = 692 divisions per unit liquid volume.

glycol has the expected very weak parent peak and an intense parent-minus-15 peak. In contrast, both the parent and parent-minus-15 peaks are intense for the trimethylsilyl derivatives of phenol, butyl mercaptan, and the cresols. Both *m*- and *p*-cresol show similar fragmentation patterns, while *o*-cresol has a much less intense parent-minus-15 peak and a more intense mass 91 than *m*- or *p*-cresol. Trimethylsilyl derivatives should aid in the analyses of mixtures containing these classes of compounds as well as in the analysis of alcohols.

Mass Spectra of Acetal-Type Compounds

Mass spectra of mixtures of oxygenated compounds frequently produce mass peaks that are not attributable to alcohols, acids, aldehydes, or other similar structural types. Some of these peaks are at odd masses and are, therefore, fragmentation peaks. They are consistently two mass units higher than fragmentation peaks from other oxygenated compounds. To produce such peaks, the oxygenated hydrocarbons must contain two oxygen atoms and no unsaturated bonds. Acetals and hemiacetals are logical possibilities. Mixtures of aldehydes and alcohols produce hemiacetals, most of which are rather unstable at room temperature (6, 60).

The general formula of the acetals is



where R_1 is hydrogen for dioxymethanes (formals) from the reaction of formaldehyde with alcohols, or CH_2 for dioxyethanes (acetals) from the reaction of acetaldehyde with alcohols, or C_2H_5 for dioxypropanes (propionals) from the reaction of propionaldehyde with alcohols.

Effusion rate measurements were made with the valve open to the mass spectrometer leak. The effusion rate with *n*-butane was the reference for calculation of apparent molecular weights. For the calculation of specific reaction rate constants, the curves obtained for mass spectral peak heights decreasing with time were corrected for normal decay of peak heights.

The complete mass spectra of the acetal-type compounds investigated have been published (50).

A series of acetals of formaldehyde, acetaldehyde, and propionaldehyde were investigated to correlate mass spectral data for analyzing mixtures of oxygenated compounds. The compounds and their sources are as follows.

Compound	Source
Dimethoxymethane (dimethylformal)	Celanese Corp.
Diethoxymethane (diethylformal)	Eastman Kodak Co.
Di- <i>n</i> -propoxymethane (di- <i>n</i> -propylformal), fractionated.....	Celanese Corp.
1,1-Dimethoxyethane (dimethylacetal)	Do.
1,1-Diethoxyethane (diethylacetal or acetal)	Eastman Kodak Co.
1,1-Di- <i>n</i> -propoxyethane (di- <i>n</i> -propylacetal), synthesized.....	Bureau of Mines.
1,1-Di- <i>n</i> -butoxyethane (di- <i>n</i> -butylacetal)	Celanese Corp.
1,1-Di- <i>n</i> -hexoxyethane (di- <i>n</i> -hexylacetal), fractionated	Carbide and Carbon Corp.
1,1-Dimethoxypropane (dimethylpropional), fractionated	Celanese Corp.
1,1-Diethoxypropane (diethylpropional), synthesized	Bureau of Mines.
1,3,5-Trioxane, sublimed	Eastman Kodak Co.
2,4,6-Trimethyl-1,3,5-trioxane (paraldehyde)	Do.
2-Methyl-1,3-dioxolane	Carbide and Carbon Corp.
Formaldehyde solution, 37 percent	Fisher Scientific Co.

Acetals

Mass Spectra.—The preferred fragmentations involve rupture of (1) a C—O bond with loss of $-\text{OR}_2$ and (2) the C— R_1 bond with loss of R_1 ; the residual mass fragments are easy to identify because of the mass difference between carbon and oxygen. Loss of $-\text{OR}_2$ produces peaks at masses 101, 87, 73, etc., whereas loss of R_1 produces peaks at 103, 89, 75, etc. These are the two strongest mass peaks in the higher molecular weight portion of each spectrum. A single acetal can be identified by application of a simple equation involving the mass fragments from loss of $-\text{R}_1$ or $-\text{OR}_2$:

$$2 \text{ times (mass of fragment from loss of } -\text{OR}_2) \text{ minus (mass of fragment from loss of } -\text{R}_1) = \text{constant.}$$

The numerical value of the constant depends on the aldehyde from which the compound is derived: 15, 43, 71, etc., respectively, for formaldehyde, acetaldehyde, propionaldehyde, etc. After the aldehyde is determined, the alcohol portion of the molecule can be identified.

The mass spectra of two dioxolanes, cyclic acetals derived from ethylene glycol, were also studied. In the spectrum of 1,3-dioxolane, the fragmentation may be considered as occurring at two bonds simultaneously to

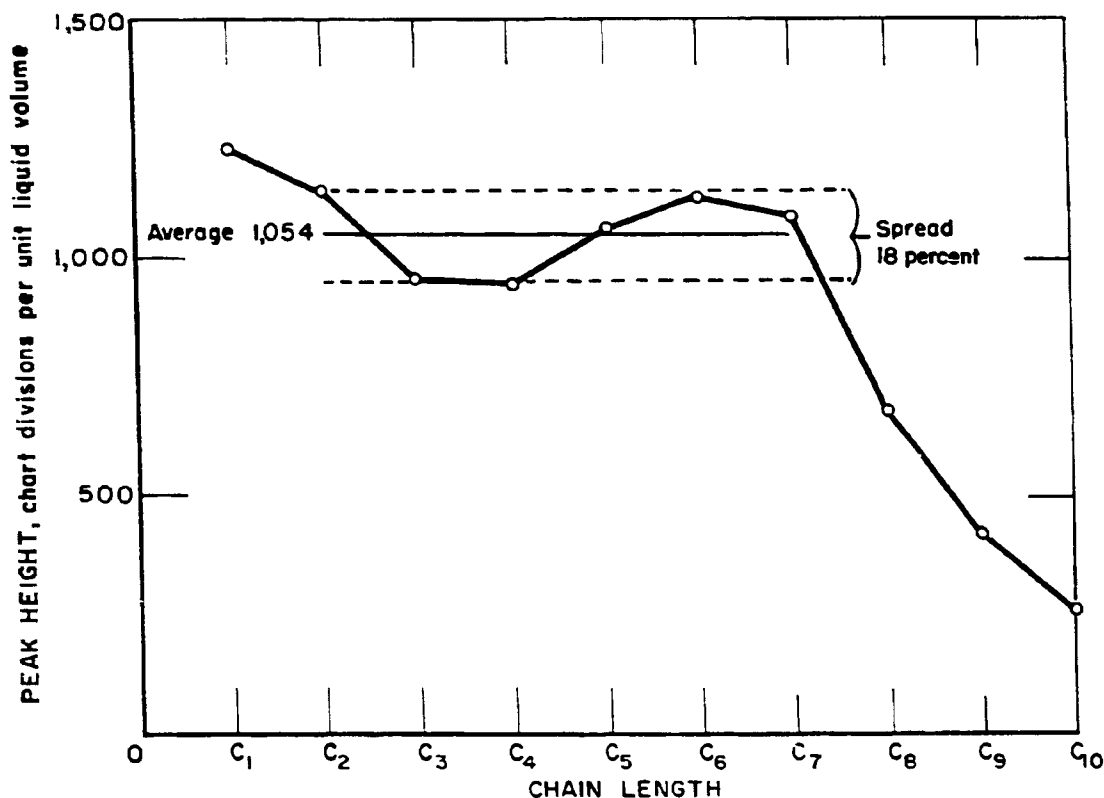
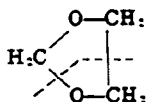


FIGURE 1.—Parent-Minus-15 Peak Intensities of Trimethylsilyl Ether Derivatives of Normal Alcohols.

produce a fairly intense peak at an even mass, 44.



In 2-methyl-1,3-dioxolane, the same type of fragmentation produces the even-numbered mass 58. Trioxane, the trimer of formaldehyde, and paraldehyde, the trimer of acetaldehyde, may also be considered cyclic acetals.

Mixtures Containing Acetals.—An acetal is easily detected in the presence of alcohol and aldehyde. Mass peaks at 75, 89, and 103, frequently found in mixtures of aldehydes and alcohols, are usually attributable to acetals. But mass 61, common in spectra of such mixtures, cannot logically occur in spectra of acetals. A fragment of mass 61 must contain two oxygens, but the smallest such fragment from acetals, $-\text{CH}(\text{OCH}_2)_2$, from dimethoxymethane (dimethyl formal), has a mass of 75. A possible explanation for the presence of unaccountable mass 61 peaks is the fragmentation of hemiacetals.

Hemiacetals

From Formaldehyde and Alcohols (Hemiformals) in the Vapor Phase.—Decomposition rate constant. The spectrum obtained from a commercial formaldehyde solution indicated the possible presence of a hemiformal. The spectrum of formaldehyde should not have mass peaks above its molecular weight, mass 30, but a commercial grade of formaldehyde vaporized into the mass spectrometer showed peaks at masses 31, 32, 33, 45, 61, and 75. Normally, methanol is added to formaldehyde solutions as an inhibitor, and is responsible for at least some of the 31, 32, and 33 peaks. The 75 peak may be explained by the formation of dimethoxymethane (dimethyl formal). But the 61 peaks and parts of the 45 and 33 peaks could not be assigned to either the formaldehyde or methanol. The only apparent explanation for the 61 peak is loss of a hydrogen atom from the hemiformal of formaldehyde and methanol, $\text{H}_2\text{C}(\text{OH})(\text{OCH}_2)$. The 45 peak also is attributed to hemiformal and results from splitting off of a hydroxyl group. Meth-

ylene glycol, $\text{CH}_2(\text{OH})_2$, a known constituent of aqueous formaldehyde solutions (92), is probably too unstable to exist in the vapor phase at a pressure of about 0.1 mm of mercury. Hall and Piret found indications in vapor density studies on alcoholic-formaldehyde solutions that methylene glycol dissociated more completely than hemiformals on vaporization (41).

A formaldehyde-methanol blend was prepared to check the spectrum obtained with commercial formaldehyde solution. The spectral peaks were essentially the same, except that no indication of dimethoxymethane (mass 75) was obtained for the blend. Extensive hemiformal formation is indicated in

TABLE 12.—Evidence of hemiformal in vapor phase of formaldehyde-methanol-water blend

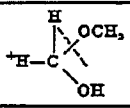
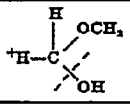
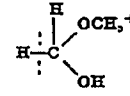
m/e	Peak height, chart divisions				Proposed structure of fragment ion
	Blend	Methanol	Formaldehyde	Residual	
29	2,160	552	1,388	220	
30	1,107	73.3	1,033.7	0	
31	1,179	942	15.2	221.8	
32	626	623.9	2.1	0	
33	75.7	9.9	65.8	
45	77	77	
61	185	185	

table 12 by the residual peaks remaining after subtraction of the spectra of methanol and formaldehyde. These residuals were larger than those from commercial formaldehyde solution, because the synthetic blend contained a much higher concentration of methanol.

To find the origin of the mass peak at 61, determination of the molecular weight of the parent structure was attempted by effusion rate measurements based on Graham's law of diffusion (24, 31). If the parent structure of that fragment were the hemiformal of methanol, $\text{CH}_2(\text{OH})(\text{OCH}_3)$, effusion rate measurements should indicate that the 61 peak is caused by loss of one hydrogen from mass 62. The measurements might have indicated that mass 61 arose from a structure of higher molecular weight, but obviously it

could not have originated from a structure with a mass less than 61. The apparent molecular weight (fig. 2) was 0.64 because of the instability of the structure producing

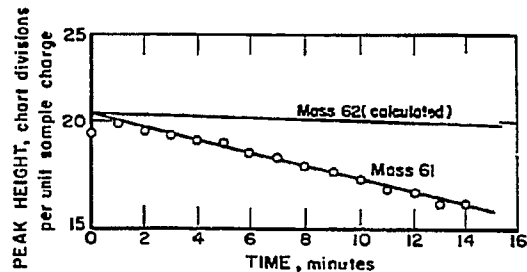


FIGURE 2.—Rate of Decomposition of Mass 61 Fragment From the Hemiformal of Methanol.

the mass 61 peak. The peak decreased rapidly during decomposition of the parent structure, hemiformal, in the vapor phase.

The logarithmic decay of the peak height for mass 61 (fig. 2) illustrates that vapor-phase decomposition of hemiformal is a first-order reaction. The specific reaction rate constant, calculated from the rate of decrease of this peak, was $0.0069 \text{ minute}^{-1}$. This procedure is a simple and accurate method for studying reactions in the vapor phase. Rate data may be obtained for either decreasing or increasing components in a reaction by following changes in peak heights of individual components.

Decomposition of the hemiformal of methanol was further observed by following temporal changes of other spectral peaks of a vaporized sample of aqueous formaldehyde-methanol. Figure 3 shows the erratic behavior of various mass peaks. Curves in figure 3 (left) represent major peaks of the principal components, formaldehyde and methanol; curves in figure 3 (right) represent peaks other than those attributable to the two major components. These latter curves may be explained by decomposition of the unstable hemiformal and the consequent decrease of ions of masses 61, 45, and 33. The structures proposed for some of these mass fragments are given in table 12. The left-hand curves also resulted from decomposition of hemiformal. During the first 30 minutes, the increasing peak heights are explained by decomposition of unstable hemiformals to formaldehyde and methanol. From 30 to 60 minutes, the decreasing peaks indicate that decomposition of hemiformal had been completed and that the normal effusion rate of the mass spectrometer had become dominant.

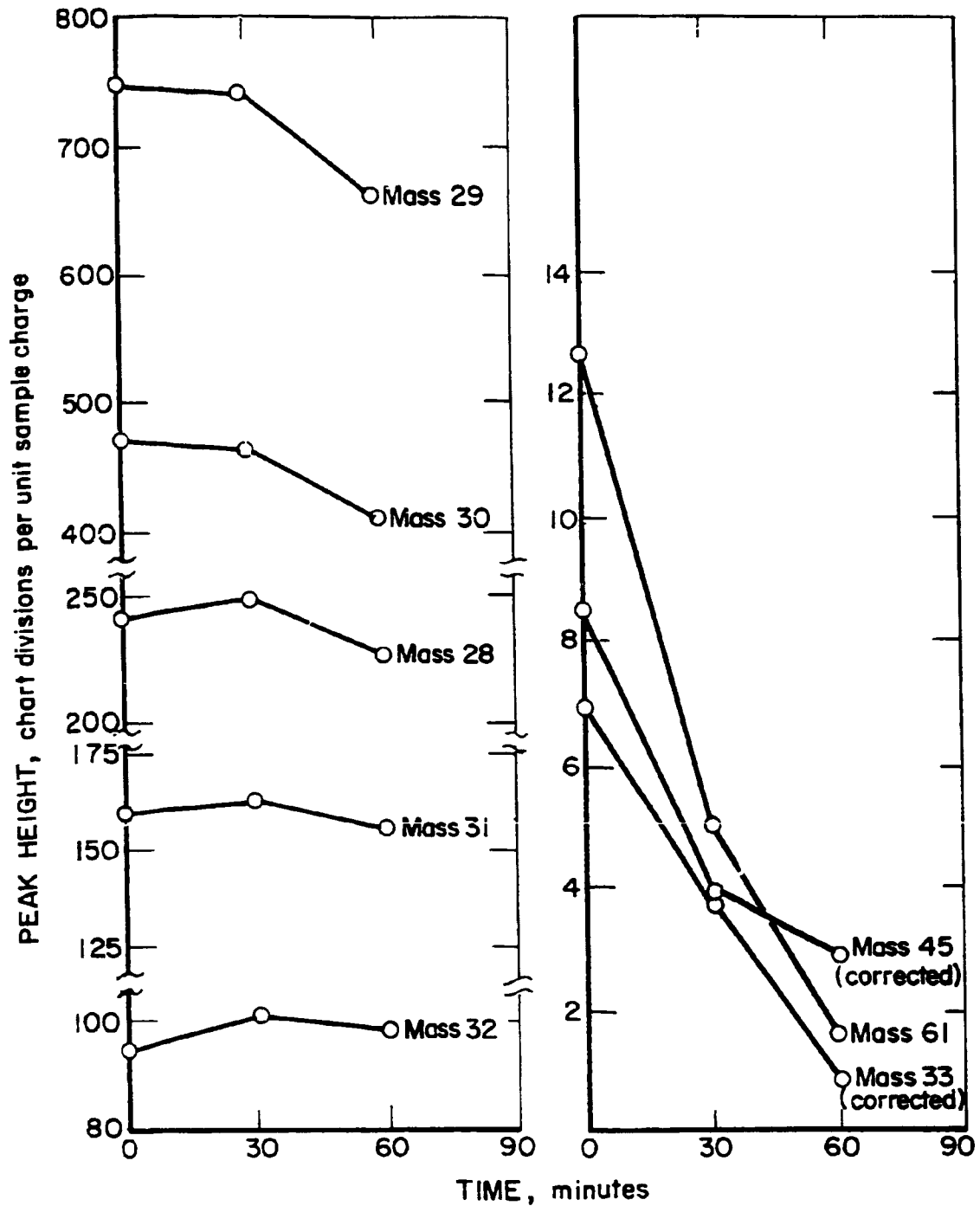


FIGURE 3.—Variation With Time of Several Mass Peaks in a Blend of Formaldehyde-Methanol-Water.

A blend of formaldehyde and ethyl alcohol in water was also investigated briefly. A peak corresponding to the 61 peak from the hemiformal of methanol was found, as expected, at mass 75 for the hemiformal of ethyl alcohol.

From Acetaldehyde and Alcohols in Vapor Phase.—Decomposition rate constant. A blend of acetaldehyde and methanol was investigated for hemiacetal formation. Hemiacetal apparently formed, but only in small concentration in the vapor phase. The spectrum, given in table 13, includes a mass 61 peak.

TABLE 13.—Evidence of hemiacetal in vapor phase of acetaldehyde-methanol blend

m/e	Peak height, chart divisions				Proposed structure of fragment ion
	Synthetic	Methanol	Acetaldehyde	Residual	
28	96.0	55.2	27.7	13.1	
29	1,152.0	492	671	-10.0	
30	67.5	58.4	7.7	1.4	
31	720.0	712	1.9	6.1	
32	470.0	470	0	
33	25.3	7.1	18.2	
43	237.0	180	27.0	
44	312.0	312	0	
45	33.7	9.7	24.0	$\begin{array}{c} \text{OCH}_3 \\ \diagdown \\ \text{CH}_2\text{CH} \\ \diagup \\ \text{OH} \end{array}$
59	5.2	5.2	$\begin{array}{c} \text{OCH}_3 \\ \diagdown \\ \text{CH}_2\text{CH} \\ \diagup \\ \text{OCH}_3 \end{array}$
61	16.6	16.6	$\begin{array}{c} \text{OCH}_3^+ \\ \diagdown \\ \text{CH}_2-\text{CH} \\ \diagup \\ \text{OH} \end{array}$
75	1.9	1.9	$\begin{array}{c} \text{OCH}_3^+ \\ \diagdown \\ \text{CH}_2-\text{CH} \\ \diagup \\ \text{OCH}_3 \end{array}$

An attempt to measure the molecular weight of the parent structure responsible for the mass 61 peak produced an impossible molecular weight of 0.068. This value indicates that the hemiacetal is less stable than the hemiformal. Decomposition of hemiacetal, as determined by decay of the mass 61 peak (fig. 4), was also a first-order reaction. The specific reaction rate constant, $0.052 \text{ minute}^{-1}$, was about 7.5 times that of the hemiformal.

The behavior of other spectral peaks was also observed. As with hemiformal (fig. 3), the peaks attributable to stable structures increased during the first 30 minutes, while the peaks for the unstable structures, masses 61, 45, and 33, decreased rapidly. The uniform rates of decrease of unstable peaks are good evidence that the peaks arose from the same structure. Structures proposed for some of these unstable peaks are given in table 13.

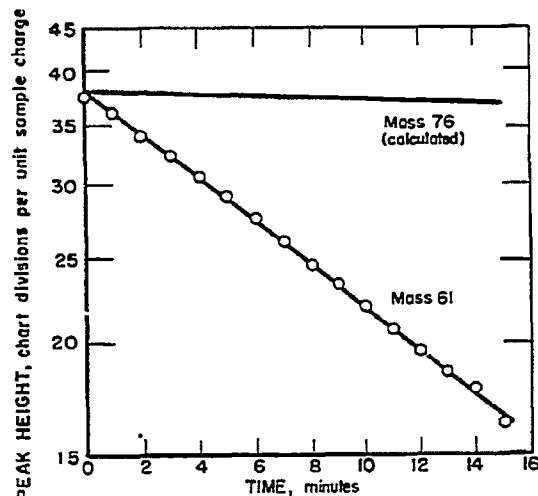


FIGURE 4.—Rate of Decomposition of Mass 61 Fragment From the Hemiacetal of Methanol.

To obtain results comparable with those from formaldehyde-methanol-water, a mixture of acetaldehyde-methanol-water was investigated. Formation of hemiacetal was not as extensive as of hemiformal. The same unstable peaks were found, but the relative intensities of hemiacetal peaks were less in the presence of water.

A mixture of acetaldehyde and ethyl alcohol was investigated. During runs on the same sample, made 30 minutes apart, rapid decay of masses 75, 61, and 47 indicated the presence of the unstable hemiacetal of ethyl alcohol. The 75 peak probably arose from loss of a methyl group.

Mixtures of Alcohol and Aldehyde

Apparent Formation of Acetals.—The mixing at room temperature of an aldehyde and an alcohol was found to produce mass peaks attributable to a trace of acetal. The persistence of these peaks indicated the stability in vapor phase of the parent substance. Table 14 gives several examples of apparent acetal formation. The acetal mass peaks were weak but had the correct relative intensities.

Mixtures of formaldehyde and methanol did not indicate formation of dimethoxymethane. All other blends, including formaldehyde-ethyl alcohol, did indicate formation of the expected acetal. The mass spectrometer is ideally suited for the detection of traces of acetals because they usually have two or more distinctive mass peaks above the mass range of the alcohol and aldehyde.

Evidence of the presence of acetals in alcohol-aldehyde mixtures is significant because

TABLE 14.—Acetals formed in alcohol-aldehyde blends, mole-percent

	Synthetic blend	MS analysis
Blend 1:		
Ethyl alcohol.....	67.6	68.2
Propionaldehyde.....	32.4	31.5
Diethoxypropane.....	0	¹ (.3)
Blend 2:		
1-Propanol.....	64.8	66.4
Acetaldehyde.....	35.2	33.6
Di-n-propoxyethane.....	0	¹ (.3)
Blend 3:		
Acetaldehyde.....	41.7	42.4
Methanol.....	58.3	57.6
Dimethoxyethane.....	0	¹ (.1)
Blend 4:		
Acetaldehyde.....	5.6	5.1
Methanol.....	7.8	7.3
Water.....	86.6	87.6
Dimethoxyethane.....	0	¹ (.03)
Blend 5:		
Ethyl alcohol.....	49.9	52.5
Acetaldehyde.....	50.1	47.5
Diethoxyethane.....	0	¹ (.1)

¹ Apparent concentration.

the formation of acetals in the absence of a dehydrating agent is not expected. However, no attempt was made to isolate the acetals from the alcohol-aldehyde mixtures; therefore, the existence of acetals is not certain.

Formation of Hemiacetals.—Hemiacetals definitely form upon mixing an aldehyde and an alcohol (6, 60). Although they are unstable in the vapor phase, hemiacetals may interfere with analysis of the alcohol and aldehyde. One can check for interference by searching the spectrum for peaks suspected of instability and observing their behavior with time. Slowly rising pressure for several minutes after expansion of the sample also is a good indication of the presence of unstable molecules that are decomposing to give two or more molecules each. Interference can be circumvented by awaiting complete decomposition of the hemicompounds after expansion of the sample into the spectrometer. After a predetermined waiting period, or after there is no further rise in micromanometer pressure, analysis may be carried out.

Mass Spectra of Ketones

Forty-two aliphatic, cyclic, and aromatic ketones ranging from 2-propanone to 7-tridecanone were investigated. The correlation study was based mainly on 35 aliphatic ketones. They are classified as methyl, ethyl, propyl, etc., on the basis of R₁, the smaller alkyl group in R₁-CO-R₂. Compounds were used as obtained, without further purification; infrared and mass spectra showed no

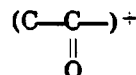
contamination by alcohols, acids, esters, or aldehydes.

Not all major fragmentation peaks result from simple bond rupture. Several rearrangement peaks, resulting from rearrangement of atoms in the molecule ion before and during fragmentation, appeared in the spectra of all the aliphatic ketones investigated. Results of the correlation study were therefore divided into two parts—normal fragmentation and rearrangement peaks. Complete mass spectra of the 42 ketones investigated have been published (81).

Normal Fragmentation Peaks

Aliphatic Ketones.—For the aliphatic ketones, major fragmentation peaks are produced by splitting on either side of the carbonyl group. Loss of the smaller hydrocarbon group, R₁, results in the first major fragment ion in the spectrum below the parent mass. Loss of the larger hydrocarbon group, R₂, also results in a major peak. This fragment is either the base (most intense) or over 40 percent of the base peak intensity for the methyl, ethyl, n-propyl, and butyl types. Three of five isopropyl-type ketones investigated are exceptions and have less intense parent-minus-R₂ peaks. Mass 43 is the base peak for all of the methyl type and for all but 6 of the 24 other aliphatic ketones. The exceptions are three ketones of the ethyl type, one of the propyl type, and two of the butyl type. Two exceptions probably result from the symmetry of the molecules, three involve loss of the larger hydrocarbon group by splitting at the carbonyl group, and one results from rearrangement.

Isotope peaks also indicate that masses 43, 57, etc., result from parent-minus-R₂ fragments for the methyl, ethyl, etc., types. For the methyl ketones, mass 44 is less than 2.9 percent of the 43 peak. Mass 43 cannot result entirely from the structure (C—C—C)⁺ and may be mainly the fragment ions



from parent-minus-R₂ fragments. For the first five of the seven ethyl ketones, the isotope values show that mass 57 consists largely of (C—C—C)⁺ ions, which are also parent-



minus-R₂ fragments. For 8 out of 11 propyl ketones and 1 of 3 butyl ketones, peaks 71 and 85, respectively, are shown by isotope measurements to arise partly from parent-minus-R₂ fragmentation.

Aromatic and Cyclic Ketones.—The mass spectra of four cyclic and three aromatic ketones were obtained. Although this is an insufficient number to provide the basis for a correlation study, certain features of these spectra should be noted. The three aromatic ketones (propyl benzyl, isopropyl benzyl, and phenyl methyl) have peaks resulting from fragmentation at the carbonyl group, similar to the aliphatic ketones. Aromatic-type fragmentation peaks are also in these spectra. The four cyclic ketones investigated show a characteristic fragmentation pattern similar to that of the corresponding hydrocarbon, but different from that of the ketones described previously. Strong peaks result from the loss of the following masses from the parent molecule: 28, 29, 42, and 43. Mass 55 is the base peak, and parent peaks have usable intensities for all four cyclic ketones.

Rearrangement Peaks

Aliphatic Ketones.—Important rearrangement peaks appear in the mass spectra of all aliphatic ketones investigated. These peaks appear at masses corresponding to the parent mass of the lower molecular weight ketones and to the parent mass +1. Therefore, rearrangement peaks from higher ketones could cause considerable analytical difficulty. The percentages of total ion current in rearrangement ions range from almost 28 percent down to less than 1 percent. The 12 ketones having the highest percentage of total ion current in rearrangement peaks have mass 58 (2-propanone parent mass) as the major rearrangement peak.

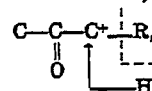
Evidence, other than the infrared spectra mentioned previously, was obtained to rule out impurities as the source of these peaks. For all higher mass ketones, mass 36 either was not present or limited the possible 2-propanone impurity to 3 percent. Masses 58 and 59 in the spectrum of 2-heptanone were investigated extensively. Determinations of rate of leak on mass 58 (24, 31) in the spectrum of this compound eliminate 2-propanone as an impurity. The mass spectrum of the heart cut from a distilled sample of 2-heptanone showed the same intensity mass 58 and 59 peaks as the original sample.

The even-mass rearrangement peaks form the series 58, 72, 86, etc., while the odd-mass rearrangement peaks include masses 59, 73, 87, etc. Except for the propyl types, the most intense rearrangement peaks in each series for any particular ketone appear at adjacent mass units. As an example, mass 58 is the most intense even-mass rearrangement peak in the spectrum of 2-heptanone and corresponds to the parent mass of 2-propanone. In

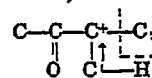
the odd-mass series of rearrangement peaks for this compound, mass 59 is the most intense peak. This fact might indicate that these two types of rearrangement peaks are formed by related processes. Rearrangement peaks appearing at parent masses of lower molecular weight ketones are in general more intense than rearrangement peaks in the odd-mass series and possibly more important analytically. The subsequent discussion will be limited to the even-mass series.

The following rules can be given regarding rearrangement peaks of aliphatic ketones as classified according to methyl, ethyl, etc., types in the tables. Possible structures are indicated.

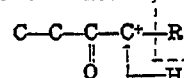
METHYL TYPE.—The most intense rearrangement peak is mass 58,



for 2-pentanone and higher molecular weight ketones without branching, or with branching beyond the third carbon atom. Because of branching on the third carbon atom, 3-methyl-2-butanone and 3-methyl-2-pentanone cannot form the mass 58 rearrangement ion easily. 3-Methyl-2-pentanone forms the mass 72 rearrangement ion,



ETHYL TYPE.—Mass 72,



is the most intense rearrangement peak for 3-heptanone and higher molecular weight ethyl-type ketones.

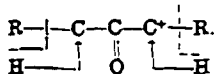
PROPYL AND ISOPROPYL TYPES.—Mass 86 is the most intense rearrangement peak of isopropyl-type ketones, starting with 2-methyl-3-heptanone. Mass 58 is the most intense rearrangement peak for *n*-propyl-type ketones, mass 86 being second most intense.

BUTYL TO HEXYL TYPES.—Mass 58 is the most intense rearrangement peak for all ketones of these types. All higher even-mass rearrangement peaks are less than 15 percent of the mass 58 intensity.

These observations regarding rearrangement peaks can be summarized as follows: The most intense rearrangement peak is mass 58, 72, or 86; many ketones have two or more intense rearrangement peaks.

Happ and Stewart (48), in their work on the mass spectra of aliphatic acids, concluded that the carbonyl carbon is included in the

mass 60 rearrangement fragment. The mass 60 rearrangement fragment for the aliphatic acids is equivalent to the ketone rearrangement peak, mass 58. If we assume that the carbonyl group is involved in the mass of the ketone rearrangement ions, the most intense rearrangement fragment for each of the methyl- or ethyl-type ketones can result from a single bond break and the rearrangement of a single hydrogen atom. However, this is not true for the range from *n*-propyl- to hexyl-type ketones, where mass 58 is the major rearrangement peak. As a minimum, two bond ruptures and the changing of position of two hydrogen atoms must be involved:



With branching on a carbon adjacent to the carbonyl group, this postulate would not hold, and a more complex mechanism would be needed. That less rearrangement occurs in such structures can be seen from the data for the isopropyl ketones. More involved methods of rearrangement, isomerization, and complete regrouping have been discussed by Langer (52).

