
Gerald Perkins

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Part of the Chemistry Commons

Recommended Citation

https://digitalcommons.lsu.edu/gradschool_disstheses/7981

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
STUDIES IN ANALYTICAL CHEMISTRY

I. NEW METHODS FOR THE DETERMINATION OF ASH IN PETROLEUM CRUDES

II. STUDIES IN OSCILLOGRAPHIC POLAROGRAPHY

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Department of Chemistry

by
Gerald Perkins, Jr.
B.S., Southeastern La. College, 1942
M.S., Louisiana State University, 1944
August, 1950
MANUSCRIPT THESES

Unpublished theses submitted for the master's and doctor's degrees and deposited in the Louisiana State University Library are available for inspection. Use of any thesis is limited by the rights of the author. Bibliographical references may be noted, but passages may not be copied unless the author has given permission. Credit must be given in subsequent written or published work.

A library which borrows this thesis for use by its clientele is expected to make sure that the borrower is aware of the above restrictions.

LOUISIANA STATE UNIVERSITY LIBRARY
ACKNOWLEDGMENT

The author wishes to express his gratitude for the help and guidance of Dr. Philip W. West, Dr. Paul Delahay, Dr. Edgar L. Compere and Dr. George C. Jaffe. He also wishes to acknowledge the assistance of his wife, Virginia H. Perkins.
# TABLE OF CONTENTS

## PART I: NEW METHODS FOR THE DETERMINATION OF ASH IN PETROLEUM CRUDES

1. INTRODUCTION AND REVIEW OF PREVIOUS WORK ........................................ 1
2. EXPERIMENTAL .................................................................................................. 3
   Preliminary studies of present methods ................................................................. 3
   Investigation of enclosed combustion methods ..................................................... 7
   Investigation of fly ash recovery methods ............................................................ 10
   Discussion of results ............................................................................................... 21
3. BIBLIOGRAPHY ................................................................................................. 22

## PART II: STUDIES IN OSCILLOGRAPHIC POLAROGRAPHY

1. INTRODUCTION AND REVIEW OF PREVIOUS WORK ........................................ 30
2. PHENOMENA OCCURRING DURING THE QUIESCENT PERIOD OF THE VOLTAGE WAVE IN THE MULTI-SWEEP METHOD ............................................. 32
   Description of the instrument ................................................................................. 35
   Technique of the measurements ............................................................................ 36
   Variation of the concentration of reducible substance during the quiescent period of the voltage wave ......................................................... 37
   Variation of the peak current during the drop life ............................................... 39
   Variation of the maximal peak current with the head of mercury .................... 41
   Variation of the maximal peak current with the shape of the voltage wave ......... 43
   Variation of the maximal peak current with the rate of potential change .......... 44
3. A SINGLE-SWEEP OSCILLOGRAPHIC POLAROGRAPHY .................................. 50
LIST OF TABLES

I. Comparison of Several Methods of Ash Determination.................. 5

II. Values of Ash Content of Various Oils as Determined by the L.S.U. Method.................................................. 18

III. Comparison of L.S.U. and A.S.T.M. Methods With Synthetic Samples.................................................. 20

IV. Determination of Rate of Mercury Flow With and Without Current Flow Through the Polarographic Cell.................. 39
# List of Figures

1. Varied Types of Apparatus for Ash Determination ........................................ 23
2. Closed System for Ash Determination ............................................................. 24
3. Drawing of Apparatus for Closed System ....................................................... 25
4. Ash Determination Bomb ............................................................................. 26
5. Fritted Glass Combustion Chamber ............................................................... 27
6. Constant Feed Apparatus .............................................................................. 29
7. Variation of Peak Current During Drop Life for Various Shapes of Voltage Wave ........................................................................................................... 62
8. Variation of Peak Current During Drop Life for Two Frequencies .................. 63
9. Variation of the Maximal Peak Current with the Rate of Potential Change for Thallous Ion ................................................................. 64
10. Variation of the Maximal Peak Current with the Rate of Potential Change for Cobaltous Ion ................................................................. 65
11. Variation of the Maximal Peak Current with the Rate of Potential Change for Thallous Ion in Several Supporting Electrolytes ......................... 66
12. Variation of the Maximal Peak Current with the Rate of Potential Change for Hydrogen Ion - Single-Sweep Contrasted with Multi-Sweep ................. 67
13. Variation of the Maximal Peak Current with the Rate of Potential Change for Cobaltous Ion - Single-Sweep Contrasted with Multi-Sweep ................. 68
14. Variation of the Maximal Peak Current with the Rate of Potential Change for Iodate Ion - Single-Sweep Contrasted with Multi-Sweep ................. 69
15. Block Diagram of a Multi-Sweep Oscillographic Polarograph ......................... 70
16. Polarographic Cell for Single-Sweep Oscillographic Polarograph ................. 71
17. Block Diagram of a Single-Sweep Oscillographic Polarograph.............. 72
18. Circuit Diagram of a Single-Sweep Oscillographic Polarograph.............. 77
19. Example of Single-Sweep Recording, Z-Modulated Horizontal Sweep, and Z-Modulated Voltage Wave......................................................... 78
20. Various Rates of Potential Change Available with the Single-Sweep Instrument................................................................. 79
ABSTRACT

STUDIES IN ANALYTICAL CHEMISTRY

These investigations were divided into two parts, comprising three studies. In the first study, present methods of determining ash in crude oils were compared. All gave similar values. Further investigation gave evidence that ash was lost during these determinations and that, as a consequence of this, the ash values obtained with these methods were in error. These methods were all similar in the respect that the oil was burned away in an open vessel, the residue was ignited to constant weight, and the gain in weight of the ignition vessel represented the weight of ash in the sample. The initial, free-burning, step appeared to be the step in which ash was lost.

Several methods for determining the ash values accurately were investigated and the most promising method was then used to check several samples of oil and several laboratory synthetic samples. The method made use of a hood to gather the ignition gases and three phthalic anhydride-packed filter units to recover the entrained ash. After evaporation of the phthalic anhydride, the recovered ash was added to the ash obtained in the ignition crucible in order to determine the total weight of ash in the sample. The oil which had been used to compare the present methods and whose ash content had been calculated by those methods to be 0.0024% showed an ash content of 0.0087% by this new method. In determining the ash content of laboratory synthetic samples the old methods, as represented by the A.S.T.M. procedure, had an average error of 30.76%, whereas, the new method, known as the L.S.U. method, had an error of only 6.1%.

viii
The second and third studies were in the field of oscillographic polarography. Irreversible electrode reactions do not give values for the current which agree with those predicted by the Randles-Sevcik equation. For an explanation of this, the phenomena which occur during the quiescent period in the voltage wave were investigated. It was demonstrated that the rate of diffusion of reduced substances within the mercury drop and the degree of irreversibility of the anodic process, which occurs during the quiescent period, contribute to the deviations from the predicted values.

Studies were made of the variation of the peak current during the drop life, the variation of the peak current with the head of mercury, the variation of the peak current with the shape of the voltage wave, and the variation of the peak current with the rate of potential change. The results obtained from these studies supported the contention that the irreversibility of the anodic process contributed to the deviations from predicted behavior.

In order to separate the influence of anodic and cathodic processes an instrument was developed which made possible an improved method of single-sweep recording. The instrument has been completely described.
PART I

I. NEW METHODS FOR THE DETERMINATION OF ASH IN PETROLEUM CRUDES
INTRODUCTION AND REVIEW OF PREVIOUS WORK

In the petroleum industry there has long existed the suspicion that present procedures for the determination of ash in crude oils give values which are inaccurate. Thus far, however, investigators have only tried to modify the present technique in such a way as to obtain reproducible results for a series of determinations on the same oil. For example, the length and temperature of ignition have been arbitrarily fixed in order to limit volatilization of ash or at least to make constant the amount of ash volatilized, and ash residues have been treated with sulfuric acid before ignition in order to eliminate volatile chlorides. Thus, errors due to loss during ignition have been essentially eliminated or standardized, but still the agreement between results remains poor.

The purpose of this investigation was to study the problem of ashing, placing particular emphasis on those steps encountered before the final ignition. The ignition is essentially a step where conditions must be fixed arbitrarily since the nature of the material defined as "ash" depends upon the temperature of the ignition. The study resolved itself into two phases: first, an investigation was conducted of methods for ashing the oil in a closed vessel from which no ash could escape; second, an investigation was made of means for recovering any ash which might be lost during the course of the existing procedures. The investigation was further designed to devise a procedure which might be used as a "yardstick" method for evaluating other techniques.

The literature covering the subject of ashing is not extensive. There has been no broad study of the problem and few references can be found which deal with it in any way. The essentials of all the current procedures
are embodied in the method described in The A.S.T.M. Standards on Petroleum Products and Lubricants for 1943 (1), which is referred to hereafter as the "A.S.T.M. Method". In this procedure a 20 gm. sample of the oil is weighed to the nearest 0.1 gm. The sample is placed in a tared platinum crucible and heated slowly to the ignition point with a bunsen flame. When the oil ignites, the burner is removed and the oil is allowed to burn freely until it has been entirely consumed. The crucible and contents, a dry cake, are removed to a burner or to a furnace and ignited to constant weight at a red heat. The increase in weight represents the weight of ash present in the sample.

The method referred to in this discussion as the "Standard Oil Method" has been described in a Standard Oil Company of New Jersey memorandum on Determination of Ash in Feed Stocks (7). It is similar to the A.S.T.M. method except that a 100 gm. sample of the oil is employed and, after having burned off the oil, the residue is ignited in a furnace at 700°C for four hours. Webber discusses a similar method for determining ash in lubricating greases (8). In this case glazed porcelain crucibles are used. Roberts, Stenzel, and Eberz (4) advocate the same method as that described in the A.S.T.M. method—50 ml. to 200 ml. according to the salt content. E. Feigl has claimed that the time necessary for determinations similar to the above is reduced without loss of accuracy by distilling off 90% of the oil from an Engler flask at a pressure of one atmosphere and ashing the residue (2).
Preliminary Studies of Present Methods

The first step in the experimental work was a study and comparison of several existing methods. The methods which were used in this study were the A.S.T.M. method, the Standard Oil method, and the Infra-Red method. The first two have already been described. In the Infra-Red method two units of a Fisher "Intra-Radiator" were used with one directed upon the surface of the oil and the other inverted to give bottom heat. This arrangement provided a temperature of approximately 180° C. A 100 gm. sample of the oil was weighed to the nearest 0.1 gm. and placed in a tared platinum dish. By means of the infra-red heat the oil was evaporated as far as possible and the remainder was burned away as in the previously described methods. The residue was ignited in a furnace at 700 degrees Centigrade for four hours, and the gain in weight represented the weight of ash in the sample.

