APPLICATIONS OF MODERN METHODS TO THE ANALYSIS OF OILS, FUELS AND LUBRICANTS

PART 1

A CRITICAL SURVEY OF METHODS OF MEASURING UNSATURATION IN MOTOR SPIRIT

PART 11

APPARATUS DESIGNED FOR THE SPECTROGRAPHIC ESTIMATION OF TRACE ELEMENTS IN OILS

by

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Thesis presented for the degree of Ph.D.,
University of Edinburgh.
October, 1948.

Preface.

An account is given of the historical development of the halogenation methods of measuring unsaturation in hydrocarbons, originating in the use of bromine for fatty oils, being replaced by iodine in one form or another, and finally reverting to the original halogen.

An original investigation is described dealing with the use of pyridine sulphate bromide for the estimation of unsaturation in motor spirit, resulting in the conclusion that although good results can be obtained for straight-chain and ring compounds, branch-chain hydrocarbons give erroneous results.

The possibilities of the Kaufmann reagent are exhaustively investigated, and although the final conclusions do not appear to provide a solution to the problem of branch-chain addition, several interesting features have arisen during the course of the work, which so far have not been specifically mentioned by other workers in this field.

The particular part played by peroxides in affecting the computation of Bromine Numbers is tentatively investigated, and the results obtained are considered by the Author to justify the further work he contemplates on this subject.

It is probable that a new method of estimating peroxide values may result from this aspect of the research.

Finally, an account is given of the probable mechanisms involved in bromination by means of the Kaufmann reagent in the light of the most recent interpretations of reactions in terms of electronic forces.

In Part 11 of this Thesis, details are given of two devices designed by the Author for use in the estimation of trace elements in oils and other compounds of an organo-metallic nature. In particular, the oil-spray blow-pipe promises to supply an answer to the need for a rapid method for the determination of additives in oils, by the application of a modified version of the original flame spectrum analysis of Lundegårdh.

The micro-filter stick offers one solution to the present difficulty of transferring small quantities of material, sithout loss, to the electrode crater, prior to spectrographic analysis.

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PART 1.

Introduction.

Most of the modern methods of estimating the amount of unsaturation in motor spirit are based on the absorption of bromine by the olefinic constituents in the hydrocarbon mixture, and it is of historical interest to record that Allen[1] was the first to employ the same halogen for the determination of the amount of unsaturated fatty acid glycerides in fats, a process which he published as far back as 1881.

Although improved by Mills,[2] the use of bromine was replaced first by Hübl's[3] iodine method, and then by the more stable and quicker acting iodine monochloride in glacial acetic acid solution introduced by Wijs[4].

It was thought for many years that this property of halogen absorption was of limited value in the study of oils derived from mineral sources, but Dunstan and Thole[5], in their work on the chemical nature of lubricating oils, used Wijs's reagent to measure the effectiveness of the separation of unsaturated from saturated hydrocarbons by means of liquid sulphur dioxide.

These authors were careful to point out the limitations of Wijs's solution, however, when applied to mineral oils, emphasising the importance of the time factor and the amount of excess reagent employed. They stated that whereas rape oil yielded a steady iodine value in three minutes, provided a reasonable excess of Wijs's solution were present, the value of a mineral lubricating oil was invariably augmented by an increase in either of the above mentioned factors.

The importance of ascertaining the degree of unsaturation in petroleum distillates, resulting from the rapid development of the internal combustion engine, led to a re-examination of the original bromination methods, and a modified version of a procedure developed by McIlhney[6] in 1899, is at present the accepted standard method of the Institute of Petroleum.

This method consists in brominating the hydrocarbon mixture with a carbon tetrachloride solution of bromine, under standard conditions of time and temperature, but on account of the unselective action of this reagent, substitution as well as addition takes place to some extent.

The fraction of bromine absorbed in this reaction depends particularly on the type of hydrocarbon present in the mixture, side-chain compounds giving abnormal results. Repeatable values may be obtained, but in view of the above findings, the Bromine Numbers so found cannot be regarded as a satisfactory measure of unsaturation in the case of an unknown motor spirit.

Johansen[7] claimed that minor modifications of the McIlhiney method gave satisfactory results, but since negative results for bromine addition were sometimes obtained, some doubt must be expressed whether the values from this method are a correct measure of either substitution or addition.

In an attempt to minimise the effect of large halogen excess and thus reduce substitution, Francis[8] developed a method by which bromine was released slowly in the reaction mixture, The latter consisted of an aqueous solution of potassium bromide-bromate acidified with sulphuric acid, successive small additions of the reagent being added to the hydrocarbon with vigorous shaking, until the faint colour of the excess halogen persisted for a specified time.

Cortese,[9] in 1929 proved that the Francis method, although reasonably good for straight-chain compounds, was unreliable for certain ring structures, a finding which was confirmed later by Mulliken and Wakeman,[10] who also stated that the accuracy was just adequate enough to establish the number of double bonds in the case of cyclic compounds and the alkadienes.

Further modifications were made on the Francis method by Thomas, Block, and Hoekstra,[11] who found that substitution could be reduced by cooling the reaction mixture at several stages. According to Bue,[12] this modification still gave high results for unsaturated branch-chain compounds, and he obtained better results by employing excess potassium bromide.

A direct titration method was introduced by Lewis and Bradstreet,[13] who used the excess potassium bromide recommended by Bue as a saturated solution in 10 per cent sulphuric acid. This they added to the hydrocarbon dissolved in carbon tetrachloride, titrating the mixture with small additions of bromide-bromate solution, shaking vigorously after each addition, and limiting the excess halogen to 1 ml. Although they eliminated the trial and error procedure of the Francis method, and the cooling recommended by Thomas, Block, and Hoekstra, unsatisfactory results were obtained for tetra- and triiso-butylene.

Green[14] repeated part of Lewis and Bradstreet's work, and whilst confirming the accuracy of the method as applied to a few straight-chain hydrocarbons, he found that, in examining a particular benzole fraction, increasing the excess reagent resulted finally in a Bromine Number of inordinately though constant high value.

Another method was suggested by Uhrig and Levin[15] who employed a solution of bromine in acetic acid to titrate a chloroform solution of the hydrocarbon direct, taking as end-point the yellow tinge of the excess bromine. After stating that they did not investigate the question of whether or not substitution occurred, owing to the "intricacy of the problem", they concluded that as their procedure used no excess bromine and yielded theoretical results, they were justified in concluding that substitution did not occur.

The most obvious weakness in this method was its inapplicability to coloured samples, which Johnson and Clark[16] overcame by a modified Francis procedure, using a carbon tetrachloride solution of the hydrocarbon mixed with glacial acetic acid, and titrating with a potassium bromide-bromate solution.

The excess halogen was determined by means of standard thiosulphate, starch being used to improve the precision of the end-point.

Branch-chain olefines, such as 3:4:4-trimethylpentene-2, 3-methyl-2-isopropyl-butene-1 and 2-ethylhexene-1 however, gave results which were 19.7, 16.3 and 18.6 per cent respectively, above the theoretical value. They concluded from these results that it would be impossible to analyse olefine mixtures quantitatively for branch-chain compounds by their method, unless only one such hydrocarbon were present and its identity known, a rather impossible prerequisite in an unknown motor spirit.

Despite these shortcomings, this method has been accepted as a tentative standard for olefines and aromatics in petroleum distillates by the American Society for Testing Materials.

The Rosenmund and Kuhnhenn Method.

For the determination of iodine values of fatty oils, Rosenmund and Kuhnhenn[17] suggested the use of pyridine sulphate bromide as a reagent capable of providing a more active halogen than the iodine monochloride used in the classical Wijs's method. In discussing the chemistry of this reagent,[18] they showed that the compounds of bromine with pyridine or quinoline are active bromine addition agents which do not take part in secondary reactions such as substitution. They therefore claimed that as substitution did not occur, the effective excess of reagent was less critical.

Bolton and Williams[19] applied this reagent to the measurement of the unsaturation of the unsaponifiable fraction of olive oil, later shown by Drummond[20] and others, to consist mainly of the unsaturated hydrocarbon squalene, and pyridine sulphate bromide is now the standard reagent for the estimation of unsaturation in all fats and fatty oils.

In dealing with the estimation of iodine value of tall oil and other similar highly unsaturated conjugated compounds, Rowe, Furnas and Bliss[21] claimed That consistently good results were obtained in the case of eight samples of commercial crude tall oil, and they proved that substitution did not take place by the following test. A sample of the crude tall oil, along with a blank, was allowed to stand for 23 days in the presence of an excess of pyridine sulphate bromide. Distilled water was added and the free bromine then removed by successive extractions with carbon tetrachloride. Acidification of the aqueous layer with sulphuric acid and subsequent oxidation with hydrogen peroxide gave a negative test for bromide ion, using the sensitive fluorescein method of detection.[17]

Further use of this reagent has been made by Angell,[22] for the estimation of ring compounds such as furfuryl alcohol, furan, and sylvan. Little, if any, substitution is said to occur, and although certain furan derivatives such as furoic acid and furfural are unaffected by this reagent, they are attacked by acidified potassium bromide-bromate solution.

Consideration does not appear to have been given to the use of this reagent for the determination of the unsaturation in other hydrocarbon mixtures such as motor spirit, but this has now been investigated by the author, vide Experimental Section, page 25.

A comparison was made between the methods of McIlhiney, Francis, and Rosenmund and Kuhnhenn, applied to the analysis of synthetic mixtures of saturated and unsaturated hydrocarbons of known Bromine Numbers.

The investigation was then continued to find out if the reaction time was a factor of importance in the bromination of a number of straight-chain and also branch-chain hydrocarbons.

It was established that in the case of the straight-chain compounds, the Bromine Numbers increased only to a slight degree, even when the reaction time was extended to one hour. Both of the branch-chain pentenes, however, gave abnormal results, even after the short reaction period of five minutes, Table 1, page 10.

It was obvious that substitution had taken place, but on account of the acidic nature of the reagent, the hydrobromic acid could not be determined by a simple titration with thiosulphate after the addition of potassium iodate.

TABLE 1.

Bromine Numbers - Pyridine Sulphate Bromide Method.

Time in Minutes:..........	5	60	Theory
Octene-1..............	142.1	144.8	
	141.8	143.6	142.5
	142.5	144.7	
	142.0	144.0	
Hexene-1..............	190.3	191.1	
	189.9	190.9	190.0
	190.2	191.3	
	190.1	191.2	
Cetene-1..............	71.0	74.6	
	71.0	74.2	71.25
	71.1	74.3	
	71.2	75.0	
Diallyl...............	390.2	390.8	
	389.8	391.1	389.4
	390.0	390.9	
	389.9	391.4	
2:4:4 Trimethylpentene-1:	168.1	185.2	
	166.7	186.5	142.5
	174.2	187.1	
	169.5	186.7	
2:4:4 Trimethylpentene-2:	177.8	253.9	
	176.8	252.9	142.5
	174.8	258.7	
	179.4	259.8	

THE KAUFMANN REAGENT.

The failure of the pyridine sulphate bromide solution to yield satisfactory results with branch-chain hydrocarbons, as already described, led to the examination of a reagent introduced by Kaufmann[23], originally for the determination of unsaturation in fatty oils, which consisted of a solution of bromine in pure methanol saturated with sodium bromide.

Kaufmann claimed that this reagent was more stable than any other bromine solution tested, due, he stated, to the fact that the halogen did not appear to exist in the free state, but was apparently loosely attached to the sodium bromide forming the tribromide, analogous to the better known triiodide. Such a solution, he observed, was ideal for bromination as it was odourless and stable, reacted more energetically than iodine and completely saturated the double bond, "without the formation of substitution products".

Although Kaufmann was no doubt correct in his statement regarding the relative reactivity of his reagent compared with iodine, the present day accepted theory, see Mechanism Section, page 60 , that bromination is affected by the active Br^+ , suggests that the halogen in such a mixture would not be so reactive as that in the McIlhiney or the pyridine sulphate bromide reagent. The bromine in the former solution is largely associated with Br^- as Br_3^-, and it therefore follows that the Br^- would depress the formation of the active Br^+ in accordance with the Law of Mass Action :-

$$Br_2 \rightleftharpoons Br^+ + Br^-$$

From a survey of bromination methods applied to measurement of unsaturation in petroleum fractions, Grosse-Oetringhaus[24], in 1938, concluded that Kaufmann's method gave reliable results. Uhrig and Levin[15], however, found that the Bromine Numbers obtained by this procedure were too high, although they did observe that theoretical results were approached when the excess halogen was at a minimum. On this fact they based the accuracy of their own method, as described on page 5.

Furthermore, Kaufmann's claim to saturation of the double bond without the formation of substitution products, appears to have been unchallenged until Jordan[25], in 1941, drew attention to the fact that the total bromine consumed was not necessarily due to addition alone.

He proved that in the bromination of synthetic styrene and purified indene, one quarter of the total bromine absorbed was present in the reaction flask as hydrobromic acid in solution.