Ketones having the highest percentage of total ion current in rearrangement peaks are methyl-type ketones, in which a simple hydrogen-transfer mechanism is sufficient.

Aromatic and Cyclic Ketones.—The mass spectra of the three aromatic ketones did not show any important rearrangement peaks. One or more rearrangement peaks (masses 29, 43, and 57) were found in the spectra of the four cyclic ketones.

Identification of Unknown Ketone

Analytical Significance of Rearrangement Peaks.—Both normal fragmentation and rearrangement peaks can be useful in identifying an unknown ketone. It is apparent that ions corresponding in mass to parent peaks of low-molecular-weight ketones, but resulting from high-molecular-weight ketones, can lead to erroneous analyses.

For methyl, propyl, butyl, and higher types without branching on a carbon atom adjacent to the carbonyl group, mass 58 rearrangement peak intensities are more than 20 percent of the 2-propanone parent sensitivity. A similar chance exists for confusing higher mass ethyl-ketones with 2-butanone. For 3-heptanone and higher molecular weight ethyl types, the sensitivity is 70 percent or more of the 2-butanone sensitivity.

It should be possible to determine the molecular weight of any ketone through 2-undecanone from the relatively intense parent peaks of these compounds. The empirical

rules, as stated in the discussion of normal fragmentation, should aid in determining the mass of each of the two hydrocarbon groups attached to the carbonyl group. Rearrangement peaks will in many instances verify these side-chain mass assignments. Even more important, rearrangement peaks should aid in determining the position of branching. Table 15 summarizes useful information ob-

TABLE 15.—Correlation of ketone structure with rearrangement peaks

	Most intense rearrangement peak			
	58	72	86	100
Methyl type:				
Straight-chain and branched beyond 3d carbon	x			
Branched on 3d carbon ¹		x		
Ethyl type: Straight-chain and branched beyond 4th carbon		x		
<i>n</i> -Propyl type: Straight-chain and branched beyond 4th carbon ¹	x		x*	
Isopropyl type: With and without other branching			x	
Butyl to hexyl types: Straight-chain and branched ¹	x			x*

¹ Only 1 example of this structure.

² Second most intense rearrangement peak.

³ Higher mass ketones studied did not include examples with branching on carbon adjacent to carbonyl group.

⁴ Second most intense rearrangement peak for butyl type.

tained from rearrangement peaks. Four examples of the identification of ketones are given in table 16, utilizing normal fragmentation and the information contained in table 15.

Identification of straight-chain ketones should be relatively easy. In many cases branching can be determined, especially if the branching is on the smaller hydrocarbon group. Although positive identification cannot always be made, the choice is limited to two or three possibilities.

Mass Spectra of Esters:

Formation of Rearrangement Ions

Mass spectral studies were made on 31 aliphatic esters, ranging from methyl formate to decyl acetate, to correlate important fragmentation peaks with molecular structures. Previous investigations of the mass spectra of esters were limited primarily to methyl (7, 42) and aromatic esters (62). Newton and Strom compared the spectra of isopropyl and isopropenyl acetate (67).

Complete mass spectra of the 31 esters have been published (80).

For this investigation the alkyl groups (R) have been designated as follows:

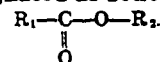


TABLE 16.—Identification of ketones from mass spectral characteristics

Molecular ion	Fragment mass ¹		Major rearrangement mass	Position of carbonyl	Branching	Possible compound
	First	Second				
142	113	85	72	Loss of mass 29 indicates smaller group is C ₂ ; rearrangement mass 72 indicates ethyl group.	Straight-chain or branched beyond 4th carbon.	3-Nonanone ² or branched C ₉ .
170	155	'	58	Loss of mass 15 indicates methyl group; rearrangement peak mass 58 supports methyl type.	Possibly branched beyond 3d carbon.	2-Undecanone ² or branched C ₁₁ .
128	85	71	86	Loss of mass 43 indicates smaller group is C ₃ ; rearrangement peak mass 86 indicates isopropyl type.	Branched in 2-position.	2-Methyl-3-heptanone ² or doubly branched C ₈ .
142	99	71	58,86	Loss of mass 43 indicates smaller group is C ₃ ; rearrangement masses of 58 and 86 indicate n-propyl type.	Straight-chain or branched beyond 4th carbon.	4-Nonanone or branched C ₉ (7-methyl-4-octanone). ¹

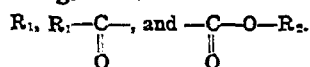
¹ First and second major peaks below parent mass.
² Denotes actual compound.

³ No second major peak.
⁴ Less intense.

The ions from normal fragmentation and from rearrangement are discussed separately.

Fragment Ions

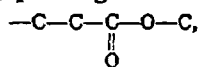
Major peaks can be correlated with the structural fragments



With only two exceptions among the examples studied (isopropyl isobutanoate and methyl hexanoate), mass ions corresponding to the structure $R_1-\overset{\text{O}}{\parallel}{\text{C}}$ have intensities at



least 30 percent of the base peak intensity. These ions form a mass series analogous to the paraffin mass series 29, 43, 57, etc. Peaks corresponding in mass to the remaining structural fragment, $-\text{O}-R_2$ (masses 31, 45, etc.), are distinctive where the alkyl group R₂ is saturated, even though their intensities are only a few percent of the base peak intensity. Mass 87, corresponding to the structure



and mass 74, a rearrangement ion, are characteristic of the higher methyl esters.

Parent and base peaks can be summarized as follows. Parent peak intensities, with few exceptions, decrease sharply with increased length of the alkyl radical R₂ that is attached to the oxygen atom. As an example, the intensity of the parent mass peak of methyl formate is 480 divisions and that of ethyl formate only 89 divisions. For the acetates through butanoates, base peaks (most intense in spectrum) are produced by either the fragment $(R_1-\overset{\text{O}}{\parallel}{\text{C}})^+$ or the alkyl group R₁⁺,



as shown in table 17. The base peak for for-

mates is mass 31, a rearrangement ion except for methyl formate.

TABLE 17.—Origin of base peaks in mass spectra of esters

Esters	Base peak, m/e	Fragment ion
Formates.....	31	Rearrangement ion, except methyl.
Acetates.....	43	$R_1-\overset{\text{O}}{\parallel}{\text{C}}^+$
Propanoates:		
Methyl and ethyl.....	29	$R_1-\overset{\text{O}}{\parallel}{\text{C}}^+$
Propyl and higher.....	57	$R_1-\overset{\text{O}}{\parallel}{\text{C}}^+$
Butanoates.....	43	$R_1-\overset{\text{O}}{\parallel}{\text{C}}^+$

Olefin-type ions forming the mass series 27, 41, etc., are 30 percent of the base peak intensity in many instances. Ions corresponding in mass to olefin molecular ions (not rearrangement ions) are discussed below under rearrangement ion correlations.

Only five comparisons could be made to show the effect of branching in the alkyl group R₂. The same major fragmentation peaks (>20 percent of base peak) appear in the spectra of normal and iso compounds of the same carbon number. Five long-chain methyl esters, investigated by Asselineau, Ryhage, and Stenhagen (7), show definite spectral changes with various R₁ alkyl groups.

Rearrangement Ions

Empirical rules have been found which relate rearrangement peaks to various ester types. Two series of rearrangement peaks were found in the mass spectra of esters. Peaks resulting from the fragment, $R_1-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$, are small; however, there are



peaks equivalent in mass to this fragment plus two hydrogen atoms. They form a series

of rearrangement peaks including masses 47, 61, 75, 89, 103, and 117. One or more of these peaks were found in the mass spectrum of each ethyl and higher ester investigated (much less intense for allyl butanoate and tertiary butyl acetate). Leak-rate determinations on mass 61 from *n*-propyl acetate and mass 75 in the spectrum of *n*-propyl propanoate eliminate the possibility that impurities are the source of these peaks (24, 31). The most intense rearrangement peak in each instance is characteristic of a particular type of ester—mass 47 for formates, 61 for acetates, etc.

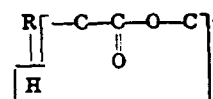
In a few instances, a major contribution is made to mass 61 by esters higher than acetates (most intense exceptions are *n*-propyl *n*-propanoate and *n*-propyl isopropanoate). For the other peaks in this series, masses 75, 89, etc., only esters of a particular type make major contributions to the characteristic rearrangement peak. This correlation is summarized in table 18. These characteristic peaks are found only when the alkyl group attached to the oxygen atom has two or more carbon atoms. Further limitations are described below.

TABLE 18.—Correlation of rearrangement peaks in mass spectra of esters

Ester correlation	Mass	Possible rearrangement structure
Ethyl and higher esters:		
Formates.....	47	$\text{H}-\text{C}-\text{O}-(+2\text{H})$ O
Acetates.....	61	$\text{C}-\text{C}-\text{O}-(+2\text{H})$ O
Propanoates.....	75	$\text{C}-\text{C}-\text{C}-\text{O}-(+2\text{H})$ O
Butanoates.....	89	$\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-(+2\text{H})$ O
Pentanoates.....	103	$\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-(+2\text{H})$ O
Hexanoates.....	117	$\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-(+2\text{H})$ O
<i>n</i> -Butanoates and higher types (not isobutanoates).....	60	$\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-(+2\text{H})$ O
Methyl esters:		
Pentanoates and higher types.....	74	$\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-\text{CH}_3(+\text{H})$ O
Ethyl esters:		
<i>n</i> -Butanoates and higher types (not isobutanoates).....	88	$\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-\text{C}-\text{CH}_3(+\text{H})$ O

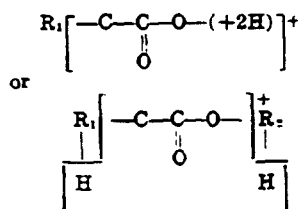
¹ Peaks in this series are weak for butanoates and higher ethyl esters.

A second series of rearrangement peaks includes masses 60, 74, 88, and 102. Mass 74 is the only intense rearrangement peak associated with methyl esters (*n*-butanoates and higher, but not isobutanoate). This mass-ion can be formed by the transfer of only one hydrogen atom,



Mass 88, characteristic of ethyl esters (butanoates and higher), can be formed in a similar manner.

Mass 60, found in the spectra of butanoates (not methyl butanoates or isobutanoates) and higher esters, could result from both rearrangement and a second structural break occurring when R₁ and R₂ contain two or more carbon atoms. Contributions to mass 60 are possible from either—



Mass 60 is not in the mass spectra of the methyl esters. The first structure is therefore consistent with the first series of rearrangements (masses 47, 61, etc.) that appear to involve the transfer of two hydrogens from R₂.

For ethyl esters and higher types the spectra indicate formation of an olefin-type ion corresponding to the alkyl group R₂, minus one hydrogen. This type of fragmentation becomes very evident for butyl and higher homologs. In several instances a typical olefin pattern is produced such as for heptyl propanoate. Alcohol and olefin spectra are similarly related (34).

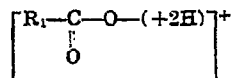
For esters having small R₂ groups, olefinic parent ions are of lower intensity and also less evident because of more intense general fragmentation at the lower masses. Olefin parent peaks are intense only for esters having intense rearrangement peaks. Neither the characteristic intense rearrangement peak nor the corresponding olefin parent appears for a compound having an R₂ group deficient in hydrogen, such as allyl butanoate, or an R₂ group with no hydrogen on particular carbon atoms, such as *tert*-butyl acetate. The characteristic acetate rearrangement peak is very weak (<10 percent of the intensity of mass 61 in *n*-butyl acetate) in the spectrum of

tert-butyl acetate. However, *sec*-butyl propanoate and all the compounds containing iso structures for R_2 groups show the typical rearrangement peaks.

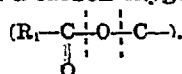
The correlation between formation of rearrangement ions and olefin parent fragments provides further evidence that the alkyl group, R_2 , is the source of hydrogen atoms in the rearrangement process. Although only one hydrogen atom would be lost in forming the olefin parent ion-fragment, the rearrangement mass corresponds to the transfer of two hydrogen atoms. Thus when one hydrogen atom is transferred, the alkyl group, R_2 , forms a positive ion; when two hydrogen atoms are transferred, a positive rearrangement ion is formed. This is supported by the observed intensities of the four peaks corresponding to these positive ions. An example is given below using heptyl propanoate, molecular weight 172.

	Intensity	Number of H atoms—	
		Rearranged	Lost after (—O—C—) break
R—C(=O)—O rearrangement ions:			
m/e 74	11.9	1	—
m/e 75	231	2	—
Olefin-type fragment ions:			
m/e 98	117	—	1
m/c 97	14.9	—	2

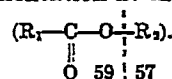
The foregoing data are also consistent with the rearrangement series observed for various types of esters (table 17). These peaks differ by 14 mass units and can be correlated on the basis of a possible rearrangement-ion mass:



These observations concerning ester rearrangement ions can be summarized as follows. For rearrangement ions to be formed, the alkyl group, R_2 , must contain at least two carbons. Two structures that do not show strong mass spectral rearrangement peaks of the above type are *tert*-butyl acetate and allyl butanoate. These exceptions could be related to a deficiency of hydrogen on particular carbon atoms in the alkyl group, R_2 , and/or a weakness of a carbon-oxygen bond



The spectrum of *tert*-butyl acetate shows intense mass 57 and 59 peaks, indicating preferential fragmentation at the oxygen atom



When rearrangement ions are observed, an olefin parent ion of carbon number corresponding to the remaining structure is also found.

Formation of Rearrangement Ions

Formation of rearrangement ions has been investigated by Langer (52), Friedman and Long (36), Honig (46), and others. Mechanisms postulated for their formation include migration of hydrogen atoms, isomerization, and complete regrouping (26, 36-37, 46, 52, 87). McLafferty has tabulated many of the positive rearrangement ions and found that intramolecular hydrogen migration can often be explained by the formation of more stable products from cleavages (61-62).

Major rearrangement peaks found in the mass spectra of ketones, acids, and aldehydes appear to be related through the common structure shown in table 19. The migration of a single hydrogen atom accounts for these rearrangement ions. As table 19 also shows, mass 62 in diethyl peroxide can be formed by the transfer of one hydrogen atom. All these examples can be explained by the formation of more stable products.

TABLE 19.—Examples of mass spectral rearrangement ions

Compound	Rearrangement peak, m/e	Possible structure
2-Pentanone	58	$\begin{array}{c} C-C-C-C-C \\ \quad \quad \\ H \quad O \end{array} \right]^+$
Butanoic acid	60	$\begin{array}{c} C-C-C-C-OH \\ \quad \quad \\ H \quad O \end{array} \right]^+$
Butanal	44	$\begin{array}{c} C-C-C-C-H \\ \quad \quad \\ H \quad O \end{array} \right]^+$
Diethyl peroxide	62	$\left[\begin{array}{c} C-C-O-O \\ + 1H \end{array} \right]^+ - C-C$
Propyl acetate	61	$\left[\begin{array}{c} C-C-O \\ + 2H \\ \\ O \end{array} \right]^+ - C-C-C$
Propyl carbonate	63	$\left[\begin{array}{c} C-C-C \\ + 3H \\ \\ O \end{array} \right]^+ - C-C-C$

Correlation of the ion-masses 47, 61, etc., with the homologous series (table 18) indicates that the mass of alkyl group R_1 remains

intact during rearrangement. Because these ions require the addition of two hydrogen atoms, an additional valence bond must be formed. A possible mechanism whereby another bond could be formed is localization of the positive charge on one of the oxygen atoms after ionization. Cummings and Bleakney (20) have evidence from mass spectra of methyl and ethyl alcohol that the charge can be localized and valence changed during electron bombardment. Friedman and Turkevich (37) concluded, from a study of the mass spectra of deuterated isopropyl alcohols, that ion structures involving a bond change of the oxygen atom account for approximately 75 percent of the observed ion yield. This finding supports the assumption of localization of charge on the oxygen atom. Collin (17) proposed localization of charge on the nitrogen atom, to explain rearrangement peaks found in the mass spectra of amines. The above evidence for localization of charge occurring during electron impact is summarized in table 20.

TABLE 20.—Formation of rearrangement ions
(Localization of charge mechanism)

Mass spectral evidence for valence change during ionization: Mass 31 in spectrum of methanol (20) is evidence that ion structure is.....	$(\overset{\ominus}{\text{C}}-\overset{\ominus}{\text{O}}\text{H})$
Spectrum of isopropyl alcohol (37) shows many ions containing.....	$(-\overset{\ominus}{\text{C}}-\overset{\ominus}{\text{O}}-)$ and $(-\overset{\ominus}{\text{C}}=\overset{\ominus}{\text{O}})$
Spectra of amines (17) indicate ionization is taking place on nitrogen atom.....	$\begin{array}{c} \oplus \quad \text{H} \\ \quad \\ \text{C}-\text{N}^+-\oplus \\ \quad \\ \text{H} \quad \text{H} \end{array}$
Ester spectra indicate rearrangement ion corresponding in mass to.....	$\left[\begin{array}{c} \text{R}-\overset{\ominus}{\text{C}}-\text{O} \\ \\ \text{O} \end{array} (+2\text{H}) \right]^+$
Possible structure resulting from localization of charge on oxygen atom is.....	$\left[\begin{array}{c} \text{R}-\overset{\ominus}{\text{C}}-\text{O}-\text{H} \\ \\ \text{O}^+ \\ \\ \text{H} \end{array} \right]^+$

The compounds listed in table 19 differ from the alcohols investigated by Cummings and Bleakney (20) and Friedman and Turkevich (37) in that, except for the peroxide, all contain a carbonyl group and some have more

than one oxygen atom. If instead of an additional valence bond forming between the O^+ and a carbon atom—for example, $-\overset{\ominus}{\text{C}}=\text{O}^+$, as these authors have described—a structure of the type $(\text{C}=\text{O}^+-\text{H})$ is formed with a rearranged hydrogen, the observed rearrangement ions can be explained. Isotope values indicate that mass 63 in propyl carbonate contains three oxygen atoms and one carbon atom, as shown in table 19. With three hydrogen atoms necessary for the ion-mass, an additional bond is required as for the esters. This again could be credited to the same mechanism.

Direct evidence for this process has been obtained from the appearance potentials of the rearrangement ions. Calculated and observed values show good agreement for mass 61 in ethyl acetate. The use of deuterated compounds would give further information.

Identification of Esters

Ions resulting from both structural breaks and rearrangements can be useful in identifying esters. Because of their relatively high volatility, esters containing 10 carbon atoms can be introduced easily into the room-temperature mass spectrometer.

Parent mass peaks cannot be used for ester analysis when alcohols or acids are present because these three classes of compounds have identical parent masses. The intense peaks resulting from the fragments R_1^+ and $\text{R}_2-\overset{\ominus}{\text{C}}-$ and the rearrangement ion masses



31, 47, 60, 61, 74, 75, and 87 should aid in determining the presence and the type of ester in an unknown mixture.

The use of rearrangement peaks for identifying esters is illustrated in figure 5, which shows the partial mass spectrum of a sample that was found by infrared analysis to contain an ester. A partial structural identification was possible from the ester rearrangement peak at mass 117, which is attributable to C_2COOR . Several peaks corresponding to olefin parent masses (70, 84, 126, and 168) are in this spectrum, typical of the peaks found in the spectra of aliphatic esters.

Another example of the use of ester rearrangement peaks is the qualitative determination of Fischer-Tropsch synthesis product distribution. The carbon number of the acid side of the esters in a mixture can be derived directly from inspection of the mass spectrum. This is illustrated in figure 6, which contains rearrangement peaks 103, 117, 131, etc., up to mass 187 corresponding to undecanoates.

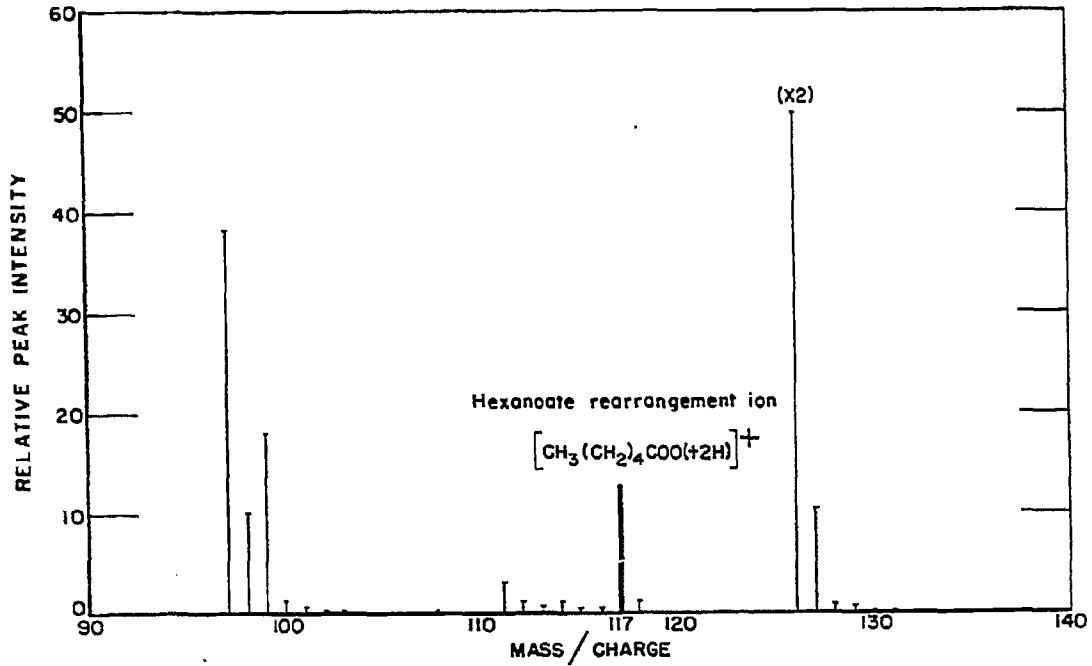


FIGURE 5.—Partial Identification of an Ester From Rearrangement Peaks.

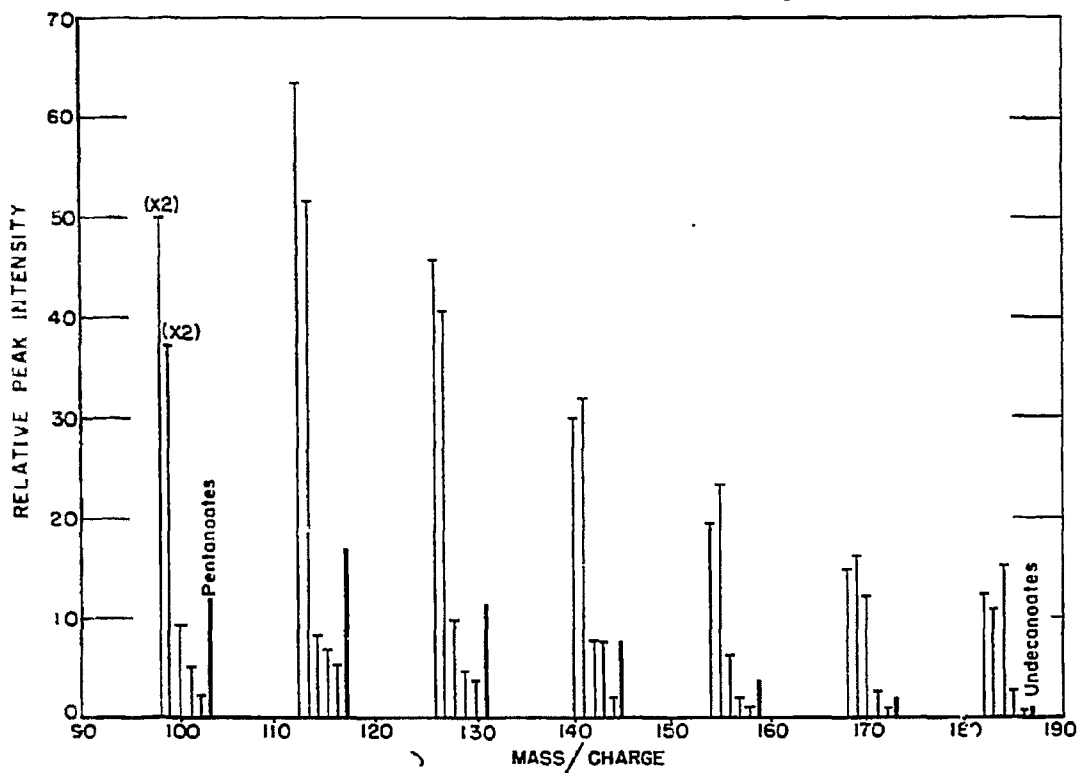


FIGURE 6.—Fischer-Tropsch Oil Product, Ester Distribution From Rearrangement Peaks.

Type-Analysis of Paraffin-Naphthene Mixtures

Mass spectrometer analysis of hydrocarbon types has been described by Brown (12). By applying sums of mass peaks which are specific for various types, Brown was able to analyze for aromatics, paraffins, combined naphthenes and olefins, and combined diolefins and cycloolefins. In the present investigation, structural types in C_6 to C_8 paraffin-naphthene mixtures were studied and a separation of the naphthenes into cyclopentane and cyclohexane derivatives obtained by mass spectral methods. A further division into monosubstituted and polysubstituted cyclopentanes and cyclohexanes was also carried out.

Detailed information can be obtained by a good fractionation of paraffin-naphthene mixtures followed by infrared analysis of many cuts but the method is tedious. Essentially each individual compound must be determined. Besides the necessity of analyzing the many paraffin compounds in the C_6 to C_8 range, the infrared method is rendered more laborious by the presence of *cis-trans* naphthene isomers. For example, 1,2,3-trimethylcyclopentane exists in three forms: *cis, cis, cis*; *cis, cis, trans*; and *cis, trans, cis*. These have different infrared spectra and so must be determined individually.





The mass spectrometric method developed is an accurate shortcut. Sample preparation consists of isolating the paraffin-naphthene portion and fractionating it into three molecular-weight cuts. Comparison analyses

are presented below to show the negligible advantage of careful fractionation into many cuts.

Mass spectra of the 36 (C_6 to C_{10}) naphthenes used in this investigation have been published (29). Only average peak values were used for the C_6 and C_7 paraffin isomers. Sensitivity coefficients were determined on a volume basis; that is, they are the actual mass peaks as read from the spectra with a standard introduction of 0.00036 cm^3 . The *n*-butane mass 43 peak sensitivity during this work was 55.2 divisions per micron.

The basic analytical scheme is indicated in table 21, which shows the different structural types, the fragmentation that takes place, and the resulting calibration mass peaks. The mass spectra of many polysubstituted cyclopentane derivatives were found to possess more intense 69 and 70 mass peaks than the cyclohexanes; conversely, the polysubstituted cyclohexanes displayed more intense 97 mass peaks. Monosubstituted cyclopentanes tend to lose the alkyl group or chain plus one hydrogen to produce strong 68 mass peaks; monosubstituted cyclohexanes behave similarly to give large 82 peaks. These were the bases for splitting the naphthenes into four different types. The fragmentation illustrated is not intended to propose a mechanism but merely to show the number of C and H atoms that are stripped off the naphthene molecule by electron bombardment, to produce the mass peaks selected for calibration. The combination of peaks chosen for calculation of total paraffins is the same as that of Brown (12).

TABLE 21.—Mass spectral type-analysis of naphthenes; general calibration mass peaks

Type No.	Type	Proposed fragmentation	Calibration peaks	
(1)	Paraffins.....	$\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-$ CH_3	$-(\text{CH}_2)$ $-(\text{C}_6\text{H}_{12})$ $-(\text{C}_7\text{H}_{14})$ etc.	43, 57, 71, 85,-
(2)	Monosubstituted cyclohexanes.....		$-(\text{---CH}_2)$ $-(\text{H})$	82
(3)	Polysubstituted cyclohexanes (dimethyl).....		$-(\text{CH}_2)$	97
(4)	Monosubstituted cyclopentanes.....		$-(\text{---CH}_2)$ $-(\text{H})$	68
(5)	Polysubstituted cyclopentanes.....		$-(\text{---CH}_2)$ $-(\text{CH}_2)_{x=0,1,2}$ $-(\text{---CH}_2)$ $-(\text{CH})$	69, 83 70

The mass peaks used for the analyses are listed in tables 22-24. In practice, three different sets of calibration data were used for analysis of the three molecular weight cuts, C₆, C₇ (+ cyclohexane), and C₈. The components of the C₆ fraction, cyclohexane, methylcyclopentane, and the five C₇ paraffins, were analyzed individually. For calculation of the dimethylcyclohexanes it was found that the sum of the 97 and 112 peaks was preferable to the 97 peak alone. The calculation for methyl-ethyl plus trimethylcyclopentanes was found to be most accurate by summing the

69, 70, 56, and 83 peaks (table 23). But a reliable alternative method consists of splitting this class of compounds into three subgroups (table 24). In each case the calibration data were arranged in sets of simultaneous equations. The necessary mass peaks were obtained from the spectra (of synthetic blends or unknowns) and calculations were carried out by the usual methods of matrix algebra. The matrix is given in table 22, the matrix for a five-component C₆ in table 23, and that for a seven-component C₆ in table 24.

TABLE 22.—Outline of type-analysis of naphthene-paraffin blends, C₇ matrix
(Compound-type numbers are in parentheses)

Calibration peak....	Cyclohexane ¹	Paraffins.....	Methylcyclohexane..	Ethylcyclopentane..	1,1-Dimethylcyclopentane. cis-1,2-Dimethylcyclopentane. trans-1,2-Dimethylcyclopentane. cis-1,3-Dimethylcyclopentane. trans-1,3-Dimethylcyclopentane.
		(1)	(2)	(4)	(5)
84.....	590.0	11.6	47.3	3.1	13.1
49+57+71+85.....	182.4	1,627.3	97.1	103.2	166.6
82.....	2.0	93.3	4.0	9.9
68.....	15.4	1.4	64.1	414.0	22.9
69+70.....	192.2	114.6	290.4	863.0	634.7

¹ Cyclohexane boils in the C₇ range.

Synthetic Blends

Accuracy of the method was tested by analysis of a 9-component C₇-cyclohexane synthetic blend and a 17-component C₈ blend. The results are shown in tables 25 and 26, respectively. For the C₈ blend two different calculation methods were found to be applicable. The general five-component calculation, based on matrix data shown in table 23, produced accurate results for the blend. Matrix data presented in table 24, in which the polysubstituted cyclopentanes were split into three subgroups [gem-trimethyls (5a), other trimethyls (5b), and the methylethyls (5c)], provides more detailed information with acceptable accuracy. The largest errors exist for the 1,2,3-trimethyls plus 1,2,4-trimethyls (5b) and the methylethyls (5c). Addition of these two answers produces a more accurate result.

Coal-Hydrogenation Gasoline

The method has been applied to the analysis of paraffins and naphthenes in gasoline obtained from vapor-phase treatment of coal-hydrogenation oil. Tables 27 and 28 demonstrate the results obtained by combining the analyses of 25 paraffin-naphthene cuts, and the comparable results obtained from analyses of C₇ and C₈ molecular-weight cuts. Components in the C₆ range were determined individually. Cyclohexane was also analyzed in the C₇ cut.