Two samples of oil were employed in these first tests, both of which were supplied by the Louisiana Division of the Standard Oil Company of New Jersey. One was designated as "Reduced Crude Feed "28", and the other "Wide Cut Paraffinic Gas Oil Feed "327". The former had an approximate ash content of 0.04% and was a thick, tarry oil. The latter had an approximate ash content of 0.0024%.

The A.S.T.M. method required approximately eight hours for a complete determination of ash, the Standard Oil method, six. This difference is probably due to the increased surface area of the platinum dish. The total time required for the Infra-Red determination was fifty-six hours, fifty of which were necessary for evaporation under the infra-red lamps. This method
is not very satisfactory due to the fact that after approximately two-thirds of the oil has evaporated a crust forms over the surface, thus preventing further evaporation. When the crust is broken it quickly reforms. Further trouble is encountered in burning away the remaining oil, which has a tendency to boil and expand under the crust, causing small eruptions which may push their way over the side of the crucible.

The results of the ignitions are presented in Table I. The A, S, T, M* method and the Standard Oil method give values of similar magnitude whereas the Infra-Red method gives values which are more consistent in themselves but somewhat higher than those of the other methods.

These higher values which were obtained with the Infra-Red method indicated that some of the ash might be lost during the burning period of the A, S, T, M* and Standard Oil methods.

In order to determine whether this was the case, a simple investigation of the ignition process was undertaken. A sample of oil was placed in one of the platinum dishes, similar to those used for the Standard Oil method, and was ignited at the surface and allowed to burn with a free flame. A clean, cold, porcelain evaporating dish was inverted in the flame. Soot deposited on the surface of the dish and collected there to a considerable depth. Periodically this deposit was carefully removed from the dish and deposited in a tared platinum crucible. (Enough of the deposit was collected to fill the crucible and the whole was weighed.) The crucible was then ignited at 700 degrees Centigrade until the weight became constant (i.e., until the carbon was completely burned away). The ash which remained was weighed and the
### TABLE I

**COMPARISON OF SEVERAL METHODS OF ASH DETERMINATION**

#### OIL A

<table>
<thead>
<tr>
<th>ASTM METHOD</th>
<th>STD. OIL METHOD</th>
<th>INFRA-RED METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0361 % ash</td>
<td>0.0374 % ash</td>
<td>0.0501 % ash</td>
</tr>
<tr>
<td>0.0394</td>
<td>0.0432</td>
<td>0.0507</td>
</tr>
<tr>
<td>0.0456</td>
<td>0.0477</td>
<td></td>
</tr>
<tr>
<td>0.0457</td>
<td>0.0427 % avg.</td>
<td>0.0504 % avg.</td>
</tr>
<tr>
<td>0.0470</td>
<td>0.0412</td>
<td>0.0470</td>
</tr>
<tr>
<td>0.0512</td>
<td>0.0442 % avg.</td>
<td>0.0470</td>
</tr>
</tbody>
</table>

Overall average for all methods ......................... 0.0449 %

Average deviation ........................................ 0.0043 %

Standard deviation ........................................ 0.0051 %

#### OIL B

<table>
<thead>
<tr>
<th>ASTM METHOD</th>
<th>STD. OIL METHOD</th>
<th>INFRA-RED METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0027 % ash</td>
<td>0.0019 % ash</td>
<td>0.0026 % ash</td>
</tr>
<tr>
<td>0.0016</td>
<td>0.0021</td>
<td>0.0029</td>
</tr>
<tr>
<td>0.0022 % avg.</td>
<td>0.0025</td>
<td>0.0028 % avg.</td>
</tr>
<tr>
<td>0.0025</td>
<td>0.0025</td>
<td>0.0025</td>
</tr>
<tr>
<td>0.0030</td>
<td>0.0024 % avg.</td>
<td>0.0024 % avg.</td>
</tr>
</tbody>
</table>

Overall average for all methods ......................... 0.0024 %

Average deviation ........................................ 0.0003 %

Standard deviation ........................................ 0.0004 %
percentage of ash in the soot was determined. Two samples of the Wide Cut Faraffinic Gas Oil yielded values of 0.10% and 0.13% for the ash content of the soot, itself.

To establish the fact that this ash was identical with the residual ash — that which was recovered after igniting the crucible in which the oil was burned — a spectrographic examination was made. Samples of both residual ash and fly ash were analyzed with a large Littrow prism spectrograph using a carbon arc as the exciting source. The samples were identical in composition with respect to the elements present, but it was noted that the relative proportions of the elements, as indicated by the line densities, varied in the two samples.

The analysis established the presence in both ash samples of the elements vanadium, iron, nickel, lead, zinc, sodium, calcium and silicon. In the residual ash vanadium and iron were present in the largest proportion while silicon was present only as a trace. In the fly ash the calcium and silicon were present in the greatest proportion whereas the iron and vanadium were present in only a small amount. The relative proportions of the other elements were little changed in both samples.

This study indicated that there is ash lost during the "free burning" process, that this ash is identical in elementary chemical composition with the residual ash, and that the lighter elements have more tendency to be lost as fly ash than do the heavier elements. In speaking of fly ash the term is used at present to include all ash carried away from the ignition crucible in any manner.
**Investigation of Enclosed Combustion Methods**

After determining that ash was being lost during the burning process it seemed logical to try to devise some method for preventing fly ash losses through elimination of the free-burning operation. This would require a new technique for ashing the oil sample. In the new method the oil would have to be burned, if burning was necessary, in such a way that the ash would be trapped in the ignition vessel. In short, it would be necessary to enclose the oil and flame entirely and allow only the exhaust gases to escape.

The apparatus necessary for this sort of a combustion could be either of two types. It could be a bomb, entirely closed or it could be a chamber from which the combustion gases would pass out through some porous medium which would retain all ash. Due to the extremely small ash values of most oils a sample size of no less than 15 gms. is almost imperative, and this consideration ruled out the use of a closed bomb. Accordingly a modified bomb was constructed which would fit the second set of requirements. It is pictured in Fig. 4. It was constructed entirely of stainless steel and consisted of two portions. The upper unit contained an inlet tube for oxygen, a needle for the introduction of the oil, and two electrodes which formed a spark gap below the needle and were designed for the ignition of the oil. The lower segment, which screwed tightly into the upper portion, was machined to hold a porous-bottom platinum crucible and was equipped with an exhaust tube whose entrance was covered with a perforated steel plate, which served as a support for the bottom of the crucible.

The oil sample, contained in a hypodermic syringe, was placed above the assembly and connected with the inlet needle. In theory, the oil was to
be fed in dropwise and ignited with the spark. Combustion, once started, would maintain itself and the exhaust gases would pass through the porous crucible and the exhaust tube. The crucible would retain the ash and after the combustion was complete it could be removed and weighed in order to determine the weight of ash.

This apparatus was constructed but was never made to work. During the tests it became apparent that one of two things was necessary in order to achieve combustion - either the oil and oxygen had to undergo some form of carburation, or the chamber had to be maintained at a high enough temperature to cause volatilization of the oil. The former expedient would prove difficult to engineer and the latter was impossible because of corrosion of the steel chamber by the oxygen at higher temperatures - the corrosion product would introduce error into the determination.

It was therefore decided to abandon the steel chamber in favor of a glass unit which would be impervious to the oxygen. With the introduction of glass as the building material it was necessary to change the design of the chamber completely. This change resulted in a simpler apparatus. This second instrument consisted of a small glass combustion chamber, connected with inlet tubes by a ground-glass joint and equipped with a fritted glass bottom, which filtered the gases and, at the same time, served as an exhaust port. The combustion was started by placing a micro-burner under the chamber and heating it before the introduction of the oil. When combustion was complete the previously-tared chamber was removed and reweighed. Its design was such that it fitted easily and securely into the pan of an analytical balance.
The oil arrived in the chamber through a porcelain tube, jacketed with a glass tube through which oxygen flowed. The end of the porcelain tube should be just inside the oxygen tube in order to achieve the best flame. The oil was fed into the chamber by a constant feed device which was constructed as follows: a constant speed motor of 1/3 rpm was attached to a worm drive fitted with a threaded collar. The movement of the collar served to press in the plunger of a hypodermic syringe which held the oil sample. The syringe fitted into the end of a stainless steel hypodermic needle, and the needle was cut short and cemented into the porcelain tube through which the oil entered the chamber. The chamber and inlet tubes are diagrammed in Fig. 5 and the constant feed device is pictured in Fig. 6.

In practice the chamber was heated to constant weight at 500 degrees Centigrade, a temperature which tests indicated did not change the weight of the glass. It was then connected to the inlet tubes and the burner was placed under it. When the chamber was sufficiently warm the oil feed device was started and the oxygen flow was connected. Ignition was spontaneous. When the oil was burned completely away the chamber was cooled, placed in a furnace at 500 degrees Centigrade to burn off any carbon which might be present, and weighed. The gain in weight represented the weight of ash.

This apparatus was tested for ease, efficiency, and continuity of combustion, and for the effect of the combustion of the glass chamber. The results showed that the flame was easily started, would maintain itself, and that the combustion was complete. No harmful effects to the chamber were noted when its dimensions were those indicated in the diagram. However, after
a period of several hours the end of the oxygen inlet tube would soften and sag and extinguish the flame. Since approximately 50 hours were necessary to burn 100 ml. of the oil a complete run could not be made with the glass inlet tube. It was necessary to use either a vycor or porcelain tube. A porcelain tip was fabricated and cemented to the injection tube, but the construction was not precise enough and did not allow a constant clearance about the whole circumference of the inner tube, a necessary factor in the production of a symmetrical and soot-free flame. The porcelain tip was discarded and an attempt was made to have the tube built of vycor. Unfortunately, this could not be accomplished and quantitative checks on this instrument could not be made.