TABLE 11

Bromination of Synthetic Styrene and Purified
I
Indene by Kaufmann Bromine Solution. (Jorden[25])

Percentage

	Addition	Absorption (based on total bromine consumed)
Styrene	51.19	98.62
Styrene	51.65	98.67
Styrene	49.52	99.14
Styrene	50.67	99.04
Indene	54.01	100.30
Indene	52.73	100.60

Based on these findings, Jordan suggested that these anomalous reactions might be due to the simultaneous action of molecular bromine and atomic bromine.

When a similar investigation was carried out on the hydrocarbons shown in Table 111, varying proportions of substitution and addition were obtained, the pentenes being outstandingly abnormal.

TABLE 111

Bromination by means of Kaufmann's Reagent.

	Percentage	
	Addition	Absorption (based on total bromine consumed)
Octene-1	85.68	99.51
Hexene-1	71.01	101.21
Octene-1	63.09	106.03
Trimethylpentene-1	24.63	101.96
Trimethylpentene-2	1.62	103.72

Bromination by means of Kaufmann's reagent was effected in a similar manner to that adopted for pyridine sulphate bromide, a glass phial containing a weighed quantity of the hydrocarbon being broken beneath the surface of a measured quantity of the reagent.

The results obtained as shown in Table 111, although not particularly good, at least confirmed the findings of Jordan that Kaufmann's reagent produced an abnormal proportion of substitution. In addition, the reagent did not appear to possess the stability claimed, as the titer dropped from N/10 to 0.95N/10 in 24 hours, and the end-point proved most unsatisfactory, having a definite tendency to recur.

The last two imperfections were largely eliminated by the purification of the methanol, as described in the experimental section vide page 34 but in order to investigate the proportion of addition and substitution in bromination by means of the Kaufmann reagent, the original method was amended for the following reasons.

Bromination procedures in general require the hydrocarbon to be dissolved in some non-polar solvent, such as carbon tetrachloride, and the reaction is terminated by the addition of an aqueous solution of potassium iodide, with the result that the mixture separates into two phases.

In the case of the Kaufmann reagent, however, the addition of the hydrocarbon dissolved in carbon tetrachloride produces a precipitate of sodium bromide from the saturated methanol solution, thereby altering the reagent from its original form. It was therefore decided that this difficulty could best be overcome by using methanol solutions of the hydrocarbons under test.

Furthermore, the complication which might follow the addition of water, i.e. the separation of the halogenated hydrocarbon in a finely divided state, continuing to react during the period of titration, was guarded against by employing a methanol solution of sodium iodide, and a normal thiosulphate solution containing the optimum quantity of methanol 40% (by volume) to yield a stable titrant. A semi-micro burette was used for the thiosulphate titration.

A comprehensive series of experiments were then carried out to investigate the relationship between the concentration of reagent and the proportion of substitution products formed, using definite quantities of various hydrocarbons dissolved in methanol.

The results showed comparatively little difference in these relationships over a wide range of reagent concentrations, but they did reveal the interesting fact that the presence of peroxides could lead to the reduction of the Bromine Number.

The Peroxide Effect.

Although the hydrocarbons used in this investigation were reasonably pure, small amounts of peroxides are generally present in olefinic mixtures unless these are freshly distilled. The presence of peroxides was observed in estimations in which insufficient Kaufmann reagent had been added for complete saturation of the double bond. In other words, the titer of the reaction mixture on addition of sodium iodide after all the bromine had been absorbed, was higher than the small amount of halogen liberated by the solvent alone.

Although the exact nature of the reaction between peroxides and acid iodide was not known, it was obvious that some correction would have to be applied to the Bromine Numbers actually found in the estimations. This allowance was arrived at by adding the standard amount of sodium iodide, 2ml. of a 50% solution in methanol, to an aliquot of the hydrocarbon dissolved in acid methanol, and titrating with standard thiosulphate after the same interval of time as that taken in the actual estimations.

The possibility of using this reaction as a basis for a method of estimating the peroxide values of hydrocarbons was considered. A similar method had been put forward by Wagner, Smith and Peters[26] in 1947, who refluxed the hydrocarbon for ten minutes with a solution of sodium iodide in isopropyl alcohol containing acetic acid.

As it was essential to establish the maximum time required for the liberation of the halogen, a series of tests were carried out in which the reaction times were increased logarithmically. It was found that the halogen liberated reached a constant amount after 40 minutes, in the case of trimethylpentene-2. and after 80 minutes for octene-1.

The figures agreed approximately with those obtained by the method of Wagner, Smith and Peters, as shown in Table 1V .

TABLE 1V .

Compariŝon of Peroxide Values obtained by the Method of Wagner, Smith and Peters,(1) and that of the Author,(11). (A) percentage Iodine liberated, (B) percentage Bromine liberated.

HYDROCARBON	1		11	
	A	B	A	B
Octene-1	1.86	1.17	1.97	1.24
	1.84	1.16	-	-
Trimethylpentene-2 ..	2.18	1.37	2.09	1.32
	2.19	1.38	-	-

Columns "A" give the iodine liberated, expressed as weight of iodine per cent of hydrocarbon weight. Columns "B" give the corresponding figures expressed as bromine. These figures are thus analogous to the Iodine and Bromine Numbers, being calculated in the same way.

In the Author's method the blanks were found to be fairly considerable, whereas those in Wagner, Smith and Peters' method were negligible

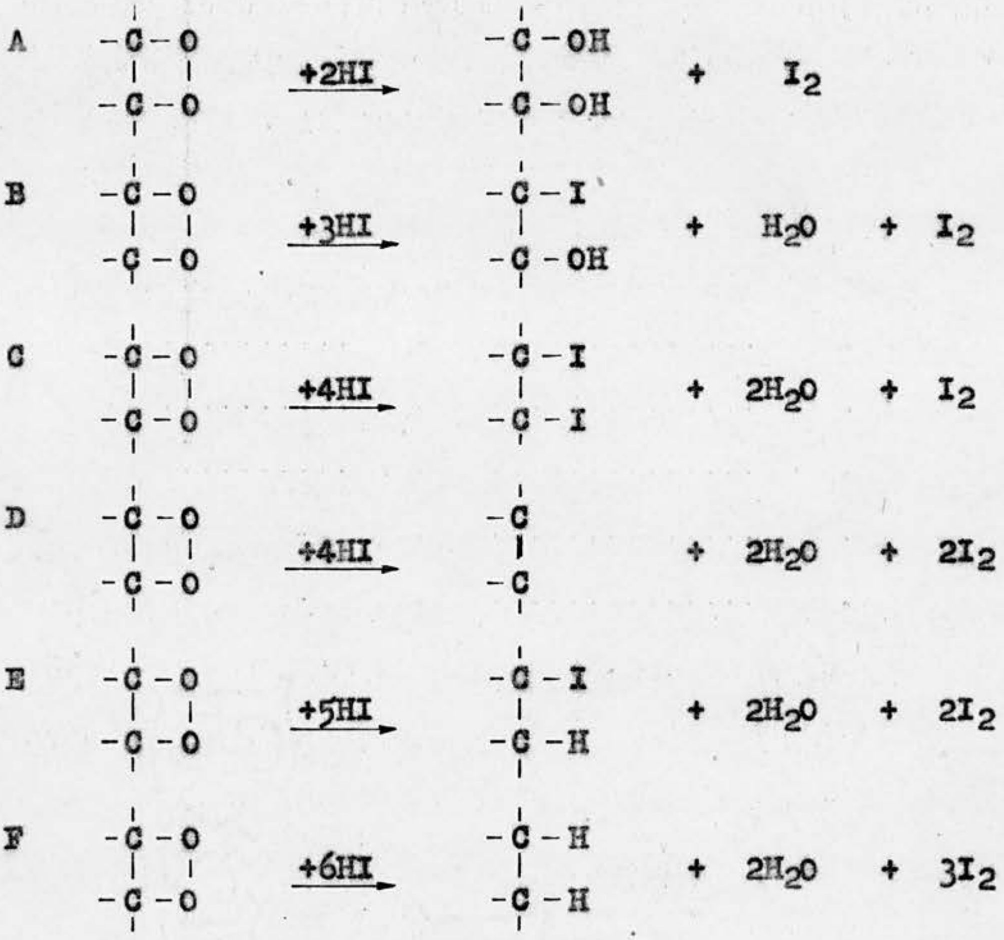
The rate of liberation of halogen, therefore, appears to be accelerated by the hydrogen ion concentration, which, being due to acetic acid, is small in the latter method. Further, the rate of liberation of halogen was found to be much smaller in the tests carried out in the hours of darkness, suggesting that the effect was photochemical.

These difficulties with the blank, necessitate that further work be carried out before the method can be adopted as a routine determination.

Note was taken of the relative proportions of iodine liberated and acid consumed in these estimations, in order to follow the course of the decomposition of the peroxide. It was found that for each atom of iodine liberated, approximately one hydrogen ion was consumed.

There appears to be a number of different ways in which peroxides may be decomposed by hydrogen iodide, as outlined on the following page.

Reactions of Peroxided Hydrocarbons with Hydrogen Iodide.



It follows from the above possibilities that if the iodine liberated and acid consumed can be shown by further investigation to be exactly equivalent, the possible compounds resulting from decomposition of peroxided hydrocarbons by hydrogen iodide, are as shown in A, D, and F. Furthermore, except in the case of A, the amounts of halogen liberated are greater than the quantities which would have been absorbed had the hydrocarbon not been peroxided, and by the factors 2 and 3 for reactions (D) and (F), respectively.

Thus the error in a Bromine Number estimation, if no correction is made for peroxides, is correspondingly greater than molecular proportions of peroxided hydrocarbon present.

As a result of these experiments, the final series of tests were made, employing the original technique of breaking a phial of the hydrocarbon beneath the surface of a measured quantity of the reagent, and the results obtained are shown in Table V.

TABLE V.

Weighed Quantities of the Hydrocarbons in Phials Broken Beneath the Surface of Aliquots of Reagent.

Hydrocarbon	Percentage			Bromine No.
	Total Absorp^n	Substit^n	Addit^n	Based on Total Absorp^n
Octene-1 (Sample A)	99.1 98.8 98.0	25.3 25.5 25.7	73.8 73.3 72.3	141.3 140.9 139.8
Octene-1 (Sample B)	98.5 98.8	23.4 22.8	75.1 76.0	140.5 140.9
Hexene-1	97.2	26.3	70.9	184.7
Diallyl	99.7 99.7	19.3 20.3	80.4 79.4	388.4 388.4
Trimethyl-pentene-1	98.5 98.6	25.3 25.8	73.2 72.8	140.5 140.6
Trimethyl-pentene-2	90.2 90.9	89.3 89.4	0.9 1.5	128.6 129.6

Conclusions regarding the use of Kaufmann's Reagent for the Determination of Bromine Numbers of Typical Unsaturated Hydrocarbons.

It has been proved that provided the Kaufmann Reagent is prepared from specially purified constituents, and subsequently corrected for any peroxide present in the hydrocarbon under test, the results obtained compare favourably with those derived from employing the present standard MaIlhiney method.

This comparison is brought out in the following table.

TABLE V1

Comparison Between Kaufmann and McIlhiney Methods.

Hydrocarbon.	Bromine Numbers. Kaufmann Method.	Theory.	McIlhiney Method.
Octene-1 (sample A)..	140.7	142.5	137.6
(sample B)..	140.7		137.7
Hexene-1	184.7	190.0	186.2
Diallyl	388.4	389.4	374.4
Trimethylpentene-1...	140.6	142.5	111.9
Trimethyplentene-2...	129.1	142.5	65.2

Branch-chain unsaturated hydrocarbons, in the opinion of the Author, cannot be satisfactorily estimated by any bromination method, due to the mechanism involved in the reaction of halogenation, vide page 60 et seq.

On the other hand, the solution of this problem may be provided by an oxidation procedure, in which the oxygen consumed is taken as a measure of unsaturation. This reaction has already been applied by Alexander[27] in the case of animal and vegetable fats, the reagent being a mixture of glacial acetic acid and sodium dichromate, and in a similar manner, Knowles[28] et alia, employ potassium permanganate as oxidising agent.

Hydrogenation must also be considered, and a claim has already been made in this field by Robb and Melville[29], who have devised a physical method for measuring the percentage of double bonds present in a mixture of olefine, saturated hydrocarbon and hydrogen, by a mercury-photosensitised dissociation of molecular hydrogen. The amount of atomic hydrogen removed from a molybdenum oxide surface which forms part of the apparatus, is estimated by a colorimetric technique for measuring the light reflected from this surface.

EXPERIMENTAL

The Rosenmund and Kunhenn Method.

The hydrocarbons used were obtained as pure, and the reagents of A.R. quality.

Preparation of Bromination Reagent.

The pyridine sulphate bromide reagent was prepared in the following manner. 40 ml of glacial acetic acid were placed in each of three Erlenmeyer flasks. To one of the flasks, 16 grams of pyridine were added, with cooling. In a similar manner, 20 grams of concentrated sulphuric acid were added carefully to the second flask. When cool, these solutions were combined by adding the sulphuric acid/acetic acid mixture to the pyridine solution. 16 grams of bromine were weighed into the third flask, and this added to the mixture of the first two solutions. The reagent thus prepared was transferred to a one litre volumetric flask, and the volume made up to the mark with glacial acetic acid. This mixture was then poured into a dark coloured Winchester quart bottle, and a litre of glacial acetic acid added.