Overlapping of the C₇ and C₈ molecular-weight cuts may require the application of a transition analysis for greater accuracy on the naphthenes. A fraction boiling between 103° and 110° C may be analyzed for methylcyclohexane, ethylcyclopentane, trimethylcyclopentanes, and paraffins. Any overlap of the paraffins was relatively unimportant since the various paraffin calibration coefficients do not vary greatly.

Caution must be exercised in analyzing for ethylcyclohexane in the presence of large amounts of methylethylcyclopentanes. The matrix shown in table 24 demonstrates rather intense mutual interference. In addition, no calibration standard is available for either *cis*- or *trans*-1,3-methylethylcyclopentane. Probably it is this compound which, in early analyses, produced high apparent concentrations for ethylcyclohexane 10°C below its boiling point. A reasonable solution to this difficulty is found in the six-component matrix described in footnote 1 of table 24, in which ethylcyclohexane and methylethylcyclopentanes are combined and calculated as a single component. Splitting these two types is still possible by combining results from matrix, table 24, with results from matrix, table 23, in which the calculation for ethylcyclohexane is more reliable. The difference between this value for ethylcyclohexane and the combined result from matrix, table 24, represents methylethylcyclopentanes.

TABLE 23.—Outline of type-analysis of naphthene-paraffin blends, 5-component C₆ matrix
 (Compound-type numbers are in parentheses)

Calibration peak	Paraffins	Ethylcyclohexane	1,1-Dimethylcyclohexane <i>cis</i> -1,2-Dimethylcyclohexane <i>trans</i> -1,2-Dimethylcyclohexane <i>cis</i> -1,3-Dimethylcyclohexane <i>trans</i> -1,3-Dimethylcyclohexane <i>cis</i> -1,4-Dimethylcyclohexane <i>trans</i> -1,4-Dimethylcyclohexane	<i>n</i> -Propylcyclopentane <i>i</i> -Propylcyclopentane	1,1-Methylethylcyclopentane <i>cis</i> -1,2-Methylethylcyclopentane 1,1,2-Trimethylcyclopentane 1,1,3-Trimethylcyclopentane <i>cis</i> , <i>trans</i> , <i>cis</i> -1,2,3-Trimethylcyclopentane <i>cis</i> , <i>cis</i> , <i>cis</i> -1,2,3-Trimethylcyclopentane <i>cis</i> , <i>trans</i> , <i>cis</i> -1,2,4-Trimethylcyclopentane <i>cis</i> , <i>cis</i> , <i>trans</i> -1,2,4-Trimethylcyclopentane (6)
	(1)	(2)	(3)	(4)	(5)
43 + 57 + 71 + 85.....	1,806.5	98.4	174.8	237.7	222.4
82.....	1.0	17.6	17.6	27.2	58.9
97 + 112.....	0	201.8	889.0	171.1	121.5
68.....	1.9	29.7	84.8	643.0	29.4
56 + 69 + 70 + 83.....	395.0	1,127.4	664.6	1,043.6	1,305.2

TABLE 24.—Outline of type-analysis of naphthene-paraffin blends, 7-component C₆ matrix¹
 (Compound-type numbers are in parentheses)

Calibration peak	Paraffins	Ethylcyclohexane	1,1-Dimethylcyclohexane <i>cis</i> -1,2-Dimethylcyclohexane <i>trans</i> -1,2-Dimethylcyclohexane <i>cis</i> -1,3-Dimethylcyclohexane <i>trans</i> -1,3-Dimethylcyclohexane <i>cis</i> -1,4-Dimethylcyclohexane <i>trans</i> -1,4-Dimethylcyclohexane (3)	<i>n</i> -Propylcyclopentane <i>i</i> -Propylcyclopentane	1,1,2-Trimethylcyclopentane 1,1,3-Trimethylcyclopentane	<i>cis</i> , <i>trans</i> , <i>cis</i> -1,2,3-Trimethylcyclopentane <i>cis</i> , <i>cis</i> , <i>cis</i> -1,2,3-Trimethylcyclopentane <i>cis</i> , <i>trans</i> , <i>cis</i> -1,2,4-Trimethylcyclopentane <i>cis</i> , <i>cis</i> , <i>trans</i> -1,2,4-Trimethylcyclopentane	1,1-Methylethylcyclopentane <i>cis</i> -1,2-Methylethylcyclopentane
	(1)	(2)	(3)	(4)	(5a)	(5b)	(5c)
43 + 57 + 71 + 85.....	1,806.5	98.4	174.8	237.7	328.8	226.1	161.0
82.....	1.0	17.6	17.6	27.2	4.6	8.5	165.6
97 + 112.....	0	201.8	889.0	171.1	299.6	150.3	114.0
68.....	1.9	29.7	84.8	643.0	44.4	24.8	21.2
69.....	25.9	79.8	217.1	641.6	406.5	202.9	160.9
70.....	192.2	29.0	119.1	144.0	155.9	833.5	270.5
83.....	3.7	918.0	84.5	119.4	182.5	44.7	648.5

¹To form a 6-component matrix from these data, use peaks 82 + 83 (row 2 + row 7) and combine proportionally type 2, ethylcyclohexane, and type 5c, methylethylcyclopentanes.

TABLE 25.—Mass spectral type-analysis of C_7 and cyclohexane paraffin-naphthene synthetic blends, volume-percent

Type	Compound	Synthetic blend	MS analysis
(1)	<i>n</i> -Heptane.....	12.4	23.0
(1)	3-Methylhexane.....	5.3	
(1)	2,3-Dimethylpentane.....	6.4	
	Cyclohexane.....	20.1	19.9
(2)	Methylcyclohexane.....	27.2	27.1
(4)	Ethylcyclopentane.....	9.0	10.7
(5)	1,1-Dimethylcyclopentane.....	6.8	19.3
(5)	<i>trans</i> -1,2-Dimethylcyclopentane.....	6.2	
(5)	<i>cis</i> -1,3-Dimethylcyclopentane.....	6.6	

TABLE 26.—Mass spectral type-analysis of C_8 paraffin-naphthene synthetic blends, volume-percent

Type	Compound	Synthetic blend		MS analysis	
				Matrix, table 24	Matrix, table 23
(1)	<i>n</i> -Octane.....	8.4	24.3	24.0	24.0
(1)	2-Methylheptane.....	5.4			
(1)	2,5-Dimethylhexane.....	5.0			
(1)	2,2,4-Trimethylpentane.....	5.5			
(2)	Ethylcyclohexane.....	11.7	10.9	11.2	
(3)	1,1-Dimethylcyclohexane.....	5.6	23.1	22.8	22.7
(3)	<i>cis</i> -1,2-Dimethylcyclohexane.....	5.9			
(3)	<i>trans</i> -1,3-Dimethylcyclohexane.....	5.8			
(3)	<i>cis</i> -1,4-Dimethylcyclohexane.....	5.8			
(4)	<i>n</i> -Propylcyclopentane.....	4.9	10.1	9.9	9.7
(4)	<i>i</i> -Propylcyclopentane.....	5.2			
(5a)	1,1,2-Trimethylcyclopentane.....	2.5	10.6	10.1	32.4
(5a)	1,1,3-Trimethylcyclopentane.....	8.1			
(5b)	<i>cis,trans,cis</i> -1,2,3-Trimethylcyclopentane.....	2.8	11.6	9.5	22.3
(5b)	<i>cis,cis,trans</i> -1,2,4-Trimethylcyclopentane.....	8.8			
(5c)	1-Methyl-1-ethylcyclopentane.....	5.3	8.6	12.8	32.4
(5c)	1-Methyl-2-ethylcyclopentane.....	3.3			

An inherent limitation in type-analyses is the loss of accuracy in analyzing one component of a given type, particularly if the calibration values for this component differ appreciably from the average calibration. In this method if only *n*-propylcyclopentane is present the application of calibration values based on *n*-propylcyclopentane and isopropylcyclopentane will produce an answer about one-third too high. Conversely the presence of only isopropylcyclopentane will produce a value about one-third too low.

Extension of this method, as described, to C_8 or higher carbon numbers, is not considered feasible. Few calibration standards are available and the numerous possible combi-

nations of substituents are expected to introduce extensive interference. Further, coal hydrogenation gasoline was found to contain C_9 and C_{10} bicyclics, which produce strong interfering 68 and 82 mass peaks. The C_9 bicyclic has been identified as hydrindane, and its interference may be removed by use of the parent peak, mass 124. The C_{10} bicyclics probably comprise a mixture such that correction for the interference would be difficult.

A simplified analysis for C_8 and above may be suitable for obtaining the limited, but useful, split into total cyclopentanes and cyclohexanes. It is probable that the higher compounds will follow the same behavior as the

TABLE 27.—*Type-analyses of C₇ paraffin-naphthene mixtures from coal-hydrogenation product*

(Boiling range 82° to 105° C)

Compound type	Combined analyses of 12 cuts, volume-percent	Analysis of combined cut, volume-percent
Cyclohexane ¹	2.5	2.4
Paraffins.....	23.7	22.8
Methylcyclohexane.....	27.1	26.5
Ethylcyclopentane.....	11.8	12.2
Dimethylcyclopentane.....	34.9	36.1

¹ The major portion of the cyclohexane distills below 82° C.

TABLE 28.—*Type-analyses of C₇ paraffin-naphthene mixtures from coal-hydrogenation product*

Compound type	Combined analyses of 13 cuts, volume-percent	Analysis of combined cut, volume-percent
Paraffins.....	28.6	26.5
Dimethylcyclohexanes.....	21.3	22.7
Ethylcyclohexane.....	8.2	11.8
1,1,2- and 1,1,3-Trimethylcyclopentanes.....	8.5	5.2
1,2,3- and 1,2,4-Trimethylcyclopentanes.....	14.7	13.4
Methylethylcyclopentanes.....	14.0	15.2
Propylcyclopentanes.....	4.7	5.2

lower homologs. This is indicated by the fact that the C₈ and C₁₀ monosubstituted compounds, the propylcyclohexanes and butylcyclohexanes and the butylcyclopentanes produce the same strong 82 and 68 peaks as the lower homologs.

ANALYSIS OF OILS DERIVED FROM COAL

Analysis of high-boiling tar acids from petroleum, coal, and neutral oils from coal has consisted largely of the laborious isolation of individual pure compounds. The procedures usually involve chemical treatment of the oil and provide only an approximation of the amount of certain compounds present in the original oil.

Routine mass spectrometric analysis of liquid products from coal hydrogenation has been limited primarily to the determination of certain hydrocarbon types (29). We normally determine total paraffins, total naphthenes, C₆ to C₁₀ alkyl benzenes, tetralin, and naphthalene in fractions boiling up to 200° C. Very little can be deduced from such spectra as to molecular weights or types of compounds present in higher boiling fractions. Adjacent mass peaks have approximately the same intensities, seldom varying by a factor >2. This nondistinct spectrum results from the presence of many compounds having similar spectra and from rearrangement ions corresponding to the molecular weights of lower members of homologous series.

Modified forms of published type-analyses

were applicable to high-boiling saturated and aromatic fractions from coal hydrogenation.

To obtain molecular weight distributions, the low-ionizing-voltage technique, described by Stevenson and Wagner (38), Lumpkin (58), and Field and Hastings (27) was applied to the saturated, aromatic, and tar-acid fractions. Thus, the combined type-analysis and low-ionizing-voltage analysis provided total percentages for types of compounds and molecular weight distribution of these compounds (78, 82-83). This approach gave detailed information for rapid product comparisons and required little preliminary processing of the samples.

Methods of Analysis

For mass spectrometric methods to be most effective, samples must first be separated by compound class. The general analytical scheme applied to these materials is shown in figure 7. The tar acids and bases are extracted from the total oil and the tar acids and neutral oils are characterized.

The neutral oil is first subjected to fluorescence indicator adsorption analysis (FIA) and drop quantities of the saturate, olefinic, and aromatic fractions are collected for mass spectrometric investigation. The aromatic fraction will contain any neutral oxygen, sulfur, or nitrogen compounds present in the total oil. The saturate and aromatic fractions are analyzed for compound types by standard type-analysis techniques and for carbon number distribution by low-ionizing voltage. The olefinic fraction is hydrogenated and the resulting saturate material is analyzed in the same manner as the original saturate fraction. After hydrogenation, the olefins and diolefins will appear as paraffins and the cycloolefins will appear as naphthenes. From type-analysis for paraffins and naphthenes, total values for each of the two groups of olefins can be obtained.

The tar-acid fraction is analyzed by the low-ionizing-voltage technique and additional information obtained from a low-ionizing-voltage spectrum of the trimethylsilyl ether of the fraction.

Type-Analysis

Type-analysis methods are based on the fact that for a given hydrocarbon type a large fraction of the total ion intensity is distributed over a small number of intense peaks which are thus characteristic of that hydrocarbon type. When the peaks in each of these groupings of characteristic peaks

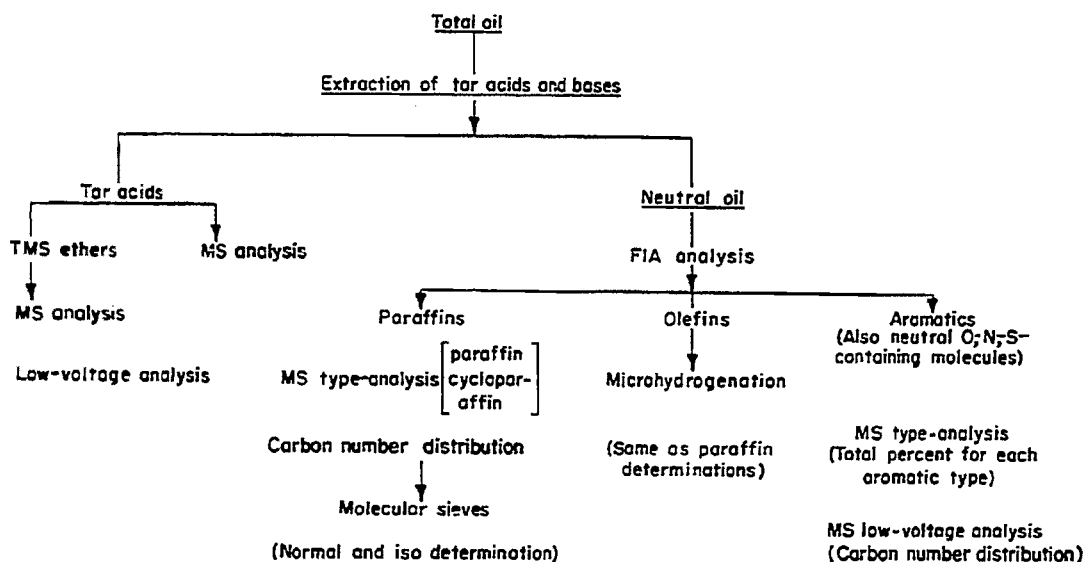


FIGURE 7.—Preliminary Separation and Mass Spectrometric Analytical Scheme for High-Boiling Oils From Coal.

are mathematically combined and treated as one peak, they provide distinctive pattern coefficients for the determination of particular hydrocarbon types.

Two type-analyses were applied to the saturated fractions. One, developed by Clerc, Hood, and O'Neal (16), is relatively independent of structural variations within each saturated type. This method is based on the constancy of total ionization over a certain portion of the spectrum. The other, developed by Lumpkin (57), does not determine monoaromatics. Being based on the spectra of specific compounds found in petroleum, it is not independent of structural variations. However, it yields relative percentages of 2-, 3-, and 4-ring condensed cycloparaffins.

Two type-analysis methods for analyzing aromatics in petroleum have been described (44, 64). Both methods determine the percentage of various 1- to 5-ring aromatic structures. Neither method is directly applicable to products from coal hydrogenation. The type-analysis matrix of Melpolder and coworkers (64) uses for calibration data average values for specific compounds found in the aromatic fraction of petroleum. Hastings, Johnson, and Lumpkin (44) derived sensitivity factors and interference coefficients from peak intensities found in particular aromatic fractions. As in the case of the saturated fraction, the Bureau investigation followed a more general approach, based on total ionization, for a type-analysis.

In this investigation, analyses were calculated as follows: For characteristic peak summations, those groupings chosen by Hastings and coworkers (44) were used; that is, summation 91 for benzenes, 117 for indans and/or tetralins, 129 for dinaphthenes, etc., 141 for naphthalenes, and 167 for acenaphthenes. Sensitivities were based on the total ionization work of Otvos and Stevenson (70), and Clerc, Hood, and O'Neal (16). Crable and Coggeshall have shown that total ionization per unit liquid volume is essentially independent of molecular weight (18). An extension of this work by Kearns and coworkers was applied to aromatics (49).

Low-Ionizing-Voltage Analysis

The first application of the low-ionizing-voltage technique, reported in the literature in 1950 by Stevenson and Wagner, was to the mass spectrometric determination of monodeuterio paraffins (88). Since 1957 this technique has been widely adopted in petroleum and chemical laboratories. Low-ionizing-voltage operation has been applied to both qualitative and quantitative determinations of organic components in complex liquid mixtures (78). In many instances only the molecular weights of the compounds present can be determined. For some mixtures the structural types can be determined, but a quantitative analysis is not possible, since calibration data are not available. However, for many aromatic-, olefinic-, and phenolic-

type compounds, calibration data are available and quantitative determinations can be made. In detecting impurities in relatively pure compounds there are advantages to obtaining a spectrum at low-ionizing voltage. For many structural types it is difficult to determine the presence of impurities having molecular weights lower than the major components, since rearrangement ions from the major component can occur at lower mass numbers. Many of these rearrangement ions can be eliminated at low-ionizing voltage, thus making detection of impurities possible.

As shown in table 29, compound types can be grouped roughly according to ionization potentials with the olefinic and aromatic types requiring the least energy to produce ionization. Many fragment ions from organic molecules require several volts additional energy compared with the molecular ion. Thus, the ionizing voltage can be adjusted to produce a spectrum consisting primarily of the parent ions of the compound types present. Electron accelerating electrodes are normally operated (~70 volts) considerably above the appearance potentials of the singly and doubly charged ions from hydrocarbons. As shown in the ionization efficiency curve, figure 8, this results not only in more intense peaks, but also in more stable operation, since any variation in electron accelerating voltage will have a minimum effect on peak intensity. Both of the above advantages are lost by operating at reduced ionizing voltages. The slope of the ionization efficiency curve is much greater, for example, at 10 volts, and also the peak intensity will be reduced for a given sample charge. The actual reduction in peak intensity will depend on the shape of the ionization efficiency curve for the particular compound being investigated. When molecular ion data obtained at 10 volts are compared with those obtained at 70 volts, reductions in peak intensities the order of a factor of 10 are quite common. This can in many instances be

TABLE 29.—Approximate ionization potentials, electron-volts

Compound class	Ionization potential
n-Paraffins (C _n -C _n)	11.2-10.2
i-Olefins (C _n -C _n)	9.7-9.5
Aromatics (C _n H _n) (lower as alkyl groups are added)	9.5
Approximate dissociation energy: Additional energy to produce fragmentation:	
C-C	~3.3
C-H	~4.2

¹ Reduced by rearrangements, etc., in certain instances.

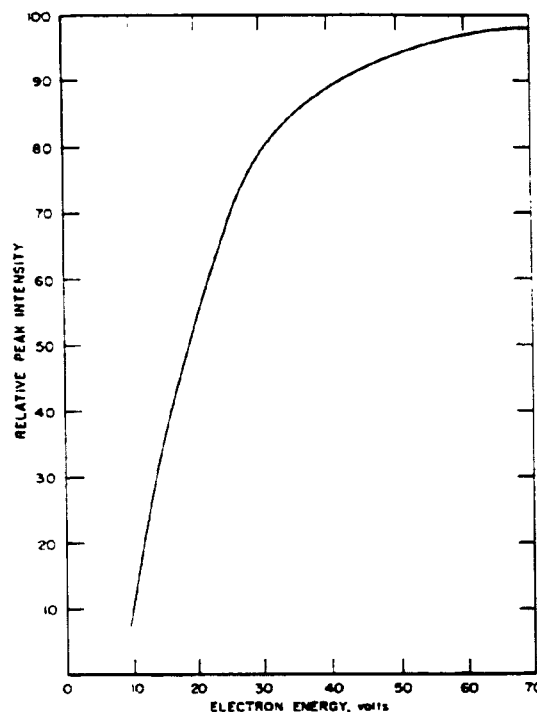


FIGURE 8.—Typical Ionization Efficiency Curve for Molecular Ions From Hydrocarbons.

compensated for by increasing the sample charge. Circuit changes necessary to operate commercially available mass spectrometers at reduced ionizing voltages have been described by Lumpkin (58).

The technique is most effective when applied to a mixture consisting of similar structural types. For a hydrocarbon mixture it is desirable to have saturated and unsaturated structures separated before the analysis. However, in certain instances it is possible to determine whether a particular peak is assignable to a saturated or unsaturated structure on the basis of spectra obtained at progressively lower ionizing voltages.

Figure 9 shows a comparison of naphthalene spectra obtained at ionizing voltages of 70 and 8.6 volts. The 8.6 volts is the indicated value, with the actual voltage being approximately 10.6 volts. In addition to the molecular ion peak, the only other peaks appearing in the 8.6-volt spectrum are from C¹³ isotopes and from impurities in the naphthalene. Impurity peaks can be seen at masses 134 and 142. Fragmentation peaks in the mass range 97 to 127 are completely missing in the spectrum obtained at low-ionizing voltage. As all even-mass peaks could be molecular ions resulting from compounds con-

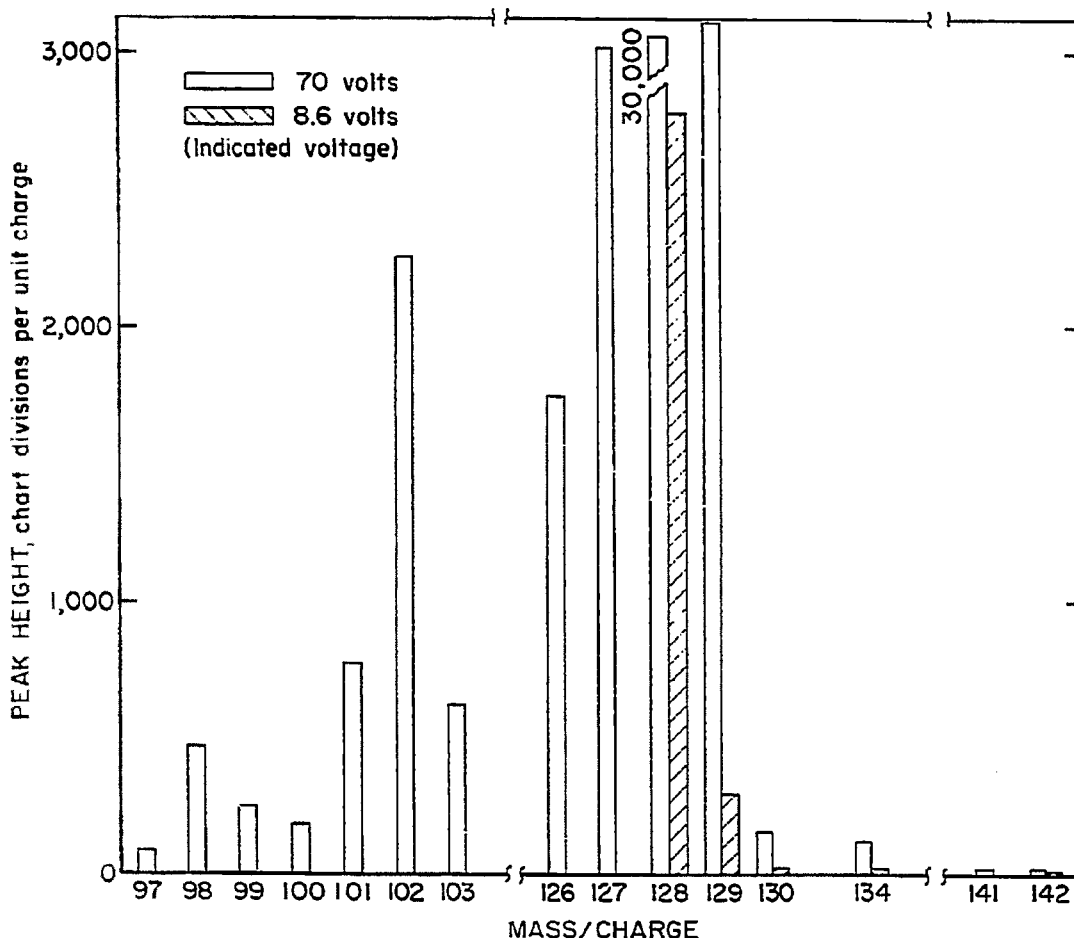


FIGURE 9.—Partial Mass Spectrum of Naphthalene, Normal and Reduced Ionizing Voltages.

taining various combinations of carbon and hydrogen, peaks occurring at masses 136, 102, 100, and 98 in the spectrum of naphthalene can be misleading. In general, rearrangement ions appearing at even masses and corresponding in mass to a radical plus a hydrogen atom have appearance potentials only a few tenths of a volt higher than the parent molecular ion. For this reason rearrangement ions cannot always be eliminated from the spectrum. In mixtures of high-molecular-weight hydrocarbons, however, all parent mass peaks of interest are above mass 100, and lower mass fragment peaks can be tolerated.

This technique can be applied to the quantitative analysis of complex mixtures provided a prior separation of compound types has been carried out. Lumpkin has observed that sensitivity factors for many homologous

series of aromatic hydrocarbons can be determined from the sensitivity factor for the initial member of these series (58).

Lumpkin's method of deriving such factors for a homologous series is based on the premises that (1) the sensitivity factors for isomers vary little, and (2) for any structural type they vary directly with reciprocal molecular weight and can be extrapolated to zero sensitivity at infinite molecular weight (58).

Kearns, Maranoski, and Crable (49) extended Lumpkin's original work on aromatics, and these methods have been applied to the aromatic fractions from the neutral oils.

To analyze the tar-acid fraction from the oil, similar information was necessary for the phenolic-type compounds (77, 83).

Therefore, sensitivity factors for phenols, dihydric phenols, alkoxyphenols, indanols,

phenylphenols, acenaphthenols, and naphthols were obtained on a unit (0.001 cm^3) liquid-volume basis (fig. 10). The order of increasing sensitivity for the phenolics is the same as for the corresponding aromatics, determined by Kearns, Maranowski, and Crable (49). These authors also investigated the variation in sensitivity with degree of substitution for alkylbenzenes. The only structural types that have shown a large variation in sensitivity with number of alkyl substituents are alkylbenzenes (49) and alkylphenols. For the bicyclic types, naphthols and indanols, average sensitivity factors permitted determinations to ± 10 to ± 15 percent of the amount present. Considerably less variation with degree of substitution was indicated for compound types having more than two condensed rings.

Variations in sensitivity factor with the number of alkyl substituents on the phenolic ring are shown in figures 11 and 12. Sensitivity factors for the monosubstituted to tetrasubstituted isomeric alkylphenols (molecular weight 150) were obtained from figure 11 and used to derive figure 12. Relative to the sensitivity factor for the monosubstituted phenol, there is a linear relationship between the sensitivity factor and the number of alkyl

substituents on the ring. This behavior also is similar to the result reported by Kearns and coworkers for the alkylbenzenes, and indicates that the appearance potential probably depends more on basic ring structure and alkyl substituents than on the presence of the hydroxyl group (49, 83). As the number of pure phenolic compounds available for calibration is quite limited compared with aromatic hydrocarbons, this correlation is useful for approximating sensitivity factors for certain phenolic types.

The number of substituents per phenolic rings can be determined for the alkylphenols using the same technique reported previously by Kearns and coworkers for alkylbenzenes (49). Tar-acid fractions (80° to 280° C) produced by the hydrogenation of Rock Springs (hvcb) 78 percent carbon coal (maf) in many instances consist primarily of phenols and indanols (fig. 13) (40). As sensitivity factors for the indanols show much less variation with degree of substitution than for the phenols, any large deviation from 100 percent must occur because improper sensitivity factors were applied for the phenols. Correct sensitivity factors can be determined from figure 11, and the average number of substituents per phenolic ring

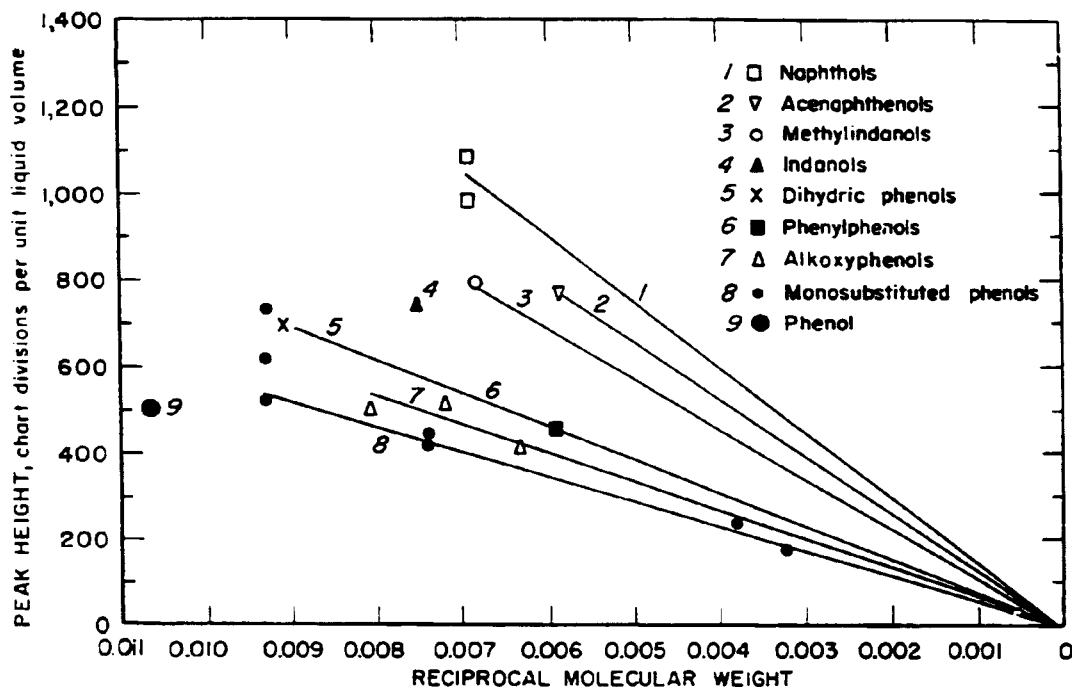


FIGURE 10.—Low-Ionizing-Voltage Sensitivity Data for Phenolic Types.

