

AMPEROMETRIC TITRATIONS OF SELECTED PETROLEUM
ADDITIVES AND SULFONIC ACIDS IN
NONAQUEOUS SOLUTIONS

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PREFACE

Special chemicals are commonly added to petroleum fuels and lubricants in order to protect storage vessels, transportation equipment and internal combustion engines from the corrosion and sludge formation caused by certain substances present in the fuels and lubricants. Each additive has properties which make it effective for protection in one or more types of fuels and lubricants.

This research was supported primarily by The Continental Oil Company through the Research Foundation of Oklahoma State University. It consisted of the polarographic study of several additives in hydrocarbon media, the hope being to develop quantitative analytical methods for some of them by employing the polarograph invented by Dr. Paul Arthur for use with high resistance nonaqueous solutions.

Since the additives are present in very small concentrations, special, often tedious, techniques normally are necessary for their quantitative estimation. Polarographic and amperometric analyses are rapid and are particularly adapted for use with solutions of low concentration. The high resistance polarograph has in addition the advantage of not having to extract the additives for analysis from the fuels and lubricants.

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CHAPTER I

INTRODUCTION

The Nature of Polarography

The common polarographic circuit for cells of low resistance is illustrated in Figure 1. The voltage from the battery is applied at a uniform rate across the cell by means of a motor driven bridge; another motor advances the chart paper of the recorder also at a uniform rate.

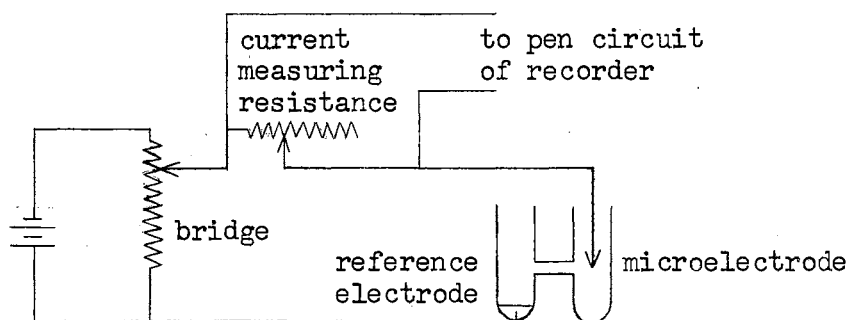


Figure 1. Circuit of Common Polarograph.

The pen circuit of the recorder measures the current as a function of the voltage drop across a standard resistor. There are several standard resistors of different sizes; these can be connected into the circuit one at a time, so that a wide range of currents can be measured. The finished polarogram is a curve showing the current for any value of the applied voltage.

The polarogram results from the fact that the microelectrode is easily polarized and, therefore, controls the flow of current through

the cell. The reference electrode is not polarized by currents of polarographic magnitude.

The commonest microelectrode is the dropping mercury electrode (D.M.E.). It consists of a reservoir containing mercury connected to a glass capillary of about 0.05 mm. internal diameter. The level in the reservoir is adjusted so that a drop falls every three to six seconds. The reference electrode is usually a saturated calomel electrode, but any stable and reproducible electrode may be used.

An explanation of the parts of the normal polarogram shown in Figure 2 aids in the understanding of polarography. As the e.m.f. supplied by the bridge to the cell is increased, the rate of current increase is small at first as shown by the line AB. This part of the curve is called the residual current. It is the sum of a condenser current and an electrochemical current. The electrochemical current results from the reduction (or oxidation) of impurities present in the solution, and the condenser current arises from the preferential adsorption of either the anions or cations of the supporting electrolyte on the surface of the D.M.E.

The electro-oxidizable or electroreducible ions or molecules can reach the surface of the microelectrode through two forces: an electrical force and a diffusion force. The electrical force is proportional to the potential difference between the microelectrode and the reference electrode; it causes the migration current. The diffusion force, which gives rise to the diffusion current, is proportional to the difference between the concentration of the reducible or oxidizable substance at the microelectrode and its concentration in the bulk of the solution.

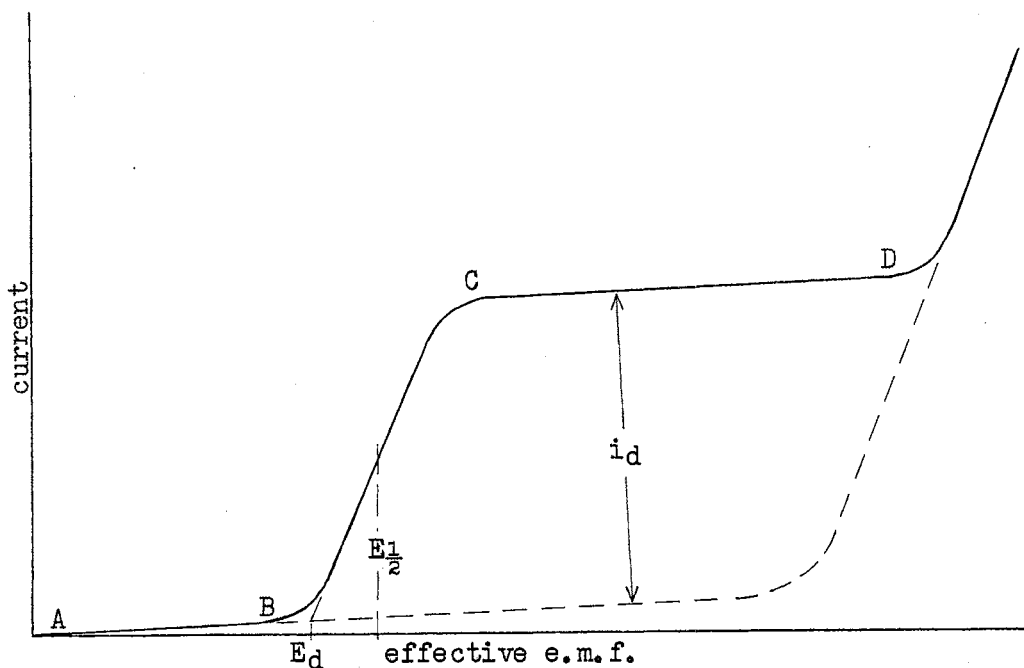


Figure 2. Normal Polarogram.

There is maintained in the polarographic solution an electrolyte at least fifty times as concentrated as the substance being analyzed. This supporting or carrier electrolyte reacts at the microelectrode only at potential differences greater than that required for the substance being analyzed and serves to minimize migration current in the wave for the substance under analysis.

As the applied potential is increased to the decomposition potential of the electro-oxidizable or electroreducible substance being analyzed, the rate of current increase (see line BC in Figure 2) becomes large compared with the slope of the residual current. At this stage, the rate of reaction at the electrode is slower than the rate of replacement of the reacted ions or molecules from the bulk of the solution. When the applied potential is great enough to cause the ions (or molecules) to react as fast as they arrive at the microelectrode from the bulk of

the solution, and when the concentration of reacting ions or molecules at the surface of the microelectrode is virtually zero, the limiting current represented by i_{CD} is reached. The current then is the sum of the residual current and the diffusion current, i_d . The limiting current is not affected greatly by a further increase in potential.

Since the magnitude of the diffusion current depends on the difference between the concentration of the ions or molecules in the bulk of the solution and the concentration at the microelectrode, and since the concentration at the microelectrode is virtually zero, the diffusion current is a measure of the concentration of the substance in the bulk of the solution.

The half-wave potential ($E_{\frac{1}{2}}$) is characteristic of the substance being oxidized or reduced. The half-wave potential is determined graphically by measuring the potential at which the midpoint of the wave, between the projected residual current line and the limiting current line, occurs.

The decomposition potential (E_d) is located at the intersection of the extrapolated residual current and wave-front lines.