Investigation of Fly Ash Recovery Methods

As heretofore stated another phase of the study of this problem was the investigation of means for recovering any ash which might be lost during the course of existing procedures. As a first step in this direction the use of some form of Gottrell precipitator was investigated. McClendon, in a determination of traces of iodine in ignition gases (3), employed a form of Gottrell precipitator with good results, and Shreve and Welborn (5) employed a Gottrell precipitator to recover solid material from escaping gases. It was constructed of 50 mm. Pyrex tubing with a piece of screen, eighteen inches long and wrapped about the outside, acting as one electrode. The central electrode was a length of 1/8 inch welding rod. Power was supplied by a pair of 12,000 volt neon sign transformers with primaries connected in parallel and secondaries connected in series.
The first precipitator constructed for the purposes of this investigation consisted of a glass chimney with an inside diameter of 50 mm and a height of 18 inches. The outer surface was silvered to a height of sixteen inches, thus allowing the glass chimney to hold a charge. At the top of the chimney was placed a platinum gauze. The gauze and silver were connected to the opposite terminals of a spark coil such as is used in demonstrations of discharges through gases. The spark coil was operated from a six-volt storage battery.

The platinum crucible was placed on a tripod below the chimney with the lip of the crucible extending somewhat into the chimney. The oil was ignited as before and allowed to burn away. The ash and soot were to be deposited on the sides of the chimney or on the gauze, from where they could be brushed into a crucible for subsequent ignition. This apparatus was a failure. The gauze soon became blocked with soot, thus destroying the draft in the chimney and allowing smoke to leak from the base. The apparatus is pictured in Fig. 1.

A second form of Gottrell precipitator was constructed which was a modification of the first type. Once again the chimney was used and, as before, was silvered on the outside. Down the center of the tube was placed a glass rod wrapped loosely with nichrome wire. The wire replaced the gauze as one terminal of the spark coil secondary while the silver remained as the other terminal. The solid matter in the gases deposited on the inside of the chimney. Later, instead of silvering the outside of the glass it was wrapped with aluminum foil.
In this apparatus, pictured in Fig. 2, precipitation was never consistently good, and the problem of recovery of the precipitated materials was a major one. Also, the precipitated soot formed streamers which would short-circuit the terminals if the glass chimney was at all dirty on the outside. The discharge would move from the aluminum, along the glass surface, into the tube, and across the streamers to the nichrome wire.

With the failure of this apparatus Cottrell precipitators and the precipitation method were abandoned in favor of absorption methods.

A train of liquid traps was designed which is pictured in Fig. 10. The ignition took place in a platinum crucible placed under a funnel-shaped hood and the ignition gases were drawn through the train by attaching the exhaust end to an aspirator or suction pump. Tests were made with a varying number of liquid traps and the traps were filled variously with water, and such solutions as ammonium hydroxide, hydrochloric acid, nitric acid. As many as four units were employed at one time, but the solid matter was not removed from the gases. The liquid traps had to be evaporated in order to recover the ash and since this required both the expenditure of considerable time and the application of a correction factor - or "blank value" - to compensate for the solids in the original solutions, a larger number of units would have been impractical. Since four scrubbers did not cleanse the gases this apparatus was also abandoned.

Entrapment of the entrained solids still seemed the most logical method for demonstrating their presence in the ignition gases and for their subsequent determination, however, the use of liquids for this purpose seemed
to offer no solution and the decision was made to find a solid filter medium with which to trap the ash. For this purpose a new apparatus was constructed which consisted of an ignition hood to collect the gases, a series of three filter units (large diameter Pyrex tubing packed with the solid filter material), three liquid traps placed after the filter units and designed to condense and collect any volatile material which might pass through the filter unit, and a suitable arrangement for applying suction to the filter trains. The apparatus is pictured in Fig. 1d.

As a filter medium surgical cotton was to be employed. This could be easily ashed to recover the solid material. A blank value would then be subtracted from the total weight of ash and the difference would comprise the weight of recovered ash. The liquid traps could be dealt with separately, and the two values combined, in the event that volatile ash was indicated.

In the course of checking the blank value (i.e., the ash content of the cotton) it was discovered that the values were not constant for the same sample of cotton. Cotton was, therefore, never employed in the filters. In its place it was necessary to substitute something which could be obtained cheaply, in quantity, in a relatively pure state, and a material which would preferably burn to gaseous products. Sucrose, which seemed to fit these requirements, was next tested. Its ash content was low but its behavior upon ignition was poor. It would expand tremendously and would froth and bubble. The frothing was severe enough to cause the loss of much solid material. Due to these disadvantages it was concluded that sucrose, while perhaps suitable, was not acceptable as a filter agent if something better could be found.
At this point another quality was added to the list of those considered desirable. If the filter material could be sublimed or evaporated the ashing step could probably be made more rapid and less troublesome.

Again with these qualities in mind a list of organic compounds was considered and phthallic anhydride was selected. Phthallic anhydride could be obtained cheaply, in large quantity, and with a negligible (less than 2 ppm) ash content. Moreover, it could be evaporated at a low temperature and its needle-like crystal structure contributed a lattice type of packing in the unit which appeared ideal for the easy passage of the gas and the efficient entrapment of the ash. Consequently, in all further work with this apparatus Baker and Adamson reagent grade phthallic anhydride was employed as the filter medium.

To insure condensation of the volatile ash a water jacket was placed around each filter unit and the liquid traps were abandoned entirely. The apparatus was modified in general design to that appearing in Fig. 1e.

The filter units were charged as follows: a circle of ashless filter paper, supported by a plug of cotton, was placed over the lower, or exhaust, stopper; finely crushed phthallic anhydride was placed over the filter paper and above that, extending for a height of about two inches, was placed coarsely pulverized phthallic anhydride crystals. The whole assembly was mounted as pictured and while the oil was burning a constant stream of air was drawn into the hood and through the system by means of the aspirators. The volume flow through the units and the number of units utilized could be controlled by the aspirators.
After the burning process was complete the crucible which held the sample was removed and heated to constant weight at 700 degrees Centigrade in a muffle furnace and the ash value obtained was termed "residual ash". The phthalic anhydride and the ashless filter paper from the filter units (together with the soot deposit from the interior of the hood and connecting tube) were transferred to a tared platinum dish and placed in an oven at 180 degrees Centigrade where the phthalic anhydride evaporated away. The crucible was then placed in a furnace at 700 degrees Centigrade and brought to constant weight. The gain in weight represented ash recovered from the ignition gases and was termed "fly ash" or "recovered ash". When the two ash values were added the total represented the true ash content of the oil.

This apparatus was first used to determine the ash content of the "Wide Cut Paraffinic Gas Oil Feed #327", one of the oils previously tested extensively with the current procedures. The results of three determinations have been tabulated below.

ASH CONTENT OF OIL B AS DETERMINED

BY THE 'LSU METHOD

0.0020 %
0.0020 %
0.0020 %
0.0020 %
0.0020 % avg.

These results were more than three times as large as those obtained by any other method. This represented quite an error for the previous methods if the LSU method were to be considered correct.

In the absence of any good method for checking the relative merits of the different procedures the ones which could logically be shown to have
the fewer sources of error could be inferred to be the more correct. To this end the apparatus was again modified in such a way as to form a "closed system" into which was introduced only filtered air. This removed the possibility of high results due to atmospheric dust. The new apparatus consisted of the previously described hood and filter arrangement placed over a large inverted beaker which was equipped with an opening in its bottom and several inlet tubes piercing its walls. The beaker was inverted in a pan of water, thus excluding the outer air entirely, and enclosed within was the tripod and ignition crucible. (A hot plate was added to keep the oil burning as its level became low in the crucible, and the wires to this hot plate passed through a packed inlet tube.) The other inlet tubes served for the introduction of air which had been filtered through a glass tube, approximately eighteen inches long, packed with glass wool which was kept wet with a heavy oil. The junction of the hood and beaker was closed with a mercury seal and a slight positive pressure was maintained at all times to insure no leakage of outside air.

With this apparatus several samples of oil were checked, and the results are listed in Table II. Since the residual ash figure is the same as that which would be obtained with the Standard Oil or the A.S.T.M. methods, the three columns — residual ash, recovered ash, and total ash — give a picture of the difference in results obtained by the two methods.

Average values have been listed in this table. The Primol D figures were checked four times, the Wide Cut Gas Oil four times, the Flask Tower Overhead, FD5458, and PD5460 each three times. The others were checked but
once. All determinations on the same oil checked within 5 ppm on total ash. The error due to fly ash was indicated to be large and was apparently at no time small enough to be disregarded.

To further check the accuracy of this method and the relative merits of the different procedures — the A.3.T.T. method and the LSU method — analyses were made of laboratory-prepared synthetic oil mixtures. This may or may not give a suitable check, since the form in which the ash is present in the oil is unknown and a synthetic oil may not have the properties of the natural oil which contribute to the formation of fly ash. However, it could indicate whether the results obtained by the new method were high.

Synthetic standard samples were made by mixing a mineral oil base with a metal naphthanate. The mineral oil base was Primol D, supplied by the Esso Laboratories. The ash value of the oil was to be used as a blank. Four determinations of this value were made by the LSU method and the following results were obtained:

Primol D ash, in ppm.

\[
\begin{array}{c}
52 \\
54 \\
55 \\
59 \\
59 \text{avg.}
\end{array}
\]

Samples of iron naphthanate and nickel naphthanate were obtained from the Esso Laboratories and analyzed for the metal as follows:

IRON NAPHTHANATE: Samples were digested in a Kjeldahl flask with concentrated sulfuric acid. No catalyst was employed. The resulting solution was evaporated to drive off most of the sulfuric acid, diluted with distilled water,
### TABLE II
VALUES OF ASH CONTENT OF VARIOUS OILS AS
DETERMINED BY THE L₃JU, METHOD

<table>
<thead>
<tr>
<th>OIL</th>
<th>RESIDUAL ASH (PPM)</th>
<th>RECOVERED ASH (PPM)</th>
<th>TOTAL ASH (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WIDE OUT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAS OIL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEED 327</td>
<td>24</td>
<td>63</td>
<td>87</td>
</tr>
<tr>
<td>PD 5458</td>
<td>28</td>
<td>72</td>
<td>110</td>
</tr>
<tr>
<td>PD 5460</td>
<td>25</td>
<td>46</td>
<td>71</td>
</tr>
<tr>
<td>Primol D</td>
<td>19</td>
<td>35</td>
<td>54</td>
</tr>
<tr>
<td>PGO FEED</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FROM FCCU</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No. 2</td>
<td>12</td>
<td>30</td>
<td>42</td>
</tr>
<tr>
<td>POLA No. 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FLASH TOWER</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OVERHEAD</td>
<td>(clay perco-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>lated and</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>vacuum dis-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>tilled)</td>
<td>5</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>76</td>
</tr>
</tbody>
</table>
and the iron precipitated with ammonium hydroxide. The iron was weighed as Fe₂O₃ and this figure was divided by the weight of the sample to give the ash factor.