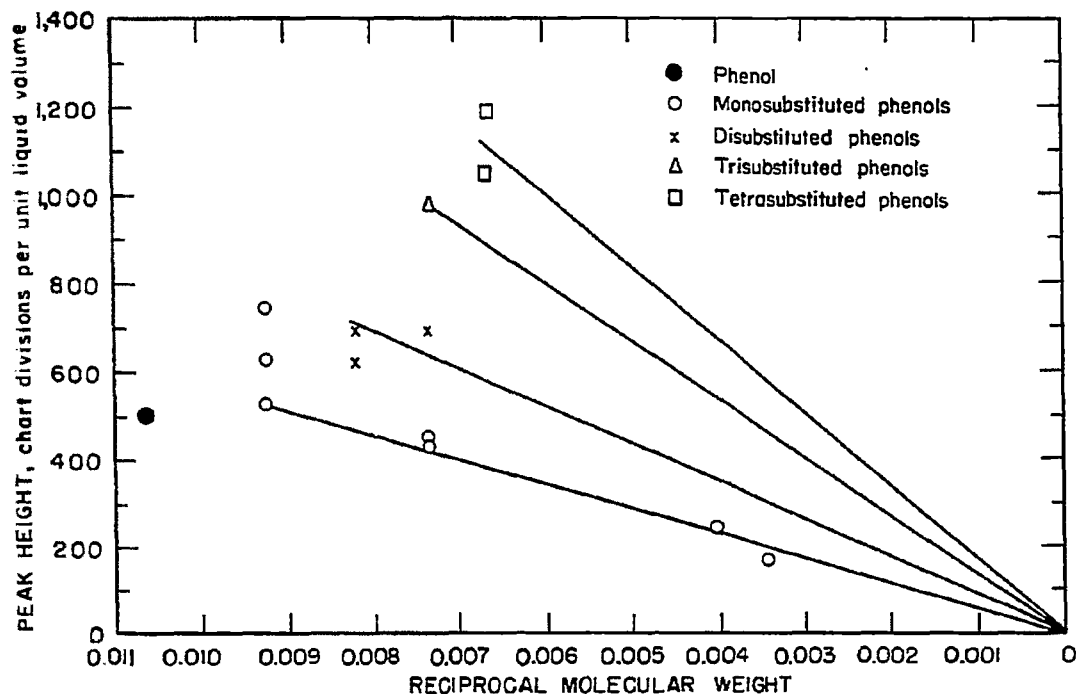


FIGURE 11.—Low-Ionizing-Voltage Sensitivity Data for Alkyl-Substituted Phenols.

can be read directly from figure 12. This method will give a maximum value for the average number of substituents, because sensitivity factors for the other structural types vary slightly, and the values used are possibly low. Application of this method to the above sample gave a value of 2.3 for the average number of substituents.

In determining sensitivity factors, the effect of the position of substituents has also

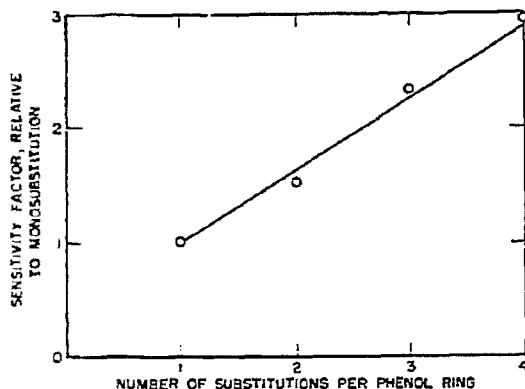


FIGURE 12.—Variation of Sensitivity Factor With Number of Alkyl Substituents on the Phenol Ring.

been investigated. Sensitivity factors determined at low-ionizing voltage for eight methylindanols, obtained from the Coal Tar Research Association, Leeds, England, are shown in table 30. These sensitivity factors can be grouped according to whether the methyl group is on the five- or six-member ring. For the examples available, methyl substitution on the six-member ring yields sensitivity factors approximately 30 percent higher than those for compounds having methyl substitution on the five-member ring. Both 4- and 5-indanols are included. The one exception to the above generalization is 5-methyl-4-indanol.

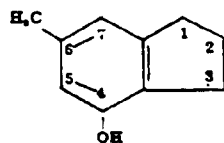
Trimethylsilyl (TMS) ether derivatives were used to verify structural types in the tar-acid fractions (53). Formation of TMS ether derivatives increases the mass of the parent molecule-ion by 72 mass units for each OH group and produces a new series of peaks free from interference by other classes of compounds. Determinations on a synthetic blend of 1- to 4-ring phenolic compounds have shown that the reaction is quantitative (table 31).

The sensitivities of the phenols and their TMS ether derivatives appear to be related (fig. 14). Sensitivity coefficients for the de-

TABLE 30.—Low-ionizing-voltage sensitivity of methylindanols, chart divisions

Compound ¹	Sensitivity/0.001 cm ²
6-Methyl-4-indanol	935
7-Methyl-4-indanol	822
7-Methyl-5-indanol	908
6-Methyl-5-indanol	882
Average	826
Average deviation from the average	=36
2-Methyl-4-indanol	738
1-Methyl-4-indanol	689
1-Methyl-5-indanol	684
5-Methyl-4-indanol	669
Average	695
Average deviation from the average	=22

¹ Example of structure: 6-Methyl-4-indanol:



derivatives are approximately 25 percent lower for 1-ring and 8 percent lower for condensed 2-ring compounds. In many instances, TMS ether derivatives could not be prepared because only limited quantities of the pure phenolic compounds were available. Quantitative data on carbon number distribution were therefore obtained from the spectrum of the original tar-acid fraction unless considerable quantities (>15 percent) of neutral material were indicated in the TMS ether spectrum.

Application of Methods

Coal-tar acids have been separated by several methods including formation of complexes, butylation, differential solubilities, etc. Following a review of existing methods, Dean, White, and McNeil concluded, "No satisfactory systematic method of analyzing coal-tar acids has yet been described" (21).

TABLE 31.—Low-ionizing-voltage analysis of a synthetic blend of phenols, volume-percent

Compound	MS analyses		Synthetic
	As phenols	As trimethylsilyl ether derivatives	
m-Cresol	30.3	28.6	31.2
m-Ethylphenol	22.2	22.1	21.1
3-Ethyl-5-methylphenol	5.9	16.1	5.9
Benzocresol	10.1	12.7	12.1
2-Methylresorcinol	4.7	5.1	5.1
5-Indanol	8.3	7.6	8.2
1-Naphthol	5.7	5.5	5.5
5-Acenaphthenol	11.6	11.2	9.9
m-Phenylphenol			
1-Pyreneol	1.2	1.1	.9

¹ Sensitivity of trimethylsilyl ether based on correlation with phenol sensitivity.

² Both compounds have molecular weight of 170; weighted sensitivity used.

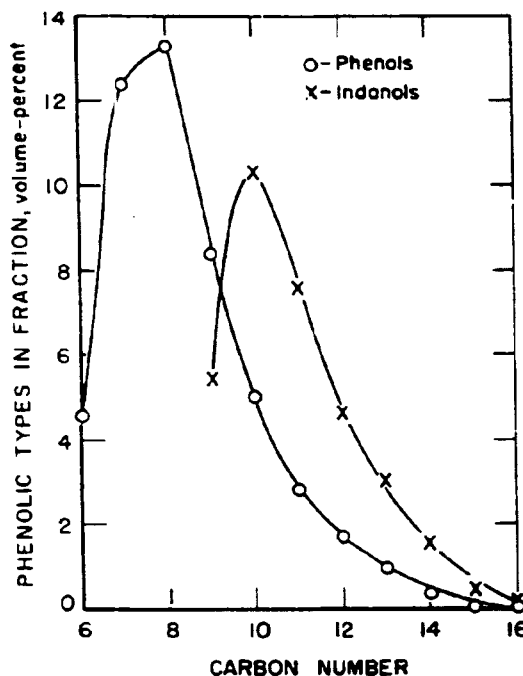


FIGURE 13.—Carbon Number Distribution of Phenols and Indanols in a Tar-Acid Fraction (80° to 280° C).

Characterization of higher boiling neutral oils from coal is equally unsatisfactory with investigations being limited to qualitative determinations or separation of the major components. The low-ionizing-voltage method provides carbon number distribution data—an intermediate step between gross characterization methods (for example, infrared, *n-d-M*) and the determination of individual components.

Tar acids and neutral oils from various coal hydrogenation oils and coal tars have been analyzed by this technique. Examples of the mixtures analyzed and data relating to their origin are given in table 32.

Sample A

In many instances, a quantitative interpretation of the spectrum was not necessary. For example, the extent of dealkylation of a tar-acid fraction (240° to 420° C) from a coal-tar distillate was determined simply from changes in peak intensity ratios. The parent mass peaks corresponded to the following compound types including alkyl derivatives: Phenols, indanols, indenols, naphthols, alkoxyphenols, acenaphthylenols and/or fluorenyls, and acenaphthenols and/or phe-

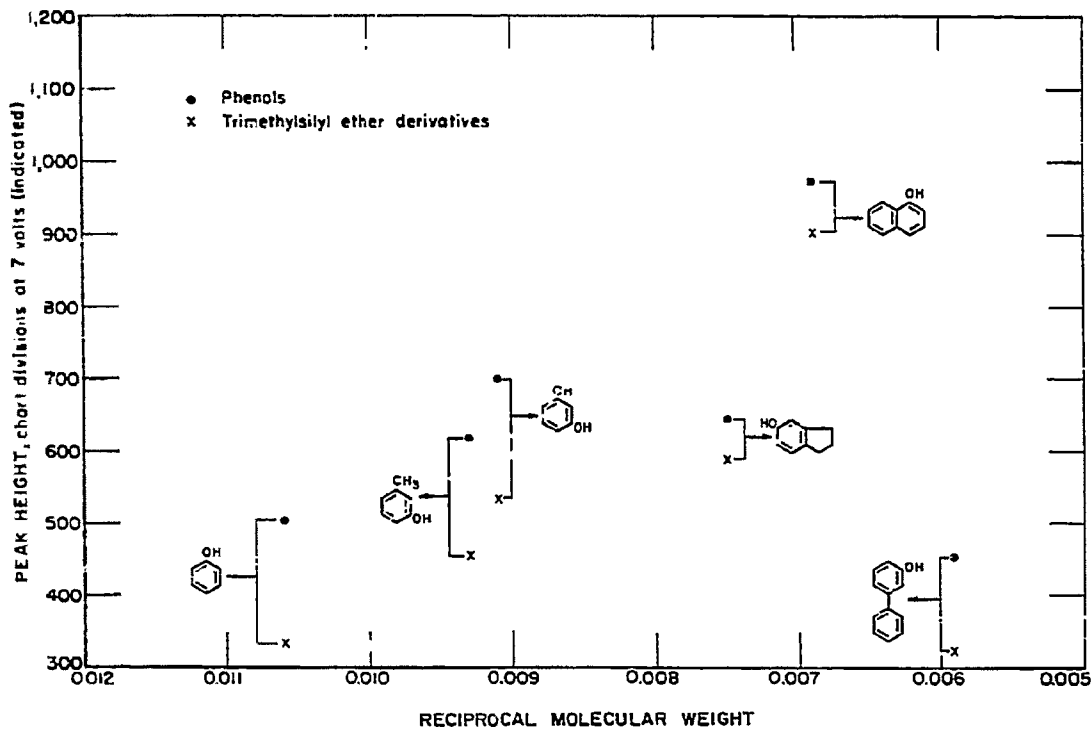


FIGURE 14.—Sensitivities of Phenols and Their Trimethylsilyl Ether Derivatives at Low-Ionizing Voltage.

TABLE 32.—Identification of samples analyzed

Designation in text	Coal	Treatment	Fraction analyzed	Source of material
A	Wyoming hvab.	Low-temperature carbonization; catalytic dealkylation of tar acids.	Tar acids < 420° C.	Bureau of Mines, Morgantown Coal Research Center.
B	British.....	Vertical retort	Tar acids 232° to 278° C.	Reference 21.
C	Texas lignite.	Low-temperature carbonization; tar acid extraction.	Tar acids.	References 8 and 48.
D	Rock Springs, Wyo., hvcb.	Hydrogenation at 465° C and 2000 psig—catalyst, 0.5 percent molybdenum.	Neutral oil, 80° to 280° C.	Bureau of Mines, Pittsburgh Coal Research Center.
E	Blended hvab.	High-temperature tar; hydrogenation at 465° C and 2,000 psig—catalyst, 2.0 percent iron.	Neutral oil, 80° to 280° C.	U.S. Steel Corp., Clairton Works.
F	Blended hvab.	Low-temperature carbonization; hydrogenation at 300° C. and 2,500 psig—catalyst, nickel on kieselguhr.	Neutral oil, 176° to 236° C.	Reference 74.
G	Subbituminous Western.	500° C carbonization.	Neutral oil, 120° to 290° C.	Union Carbide Olefins Co.

nylphenols. Results obtained on the phenols are shown in figure 15. The intensities of the parent masses 94 to 164 were considerably increased after cracking. Also, the maximum peak intensity for the cracked sample occurred one carbon number less than in the spectrum of the original sample. This information was sufficient to enable the course of the catalytic cracking operation to be followed.

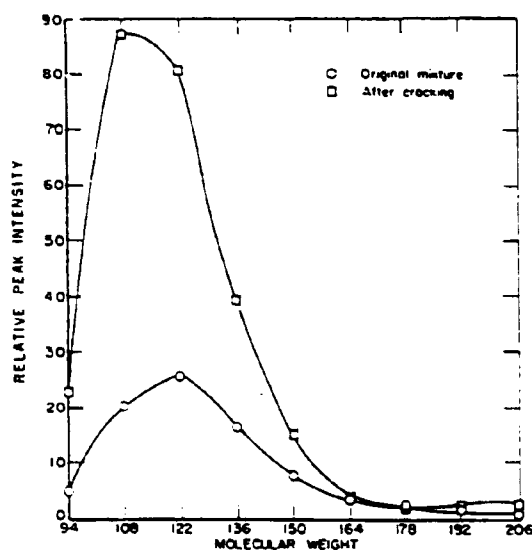


FIGURE 15.—Catalytic Cracking of Phenols From Coal-Tar Distillate as Evidenced by Low-Ionizing-Voltage Mass Spectra.

Sample B

When the desired pure compounds are not available for synthetic mixtures, determinations on samples previously analyzed by other methods are helpful in evaluating a new technique. To compare the total phenol and indanol values at various carbon numbers with values obtained by chemical methods, six fractions of tar acids boiling between 232° and 278°C from a vertical retort operation were obtained from the Coal Tar Research Association. These fractions, containing primarily phenols and indanols, had been analyzed for specific compounds (21). The British data for two fractions shown in table 33 represent sums of values found for specific compounds at a particular carbon number but are not necessarily complete analyses. In general, values obtained by low-ionizing voltage were somewhat higher than those obtained chemically.

TABLE 33.—Analyses of high-boiling tar acids from Coal Tar Research Association (CTRA), Leeds, England, volume-percent

	Mass spectral		CTRA	
	Phenols	Indanols	Phenols	Indanols
FRACTION WITH bp. OF 241.5° TO 244.6° C				
C	0.2			
C ₆	.4			
C ₇	35	22	32	20
C ₈	34	5.5	13	
C ₉	3.3	.3		
C ₁₀	.3	.08		
FRACTION WITH bp. OF 247.5° TO 249.8° C				
C	0.1			
C ₆	.2			
C ₇	10	21	16	20
C ₈	43	17	21	20
C ₉	4.7	3.1		
C ₁₀	.8	.2		
C ₁₁	.1	.07		

Sample C

A quantitative analysis of a tar-acid fraction from low-temperature tar derived from lignite is shown in table 34 (8, 48). This sample contained a larger variety of phenolics than the coal-hydrogenation product and illustrates a broader application of the method. Six of the seven structural types showed one well-defined maximum; the series of dihydric phenols showed two, possibly because of the presence of anthrols and/or phenanthrols which occur at the same parent mass series as the dihydrics above mass 194. Approximately 83 percent of the tar-acid fraction consisted of compounds with 6 to 22 carbon atoms. This total appears reasonable as some neutral material probably remained in the sample. The data were verified by a spectrum of the trimethylsilyl ether derivatives.

Analysis of Neutral Oils Derived From Coal Sample D

Table 35 shows the analysis of a sample consisting primarily of neutral oil, obtained by blending fractions of coal-hydrogenation oil (80° to 280° C) as a preliminary step in preparing a jet fuel. Carbon number distribution data for the following compound types including alkyl derivatives are shown in figure 16: Benzenes, indans, and phenols. Further hydrogenation to convert aromatics to naphthenes, as described by Schlesinger and coworkers (74), is required for this material to meet JP-4 jet fuel specifications.

Sample E

Data on distillable neutral oil (80° to 280° C) obtained from hydrogenated high-temperature tar are shown in table 36. This material was prepared by a single pass hy-

TABLE 34.—Mass spectral analysis of methanol-extract of low-temperature tar from Texas lignite, volume-percent

	Compound types and alkyl derivatives						
	Phenols	Dihydricphenols	Indenols	Indanols	Naphthols	Acenaphthenols	Acenaphthylenols
1	3.7	0.4					
2	2.4	.5					
3	7.7	1.0					
4	4.4	1.0					
5	1.7	.5	2.0	0.9			
6	1.3	.5	2.5	2.8			
7	1.4	.5	1.8	2.5	1.8		
8	1.0	.8	1.1	1.6	2.2	0.2	0.1
9	.6	1.0	.8	.8	1.5	.7	.5
10	.5	.8	.7	.8	.5	1.3	.9
11	.5	.5	.5	.5	.5	1.3	1.0
12	.5	.4	.4	.4	.5	.8	.8
13	.5	.4	.4	.4	.5	.5	.5
14	.5	.4	.4	.4	.5	.4	.5
15	.5	.4	.4	.4	.5	.4	.5
16	.5	.4	.4	.4	.5	.4	.5
17	.5	.4	.4	.4	.5	.4	.5
18	.5	.4	.4	.4	.5	.4	.5
19	.5	.4	.4	.4	.5	.4	.5
20	.5	.4	.4	.4	.5	.4	.5
21	.5	.4	.4	.4	.5	.4	.5
22	.5	.4	.4	.4	.5	.4	.5
23	.5	.4	.4	.4	.5	.4	.5
24	.5	.4	.4	.4	.5	.4	.5
25	.5	.4	.4	.4	.5	.4	.5
26	.5	.4	.4	.4	.5	.4	.5
27	.5	.4	.4	.4	.5	.4	.5
28	.5	.4	.4	.4	.5	.4	.5
29	.5	.4	.4	.4	.5	.4	.5
30	.5	.4	.4	.4	.5	.4	.5
31	.5	.4	.4	.4	.5	.4	.5
32	.5	.4	.4	.4	.5	.4	.5
33	.5	.4	.4	.4	.5	.4	.5
34	.5	.4	.4	.4	.5	.4	.5
35	.5	.4	.4	.4	.5	.4	.5
36	.5	.4	.4	.4	.5	.4	.5
37	.5	.4	.4	.4	.5	.4	.5
38	.5	.4	.4	.4	.5	.4	.5
39	.5	.4	.4	.4	.5	.4	.5
40	.5	.4	.4	.4	.5	.4	.5
41	.5	.4	.4	.4	.5	.4	.5
42	.5	.4	.4	.4	.5	.4	.5
43	.5	.4	.4	.4	.5	.4	.5
44	.5	.4	.4	.4	.5	.4	.5
45	.5	.4	.4	.4	.5	.4	.5
46	.5	.4	.4	.4	.5	.4	.5
47	.5	.4	.4	.4	.5	.4	.5
48	.5	.4	.4	.4	.5	.4	.5
49	.5	.4	.4	.4	.5	.4	.5
50	.5	.4	.4	.4	.5	.4	.5
Total ¹	31.8	7.9	10.9	12.7	9.0	5.6	5.0

¹ Grand total, 82.9 volume-percent.

drogenation of top tar at 3,000 psig and 465° C. The aromatic portion, comprising 97 percent of the neutral oil, was analyzed both by low-ionizing voltage and conventional type-analysis. The type-analysis was based on a variation of the method described by Lumpkin (58). Results of the low-ionizing-voltage analysis are shown as summations of the various values obtained at each carbon number. The results compared favorably, with the exception of the indenenes. These deviations possibly arise from contributions to the spectrum by the additional structural types indicated in the low-voltage analysis including phenylnaphthalenes and/or methyl-enphenanthrenes and pyrenes and/or fluor-

anthenes. Sensitivity factors for the type-analyses were based on total ionization techniques and should be quite accurate. The analysis by low-ionizing voltage totaled 101.3 percent before normalization, indicating that reasonable sensitivities were used. Although the analysis of this complex mixture cannot be confirmed by other instrumental or chemical methods, agreement between the two mass spectrometric methods indicates the data are valid.

Sample F

As a further application of the technique to neutral oil, three fractions (bp 176° to 236° C) of saturated hydrocarbons produced by hydrogenation of low-temperature tar were analyzed (74). These samples were also of interest because of their possible application as jet fuels. The type-analysis (table 37) indicates the samples consist primarily (~95 percent) of condensed and noncondensed cycloparaffins. The relative amounts of condensed and noncondensed structures were determined and also the ratio of the C₅ to C₆ rings for the noncondensed structures. Carbon number distributions for the cycloparaffins are first approximations as only limited

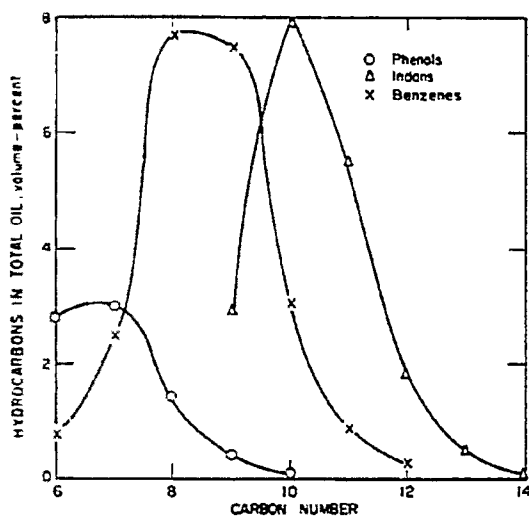


FIGURE 16.—Carbon Number Distribution of Phenols, Indans, and Benzenes in Blended Fractions (80° to 280° C) of a Coal-Hydrogenation Oil.

TABLE 35.—Mass spectral analysis of a coal-hydrogenation oil, volume-percent

Compound type, including alkyl derivatives	Coal-hydrogenation oil
Indans, tetralins	19.0
Benzenes	23.1
Paraffins	16.7
Noncondensed cycloparaffins	22.5
Condensed cycloparaffins	4.0
Naphthalenes	3.7
Olefins	2.0
Indenes	.7
Acenaphthenes	.5
Phenols	7.8

TABLE 36.—Mass spectral analysis of distillable neutral oil from hydrogenation of a high-temperature tar, volume-percent

Compound type, including alkyl derivatives	Low-voltage analysis	Type-analysis
Benzene	18.1	9.1
Indane, tetraline	10.6	12.9
Naphthalenes	28.1	22.2
Acenaphthylene, fluorene	14.0	13.3
Acenaphthene, biphenyls	18.7	24.2
Phenanthrenes, anthracene	8.8	8.2
Indenes	5.7	10.1
Phenylanthracene, methylphenanthrenes ¹	5.4	
Pyrene, fluoranthene ²	.6	

¹ Average of disubstitution assumed.

² Identification not certain; not included in type-analysis matrix.

calibration data are available. For the samples shown in table 37, values above 10 percent are probably good to ± 10 percent of the amount shown. Below 10 percent, values could be in error as much as ± 50 percent. The fractions show a progressive increase in the carbon number at which maximum concentration occurs.

TABLE 37.—Mass spectral analysis of saturated neutral oils produced by hydrogenation of low-temperature tar, volume-percent

Boiling range, °C	Type-analysis				Low-voltage analysis, total condensed and noncondensed cycloparaffins						
	Naphthalene	Noncondensed cycloparaffins		Condensed cycloparaffins	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆
		Total	Ratio, C ₃ /C ₆ rings								
175-198	0.4	47	4.9	51	25	60	12				
203-224	Trace	28	1.8	67	1	28	60	6			
217-236	Trace	20	1.5	77			5	42	32	13	4

ues based on mass spectrometric data for average molecular weight, total rings per molecule (R_T), aromatic rings per molecule (R_A), double bonds per molecule ($N^=$), and the atom ratio (H/C) is given in table 38. Reasonable agreement is shown in these data indicating the validity of the mass spectrometric method.

TABLE 38.—Analysis of 120° to 290° C fraction of neutral oil from carbonization of subbituminous Western coal at 500° C. Comparison of n-d-M and mass spectral results

	Union Carbide—n-d-M method	Bureau of Mines—MS analysis
Average molecular weight	1152 \pm 3	156
R _T (total rings/molecule)	1.29	1.05
R _A (aromatic rings/molecule)	.69	.60
N ⁼ (double bonds/molecule)	.38	.39
H/C (atom ratio)	1.52	1.51
Ultimate	1.48 \pm .03	

¹ Determined from boiling range.

² Cycloparaffins considered as all single ring; minimum.

³ Half of olefins considered as containing 2 double bonds.

Sample G

A sample of neutral oil (bp 120° to 290° C) from the carbonization at 500° C of a subbituminous western coal was obtained from the Union Carbide Olefins Co. This sample had been subjected to extensive investigation including the determination of physical properties, FIA analysis, n-d-M calculations, etc. The Bureau of Mines FIA analysis agrees quite well with the estimated percentages given by Union Carbide as shown in table 38. Table 39 shows type-analyses for the compound types in the three fractions. Analysis of the olefinic fraction, after hydrogenation, indicated this fraction consisted of approximately 10 percent cyclic structures.

The 12 homologous series can be associated with the compound types shown in table 40 and complete carbon number distribution data for these structural types are given in table 40. Carbon numbers of the various components range from C₆ to C₁₃. Approximately 2 percent of tar acids remained in this neutral oil. A comparison of calculated val-

TABLE 39.—Mass spectral analysis of 120° to 290° C fraction of neutral oil from carbonization of subbituminous Western coal at 500° C, volume-percent

Compound type, including alkyl derivatives ¹	Bureau of Mines analysis		Union Carbide estimate
	MS	FIA	
Saturates:			
Paraffins	12.6	16.4	17
Noncondensed cycloparaffins	3.2		
Condensed cycloparaffins	.6		
Olefins:			
Olefins and diolefins	19.2	21.5	25 \pm 5
Cycloolefins	2.3		
Aromatics:			
Unsaturated aromatics (isdenes)	7.1	62.1	58 \pm 5
Alkylbenzenes	23.4		
Acenaphthene and/or diphenyls	2.8		
Naphthalenes	14.8		
Indane, and/or tetralins	12.0		
Phenols, monohydric and dihydric	2.0		

¹ Possibly up to 8 percent of molecules containing N, S, or O, other than phenols, are not identified. Probably distributed among aromatic and olefinic types.

A minimum of 77 components is indicated in this mixture, and since the method does not determine individual isomers or various structural types having identical molecular weights, the actual number is probably many times this figure.

SPECIAL ANALYTICAL TECHNIQUES

Mass spectrometer analyses of certain types of compounds present unique problems. These problems arise from (1) similarity of mass spectra, (2) chemical reactivity, (3) adsorption in the mass spectrometer, (4) trace impurities in calibration compounds, (5) the need for very accurate analyses of trace components in the presence of interfering compounds, etc.

The similarity of mass spectra of various hydrocarbons is both an advantage and a disadvantage analytically. Type-analyses have been devised based on these similarities and, where only general information is required, these data are usually sufficient. However, for product characterization, values for individual components are desirable. Two approaches were used to reduce spectral interferences, separation by molecular sieves and reactions to form noninterfering species.

The ratio of branched to normal hydrocarbons from C_{11} through C_{18} in the Fischer-Tropsch product was determined for each carbon number using molecular sieve techniques to separate the normal hydrocarbons from the remainder of the hydrogenated product (68, 79). A different approach was

used to determine the ratio of branched to normal hydrocarbons in the charcoal trap product of the Fischer-Tropsch synthesis. A hydrochlorination reaction was applied in determining the isobutene and isopentene in this synthesis product (63).

Chemical reactivity difficulties arise when material present in the mass spectrometer inlet system is attacked by compounds such as nitrogen dioxide. Conditioning procedures were devised to permit analyses for oxides of nitrogen (33).

Adsorption in the mass spectrometer inlet system is responsible for the difficulty in analyzing for hydrogen sulfide and for vapor-phase water. Procedures to minimize this effect were devised.

The presence of trace impurities in calibration standards is of paramount importance in certain analytical problems. The accuracy of the calculation of equilibrium constants for the reaction of $H_2 + D_2 \rightleftharpoons 2HD$ is dependent on knowledge of the spectra of each of these gases and the purity of the calibration materials. The mass spectrum of hydrogen deuteride was obtained and the equilibrium constants calculated (31).

Mass Spectrometric Determination of the Ratio of Branched to Normal Hydrocarbons Up to C_{18} in Fischer-Tropsch Product

The Fischer-Tropsch synthesis is being investigated by the Bureau of Mines as a means of converting coal to hydrocarbons. Gaseous

TABLE 40.—Mass spectral carbon number distribution data for neutral oil (bp 120° to 290° C) from the 500° C carbonization of a subbituminous Western coal, volume-percent

	$C_nH_{2n+2}O_y$											
	0 -6	0 -8	0 -10	0 -12	0 -14	0 -16	0 -18	0 -20	0 -22	0 -24	0 -26	0 -28
	Benzenes	Indans and/or tetralins	Indenes and/or dihydronaphthalenes	Naphthalenes	Acenaphthenes and/or diphenyls	Fluorenes and/or acenaphthylenes	Paraffins	Monocyclics and diocyclics	Cycloolefins	Naphthalenes	Phenols	Dihydric phenols and/or alkoxyphenols
C ₇	0.1							0.3				0.1
C ₈	5.2							1.0				1.0
C ₉	5.1	0.3					0.5	1.9			0.1	1.1
C ₁₀	4.4	1.5	0.1				1.5	3.8			1.5	
C ₁₁	22.7	5.4	1.3				1.1	6.6			1.5	
C ₁₂	12.0	3.4	1.1	1.2			1.6	3.1			1.1	
C ₁₃	1.6	5.4	1.1	3.5	0.3		1.6	1.6			1.1	
C ₁₄	1.2	1.3	1.1	1.9	1.1	0.3	1.1	1.1			1.1	
C ₁₅	3.5	3.9	1.4	1.7	1.1	1.1	1.7	1.1			1.1	
C ₁₆	3	1	1.4	1.1	1.1	1.1	1.5	1.3			1.1	
C ₁₇							1.3					
C ₁₈							1					
Total	23.4	12.0	6.3	14.9	2.8	0.8	12.6	19.2	2.3	3.8	1.4	0.6

and liquid hydrocarbons from the Fischer-Tropsch synthesis have been studied by several investigators including Anderson, Friedel, and Storch (3); Weitkamp, Seelig, Bowman, and Cady (94); Bruner (15); and Gall and Kipping (38). While carbon number distribution data for the hydrocarbons have in certain instances been obtained up to C_{20} , information concerning the ratio of branched to normal hydrocarbons in Fischer-Tropsch product is not available above C_6 . The desired information can be obtained for the paraffins plus olefins in the product if hydrogenated material is analyzed. The purpose of this investigation was to derive methods for determining carbon number distribution data, and the ratio of branched to normal paraffins, in hydrogenated fractions of Fischer-Tropsch synthesis product.

Theoretical chain branching schemes for the hydrocarbons in Fischer-Tropsch product have been proposed by Anderson, Friedel, and Storch and others (3, 28, 95-96). The carbon number distribution for the hydrocarbons is also predicted by these schemes. Previous investigations have shown that these chain branching schemes adequately describe the synthesis product up to C_6 (3). For these comparisons, the individual isomers for the C_7 to C_8 hydrocarbons were determined.