Aqueous 10% potassium iodide and standard N/10 sodium thiosulphate were prepared in the usual manner, no stabilising agent being added to the latter.

Procedure: The appropriate quantity of motor spirit may be measured by means of a calibrated pipette, but the following technique was found to give excellent results. A glass vessel was constructed from the bottom 1½ inch portion of a thin-walled test-tube drawn out to a thick capillary and then further drawn down to a hair capillary, 1 inch in length. After weighing, the tube was warmed in the flame of a bunsen, withdrawn from the latter and then the capillary was immersed in the sample. On cooling somewhat, the requisite amount of liquid was sucked up into the tube, which was allowed to cool completely before inverting to allow the liquid to flow into the wider section. In this way, the loss of high vapour pressure constituents in the hydrocarbon mixture which could occur in using a pipette, was avoided.

After the second weighing, the tube was dropped into a bottle of the type used for iodine value determinations, which contained 25 ml. of carbon tetrachloride and an ordinary glass marble. The pyridine sulphate bromide reagent was added from a burette, the stopper replaced and the weighing tube broken by the impact of the marble on shaking the bottle.

An interval of five minutes was allowed to elapse, before the excess halogen was determined by addition of 10 ml. of the potassium iodide solution, and titration with the standard thiosulphate.

The Bromine Number was computed in the usual way from the formula (A - B) x 8 x N/w, in which A - ml. standard thiosulphate equivalent to the reagent used in the blank, B = ml. thiosulphate equivalent to the excess reagent, N = normality of the standard thiosulphate solution, and w = weight of sample in grams.

The results given in Table V11 form an interesting comparison between the methods of McIlhiney (A), Francis (B) and the Rosenmund and Kuhnhenn procedure already described, (C).

TABLE V11

Comparison Between the Methods of McIlhiney (A), Francis (B) and the Rosenmund-Kuhnhenn Procedure(C)

Hydrocarbons.	Bromine Numbers A	 B	 C
Shale Oil Fractions.			
No.1	103.1 -	102.1 103.0	100.6 102.0
No.2	83.0 83.2	83.1 83.1	83.5 82.6
No.3	65.1 67.8	74.5 74.7	73.2 72.6
No.4	57.9 56.9	71.4 71.1	71.4 72.2
No.5	51.3 51.8	63.4 -	62.8 62.9
No.6	36.5 37.6	49.7 50.1	50.9 50.6
No.7	51.9 52.0	62.5 62.7	59.3 -
Old cracked spirit	-	47.9 48.2	47.9 47.2
Straight Hydrocarbons			
Benzene, redistilled ..	nil	nil	nil
Cyclohexane	nil	nil	nil
Cyclohexene, commercial, redistilled	182.2	-	182.1
+ Cyclohexene	-	182.9	191.2
* Oxtene-1 and -2	-	140.0	142.2

+ Organic Synthesis, V, X11, 33.

* Whitmore and Herndon, J. Amer.Chem.Soc.,1933,55, 3428.

Table V111 gives the results obtained in applying method (C) to the analysis of synthetic mixtures of saturated and unsaturated hydrocarbons of known Bromine Number.

TABLE V111

Analysis of Synthetic Mixtures by Method C

HYDROCARBON.	Bromine Number.		Percentages.		
			Olefines.		Excess
	Theory	Found.	Actual	Found.	Reagent (Calc).
Octene in Benzene					
No.1	35.5	35.7	24.9	25.0	36
No.2	35.9	36.1 36.0	25.3	25.4 25.3	167 643
No.3	71.2	71.6 71.5	50.1	50.3 50.3	242 412
No.4	95.9	95.7 95.7	67.7	67.3 67.8	359 333
Cyclohexene in benzene.					
No.5	61.6	60.7 61.3	33.9 33.9	33.7 33.4	273 200
No.6	48.2	48.9 49.7	26.5	27.3 26.9	296 436
Cyclohexene in Cyclohexane.					
No.7	37.5	37.9	20.6	20.8 20.8	348 258

The investigation was then continued to find out whether time was an important factor in the bromination of a number of straight-chain and also side-chain hydrocarbons.

The following are a few typical examples:-

TABLE 1X.

Bromine Numbers - Pyridine Sulphate Bromide Method.

Time in Minutes:	5	60	Theory
Octene-1	142.1	144.8	
	141.8	143.6	142.5
	142.5	144.7	
	142.0	144.0	
Hexene-1	190.3	191.1	
	189.9	190.9	190.9
	190.2	191.3	
	190.1	191.2	
Cetene-1	71.0	74.6	
	71.0	74.2	71.25
	71.1	74.3	
	71.2	75.0	
Diallyl	390.2	390.8	
	389.8	391.1	389.4
	390.0	390.9	
	389.9	391.4	
2:4:4 Trimethylpentene-1:	168.1	185.2	
	166.7	186.5	142.5
	174.2	187.1	
	169.5	186.7	
2:4:4 Trimethylpentene-2:	177.8	253.9	
	176.8	252.9	142.5
	174.8	258.7	
	179.4	259.8	

These results proved that this method, although satisfactory for straight-chain unsaturated hydrocarbons, was not suitable for branch-chain compounds.

For this reason, consideration was than given to the use of the Kaufmann Reagent.

THE KAUFMANN REAGENT.

Preparation of Reagent.

A saturated solution of sodium bromide in A.R. quality methanol was first prepared, and to this the requisite quantity of redistilled bromine to give a decinormal solution was added from a calibrated pipette.

Procedure.

In the preliminary trials with this reagent, the same technique as that adopted for the pyridine sulphate bromide solution was employed, aqueous potassium iodide being added before titrating the unabsorbed halogen with the standard thiosulphate solution. A 2% solution of potassium iodate was added to the flask after the first titration had been completed, so that an estimation of substitution could be obtained, the bromine released by the hydrobromic acid being multiplied by two in order to arrive at the corresponding substitution equivalent. The fraction of halogen absorbed by addition only was derived by subtracting from the total absorption, i.e. the first titration of thiosulphate after the sodium iodide addition, twice the second titration.

The results obtained in this manner for a few hydrocarbons are shown in the following Table.

TABLE X

Bromination by means of Kaufmann's Reagent
Bromine Number based on Total Absorption.

Hydrocarbon	Bromine Number		Substn.	Addtn.
	Detmnd.	Theory	(Detmnd)	(Diff.)
Octene-1............	141.8	142.5	20.3	121.5
	142.1		-	-
Hexene-1...........	192.3	190.0	-	-
	196.3		-	-
Cetene-1............	75.6	71.3	-	-
	78.8			
Trimethylpentene-1..	145.3	142.5	109.5	35.8
	149.0		-	-
Trimethylpentene-2..	147.8	142.5	147.8	-ive
	150.0		150.0	-ive

Although these preliminary tests were not particularly encouraging, they served to confirm the findings of Jordan, vide page 12, namely, that this reagent was characterised by a rather abnormal proportion of substitution, especially in the reaction with the two branch-chain hydrocarbons.

Furthermore, the reagent was unstable, and the endpoint proved to be very unsatisfactory. Although starch was used, the blue colour reappeared in a few seconds after its initial disappearance.

It was thus apparent that no reliable results could be obtained until these unsatisfactory features of the method had been solved. These defects were traced, at least in part, to the use of methanol of doubtful purity. It was found that (a) a relatively large amount of acidity was present in the reagent due it was thought, to the substituting action of the bromine on impurities in the methanol, and (b) the recurring endpoint was not apparently brought about by atmospheric oxidation of the hydrogen iodide present, or to photochemical action, since the reaction persisted in an atmosphere of nitrogen and also under illumination by filtered light of negligible actinic value.

Purification of Reagent Constituents.

Purification of the reagents was effected in the following manner. The bromine was distilled over potassium bromide, the middle fraction being collected.

The methanol was treated with excess bromine and allowed to stand overnight before decolorisation was carried out by addition of anhydrous sodium sulphite. After drying over sodium, the alcohol was distilled through a twelve bulb fractionating column, the fraction distilling between 65°C. and 65.5°C. being collected. Bromine was added to this cut, and after standing overnight, redistillation was carried out. The purified alcohol was tested with aqueous iodide/iodate solution and found to be free from hydrobromic acid.

The reagent made up from these purified constituents, proved to be more stable, and gave a much sharper end-point, the use of starch being necessary.

Relationship between Quantity of Reagent used and Reaction Products formed.

The next series of experiments were designed to investigate the relationship between the relative proportions of substitution and addition products formed by the action of varying amounts of decinormal Kaufmann reagent on definite aliquots of decinormal solutions of hydrocarbons dissolved in the same solvent as that used for the preparation of the reagent, i.e. purified methanol saturated with sodium bromide - vide page 34 .

The procedure was as follows:
The definite volume of hydrocarbon solution was pipetted into an iodine value type of flask, and the Kaufmann reagent added from a burette. After a reaction time of five minutes, 2 ml. of the methanol solution of sodium iodide were added and the liberated iodine titrated with decinormal thiosulphate until the faint brown tint disappeared. 0.5 gram of potassium iodate in the form of a fine powder was then added, and the halogen, corresponding to the hydrobromic acid formed by the substitution action, titrated with the thiosulphate solution.

The difference between the reagent blank and the first thiosulphate titration figure represented the total bromine absorbed, and the second thiosulphate titration multiplied by two gave the amount of substitution.

TABLE X1

OCTENE-1.

25 ml. of an N/10 solution of actene-1 in methanol saturated with sodium bromide, treated with varying volumes of Kaufmann reagent. Reaction Time: 2 minutes.

Volume of Kaufmann Reagent(ml)	N/10 Bromine Equivalent.	Thiosulphate. Titration to		Percentage.	
		NaI	KIO$_3$.	Absorpn.	Substn.
4.0	4.20	*0.30	0.29	-	14.9
8.0	8.40	0.35	0.86	-	24.4
12.0	12.60	0.42	1.32	-	21.7
16.0	16.80	0.42	1.95	-	23.8
20.0	21.00	0.48	2.50	-	24.4
24.0	25.20	1.21	2.90	96.0	24.2
30.0	31.50	7.24	2.99	97.0	24.7
37.5	39.40	14.89	3.30	98.0	26.9
45.0	47.40	22.78	3.28	98.5	26.7

These results indicate a slight upward trend in total absorption and substitution with increasing concentration of bromine.

* Peroxide Effect - vide pages 46 and 52.

TABLE X11

HEXENE-1.

25 ml. of an N/10 solution of hexene-1 in methanol saturated with sodium bromide, treated with varying volumes of Kaufmann reagent. Reaction Time:- 5 minutes.

Volume of Kaufmann Reagent(ml)	N/10 Bromine Equivalent.	Thiosulphate Titration to		Percentage	
		NaI	KIO_3	Absorpn.	Substn.
4.0	4.05	0.62	-	-	-
8.0	8.10	0.55	0.58	-	15.4
12.0	12.15	0.41	1.18	-	20.1
16.0	16.20	0.42	1.70	-	21.5
20.0	20.25	0.30	2.30	-	23.1
24.0	24.30	2.07	2.53	88.9	22.3
28.0	28.35	6.58	2.42	87.1	22.2
32.0	32.40	10.20	2.50	88.8	22.5
40.0	40.50	18.15	2.58	89.4	22.5

The total absorption in the case of this hydrocarbon is relatively low, and there are very slight upward trends similar to those found in octene.

TABLE X111

CETENE-1.

25 ml. of an N/10 solution of cetene-1 in methanol[+] treated with varying volumes of Kaufmann reagent.

Reaction Time: 5 minutes.

Volume of Kaufmann Reagent (ml)	N/10 Bromine Equivalent.	Thiosulphate Titration to		Percentage.	
		NaI	KIO_3	Absorpn.	Substn.
4.0	4.89	0.91	0.82	-	41.3
8.0	9.87	1.13	1.77	-	40.5
12.0	14.76	1.53	2.49	-	37.7
16.0	19.54	1.91	3.30	-	37.4
20.0	24.25	2.77	4.27	88.4	39.4
24.5	29.92	8.18	4.00	88.8	36.8
28.0	34.20	12.42	3.99	88.9	36.7
32.0	39.08	17.20	4.05	89.3	37.0
40.0	48.85	26.95	3.85	89.4	35.2

[+] On account of the limited solubility of the cetene in the usual solvent, i.e. methanol saturated with sodium bromide, the latter was omitted.

Although this hydrocarbon shows a very slight upward trend with respect to total absorption, the substitution tends to fall.

TABLE XIV
DIALLYL.

25 ml. of an N/10 solution of diallyl in methanol saturated with sodium bromide, treated with varying volumes of Kaufmann reagent. Reaction Time:- 5 minutes:

Volume of Kaufmann Reagent (ml)	N/10 Bromine Equivalent	Thiosulphate Titration to		Percentage.	
		NaI	KIO_3	Absorpn.	Substn.
4.0	5.58	0.21	0.46	-	17.1
8.0	11.16	0.40	0.92	-	17.1
12.0	16.74	0.28	1.47	-	17.9
16.0	22.32	0.40	1.87	-	17.1
20.0	27.90	3.72	2.19	96.7	18.1
24.0	33.48	9.48	2.10	96.0	17.5
28.0	39.06	15.07	2.19	96.0	18.2
34.0	47.43	23.34	2.30	96.4	19.1
40.0	55.79	31.73	2.11	96.2	17.5

This hydrocarbon shows little if any trend with regard to either total absorption or substitution.