NICKEL NAPHTHANATE: Samples were digested and evaporated as for the iron and the nickel was weighed after electro-deposition on a platinum gauze electrode. This weight was converted to the oxide and divided by the weight of sample to give the ash factor.

The synthetic oils were made as follows: a tared platinum crucible was placed on the balance pan and in the bottom was placed a small drop of the naphthanate. This was weighed and the weight of the naphthanate was calculated. Primol D was then added to the crucible until the sample weight was approximately 20 gm. The weight of the Primol D was determined. The crucible was warmed and the naphthanate diffused throughout the solution. The sample was then ashed. Three samples of the iron synthetic and two samples of the nickel synthetic were analyzed.

The results of the five runs are presented in Table III. The amount of ash in the Primol D was added to the amount of metal ash present in the form of the naphthanate and the total amount of ash recovered was compared with this value. In order to remove any question as to the actual amount of ash in the mineral oil base it was employed as a blank, and the value added to the calculated result was based on the ash value of 55 ppm. for the LSU method and an ash value of 19 ppm. for the A.S.T.M. method. These figures were derived from the average of four ash determinations by each method.

The metals used in these determinations, iron and nickel, were
<table>
<thead>
<tr>
<th></th>
<th>LSU</th>
<th>ASTM</th>
<th>LSU</th>
<th>ASTM</th>
<th>LSU</th>
<th>ASTM</th>
<th>LSU</th>
<th>ASTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primol D blank for LSU method (ppm)</td>
<td>52</td>
<td>55</td>
<td>53</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primol D blank for ASTM method (ppm)</td>
<td>18</td>
<td>19</td>
<td>18</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wt. of ash added as Iron Naphthanate (ppm)</td>
<td>34</td>
<td>34</td>
<td>78</td>
<td>78</td>
<td>62</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wt. of ash added as Nickel Naphthanate (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>179</td>
<td>179</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Total wt. of ash to be recovered (ppm)</td>
<td>86</td>
<td>52</td>
<td>133</td>
<td>97</td>
<td>115</td>
<td>80</td>
<td>254</td>
<td>198</td>
</tr>
<tr>
<td>Amount recovered (ppm)</td>
<td>80</td>
<td>34</td>
<td>157</td>
<td>91</td>
<td>110</td>
<td>58</td>
<td>263</td>
<td>201</td>
</tr>
<tr>
<td>Error (ppm)</td>
<td>6</td>
<td>18</td>
<td>4</td>
<td>6</td>
<td>5</td>
<td>22</td>
<td>29</td>
<td>3</td>
</tr>
<tr>
<td>Percent error</td>
<td>7</td>
<td>34.6</td>
<td>3</td>
<td>6.2</td>
<td>4.5</td>
<td>27.5</td>
<td>12.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>
metals which did not appear to a great extent in the fly ash which had been examined spectrographically. Therefore, the A.$T$.M. method and the LSU method should both have been close to the correct value - and the A.$T$.M. method should have shown better results than in the case where calcium, silicon, or sodium were the metals under investigation. These checks, then, gave the A.$T$.M. method the best possible chance to be correct.

As can be seen from an inspection of the results the A.$T$.M. method was much farther from the correct value than was the LSU method. If it had been assumed that the LSU method was correct and a value of 55 ppm. had been used in computing the ash in the blank for each method the results of the A.$T$.M. method would have been much farther from the correct values.

Discussion of Results

Present methods of ashing crude oil do not take into consideration any loss of ash which might occur during the ignition, or free-burning, step which is common to all of them. This research has demonstrated that ash may be recovered from the gases formed during the ignition step which is identical in chemical composition with the ash remaining in the ignition crucible. It may be inferred that this recovered ash originally came from the oil sample and represents an error in method for the existing procedures. With the phthallic anhydride filter apparatus which was designed during the course of this investigation the lost ash can be recovered and the error of existing methods evaluated. Several samples of oil were checked and this error was found to be so large that in no instance could it be considered negligible. The apparatus was checked with synthetic samples and found to give accurate results.
BIBLIOGRAPHY

(1) A.S.T.M. Standards on Petroleum Products and Lubricants, 1943
(2) Feigl, B., Petroleum Zeitung, 34, No. 2; Motorenbetrieb u. Maschinen
Schmier, 11, No. 1, 5-8 (1938)
(3) McClendon, J. F., "The Determination of Traces of Iodine I", Journal
of the American Chemical Society, 52, 1093-99
(4) Roberts, C.H.; Stenzel, R.W.; and Sberz, W. F., "Determination of
Salts in Crude Oil, Part III; Analytical Methods", Petroleum Engineer,
10, No. 6, 42-46, (1938-39)
(5) Shreve, R. N. and Welborn, R. W., "Catalytic Oxidations of the Naph-
thalene Series", Industrial and Engineering Chemistry, 37, No. 3, (1945)
(6) Simpson, T. N., Chemist Analyst, 27, 44, (1938)
(7) Standard Oil Co. of New Jersey, Louisiana Division, Memorandum On De-
termination of Ash in Feed Stocks, Oct. 21, 1946
Journal of the Institute of Petroleum, 36, 273-93, (1940)
VARIED TYPES OF APARATUS FOR ASH DETERMINATION

(a)

(b)

(c)

FIG. 1
FIGURE 2
CLOSED SYSTEM USED FOR ASH DETERMINATION

PHTHALIC ANHYDRIDE
COTTON
SUCTION
MERCURY OR WATER SEAL
PLATINUM CRUCIBLE
HOT PLATE
TRIPOD
FILTERED AIR INLET
PRESSURE EQUALIZER
PAN OF WATER
Four liter beaker with three diagonal inlet tubes arranged symmetrically about the container approximately as shown and of the specified dimensions, and two more inlet tubes arranged one above and one below the diagonal ones as shown. The top of beaker to have a round opening, rimmed by a depression as indicated above.
A hypodermic needle, A, is cemented into a porcelain tube, B, and both are cemented into a ground-glass joint, C. This assembly fits into the joint C* which is attached to the oxygen nozzle, D, and the oxygen inlet tube, E. The combustion chamber, F, with fritted-glass end, G, fastens to the inlet tubes at ground-glass joint, D-D*. J is an extension for the oxygen inlet and H is a hypodermic syringe.
FIG. 5
FRITTED-GLASS COMBUSTION CHAMBER
PART II

STUDIES IN OSCILLOGRAPHIC POLAROGRAPHY
INTRODUCTION AND REVIEW OF PREVIOUS WORK

The cathode-ray oscillograph has been used as an indicating and recording device for data obtained through the principles of polarography. The horizontal deflection in the cathode-ray tube is proportional to the difference of potential applied to the polarographic cell and the vertical deflection is proportional to the current flowing through the cell. The resulting oscilloscope pattern gives a graphical representation of current as a function of applied voltage.

The magnitude of the current flowing through the cell at any moment is a function of the size of the mercury drop at that moment. This has led to the development of two techniques for recording the wave. The first, known as the single-sweep method and suggested and used by Randles (19), utilizes an instrument also described by Weismann (24) which employs a relay, in conjunction with suitable electronic circuits and actuated by the sudden variation in current at the fall of a drop, to apply a single, sawtooth sweep of potential to the cell. Due chiefly to the method of synchronizing the voltage sweep with the fall of the drop this method is not too accurate.

The second technique is one which records waves throughout the life of several drops. It is known as the multi-sweep method. The wave of maximum height corresponds to the maximum size of the mercury drop, and, since the mercury drop attains its maximum size at the moment of falling, this size is reproducible. Waves are recorded during the life of several drops in order to insure that maximum height will be obtained. This method has been developed and discussed by Delahay (6), who at first utilized a saw-tooth voltage wave, but who later changed to a saw-tooth wave with a quiescent period. He has reported better results with this latter type of wave.
Oscillographic techniques in polarography were also employed by Matheson and Nichols (17), pioneers in the field. Heyrovsky (10, 11, 12, 15, 14, 15), Bieber and Trumpler (1), and Sevoik (23) have utilized oscillographic polarography in the study of the reversibility of various reactions. Muller; Garman; Dros, and Petras (18) and later Boeke and van Súchtelen (2) have used oscillographic techniques for the determination of half-wave potentials. Ben (5) and Reboul and Ben (22) used the oscillograph in a study of the variations of polarographic current during the formation of a mercury drop at the electrode. These latter methods are not techniques which are suitable for application in quantitative analysis.

The waves obtained as the result of the oscillographic method do not have the same configuration as the conventional polarographic wave. The oscillographic waves exhibit a peak, or "maximum", due to transitory phenomena, after which the current falls off to a constant value. The magnitude of this maximum, which is designated as the "maximal peak current", is the significant measurement in oscillographic polarography. Randles (20) and Sevoik (23) have derived an expression for the wave height which, after numerical simplification by Delahay (8), may be written in the following manner:

\[ I = 2.344n^{3/2} m^{2/3} t^{2/3} v^{1/2} D^{1/6} \quad (1) \]

where:

- \( I \) = maximal peak current in microamperes
- \( n \) = number of electrons involved in the reaction at the electrode
- \( D \) = the diffusion coefficient of the substance reacting at the electrode in cm.\(^2\) sec.\(^{-1}\)
m = the rate of mercury flow in mg. per sec.

t = the drop time in seconds

v = the rate of potential change at the dropping mercury electrode

in volts per second

C = the concentration of the substance reacting at the electrode

in millimoles per liter

The numerical constant 2544 is given by Randles. Seveik reported
1852, but the value given by Randles was found to be correct by Delahay (8).