Several mass spectrometric methods for determining the ratio of branched to normal paraffins have been described. In all of these methods, certain assumptions have been made concerning fragmentation patterns and sensitivity factors for the branched paraffins. In the first investigation of this type, O'Neal and Wier assumed that the pure compound, 3-ethyl tetracosane, was representative of the isoalkanes in petroleum waxes (69). Brown, Skahan, Cirillo, and Melpolder "felt that an average isoparaffin would dissociate so as to lose 43 mass units," and, therefore, used peaks corresponding to (molecular weight -43 mass units) for isoparaffin determinations (13). Ferguson and Howard described a method for determining the iso-to-normal paraffin ratio in gasoline-range petroleum (25). The same authors used thermodynamic equilibrium data of Prosen, Pitzer, and Rossini to weight individual C_6 to C_8 isoparaffins and obtain representative sensitivity factors at each of these carbon numbers (71). Using molecular sieve techniques, average isoparaffin sensitivities were also obtained for the C_9 to C_{11} paraffins in representative gasolines. In this instance, Ferguson and Howard had to assume that a representative fraction of isoparaffins was obtained by the molecular sieve technique, because very few

pure isoparaffins above C_{10} are available for synthetic blend determinations.

O'Connor and Norris described a complete analytical scheme for characterizing the compound types in the light-gas oil (100° to 650°) fraction of petroleum (68). Molecular sieves were used in determining total percentages of normal paraffins and straight-chain olefins; however, carbon number distribution data were not obtained. Excellent results were reported on synthetic blends prepared from the limited number of pure compounds available. For the isoparaffins, 2-methyldecane was the highest molecular weight compound included in the blends. Using their method, n-pentane must be refluxed through the sieves for approximately 100 hours if the normal paraffins up to C_{22} are desired for a carbon number distribution determination by gas chromatography or other method.

Branched-chain hydrocarbons in Fischer-Tropsch synthesis product consist primarily of mono-substituted and dimethyl-substituted compounds. While this mixture is less complex than that found in petroleum, the methyl branched compounds, particularly those having methyl branching near one end of the alkyl chain, should cause the most difficulty with separations by molecular sieve material. In the present investigation, molecular sieve techniques were used to obtain the ratio of branched to normal paraffins in the range C_{11} to C_{14} in hydrogenated fractions of Fischer-Tropsch product. The product was produced at 265° C using an ammonia synthesis catalyst composed of Fe_3O_4 , MgO, and K_2O . The synthesis was carried out with $1H_2$ -to-1CO gas at 21.4 atmospheres. After hydrogenation and removal of the oxygenates, the remaining product consisted of the same major types of hydrocarbons found in petroleum: Paraffins, naphthenes, and monoaromatics. Information derived from this investigation concerning the use of molecular sieves should therefore be applicable to liquid fractions of petroleum origin. While the purpose of this investigation was to determine the adequacy of the chain branching schemes in describing the distribution of C_{10} to C_{20} synthesis product, agreement between theoretical and experimental data also indicates the validity of molecular sieve separation in this range.

Experimental Procedure

Separation and Sample Preparation.—Fractions of the product investigated boiled in the ranges 170° to 323° C, 323° to 390° C, and $>390^\circ$ C residue. This included all paraffins and olefins having more than 10

carbons. The 323° to 390° C fraction was intermediate between the liquid and residue product and was the smallest of the three fractions. The flow diagram, figure 17, gives the sample handling and preparation for

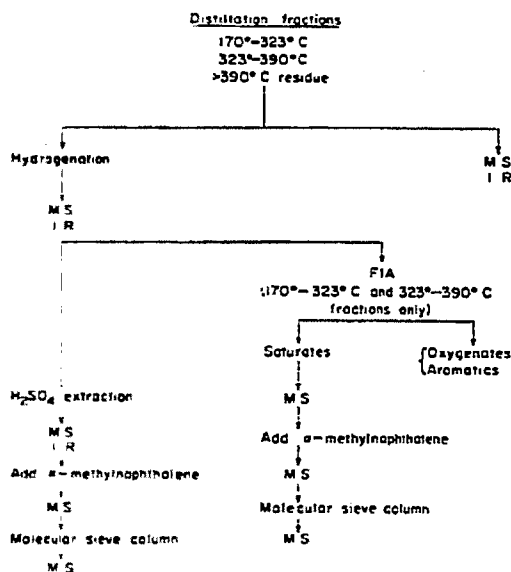


FIGURE 17.—Separation and Analysis of $>170^{\circ}$ C Fraction of Fischer-Tropsch Synthesis Product.

the spectrometric investigation. Hydrogenation was carried out at 185° C for about 16 hours on Raney nickel catalyst. The three fractions were then investigated by infrared and found to be free of olefins. Oxygenated material was removed from the three fractions by sulfuric acid extraction, and infrared (IR) determinations showed these samples were free of hydroxyl and carbonyl groups. The fluorescent indicator adsorption technique (FIA) was also applied to a portion of the 170° to 323° C and 323° to 390° C fractions after hydrogenation. Drop quantities of the saturates were collected from the FIA for spectrometric investigation. Results obtained by this separation method were consistent with those from the acid extraction technique.

Carbon number distribution data were then obtained for the paraffinic hydrocarbons in all three fractions. Prior to molecular sieve separation, approximately 10 percent by volume of α -methylnaphthalene was added as an internal standard to a portion of the saturate concentrate collected from FIA. Removal of normal paraffins by the molecular sieves re-

sulted in a reduction in parent peak intensities. Thus, comparison of mass spectra obtained before and after sieve treatment, following adjustment to bring internal standard peaks to the same intensity, permitted determinations for normal and branched paraffins.

Mass Spectrometric Calibration Data.—Mass ions corresponding to the molecular weights of the paraffins were used. Appropriate calibration data covering the mass range of interest were needed for both the normal and branched-chain paraffinic structures (fig. 18). As pure normal paraffins are available to C_{30} , data were easily obtained for the normal compounds (curve 1). The problem with the branched compounds consisted not only of obtaining the proper pure compounds (very few available above C_9) but also of weighting the calibration data. Two approaches were used to determine the sensitivities shown in figure 18: (1) The branched components in hydrogenated Fischer-Tropsch product were isolated by distillation and molecular sieve techniques and sensitivities for the total branched paraffins C_{10} to C_{20} determined from actual product (curve 4); data from fractions of branched paraffins consisting primarily of single carbon numbers, C_{11} to C_{14} , were combined with data from a broader fraction in establishing curve 4; (2) Sensitivity factors based on data for the mono-substituted and dimethyl-substituted compounds, major components in Fischer-Tropsch product, were extrapolated from C_9 and lower carbon numbers (curve 3). Good agreement is shown between sensitivity factors obtained by the two methods. More highly branched compounds having lower sensitivity factors were not considered in deriving curve 3. It is therefore reasonable that curve 4 gives slightly lower sensitivity factors than curve 3. Theoretical weighting factors for combining normal and total branched paraffins were used in obtaining sensitivities for the total paraffin at each carbon number (curve 2) (3).

Molecular Sieve Technique.—Three molecular sieve techniques were investigated: (1) Simple mixing of the sample and sieve material (56); (2) the vacuum evaporation method developed by Nelson, Grimes, and Heinrich (66); and (3) an elution technique developed by O'Connor and Norris (68). The elution technique gave a better separation of normal and branched components (above C_{10}) in synthetic mixtures and was therefore used in characterizing the 170° to 323° C and 323° to 390° C fractions.

Briefly, the technique is as follows. Be-

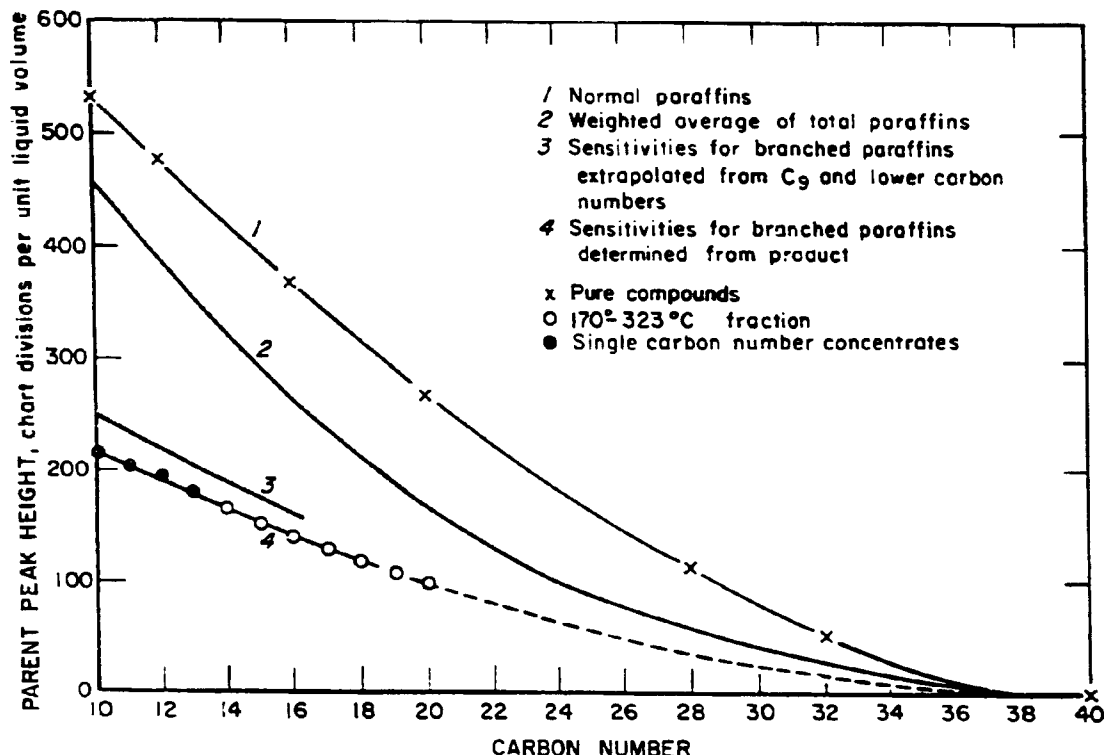


FIGURE 18.—Sensitivity Data for Paraffins in Fischer-Tropsch Product.

tween 0.2 and 0.5 ml of sample containing about 10 percent by volume of α -methylnaphthalene is charged to the column, followed by approximately 8 ml of isopentane that has previously been put through a molecular sieve column to remove any traces of normal components. The material collected is then stripped of most of the isopentane—with approximately 25 percent isopentane remaining in the final mixture. Recovery of the normal components from the sieve material is not necessary, as changes in the intensities of the molecular ions and internal standard after sieve treatment can be used to calculate the normal paraffins.

Synthetic mixtures were prepared to determine whether (1) molecular sieves are effective in removing normal paraffins from actual Fischer-Tropsch product, and/or (2) during the stripping operation only isopentane and not portions of the sample or internal standard are removed. A blend was prepared consisting of approximately 40 percent n -C₁₆ and the remainder 170° to 323° C product. The n -C₁₆ was completely removed by sieve treatment. A second mixture was prepared consisting of 0.3 ml of 170° to 323°

C product (including approximately 10 percent α -methylnaphthalene as internal standard) and 8 ml of isopentane. After stripping the isopentane, the same mass spectrum was obtained as before addition of the isopentane.

Results

A summary of the carbon number distribution data for the three fractions is shown in table 41. Paraffin-naphthene type-analysis results for total percentages of these two structural types are also given (29). The naphthene content is ~2 percent in the first two fractions and then rises to 16 percent in the >390° C residue. Values for the oxygenates were obtained by summing the infrared functional group determinations for the hydroxyl and carbonyl group containing compounds. In these fractions of hydrogenated product there is a trend toward increased oxygenate and decreased paraffin content with increasing carbon number. Determinations on the >390° C residue were made to C₃₅, the highest carbon number with readable peaks. The composite analysis of the total (last column) was based on a summation

TABLE 41.—Carbon number distribution for paraffins in hydrogenated fractions of Fischer-Tropsch product, volume-percent

	Boiling range, °C			Composite ¹ boiling at >170° C
	170° to 323° C	323° to 390° C	>390° C	
Fraction of total boiling at >170° C.....	36.8	13.3	49.9	100
Oxygenates.....	20.6	35.8	34.6	29.6
Naphthenes.....	2.4	1.6	16.4	9.3
Paraffins.....	77.0	62.6	49.0	61.1

DISTRIBUTION FOR PARAFFINS

C ₉	3.7			21.5
C ₁₀	12.1			4.9
C ₁₁	11.7			4.7
C ₁₂	11.1	0.2		4.3
C ₁₃	10.3	.28		4.0
C ₁₄	8.9	1.3		3.6
C ₁₅	7.0	3.4		3.2
C ₁₆	4.8	6.3		2.7
C ₁₇	2.9	8.4		2.3
C ₁₈	1.8	9.7		2.1
C ₁₉	1.1	9.4	0.25	1.9
C ₂₀71	8.1	.79	1.8
C ₂₁43	6.0	1.5	1.7
C ₂₂27	3.9	2.1	1.6
C ₂₃20	2.7	2.7	1.7
C ₂₄		1.5	2.9	1.6
C ₂₅		1.1	3.1	1.4
C ₂₆50	3.1	1.5
C ₂₇			3.1	1.4
C ₂₈			3.2	1.4
C ₂₉			3.0	1.4
C ₃₀			2.7	1.3
C ₃₁			2.3	1.0
C ₃₂			2.3	0.90
C ₃₃			1.9	.80
C ₃₄			1.8	.82
C ₃₅			1.4	.63
C ₃₆			1.5	.60
C ₃₇			1.4	.50
Aromatics and higher molecular weight paraffins.....			3.0	3.9

¹ Determined from peak summations, based on volume fractions.² Not total C₂₉; lower boiling fraction contained C₉ but not C₁₁.

of peak intensities in the three fractions, weighted according to the volume fraction of each, rather than a summation of percentages shown for the three fractions. This was done to eliminate any errors that might occur by applying weighted sensitivity factors if either branched or normal material was concentrated in the low- or high-boiling ends of the fractions. Figure 19 shows the volume-percent of paraffin at each carbon number from C₁₁ to C₃₄ for the hydrogenated product. Values from C₂₂ to C₃₀ are quite similar.

Table 42 shows a summary of the determinations for normal paraffins from C₁₁ through C₁₈ using molecular sieve separations. Predicted values according to the chain growth scheme of Anderson, Friedel, and Storch (discussed later) are also shown (3).

The carbon number distribution for normal paraffins in the 170° to 323° C fraction was also determined by an independent mass spectrometric method (courtesy, Atlantic Re-

TABLE 42.—Determination of n-paraffins in hydrogenated Fischer-Tropsch synthesis product, bp >170° C, volume-percent

	Total paraffin at each carbon number appearing as n-paraffin	
	Experimental	Predicted ¹
C ₁₁	74.1	71.3
C ₁₂	70.2	68.4
C ₁₃	65.6	65.7
C ₁₄	62.1	63.1
C ₁₅	58.2	60.6
C ₁₆	54.0	58.2
C ₁₇	50.7	55.9
C ₁₈	47.9	53.8

¹ Reference 3.

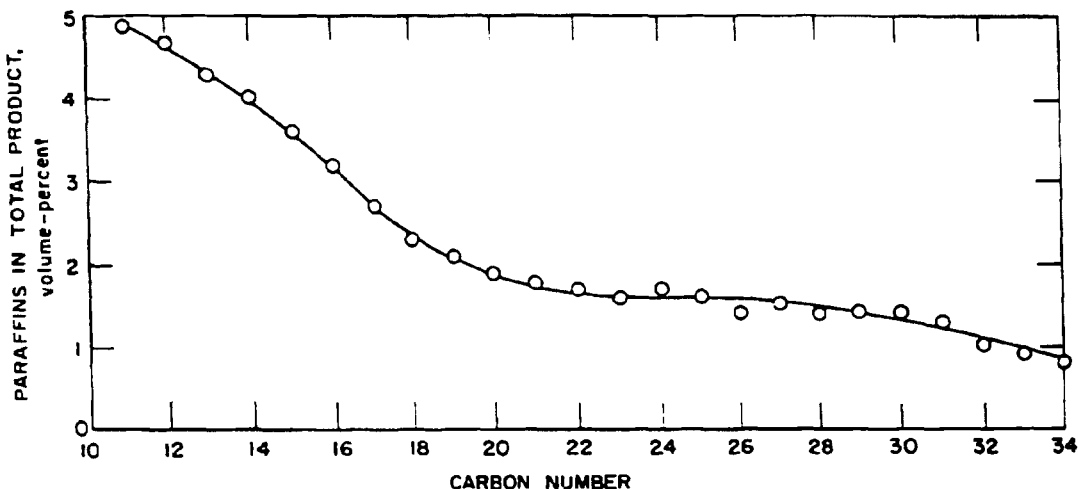


FIGURE 19.—Carbon Number Distribution for Paraffins in Hydrogenated Fischer-Tropsch Product, bp >170° C.

fining Research Laboratory). This method is based on a matrix operation involving over 700 coefficients (13).

TABLE 43.—Distribution of normal paraffins in 170° to 323° C fraction of Fischer-Tropsch synthesis product, volume-percent

	Molecular sieve MS analysis	MS matrix calculation ¹
C	1.6	1.6
CC	3.2	3.2
CCC	13.2	13.0
CCCC	11.3	10.5
CCCCC	10.6	9.2
CCCCCC	9.1	8.4
CCCCCCC	7.3	7.6
CCCCCCCC	5.3	5.8
CCCCCCCCC	3.5	4.0
CCCCCCCCCC	2.0	2.8
CCCCCCCCCC	1.2	1.9
CCCCCCCCCC	.7	1.0

¹ Courtesy Atlantic Refining Co., reference 13.

Results shown in table 43 are in good agreement considering the complexity of the mixture. For normal paraffins >5 percent, values obtained by the two methods show differences of less than 15 percent of the amount present.

Discussion of Results

Anderson, Friedel, and Storch derived the following expression to describe the carbon number distribution for Fischer-Tropsch product (3):

$$\phi = kF_n a^{n-2} \quad (1)$$

or

$$\log(\phi_n/F_n) = n \log a + \log(k/a^2) \quad (2)$$

where ϕ_n = number of moles containing (n) carbon atoms,

F_n is a function of (f), a constant representative of the extent of branching, and (k) and (a) are constants.

As a plot of $\log(\phi_n/F_n)$ versus (n) should be linear (equation 2), this expression can be used to examine experimental data. Figure 20 shows the agreement between the present data for total paraffins and predicted values based on a branching factor $f=0.045$.

Values for normal paraffins determined in this investigation by the combined molecular sieve-mass spectrometric technique agree with the isomer distribution predicted by Anderson, Friedel, and Storch. Determinations made by an independent method (table 43) also support the validity of molecular sieve separations for paraffins to approximately C₂₀. Predicted values for the normal paraffins shown in table 42 are based on a chain growth calculation that considers only monomethyl and dimethyl branched isomers (8). The calculation of the total branched paraffin at each carbon number above C₃ is not feasible using methods described in the literature. Contributions by other branched structures will result in the predicted value for the total branched paraffins being low and the normal isomers high. However, branched paraffins other than monomethyl or dimethyl have been found only as minor components (total <0.5 percent for C₆) in previous investigations (94). The trend for predicted values for the normal paraffins to be increasingly larger than the experimental values, from C₁₄ to C₁₈ (table 42), possibly indicates that contributions from the other branched isomers become significant at higher carbon numbers.

Results obtained on Fischer-Tropsch product produced at 265° C with an iron catalyst are also consistent with results reported by Gall and Kipping under similar synthesis conditions (38). Gall and Kipping found in

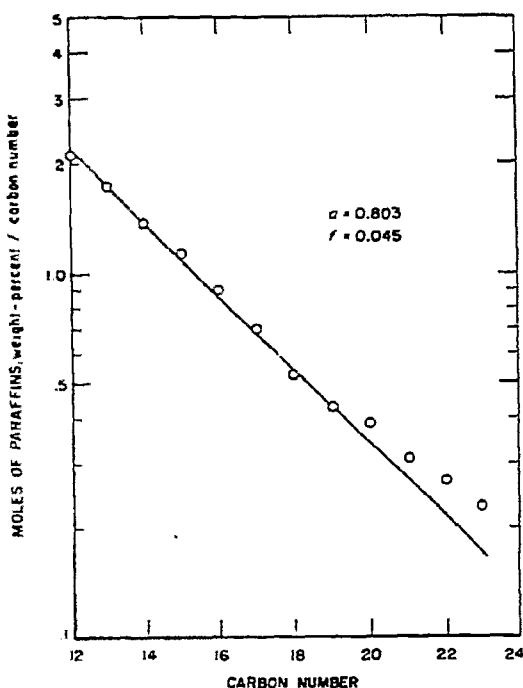


FIGURE 20.—Predicted Values for Carbon Number Distribution of Paraffins in Hydrogenated Fischer-Tropsch Products, bp >170° C.

their study of the C₅ to C₈ paraffinic fraction of synthesis product that the proportion of branched-chain isomers increases regularly with synthesis temperature; that is, the (f) factor increases with increasing synthesis temperature. Extrapolating the C₅ to C₈ data obtained by Gall and Kipping to higher carbon numbers (fig. 21) indicates that, for 265° C operation, the paraffin fraction should consist of approximately 64 percent normal paraffins at C₁₄. The present investigation gave a value of 62 percent normal paraffin at C₁₄.

For product obtained with an iron catalyst, Anderson and coworkers have shown that predicted values for isomer distribution, using a branching factor of 0.115, show excellent agreement with their experimental values. However, the experimental data of Weitkamp (94) and Bruner (15) used for this comparison were obtained under high-temperature-synthesis conditions. The product with which Weitkamp dealt was produced at 315° C, and the product Bruner analyzed is described as being produced between 290° and 370° C. These data from high-temperature operations are also consistent with the data Gall and Kipping obtained at 315° C (fig. 21). The carbon number distribution data, and also the ratio of branched to normal hydrocarbons determined 10 carbon numbers higher than in previous investigations, tend to support the work of Gall and Kipping in the temperature variation of isomer distribution.

Data shown in figure 20 imply that one value for (a) and (f) in the chain-growth

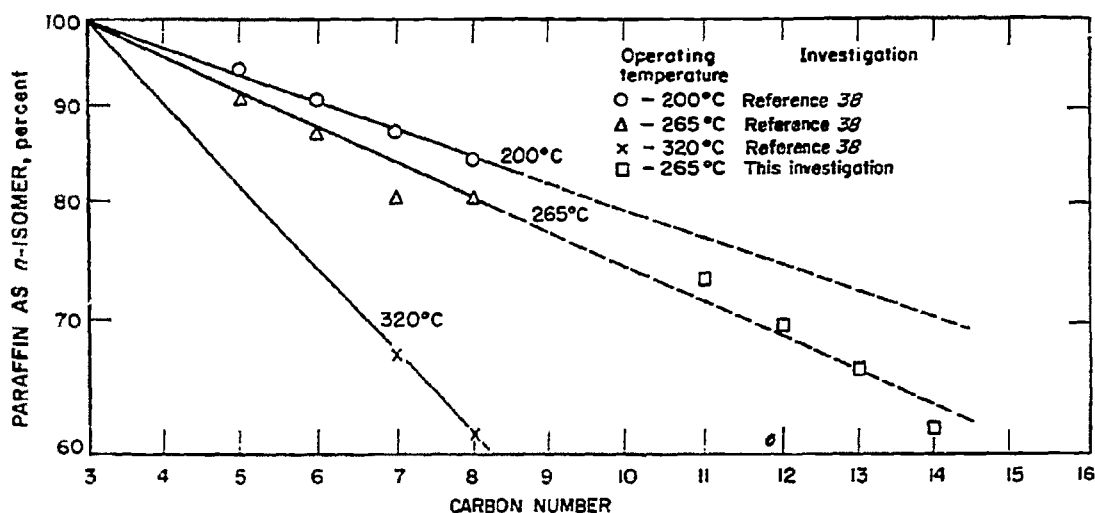


FIGURE 21.—Variation in Proportion of n-Isomer With Carbon Number for Paraffins (Logarithmic Plot).

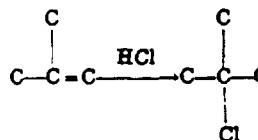
scheme will not apply over the entire molecular weight range, and a change in these constants must be made at approximately C_{20} . Anderson has noted that a similar plot of Weitkamp's data is linear for the range C_2 to C_{14} with $a = 0.6185$ and $f = 0.115$ (2). The deviation found in the plot of the Weitkamp data is in the same direction as found in the present investigation. Anderson also noted that carbon number distribution data obtained for synthesis product produced with a cobalt catalyst gave a linear plot from C_2 to C_{20} with $a = 0.836$ and $f = 0.035$. Thus, for the lower branching factor (f), the chain-growth scheme was found to apply over a much wider carbon number range. The present data are linear from at least C_{12} to C_{30} and are more in line with the data for product from cobalt catalyst. This would indicate that the chain-growth scheme adequately describes the product from low-temperature operations, but not the extensively branched product obtained at approximately 300°C . Perhaps other terms to describe cyclization or the role of oxygenated compounds are required.

Analysis of Butenes and Pentenes by Hydrochlorination

Determination of the amounts of the individual butenes present in a butene mixture is complicated by the similarity of their mass spectra. A procedure was described by Melpolder and Brown (63) for converting the isobutene in samples to *tert*-butyl chloride prior to mass spectrometric analysis. Isobutene is then determined in terms of the chloride and the separation of the isomers is simplified. Melpolder and Brown have also ascertained that in pentene mixtures only 2-methyl-1-butene and 2-methyl-2-butene react to form *tert*-amyl chloride when treated with HCl.

The procedure for the addition of a chlorine atom to the tertiary carbon at the double bond involves the reaction with HCl at reduced temperature and pressure. A portion of the sample is placed in a blending system and frozen down with liquid N_2 ; then the air is pumped off. When the sample has returned to room temperature, an equal portion of HCl is added and the mixture alternately cooled and warmed to complete the reaction. When a large percentage of isobutene is present, precaution must be taken not to exceed the vapor pressure of *tert*-butyl chloride—200 mm of mercury at room temperature.

This reaction is quantitative and can be carried out in about 30 minutes.



The mass spectrum of *tert*-butyl chloride has major peaks at m/e 77, 57, and 41. The major peaks in the mass spectrum of *tert*-amyl chloride are at m/e 91, 77, 71, 55, 43, and 41. Masses 77 and 91 can be used to correct the spectrum of the butene mixture for the contributions of the chlorides and to calculate the partial pressure of the chlorides in the mixture. The percent of the chloride is equivalent to the amount of isobutene or isopentene in the original mixture.

Before applying this method to the analysis of unknown hydrocarbon mixtures from the Fischer-Tropsch synthesis, synthetic blends were first analyzed. Initial work was carried out with the synthetic mixtures of C_4 and C_5 hydrocarbons shown in table 44. This work was then extended to include a blend similar to the mixtures found in the charcoal traps from the catalyst-testing units to attempt a separation of butenes in the presence of many interfering compounds. The resulting data, table 45, indicate that this procedure should give reliable results on this type of sample.

TABLE 44.—Mass spectral analysis of synthetic blends of C_4 and C_5 hydrocarbons, mole-percent

	1-Pentane	Isopentane	1-Butene	Isobutene
Synthetic blend.....	23.0	2.0	70.0	5.0
Analysis 1.....	22.4	12.2	70.0	5.4
Analysis 2.....	22.8	12.1	70.0	5.1

¹ Determined as *tert*-amyl chloride.

² Determined as *tert*-butyl chloride.

TABLE 45.—Mass spectral analysis of a synthetic blend of C_4 to C_5 hydrocarbons, mole-percent

	Synthetic	Analysis
n-Hexane.....	0.3	0.3
1-Butene.....	5	6
n-Pentane.....	2.2	2.2
1-Pentene.....	5.0	5.2
n-Butane.....	10.0	8.6
Isobutane.....	1.0	1.0
1-Butene.....	39.8	38.7
Isobutene.....	2.0	1.8
Propane.....	83.2	84.9
Propene.....	6.0	6.7

¹ Determination made from *tert*-butyl chloride.

Mass Spectrometric Analysis of Mixtures Containing Nitrogen Dioxide

Chemical determination of oxides of nitrogen has been the subject of considerable study (47, 98). Nitrogen dioxide has behaved erratically in the mass spectrometer and has resisted accurate analysis by this method. This investigation was concerned with means of eliminating the instrumental instability and devising techniques for the analyses by mass spectrometer alone of nitrogen dioxide, nitric oxide, and other gases in multicomponent mixtures (33).

Materials

Mathieson nitrogen dioxide in a glass bulb was frozen in a Dry Ice bath and evacuated for 30 minutes to remove volatile impurities. Nitric oxide cannot be removed in this way because of the formation of solid nitrogen trioxide. Oxygen was added to the bulb and the mixture was frozen in order to convert any nitric oxide to nitrogen dioxide. Pumping away the excess oxygen produced a reliable sample of the dioxide. For sampling from cylinders only a very short section of tubing, inert plastic rather than rubber, should be used.

Synthetic nitrogen dioxide was prepared by reacting synthetic nitric oxide with oxygen. The product was frozen in Dry Ice and excess oxygen was pumped off. The mass spectrum was identical to the spectrum of purified Mathieson nitrogen dioxide.

Mathieson nitric oxide was frozen in liquid nitrogen, and volatile impurities were pumped off. The cylinders used in this work contained about 1 percent of carbon dioxide and perhaps nitrous oxide in smaller concentrations. Either carbon dioxide or nitrous oxide impurities can be prevented from entering the spectrometer by sampling at a temperature slightly above liquid nitrogen temperatures. This was done by freezing the sample, then suspending it slightly above the surface of the liquid nitrogen bath before opening the stopcock.

Synthetic nitric oxide was prepared by dissolving 0.5 gram of potassium nitrate, recrystallized three times and dried for 2 hours at 100° C in 12.5 ml of 95 percent sulfuric acid. The solution was placed in a 100-ml sample bulb which was then frozen in Dry Ice and evacuated. Mercury was sucked in through the stopcock bore and allowed to react. The mixture was frozen in liquid nitrogen in order to pump off any traces of air, and samples were taken with the bulb suspended above liquid nitrogen. The mass

spectrum showed no nitrous oxide or carbon dioxide.

No chemical or other tests for impurities were made on these compounds. The same gas used for calibration of the spectrometer was used for preparation of the synthetic blends.

Stopcock Greases—Four lubricants were tested: Apiezon L, Consolidated grease (grade B), Dow Corning high-vacuum, silicone, and Perfluoro (FCX-759, furnished by E. I. du Pont de Nemours & Co., Inc.). The same mixture of nitrogen dioxide and helium was placed in four sample bottles, stopcocks of which were lubricated with these greases. Helium served as an internal standard to check for loss of the dioxide by sorption or by formation of nonvolatile products. Duplicate analyses of the helium to nitrogen dioxide ratio and of the volatile reaction products were made at intervals over a 12-day period. The first of these analyses produced the most information because an appreciable percentage of this sample was the gas trapped in the stopcock bore where the ratio, lubricant to gas, was the greatest.