High Resistance Polarography

The essential differences between the low resistance polarograph and the high resistance polarograph are shown in Figures 1 and 3. It will be noted that the former uses one reference electrode and one microelectrode. The e.m.f. applied across the electrolysis cell is assumed to be the effective e.m.f. between the electrodes. This is essentially true when the cell resistance is negligible, because the iR -drop is an insignificant fraction of the applied voltage. The

applied voltage is used in two ways:

$$E_{\text{applied}} = E_{\text{effective}} + iR.$$

Consequently, when high resistances are encountered, iR -drop cannot be ignored. In order to correct for the iR -drop, the high resistance polarograph employs two reference electrodes and one microelectrode. The polarizing potential is applied from a motor driven bridge across the microelectrode and one reference electrode, the electrolysis reference electrode (E.R.E.). The iR -drop occurs in this arm of the cell, but the voltage across this branch (the applied voltage) is not measured. The effective potential is measured across the microelectrode and the other

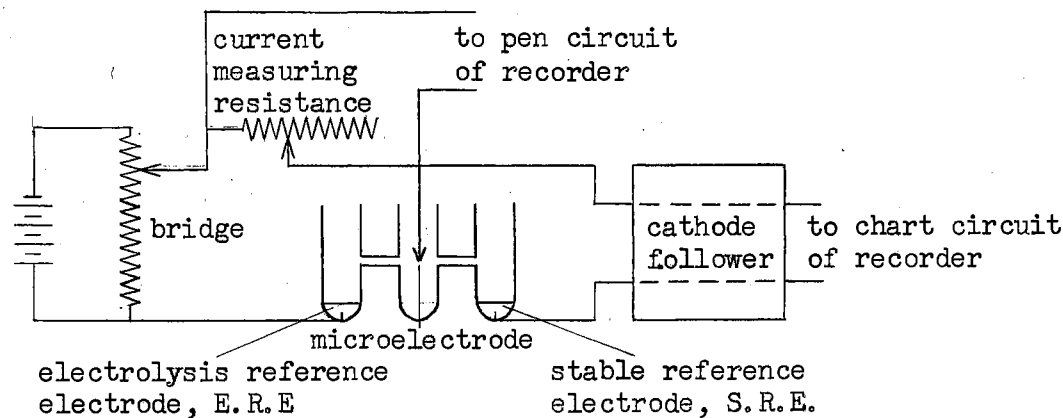


Figure 3. Circuit of High Resistance Polarograph.

reference electrode, the stable reference electrode (S.R.E.). A high input impedance cathode follower in the circuit permits this to be done without drawing appreciable current.

Other conditions being constant, the position of any point on a polarogram with respect to the zero effective voltage is determined by the nature of the reference electrode; in high resistance polarography any point on the polarogram is dependent upon the nature of the stable reference electrode only. In either case, if this reference electrode is

changed, the net effect is to shift the entire polarogram to the right or left.

The D.M.E. in contact with a solution but in open circuit with the two reference electrodes assumes a potential that is dependent upon the nature of the solution and is independent of either reference electrode. The cathode follower connected across the D.M.E. and S.R.E., which is essentially open circuit because of the high input impedance of the cathode follower, measures the difference of the potentials of the two electrodes. When the circuit between the D.M.E. and the E.R.E. is closed, the D.M.E. tends to assume the potential imposed upon it by the E.R.E. Since at least a minute amount of current must flow, however, the D.M.E. assumes a voltage equal only to the E.R.E. voltage minus the iR-drop in the cell. When the reference electrodes are both the same kind, the closed circuit voltage must always be closer than the open circuit voltage to the zero voltage axis. This is another way of stating that the measured potential difference is less when some of the applied potential difference is consumed as iR-drop.

One part of the starting procedure for making full polarograms with the high resistance polarograph, using the D.M.E. as cathode, is to mark the zero current position (that is, with open circuit between the D.M.E. and E.R.E.) before throwing the microelectrode switch to the "CATHODE" position and starting the motor driven bridge. The zero current mark is an important reference point for current measurements and for comparing polarograms.

Amperometric Titrations

The essential difference between analysis by ordinary polarography

and analysis by amperometric titrations is that in the former the concentration of the unknown is determined by measuring the diffusion current of the polarogram, and in the latter the current which passes through the titration cell at a suitable effective e.m.f. is measured as a function of the volume of a suitable titrating solution. The end point of the titration is the point of intersection of the two lines giving the change in the current before and after the equivalence point.

Figure 4 illustrates the following explanation of an amperometric titration.

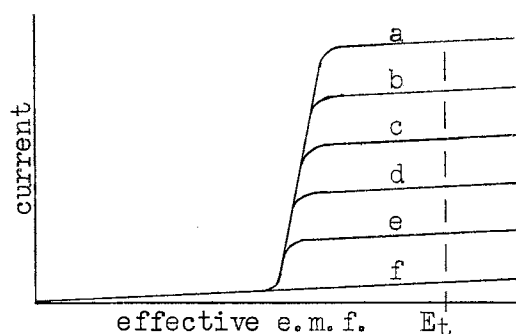


Figure 4. Illustration of Amperometric Titration.

If, for example, the ion being titrated is Pb^{++} and the titrant is $SO_4^{=}$, the full polarogram before the addition of any titrant is represented by curve a. After the addition of a certain volume of titrant, a full polarogram appears as curve b. After the addition of another quantity of titrant equal to the first addition, the complete polarogram appears as c. When the stoichiometric quantity of sulfate has been added, curve f is obtained and, since sulfate ions are not reducible polarographically, essentially this same curve will be obtained even with further additions of titrant. A graph of the currents at E_t vs. volume will be like that in Figure 5, curve c, the break in the curve

being the end point in the amperometric titration.

There are many possible combinations of unknown and titrant for amperometric titrations, and many different types of titration curves result. The three most commonly encountered types are as follows:

1. If both the titrant and the titrated substance give waves which are topped at the selected voltage and if the product of their reaction with each other is insoluble or does not give a wave, the current decreases before the end point and increases beyond the end point as in Figure 5, curve a.

2. If the titrant reacts at the microelectrode but the titrated substance does not, the current remains constant before the end point and increases past the end point as in Figure 5, curve b.

3. If the titrant does not react at the microelectrode but the titrated substance does, the current decreases before the end point and remains constant after the end point as in Figure 5, curve c.

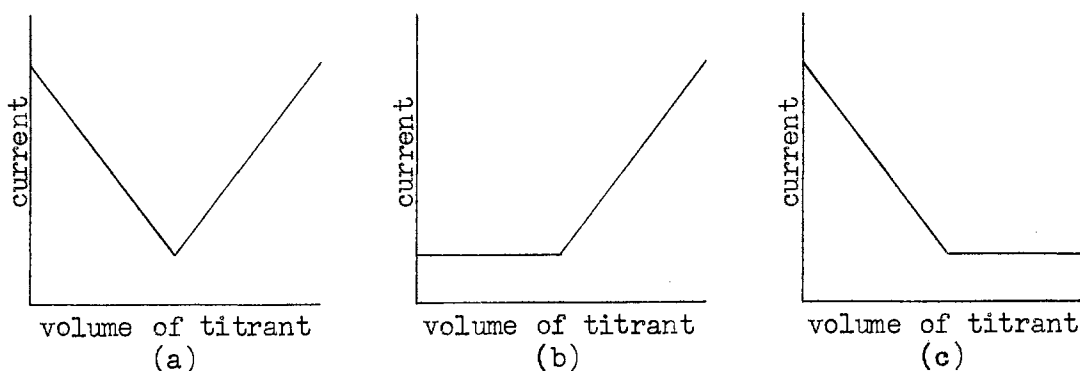


Figure 5. Three Common Amperometric Titration Curves.

If the concentration of the titrant is five to ten times the concentration of the titrated substance, the volume change of the solution during the titration can be neglected. When the volume change is appreciable during the titration, the end point is sometimes less easy

to locate owing to flattening of the angle of intersection and to curvature of the lines. In such cases results can be improved by multiplying the individual current readings by a correction factor.

$$i_{\text{correct}} = i_{\text{measured}} \left(\frac{V + v}{V} \right)$$

where V is the original volume of solution and v is the total volume of titrant added in order to obtain the measured current reading.

The advantages and disadvantages of amperometric titrations have been summarized by Kolthoff and Lingane (27). These are as follows:

1. In general very dilute solutions can be titrated with a high degree of accuracy. Naturally, amperometric titrations are subject to the ordinary sources of error of volumetric determinations (instrumental errors, coprecipitation, etc.).

2. Precipitation titrations can be performed even when the solubility is relatively great, but solubility equilibrium must be attained relatively quickly or the titration becomes much more difficult.

3. Foreign electrolytes which do not yield diffusion currents at the effective e.m.f. used for the titration do not interfere. Their presence is actually desirable in amperometric titrations to eliminate the migration current. Foreign substances which do not interfere in the titration reaction but which yield diffusion currents at the effective e.m.f. used for the titration must not be present in concentrations many times larger than that of the substance titrated. In their presence the relative changes in the current during the titration become smaller.

4. Substances which are not reduced or oxidized can be titrated if the titrant yields a diffusion current which is proportional to the concentration. This is the basic titration curve illustrated in Figure 5, curve b.

5. Many titrations can be carried out rapidly because only a few measurements of current before and after the end point need be recorded.

6. It is immaterial whether the reaction which takes place during the titration is reversible or irreversible.

7. In routine work it is possible to simplify the polarographic equipment required.

8. Amperometric titrations, in general, yield more accurate results than direct polarographic measurements, because the titration curve is the mean of several measurements.