The term v is equal to the magnitude of the potential difference which is ap-
plied to the polarographic cell, in the form of a saw-tooth wave, divided
by the time interval in which this potential is impressed on the cell. This
is a term which is not found in the Ilkovic equation. The exponent of t is
also different from that found in the Ilkovic equation. Taking these differ-
ences into consideration it can be seen that the current obtained in oscil-
lographic polarography should be much larger than that obtained in convention-
al polarography.

The application of the Randles-Seveik equation to the case of re-
versible reactions by Delahay (8) has demonstrated its validity. On the other
hand, he has reported that irreversible reactions give deviations from the
behaviour predicted by the equation. In these reactions the maximal peak
current was much smaller than that indicated by the Randles-Seveik equation.
Furthermore, it was not proportional to \( v^2 \). According to Delahay, this dif-
ference in current from the predicted value could be explained as being due
to the rate of the electrode reaction. Delahay further reported that, for
irreversible reactions, the current was not independent of the head of mercury.
Since \( m \) is proportional to the head of mercury, \( h \), and \( t \) is inversely proportional to \( h \), I should be independent of the head of mercury (16). No explanation was offered.

The scope of this investigation was designed to include a study of these discrepancies - the extent and nature of their deviations from the behaviour predicted by the Randles-Sevcik equation and an explanation for these deviations. Since the influence of the anodic as well as the cathodic process would be a contributing factor to any deviations, it was necessary to divorce the one from the other in order to study the effect of each. This could be done by utilizing the single-sweep method. The single-sweep method is of further importance in analytical applications for, not only does it eliminate the influence of the anodic process and thus decrease the deviations from the Randles-Sevcik equation, but it also eliminates errors due to fluctuations in the drop time, the nature of which have been discussed by Delahay and Stiehl (9).

Consequently, single-sweep studies were conducted and the knowledge obtained not only explained the role which the anodic process played in the deviations from predicted behaviour, but also verified predictions which had been made concerning these deviations. An instrument was developed which would make possible the recording of a single sweep of potential at the same moment in the life of each drop. Its design included a means of detecting the fall of the mercury drop and circuits for the application of a potential wave of variable shape and frequency at a determinate time after the fall of the drop. It is an instrument which is suitable for analytical determinations and which incorporates all the advantages of the single-sweep method described above.
I. PHENOMENA OCCURRING DURING THE QUIESCENT PERIOD OF THE VOLTAGE WAVE IN THE MULTI-SWEEP METHOD

In oscillographic polarography a potential difference is applied to the polarographic cell in the form of a saw-tooth voltage wave with a quiescent period. As the potential increases linearly some ions or molecules present in the solution are reduced at the dropping-mercury cathode, causing a corresponding current wave in the cell circuit. At the end of the voltage sweep the potential drops to its initial value. During the quiescent period between voltage waves the ions or molecules which have been reduced are generally reoxidized. Because of this anodic process, the concentration of reducible substance at the surface of the mercury drop changes. For this reason it was suspected that some part of the discrepancies between the experimental results and the wave height calculated by the Randles-Sevcik equation are caused by the anodic process occurring during the quiescent period between voltage waves.

In order to study the influence of the anodic process the following three procedures were utilized: (1) The length of the quiescent period is varied. Thus, with all other conditions remaining constant, any variation in the maximal peak current due to the change in the length of the quiescent period will afford information concerning the dependence of the maximal peak current upon the quiescent-period phenomenon (i.e., anodic process).

(2) Ordinarily, in the multi-sweep method, many sweeps of potential occur during the life of one drop. Any effect upon the height of the current wave due to an incomplete return to initial conditions during the quiescent period
will, of course, be cumulative during the life of the drop, and initial conditions will not be restored until a new drop is formed. Consequently, an indication of the effect of the anodic process occurring during the quiescent period is obtained by recording the successive waves occurring during the life of a single drop.

(5) The effect of the anodic process is entirely eliminated by utilizing a single sweep of potential. If a single sweep of potential is impressed upon the polarographic cell the current will depend entirely upon the initial conditions in the system and the nature of the cathodic process. Comparison of the results obtained by this method and those obtained by the multi-sweep method will give further indications of the nature of the anodic-process phenomenon.

All measurements were made by the method previously reported by Delahay and Stiéh1 (9) and the work was carried out with all solutions at a temperature of 30.5°C.

Description of the Instrument

The instrument which was used in these studies has been described by Delahay (6, 7) and by Delahay and Stiéh1 (9), and is schematically shown in Fig. 15.

The saw-tooth voltage generated by the time basis of a cathode-ray oscillograph was modified in order to introduce a quiescent period. The circuit labeled B in the diagram accomplished this. The re-formed wave had the shape pictured in the diagram.

The voltage wave was applied to the polarographic cell, C, connected in series with a calibrated resistance. The potential difference developed
between the terminals of the calibrated resistance was applied, after amplification, to the vertical deflection plates of the cathode-ray tube.

The saw-tooth voltage wave is also applied, after amplification, to the horizontal deflection plates of the cathode-ray tube. The shape of the voltage wave was determined by replacing the polarographic cell by a voltage divider connected to the vertical deflection amplifier of the cathode-ray oscilloscope.

**Technique of the Measurements**

In the oscillographic method of recording polarographic data the permanent records which were obtained by photographing the trace on the face of the cathode-ray tube presented the data graphically in the form of a curve. In order to interpret these quantitatively it was necessary to convert the coordinate readings from units of length to microamperes or to volts, as the case may have been. This entailed a mathematical calculation. A list of the various measurements which were necessary and the nature of the calculations which were used to evaluate them follows:

1. **Calibration of the Vertical Deflection of the Oscilloscope**

   For each series of measurements it was necessary to determine the sensitivity of the vertical deflection amplifier in millivolts per millimeter deflection. This measurement was repeated periodically in order to insure that no error would be introduced through fluctuations in sensitivity. Five millivolts was obtained from a potentiometer which had been previously balanced against a standard cell and was applied to the vertical deflection amplifier. The circuits which accomplished this have been described elsewhere (9). The initial trace on the oscilloscope and the displacement of the trace
due to the application of the five millivolts were photographed on the same film and the distance between the two traces was measured.

(2) Current Wave Height in Microamperes

The current flowing in the circuit of the polarographic cell passed through a known and variable resistance $R$ and the potential difference developed across this resistance was applied to the vertical deflection amplifier and subsequently to the vertical deflection plates of the oscillograph. If the height of the wave was designated as $H$ and the height of the deflection due to the five millivolts, as measured above, was designated as $D$, then, according to Ohm's law:

$$I = E \times \frac{1}{R} \quad (2)$$

or, after substituting the appropriate values:

$$I = \frac{H \times 5 \times 10^{-3} \times \frac{1}{R}}{D} \quad (3)$$

where the units of $H$ and $D$ were the same. This value for the current in amperes was subsequently converted to microamperes.

(3) Frequency of the Voltage Wave

A sixty cycle signal was applied to the vertical deflection plates of the oscilloscope while the voltage wave was applied to the horizontal deflection plates. If $n$ was the number of cycles present in the resulting sine-wave pattern then the frequency of the voltage was given by $60/n$.

(4) Voltage Wave Height and Rate of Potential Change

The voltage wave which was impressed across the polarographic cell could be applied through a voltage divider to the vertical deflection plates of the oscilloscope. The resulting picture was photographed. If the height
of this wave was designated as \( h \) and the height of the deflection caused by
the five millivolts was designated as \( D \), then:

\[
E = \frac{h \times 5 \times 10^{-2}}{D} \times \frac{1}{\text{voltage divider ratio}} \quad (4)
\]

This gave the amplitude of the potential wave in volts.

The time for one complete voltage wave was equal to the reciprocal
of the frequency. One complete wave of total period, \( p \), had a quiescent
period, \( q \). The fraction \( \frac{p}{q} \) when multiplied by \( 1/f \), where \( f \) is the fre-
quency, gave the time, in seconds, during which the voltage was changing.

If the rate of potential change was designated as \( V \), then:

\[
V = \frac{E \times f \times p}{p - q} \quad (5)
\]

(5) Drop Time

The drop time was determined by measuring, with a stopclock, the
time necessary for the fall of ten mercury drops and dividing this value by
ten.

(6) The Rate of Flow of Mercury Through the Capillary

The mass of fifty mercury drops was determined on an analytical bal-
ance and divided by the time required for their passage through the capillary.

---

Variation of the Concentration of Reducible Substance

During the Quiescent Period of the Voltage Wave

Before the first sweep of potential occurs in the earliest stage
of a new mercury drop, the concentration, \( C_0 \), of reducible material at the
surface of the electrode is equal to the bulk concentration \( C_0 \). During the
sweep of potential the reducible material reacts at the electrode and \( C_s \) decreases progressively. Concentration \( C_s \) is thus smaller than \( C_0 \) at the beginning of the quiescent period following the first sweep of potential. Reducible material will, therefore, diffuse toward the electrode during the quiescent period. If equilibrium could be reached at the end of the quiescent period, \( C_s \) would then be equal to \( C_0 \). During the quiescent period the material which has been reduced during the preceding sweep of potential may be reoxidized (7) to the original reducible form. In the case of a reversible electrode reaction the anodic process is completed before the end of the quiescent period. Concentration \( C_s \) is then practically equal to \( C_0 \) before the second sweep of potential occurs. This process repeats itself during the life of the mercury drop, \( C_s \) being equal to \( C_0 \) before each sweep of potential. As a result, the maximal peak current practically obeys the Randles-Sevcik equation.

If a metal soluble in mercury is formed by reduction of a cation, this metal diffuses toward the center of the drop during the sweep of potential. During the following quiescent period the metal is reoxidized and the metal which has diffused inside the drop now diffuses toward the surface. This diffusion process may limit the rate of the reoxidation reaction occurring during the quiescent period even in the case of a reversible electrode reaction. However, this effect is generally negligible when the rate of potential change is smaller than fifty volts per second, the quiescent period being of the same order of magnitude as the period of the voltage wave.

In the case of an irreversible electrode reaction the rate of the anodic process greatly depends upon the value of the potential of the dropping-
mercury electrode during the quiescent period. If the anodic process requires a large overvoltage, the rate of reoxidation may be very small. If the over-voltage is small, reoxidation may proceed to a large extent. Very often the anodic process will not be completed before the next sweep of potential occurs. As a result, the concentration \( C_0 \) before each sweep of potential decreases as the drop grows. The maximal peak current is actually measured for a concentration of reducible substance smaller than the bulk concentration \( C_0 \). The Randles-Sevcik equation therefore cannot be applied to an irreversible electrode reaction when the multi-sweep method of measurement is used.