Determinations based on the internal standard indicated that some loss of nitrogen dioxide in the grease of the stopcock bore occurred in all cases. The duplicate analyses showed that the total amount lost was negligible. Analyses of the gaseous decomposition products produced the following order of preference: Silicone, Perfluoro, Consolidated, and Apiezon. Apiezon reacted to a much greater extent than any of the others, as evidenced by appreciable formation of nitric oxide, carbon monoxide, and carbon dioxide. No volatile reaction products were found with the silicone grease.

Preferential loss of nitrogen dioxide in the grease can be minimized by discarding the gas in the stopcock bore with a preliminary flushing. If L-type stopcocks are used the flushing operation is still desirable.

Diffusion-Pump Oil.—Only silicone pumping fluid (Dow Corning No. 703) was used in the vacuum pump of the gas-handling system. Nitrogen dioxide reacts rapidly with the oil at room temperature to form brownish addition products. The reaction is not reversible, even at elevated temperatures. Twenty millimeters of nitrogen dioxide were completely taken up after standing in contact with silicone pump oil. The pressure decreased to 0.001 mm and remained there even after heating. This indicates that there is no formation of volatile reaction products which might give spurious peaks in the mass spectrum of nitrogen dioxide. The only dele-

terious effect is eventual deterioration of the pumping fluid. This process is slow because the pump was exposed to nitrogen dioxide pressures of less than 0.1 mm of mercury. In 9 months of parttime operation with nitrogen dioxide and nitric acid the pump oil was changed only once.

Apparatus.—A Consolidated Electroynamics model 21-103 mass spectrometer was used in this work. The gas-handling system of this instrument is constructed of stainless steel and utilizes stainless steel bellows valves. Samples were admitted directly into the glass expansion bottle through a blind flange on the left side of the gas-handling system. A glass manifold with four tapered joints was connected to this flange so that several samples could be handled without breaking the vacuum and risking contamination.

Pressure measurements were made on the Consolidated micromanometer which operates in the micron range.

Nitrogen Dioxide

Instability.—The erratic behavior of nitrogen dioxide in the mass spectrometer is attributable to chemical reactivity. Under normal temperature and pressure conditions this substance exists as an equilibrium mixture of the tetroxide and the dioxide according to the equation $N_2O_4 \rightleftharpoons 2NO_2$.

Equilibrium data (91) for this system permit calculation of the relative amounts of dinitrogen tetroxide and nitrogen dioxide existing at normal temperature and pressure. Under the conditions of mass-spectrometer investigation the usual pressure range is around 100 microns. At this pressure the equilibrium mixture is 99.9+ percent of nitrogen dioxide. Pressure measurement in the micron range, by means of the micromanometer, obviates the necessity for any correction for the equilibrium, and analytical results are in terms of nitrogen dioxide. Obviously, the equilibrium is not involved in the question of instability.

It is generally known that traces of reactive materials are always present in the high-vacuum system of the mass spectrometer. Adsorbed water is one such substance. Others are carbon and polymerized hydrocarbons. Although no stopcock grease exists in the metal gas-handling system, traces of reactive nonvolatile materials accumulate from samples and from pump oil.

Nitrogen dioxide apparently reacts with these carbonaceous materials to produce spectral instability. Evidence of reaction was found in the appearance of nitric oxide, carbon monoxide, carbon dioxide, and water

in the mass spectrum of nitrogen dioxide. In the same manner carbon monoxide and carbon dioxide appear in the mass spectrum of oxygen.

Nitrosation and/or nitration reactions apparently occur to some extent. A nitrosate arises from addition of two molecules of nitrogen dioxide to a double bond, producing a nitroso group on one carbon and a nitrate on the other. Formation of such species would remove molecules of nitrogen dioxide completely from the gas phase without producing any volatile product that might be detected in the mass spectrum. A good indication of this reaction was found in the nitric oxide, mass 30, background which persisted for some time after nitrogen dioxide runs had been completed. There was no nitrogen dioxide, mass 46, background. Thermal decomposition of the nitrosates of 1-hexene and butadiene and of nitrated cellulose have shown that nitric oxide, but no nitrogen dioxide, is given off.

Conditioning of the system, to reach a point of stability with respect to nitrogen dioxide, involves diminution of troublesome reactions by prior treatment of the system with excess nitrogen dioxide. Elimination of these reactions is never realized because carbon monoxide and carbon dioxide appear in all nitrogen dioxide spectra. But, with proper conditioning, the spectrometer reaches a steady state, after which the amounts of carbon monoxide and carbon dioxide formed become fairly constant for a given nitrogen dioxide pressure.

Conditioning Procedure.—EARLY NITROGEN DIOXIDE RUNS—Conditioning of the mass spectrometer normally refers to treating a new filament by exposing it to high-pressure 2-butene in order to achieve stable operating characteristics. With a reactive substance such as nitrogen dioxide, the conditioning procedure must involve the entire high-vacuum system to which the gases to be analyzed will be exposed.

Daily conditioning of the mass spectrometer was achieved initially by the following treatment:

1. Overnight (8 hours) treatment of both gas-handling system and filament with 100 microns of nitrogen dioxide in the expansion bottle behind the mass spectrometer leak.
2. Three nitrogen dioxide runs at pressures of 200 microns.

After this treatment the spectrometer was ready for analyses. If samples with nitrogen dioxide partial pressures below 200 microns were to be analyzed, the spectrometer was given the following treatment in order to maintain stability:

3. Nitrogen dioxide at a pressure of 100 microns for 20 minutes every 2 hours.

4. Nitrogen dioxide at a low pressure, about 10 to 20 microns, for 5 minutes.

During any break in operation, conditioning was maintained by the following treatment:

5. Nitrogen dioxide at a pressure of 100 microns until operation was resumed.

It was apparent that once the mass spectrometer was stabilized with respect to nitrogen dioxide, it had to be kept in contact with appreciable pressures of nitrogen dioxide almost continuously.

After conditioning, the data in figure 22 were obtained. The spectrometer was ad-

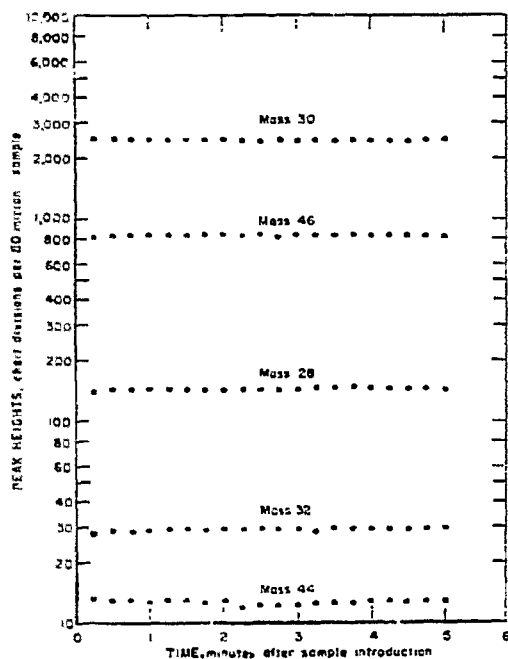


FIGURE 22.—Preliminary Test for Proper Conditioning With NO_2 . Separate 80-Micron Samples Used for Determination at Each Mass.

justed for one mass, nitrogen dioxide was introduced, and the mass peak was scanned immediately. The same peak was rescanned every 15 seconds for 5 minutes. A different sample for each mass peak was introduced and run in the same manner. All of the mass peaks were practically maximized, even at 15 seconds. Without proper conditioning, similar experiments produced erratic results. Figure 23 illustrates an additional necessary test for conditioning. Constancy must be

attained for the 46- and 30-mass peaks for successive nitrogen dioxide samples, as shown by curves *b* of figure 23.

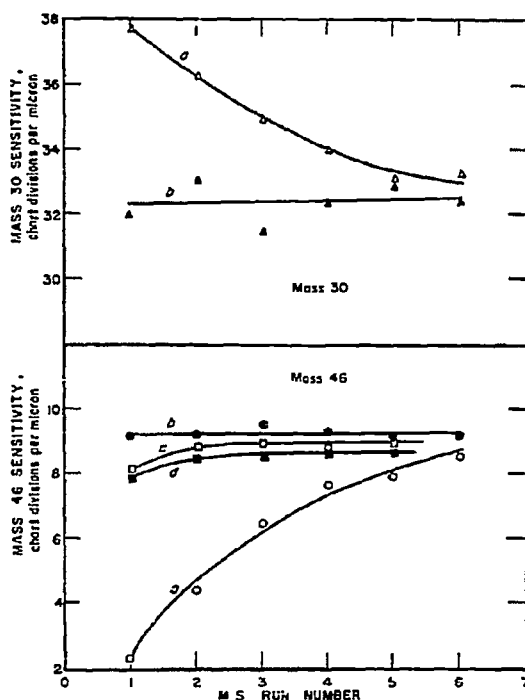


FIGURE 23.—Test for Proper Conditioning with NO_2 by Consecutive Runs.

LATER NITROGEN DIOXIDE RUNS.—The rigorous conditioning described above was found to be the minimum treatment necessary during the first few weeks of handling nitrogen dioxide samples. Curves *a* of figure 23 illustrate the extensive reaction and consequent loss of nitrogen dioxide suffered when no conditioning was applied. Curve *c* of figure 23 shows that, after 8 months of operation, the nitrogen dioxide spectrum rapidly approached stability each day, even without conditioning. No advantage was found in conditioning of the gas-handling system only (curve *d*, fig. 23), which indicates that the slight conditioning now necessary is required only for the inlet line and ionization chamber. Further indications that the gas-handling system was well conditioned after 8 months was found in the lack of any appreciable nitrogen dioxide reaction overnight. A sample of nitrogen dioxide was run, then allowed to remain in the gas-handling system for 8 hours. The spectrum of this sample the following morning was almost iden-

tical. Also, the sample pressure according to the micromanometer did not change.

Nitric Acid Conditioning.—An alternative conditioning procedure utilized fuming nitric acid vapors (35). The strong oxidizing property decreased the time involved, but the material was more difficult to handle.

With a tungsten filament, reversion to routine operation is achieved readily by treatment of the mass-spectrometer filament with 2-butene. No adverse effect on the spectrometer filament was realized. The first filament was subjected to nitrogen dioxide and/or nitric acid about 30 hours per week over a period of 5 months. The total life of the filament was 8 months, which is about average for our instrument.

Nitrogen Dioxide Mass Spectra.—The mass spectrum of nitrogen dioxide varies with the partial pressure of the substance. The spectrum is discussed in terms of pressure in microns, which refers to the pressure

in the expansion bottle, behind the goldfoil leak of the Consolidated spectrometer. Spectra for various pressures are listed in table 46.

SPECTRA FOR PRESSURES ABOVE 15 MICRONS.—Columns 2 to 7 of table 46 give the spectra for pressures between 200 and 13 microns. The principal peaks in the spectra are found at masses 46, 30, 16, and 14, which are attributable to ionization and fragmentation of the nitrogen dioxide molecule. Above 15 microns the sensitivities (and patterns) for these principal peaks are almost constant and independent of pressure (figs. 24-25). The reproducibility is indicated by the straight lines obtained. Consistency of mass 46 sensitivities is shown further in figure 25 by six consecutive runs in the region of 75 microns. Day-to-day reproducibility of sensitivities (and patterns) for all four principal mass peaks were generally comparable to the results for hydrocarbon gases.

In addition to the expected isotopic masses

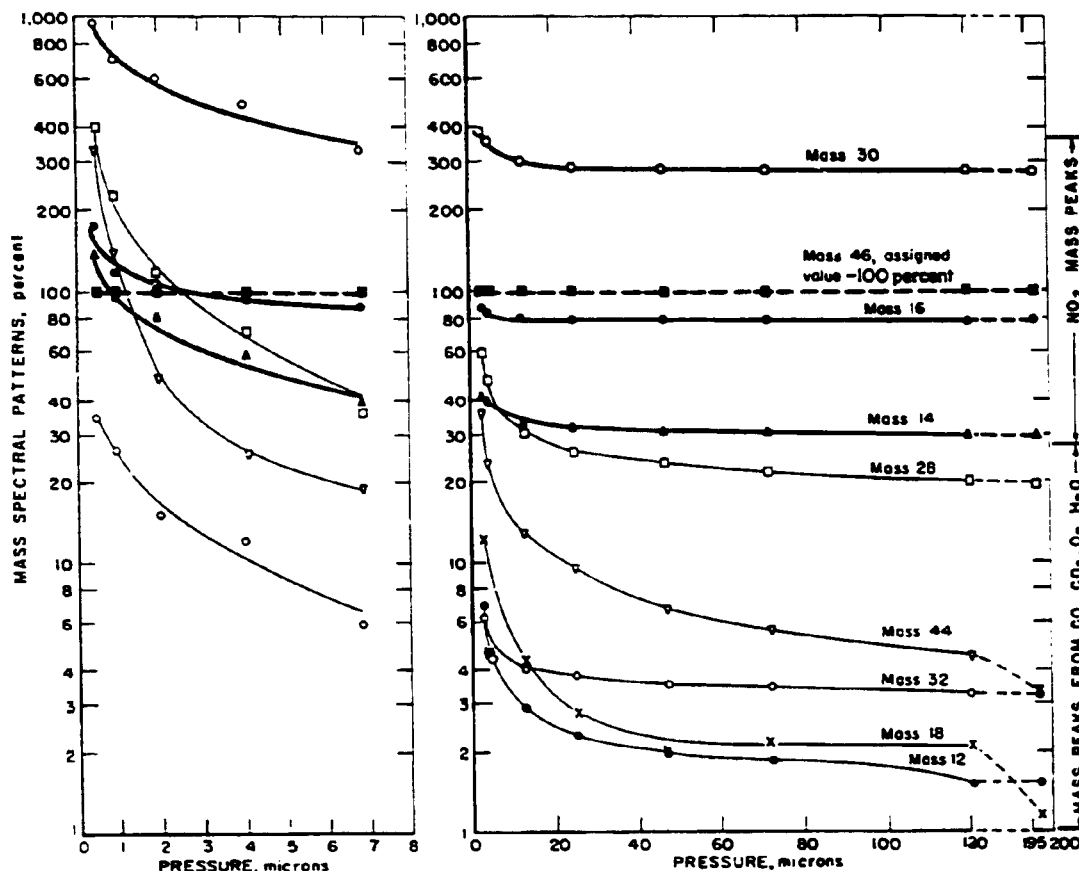


FIGURE 24.—NO, Mass Spectral Patterns at Various Pressures.

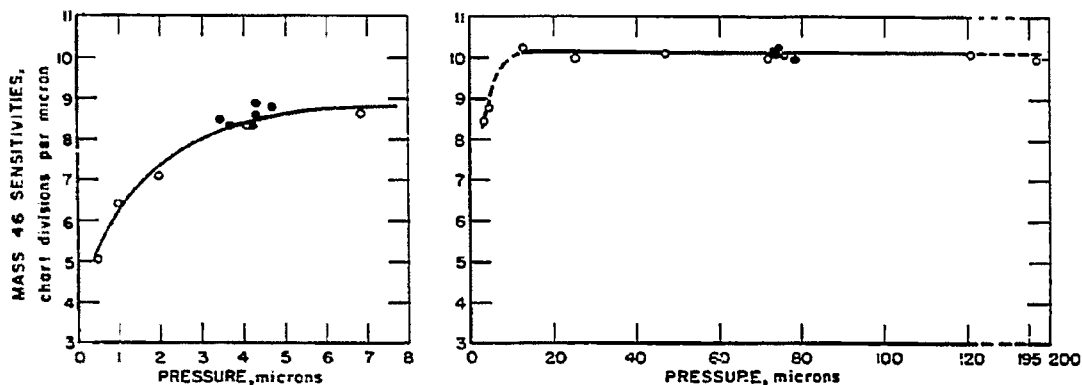


FIGURE 25.— NO_2 Mass Spectral Sensitivities at Various Pressures. Reproducibility Near 4 and 75 Microns Is Indicated by Sets of Six Consecutive Runs (\bullet), Made Several Weeks Later (\circ —Butane 58 Peak Sensitivity = 7.73 Divisions Per Micron).

there are other peaks which are not attributable directly to fragmentation of the nitrogen dioxide molecule. The 28 peak is produced by carbon monoxide, and the smaller 44 peak is mainly attributed to carbon dioxide. The 12 peak checks these assignments. The 22 peak shows that practically all of the 44 peak is carbon dioxide, instead of nitrous oxide which has no doubly ionized 22 peak at pressures of 40 microns. The 32 peak is attributable to oxygen from the slight decomposition of nitrogen dioxide according to the equation $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$. A small peak for water was usually but not always produced by nitrogen dioxide.

The apparent concentrations of water, carbon monoxide, carbon dioxide, and oxygen, which were found in the mass spectrum of

nitrogen dioxide, were not as large as the pattern values indicated. Concentrations for a typical run at 100 microns are listed in table 47. The amounts formed depend on the condition of the system. Since the apparent components were produced by pure nitrogen dioxide, the 44, 32, 28, 18, and 12 mass peaks were treated not as impurity peaks but as parts of the nitrogen dioxide spectrum. On a particular day at a given pressure these minor mass peaks were nearly as reproducible as the principal mass peaks.

Spectral patterns may not be reproducible with different filaments. Comparison of spectra from two filaments showed that the 30, 16, 14, and 32 peaks were appreciably higher with respect to the parent mass 46, for the second filament (table 48). The decreased

TABLE 46.—Mass spectral patterns of NO_2 at various pressures

Pressure . . . μ	197.1	120.7	72.1	47.2	25.4	13.0	4.7	3.4	6.83	4.04 ¹	1.96 ²	0.97 ³	0.49 ⁴
Mass. percent of mass 46 peaks:													
12	1.53	1.51	1.35	1.97	2.29	2.86	4.6	6.9	4.4	4.0	13	24	30
14	29.0	29.2	29.9	30.6	31.6	32.7	40.0	41	39.5	59.6	81	96	140
16	.70	.75	.83	1.03	1.13	1.65	2.9	3.5	2.1	4.4	9		
18	78.4	77.6	78.6	78.3	78.8	80.6	81.5	83.5	88.4	95.5	109	118	175
19.6 ⁵	.19	.20	.19	.19	.24	.33	4.6	12					
22	.05	.07	.08	.08	.12	.15							
23 ²	.20	.21	.18	.16	.12	.03							
28	19.4	19.9	21.3	23.7	25.6	30.1	46.3	59.3	35.9	71.8	117	222	400
29 ⁴	.30	.34	.33	.23	.39	.59	.5	.4					
30	275	280	278	282	289	305	352	382	336	439	604	706	965
31 ⁴	.99	.97	1.06	1.03	1.14	1.35	1.0	1.0					
32	3.23	3.23	3.42	3.53	3.79	3.99	4.4	6.2	5.9	12	15	26	35
44	3.32	4.43	5.58	6.60	9.35	12.9	23	38	19	26	48	140	340
46	100	100	100	100	100	100	100	100	100	100	100	100	100
47 ⁴	.40												
48 ⁴	.38												
Sensitivity of mass 46, divisions per micron ¹	9.96	10.1	10.0	10.1	10.0	10.25	8.8	8.5	8.64	8.33	7.1	6.4	5.1

¹ Spectra obtained with blend of 2 percent NO_2 in helium. Effective NO_2 pressures calculated on this basis.

² Metastable ion.

³ Doubly charged ion.

⁴ Isotope peak.

⁵ n-Butane mass 58 sensitivity 7.73 divisions per micron; n-butane 43/58 ratio, 7.87.

TABLE 47.—*Apparent impurities produced in spectrometer by nitrogen dioxide, microns*
(Typical data at 100 and at 5 microns after 8 months of NO₂ runs)

Compound	100 μ of NO ₂	5 μ of NO ₂
H ₂ O	0.2	0.2
CO	3.2	.5
CO ₂	.2	.1
O ₂	1.2	.1

44, 28, 18, and 12 peaks were attributed to decreased carbon dioxide, carbon monoxide, and water through improved conditioning with time. Temperature effects were investigated only slightly. Results indicated that the nitrogen dioxide spectrum is temperature-sensitive. The larger parent peak sensitivities and smaller pattern values, which resulted from operation at temperatures lower than the usual 250° C, should promote more accurate analyses of mixtures.

TABLE 48.—*NO₂ patterns at 100 microns obtained with two different mass-spectrometer filaments, percent of mass 46 peaks*

Mass	Filament 1 ¹	Filament 2 ¹
12	1.68	1.45
14	29.6	40.2
16	78.1	92.3
18	2.13	0
28	20.6	15.8
30	279	298
32	3.32	4.19
44	5.00	3.39
46	100	100

¹ Sensitivity of mass 46, in divisions per micron, 10.1 for filament 1; 9.10 for filament 2.

² Decreased peaks for CO, CO₂, and H₂O are attributable to improved conditioning with time.

SPECTRA FOR PRESSURES BELOW 15 MICRONS.

—In contrast to the approximate constancy of spectra for pressures above 15 microns, measurements below 15 microns showed large variations with decreasing pressure (figs. 24–25, and the last seven columns of table 46). An important reason for this variation is the decomposition of nitrogen dioxide according to the reaction $\text{NO}_2 \rightleftharpoons \text{NO} + \text{O}$, which becomes important in this pressure range. Formation of nitric oxide increases rapidly with decreasing pressure but the accompanying increase in peaks due to atomic and molecular oxygen were not as large as expected. Instead, the oxygen produced carbon monoxide and carbon dioxide which increased rapidly with decreasing pressure.

The rapid changes in pattern and sensitivity at low pressures are not insurmountable difficulties. Good reproducibility at a given pressure was shown by mass 46 sensitivities

for six successive runs in the region of 4 microns (fig. 25). Mass 46 sensitivities were fairly reproducible from day to day; all of the other mass peaks were reproducible only on the same day. Although the apparent impurities are large, as shown for 5 microns of nitrogen dioxide in table 47, their stability on any given day permits accurate analyses. Spectra for nitrogen dioxide partial pressures below 0.5 micron are possible by utilization of a higher electron catcher current. Patterns and sensitivities obtained at 50 microamperes compared favorably with results at the usual setting of 10 microamperes (tables 49–50).

TABLE 49.—*NO₂ mass spectral patterns¹ at ionizing currents of 10 and 50 μa*

Ionizing current	Effective pressure, microns			
	4.71		0.60	
	10 μa	50 μa	10 μa	50 μa
Mass, mole-percent:				
12	3.7	4.0		
14	53.8	50.7	56	53
16	82.0	81.4	87	82
18	9.1	10.0	30	30
28	55.6	55.9	66	66
30	650	437	500	504
32	7.1	7.3	10	11
44	9.9	11.9	20	22
46	100	100	100	100
Sensitivity of mass 46, divisions per micron	8.1	8.5	2.5	2.9

¹ Pattern values are lower than corresponding values in table 46, because of better conditioning on this particular day.

² Spectra obtained with blend of 2 percent NO₂ in helium. Effective NO₂ pressures calculated on this basis.

TABLE 50.—*Mass spectral synthetic blend analysis at 50 μa, mole-percent*
(Total pressure, 100 microns)

	NO ₂	NO	CO	CO ₂	N ₂	He
MS analysis	0.65	0.44	0.36	0.54	0.41	97.4
Synthetic blend	.75	.54	.54	.54	.54	97.1

Mass Spectra of Nitric Oxide and Nitrous Oxide

The mass spectra of nitric oxide and nitrous oxide are shown in table 51, along with a comparison spectrum of nitrogen dioxide. The principal peaks of nitric oxide, 30, 16, and 14, are attributed to ionization and fragmentation of the nitric oxide molecule. The 12 and part of the 28 peak are due to carbon monoxide. The remainder of the 28 peak is attributed to nitrogen, which was present probably because of slight nitric oxide decomposition according to the equation, $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$. Mass 32 for oxygen does not appear in the spectrum, but this may be due to reaction to form carbon monoxide or nonvolatile products. The nitric oxide spectrum was constant and independent of par-

tial pressure. No conditioning was required; the small peaks due to carbon monoxide were

TABLE 51.—Mass spectral patterns of nitric oxide, nitrous oxide, and nitrogen dioxide

	NO	N ₂ O	NO ₂
Mass, percent of molecular-ion peaks:....			
12.....	0.31	0.14	1.45
14.....	12.1	16.8	40.2
15.....	2.53	.14	.77
16.....	2.75	6.05	92.3
19.6.....			1.24
22.....		0	
23.....			1.22
28.....	5.64	18.1	15.8
29.....	.05	.23	.41
30.....	100	38.3	298
31.....	.37	.13	1.08
32.....	.23	.15	4.19
44.....		100	.39
45.....		.75	
46.....		.21	100
47.....			.39
48.....			.36
Sensitivity of molecular-ion divisions per micron ²	44.6	33.0	9.10

¹ Metastable ion.

² Doubly charged ion.

³ n-butane mass 58 sensitivity, 7.73 divisions per micron.

constant and were considered as part of the nitric oxide pattern.

The principal peaks of nitrous oxide are the 44, 30, 28, 16 and 14. Besides isotope peaks there was only one other peak, a small mass 12 for carbon monoxide. But the contribution of carbon monoxide to the 28 peak was less than 10 percent of the total.

Analysis of Nitrogen Dioxide in Mixtures

Synthetic Blends.—Blends were prepared both by mixing in the instrument by means of the micromanometer and in a conventional blending system. The former method has the disadvantage that the blend cannot be retained for future runs, but the elimination of reaction or contamination in an auxiliary blending system is an important advantage. The blend analyses are tabulated in table 52. In all cases nitrogen dioxide calibrations were made at the same time, although past calibrations were often applicable. Conditioning of the system for nitrogen dioxide does not

TABLE 52.—Mass spectral analyses of synthetic blends containing NO₂ and NO, mole-percent

Blend	A	NO ₂	NO	N ₂ O	CO ₂	CO	N ₂	O ₂	H ₂ O	H ₂	He
Synthetic Blends Prepared Directly in Mass Spectrometer; Micron Pressure Measurements by Micromanometer											
1	{ MS analysis.....	91.2	8.7								
	{ Synthetic.....	91.2	8.8								
7	{ MS analysis.....	90.5	9.5								
	{ Synthetic.....	90.0	10.0								
3	{ MS analysis.....	85.3	14.7								
	{ Synthetic.....	85.3	14.7								
4	{ MS analysis.....	90.6	9.4								
	{ Synthetic.....	90.4	9.6								
5	{ MS analysis.....	94.5	5.5								
	{ Synthetic.....	94.9	5.1								
6	{ MS analysis.....	49.0	50.8	.2							
	{ Synthetic.....	49.8	50.2	0							
7	{ MS analysis.....	78.3	4.7	5.0	5.6		6.4				
	{ Synthetic.....	78.9	5.0	5.4	5.3		5.4				
8	{ MS analysis.....	74.4	4.9	5.0	5.1	4.5	6.1				
	{ Synthetic.....	74.3	5.1	5.3	4.9	4.7	5.7				
9	{ MS analysis.....		60.3						39.7		
	{ Synthetic.....		59.0						41.0		
10	{ MS analysis.....		5.3	3.9	13.1	13.1	16.2	4.3	44.1		
	{ Synthetic.....		5.1	4.0	13.2	13.3	16.3	4.3	43.8		
11	{ MS analysis.....			15.1	15.2	15.3	31.0	8.3		15.1	
	{ Synthetic.....			15.0	15.0	15.1	31.6	8.4		14.9	
12	{ MS analysis.....		9.4	10.1	12.1	12.4	25.2	6.7		12.1	
	{ Synthetic.....		10.2	9.6	12.0	12.0	25.4	6.8		11.9	
13	{ MS analysis.....		11.0	11.1	14.1	13.5	14.1	28.6	7.6		
	{ Synthetic.....		11.6	11.2	13.6	13.6	13.7	28.7	7.6		
Synthetic Blends Prepared on Conventional Blending Systems With Mercury Manometer											
A	{ MS analysis.....	6.6	5.0		4.9	4.7	4.8				74.0
	{ Synthetic.....	7.0	4.9		4.9	4.9	4.9				73.4
B	{ MS analysis.....	6.3	5.2		4.9	4.4	5.2				74.0
	{ Synthetic.....	7.2	4.9		4.9	4.9	4.9				73.3
C	{ MS analysis.....	6.5	4.6		4.9	3.4	5.4				75.2
	{ Synthetic.....	7.1	4.9		4.9	4.8	4.9				73.4

change the spectra of other components. Conversely, the presence of other components apparently has no effect on the spectral behavior of nitrogen dioxide. Even nitric oxide and oxygen, which react spontaneously at atmospheric pressure, formed no nitrogen dioxide at 90 microns. This was demonstrated by blending nitric oxide and oxygen to a pressure of 90 microns in the spectrometer; after 30 minutes no 46 peak for nitrogen dioxide had appeared (table 53).

Blends 1, 2, 4, and 5 contained 10 percent or less nitric oxide and 90 percent or more nitrogen dioxide. For such samples, frequent calibration of patterns were necessary to obtain high accuracy. The calibration of the 30 peak from nitrogen dioxide is critical because of the large correction which must be made before nitric oxide can be calculated. Greatest accuracy was obtained by alternating samples with nitrogen dioxide calibration runs and by correcting for the mass 30 background. Lower accuracy, within 1 percent, was possible for mixtures of 10 percent nitric oxide and 90 percent nitrogen dioxide by the simple difference method; in this case no pattern calibration was needed.

Mixtures containing water and nitrogen dioxide were analyzed with some success (blends 9-10). Preparation of blends in the spectrometer was subject to some error because of adsorption of water. Preliminary flushing with water and addition of water as the last component of a blend helped to minimize adsorption trouble. Nitrogen dioxide and water calibration runs were alternated with no adverse effects on reproducibility for either compound. Nitric acid produced a parent peak at mass 63, but no 63 peak was observed in the spectra of blends 9 or 10. Formation of nitric acid would not be expected since blending was carried out at micron pressures.

TABLE 53.—Nonreactivity of NO and O₂ in micron pressure range¹, mole-percent

	NO	O ₂	NO ₂
Original analysis.....	57.4	32.6	0.0
Analysis 5 minutes later.....	57.4	32.6	0
Analysis 30 minutes later.....	57.7	32.3	0

¹ Total pressure of NO + O₂ mixture = 89.7 microns.

Nitrous oxide and carbon dioxide, in blends 11, 12, and 13, were split by means of the double charged ion at mass 22, which occurs only in the carbon dioxide spectrum.

Analysis of a blend containing only 0.75 percent of nitrogen dioxide was carried out at an electron catcher current of 50 micro-

amperes (table 50). The analysis was made with a total pressure of 100 microns; no attempt was made to concentrate the nitrogen dioxide with a refrigerant.

Procedure for Analysis of Nitrogen Dioxide.—Analysis of mixtures containing nitrogen dioxide can be carried out by the following procedure:

Construct a working curve of partial pressure of nitrogen dioxide versus mass 46 peak height (fig. 26).

Prepare a table, or graphs, of pattern values at various partial pressures of nitrogen dioxide (table 46 or fig. 24).

Apply the nitrogen dioxide mass 46 peak height for the unknown to the working curve and obtain the partial pressure.