9. The results of the titration are independent of the characteristics of the capillary.

10. Temperature does not have to be known as long as it is kept constant during the titration.

11. In polarographic determinations the values of the diffusion current are more or less dependent upon the kind and concentration of supporting electrolyte. In amperometric titrations one is interested only in the relative change in the current, and the supporting electrolytes have no effect upon the results as long as they do not interfere with the titration reaction.

CHAPTER II

HISTORY

The dropping mercury electrode was used by Kucera in 1903 to study the electrocapillary curve of mercury in various solutions (29). He noticed inflections in the electrocapillary curve when reducible substances were present. At the suggestion of Kucera, Heyrovsky investigated further, and from his work polarography was developed (14, 15). Although the use of the D.M.E. as an indicator electrode in titrations was a logical development of polarography (16), even earlier, in 1897, Salomon gave the first description of an amperometric titration and mentioned the principle upon which it and all other amperometric titrations are based (43, 44). A dilute potassium chloride solution containing two silver electrodes connected in a circuit with a galvanometer and an applied e.m.f. of 0.1 volt was titrated with silver nitrate. The current remained small until after the equivalence point when the electrodes became depolarized, causing a sudden, large deflection of the galvanometer. The current magnitude past the end point was proportional to the concentration of silver ions.

The words "polarograph" and "polarogram" were coined by Heyrovsky and Shikata in 1925 (18). "Amperometric titration" was coined by Kolthoff and Pan in 1939 (28).

Half-Wave Potential

The half-wave potential is of interest in amperometric titrations

only as an aid in determining a suitable voltage for a titration.

Theories of half-wave potential have been given by Heyrovsky and Ilkovic (17) and have been useful in determining the reversibility of electrode reactions.

Diffusion Current Theory

The derivation of the Ilkovic equation (21, 22) for the current of the D.M.E. is given below. This is taken from the straightforward presentation by Meites (35).

Assume that a small plane solid electrode is placed in a solution containing a reducible ion, and that these ions can reach the surface of the electrode from only one direction (linear diffusion). The observed diffusion current is given by the equation

$$i_T = nFAC \sqrt{\frac{D}{\pi T}} \quad (1)$$

where \underline{n} is the number of faradays consumed per mole of substance reduced at the electrode (i.e., the number of equivalents per mole), \underline{F} is the faraday (coulombs/gram equivalent), \underline{A} is the area of the electrode (cm.²), \underline{C} is the concentration of reducible ion (moles/1000 cm.³), \underline{D} is the diffusion coefficient of the reducible ion (cm.²/sec.) and $\underline{i_T}$ is the current at that instant (amperes).

The drops produced by a conventional D.M.E. are very nearly spherical, so that the volume of a drop \underline{T} seconds after it has begun to form is

$$V = \frac{4}{3} \pi r^3 = \frac{mT}{d}$$

where \underline{r} is the radius of the drop (cm.) at time \underline{T} , \underline{m} is the rate of flow of mercury into the drop (g./sec.), and \underline{d} is the density of mercury (g./cm.³). This equation is solved for \underline{r}^2 , and both sides of the

resultant equation are multiplied by 4 to obtain the area of the drop at time T:

$$A = 4\pi r^2 = 4\pi \left[\frac{3mT}{4\pi d} \right]^{2/3}.$$

This is substituted into equation (1), giving

$$i_T = (36)^{1/3} \pi^{-1/6} d^{-2/3} n F D^{1/2} C_m^{2/3} T^{1/6}. \quad (2)$$

Changing the units of i_T to microamperes, of C to millimoles per liter, of m to mg./sec., and introducing the numerical values of d at 25°C (13.6 g./cm³), π , and F (96,500 coulombs/gram equivalent) gives

$$i_T = 464 n D^{1/2} C_m^{2/3} T^{1/6}.$$

The average current is obtained by integrating over the life of the drop, in order to obtain the number of microcoulombs which flow during that time, and dividing the result by the drop time t (seconds), the length of time that elapses between the instants at which two successive drops fall. This gives

$$i_d = \frac{1}{t} \int_0^t i_T dT = 398 n D^{1/2} C_m^{2/3} t^{1/6}. \quad (3)$$

In this derivation it is assumed that the reducible ions reaching each small segment of the drop surface come from only one direction, i.e., that parallel to the axis of a cylinder. Actually they come from points within a cone whose apex is at the center of the drop, so that the diffusion is radial rather than linear. Since the volume bounded by the cone is greater than that bounded by the cylinder, the current predicted by equation (3) is too small. Much better agreement with experimental results is secured by multiplying the right-hand side of equation (3) by $(7/3)^{1/2}$, giving

$$i_d = 607 n D^{1/2} C_m^{2/3} t^{1/6}. \quad (4)$$

This average current, i_d , is the theoretical current which, if allowed to flow for a length of time equal to the drop time, would pass

the same number of microcoulombs as would the drop itself during its actual life.

The diffusion current constant, I_d , is obtained from the Ilkovic equation:

$$I_d = 607 nD^{1/2} = \frac{i_d}{C_m^{2/3} t^{1/6}}$$

I_d should be constant for any particular ion in a given combination of supporting electrolyte and solvent at constant temperature.

The Ilkovic equation is not wholly adequate, since it does not account for the observed variations of the diffusion current constant with the characteristics of the D.M.E. Strehlow and von Stackelberg (46) and Lingane and Loveridge (32) independently demonstrated that the fault of the Ilkovic equation was due to the neglect of the curvature of the electrode surface. The Ilkovic equation as modified by these men is

$$i_d = 607 nD^{1/2} C_m^{2/3} t^{1/6} \left[1 - \frac{AD^{1/2} t^{1/6}}{m^{1/3}} \right]$$

where A was evaluated as 17 by Strehlow and von Stackelberg and as 39 by Lingane and Loveridge. The correction term itself is not large, but it is not negligible in accurate work.

Amperometric Titrations

The amount of reported amperometric work in which organic solvents are used is comparatively small, and information about the use of anhydrous organic solvents is rare.

Compounds containing positive chlorine and bromine were titrated in water-chloroform-methanol mixtures with sulfur dioxide in pyridine by Freedman (8).

Kolthoff and Harris (25) developed a method for titrating mercaptans in ammoniacal ethanol-water solutions with silver nitrate. They later (26) used essentially the same method to determine primary and tertiary mercaptans in mixtures of the two. One aliquot was titrated with silver nitrate to determine the total mercaptan present, and another aliquot was titrated with iodine to determine the quantity of primary mercaptan. Grimes, Pucket, Newby and Heinrich (11) adapted this titration to the determination of mercaptan sulfur in hydrocarbons. Liquid hydrocarbon samples were dissolved in ammoniacal water-acetone solution and titrated with silver nitrate. Gaseous mercaptan samples were dissolved in a solution of excess silver nitrate in acetone, aqueous ammonia was added and the excess silver was titrated with standard mercaptan. Rosenberg, Perrone and Kirk (42) determined the sulfhydryl group in bovine serum albumin in water-ethanol solutions by titrating with aqueous silver nitrate.

Mann (34) detected acid-base end points in water-ethanol solutions by following the change in polarization current between platinum or aluminum electrodes in combination with quinhydrone. A study of the solubility of dimethylglyoxime in water-ethanol solutions was performed by Stromberg and Zelyanskaya (47) with the aid of amperometric titrations. Zhdanov, Tseitlin and Yakubov (50) titrated salts of copper, zinc and cobalt in water-ethanol solutions with anthranilic acid.

In water-acetone solutions, chloride and bromide were titrated by Laitinen, Jennings and Parks (30), and chloride was titrated by Deschamps (6). Silver nitrate was the titrating agent.

Lead nitrate was used by Gordon and Urner (10) to titrate sulfates in water-2-propanol solutions. Detty, Heston and Wender (7) titrated

3-hydroxyflavone in water-2-propanol solutions with cupric sulfate.

The formation of insoluble complexes by the combination of 2-mercaptothiazole with cupric and silver ions was used by Liberti and Cervone (31). They developed methods for titrating the cupric ion in water-acetic acid solution with 2-mercaptothiazole and for titrating 2-mercaptothiazole in ammoniacal water-ethanol solutions with the silver ion.

Some photographic developers were titrated in 50% water-50% sulfuric acid solutions with potassium dichromate by Zyka (51).

A method for direct titration of some unsaturated organic compounds with bromine solution was developed by Tomicek, Blazek and Roubal (48). The solvent was glacial acetic acid. The same solvent was used by Hinsvark and Stone (19) for a titration of oxalic acid with ammonium hexanitratocerate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

Most of the aforementioned work was performed without the use of the dropping mercury electrode. Either a polarization cell with two identical electrodes or a solid indicator electrode with a reference electrode was used.