**Variation of the Peak Current During the Drop Life**

The influence of the decrease in concentration \( C_0 \) was studied quantitatively by measuring the height of each wave occurring during the life of one drop. This method has already been applied by Delahay (6). The logarithm of the current corresponding to each peak was plotted against the logarithm of the time at which the peak occurred. A straight line having a slope 0.66 should have been obtained if the Randles-Sevcik equation was applicable (see formula 1). The method was applied to the reduction of \( Co \) ion in order to study the various factors affecting the decrease in concentration \( C_0 \). The data has been presented graphically in figures 7 and 8. Before applying this method it was necessary to ascertain that the rate \( m \) of the flow of mercury did not vary during the drop life. This was verified indirectly by measuring \( m \) when the cell was disconnected and when an oscillographic wave was being recorded. The values of \( m \), which have been recorded in Table IV, were practically the same in both cases.
(1) Influence of the shape of the voltage wave.

In figure 7 were plotted the values of log I versus log t for a $10^{-5}$ molar cobalt nitrate solution for three shapes of the voltage wave characterized by a relatively short, a medium, and a long quiescent period. The slope of the plot log I vs. log t decreased as the drop grew. In the early stage of the drop the slope was practically 0.66 and was independent of the shape of the voltage wave. The slope for the final stage of the mercury drop was smaller than 0.66 because of the decrease in the surface concentration $C_0$. This slope decreased when the ratio of the quiescent period $q$ to the period $p$ of the voltage wave decreased as shown by the following results:

For $q/p$ equal to 0.14, 0.53, and 0.82 the slope for the final stage of the drop was 0.51, 0.57, and 0.60 respectively.

(2) Influence of the rate of potential change

When the rate of potential change was increased, the quiescent period became shorter. Thus, less time was available to the anodic and diffusion processes occurring during the quiescent period. Voltage waves of two frequencies were employed in this study - four sweeps per second and ten sweeps per second. The ratio $q/p$ was 0.52 in each case, and the resulting rates of potential change were 9.0 volts per second and 23.5 volts per second, respectively. As a result, the decrease in the concentration $C_0$ measured before each sweep of potential was more pronounced when the rate of potential change was increased and the slope of the plot log I vs. log t for the final stage of the drop became smaller. In the case of the cobaltous ion presented in Fig. 8 this slope was 0.62 when the rate of potential change was 9 volts.
per second, and it was only 0.58 when the rate of potential change was 23.5 volts per second. Experiments could not be carried out at higher rates of potential change because the numerous waves thus obtained could no longer be resolved.

(3) Influence of the concentration of reducible substance

Experiments were carried out with solutions of cobaltous nitrate of concentrations which varied from $2 \times 10^{-4}$ to $10^{-5}$ molar. No appreciable variation of the slope of the plot log I vs. log t for the final stage of the drop was detected when the conditions were as follows: freq. = 6 sweeps per sec., rate of potential change = 15.8 volts per second, $q/p = 0.52$. The slope which was equal to $0.50 - 0.01$, was not affected by a change in the concentration of reducible substance.

**Variation of the Maximal Peak Current With the Head of Mercury**

According to the Randles-Sevcik equation the height of an oscillographic wave is proportional to the factor $(mt)^{2/3}$ ($20, 23$), $m$ being the rate of flow of mercury and $t$ the time of the drop life at which the wave height is measured. When the multi-sweep method is employed, $t$ is practically equal to the drop time ($6$). Since the product $mt$ is practically independent of the head of mercury ($15$), the maximal peak current should also be independent of the head of mercury. This was actually observed in the case of reversible electrode reactions ($6, 8$). For irreversible electrode reactions, on the other hand, it has been observed that the maximal peak current increases with the head of mercury ($8$). This abnormal behavior can now be explained in the following manner.
In the previous section it was shown that the concentration $C_0$ of reducible material at the surface of the electrode decreases from one sweep to another. When the head of mercury is increased, the drop time, and consequently the number of sweeps of potential per drop, decreases. As a result the decrease in $C_0$ is smaller when the head of mercury is increased and, therefore, the maximal peak current increases.

**Variation of the Maximal Peak Current With the Shape of the Voltage Wave**

Oscillographic waves were recorded for various shapes of the voltage wave at different frequencies. The results for the reduction of thallous and cobaltous ions have been presented in figures 9 and 10. The shape of the voltage wave has been characterized by the ratio, $q/p$ of the quiescent period, $q$, to the period, $p$, of the voltage wave. In the case of the thallium ion the electrode reaction was reversible and there was practically no influence of the shape of voltage wave on the maximal peak current. (Figure 9). In the case of the irreversible reduction of cobaltous ion, on the other hand, the maximal peak current depended greatly on the shape of the voltage wave (figure 10). This phenomenon was interpreted in the following manner.

In the case of a reversible electrode reaction there was practically no variation of concentration $C_0$ from one sweep to another, even when the quiescent period was relatively short. Therefore, the maximal peak current for a given rate of potential change did not depend upon the shape of the voltage wave.

In the case of an irreversible electrode reaction the concentration $C_0$ varied from one sweep to another. When the quiescent period became longer for a given rate of potential change more time was available to the anodic
and diffusion processes. The decrease in concentration $C_0$ for the drop life was less pronounced and the maximal peak current increased accordingly.

**Variation of the Maximal Peak Current With the Rate of Potential Change**

It has been previously reported that, for irreversible electrode reactions, if the current $I$ is plotted as a function of the term $\sqrt{v}$ the line is not straight at the higher rates of potential change ($\theta$). This can be seen from a comparison of the data which has been presented in figures 9 and 10. For thallium, which gives a reversible electrode reaction, the plot of $I$ vs. $\sqrt{v}$ is a straight line which would pass through the origin. For cobalt, on the other hand, each curve in the series plotted in figure 10 should pass through the origin. If the curves had been continued to the origin they would have shown a tremendous decrease in slope at the higher rates of potential.

This may be explained as follows. In the case of an irreversible electrode reaction the decrease in concentration, $C_0$, from one sweep to another is more pronounced when the rate of potential change increases. This decrease in concentration $C_0$ together with the effect of the rate of the electrode reaction accounts for the curvature in the plot of $I$ vs. $\sqrt{v}$.

For a reversible electrode reaction, on the other hand, the concentration $C_0$ remains practically constant from one sweep to another and the maximal peak current is proportional to $\sqrt{v}$ as predicted by the Randles-Sevcik equation. Actually, when the rate of potential change is of the order of one hundred volts per second a slight decrease in $C_0$ may occur and the diagram $I = f(\sqrt{v})$ exhibits a curvature at these high values of $v$ ($\theta$). In order to separate the influence of the rate of the cathodic process from the influence of variations in concentration, $C_0$, it is necessary to record only a single
wave at a given stage of the drop life.

Experimental methods for the recording of oscillographic waves by the single-sweep method have been described by Randles (19) and by Weidemann (24). Such instruments as these authors describe were not available at the time of this investigation, and a simpler method, whose description follows, was devised.

The saw-tooth wave generator of the instrument previously described (6, 7, 9) was replaced by a manually operated single-sweep circuit. This substitution is readily made in most commercial cathode-ray oscillographs. However, the manual method could not accurately produce a sweep at a predetermined time. For this reason the moment in the life of the mercury drop at which the sweep occurred was determined by adding a "pilot-ion" to the solution which was being investigated. This pilot-ion should be reduced reversibly at the dropping-mercury electrode and its wave should, at least approximately, obey the Randles-Sevcik equation. It could then be assumed that the height of the pilot-ion wave was the same, under identical conditions, whether it was determined by the single-sweep method or by the multi-sweep-method. Thallous ions almost fulfills this condition and was used in the following investigations at a \( 10^{-3} \) molar concentration. Waves were recorded by the single-sweep method for the mixture of the thallous ion and the substance being investigated. Since the time of the life of the mercury drop at which the sweep of potential occurred was not known, wave heights of the investigated substance were corrected by the following formula:

\[
I = \frac{(I_{T1})^2}{(I_{T2})^3} \times I \quad (6)
\]
in which \( I_s \) is the height of the investigated substance corresponding to the maximum size of the drop,

\( I \) is the height of the same wave at the time of the single-sweep recording, and

\((I_{T1})_m \) and \((I_{T1})_s \) are the heights of the thallous-ion wave by the multi-sweep and by the single-sweep method respectively.

All wave heights appearing in the equation are measured at the same rate of potential change.

It should be pointed out that this equation did not take into account the variation of the size of the mercury drop between the time of the Tl ion wave and the wave of the investigated substance. This effect was, however, negligible — especially when the rate of potential change was of the order of 10 volts per second or more, as was the case.

The rate of potential change in the single-sweep method was measured by recording the voltage wave applied to the cell and by calibrating the horizontal time axis with a 60 c.p.s. sine wave. All results were obtained at a temperature of 30.5°C.

The wave height for Tl ion determined by the multi-sweep method was plotted against the square root of the rate of potential change in Fig. 11 for the three supporting electrolytes used in this investigation. Fig. 19 is an example of single-sweep recording. Wave heights of \( H^- \), \( C_2O_4^- \), and \( 1O_3^- \) ions determined by the single-sweep and multi-sweep methods were plotted against the square root of the rate of potential change in Figures 12, 13, and 14. Theoretical wave heights calculated from the Randles-Sevcik equation were also
plotted on each graph. Diffusion coefficients at infinite dilution corrected for the temperature of 30.5°C, were used in the calculation (16). It was assumed that the temperature coefficient was 2% per degree for the investigated ions. The diffusion coefficient of Co was taken equal to the coefficient for Ni ion because of the lack of data.

Figure 11 shows that the experimental wave heights were smaller than the wave heights calculated by the Randles-Sevcik equation. The discrepancy, however, was smaller than Fig. 11 indicates because the actual diffusion coefficient of the Tl ion was smaller than the coefficient, at infinite dilution, used in the calculation of Curve II. Fig. 11 also shows that the discrepancy between experimental and calculated wave heights increased with the rate of potential. As it has been previously pointed out, the difference was due to the following effects: incompleteness of the anodic process, influence of the resistance of the circuit (9) and possibly slight irreversibility of the cathodic process (8).