Select the proper pattern values, or run calibration patterns on pure nitrogen dioxide at partial pressures corresponding to those found in the mixtures.

Subtract the nitrogen dioxide contribution from the mixture spectrum and proceed with analysis in the usual way.

The applicability of previously determined working curves of peak heights versus nitrogen dioxide partial pressure must be checked daily. Since the spectrometer must be conditioned with nitrogen dioxide, it is appropriate to check for sensitivity variations with nitrogen dioxide itself, rather than with some standard compound.

ANALYSIS OF SAMPLES CONTAINING MORE THAN 15 MICRONS (AFTER EXPANSION) OF NITROGEN DIOXIDE.—The working curve is a straight line for partial pressures above 15 microns, and therefore is easily corrected if a sensitivity check indicates a shift. Patterns are nearly constant in this pressure range and are also easy to adjust.

ANALYSIS OF SAMPLES CONTAINING LESS THAN 15 MICRONS (AFTER EXPANSION) OF NITROGEN DIOXIDE.—The working curve is not linear for partial pressures below 15 microns and accordingly should be checked at two or more points. Since all the pattern values in this low-pressure range vary from day to day, nitrogen dioxide patterns must be run on the same day and at the same partial pressure as that found in the samples. This means running calibrations after the samples instead of before.

Analysis is simplified if most of the pattern values can be ignored. For many analyses of samples containing less than 15 microns of nitrogen dioxide, only the 46 and 30 mass peaks are needed.

The ultimate limit of detectability for nitrogen dioxide, using the 46 peak and a catcher current of 50 microamperes, is about

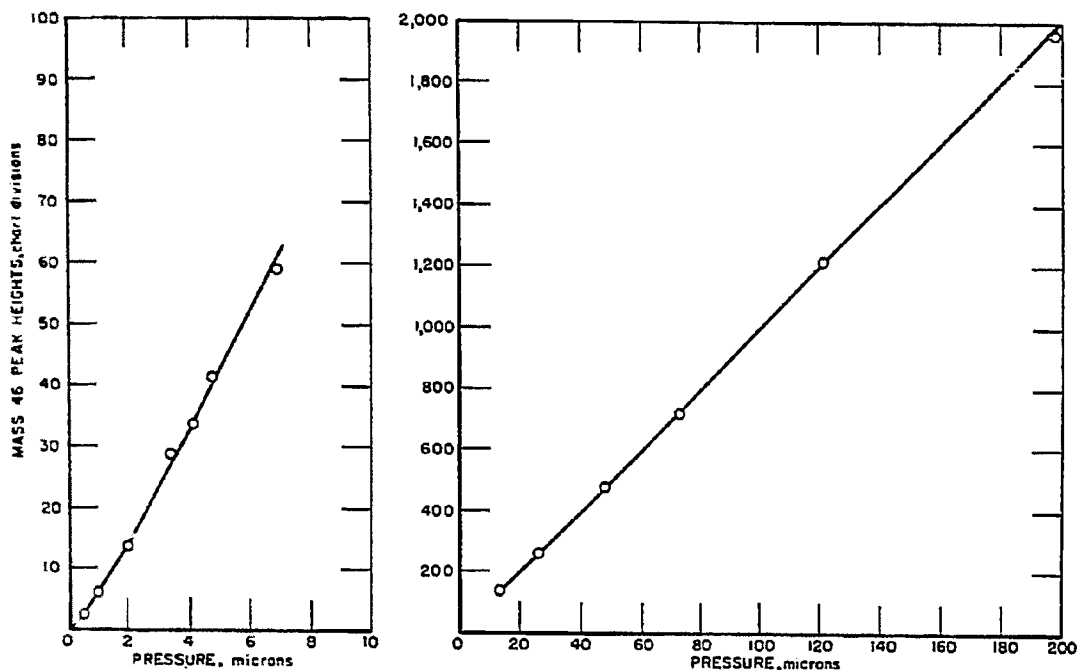


FIGURE 26.—Working Curve; NO_2 Pressure Versus Mass 46 Peak Heights.

0.05 mole-percent, or 0.05 micron partial pressure with a total pressure of 100 microns. Concentration by refrigerant can lower this limit by a large factor, depending on the other constituents present. Concentration by refrigerant may be usable on some mixtures for a purpose other than analysis of traces of nitrogen dioxide. The method can be applied to fractionate a sample containing less than 15 microns of nitrogen dioxide in order to raise the partial pressure into the less troublesome region above 15 microns.

Mass Spectrum of Nitric Acid

In investigating the mass spectrum of nitrogen dioxide, reproducible spectra were obtained only after the instrument had been conditioned by long exposure to nitrogen dioxide (33). Red-fuming nitric acid was investigated because of its importance in rocket propulsion. Reproducible mass spectra were obtained after conditioning with nitrogen dioxide or nitric acid.

Experimental

Liquid red-fuming nitric acid (reagent grade) was pipetted from a 0.020-ml micro-pipet through a silicone-lubricated ground joint into a 250-cm³ sample bottle that had been flushed with nitric acid vapor. The

sample bottle was immediately sealed with a ground joint and stopcock assembly, and the bulb was immersed in liquid nitrogen to freeze the acid; the bottle was evacuated and then was brought back to room temperature. Portions of this gas sample were introduced.

Daily conditioning of the mass spectrometer was necessary initially.

This involved overnight (8 hours) treatment of both gas-handling system and filament with 100 microns of nitrogen dioxide or nitric acid in the expansion bottle behind the mass spectrometer leak and three nitric acid runs at pressures of 200 microns. During any break in operation, conditioning was maintained by treatment with nitric acid at a pressure of 100 microns until operation resumed. Eventually the conditioning procedure was shortened to running 100 microns of nitric acid for 1 hour.

Reversion to routine operation on hydrocarbon samples was achieved readily by treatment of the mass spectrometer filament (tungsten) with 2-butene.

Synthetic blends were prepared at micron pressures in the gas-handling system of the spectrometer. Immediately following analysis the blends were discarded.

Results and Discussion

The spectrum of red-fuming nitric acid is

shown in table 54. Reproducibility is illustrated by spectra from duplicate sample introductions. The apparent assignments are given for the various ions of the spectrum. In the mass spectrum of both nitrogen dioxide and nitric acid, ions containing carbon

(masses 44, 28, and 12) are unavoidable in an instrument used for mass-spectral determinations on hydrocarbons. Nevertheless, analytical applications can be made, as the mass-spectral peaks for these carbon-containing ions become reproducible (table 54).

TABLE 54.—*Successive mass spectral patterns of red-fuming nitric acid*

<i>m/e</i> , percent of mass 46 peak:	Relative intensity			Apparent assignment
	HNO ₃		NO ₂ ¹	
	A ²	B ²		
12	0.58	.056	1.45	C ⁺
14	10.4	9.02	40.2	N ⁺
16	21.7	19.8	92.3	O ⁺
17	24.4	24.8		HO ⁺
18	49.4	53.6	0	H ₂ O ⁺
28	20.0	20.4	15.8	CO ⁺ , N ₂ ⁻
30	85.7	84.4	298	NO ⁺
32	3.63	3.61	4.19	O ₂ ⁺
44	2.19	2.22	1.39	CO ₂ ⁺
46	100	100	100	NO ₂ ⁺
63	2.07	2.04		HNO ₃ ⁺
73	.96	.78		
75	.21	.24		
77	.11	.12		
79	.26	.25		
81	.13	.11		
Sensitivity of molecular ion, in divisions per micron:				
Molecular ion	.268	.259	9.10	
<i>n</i> -Butane mass 58	6.35	6.35	7.73	
Pressure, microns	119.4	114.1	100	

¹ Nitrogen dioxide pattern included for comparison.

² Duplicate sample introduction.

³ CO₂ and H₂O peaks in NO₂ spectrum vary considerably with extent of conditioning.

⁴ Molecular ion underlined.

No investigation was made into the origin of the small mass peaks at 73, 75, 77, 79, and 81. Obviously they cannot be attributed to fragmentation of nitric acid, molecular weight 63, but they may be due to higher molecular weight constituents in the acid, anomalous effects in the spectrometer, or reaction products from sample handling.

Successful mass spectral analyses of two-component blends of red-fuming nitric acid and nitrogen dioxide were carried out (table 55). After preparation of the blends in the mass spectrometer sampling system at micron pressures, duplicate spectral scans were made. The first scan was considered a conditioning run; analyses were carried out on the second scan. Nitric acid was calculated from the mass 63 peak, and nitrogen dioxide from the mass 16 peak. Mass 16 suffers less than mass 30 from the interference of nitric acid. Mass 30 may also be used for calculation of nitrogen dioxide in the presence of nitric acid; because of its greater sensitivity, the mass 30 peak should be advantageous for

analyzing small concentrations of nitrogen dioxide.

Rhenium filaments are expected to reduce conditioning procedures and the production of interfering carbon-containing ions, and to afford greater sensitivity and accuracy of analyses of both nitric acid and nitrogen dioxide (73).

For analysis of liquid mixtures of nitrogen dioxide and nitric acid, where large samples are available, volumetric methods are more accurate than the mass spectral method. For analysis of the vapor phase or of trace quantities of liquid, the mass spectral method is more accurate.

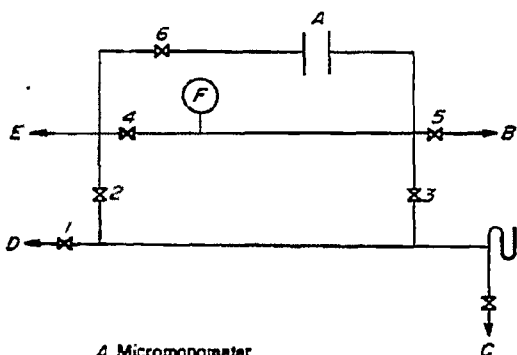
Determination of H₂S and Vapor-Phase H₂O

The accurate determination of H₂S by mass spectrometry is very difficult. The early instruments were equipped with mercury manometers for measuring the pressure in the inlet system and the inlet system itself was

made of glass with glass stopcocks. The H_2S reacted with the mercury in the manometer and was adsorbed by the stopcock grease. Thus, mass spectrometer analyses were always low and the H_2S in the stopcock grease was eluted as background in subsequent samples. Inlet systems supplied with instruments produced since about 1950 are metal with metal valves replacing the stopcocks. The micromanometer has replaced the mercury manometer, which, while still connected, can be isolated from the system. The only adsorption in the present system is in the stopcock grease of the sample bottle itself and possibly in residues accumulated in the gas-handling system over long periods of time. The presence of such residues is demonstrated by the radical conditioning necessary to obtain constant NO_2 spectra as described previously.

The analytical work required for the H_2S equilibrium study, carried out by the Indirect Coal Conversion Processes Group, necessitated the development of a technique for obtaining rapid analyses for H_2S in the presence of CO_2 and H_2O vapor. Since the water was in the vapor phase, the instrument had to be conditioned for both H_2O and H_2S . The following technique, using the flow system shown in figure 27, enabled reasonable analyses to be obtained for both of these troublesome components.

1. A CO_2 calibration was obtained following normal procedure and the mass spectrometer pumped out.



- A Micromanometer
- B To Isatron and analyzer tube
- C Gas sample inlet
- D To orifice liquid sample inlet
- E To vacuum pumps
- F 3-liter expansion volume

FIGURE 27.—Schematic Diagram of Flow System in Mass Spectrometer Inlet System.

2. The sample bottle was attached to the inlet system (C) and the system pumped to the sample-bottle stopcock.

3. A water sample was introduced through the orifice (D) with valves 2 and 3. A small amount of the water sample was bled through valve 3 into the remainder of the gas-handling system, the isatron, and the analyzer tube. After 5 minutes, with valves 2 and 3 closed, the system was pumped out, two calibration samples were bled from valve 3 and calibration spectra were obtained.

4. The water was then pumped from the entire system.

5. A flush sample was taken from the sample bottle and, after 5 minutes was allowed for conditioning, the system was then pumped out again.

6. A sample was admitted to the instrument and duplicate runs made.

7. A 5-minute sample flush was made from each successive sample bottle.

The following data obtained for H_2S by this technique were compared with the synthetic values, Tutwiler analyses, and methylene blue determinations:

Synthetic	Tutwiler	Methylene Blue	Mass spectrometer
2.5	2.0	1.2	2.3
1.0	1.0	.5	1.0
.6	.7	.6	.5
.3	.3	.3	.1

The Tutwiler method, used to determine hydrogen sulfide in concentrations between 0.05 and 10 percent by volume, covers the range of the synthetic blends adequately. The methylene blue method is recommended for the analysis of sulfur as hydrogen sulfide in the lower concentrations and is applicable at the 0.5-percent level. The mass spectrometric analyses compare favorably with the Tutwiler at the higher concentrations but do not appear usable for concentrations less than 0.5 percent.

Mass Spectrum of Hydrogen Deuteride (HD)

The direct chemical preparation of hydrogen deuteride, 99+ percent pure, was reported by Wender, Friedel, and Orchin (97). The fragmentation pattern under electron impact of this compound is of theoretical importance for comparison with the fragmentation patterns of H_2 and D_2 , and is of analytical importance for determination of hydrogen-deuterium mixtures, as in the calculation of equilibrium constants for the reaction of $H_2 + D_2 \rightleftharpoons 2HD$ (81). The unknown production of D^+ , mass 2, from fragmentation of HD interferes with the analysis

TABLE 55.—*Mass spectral analyses of synthetic blends of nitric acid and nitrogen dioxide, mole-percent*

	Blend ¹	Synthetic blend	MS analysis
1	HNO ₃ (mass 63).....	71.1	68.7
	NO ₂ (mass 46).....	28.9	31.3
2	HNO ₃	90.3	91.0
	NO ₂	9.7	9.0
3	HNO ₃	94.6	93.9
	NO ₂	5.4	6.1

¹ Blends prepared directly in mass spectrometer. Micron pressure measurements by micromanometer.

of H₂. This interference has been supposed slight, as is the unknown interference of D⁺ from D₂ (9), but if neglected can produce errors of several percent in calculation of equilibrium constants.

The relative abundance of D⁺ from HD cannot be determined directly because of the interference of unknown H₂ impurity. This difficulty was circumvented by measurements of rates of diffusion through the leak system of the mass spectrometer (24). Relative rates for H₂, measured at mass 2, and for HD, measured at mass 3, were found to be 12.72 and 10.46 percent per minute, respectively. These two values were plotted versus H₂ and HD percentages, and a straight line

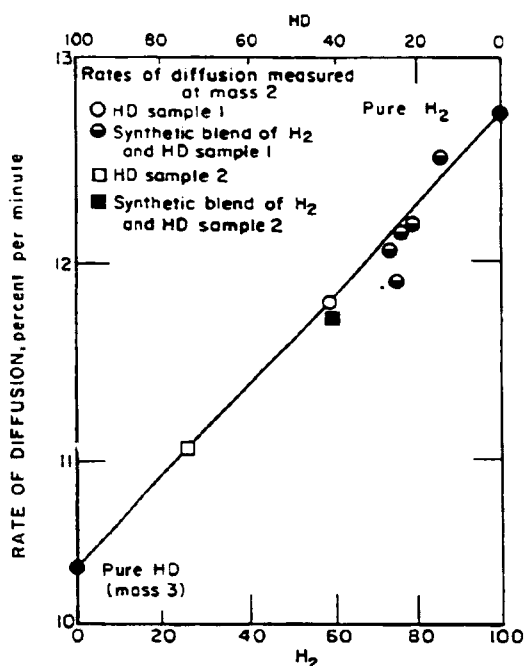


FIGURE 28.—Rate of Diffusion Curve for Determination of H₂ Impurity and Relative Abundance of D⁺ From HD.

was drawn between them (fig. 28). Then, measurements were made at mass 2 for two samples of HD with unknown H₂ impurity; thus, the rates of diffusion were due to mixtures of HD and H₂.⁴ The rate values were applied to the straight-line plot and the percentages of D⁺ and H₂⁺ which comprised the mass 2 ion peak were read from the abscissa. From these values the percentages of H₂ impurity and the relative abundance of D⁺, 1.13±0.05, were determined. Composition of one high-purity HD sample was found to be 98.8 percent HD, 0.4 percent H₂, plus 0.8 percent D₂, determined by direct analysis, compared with 99 percent HD by chemical analysis. Linearity of the relationship, rate of diffusion versus concentration, was checked by measuring the rates for six synthetic blends of HD plus small amounts of H₂. The resulting points fit the straight line within experimental error of the measurements (fig. 28).

The relative abundances of all ions from HD, H₂ (100 percent), and D₂ (99.2 percent

TABLE 56.—*Mass spectra of H₂, HD, and D₂*

	Ion	H ₂	HD	D ₂
Mass, percent of molecular-ion peak:	H ⁺	2.01	0.82	21.06
	H ₂ ⁺ or D ⁺	100.0	1.13
	HD ⁺	100.0
	D ₂ ⁺	100.0
Sensitivity of molecular ion, divisions per micron	H ₂ ⁺ from H ₂	25.4	25.5	25.6
	D ⁺ from D ₂	21.9

¹ Corresponding value from reference 9 is 2.82.

² Corresponding value from reference 9 is 1.32.

³ Corresponding value from reference 9 is 1.9.

D₂, 0.8 percent HD) are given in table 56. Data were obtained with 70-volt electrons and magnetic scanning. It will be noted that the total monatomic ions from H₂ and HD are practically equal and are twice the amount of monatomic ions obtained from D₂. The values for H⁺ and D⁺ from H₂ and D₂, obtained by Bauer and Beach (9) with 70-volt electrons, are included in the table. Absolute values of the two sets of data were not expected to compare; but the ratios, H⁺ from H₂/D⁺ from D₂, compared exactly with each other and quite well with Stevenson's calculated value (86). The relative sensitivity coefficients (ionization of the parent molecule per unit pressure) from four sets of data for H₂, HD, and D₂ were essentially equal, as expected (45).

Equilibrium constants at 500° C for H₂ +

⁴ Rate measurements were made in 8 minutes or less to minimize possible diffusion separation; linearity of the semilog plots of diffusion rates indicated that separation, if any, was negligible.

$D_2 \rightleftharpoons 2HD$ were calculated, using the calibration data in table 56, for three samples equilibrated over an iron catalyst. The corrected average $K_{300^\circ C}$ in table 57 is 3.87 ± 0.02 , as

TABLE 57.—*Calculation of equilibrium constants at 500° C¹ for $H_2 + D_2 \rightleftharpoons 2HD$ from mass spectral analyses*

Sample	Mass 2 corrected for D ⁺ from HD			$K_{300^\circ C}$	No HD correction $K_{300^\circ C}$
	D ₂ , percent	HD, percent	H ₂ , percent		
A.....	39.1	46.5	14.4	3.84	3.71
A.....	38.8	46.6	14.6	3.84	3.71
B.....	41.6	45.5	12.9	3.86	3.71
B.....	41.6	45.5	12.9	3.86	3.72
C.....	55.1	38.1	6.8	3.90	3.68
C.....	55.2	38.1	6.7	3.90	3.68
Average.....				3.87 ± 0.02	3.70 ± 0.02

¹ Reference 75, $K_{468^\circ C} = 3.75 \pm 0.07$. Theoretical, $K_{468^\circ C} = 3.82$; $K_{300^\circ C} = 3.82$.

compared to the theoretical value of 3.83 (99). If mass 2 values are not corrected for D⁺ ions from HD, in these samples of low H₂ content, the average $K_{300^\circ C}$ is low, 3.70 ± 0.02 . This correction was not used by Rittenberg, Bleakney, and Urey (72) in determining equilibrium at 468° C; however, with ± 35 percent H₂ the correction is less important. Their results produce an average $K_{468^\circ C}$ of 3.75 ± 0.07 , as compared to the theoretical value of 3.82.

INSTRUMENTATION AND STUDIES OF ANOMALOUS PEAKS

Mass spectrometers using tungsten filaments commonly exhibit a phenomenon known as gas sensitivity in which the behavior of the instrument, when running a given gas, depends on the nature of the gases which were introduced previously. It has been customary to condition the filament periodically with a gas such as 2-butene to prevent gas sensitivity. With the advent of the high-temperature mass spectrometer, this problem became more serious since the samples frequently caused gas sensitivity after only a few hours of operation.

Robinson and Sharkey (73) and Sharkey, Robinson, and Friedel (77) have studied the conditions causing gas sensitivity and recommended the use of rhenium, rather than tungsten, for the electron emitter in the mass spectrometer.

Other problems investigated concern reproducible pressure measurements (59) and sample volumes (32) for the routine operation of the mass spectrometer. In routine gas analysis, it is advantageous to employ constant pressure samples. With the automatic

manometer, a standard volume of gas can be introduced rapidly and the calculating time is reduced. For the analysis of liquids, it is essential that a constant volume of sample is introduced. The self-filling micropipet permits rapid and reproducible sample introductions.

Anomalous negative peaks have been observed in the mass spectra of several gases including O₂, N₂, CO and CO₂. A study was made of this phenomena, and a mechanism was proposed (75).

Conditioning of Mass Spectrometer Filaments: Tungsten Carbide Formation

The so-called conditioning of mass-spectrometer filaments is a technique employed by all users of analytical mass spectrometers. This investigation was undertaken to determine the process by which tungsten-filament conditioning takes place and also to determine the structural differences that exist between a well-conditioned filament and a so-called nonrecoverable filament. The conditioning technique is somewhat arbitrary but usually consists of introducing 2-butene or some other olefin into the mass spectrometer until the filament current becomes stable. The pressures employed are approximately 10 times the normal operating pressure of the mass spectrometer. During this conditioning period, a current drop of 20 to 30 percent is usually observed. Further conditioning, at least for a short period, such as 1 hour, results in little or no further decrease in the current. After stable current conditions have been reached, it is usually found that reliable and reproducible spectral peak intensities for hydrocarbons and other classes of compounds can be obtained.

If the conditioning process is not repeated periodically, it is found in some instances that the filament current will change with admission of samples. In most instances, stable filament operation at the minimum current value can again be achieved simply by reconditioning. However, in certain others the reconditioning results in increased filament current, and this is termed a non-recoverable filament. These filaments are discarded, resulting in lost operating time for the mass spectrometer while a new filament is being installed. This problem is particularly acute in high-temperature mass spectrometry. At times filaments have become unstable in a few hours of operation, and it has been necessary to attempt various empirical methods of recovery.

Information related to the carbiding of tungsten filaments has been published by Andrews (4), Dushman (23), and Strong (89). The information issued by the last two authors has been collected from a variety of sources. This problem is of interest to the lamp industry, and most of the information in the above references is related to tungsten filaments as used in lamps.

A tungsten filament forms the carbide W_2C after a carbon content of approximately 3 percent is reached. Further addition of carbon results in the formation of the carbide WC, and complete conversion of the filament into the carbide WC is achieved at a carbon content of 6.12 percent. Drastic changes in the cold conductance of the filament result from the formation of W_2C and WC, as shown in figure 29. At elevated temperatures, these changes are not as pronounced; there is approximately a difference of a factor of 2 in conductance between pure tungsten and pure W_2C at 2,200° K. Andrews (4) was able to correlate the cold conductance of tungsten filaments with the carbon content.

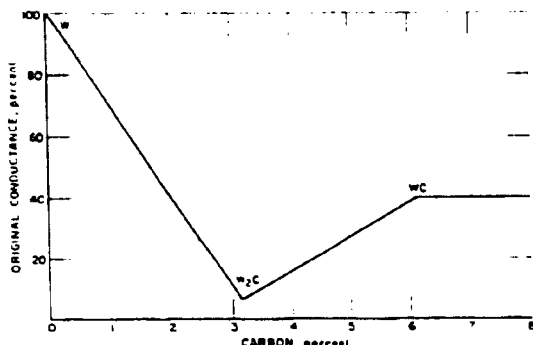


FIGURE 29.—Change of Conductance With Carbon Content for Tungsten at Room Temperature.

As used in the mass spectrometer, filament emission is regulated at a constant value by varying the current through the filament. The decrease in filament current observed as conditioning proceeds could therefore result from decreased conductivity of the filament or from an increase in efficiency of electron emission from the surface. This latter effect would result from a decrease in the work function of the surface. It has been shown by several investigators, including Klein (51), that the work functions of tungsten and tungsten carbides are approximately the same. This, coupled with the change in conductivity observed by Andrews (4) for carbided tungsten filaments, makes it appear definite that the current change observed

during mass-spectrometer conditioning results from a bulk, not a surface, change. Changes in filament current must therefore result from the presence of varying amounts of W, W_2C , and WC. These changes are observable in X-ray diffraction patterns.

The rate of conditioning is limited by two factors: First, the rate of decomposition of the hydrocarbon on the tungsten surface, which is primarily a supply problem, and second, the rate of diffusion of carbon into the tungsten, which is primarily a function of the filament temperature. Some general observations made by Andrews (4) and Dushman (23) concerning the formation of tungsten carbides follow. Conditioning can be done by almost any hydrocarbon; however, when an oxygen atom is present in the molecule, conditioning proceeds more slowly. As an example, alcohol carbonizes roughly one-tenth to two-tenths as rapidly as naphthalene. These observations also include the facts that the decomposition of a hydrocarbon on a filament surface proceeds much more rapidly on W_2C than on WC or carbon, and the diffusion of carbon through WC is much slower than through W_2C . As a result of the latter property, carbon will tend to accumulate on the surface when the supply of hydrocarbon is excessive; a condition whereby tungsten or W_2C is the emitting surface of the filament therefore appear desirable.

Below 2,400° K, carbides decompose slowly; above 2,700° K carbides decompose very rapidly, and pure W_2C will become almost pure tungsten within 8 hours. Carbon can be removed rapidly by flashing a filament in hydrogen. The effect of oxygen on a heated tungsten filament containing carbides is to remove carbon through the formation of CO_2 at lower temperatures and the formation of CO at higher temperatures. Andrews (4) examined various tungsten-lamp filaments under a microscope and found definite ring formation. These rings were identified as tungsten and the carbides of tungsten.

For this study, X-ray diffraction techniques were used in addition to microscopic examination of selected sections of the filaments. The filaments investigated were first divided into segments approximately 1/32-inch long. Individual segments were then studied by X-ray diffraction for the presence of tungsten and tungsten carbides. Representative segments were mounted and observed under an optical microscope.

Tests were carried out by preparing for examination a well-conditioned mass-spectrometer filament and also an over-conditioned mass-spectrometer filament. New, unused

filament assemblies were used in both instances. The well-conditioned filament was prepared by conditioning with 2-butene for approximately 5 hours, during which time the current dropped from 5.0 to 4.1 amperes. For the last hour the filament current remained steady, indicating that the current had reached a minimum value. This filament was then conditioned with *n*-butane for 1 hour and removed immediately without further heating.

The overconditioned filament was also prepared using a new filament. 2-Butene at a pressure of 500 microns was introduced for 25 consecutive hours. The current declined to 4.0 amperes after approximately 4 hours and showed only a slight change to 3.7 amperes during the next 6 hours. After 10 hours, the conditioning sample was pumped out and then readmitted. Overconditioning of the filament was indicated, as the current increased to 4.1 amperes during the pumpout. To insure overconditioning, 2-butene was admitted overnight for 13 additional hours.

The conditioning and deconditioning of a third mass-spectrometer filament was studied during mass-spectrometer operations, but this filament was not examined by X-ray diffraction. This filament was subjected to repeated overconditioning and deconditioning to verify the theory discussed below.

X-ray diffraction results on the well-conditioned filaments are shown in figures 30 and 31. Cross sectional diagrams based on these results are also given. Only α -W₂C

was observed in the diffraction patterns; however, the phase β -W₂C exists at temperatures above 2,600° C.

For both filaments, segments near the end-posts are almost pure tungsten. This would be expected, since these sections are relatively cool during operation and there would be very little chance for hydrocarbon decomposition or carbon diffusion in these regions. The entire length of the well-conditioned filament was found to have a core of tungsten. Center segments corresponding to two-thirds of the filament length have α -W₂C as their major surface component. Sections between the end-posts and the center section are comprised of W and WC. A major difference between the well-conditioned and overconditioned filaments is the presence of the carbide WC over the entire hot portion of the overconditioned filament.

These structural differences and also the observed current changes can be interpreted in terms of the variation of conductance with carbon content as shown in figure 32. A well-conditioned filament will, during normal operation, have a carbon content of 3 percent near the surface, corresponding to α -W₂C. The minimum conductance state is probably fairly broad, extending over several tenths of 1 percent of carbon. This will be the region of most stable operation, with the filament current constant and the ion source operating at approximately constant temperature. The addition and loss of small percentages of carbon will occur slowly as

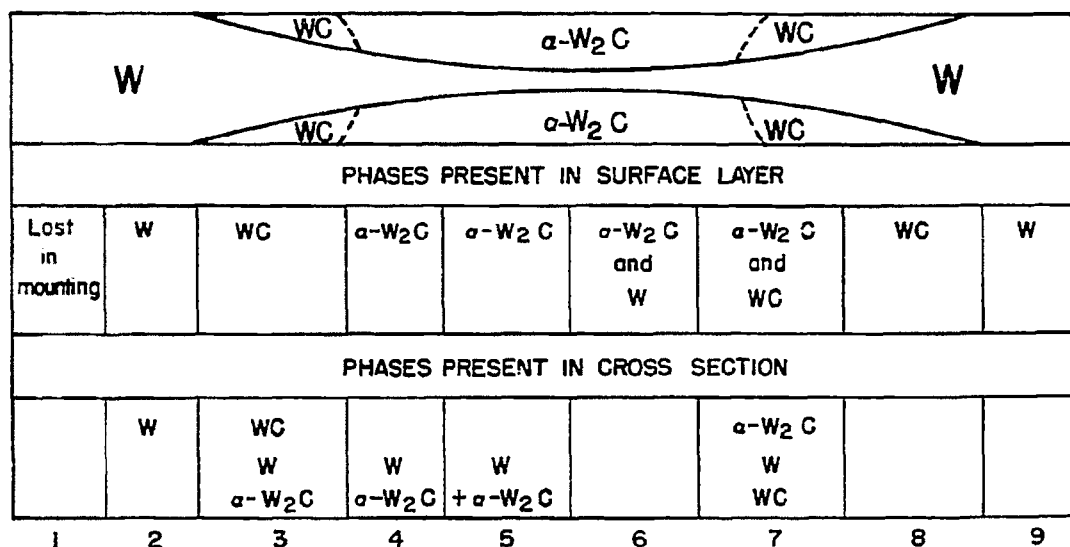


FIGURE 30.—Schematic Diagram of a Longitudinal Section of a Well-Conditioned Filament Showing Locations of Crystalline Phases.