Several methods have been devised for using high resistance solutions in polarography. A conventional polarograph with an electromechanical device for instantaneous resistance compensation was reported by Nicholson (36). This device applies by means of the pen drive circuit in the recorder a corrective voltage which is at all times equal and opposite to the iR -drop in the cell and the current measuring resistor. Jackson and Elving (24) described an iR -drop compensator in which the iR -drop of a small resistance in series with the electrolysis cell is made equal to the iR -drop of the cell by amplification. This

amplified voltage automatically adds to the bridge voltage and compensates for the iR -drop of the cell. The compensator is used with a conventional polarograph. In the evaluation of the compensator, the solvent-electrolyte system of 0.10M lithium chloride in 1:1 2-propanol-2,2,4-trimethylpentane was used. This same system was employed in some of the research reported here. Jackson and Elving encountered much lower cell resistance; this fact can be explained by cell design. Adams and Voorhies (1) described an automatic recording instrument for voltammetry at controlled current. More recently, Sawyer, Pecsok and Jensen (45) described an automatic recording polarograph using two reference electrodes. Both Adams and Sawyer employed principles similar to those used in the Arthur polarograph. The highest cell resistances reported with these other instruments were only approximately 3×10^4 ohms. In 1952 Ilkovic (23) presented a paper describing an automatic iR -drop compensator, but no details were available in this country.

CHAPTER III

SCOPE OF INVESTIGATION

The purpose of this research was to study several additives supplied by the sponsor and to develop quantitative analytical methods for the more promising ones. The additives finally chosen for study were those representing classes or types of wide use.

The basic apparatus employed was that already proven reliable by past work in high resistance polarographic studies in this laboratory. In the development of the analytical methods, the main point of this research always was to avoid any kind of preliminary separation procedure.

CHAPTER IV

APPARATUS

The high resistance polarograph was, except for the cathode follower, that developed by Arthur and Lloyd (33, 3). The cathode follower used in this research was selected on the basis of its operating characteristics as described by Gucker and Peterson (12). It was powered with a single ninety-volt dry battery and a single six-volt automobile battery. This cathode follower was designed as a differential type, but the circuit with one input side short-circuited served excellently as the high input impedance stage necessary in the high resistance polarograph.

The electrolysis cell was essentially that developed by Ulrich and VanderKam (49). It is shown with other parts in Figure 6. The connecting arms were packed with absorbent cotton which was then saturated with a saturated solution of lithium chloride in acetone. The parts of the cell arms outside the fritted discs were also packed with absorbent cotton which in this case was saturated with the solution of carrier electrolyte in alcohol used to prepare the alcohol-hydrocarbon solution within the cell. Nitrogen escaped at the top of the electrolysis cell through the spaces around the degassing tube and the burette tip. The space between the D.M.E. and its aperture in the cell top was closed with a short piece of surgical rubber tubing.

The stable reference electrode and the electrolysis reference

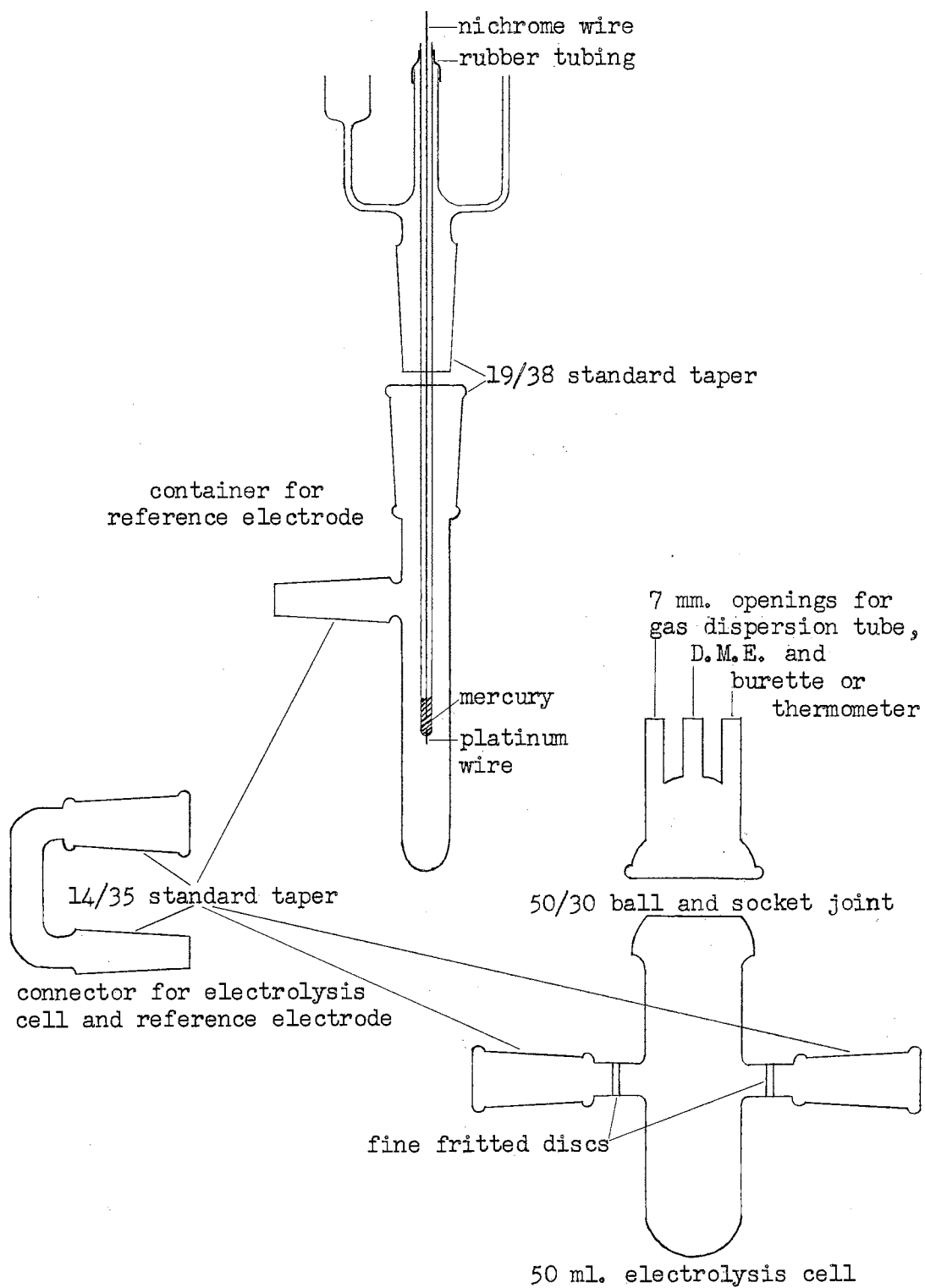


Figure 6. Electrolysis Cell Assembly.

electrode were both acetone saturated calomel electrodes of the type described by Arthur and Lyons (4).

Resistance measurements were made with an Industrial Instruments, Inc. Conductivity Bridge, Model RC 16B.

Mercury purification apparatus consisted of a Type "G" Mercury Filter and a Mercury Oxifier from Bethlehem Apparatus Company and a vacuum still from Gaertner Scientific Company.

The dropping mercury electrode assembly was that described by Lloyd (33).

The pH meter used in this research was a Beckman pH Meter, Model H2.

All amperometric titrations except those noted were performed with the cell in an oil bath thermostat at $25.0 \pm 0.1^\circ \text{C}$.

CHAPTER V

REAGENTS

Acetic acid - Baker and Adamson reagent grade was used without further purification.

Acetone - Fisher Scientific reagent grade and Brothers Chemical reagent A.C.S. grade were dried over anhydrous potassium carbonate and distilled from fresh anhydrous potassium carbonate.

Arsenious oxide - Baker and Adamson primary standard was used without further purification after being dried overnight at 110° C.

Benzenesulfonic acid was prepared by making a saturated solution of sodium benzenesulfonate, transferring a portion of the liquid to another container, adding to this volume of liquid approximately five times as much concentrated hydrochloric acid, filtering, and evaporating the filtrate in a vacuum desiccator.

1-Butanol - Harshaw Chemical pure grade was allowed to stand overnight with potassium hydroxide dissolved in it, distilled through a six-ball Snyder column and redistilled through the same column from anhydrous potassium carbonate.

2-Butanone - Unlabelled practical grade supplied from the storeroom of O.S.U. was used without further purification.

Chromic sulfate - Mallinckrodt analytical reagent grade, $\text{Cr}_2(\text{SO}_4)_3 + \text{Aq.}$, was used without further purification.

Cupric chloride - Eimer and Amend tested purity reagent grade was

used without further purification.

2,5-Dimethylbenzenesulfonic acid - Eastman Kodak white label grade was used without further purification.

Ethanol - Unlabelled absolute supplied from the storeroom of O.S.U. was used without further purification.

1-Hexanol - Matheson, Coleman and Bell practical grade was used without further purification.

Hydrochloric acid - Baker and Adamson reagent grade was used without further purification.