In the case of the H wave shown in Fig. 12, wave heights by the single-sweep and multi-sweep methods were comparable although heights obtained by the former method were larger than those obtained by the latter. The discrepancy between experimental and calculated values was thus, mainly, caused by the irreversibility of the cathodic process (Curves II and III). For Co ion the difference between wave heights by the single-sweep method and by the multi-sweep method was large. The anodic process occurring during the quiescent period was thus far from being completed before a new sweep of potential occurred in the multi-sweep method. The case of the iodate wave recorded with
an alkaline supporting electrolyte was even more striking (Curves I and II). The anodic process (i.e., the oxidation of iodide to iodate) practically did not occur during the quiescent period of the voltage wave.

From the experimental data of Figures 12, 13, and 14 it may be concluded that the incompleteness of the anodic process occurring during the quiescent period of the voltage wave caused a large decrease in the height of irreversible cathodic waves measured by the multi-sweep method. The difference was due to the irreversibility of the anodic process and to the diffusion of the reduced material during the anodic process either in the mercury drop or in the solution. The influence of the latter phenomenon is, however, much smaller than that of the former, as shown by the fact that reversible waves almost obey the Randles-Sevink equation. Because of this diffusion phenomenon a slight difference in wave height was to be expected even for a reversible electrode process when both single-sweep and multi-sweep methods are applied. Therefore, the assumption which was made that the height of the Tl wave determined by either method is the same, is only correct as a first approximation.
II. A SINGLE-SWEEP OSCILLOGRAPHIC POLAROGRAPH

It has been reported by Delahay (6) and by Delahay and Stiehl (9) that the drop time fluctuates from one drop to another in the multi-sweep method. In the foregoing study of irreversible electrode reactions, in which a single voltage sweep was achieved with a manually driven circuit, it was found that the irreversibility of the anodic process contributed considerably to the decrease in the concentration of reducible substance at the surface of the dropping mercury electrode during the life of a drop. In order to eliminate these undesirable effects, circuits were designed which would produce a single voltage sweep of variable magnitude and rate of potential change at a determinate and reproducible time in the life of the mercury drop.

Description of the Instrument

The principles of the circuit can be seen from the block diagram, Figure 17, and from the circuit diagram, Figure 18. The platinum contacts, placed below the mercury capillary are short-circuited by the mercury drop as it falls. The ensuing voltage pulse is amplified by three amplifier stages and activates a relay in the plate circuit of the last amplifier. When this relay closes it charges a condenser, whose discharge takes place when the relay reopens. The discharge of this condenser introduces a time delay. The time of the delay can be varied. After a prescribed time the voltage drops to a sufficiently low value so that the following tube ceases to conduct. While this tube is conducting, two relays in its plate circuit are closed, applying a blanking pulse to the cathode-ray tube and actuating a time, which measures the time of delay. When the relay opens a saw-tooth voltage wave is
generated. This wave is amplified in the following tube and applied to the polarographic cell. The current in the cell circuit flows through a calibrated resistance and the potential difference developed across this resistance is amplified and applied to the vertical deflection amplifier of the cathode-ray oscillograph.

**Description of the Polarographic Cell**

The design and fabrication of the electrode arrangement which detected the fall of the mercury drop was the result of much experimental work. Several factors contributed to the necessity for critical adjustments to the electrodes themselves, and to the resistance in the grid circuit of the first amplifier tube. If the potential across the electrodes was too large the mercury drop was caught, thus causing a permanent short circuit. It also appeared that if the current flow between the electrodes and between the electrodes and the quiet mercury pool were too high the mercury drops were caught. The shape and relative positions of the two electrodes contributed to the phenomenon. Consequently, it was necessary to add sufficient amplifier stages so that small potentials could be used at the electrodes. It was further necessary to have separate power supplied for the amplifier circuit and the remainder of the circuits in order to minimize current flow between the platinum electrodes and the quiet mercury pool. The shape of the electrodes which best suited their function was arrived at by experiment. One electrode was made large and flattened to a spade shape at the end while the other electrode was a thin, needle-like wire whose end pointed toward the center of the flattened portion of the other electrode. The complete polarographic cell arrangement is pictured in Figure 16.
Technique of the Measurements

Sensitivity: The sensitivity of the amplifier was determined, as in the multi-sweep method, by applying five millivolts to the vertical deflection amplifier and measuring the resulting deflection of the cathode-ray tube trace. The five millivolt deflection is obtained by adjusting \( p_4 \) until the meter \( M_2 \) reads one volt and then making a simultaneous recording with \( S_3 \) first in position II, for zero potential, and then in position III, for five millivolts.

Rate of Potential Change: The rate of potential change which is adjusted by multi-position switch \( S_4 \), was calculated differently than in the multi-sweep method. Due to the longer lengths of time of voltage sweep which were available with this instrument, calibration of the time basis with a sixty cycle signal would have produced more cycles on the oscilloscope trace than could have been resolved. For this reason a square wave generator, connected to the Z modulation input of the cathode-ray oscillograph was used. Its frequency could be set at a low value and measured with the sixty cycle voltage. When the square wave was applied to the Z modulation input the horizontal sweep of the cathode-ray tube was broken into a series of dots. The time represented by the distance between each dot was equal to the reciprocal of the frequency of the square wave. This value multiplied by the number of dots present gave the total time. In order to find the rate of potential change, the voltage, as calculated by Equation 4, was divided by the time, in seconds, required for the voltage sweep. The various rates of potential change available in the instrument are shown in Figure 20, which also shows the excellent linearity of the voltage wave.
Initial Potential and Amplitude of Voltage Wave: The initial potential, which is adjusted for amplitude by \( p_2 \) and \( p_3 \) and for sign by switch \( S_6 \), was measured on the meter \( H_1 \), whose circuit is closed by switch \( S_7 \). The amplitude of the voltage wave is adjusted by means of the multi-position switch \( S_2 \) and is measured in the same manner as it was measured in the multi-sweep method. The wave is applied to the oscilloscope, through the voltage divider \( r_{67} - r_{58} \), when \( S_8 \) is in position IV.

Time of the Voltage Sweep: The time at which the sweep occurs after the fall of the mercury drop is adjusted by means of the multi-position switches \( S_2 \), a coarse adjustment, and \( S_3 \), a fine adjustment. This time was measured in the following way. When the drop fell, relays actuated a timer. This timer then operated until the start of the voltage sweep. Thus, the time of the beginning of the sweep was equal to the sum of the elapsed time, as shown by the timer, and the time lag between the fall of the mercury drop and the activation of the relay which controlled the timer. The time of the recording of any particular wave was equal to the sum of these two values and the time which elapsed between the start of the voltage sweep and the recording of the wave.

The time lag in the relay circuit is measured by plotting \( I \) against \( t \) for some reversibly-reduced ion. When \( I \) is zero, \( t \) should be zero, but, due to the lag in the relay, \( t \), as represented on the graph, will actually have a negative value. The absolute magnitude of this negative value gives the magnitude of the time lag in the relay circuit. The time which elapsed between the start of the voltage sweep and the recording of a wave was determined by photographing, on the same film, the current wave and the \( z \)-modulated horizontal sweep.
The number of dots between the start of the wave and the peak of the recorded wave gave the elapsed time. The appearance of the Z-modulated horizontal sweep, the voltage wave, and the recorded current wave, as obtained with the instrument, are shown in Figure 19.
SUMMARY

In earlier pages the advantages of the single-sweep method have been discussed. It has been stated that earlier single-sweep instruments have not been suitable for accurate analytical work. The instrument designed during this investigation, on the other hand, has none of the features which made the earlier instruments unreliable. However, further experimental work will be necessary in order to ascertain whether or not the present instrument is free from other sources of error. It should be verified that the current is actually a function of $t^{2/3}$ and $m^{2/3}$ and the accuracy of the instrument should be checked by determining $I$ as a function of concentration for several ions.

NOTE:

The material in this thesis has been made the subject of four papers. Two have been submitted for publication - one of which has been accepted - and two are to be submitted in the near future.
BIBLIOGRAPHY

(3) Bon, F.: Compt. Rend., 222, 286, (1946)
(7) Delahay, P.: Ibid., 54, 402, (1950)
(8) Delahay, P.: Ibid., 54, 630 (1950)
(9) Delahay, P. and Stiehl, G. L.: Ibid., (in course of publication)
(10) Heyrovsky, J.: Chem. Lstvy, 35, 155 (1941)
(19) Randles, J. E. B.: Analyt., 72, 301, (1947)


(22) Reboul, G. and Ben, F.: *Compt. Rend.*, 224, 1265, (1947)


### TABLE IV

Rate of flow of mercury during wave recording vs. rate for a disconnected cell.

10^{-3} molar Co^2+ ion in 1 molar potassium chloride

<table>
<thead>
<tr>
<th>Head of mercury (mm)</th>
<th>Rate of flow of mercury (mg per sec.)</th>
<th>Rate of flow of mercury (mg per sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>555</td>
<td>0.401</td>
<td>0.402</td>
</tr>
<tr>
<td>465</td>
<td>0.594</td>
<td>0.590</td>
</tr>
<tr>
<td>619</td>
<td>0.797</td>
<td>0.791</td>
</tr>
<tr>
<td>757</td>
<td>0.985</td>
<td>0.979</td>
</tr>
</tbody>
</table>
**Figure 7:** Variation of peak current during drop life for various shapes of voltage wave.

$10^{-3}$ molar cobaltous ion in 1 molar KCl.

$m = 1.79$ mg. per sec.; $a = 6$ sweeps per sec.; $v = 7.10$ volts per sec. (curve I); $v = 15.8$ volts per sec. (curve II); $v = 45.8$ volts per sec. (curve III).

$q/p = 0.14$ (curve I), $q/p = 0.53$ (curve II), $q/p = 0.83$ (curve III)

**Figure 8:** Variation of peak current during drop life for two frequencies.

$10^{-3}$ molar cobaltous ion in 1 molar KCl.

$m = 1.79$ mg. per sec.; $q/p = 0.52$

Curve I: $a = 4$ sweeps per sec.; $v = 9.0$ volts per sec.

Curve II: $a = 10$ sweeps per sec.; $v = 25.5$ volts per sec.