TABLE XV

2:4:4 Trimethylpentene-1

25 ml. of an N/10 solution of 2:4:4 trimethylpentene-1 in methanol saturated with sodium bromide, treated with varying volumes of Kaufmann reagent. Reaction Time: 5 minutes.

Volume of Kaufmann Reagent (ml)	N/10 Bromine Equivalent	Thiosulphate Titration to		Percentage	
		NaI	KIO_3	Absorpn.	Substn.
4.0	4.74	0.26	1.41	-	62.9
8.0	9.48	0.44	2.94	-	65.1
12.0	14.22	0.53	4.56	-	66.6
16.0	18.96	0.73	6.76	-	68.7
20.0	23.71	2.42	7.97	85.2	69.7
24.0	29.63	7.47	7.60	86.6	70.1
28.0	33.18	11.51	7.54	86.7	69.5
32.0	37.98	16.11	7.65	87.5	69.6
36.0	42.66	20.91	7.70	87.0	70.8
40.0	47.41	25.42	7.68	88.0	70.0

The trend in this case is slightly upward in both total and substitution percentages.

TABLE XV1

2:4:4 Trimethylpentene-2

25 ml. of an N/10 solution of 2:4:4 trimethylpentene-2 in methanol saturated with sodium bromide, treated with varying volumes of Kaufmann reagent. Reaction Time: 5 minutes.

Volume of Kaufmann Reagent(Ml)	N/10 Bromine Equivalent	Thiosulphate Titration to		Percentage	
		NaI	KIO_3	Absorpn.	Substn.
4.0	7.45	0.69	3.31	-	98.0
8.0	11.91	0.94	5.28	-	96.1
12.0	17.90	0.75	8.68	-	95.6
16.0	23.84	1.25	10.94	90.4	96.8
20.0	29.80	7.06	10.90	91.0	95.7
24.0	35.75	12.62	11.16	92.5	96.5
28.0	41.73	18.44	11.35	93.2	96.6
32.0	48.43	24.75	11.38	94.7	96.1

With the exception of diallyl, the only trend shown by these experiments was the slight increase in absorption with increasing concentration of bromine, and it was considered that the low figures for total absorption may have been due to addition of hydrobromic acid brought about by the competition of the H^+ with the Br^+ in the attack on the lone electron pair.

To test this theory, another series of experiments were carried out, in which the former procedure was reversed, the reagent being added to the flask first in one addition, and the hydrocarbon solution subsequently added dropwise from a burette. In effect, this method would ensure an excess of bromine being present, at least in the initial stages of the reaction.

TABLE XV11

OCTENE-1.

25 ml. of an N/10 solution of octene-1 in methanol saturated with sodium bromide, added dropwise to measured volumes of Kaufmann reagent. Reaction Time:- 5 minutes.

Volume of Kaufmann Reagent (ml)	N/10 Bromine Equivalent	Thiosulphate Titration to		Percentage	
		NaI	KIO_3	Absorpn.	Substn.
10.0	10.47	0.42	1.09	-	21.7
18.0	18.84	0.59	2.08	-	22.8
26.0	27.21	3.52	2.77	94.8	23.4
34.0	35.58	11.79	2.85	95.2	24.0
42.0	43.96	20.01	2.96	95.8	24.7
50.0	52.33	28.00	3.14	97.3	25.8

The total absorption obtained in these experiments was less than that recorded in the first series, vide page 36 but the substitution percentage was much the same.

TABLE XV111

HEXENE-1

25 ml. of an N/10 solution of hexene-1 in methanol saturated with sodium bromide, added dropwise to measured volumes of Kaufmann reagent. Reaction Time: 5 minutes.

Volume of Kaufmann Reagent (ml)	N/10 Bromine Equivalent	Thiosulphate Titration to		Percentage	
		NaI	KIO_3	Absorpn.	Substn.
10.0	10.90	0.89	0.80	-	16.0
18.0	19.62	1.24	1.78	-	19.4
26.0	28.34	6.47	2.16	87.5	19.8
34.0	37.06	15.63	2.13	85.7	19.9
42.0	45.78	23.93	2.18	87.4	20.0
50.0	54.50	33.09	2.10	85.6	19.6

As in the case of Octene-1, the total absorption results were less by this method than those shown on page 37 .

TABLE X1X

2:2:4 Trimethylpentene-1

25 ml. of an N/10 solution of 2:4:4 trimethylpentene-1 in methanol saturated with sodium bromide, added dropwise to measured volumes of Kaufmann reagent. Reaction Time; 5 minutes.

Volume of Kaufmann Reagent (ml)	N/10 Bromine Equivalent.	Thiosulphate Titration to		Percentage	
		NaI	KIO_3	Absorpn.	Substn.
10.0	11.68	0.65	4.10	-	74.3
28.0	32.71	8.13	9.59	98.3	78.0
26.0	30.37	5.80	9.32	98.3	75.9
34.0	39.72	15.02	9.64	98.8	78.1
42.0	49.06	24.86	9.42	96.8	77.9

This hydrocarbon showed an increase in both total absorption and substitution, compared with the results of the first test, vide page 40.

TABLE XX

2:4:4 Trimethylpentene-2

25 ml of N/10 solution of 2:4:4 trimethylpentene-2 in methanol saturated with sodium bromide, added dropwise to measured volumes of Kaufmann reagent. Reaction Time: 5 minutes.

Volume of Kaufmann Reagent (ml)	N/10 Bromine Equivalent	Thiosulphate Titration to		Percentage	
		NaI	KIO_3	Absorpn.	Substn.
10.0	11.14	0.76	4.92	-	94.8
18.0	20.05	1.10	9.03	-	95.3
26.0	28.96	5.90	10.95	92.2	95.0
34.0	37.88	14.60	11.10	93.1	95.4
42.0	46.79	23.42	11.43	93.5	97.8
50.0	55.69	31.40	11.69	97.2	96.3

In this case, both the total absorption and the substitution tend to increase with increase in the amount of reagent.

Observations on the foregoing two series of Tests.

As outlined on page 35, these experiments were designed to investigate the effect of varying the amounts of the Kaufmann reagent on definite aliquots of hydrocarbon dissolved in methanol, with particular respect to the preportions of substitution and addition products formed.

The results indicated in the first place that comparatively little change in these proportions took place with varying amounts of reagent. Secondly, they showed that although the total absorption was consistently low, this discrepency was not reduced to any appreciable extent by the use of excess reagent.

Another interesting observation was made, namely, that in every case in which the hydrocarbon solution was treated with insufficiant reagent to effect full bromination, as indicated by the complete discharge of colour, although the mixture contained no free halogen, iodine was liberated on addition of the sodium iodide solution. The figures concerned are indicated in red in the tables, but the following example illustrates the point.

TABLE XX1

Addition of Insufficient Kaufmann Reagent for Full Bromination to N/10 Octene-1 Solution in Methanol Saturated with Sodium Bromide.

N/10 Solutions.	Volumes Used.
Octene-1...........................	25 ml.
Kaufmann Reagent	8.1 ml.
Thiosulphate Equivalent to Iodine liberated after addition of sodium iodide solution	0.55 ml.

This abnormal result was ascribed in part to the presence of peroxides in the hydrocarbon, interacting with the sodium iodide in the presence of the hydrobromic acid formed by the substitution action of the reagent on the hydrocarbon. It was also considered that traces of impurities still remaining in the methanol might have been contributing to this effect by forming, on addition of sodium iodide, unstable iodo-compounds which liberated iodine on decomposition.

Experiments were carried out to elucidate, in the first place, the conditions under which halogen could be liberated from the methanol solvent used in the preparation of the Kaufmann reagent, after the addition of sodium iodide.

The Influence of Temperature.

Two solutions (50 ml.) of hydrobromic acid (N/10) in methanol saturated with sodium bromide were each treated with 2 ml. of a saturated methanol solution of sodium iodide, and allowed to stand for 15 minutes, one sample at 2'C. and the other at 22'c. On titrating with normal thiosulphate, the former gave the lower figure, but the end-point recurred badly, whereas the latter gave a stable end-point.

Finally, however, when the lower temperature test was allowed to attain room temperature, a stable end-point was obtained, which was in agreement with that of the other sample, thus:-

TABLE XX11

Temperature Effect on the Liberation of Iodine from Sodium Iodide in a Methanol Solution of Hydrobromic Acid.

	Test A.	Test B.
Temperature	2'C.	22'C
Reaction Time	15 minutes.	
Thiosulphate Required (N/10).	0.285 ml.	0.450 ,1.

After allowing the temperature of the Test A mixture to rise to 22'C., the thiosulphate requirement rose to 0.450 ml.

Conclusion.

It was thus established that a stable end-point could be attained in the presence of hydrobromic acid and that the rate of liberation of halogen was accelerated at higher temperatures.

The Influence of Water

50 ml. aliquots of N/10 hydrobromic acid solution in methanol saturated with sodium bromide were treated with different quantities of water, and allowed to react for definite time intervals in the presence of 2 ml. of the methanol solution of sodium iodide, and then titrated with thiosulphate solution.

The results of this test proved that water influenced the reaction in the following manner, (a) by slowing down the liberation of halogen, and (b) by slightly reducing the titration figure when the end-point reached final stability. Thus, 2 ml. of added water reduced the thiosulphate requirement from 0.450 ml. to 0.398 ml., and 25 ml. reduced this figure to 0.359 ml., the time taken for full liberation being 30 minutes, compared with 15 minutes required at ordinary temperature for the anhydrous methanol, as shown on page

TABLE XX111

Volume of Added Water	Reaction Time	N/1 thiosulphate.
nil	15 mins.	0.450 ml.
2 ml.	5 mins	0.300 ml.
2 ml.	30 mins.	0.398 ml.
25 ml.	30 mins.	0.359 ml.

Conclusion.

It was concluded from these results that it was advantageous to use anhydrous methanol so as to ensure a rapid liberation of halogen and a constant stable end-point.

The Influence of Hydrobromic Acid.

Hydrobromic acid was added to the methanol used for the preparation of the Kaufmann reagent, in the first instance, during exploratory tests designed to determine whether the presence of this acid was responsible for the fact that the figures obtained for bromination, based on total absorption, were usually below 100 per cent. It was considered possible that addition of hydrobromic acid was the cause of this discrepancy.

The first point established was that a solution of hydrobromic acid in methanol, saturated with sodium bromide, was perfectly stable, as shown in the following table :-

TABLE XXIV.

Effect of Hydrobromic Acid on Kaufmann Reagent Solvent, (Methanol saturated with NaBr).

10.ml. of approximately N/10 hydrobromic acid dissolved in Methanol saturated with NaBr.

Reaction time	10 mins.	2 hrs.	18 hrs.
Halogen released on addn. of sod. iodide, N/1 thiosulphate Titration (ml.)	0.025	0.025	0.025
Halogen released on addn. of pot. iodate, hydrobromic acid in terms of N/1 thiosulphate	0.955	0.955	0.950

Furthermore, the added acid did not react with hydrocarbon dissolved in methanol solvent in the absence of bromine.

TABLE XXV

Effect of Hydrobromic Acid on Hydrocarbon dissolved in approximately N/10 Hydrobromic Acid in Methanol Saturated with Sodium Bromide.

10 ml. of N/10 Octene-1 dissolved in the above acid solvent.

Reaction Time	10 mins.	2 hrs.	18 hrs.
Halogen released on addn. of Sodium Iodide in terms of N/1 thiosulphate (ml.)	0.028	0.034	0.030
Halogen released on addition of Pot. Iodate, Hydrobromic Acid in terms of N/1 Thiosulphate	0.956	0.946	0.950

It was considered, moreover, that the presence of bromine would not cause the addition of HBr at the double bond, vide Mechanisms, page 68

Having thus established the fact that at least part of the abnormal release of halogen referred to on page 47 was due to impurities in the methanol, attention was then turned to the contributory effects resulting from the presence of peroxides in the hydrocarbons used.

Peroxide Effect.

The following method was devised to investigate the decomposition of peroxides by an acid solution of methanol saturated with sodium bromide in the presence of sodium iodide.

Procedure.

20 ml. aliquots of methanol saturated with sodium bromide containing hydrobromic acid equivalent to N/50 strength, were measured into iodine value flasks. To each sample, 1.5 ml. of trimethylpentene-2 were run in from a micro-burette, and 2 ml. of a 50% methanol solution of sodium iodide,(W/V), added. The samples were left for varying times, in logarithmic progression, and blanks on the solvent were carried out simultaneously with each sample. The following results were obtained :-

TABLE XXV1

Decomposition of Peroxides in Trimethylpentene-2 by N/50 HBr in MeOH saturated with NaBr in the presence of NaI.