Iodine - Fisher certified reagent grade was resublimed with potassium iodide and ignited lime according to the method given by Pierce and Haensch (40).

Kerosene - Conoco water-white grade was used without further purification.

Ligroine - Eastman Kodak practical grade was used without further purification.

Lithium chloride - Mallinckrodt analytical reagent grade was used after it was dried for several days at 110°-115° C.

Lithium nitrate - Mallinckrodt analytical reagent grade was used after it was dried for several days at 110°-115° C.

Mercuric chloride - Merck reagent grade was used without further purification.

Mercurous chloride - Mallinckrodt analytical reagent grade and Fisher certified reagent grade were used without further purification.

Mercury was reclaimed from used polarographic laboratory stock by filtration with a gold filter, oxidation of base metals with a mercury oxidizer and distillation under vacuum.

Methanol - Baker analyzed reagent grade absolute was used without further purification.

para-Methylbenzenesulfonic acid - Eastman Kodak white label grade was used without further purification.

2-Naphthalenesulfonic acid - Eastman Kodak white label grade was used without further purification.

Nitrogen - Water-pumped Linde and Airco were used after passing successively through three towers of alkaline pyrogallol or chromous sulfate-sulfuric acid-amalgamated zinc, a tower of sulfuric acid and two towers of the solvent electrolyte system. The chromous sulfate towers were adopted after several pyrogallol solutions were expended rather quickly. Pyrogallol has no indicator, but when solutions of the blue chromous ion are expended, the green chromic ion appears. Rapid expenditure of the pyrogallol occurred after switching from Linde to Airco nitrogen. A direct comparison of the two brands with the same solution showed that the Airco contained at least five times as much oxygen as the Linde.

The chromous scrubbers were prepared in a manner adapted from the procedure described by Altieri (2). Three pounds of twenty-mesh reagent grade zinc were added to a solution of 21 g. of mercuric chloride dissolved in 500 ml. of water. This was shaken occasionally for about fifteen minutes, separated by decantation and washed with water. The zinc was divided approximately equally among three 250 ml. towers. To each tower were added 75 ml. of 0.10M sulfuric acid solution and 75 ml. of chromic sulfate solution, the latter consisting of 100 g. of chromic sulfate in 225 ml. of solution. The towers were closed immediately. After a few hours the blue chromous ion was in evidence. Two towers

were adequate, but the third tower was included in the event that the first tower became expended during a long set of experiments.

1-Octanol - Matheson, Coleman and Bell white label grade was used without further purification.

3-Pentanone - Matheson, Coleman and Bell white label grade was used without further purification.

Petroleum ether - Baker reagent grade, b.p. 60°-110° C., was used without further purification.

Potassium hydroxide - Baker and Adamson reagent grade was used without further purification.

Potassium iodide - Fisher certified reagent grade was used without further purification after being found iodate-free by testing with sulfuric acid and starch as recommended by Pierce and Haenisch (39).

1-Propanol - Matheson, Coleman and Bell practical grade was used without further purification.

2-Propanol - Baker analyzed reagent grade and Brothers Chemical were used without further purification.

Sodium benzenesulfonate - Fisher Scientific C.P. was used without further purification.

Sodium borate - Mallinckrodt analytical reagent grade was used without further purification.

Sodium dinonylnaphthalenesulfonate was supplied by the sponsor and was used without further purification.

Sodium hydroxide - Fisher Scientific reagent grade was used without further purification.

Sodium 2-naphthalenesulfonate was prepared by treating a solution of 2-naphthalenesulfonic acid with a solution of saturated sodium

hydroxide, filtering, and washing the salt five times with distilled water.

Sodium thiosulfate - Baker analyzed reagent grade was used without further purification.

Starch - Baker analyzed reagent soluble potato powder for iodometry was used without further purification.

Sulfuric acid - Baker and Adamson reagent grade was used without further purification.

Tetra-n-butylammonium iodide from stock on hand prepared by Lloyd (33) was used without further purification.

Tetraethylammonium bromide - Eastman Kodak white label grade was recrystallized twice from ethanol (13).

Tetramethylammonium chloride - Eastman Kodak practical grade was purified by the method of Pickard and Neptune (37). It was dissolved and filtered in hot 25% methanol in acetone. This solution was added to 100-110 ml. of acetone and allowed to cool. The crystalline product was separated by filtration and stored in a vacuum desiccator.

2,2,4-Trimethylpentane - Conoco reference grade, supplied by the sponsor, was used after simple distillation.

Zinc - Baker analyzed reagent grade was used without further purification.

CHAPTER VI

EXPERIMENTAL PROCEDURE

Mixed Solvents

Since 1-butanol, 1-hexanol, 1-octanol, 2-butanone and 3-pentanone all had been employed successfully in earlier polarographic work in this laboratory, experiments were run to determine how well these would mix with petroleum products. Kerosene was used as representative of petroleum fractions. One-to-one (by volume) stable solutions were readily obtained with all the solvents listed. Stable solutions also resulted when the alcohols had enough lithium chloride dissolved in them to make the resulting solutions 0.05-0.10M.

Polarograms of butanol-kerosene solutions gave excellent carrier waves with, however, additional waves due to reducible substances present in the kerosene. These waves demonstrated the fact that polarographic waves of a very usable type were readily obtained in such solvents, but they were undesirable otherwise. Since polarograms must be examined closely in an investigation such as this, the presence of an extra wave can be an insurmountable difficulty at first. This is especially true in work which involves mixed solvents of hydrocarbons and alcohols, a relatively new and almost totally unexplored field. Consequently, other representative petroleum products were tried. Ligroine was as bad or worse than kerosene. Much better results were obtained with reagent grade petroleum ether but, because of its volatility,

evaporation was quite pronounced. Although presaturation of the degassing nitrogen corrected this, there was still the difficulty that, because of the wide range of boiling points of the hydrocarbons in the petroleum ether, the composition of the solution under analysis undoubtedly changed somewhat.

Kerosene probably could have been purified suitably (20), and the slight composition change in the solution with petroleum ether might not have been serious as long as the volume remained constant, but the sponsor, Continental Oil Company, solved the problem with a large supply of 2,2,4-trimethylpentane of good purity. This was distilled with simple apparatus to remove some light solids which probably were originally in the shipping container, but no difference could be detected polarographically between that which was used directly from the container and that which was distilled.

This research was started using 1-butanol, which was selected because it was believed to be suitable for forming solutions with a wide range of hydrocarbons. After the preliminary investigations, however, 2-propanol was used instead. A comparison of the two alcohols shows 1-butanol to be somewhat less volatile and perhaps, due to its greater molecular weight, a better solvent for higher molecular weight hydrocarbons, but this was not noted experimentally. One-to-one solutions of 2-propanol and 2,2,4-trimethylpentane were readily formed regardless of the supporting electrolyte present in the 2-propanol. Presaturation of the degassing nitrogen was still found to be necessary, however.

The advantages of 2-propanol are its commercial availability in highly pure form at low cost. Reagent grade 2-propanol purified in the manner described earlier was compared polarographically with the

unpurified stock. The results showed no discernible difference.

Supporting Electrolytes and Cell Resistances

In the event that at a later date a reduction in resistance of the solutions under study might have been desirable and might have been accomplished by a change of supporting electrolyte, the specific conductivities of 0.10M solutions of tetramethylammonium chloride, tetraethylammonium bromide, tetra-n-butylammonium iodide and lithium chloride in 1-butanol were determined. They were found to be, respectively, 2.1×10^{-3} , 3.2×10^{-3} , 2.7×10^{-3} and 2.0×10^{-3} ohms⁻¹.

Tetramethylammonium chloride was employed as supporting electrolyte for preliminary experiments because of its high negative decomposition potential. After the preliminary work was done, lithium nitrate and lithium chloride were employed. Actual cell resistances in this work ranged from 0.4 to 1.4 megohms for the D.M.E.-E.R.E. branch and between 0.1 and 0.8 megohm for the D.M.E.-S.R.E. branch.

Burettes

Except for some early experiments, microburettes with capacities of five milliliters were used for the amperometric titrations. These burettes had graduations of 0.01 ml., and the nearest 0.001 ml. could be estimated with the aid of a magnifier.