**Figure 9:** Variation of maximal peak current with the rate of potential change.

$10^{-3}$ molar thallous ion in 0.5 molar KNO$_3$

$m = 1.79$ mg. per sec.; $t = 5.00$ sec.

**Figure 10:** Variation of maximal peak current with the rate of potential change.

$10^{-3}$ molar cobaltous ion in 1 molar KCl.

$m = 1.79$ mg. per sec.; $t = 5.00$ sec.

**Figure 11:** Variations of the maximal peak current with the square root of the rate of potential change for $10^{-3}$ molar thallous nitrate solution in various supporting electrolytes.
Curve I: experimental curve; Curve II: calculated curve

**Figure 12:** Variation of the wave height with the square root of the rate of potential change. Single-sweep method vs. multi-sweep method. 

10^-3 normal H_2SO_4 in 0.5 molar lithium sulfate

m = 0.98 mg. per sec.; t = 3.56 sec., q/p = 0.57 - 0.07

(q = quiescent period of the voltage wave, p = total period of the voltage wave)

Curve I: multi-sweep method; Curve II: single-sweep method; Curve III: calculated by means of the Randles-Sevcik equation.

**Figure 13:** Same type of curve as Figure 12 for 10^-3 molar cobalt nitrate in 1 molar sodium sulfate.

m = 0.98 mg. per sec.; t = 4.30 sec., q/p = 0.54 - 0.04

**Figure 14:** Same type of curve as Figure 12 for the case of 10^-3 molar potassium iodate in 0.5 molar NaOH.

m = 0.98 mg. per sec.; t = 5.70 sec.; q/p = 0.80 - 0.10

**Figure 15:** Block diagram for a multi-sweep oscillographic polarograph.

**Figure 16:** Polarographic cell construction in single-sweep oscillographic polarograph. Shaded areas represent mercury. Exterior shaded rectangle represents a clamp.

**Figure 17:** Block diagram of a single-sweep oscillographic polarograph.

**Figure 18:** Circuit diagram of a single-sweep oscillographic polarograph.

**Figure 19:** Upper: Recording made with the single-sweep oscillographic polarograph. 10^-3 cobaltous ion.

Lower: Z-modulated voltage wave.
Figure 20: Variation of voltage with time for different settings of the rate of potential change control on the single-sweep oscillographic polarograph.
FIG. 7
VARIATION OF PEAK CURRENT DURING DROP LIFE FOR VARIOUS SHAPES OF VOLTAGE WAVE
FIG. 8

VARIATION OF PEAK CURRENT DURING DROP LIFE FOR T.C.
FREQUENCIES
FIG. 9

VARIATION OF THE MAXIMAL PEAK CURRENT WITH THE RATE OF POTENTIAL CHANGE FOR THALLIOUS ION

+ curve I: $\alpha/\beta = 0.08 \pm 0.02$

$\times$ curve II: $\alpha/\beta = 0.25 \pm 0.05$

$\bullet$ curve III: $\alpha/\beta = 0.50 \pm 0.05$

$\Delta$ curve IV: $\alpha/\beta = 0.68 \pm 0.07$

$I \times 10^{-6}$ (amp.)

$\sqrt{2}$ (volts/sec.)
FIG. 10

VARIATION OF THE AXIAL PEAK CURRENT WITH THE RATE OF POTENTIAL CHANGE OR COSALICIOUS ACH
VARIATION OF THE MAXIMAL PEAK CURRENT WITH THE RATE OF POTENTIAL CHANGE FOR THALLOUS ION IN SEVERAL SUPPORTING ELECTROLYTES
FIG. 16

VARIATION OF THE AXIAL PEAK CURRENT WITH THE RATE OF POTENTIAL CHANGE FOR HYDROGEN ION -- SINGLE-SHIFT CONTRASTED 1TH--MLII-SLEEP
FIG. 14

VARIATION OF THE MAXIMAL PEAK CURRENT WITH THE RATE OF
POTENTIAL CHANGE FOR IODATE ION -- SINGLE-STEP CON-
TRASTED WITH ULTRASTEP
BLOCK DIAGRAM
OSCILLOGRAPHIC POLAROGRAPH

FIG. 10
POLAROGRAPHIC CELL FOR SINGLE-SLEEP OSCILLOGRAPHIC POLAROGRAPH
KEY TO SYMBOLS IN FIGURE 13

\[ \begin{align*}
\text{r}_1 & : 33,000 \text{ ohms, 1 watt} \\
\text{r}_2 & : 4.7 \text{ megohms, 2 watts} \\
\text{r}_3 & : 1,000 \text{ ohms, 2 watts} \\
\text{r}_4 & : 82,000 \text{ ohms, 5 watts} \\
\text{r}_5 & : 1.0 \text{ megohm, 1 watt} \\
\text{r}_6 & : 1,000 \text{ ohms, 2 watts} \\
\text{r}_7 & : 82,000 \text{ ohms, 1 watt} \\
\text{r}_8 & : 330,000 \text{ ohms, 5 watts} \\
\text{r}_9 & : 500,000 \text{ ohms, 2 watts} \\
\text{r}_{10} & : 2,200 \text{ ohms, 1 watt} \\
\text{r}_{11} & : 5,000 \text{ ohms, 25 watts adjustable} \\
\text{r}_{12} & : 4.7 \text{ megohms, 1 watt} \\
\text{r}_{13} & : 10,000 \text{ ohms, 5 watts} \\
\text{r}_{14} \text{ to } \text{r}_{22} & : 220,000 \text{ ohms, 1 watt} \\
\text{r}_{23} \text{ to } \text{r}_{32} & : 22,000 \text{ ohms, 1 watt} \\
\text{r}_{33} & : 1.5 \text{ megohm, 1 watt} \\
\text{r}_{34} & : 1.2 \text{ megohms, 1 watt} \\
\text{r}_{35} & : 820,000 \text{ ohms, 1 watt} \\
\text{r}_{36} & : 680,000 \text{ ohms, 1 watt} \\
\text{r}_{37} & : 390,000 \text{ ohms, 1 watt} \\
\text{r}_{38} & : 270,000 \text{ ohms, 1 watt} \\
\text{r}_{39} & : 220,000 \text{ ohms, 1 watt}
\end{align*} \]
120,000 ohms, 1 watt
100,000 ohms, 1 watt
39,000 ohms, 1 watt
27,000 ohms, 1 watt
12,000 ohms, 1 watt
22,000 ohms, 2 watts
1.0 megohm, 2 watts
4.7 megohms, 2 watts
15 ohms, 1 watt
10,000 ohms, 25 watts
7,000 ohms, 10 watts
5,000 ohms adjustable, 10 watts
0-9,999 ohms decade resistance accuracy 0.1%
0 to 90 ohms in 10 ohm step, accuracy 0.1%
10,000 ohms, accuracy 0.1%
10 ohms, accuracy 0.1%
2000 ohms, accuracy 0.1%
45,000 ohms, 5 watts
1.0 megohm, 1 watt
10,000 ohms
10 ohms, wired
100 ohms, wired
1,500, wired
200 ohms, wired
$P_6$ 10,000 ohms

$C_1 = C_5$ 25 microfarads, electrolytic, 25 volts

$C_2 = C_5$ 0.5 microfarads, paper, 600 volts

$C_4$ 4 microfarads, electrolytic, 450 volts

$C_6$ 1 microfarad, paper, 600 volts

$C_8$ 2 microfarads, oil, 1000 volts

$C_9$ 0.01 microfarad, paper, 600 volts

$C_{10}$ 100 microfarads, electrolytic, 25 volts

$T_1, T_2$ 6 S J 7

$T_4$ V R 150

$T_6$ 6 V 6

$R_1$ S.P.D.T. relay

$R_2$ D.F.D.T. relay

$R_3$ S.P.S.T. relay

$M_1$ 0-200 microammeter

$M_2$ 0-1 voltmeter (at least 5,000 ohms volts)

$B_1$ 22.5 volt battery, "B" supply

$B_2$ 15 volt battery, "C" supply

$B_3$ 4.5 volt battery, "C" supply

$B_4$ 6 volt battery, "A" supply

$B_5$ 1.5 volt battery, "B" supply

$B_6$ 3 volt battery, "B" supply

$B_7$ 90 volt battery, "P" supply

$B_8$ 45 volt battery, "B" supply
R_2 \quad 67.5 \text{ volt battery, "B" supply}

t_1, t_2 \quad \text{to platinum electrodes of polarographic cell}

t_3 \quad \text{to "Z modulation" terminal of C.R. oscillograph}

t_4 \quad \text{to output of square wave generator}

t_5, t_6 \quad \text{connected in series with electric timer}

t_7 \quad \text{to input of X amplifier of C.R. oscillograph}

t_8, t_9 \quad \text{to polarographic cell}

t_{10} \quad \text{to input of Y amplifier of C.R. oscillograph}
CIRCUIT DIAGRAM OF A SINGLE-SWEEP OSCILLOGRAPHIC POLAROGRAPH

FIG. 18
FIG. 19

Example of single-sweep recording, Z-modulated horizontal sweep, and Z-modulated voltage wave.
VARIOUS RATES OF POTENTIAL CHANGE AVAILABLE WITH THE SINGLE-SLEEP INSTRUMENT
Gerald Perkins, Jr., was born August 12, 1921, in the city of New Orleans. In 1931 he moved to Hammond, Louisiana and his high school education was obtained at Eastman High School in that city. In 1937 he entered Southeastern Louisiana College in Hammond and finished, with the Bachelor of Science degree, in 1942. In July, 1942 he entered graduate school at Louisiana State University. He volunteered for the naval service in 1944 and was commissioned an Ensign. His Master of Science degree was granted in June, 1944 by Louisiana State University.

While serving in the United States Navy he studied at Princeton University and the Massachusetts Institute of Technology. Upon completion of this work he was assigned overseas duty as an electronics officer. Upon his return to inactive duty he re-enrolled in Louisiana State University to work toward the PhD. He is now a candidate for this degree.
Candidate: Gerald Perkins, Jr.

Major Field: Chemistry

Title of Thesis: Studies in Analytical Chemistry
   I. New Methods for the Determination of Ash in Petroleum Crudes
   II. Studies in Oscillographic Polarography

Approved:

[Signatures and signatures of the examining committee members]

Date of Examination: July 25, 1950