Test No.	Time in mins.	Volume of N/10 thiosulphate in ml. after addition of NaI		KIO$_3$		Iodine liberated.	Acid consumed.
		Sample	Blank	Sample	Blank	in ml.	
1	1	0.60	0.20	6.70	6.80	0.40	0.10
2	2.5	0.80	0.25	6.55	6.85	0.55	0.30
3	5	1.40	0.30	5.90	6.70	1.10	0.80
4	10	1.50	0.35	5.80	6.65	1.15	0.85
5	20	1.95	0.45	5.35	6.60	1.50	1.25
6	40	2.40	0.65	4.90	6.35	1.75	1.45
7	80	2.85	0.95	4.35	6.05	1.90	1.70
8	160	3.30	1.50	3.95	5.50	1.80	1.55
9	1280	5.00	3.20	2.25	3.90	1.80	1.65

It will be observed that the halogen liberated approaches a stationary value at 40 minutes, and remains at this figure over a considerable period of time.

A similar series of tests were carried out with octene-1, and the results obtained are shown in the following table:-

TABLE XXV11

Decomposition of Peroxides in Octene-1 by N/50 HBr in MeOH saturated with NaBr, in the presence of NaI

Test No	Time in mins.	Volume of N/10 thiosulphate in ml. after addition of				Iodine Liberated.	Acid Consumed.
		NaI		KIO_3			
		Sample	Blank.	Sample	Blank.	in ml.	
1	5	0.9	0.4	5.9	6.5	0.5	0.6
2	10	1.1	0.4	5.7	6.5	0.7	0.8
3	20	1.6	0.45	5.2	6.4	1.15	1.2
4	40	1.8	0.5	4.9	6.4	1.3	1.5
5	80	2.2	0.6	4.5	6.2	1.6	1.7
6	160	2.5	0.8	4.3	6.0	1.7	1.7
7	320	2.6	0.9	4.1	5.9	1.7	1.8

In this case, the halogen liberated approaches a stationary value after 80 minutes.

The blanks on the reagents will be seen from the above tables to be fairly considerable, and it appears that, other factors being equal, the rate of liberation of halogen is constant, (Table XXV1).

This fact and the observation that the rate of liberation evidently decreased considerably during the hours of darkness, suggested that this was a photochemical effect.* It would, moreover, appear to be governed by the hydrogen ion concentration, since the blank in the Wagner, Smith and Peters' method, using acetic acid was negligible.

TABLE XXV111

Rate of Halogen Liberation from Acid Iodide in Methanol.

A	B	C	D
5 - 10	0.05	0.010	ca 1.30 pm.
10 - 20	0.10	0.010	ca 3.00 pm.
20 - 40	0.20	0.010	ca 3.00 pm.
40 - 80	0.30	0.0075	ca 3.00 pm.
80 - 160	0.55	0.0069	ca 3.00 pm.
160 - 280	0.80	0.0066	ca 4.00 pm.
*280 - 1250	0.90	0.0009	5 pm. - 9 am.

A - Time interval between determinations.

B - Difference in titer of determinations.

C - Ratio B/A (ml. per minute).

D - Actual times of the intervals.

Corrections for peroxides in hydrocarbons.

On the basis of the previous experiments, the following procedure was adopted to arrive at the corrections to be applied to the various hydrocarbons tested.

Procedure:

A phial of the hydrocarbon was broken under 20 ml. of the acid methanol saturated with sodium bromide solution, and allowed to stand for 2 minutes. 2 ml. of the sodium iodide solution were added, and after exactly 10 minutes, the reaction was stopped by adding 50 ml. of water. The halogen was titrated with N/10 thiosulphate, starch being used to sharpen the end-point. 10 ml. of 2% aqueous potassium iodate were then added, and the acidity titrated. 20 ml. of the solvent alone were similarly treated. The results are expressed in the following tables.

TABLE XX1X

Peroxide Determination.

Hydrocarbon.	Weight taken (grams).	Iodine		Acidity of		Iodine Liberated.	Hydrogen Iodide Absorbed.
		From Blank	From Sample.	Sample	Blank.		
Octene-1 (sample A).	0.953	0.4	1.10	4.55	5.30	0.70	0.75
(sample B).	1.011	0.4	0.55	5.05	5.30	0.15	0.25
Hexene-1 ..	0.683	0.4	1.10	4.55	5.30	0.70	0.75
	0.833	0.4	1.15	4.45	5.30	0.75	0.85
Diallyl ..	0.657	0.4	0.40	5.30	5.30	nil.	nil.
	0.607	0.4	0.40	5.30	5.30	nil.	nil.
T.M.P.-1 .	0.763	0.4	0.40	5.30	5.30	nil.	nil.
	0.679	0.4	0.40	5.30	5.30	nil.	nil.
T.M.P.-2 .	0.858	0.4	0.95	5.00	5.30	0.45	0.30
	0.712	0.4	0.95	4.90	5.30	0.45	0.40

These figures correspond to the following corrections expressed as the percentage to be added to the estimated percentage total absorption and percentage substitution.

TABLE XXX

Corrections Due to Peroxide.

	Percentage.			
	Total Absorption		Substitution.	
Hydrocarbon.	Determined	Average	Determined	Average.
Octene-1				
(sample A)..	0.82	0.80	1.77	1.80
(sample B)..	0.17	0.20	0.50	0.50
Hexene-1 ...	0.86 0.77	0.80	1.85 1.73	1.80
Diallyl	nil.		nil.	
T.M.P.-1 ...	nil.		nil.	
T.M.P.-2 ...	0.59 0.79	0.70	1.38 0.79	1.10

The method of calculating the corrections is similar to that used for the estimations, viz.

$$\frac{\text{ml. thio. (N/10)}}{\text{weight taken}} \times \frac{\text{Equivalent Wt.}}{10,000} \times 100 = \text{Correction for Total Absorpn.}$$

$$\frac{2 \times \text{ml. thio (N/10)}}{\text{weight taken}} \times \frac{\text{Equivalent Wt.}}{10,000} \times 100 = \text{Correction for Substitution.}$$

Equivalent Weight = 10,000 wt. of N/10 thio.

These corrections have been applied to the following Table:

TABLE XXX1

Bromine Numbers Corrected for Peroxide, Excess Reagent Treated with Weighed Amounts of Hydrocarbon.

Hydrocarbon.	Percentage.			Bromine Number.	
	Total Absorpn.	Substn.	Addn.	Based on Total A Absorpn.	Theory.
Octene-1 (sample A)	99.1	25.3	73.8	141.3	
	98.8	25.5	73.3	140.9	142.5
	98.0	25.7	72.3	139.8	
Octene-1 (sample B)	98.5	23.4	75.1	140.5	142.5
	98.8	22.8	76.0	140.9	
Hexene-1	97.2	26.3	70.9	184.7	190.0
Diallyl	99.7	19.3	80.4	388.4	
	99.7	20.3	79.4	388.4	389.4
Trimethyl-pentene-1	98.5	25.3	73.2	140.5	
	98.6	25.8	72.8	140.6	142.5
Trimethyl-pentene-2	90.2	89.3	0.9	128.6	
	90.9	89.4	1.5	129.6	142.5

MECHANISM OF BROMINATION BY MEANS OF KAUFMANN'S REAGENT.

The view was expressed by Lowrie[30] in 1923, that the double bond in organic chemistry reacted generally as if it contained one co-valency and one electro-valency. and that ethylene may therefore be written $\overset{+}{C}H_2-\overset{-}{C}H_2$. The modern terminology for this is that by an electromeric change, double bonds are electronically activated, in the following manner :-

$$>C = C< \longrightarrow >\overset{\delta+}{C} - \overset{\delta-}{C}<$$

It is now well established that halogen addition is brought about by the attack of a positively polarised (cationoid) halogen upon a negative centre at one of the unsaturated carbon atoms. There are four examples of particular reactions which confirm this statement.

(1). Bromine addition is accelerated when the unsaturated molecule contains electron-releasing groups relative to hydrogen, whereas retardation is observed when electron-attracting groups are present.[31] The relative rates of bromine addition are given in Table 1.

TABLE 1.

Compound	$CMe_2=CMe_2$	$CHMe=CH_2$	$CH_2=CH_2$	$CHMe=CHCOOH$	$CHBr=CH_2$
Relative Rate	14.0	2.03	1	0.26	small

(2). In an unsymmetrical unsaturated compound, when iodine monochloride is added, the more positive iodine attacks the negatively polarised carbon atom.[32]

$$CH_2{=}CH.COOH + ICl \longrightarrow CH_2Cl.CHI.COOH$$

(3). When the seat of unsaturation is contained in an ion, halogen addition is facilitated. Sodium acrylate in water adds bromine more readily than does acrylic acid.[33]

(4). If ethylene is treated with bromine water containing sodium chloride, iodide and nitrate, the products have the formulae, $CH_2Br.CH_2Cl$, $CH_2Br.CH_2I$, $CH_2Br.CH_2ONO_2$, respectively.[34] The anions thus compete for attachment to the second carbon atom of the double bond, and the first carbon atom, which must be negative, is attacked by the positive bromine.

The pioneer in the field of kinetics of bromine addition to olefinic compounds was P.W. Robertson, whose first paper on the subject was published in 1937.[35] He and his collaborators accepted the conception already mentioned, that the positive atom of the polarised bromine molecule attaches itself with effective impact to the negative carbon of the ethylenic system, whereupon the resulting positive charge ofthe second ethylenic carbon atom is neutralised by the negative bromine ion which has a momentary existence.

These fundamental factors may be employed in the explanation of the mechanism which takes place in the action of Kaufmann's reagent on the unsaturated hydrocarbons used in this investigation.

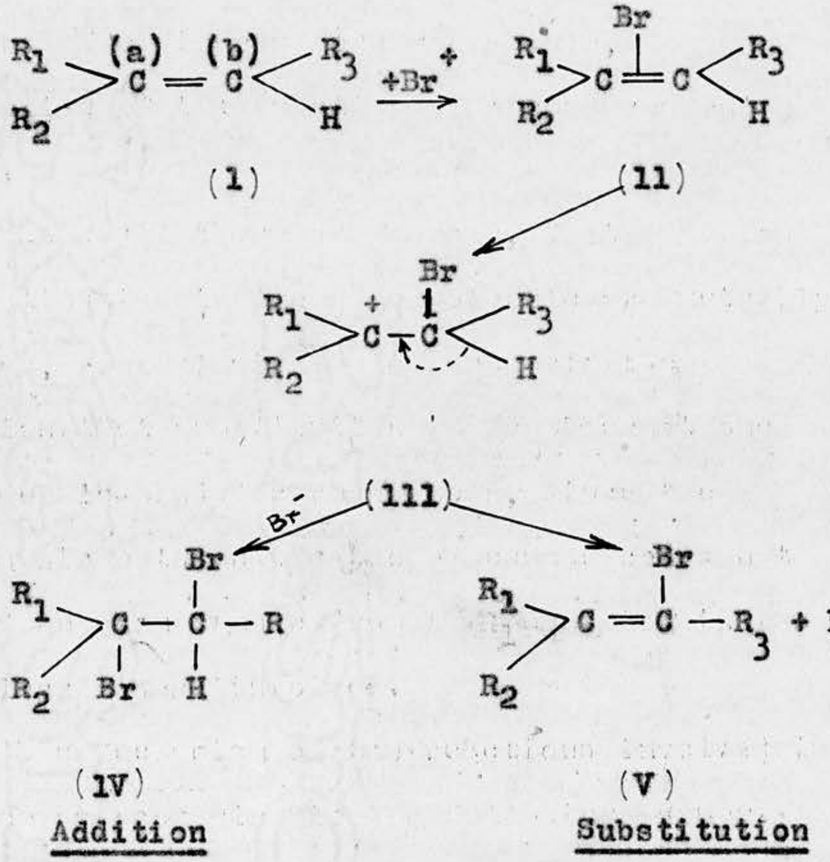
In all the hydrocarbons examined, substitution as well as addition was found to occur, and the total amount of reacting bromine was found to be approaching that required for complete addition. The figures were repeatable, irrespective of the quantity of excess reagent present.

It would therefore appear, that addition and substitution in the same molecule are mutually exclusive, a conclusion which supports the contention that substitution takes place at one of the double-bonded carbon atoms, since the relationship between the two processes could not exist if an atom remote from this position in the same molecule were involved.

The mechanism of the reactions involved is envisaged as occurring in the following manner.

As few unsaturated hydrocarbons are symmetrical about the double bond, this disproportion is reflected in the electronic charges about this linkage, brought into operation by the differences in the electron-donating properties of the groups associated with the two double-bonded carbon atoms.

When these effects are considered in relation to the possibilities of addition and substitution in unsaturated hydrocarbons, an argument can be made as follows. Consider in the first place the highly unsaturated branch chain hydrocarbons which have been found in this investigation, and by other workers to give the most anomolous results.



Thus in the hydrocarbon(1) the concentration of electrons on atom (a), is determined by the total electron donating strength of $R_1 + R_2$ as compared with that of R_3.

At stage 11, the Br$^+$ os depicted as adding itself on to the π electrons of the ethylenic linkage, these electrons being regarded as available for dative bond formation. The -ive charges on atom (a) direct the change (11) to (111), the π electrons migrating to form the C-Br co-valent link on atom (b).