A microburette had many advantages for this work. One of the first things learned about these amperometric titrations was that the starting ratio of alcohol to hydrocarbon in the titration cell could not be changed much without causing the titration curve to deviate from straight lines. This problem was solved at first, when a larger burette was used,

by the preparation of titrants of 1:1 2-propanol-2,2,4-trimethylpentane with the same concentration of carrier electrolyte as the solution in the cell. The hydrocarbon, however, affected the silicone stopcock grease. After a few hours the stopcock became difficult to turn and the burette tip became clogged. The addition of a small quantity of more concentrated titrant in 2-propanol alone, which did not affect the stopcock grease appreciably, obviated the necessity of using carrier electrolyte and mixed solvents. This approach had the further advantage of not introducing an appreciable quantity of oxygen into the cell with each addition of titrant in those cases in which the titrant accidentally had come into brief contact with air during the operation. This advantage was greatest at the lowest concentration of unknown and the highest sensitivity setting of the polarograph. In addition, when small volumes of titrant were used, no correction was needed for current measurements because of increased volume of solution in the cell. It was possible to fit microburettes close to and parallel with the D.M.E. and to hold them to the supporting apparatus of the D.M.E. with a small piece of wire. The extra weight was easily supported. A larger burette required a separate support and an angled extension tip attached to the tip of the burette.

The disadvantage of microburettes for this type of work is the greater proportional error of the solution clinging to the burette tip when compared with a larger burette. It was impossible, with the apparatus employed, to touch the burette tip with anything or to touch the tip to the inside of the titration cell. The greatest possible error in displacement of the entire titration curve was less than 0.01 ml. This was less than 2% if the volume of titrant at the stoichiometric

point was 0.5 ml. Since a titration curve is the result of several additions of titrant, the errors among the individual points relative to each other tend to average out when the lines are drawn through the points.

The two types of microburette arrangements are illustrated in Figures 7 and 8.

Figure 7 shows the earlier type used with cupric chloride titrants only. Each burette filling was degassed with nitrogen saturated with 2-propanol. To fill the burette, the gas dispersion tube was raised above the surface of the liquid, and the burette was lowered until the outside of the standard taper joint fitted tightly into the rubber tubing. Nitrogen pressure then forced titrant into the burette. This apparatus was satisfactory for checking the variance of end points of several titrations with the same burette filling, but it had the disadvantage of a possibility of a change in concentration of titrant if the nitrogen was not completely saturated with 2-propanol. Another disadvantage was that the long test tube over the top of the burette did not keep air completely out of contact with the solution. The Parafilm seal let nitrogen out during the degassing period and a small amount of air in when solution was allowed to run out from the burette.

The other microburette assembly shown in Figure 8 was devised when the potassium hydroxide in 2-propanol, which destroys silicone type stopcock grease, was used as titrant. The titrant was degassed in a 500 ml. polyethylene wash bottle; nitrogen entered the bottle through tubing slipped over the spout of the wash bottle. The screw cap was loosened slightly to allow escape of nitrogen. The cap was tightened at the end of the degassing, and the spout was pulled up so that its interior end was above the surface of the liquid. The degassing tubing

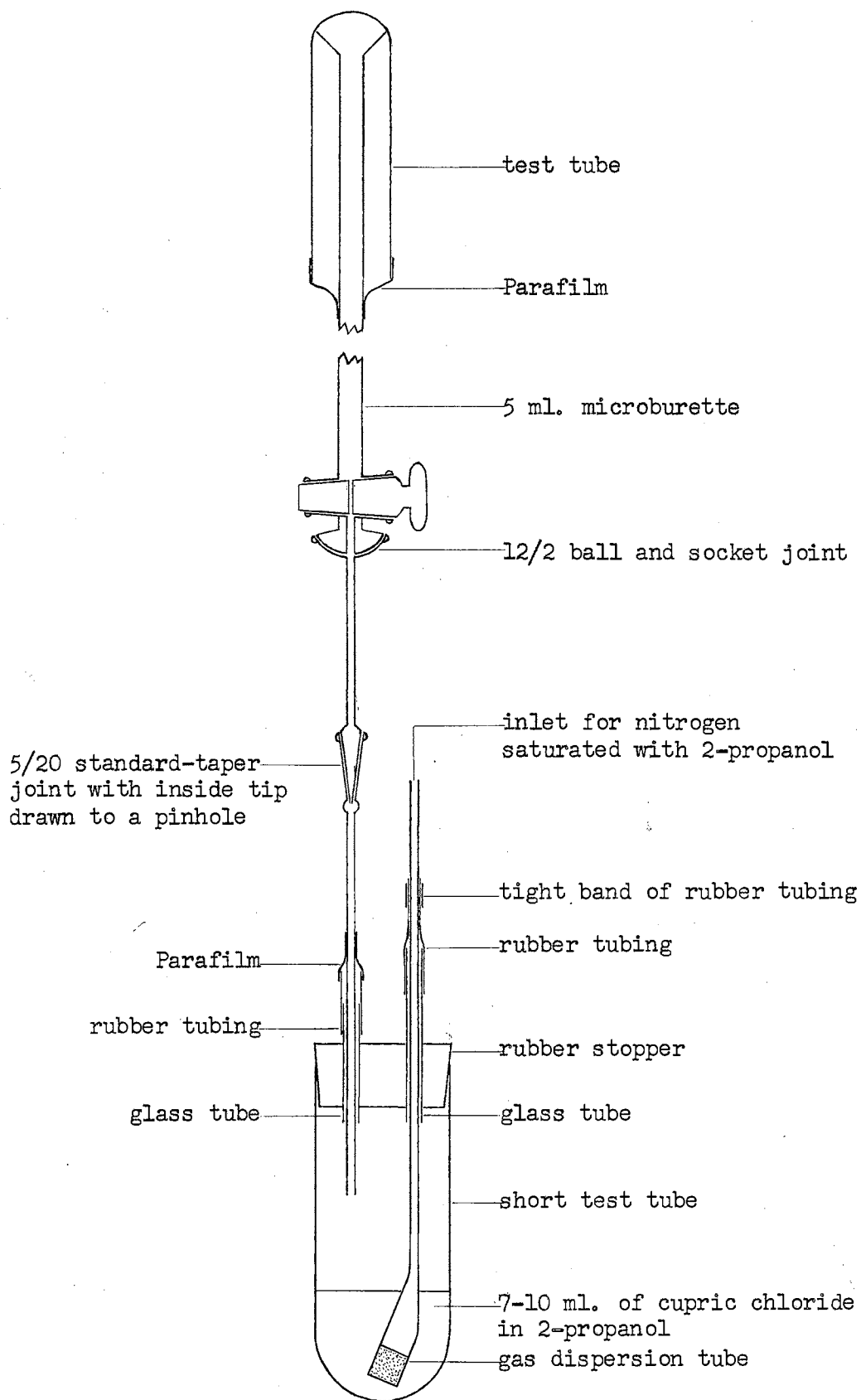


Figure 7. Cutaway View of Apparatus for Degassing Titrant and Filling Microburette (Degassing Position).