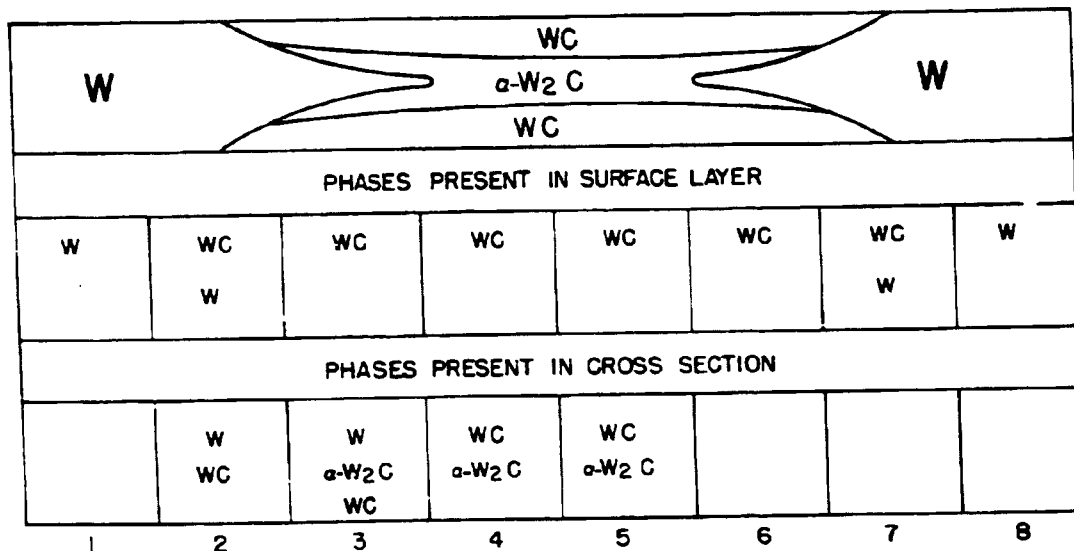


FIGURE 31.—Schematic Diagram of a Longitudinal Section of an Overconditioned Filament Showing Locations of Crystalline Phases.

samples containing hydrocarbons and/or oxygenated compounds are introduced. Overconditioning should take place slowly, because hydrocarbon decomposition is slower on WC and carbon than on α -W₂C.

An increase in filament current resulting from the loss of carbon can therefore be easily corrected by reconditioning. An increase in filament current, resulting from the carbon

content being considerably above the 3-percent value, corresponds to filament conductance values on the right-hand portion of the curve. The addition of carbon by conditioning will simply result in a further increase in filament current. Operation with the carbon content between 3 and 6 percent can therefore be correlated with observed operating characteristics of an overconditioned fila-

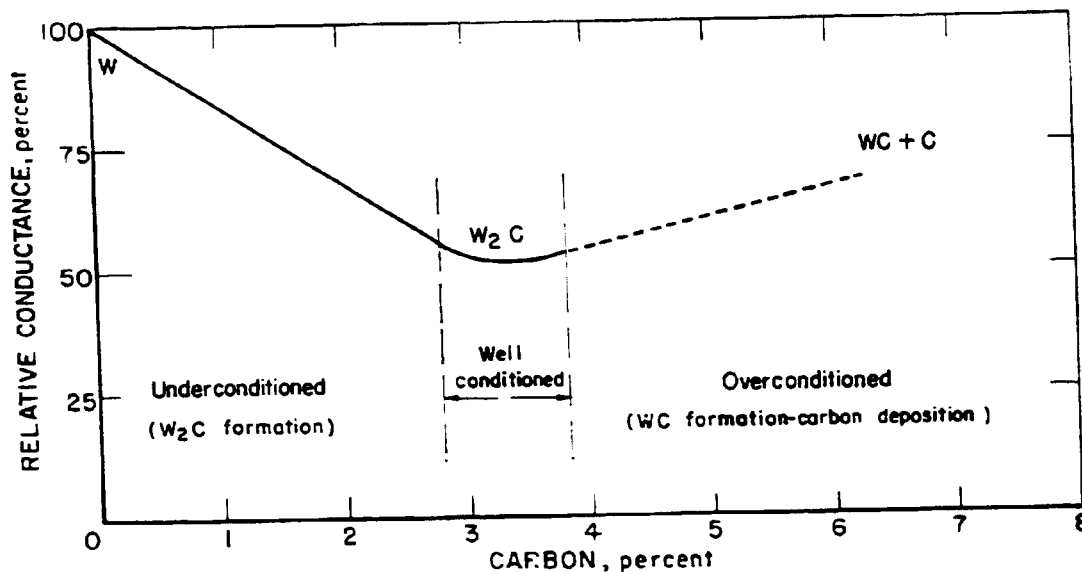


FIGURE 32.—Conductance Change With Carbon Content for a Tungsten Filament at 2,475° C.

ment. As carbon diffuses more slowly in the carbide WC than in α -W₂C, carbon will accumulate on the surface of an overconditioned filament. It appears that the one major difference between a well-conditioned and overconditioned filament is the presence of α -W₂C on the surface of the well-conditioned filament with the possibility of further carbon uptake.

This theory has been verified by tests on a filament during actual instrument operation. Figure 33 shows the tests performed and the resulting changes in filament current. This filament was overconditioned by the introduction of 2-butene at high pressure until an overconditioned, unsteady state was reached. High-pressure oxygen was then introduced, after which the filament current declined to its previous normal operating value. This cycle was reproduced three times by the alternated introduction of high-pressure oxygen and hydrocarbon. After the final introduction of oxygen, the filament was left in

good operating condition, as judged by the filament current. After these tests, this filament operated several months, during which time stable operating conditions were maintained.

The results of this investigation give a basis for many of the observations derived from empirical tests made in the past. It has been observed that unstable operation resulting from the repeated analysis of mixtures of aromatic compounds could be corrected by introducing oxygen. This is simply a case of deconditioning the filament after it had been overconditioned with aromatic compounds. It has also been observed that increasing the operating temperature of the ion source improved the stability of operation when samples consisting almost entirely of hydrocarbons are introduced repeatedly. Any increase in filament temperature, resulting from an increase in temperature of the ion source heater, should reduce WC formation and carbon accumulation on

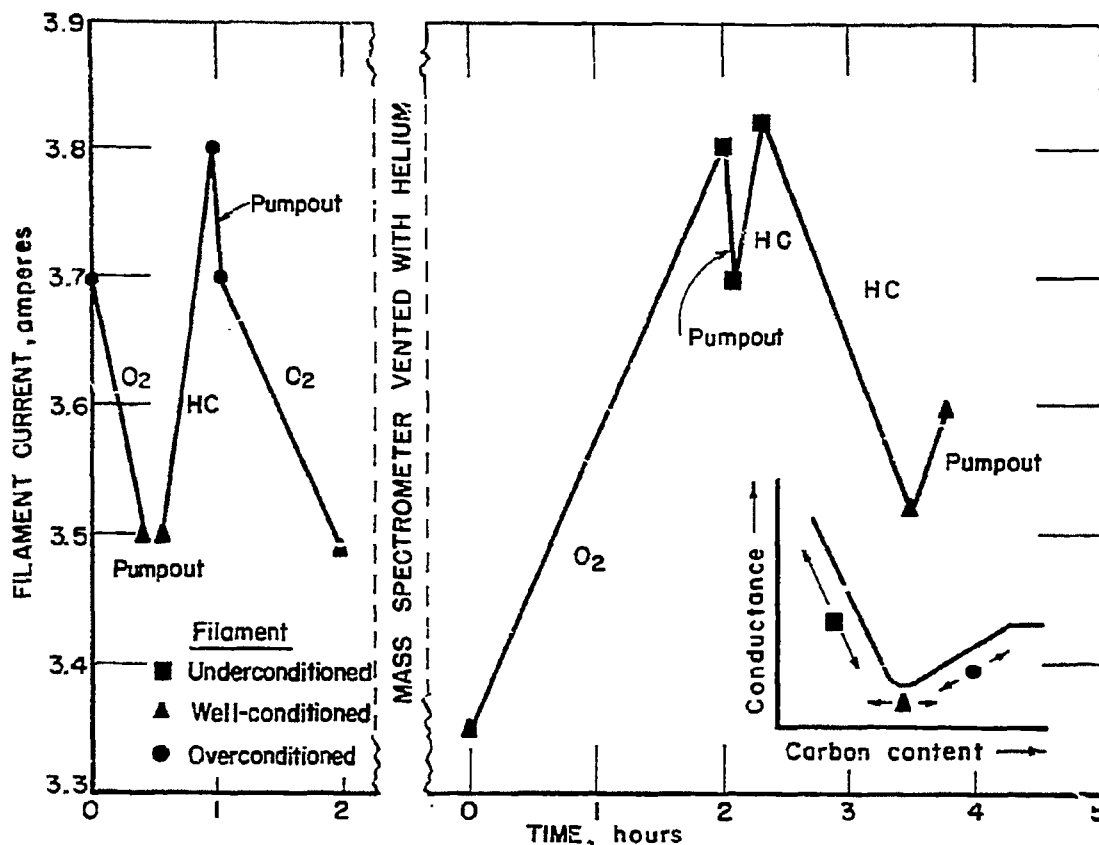


FIGURE 33.—Current Changes Observed With the Introduction of Oxygen or Hydrocarbon.

the filament surface, as carbon will diffuse more rapidly with increased filament temperature. In high-temperature mass spectrometry there is a very definite limit to the sample pressure that can be used and still retain stable current conditions; experience indicates this limit is roughly 50 microns. When this pressure limit is exceeded, definite current changes are observed with each sample introduced. This also can be explained in terms of overconditioning and carbon deposition on the surface of the overconditioned tungsten filament.

Several mass-spectrometry laboratories, particularly those having high-temperature mass spectrometers, have reported instances of filaments deforming after being used a relatively short time. This deformation in the center section of the filament displaces the emitting tungsten surface relative to the slit and renders the filament useless. This has been attributed to high-voltage arcing creating a hot spot in the center of the filament. Bowing of tungsten filaments has occurred, however, in instances where the high voltage has not been applied in the mass spectrometer. Thus, it is felt that this deformation is also related to the conditioning process and carbide formation. The density of tungsten is 19.3, while the densities of W₂C and WC are 16.1 and 15.7, respectively. As the densities of the two carbides are appreciably lower than the density of tungsten, deformation of the tungsten filament could result from excessive carbide formation.

The results of this investigation should not only provide a technique for increasing the usable life of tungsten filaments but also indicate how more stable mass-spectrometer operation can be obtained.

Rhenium Filaments for Mass Spectrometry

Many properties of rhenium and its possible applications in electronics had been investigated by Sims (84). Several of these properties make rhenium a desirable electron emitter. It melts at approximately 3180° C, only 232° below tungsten and its thermionic work function is 4.80 volts, compared with 4.56 for tungsten. Rhenium is considerably more resistant than tungsten to the water cycle, a major advantage in mass spectrometry since many samples contain large percentages of water. Further, rhenium remains ductile at all temperatures and therefore is less likely to be ruptured by thermal or mechanical shock. It is easily spot welded and its carbides are unstable. For the same emis-

sion density, its evaporation rate is about 150 times that of tungsten (though still only about one-fortieth that of carbon). One may expect a service life of a rhenium emitter, limited by evaporation alone, to be at least several months at the emission densities ordinarily used in analytical mass spectrometers.

Rhenium emitters have been used in two analytical mass spectrometers for several years. The tungsten wire on a standard filament assembly for a Consolidated type 21-103 mass spectrometer was replaced with a rhenium wire of the same diameter (0.007 inch). Both rhenium and tungsten heaters have been used on assemblies having rhenium filaments. Satisfactory operation was obtained, and the temperature of the ion source could be controlled at the usual 250° C. For the same emission, rhenium filaments required less current than tungsten filaments, 3.0 instead of 3.8 amperes. Rhenium filaments in the heated-inlet mass spectrometer were exposed for several months to the same variety of high-molecular-weight aromatic compounds that caused difficulty with tungsten filaments. Operation was satisfactory at all times, without evidence of gas sensitivity or loop formation.

As expected, rhenium emitters did not form solid carbides. Repeated attempts to "condition" rhenium filaments were unsuccessful, the filament current remaining essentially constant at 3.0 ± 0.05 amperes during 4 hours of treatment with 2-butene. The absence of carbides was verified by X-ray analysis of a rhenium emitter that had been used for over 3 months. On several occasions filament emission increased slightly over 8-hour periods. This variation was not associated with the introduction of individual samples but appeared to be related to gradual contamination of the ion source. This condition was completely cured by pumping overnight. Improved temperature stability is indicated by the mass 127/mass 225 pattern of normal hexadecane. Measured over 3-week periods, the average deviation from the average pattern was 0.8 percent with rhenium and 2.2 percent with tungsten. The ion source heater had to be adjusted several times each day when the tungsten emitter was in use. Better temperature stability of the rhenium filament is of considerable advantage in low ionizing voltage and appearance potential work. Rhenium emitters have been found durable enough to be used in analytical mass spectrometers. Above-average life of the ion source (period before dismantling and cleaning is required) has been realized repeatedly in the mass spectrometer with heated inlet

since rhenium has been in use. Comparative background tests, made by introducing 100 microns of oxygen into instruments having rhenium and tungsten emitters, indicated a reduction in the CO_2 background by a factor of about 5 with rhenium filaments.

These advantages were observed primarily in using the heated-inlet mass spectrometer with samples containing high percentages of aromatic compounds.

Automatic Manometer for Constant-Pressure Gas Sampling

In routine mass-spectrometric analysis of gases, pressures are measured by manometric methods. Such measurement often requires manipulation of stopcocks or valves to obtain pressures in the desired range; constant pressures are nearly impossible to obtain in this way. A simple method was therefore sought to produce constant pressure automatically.

The device developed is a manometer with a fine-porosity sintered-glass disk built into one leg; some restriction is needed between the legs of the manometer to retard the mer-

cury flow when sampling is done at near atmospheric pressures. The device is placed at the inlet of the spectrometer's gas-sampling system.

Operation is illustrated by the three positions of the mercury column shown in figure 34. The first drawing shows the position with the sample-inlet system evacuated. An auxiliary vacuum pump continuously exhausts the right side of the sintered disk. In the second, the sample is admitted to the inlet system and forces the mercury column to the position indicated. The auxiliary pump immediately begins to remove excess sample through the sintered disk and reduces the pressure to the desired value. Pumping stops sharply when mercury reaches the top of the sintered disk; overshoot is not a serious problem because pumping slows progressively as more and more of the disk becomes covered by mercury. The time required to reach the cutoff point is about 10 seconds. Pressure of the sample is determined by the difference in the two legs of the manometer, but because of sticking or slight

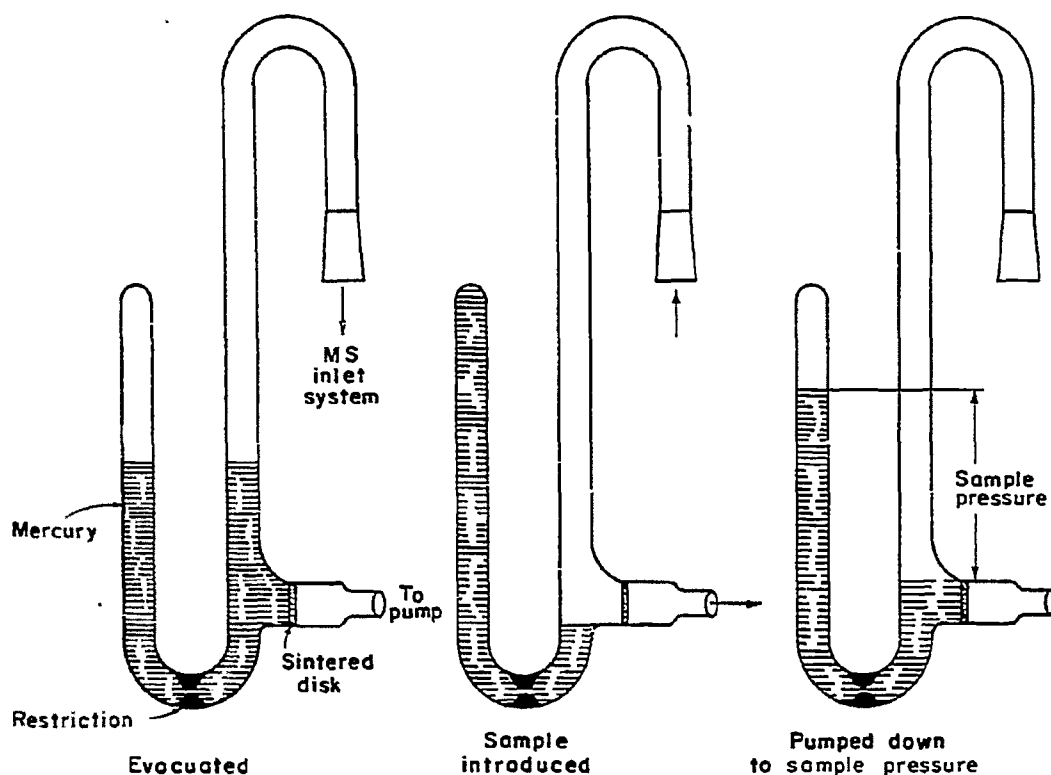


FIGURE 34.—Manometer for Obtaining Uniform Gas Pressure During Sampling.

overshooting this difference is not always an accurate measurement of pressure. To obtain the true sample pressure delivered by the device an accurate auxiliary manometric device must be used.

Two different sampling manometers were constructed to operate at pressures of 28 and 70 mm. Measurements on samples of air were made with a micromanometer after an 8.6-cm³ sample had been expanded into a 3.3-liter volume.

In the 70-mm (183-micron) tests pressures measured were 182.7, 183.1, 183.1, 182.7, and 183.1 microns, with a mean of 182.9 microns, a spread of 0.4 micron (0.22 percent), and a standard deviation of 0.2 micron (0.12 percent). The deviations include errors of volume expansion and of the micromanometer.

Table 58 shows the reproducibility of the 28-mm (72-micron) samples as well as the results of two extremes of operation: Data in the top half were obtained by introducing a sample of air by opening the system rapidly to full atmospheric pressure; data in the bottom half are for samples of slightly over 28-mm introduced slowly and with extreme care, so that the sintered disk was barely uncovered. The difference in average pressures, 0.5 micron (0.19-mm), is presumably due to the slightly different momenta with which the mercury approaches the cutoff point. In each series of runs the percentage values for spread and standard deviation are extremely low; best results are obtained by rapid introduction. The overall values for both rapid and slow introductions show fairly good reproducibility: For a 28-mm sampling device the standard deviation, 0.44 percent, represents a pressure deviation of 0.12-mm.

TABLE 58.—*Reproducibility of constant-pressure gas samples, with various introduction methods*

Method	Microns	Percent
Rapid, atmospheric pressure: Introduction:		
1.....	72.2	
2.....	72.1	
3.....	72.1	
4.....	72.2	
5.....	72.3	
Mean.....	72.2	
Spread.....	.2	.3
Standard deviation.....	.08	.11
Slow, low pressure: Introduction:		
1.....	72.5	
2.....	72.8	
3.....	73.0	
4.....	72.7	
5.....	72.7	
Mean.....	72.7	
Spread.....	.5	.7
Standard deviation.....	.18	.25
Overall total:		
Mean.....	72.46	
Spread.....	.9	1.2
Standard deviation.....	.32	.44

1 ~ 28 mm.

As the sample pressure is reduced by pumping through a sintered disk, possible fractionation of the sample had to be checked. A sample of gas containing two components of different molecular weights, hydrogen and carbon monoxide, was introduced at atmospheric pressure. After automatic reduction of the pressure to 28-mm, mass-spectrometric analyses were made. Data in table 59 do not indicate fractionation within experimental error for either rapid or slow introduction of the sample.

TABLE 59.—*Mass spectral test for fractionation through sintered disk. Determination of ratio of components in a 1 to 1 mixture of H₂ and CO*

[Pressure, 28mm; known ratio of H₂ to CO, 0.981]

Method	Ratio, H ₂ /CO
Rapid, atmospheric pressure: Introduction:	
1.....	0.983
2.....	.980
3.....	.980
4.....	.982
5.....	.983
Average.....	.983
Slow, low pressure: Introduction:	
1.....	.980
2.....	.983
3.....	.981
4.....	.982
5.....	.986
Average.....	.982

This apparatus may be built so that the range of pressure can be changed. However, simplicity renders interchangeable units preferable. The unit has not been applied at pressure greater than 120-mm.

Uniform pressures of samples enable easier checking and comparing of results; delicate control of valves to get nearly uniform pressure is replaced by automatic operation; and analytical accuracy is increased somewhat by the high precision of measurement of calibration and sample pressures.

Self-Filling Micropipet for Liquid Introduction

Analyses of liquid mixtures by mass spectrometer require introduction of minute amounts of calibration liquids (on the order of 0.001 ml) and measurement of these amounts to about 1 percent. Sample introduction usually consists of expanding the liquid directly into the high-vacuum system of the spectrometer by touching a pipet to a sintered-glass disk under mercury (90). Two methods for quantitative measurement of small amounts of liquid have been published: The volume of liquid is measured by a micropipet constructed of thermometer tubing (90), or the pressure of the expanded vapor is measured by a specially designed micro-

manometer which operates in the pressure range of 0 to 100 microns of mercury (100).

The method herein described is a volume-measuring modification which is simple, time saving, and sufficiently accurate, and involves no reading errors. The method requires only the usual mercury-sintered disk valve and a self-filling 0.001-ml micropipet (1, 10) (fig. 35; available commercially in sizes 0.001 to 0.010-ml).

The methods permit sufficiently good quantitative analysis, as shown by the reproducibility tests in table 60 for *n*-heptane, *n*-octane, *n*-nonane, and a xylene mixture, both with air flowing through the capillary and with mercury sealing. Precision of both methods apparently decreases with the vapor pressure. The airflow method is somewhat more precise in all four cases; accuracy of this method is demonstrated by analyses of a

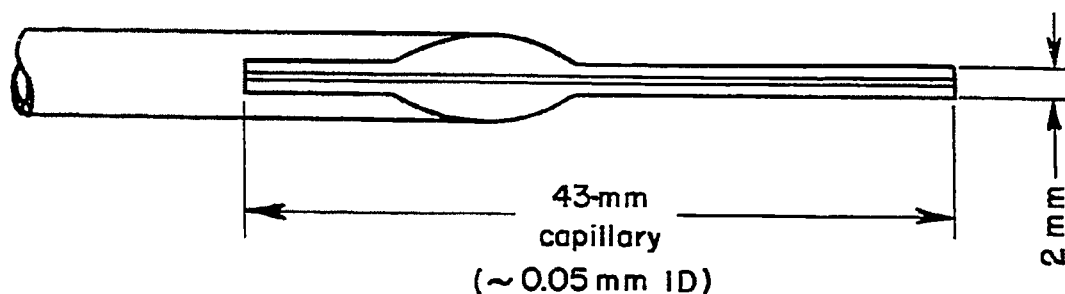


FIGURE 35.—Self-Filling 0.001-ml Micropipet.

When dipped in a liquid, the small section of capillary tubing becomes filled only to the top by capillary action; then the liquid is delivered completely to the vacuum system by touching the pipet tip to the sintered disk under mercury. Air is allowed to flow through the capillary following the sample until all visible droplets of liquids are swept into the instrument. As the amount of air thus introduced is immaterial to analysis, the mass peaks for air need not be measured. Quantitative results for hydrocarbons appear to be best if the pressure of sample plus air in the 4-liter vacuum system is kept near a Pirani gage reading of 0.20 ± 0.03 mm. Under these conditions the amount of air represents 20 to 30 percent of the total; no detrimental effects on the mass spectrometer filament have been noted. An alternative method, sealing with mercury, consists of filling the capillary with the sample and then pouring enough mercury into the pipet to cover the upper tip. Thus mercury, instead of air, flows through the capillary following the liquid sample.

typical six-component synthetic blend, mainly octanes (table 61). Some inconsistency is expected for the mercury-seal method, inasmuch as droplets of liquid occasionally are trapped inside the capillary by mercury. Use of this method is essential when air must be excluded.

Calculating time is appreciably decreased by the use of this pipet. It is not necessary to calculate percentage patterns from the spectra of pure calibration compounds, because the amount of sample and therefore the spectral peak height are always the same, within experimental error. For the same reason, sensitivity coefficients (peak heights/sample pressure or volume) are not needed, for the peaks themselves serve this purpose. Because the partial volumes of the constituents add up to near 1.0, approximate percentages are obtained immediately, although normalization to 1.0, or 100 percent, is usually necessary.

Application with increased accuracy to C_4 alcohols, C_3 acids, and other oxygenated compounds was obtained by a modification of the

TABLE 60.—Reproducibility of liquid introduction into mass spectrometer by 0.001-ml self-filling micropipet

Component	Mass	Average peak height ¹		Maximum spread, percent		Average deviation from average, percent	
		Airflow	Mercury seal	Airflow	Mercury seal	Airflow	Mercury seal
<i>n</i> -Heptane	100	550 (5)	500 (5)	1.8	4.6	0.6	1.4
<i>n</i> -Octane	114	281 (5)	271 (5)	2.8	8.5	.7	2.0
<i>n</i> -Nonane	128	225 (5)	225 (7)	4.5	7.3	1.6	2.5
Xylenes	106	213 (6)	212 (6)	3.8	8.6	1.2	2.1

¹ Figures in parentheses represent number of runs.

mercury seal method, which consists of forcibly squirting sample and mercury through the pipet and onto the sintered disk.

TABLE 61.—Mass spectral analyses of synthetic blend introduced with 0.001-ml self-filling micropipet, volume-percent¹

Component	Synthetic blend	MS analysis 1	MS analysis 2
n-Nonane	8.2	3.5	3.9
n-Octane	74.3	73.2	75.3
2-Methylheptane	7.0	6.9	7.0
3-Methylheptane	6.9	7.2	6.4
4-Methylheptane	2.9	4.3	2.9
n-Heptane	5.2	4.9	4.5

¹ Airflow method used for calibration and samples.

Anomalous Negative Peaks in Mass Spectra

In the mass spectra of the gases O₂, N₂, CO, and CO₂, negative peaks have been found approximately two mass units lower than the peaks of the positive molecular ions. Arnot (5) and Sloane and Press (85), using mass spectrometer tubes of special design, observed negative peaks corresponding roughly in mass to positive ions of these gases.

The mechanisms for negative ion formation that seem most probable are those proposed by Arnot (5). In both processes the positive ion captures an electron at the metal surface and is neutralized but left excited. This is followed by either (1) capturing another electron to form a negative ion of the same type, or (2) transferring the energy of the positive ion to another type atom on the surface, which in turn captures an electron to form a negative ion of another type.

Negative peaks have been observed with various ion sources while using the same analyzer section of the mass spectrometer tube. This indicates that the source of the negative peaks is in the region of the exit slit of the analyzer section and probably

arises from a nonconducting layer on the exit slit plate. A schematic diagram of this possible source of negative ions from carbon monoxide is given in figure 36. With field conditions set to focus positive ions of mass 26, mass 28 ions will have a larger radius and strike some point (as shown) on the exit slit plate. This spot on the plate will then act as the source of negative ions, which are deflected by the magnetic field, collected, and recorded as a negative peak at 26.2 on the mass scale. The difference in radius of the "mass 26.2" and mass 28 ions is approximately 2 mm. Assuming that the negative ions CO⁻ are formed with very low energy, the radius of the path of these ions would be about this value, making it possible for them to be collected. In figure 37 is shown a negative peak near mass 26.2 on the portion of a CO spectrum.

Table 62 gives the ratio of negative to positive ions for the gases studied thus far. These values are of the same order of magnitude as the probabilities of conversion given by Arnot (5) for O₂, 0.42×10^{-4} , and for CO₂, 2.3×10^{-4} .

The negative ion N₂⁻ is known to be unstable and was not detected by Arnot (5), but in the present work on N₂ a negative peak near 26.2 was found. This may be due to a

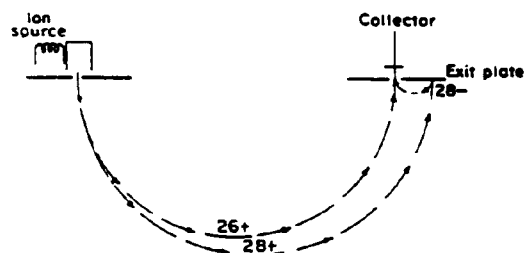


FIGURE 36.—Possible Source of Negative Peaks.

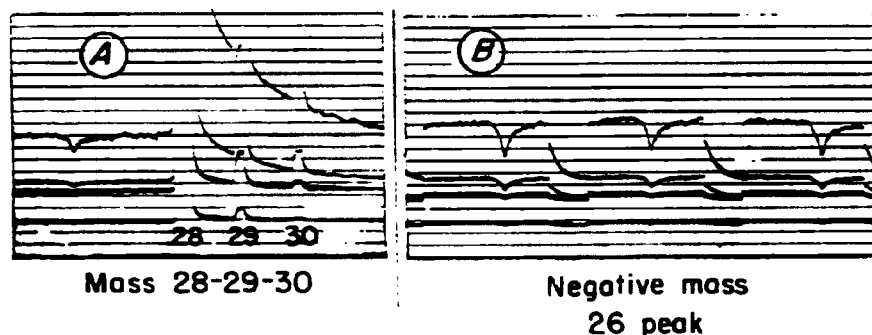


FIGURE 37.—A, Portion of CO Spectrum; B, Reproducibility of Negative Mass 26 Peak.

negative ion of another type, according to Arnot's second mechanism. However, the detection of N_2^- is feasible in the present case because of the short distance traversed to the collector. Further, negative peaks in the spectra of all four gases appear to have the same shape. If a transfer of energy were involved, the ions formed would possibly have a large energy spread giving broad peaks. Therefore, the negative peak in the spectrum of N_2 is probably due to N_2^- .

It was difficult to relate peak height to pressure accurately because of the size of the peak; however, as nearly as could be

determined, this relationship was linear up to three times normal operating pressure. Any negative ions from hydrocarbons formed by this process would not be detected because of the much larger positive ion peaks occurring at the same masses.

TABLE 62.—*Ratio of negative to positive ion peaks*

<i>Gas</i>	<i>Ratio</i>
N_2	2.9×10^{-4}
O_2	3.5×10^{-4}
CO.....	4.5×10^{-4}
CO_2	5.9×10^{-4}

CONCLUSIONS

The analytical techniques described resulted from studies of the mass spectra of alcohols, ketones, esters, acetals, trimethylsilyl ether derivatives of alcohols, paraffins, and naphthenes. These techniques made possible qualitative and, in some instances, quantitative analyses of complex mixtures from the Fischer-Tropsch synthesis. Methods developed for obtaining mass spectra at low-ionizing voltage yielded carbon number distribution data for saturate, aromatic, and tar acid fractions of oils derived from coal.

Extension of this investigation to higher boiling fractions (bp $>300^{\circ}\text{C}$) will be limited by (1) availability of pure compounds for calibration, (2) vapor pressures of samples, and (3) resolving power of the instrument. Lack of pure compounds will probably not be a serious handicap for at least semiquantitative analyses.

Use of low-ionizing techniques will probably increase. Indications are that the large

est deviations in sensitivity with degree of substitution occur for the alkylbenzenes and alkylphenols. Only relatively minor variations in sensitivity factors occur at a given carbon number for other types having an aromatic ring structure. Extrapolation to zero sensitivity at infinite molecular weight appears satisfactory for obtaining approximate sensitivities for phenolic as well as neutral material.

Shortage of pure compounds will limit the investigation of synthetic mixtures that should accompany the extension of any method. The limitation of resolving power is being overcome by the adaptation of double focusing instruments for analytical work. The most serious limitation is probably low vapor pressure. Extension of mass spectral techniques to material of higher molecular weight will therefore depend largely on the development of techniques for obtaining ionic species representative of the sample.

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