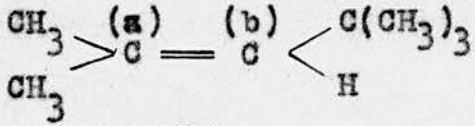
The stability of the molecule may be attained by (1) the atom (a) may complete its octet by uniting with a Br$^-$ion or (2) a substituent on (b) may be released as a positive ion, and the vacated electron pair will then swing back to reform the double bond. The most likely substituent to be released in the one most stable as a positive ion, namely, the H$^+$ion, particularly as the solvent is polar.

Mechanism (1) thus leads to addition, and (2) to substitution, and the effect of the substituents on (a) and (b) in determining which reaction predominates may be explained as follows.

In the formation of (1V) from (111), it is considered probable that the entering Br$^-$ is attracted by electrostatic forces, whence it follows that the less the positive charge on (a), the less the probability of this occurring before the competing mechanism (111) $\rightarrow$ (V) + (H$^+$) occurs.

Thus the electron deficiency at atom (a) stage (111), will be partly compensated by electron displacement towards this atom brought about largely by R_1 and R_2, the degree of compensation being determined by the strength of these groups.

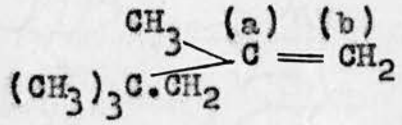
It seems reasonable, therefore, to expect that strong electron donating groups on (a) would give rise to a relatively large proportion of substitution as compared with addition, a deduction which appears to be borne out experimentally in the case of 2:4:4 trimethylpentene-2 (V1).



(V1)

Here the carbon atom marked (a) has two strongly electron-donating methyl groups, while (b) has one weakly electron-donating <u>ter</u>-butyl group. The concentration of charge on (a) will therefore be large and favour substitution. In point of fact, the substitution/addition ratio found experimentally in 89.4/1.5.

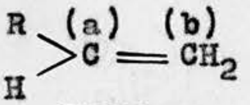
In the case of 2:4:4 trimethylpentene-1 (V11)



(V11)

instead of two strongly electron-donating methyl groups, there is only one methyl group and a weak <u>neo</u>-pentyl group. The concentration of electrons on (a) although large, will not be so great as that on the corresponding atom in (VI), and the substitution/addition ratio should therefore be smaller. Experimental results once again favour this theory, the figures being 73/25.5

Considering now the straight chain hydrocarbons, hexene-1, octene-1 and cetene-1.

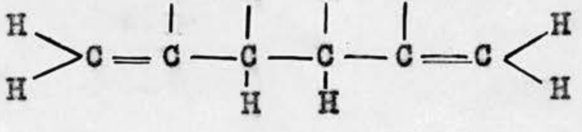


VIII

R = C_4H_9, C_6H_{13}, and $C_{14}H_{29}$.

All these groups have weak electron-donating properties, so that a relatively small amount of substitution may be expected at (b). The ratios established experimentally were 26/74, 35/75 and 37/63, respectively.

Finally, in the case of diallyl (IX) a relatively weak concentration of electrons may be expected on the 2 - and 5 - position atoms, so that a small amount of substitution on the 1- and 6- positions appears probable.



(IX)

The substitution/addition ratio actually obtained was 18/82.

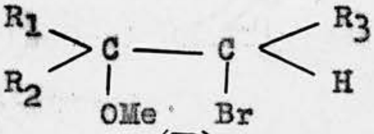
Abnormal Reactions.

A.

The first and most obvious abnormal reaction, is the possibility of substitution remote from the double bond. This will give rise to abnormally high figures for total absorption and also for substitution, but results in general indicate that this does not occur, the tendency being for the estimated values to be slightly less than those required for theory.

B.

The formation of compounds such as (X) has been reported by Jackson[36] in the course of work on bromination in methanolic solution.

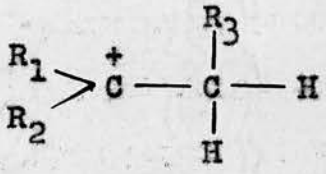


(X)

Although the double bond has been removed, this reaction is tantamount to a substitution, since from the bromine molecule, one atom goes off as Br^-, a hydrogen ion being produced from the MeOH molecule. This would explain why no further substitution occurs after entry of one bromine atom, since the double bond is removed. It is not considered that this reaction can be much in evidence when the Kaufmann reagent is used, as competition from bromide ions would minimise the degree of entry of the MeO radicle. The overall bromine absorption would in any case be unaffected.

Addition of Hydrobromic Acid.

C.



$R_1R_2\overset{+}{C}-\underset{H}{\overset{R_3}{C}}-H$

(XI)

This can only be envisaged as attack by the hydrogen, or rather the $MeOH_2^+$ ion, on the π electrons of the double bond, followed by isomerisation to the carbonium ion (XI) which thus reacts with a bromide ion.

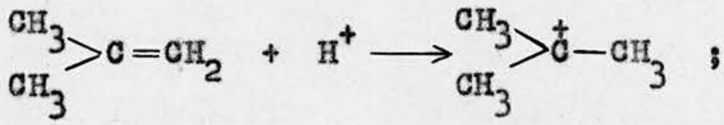
This reaction does not occur in the absence of bromine, since solutions of hydrocarbon in acid methanol are quite stable, vide page 51 Table XXV so that in the process suggested above, the $MeOH_2^+$ or H^+ ions would compete with the Br^+. Since the latter is activated, whereas the former are not, it is not considered that this reaction will occur to any appreciable extent. In this connection, reference may be made to Table XXXI page 59. The total absorption figures approach 100 per cent except in the case of trimethylpentene-2, where the difference amounts to almost 10 per cent. This is obviously not due to hydrobromic acid addition, which could only take place at the expense of the acid produced in the substitution reaction. The estimated value of the latter would thus be reduced by twice the above mentioned 10 per cent discrepancy.

Possibility of Low Results through Dimerisation.

D.

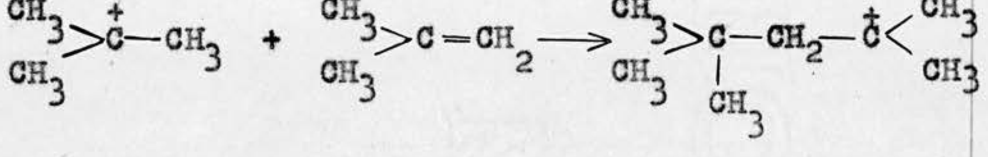
Bergmann[37] in his paper on the dimerisation reactions of unsaturated hydrocarbons, deals largely with the formation of new olefins by "migratory dimerisation" brought about initially by the migration of a hydrogen atom. He produces evidence to show how the degree of assymmetry favours dimerisation reactions, citing amongst other hydrocarbons, styrene[38] and indene[39].

The mechanism which he and also Birch and Dunstan[40] in their work on olefine- isoparaffin addition reactions, appear to favour, is that of Whitmore[41] who suggests in the case of isobutylene, the addition of a proton, e.g.



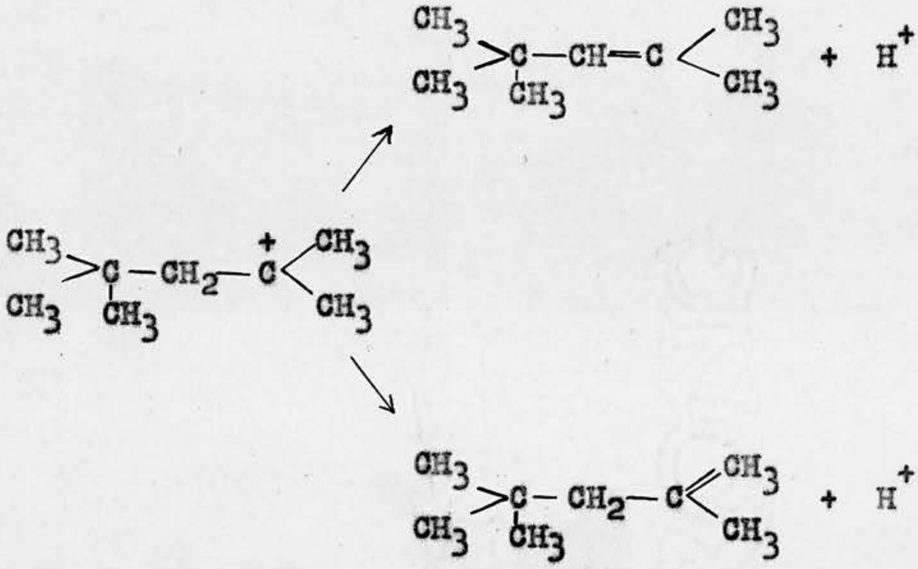
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=CH_2 + H^+ \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\overset{+}{C}-CH_3 \;;$$

the positive carbonium ion so formed acts like a proton and adds on to another molecule of hydrocarbon:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\overset{+}{C}-CH_3 + \begin{matrix}CH_3\\CH_3\end{matrix}\!>C=CH_2 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\underset{\overset{|}{CH_3}}{C}-CH_2-\overset{+}{C}\!<\begin{matrix}CH_3\\CH_3\end{matrix}$$

finally a proton is released, and a double bond formed to give the dimer:

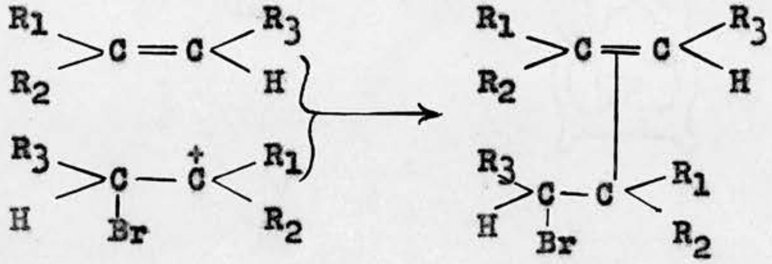


A somewhat similar mechanism may be advanced to support the contention that the low results obtained , particularly in the case of trimethylpentene-2, may be due to dimerisation brought about in the following manner.

The π electrons in the unsaturated hydrocarbon molecule (X11), may be attacked by the carbonium ion (X111), formed by the addition of Br^-, to produce (X1V) thus :-

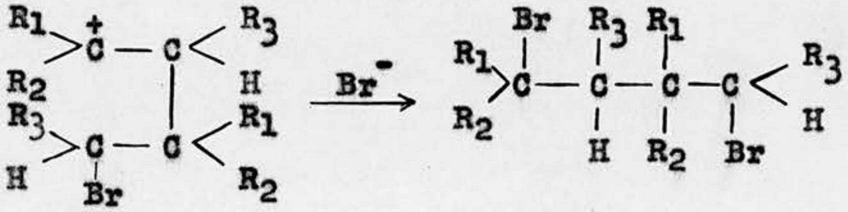
(X11)

(X111)



(X1V)

By isomerisation (X1V) goes to (XV), and to complete the stable dimer, a bromide ion is added :-



(XV) (XV1)

In the initial stages of this suggested series of reactions, the carbonium ion (X111) would act in competition with Br^+, hence dimerisation is most likely to occur with low bromine concentration and high hydrocarbon similar to the case for HBr addition suggested in "C".

Low bromide concentration would also favour this effect, sonce the carbonium ion would have a better chance of uniting as indicated, before being attacked by the Br^-.

The author intends to test this theory by (a) brominating trimethylpentene-2 in the absence of NaBr to reduce the Br^- to a minimum, in order to compare the results for absorption with those obtained with Kaufmann's reagent, and (b) by preparing a sufficient quantity of the products of bromination for identification and estimation.

Conclusions

From the foregoing discussion, it is apparent that the celerity of reaction between bromine and olefinic hydrocarbons in general must not be interpreted as evidence of a simple reaction mechanism.

The picture presented conforms to the present-day theories as revealed by kinetic investigations, but the probabilities illustrated by the examples A, B, C and D typify a complexity which belies the common assertion that addition reactions are straightforward and easy.

Addition is recognised as a characteristic property of unsaturated hydrocarbons, but this investigation has proved, in the variation of reactivity shown by the two trimethylpentene isomers towards bromine, that as Williams[42] so aptly phrases it "far from being an automatic trap for unwary halogen, the double bond is rather an objective to be sprung only by subtle and devious attack".

****

SUMMARY.

A historical treatment has been applied to the evolution of methods employed to measure the degree of unsaturation in hydrocarbon oils.

An original application of pyridine sulphate bromide to the estimation of the degree of unsaturation in motor spirit has been elaborated, and the use of Kaufmann's reagent for a similar purpose has been fully investigated. In connection with the latter reagent, the influence of peroxides on the value of Bromine Numbers has proved of sufficient interest and importance to justify further work on this subject.

In conclusion, a short account of the mechanisms involved in halogenation by means of Kaufmann's reagent is given, the interpretations of the reactions being based on recent work on the chemical kinetics of organic reactions in liquid systems.

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PART 11

AN OIL-SPRAY BLOW-PIPE FOR THE ESTIMATION OF TRACE ELEMENTS IN OILS.

Introduction.

Although most applications of the spectrograph have been made in the field of absorption spectroscopy, particularly in the infra-red and ultra-violet ranges, the use of emission spectroscopy has been suggested to cover the examination of inorganic additives, which within recent years have found increasing applications in the field of oil technology. Some of the compounds employed for this purpose are organo-metallics, such as the detergents aluminium naphthenate and the calcium salts of chloro-stearic acids, as well as the corrosion inhibitors in crank-case lubricating oils which contain lead, tin, bismuth or chromium, and in the field of motor spirits, we have the well known anti-knock compound, tetra-ethyl lead.