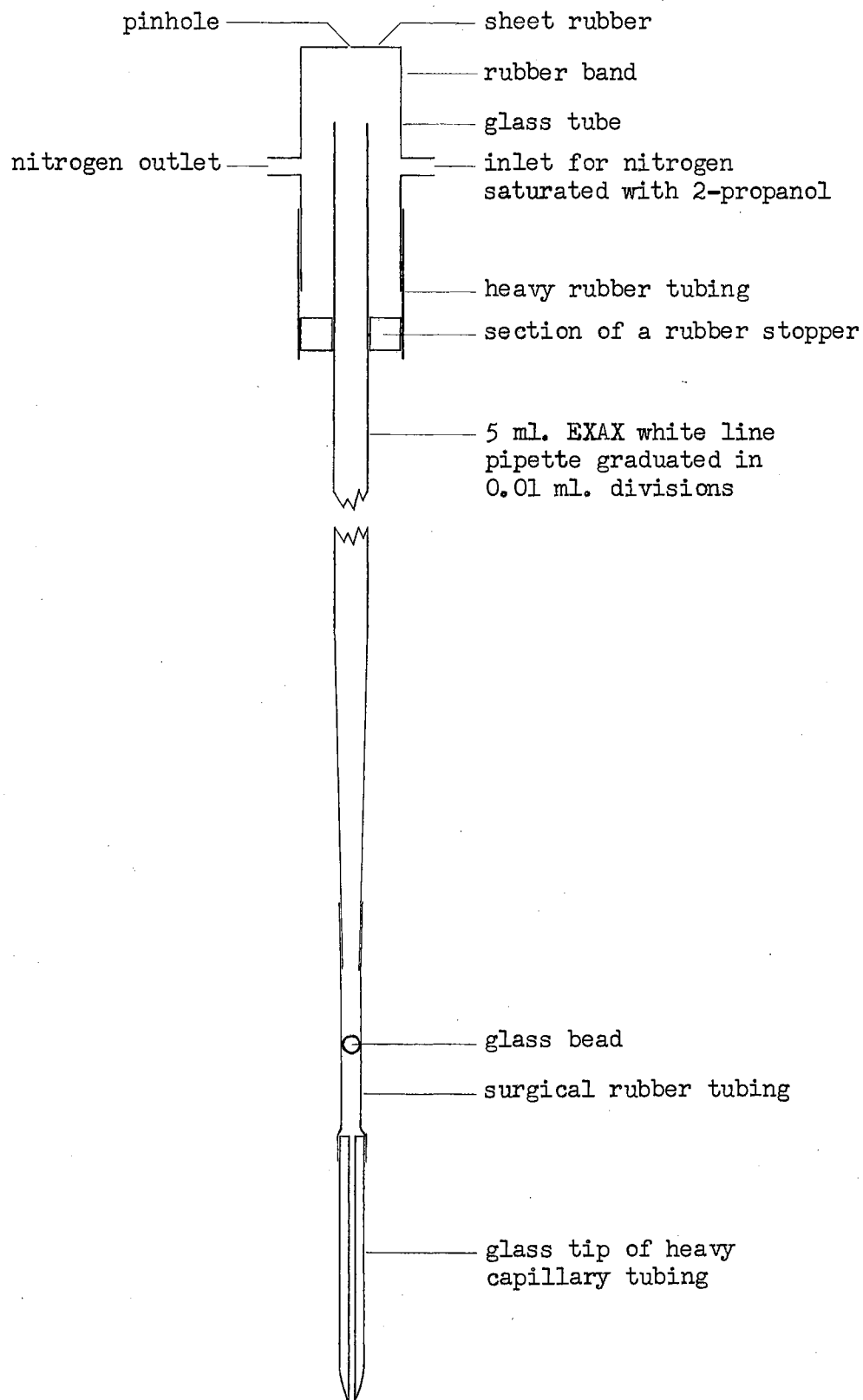


Figure 8. Cutaway View of Microburette Assembly for Standardized Titrants.

was removed, and the exterior end of the spout was capped with a short piece of Tygon tubing with one end closed. The procedure for filling the burette was the following: the cap on the spout was removed, the spout was pushed down so that its interior end was below the surface of the liquid, the exterior end of the spout was inserted into the small hole in the rubber diaphragm, a couple of milliliters were squirted into the nitrogen-filled space adjacent to the top of the burette to clear the spout of any air which had entered it, the spout was inserted into the burette, and the burette was filled to its top. The rubber tubing above the bead was squeezed to free trapped bubbles, solution was run out until the meniscus reached the graduations, and the burette was inserted quickly into the nitrogen atmosphere of the titration cell.

This burette assembly was used for all the titrations in which standardized titrants, both potassium hydroxide and cupric chloride, were employed.

No noticeable evaporation occurred with either burette arrangement.

Preliminary Investigations

Several additives were supplied by the sponsor. Three of them, Santolene J, Tenamene 60 and sodium dinonylnaphthalenesulfonate, were selected as being characteristic of the general types after some study and preliminary experiments. The last-named is available as the active agent in an additive preparation named Nasul SS. Most of the research was on these three and on sulfonic acids, the latter being investigated as part of the work on the sulfonates. The complete investigations of these selected additives, including their preliminary investigations, follow this section presenting the preliminary investigations of all of

the incompletely-studied additives.

Di-tertiary-butyl-para-cresol. A hindered phenol, 4-methyl-2,6-di--t-butylphenol, this was supplied as a pure white crystalline compound. Cathodic waves were attempted using a D.M.E. and 0.10M lithium chloride in 1-butanol. Results were entirely negative. Anodic waves were then attempted using a platinum, and later a gold, rotating microelectrode. Lithium chloride, sodium hydroxide and potassium hydroxide were used as carriers in 1-butanol. The latter two carriers were used because in aqueous solutions higher pH results in greater ease of oxidation of phenols in general. An apparatus was devised so that the solutions could be degassed and kept under an atmosphere of nitrogen. No waves were obtained, but in every case the recorder pen became jittery, a phenomenon which might have been caused by adsorption of the phenol at the microelectrode. These were the only experiments involving use of rotating microelectrodes in this research. All other work was done with the cathodic D.M.E.

Paradyne HO-2 Enjay. The active agent in this liquid additive was described as a mixture of barium, calcium and sodium sulfonates. A solution of 29 mg. in 25 ml. of 0.10M tetramethylammonium chloride in 1-butanol yielded two waves, one of questionable origin at -0.49 volt and the other at -1.71 volts. The second wave was approximately three times the height of the first.

Oronite Dispersant FO. This liquid additive was described as 40% sulfonates, the active part, and 60% hydrocarbon and 2-propanol. A 25 mg. sample in 25 ml. of 0.10M tetramethylammonium chloride in 1-butanol gave a wave which had a half-wave potential of -1.95 volts and which ran into the carrier decomposition curve.

Nasul EDS. This additive was ethylenediamine dinonylnaphthalene-sulfonate supplied as 50% sulfonate in 46% mineral seal oil and 4% unsulfonated oil. A 40 mg. sample in 20 ml. of 0.10M tetramethylammonium chloride gave a wave having a half-wave potential of -1.50 volts. In 0.10M lithium chloride in 1-butanol, Nasul EDS gave a half-wave potential of -1.57 volts, and ethylenediamine gave a similar wave having a half-wave potential of -1.63 volts. The latter was run because it was believed that ethylenediamine was the polarographically-active part of the molecule.

Paradyne HO-4 Enjay was described as perhaps having a primary amine as the active group, the material having a base number of 219 and containing 5% nitrogen. A wave did not appear from a 35 mg. sample in 25 ml. of 0.10M tetramethylammonium chloride in 1-butanol. (A similar result was obtained with Santolene J, a supposedly similar substance.)

Santolene H. No information was given concerning the composition of this liquid. A wave did not appear from 42 mg. in 50 ml. of 0.10M tetramethylammonium chloride in 1-butanol.

DuPont FOA-2 was described as a mixture of 80% lauryl methacrylate and 20% diethylaminoethyl methacrylate supplied 50% in kerosene. Two waves were obtained from 32 mg. in 25 ml. of 0.10M tetramethylammonium chloride in 1-butanol. The first wave had a half-wave potential of -0.88 volt, and the second wave, about four times as high as the first and running into the carrier decomposition curve, had a half-wave potential of -1.91 volts.

Gulf 178. This substance was described as containing an amine soap or possibly an amide. A 24 mg. sample in 20 ml. of 0.10M tetramethylammonium chloride in 1-butanol gave a wave having a half-wave potential

of -1.90 volts, which was very near the carrier decomposition curve.

Santolene C. This liquid additive was described as probably a dimerized acid. The acid and saponification numbers were given as 95 and 96, respectively. A sample of 27 mg. in 20 ml. of 0.10M tetramethylammonium chloride in 1-butanol gave a wave with a half-wave potential of -1.88 volts.

According to information supplied by the sponsor, Santolene C is presently determined by a process of extraction followed by aqueous amperometric titration with cupric acetate. Consequently, a 27 mg. sample of Santolene C in 10 ml. of petroleum ether was added to 20 ml. of degassed 0.10M tetramethylammonium chloride in 1-butanol, degassed further, and titrated with $2.0 \times 10^{-3}M$ cupric acetate in 1-butanol. A copper wave appeared and increased linearly with concentration, but no effect on the wave supposedly caused by Santolene C was observed.

A solution of 40 mg. of Santolene C in kerosene was shaken with hydrochloric acid (1 volume of concentrated hydrochloric acid plus 4 volumes of water), washed with water, mixed with 10 ml. of 0.10M tetramethylammonium chloride and titrated amperometrically with a saturated solution of cupric acetate in 0.05M tetramethylammonium chloride in 1-butanol. The titrant was prepared as $1.0 \times 10^{-3}M$, but not all of the cupric acetate dissolved. Another similar acid treatment, wash and amperometric titration were carried out using reagent grade petroleum ether. This time the titrant was $2.0 \times 10^{-3}M$ cupric acetate in only 1-butanol. Neither titration was successful.

A reverse titration was performed by titrating a 25 ml. solution of $1 \times 10^{-3}M$ cupric acetate in 0.10M tetramethylammonium chloride in methanol with a solution of 0.126 g. of Santolene C in 25 ml. of 0.10M

tetramethylammonium chloride in methanol. Each addition of the Santolene C solution decreased the height of the wave of the cupric ion, and a green precipitate formed during the titration. The fact that the precipitate appeared in methanol but not in the petroleum ether-butanol solutions indicated that a successful titration with the cupric ion probably would have to be based on the insolubility of the cupric ion-Santolene C combination. Further experiments with this additive were not performed because of interest in other additives.

Santolene J

This additive was a dark brown liquid described by the sponsor as a mixture of amines of high molecular weights. In an exploratory experiment the curves of 50 ml. of 0.10M tetramethylammonium chloride in 1-butanol both with and without 0.375 g. of Santolene J were almost identical.