No matter in what organic medium the additive may be dissolved, the procedure adopted in most spectrographic laboratories devoted to the examination of petroleum products, has been to destroy the organic matter in the first instance, and subsequently to examine the residue or ash for the metallic constituents. For example, Russell[1], transfers an aliquot of the solid ash to the electrode crater, whereas Fred, Nachtried and Tompins[2], evaporate a portion of the solution of the inorganic constituents from the crater of a pure copper electrode, which is subsequently sparked.

It is open to doubt whether the ordinary spectrographic methods applied in such a manner, offer any advantages over the well-established micro-chemical or colorimetric methods. All these procedures have the common failing that ashing by combustion almost invariably leads to losses due to either mechanical entrainment in the products of the ignition, or to volatilisation of the oxides. If wet methods of oxidation are employed, there is a danger from spurting loss or contamination from the reagents or the vessel in which the treatment is carried out.

The difficulties enumerated above appear to have been overcome by a method introduced by Calkins and White[3], who employed pure graphite electrodes which were heated electrically to a white heat and then plunged into the oil under examination. The quenched electrode acted as a wick and sucked up a portion of the oil which filled the spaces formerly occupied by gases in the graphite.

They claimed that by means of their special rapid spectrographic technique, a quantitative analysis of phosphorus, calcium, barium, zinc and lead in lubricating oils or lubricating oil additives could be made in a few minutes. It was admitted, however, that the results obtained with tetra-ethyl lead were not so satisfactory.

There is another spectrographic technique, however, which does not appear to have been applied to the estimation of trace elements in oils. This method was first introduced by Lundegårdh[4], for the spectrographic analysis of aqueous solutions of inorganic salts. These were sprayed into an air-acetylene flame which raised the metallic atoms to their excitation temperature, the spectra being recorded photographically in the usual manner.

Klemperer[5] appears to have pioneered the spectral analysis of elements in solution by introducing an electrolytical spray apparatus, based on the work of Kirchoff, Bunsen, Beckmann and others. This apparatus, according to Lundegårdh[6], was somewhat complicated and difficult to handle, and he preferred to use a modification of a nozzle spraying apparatus designed much earlier by Gouy[7]. The air required for the air/acetylene flame was passed through a vessel containing the solution of the sample, and the latter was carried to the flame in the form of a fine mist.

The emission spectra of the metallic constituents in the solution under test, were recorded photographically and estimated by means of a photometer.

Improvements and simplifications in the original apparatus are depicted in the sketch below, the nozzle being introduced in 1936[8], and the burner in 1938[9].

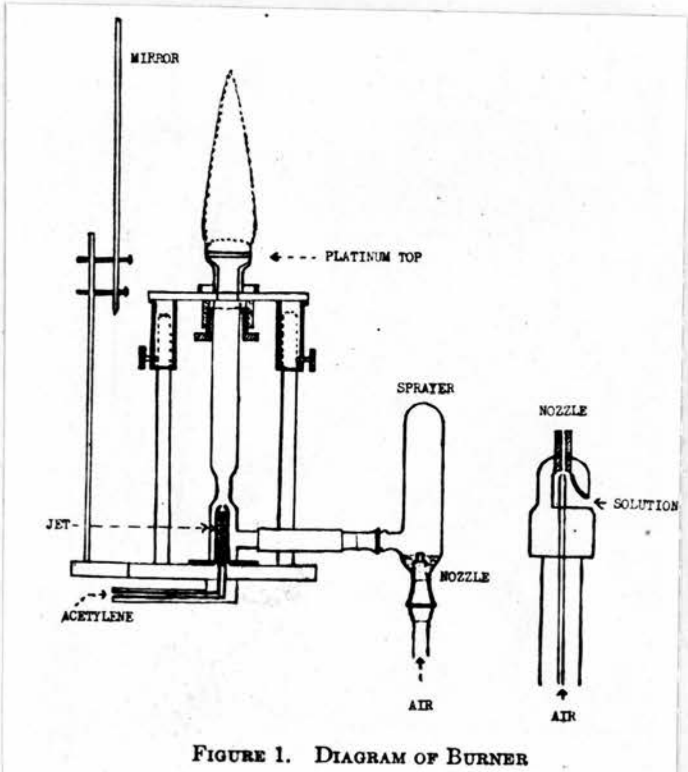


FIGURE 1. DIAGRAM OF BURNER

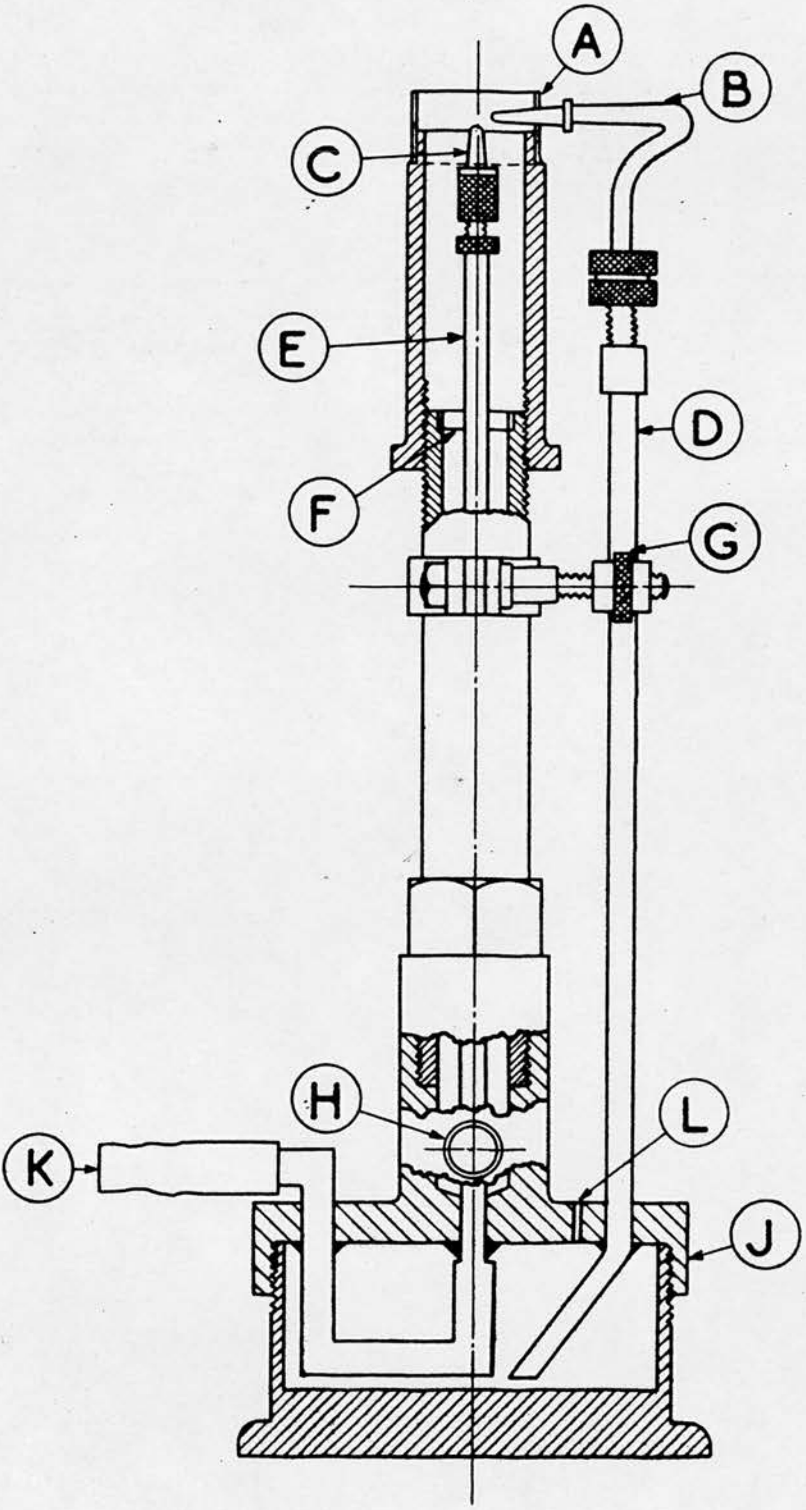
An apparatus of this type was used by Griggs, Johnstin and Elledge[10], for the mineral analysis of biological materials, the inorganic constituents being isolated by oxidation of the organic matter with nitric acid and perhydrol at 140'C. In the course of their remarks on the preparation of the samples, they make the interesting statement that dry-ashing at 400'C was accompanied by a loss of about 30 per cent of the total potassium and by as much as 10 per cent of the calcium[11].

Description of Apparatus.

The instrument designed by the author is essentially an oxy-coal gas blow-pipe in a form which resembles an ordinary bunsen burner. The hydrocarbon gas passes up the main tube and is burned at the top which is protected by a platinum collar.

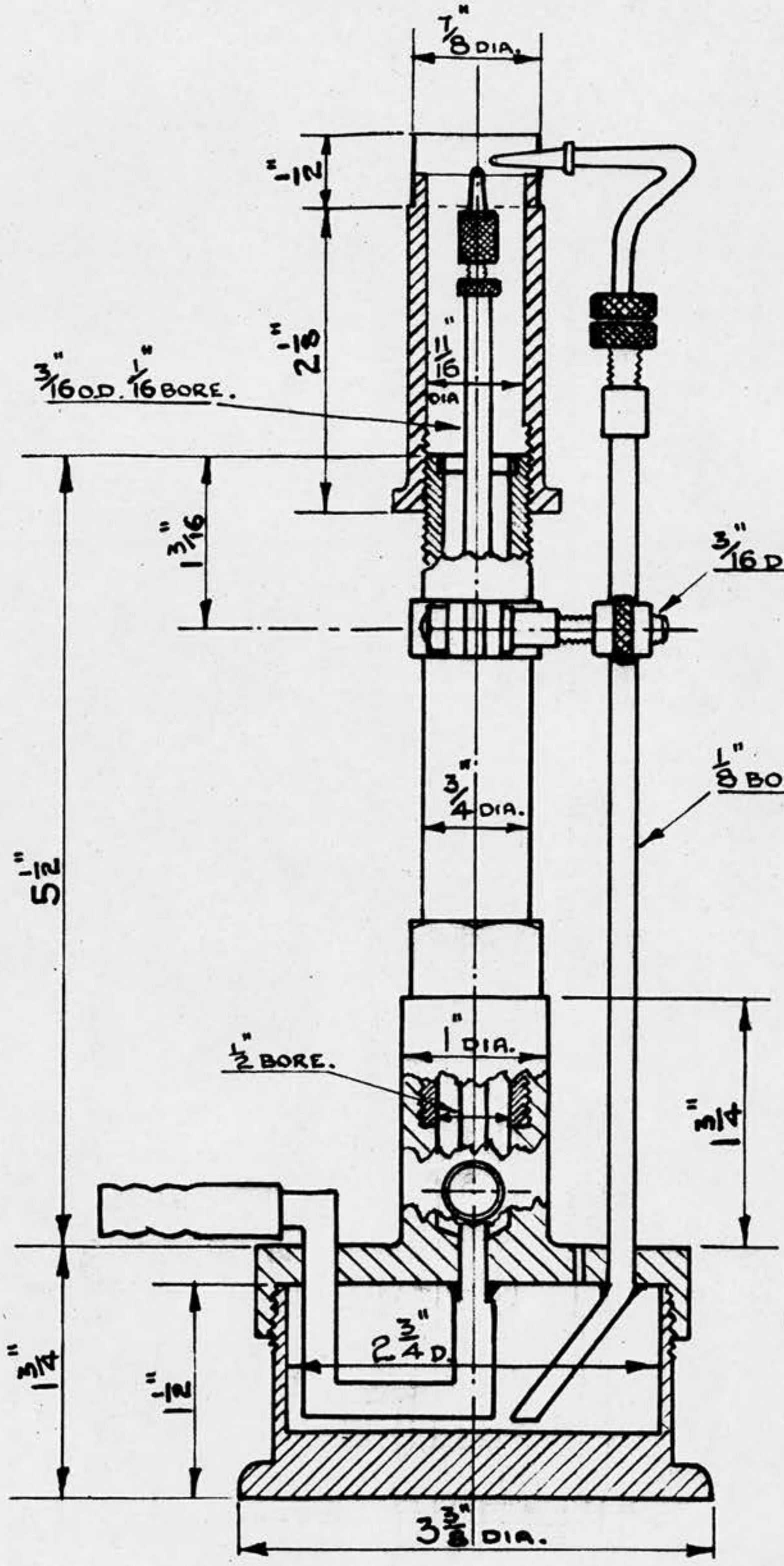
The base of the burner accommodates the sample dissolved in a suitable solvent in a compartment through which two narrow bore brass tubes pass, one centrally up the blow-pipe to a platinum jet, and the other externally terminating in another platinum jet. The former conveys a stream of oxygen which in passing the latter at high velocity, sucks up the sample from the reservoir and delivers it to the coal gas flame in the form of find spray.

In this proto-type model, a circular reflector is employed which incorporates a sliding aperture, the position of the latter being varied in order to facilitate the examination of the flame along its entire length for the determination of the point of maximum emission. For standardisation of gas pressures, calibrated manometers are incorporated in the respective pipe lines.

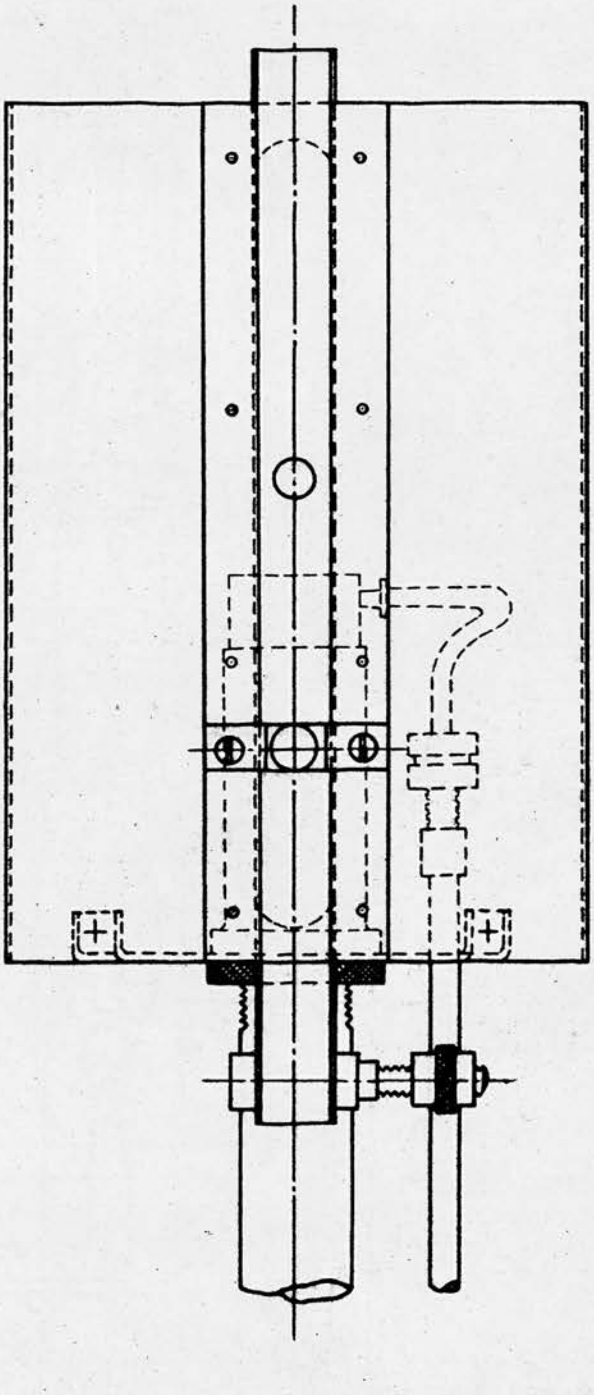


A	PLATINUM GUARD.
B	OIL JET REMOVABLE PLAT. NOZZLE.
C	OXYGEN JET PLAT.
D	OIL FEED PIPE.
E	OXY. JET FEED PIPE.
F	ANTI EXPLOSION GAUZE.
G	OIL JET DISTANCE REGULATOR.
H	COAL GAS INLET.
J	OIL RESERVOIR.
K	OXYGEN FEED TO JET.
L	VENT HOLE.

ARRANGEMENT
OF
OIL SPRAY BLOW PIPE



SECTIONAL DRAWING
OF
OIL SPRAY BLOW PIPE



ARRGT. OF CIRCULAR REFLECTOR
WITH ADJUSTABLE APERTURE.

EXPERIMENTAL

Technique.

The technique employed in these preliminary experiments was the "total energy method," which is based on the fact that if the same amount of sample is consumed in unit time, the resultant spectrographic line densities will be a function of concentration.

These essential features are effected by burning the oil solution for a definite period of time, the oxygen and coal-gas feed rates being maintained at a constant value.

Internal Standard.

Most spectrographic methods are based on the use of an internal standard, which serves as a means of checking the conditions of exposure for each analysis. In metallurgical spectrography, the major constituent of the alloy is generally used as the internal standard because the spectral line density due to this element is relatively independent of concentration.

In dealing with the analysis of biological materials in which case no single element is present in sufficiently high concentration to act as an internal standard, a definite quantity of a known element in the form of a salt, is added to the inorganic residue of the sample, in a proportion which approximates to 98 per cent of the total.

Oils, of course, are in a similar category to biological materials, but there are obvious difficulties in adding a suitable internal standard element to an oil particularly when the latter is used as an oil and not as a residual ash. In such cases, the density of the spectrogram on those portions of the film which are free from lines or bands, may be taken as an internal standard, when integrated over the period of the particular exposure time selected as a result of experiment.

Analytical Curve.

Procedure: 25 ml. of a solution of leaded motor spirit in ligroin, of composition shown in column 2 of Table, were used in each determination. In deriving the curve, "concentration of lead" was plotted against "-log ratio" of lead line density/ background, the logarithms used being the true logs. as distinct from the usual forms shown in the previous column on the table. This was necessary, since a logarithmic scale was employed for plotting purposes.

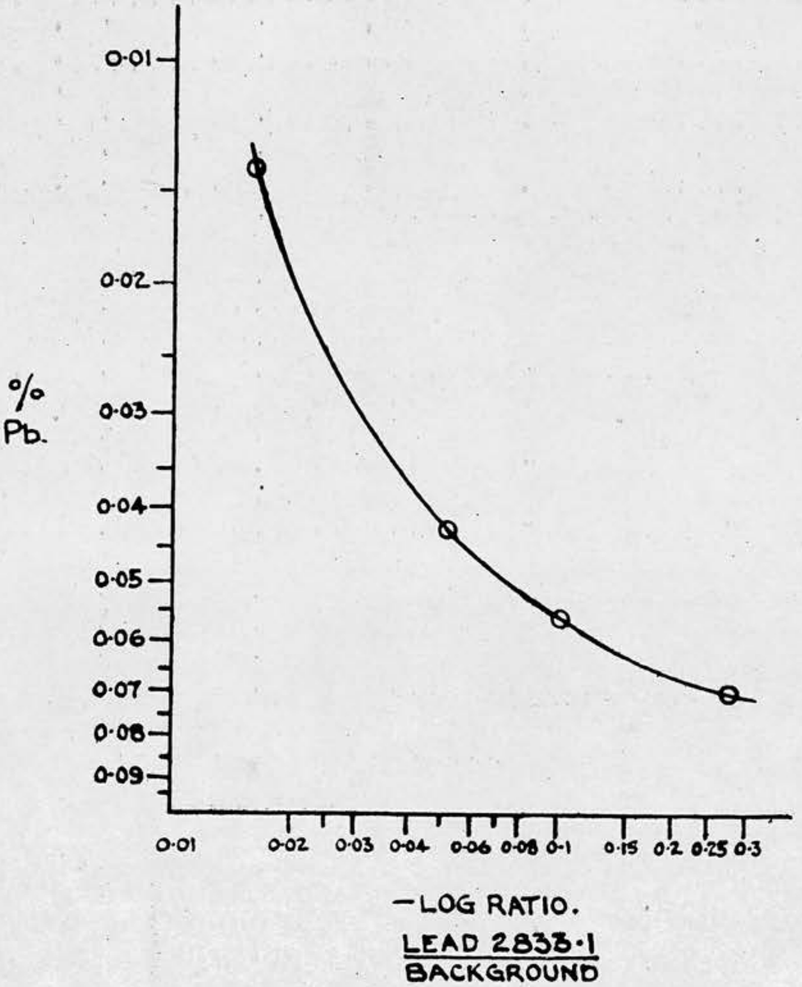
Analytical Curve

TABLE 1.

Spectrographic Analytical Results on Motor Spirit Containing 3 ml. of Tetraethyl Lead per Gallon.

Diluent .... Ligroin

Test		Densitometer Readings		Log	-log	Concentn
No.	Test Solution.	Pb. 2833.1	Background	Ratio	Ratio	%age Pb.
1	Diluent.	-	-	-	-	nil.
	Sample Diluent.					
2	5ml.+ 20ml.	41.65	43.25	1.984	0.016	0.014
3	10ml.+ 15ml.	40.25	40.40	1.998	0.002	0.028
4	15ml.+ 10ml.	39.20	44.20	1.948	0.052	0.042
5	20ml.+ 5ml.	36.25	46.00	1.897	0.103	0.056
6	Sample	19.60	37.15	1.722	0.278	0.070



ANALYTICAL CURVE—LEAD IN PETROL.

Except for Test No.3., which is obviously abnormal, the values obtained were located on an excellent smooth curve, suggesting that the figures were sufficiently good to indicate the success of the method.

Conclusions.

An apparatus has been designed which according to preliminary experiments promises to provide a means of estimating quantitatively the lead content of motor fuel containing this element as an additive.

These experiments are being continued, in the belief that the apparatus may be of more general use in the estimation of oil additives, as well as in the wider field of organometallic compounds.

Like all proto-types, this apparatus is not free from defects, which these tests have served to reveal, and a model of improved design is in the process of construction.

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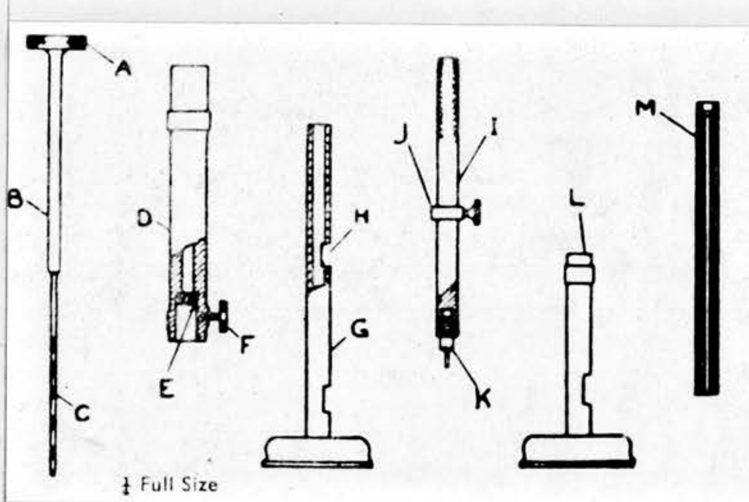
A MICRO FILTER STICK FOR USE IN SPECTROGRAPHIC ANALYSIS.

The employment of the spectrograph for the analysis of microchemical quantities of solids generally requires the transfer of the materials to the cathode crater from one of the many types of filters recently described by Wyatt.[1] This transfer may be effected by the method used, for example, by Harper and Strafford,[2] in their work on the spectrographic estimation of traces of arsenic in foodstuffs, but whatever the particular procedure adopted, it requires extremely careful manipulation to avoid mechanical loss.

The elimination of this danger and a speeding up of the analysis may be effected by the conversion of the cathode carbon itself into a filter stick, similar in shape to that designed by King.[3] This can be carried out readily by means of the hand-operated tool shown in the sketch on the next page. This tool is much more easily controlled than a power-driven lathe or drill.

Filter stick drill and crater cutter.



¼ Full Size

A. Nurled handle.
B. Drill mount.
C. Drill 1/16" diameter.
D. Sleeve guide.
E. Guide plate with centre hole.
F. Fixing screw.
G. Carbon holder.
H. Slots for holding carbon when drilling.
I. Recess cutter.
J. Recess depth stop.
K. Cutter head, interchangeable.
L. Holder for short lengths of carbon.
M. Carbon filter stick.

Procedure:

The carbon is placed in holder G, and the guide D superimposed so that the underside of the guide plate E, rests on the top edge of G, and then screw F is tightened. The drill C is inserted and slight downward pressure applied, the handle then turned in a clockwise direction. The length drilled is registered on the inscribed mount B, and for 6-inch carbons it has been found expedient to drill rather more than 3 inches into one end of the carbon, which is then reversed and the remaining length drilled from the opposite end. The drill and sleeve are removed, and the recess cutter is positioned by inserting the guide pin in the hole of the drilled carbon. The recess guide stop is moved up the inscribed shank of the cutter a distance equal to the required depth of the crater, the fixing screw tightened, and the recess cut by revolving the tool until the stop makes contact with the top of the carbon holder. By choosing a suitable design of cutter head, any desired shape of crater may be formed, for example, that used by Mitchell.[4]

The tiny filter paper disc which fits into the recess is cut by means of a cork borer, and the usual microfiltration technique is used, filtering preferably, from a centrifuge. A fresh crater may be cut when distortion takes place as a result of arcing, a new flat surface being obtained by rubbing down on emery paper.

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Acknowledgements.

The author wishes to record his appreciation of the help received from the Anglo-Iranian Oil Company, in supplying the samples of hydrocarbons; Messrs Babcock & Wilcox, Ltd., for spectrographic assistance; and the Railway Executive Committee for laboratory facilities.

He is also greatly indebted to Prof. H.B. Nisbet, Heriot-Watt College, who supervised the work, for his keen interest and helpful suggestions during its development.