Since the additive was an amine, it was reasoned that a copper complex could be formed, and that a wave due to the copper complex would appear in a polarogram. Different weights of Santolene J, 60, 20, 6.0 and 2.0 mg., in 10 ml. kerosene samples were shaken with dry cupric chloride dihydrate for one hour, separated from the solid cupric chloride by suction filter, diluted to 25 ml. with kerosene, and mixed with 25 ml. of 0.10M lithium nitrate in 1-butanol; this was done quantitatively. A polarogram of each solution showed a new wave. Considering the cathodic part of this wave, the half-wave potential was in the neighborhood of 0.0 volt. A comparison of the currents with one another showed that the currents obtained were not proportional to the concentration of Santolene J.

The experience with the kerosene demonstrated that other polarographically active substances ordinarily might be present in petroleum products in concentrations greater than that of an additive. This meant that either a separation had to be performed as a preliminary to polarographic analysis, or an amperometric titration had to be developed, if the analytical methods developed during this research were to be practical. The amperometric technique was chosen as promising greater simplicity and speed in view of the inherent ability of the Arthur polarograph to handle solutions of very high resistance.

A sample of 30 mg. of Santolene J in a 50 ml. solution of 0.05M lithium nitrate in 1:1 2-propanol-2,2,4-trimethylpentane was titrated with a saturated solution of cupric acetate in methanol. The titrant was prepared as 0.0100M cupric acetate, but not all of the salt dissolved. Complete cathodic polarograms from the zero current axis were made after each addition of titrant. The current vs. volume curves at zero and at -0.19 volt both gave sharp breaks at 14.8 ml. The current measurements at -0.19 volt were at approximately the top of a wave which began to appear after the addition of about 10 ml. and which increased markedly after the break in the titration curve. Because of the sharp rise past the break, this wave was believed to be due entirely to cupric ions. Another wave appeared after the first addition of the titrant. Its decomposition potential was 1.0 volt; due to the curved wave front the half-wave potential could not be determined. The wave height increased and then decreased during the titration; after the addition of 20 ml. it had almost disappeared. A green precipitate formed during the titration.

Because the end points with currents measured at the two voltages

were the same, and since the oxygen wave does not appear on the positive side of the zero voltage axis, it was reasoned that degassing could be eliminated, the solution could be left exposed to the atmosphere during the titration, and the current measurements could be made at zero voltage. Two such titrations were performed employing a 10.0 mg. sample and a 3.0 mg. sample with the same titrant and supporting electrolyte as above. The end points were 3.5 ml. and 1.15 ml., respectively. In each of the two titrations, the titration curve past the end point was straight to about 5 ml. past the end point. There it curved upward. This was suspected as being due to the radical change in the composition of the solution caused by the addition of the methanol titrant. A problem similar to this does not occur in aqueous amperometry. Because of the curving and the lack of experience at the time, neither of the end points was considered as certain. Also, while the agreement between the end points of the 10.0 mg. and 3.0 mg. samples was good, their agreement with the 30 mg. sample was not. The solutions were not thermostated.

In order to put the titrations on a quantitative basis, it was desired to have a copper salt which would dissolve completely in the same solvent mixture in which the Santolene J solutions were titrated. Reagent grade cupric chloride dihydrate met the requirement. This salt was easily handled with no special precautions necessary. The titrant was prepared by dissolving the appropriate weight of salt for 50 ml. of cupric chloride in 25.0 ml. of a solution of 0.20M lithium nitrate in 1-butanol and diluting to 50.0 ml. with the same volume of 2,2,4-trimethylpentane. A 30.0 mg. sample of Santolene J solution exposed to the atmosphere was titrated. An excellent titration curve was obtained; the end point was 7.15 ml. Again no thermostat was used.

This was the first of a series of forty-five titrations of Santolene J solutions exposed to the atmosphere. A thermostat was used for the last thirty-one titrations. The majority of the titrations were on 10.0 mg. samples in 1:1 1-butanol-2,2,4-trimethylpentane, but samples ranging from 30.0 mg. to 0.100 mg. were titrated, and 1:1 2-propanol-2,2,4-trimethylpentane was used for about one-fourth of the experiments.

It was determined early in these experiments that lithium nitrate as supporting electrolyte gave better titration curves than lithium chloride. In lithium nitrate solutions more of the cupric ion wave appeared before the zero voltage axis. The difference between the electrolytes was measured by comparing 0.10M solutions of lithium nitrate and lithium chloride in 1:1 2-propanol-2,2,4-trimethylpentane in the same titration cell within five minutes of one another. The two differed by 0.08 volt; the zero current mark of the lithium chloride was 0.02 volt on the negative side of the zero voltage line, and that of the lithium nitrate was 0.06 volt on the positive side.

The results of the titrations in which the solutions were exposed to the air were consistently favorable enough so that continued work seemed justified, but results were never good enough to justify setting up this type of titration for a final statistical evaluation. However, during the course of these titrations, peculiarities and properties of the additive and of the whole system were noted; also, other experiments were performed which aided in understanding these peculiarities.

With 30 mg. samples in 1-butanol-2,2,4-trimethylpentane solutions, green solutions and copious green precipitates were observed during and immediately after the titrations; 10 and 5 mg. samples had green solutions but no precipitates immediately after the titrations. After

standing overnight, the solutions of the 30 and 10 mg. samples were colorless and green precipitates were present; the 5 mg. solutions still had green color but no precipitates. In 2-propanol-2,2,4-trimethylpentane solutions, copious green precipitates were observed during and immediately after the titrations of 10 and 30 mg. samples. A comparison of these results with those above showed that the green Santolene J complex precipitated more readily in the 2-propanol solutions.

In the 10 and 5 mg. titrations in 1-butanol-2,2,4-trimethylpentane solutions, even though no precipitate was visible to the unaided eye and the solution appeared green, it was believed that the titrations involved precipitations. This was proven to be the case by a titration of a 5 mg. sample in which, after each addition of titrant, the room was darkened and a narrow beam of bright light was passed through the solution in the titration cell. No Tyndall effect was present at first, but one appeared before the end point was reached, increased during the remainder of the titration, and appeared strongest at the end of the titration. In ordinary light the solution appeared perfectly transparent to the unaided eye. Two solutions of 10.0 mg. samples, each containing a pinch of very fine ground glass, were titrated. It was believed that the ground glass might have an accelerating effect on the precipitation, and that this might improve results. A comparison of these results with others did not show any noticeable difference.

Whether the overall concentration of supporting electrolyte was 0.05M or 0.10M seemed to make little difference except that there were indications that the visible precipitate might have appeared faster in 0.10M solutions.

There were some results that indicated the possibility that changes

in the composition of the additive might have occurred during the time it had been stored in the concentrated form. In order to obtain an additive about which more was known, the additive supplied by the sponsor was distilled at reduced pressure. A simple distillation was carried out at a pressure range of 0.5-1.5 mm. of mercury. The distilling range was 54-110° C. The distillate was clear with a very slight yellowish tint. This distillation was performed when slightly less than half of the forty-five aforementioned titrations had been completed. The distillate was used exclusively thereafter for all experiments.

Titrations of the additive with standardized hydrochloric acid were carried out by dissolving accurately weighed samples in 25 ml. of absolute ethanol and adding 25 ml. of water. Both methyl orange and a pH meter were used to determine end points and each gave satisfactory results. The weight of Santolene J in the alcohol-water mixture had to be 0.5 g. or less for homogeneity. The equivalent weight determined by this means was 207. A molecular weight determination by the freezing point depression of benzene showed an average molecular weight of 208. These experiments indicated that there was one reactive amine group per molecule. Saturated aliphatic amines with thirteen and fourteen carbon atoms have molecular weights of 199 and 213, respectively.

Silver nitrate as titrant was used for one 10 mg. sample, but even though a brown precipitate formed, the titration plot was a straight line that continued even beyond the theoretical end point. The carrier-solvent system for both titrant and titrated solution was 0.10M lithium nitrate in 1:1 2-propanol-2,2,4-trimethylpentane.

Based upon the form of curve obtained, the practical amperometric titration limits indicated by all the experiments were 5 mg. and 1 mg.

for 1-butanol and 2-propanol, respectively, in combination with 2,2,4-trimethylpentane, the total volume being 50 ml.

When continued titrations of solutions exposed to the atmosphere did not yield desired results, titrations were made on degassed solutions in an atmosphere of nitrogen. For this work the burette assembly previously mentioned and shown in Figure 7 was devised. Only solutions of 0.05M lithium nitrate in 1:1 2-propanol-2,2,4-trimethylpentane were used for the remainder of the work on Santolene J.

Several blank titrations were made. The set of points for each blank resulted in a very straight line. The lines of the 0.050M cupric chloride blanks passed through the origin in each case, and the line of the 0.0050M cupric chloride blank passed through the current axis slightly above the origin.

The results of the blank titrations were important for several reasons. They indicated that the method of making current measurements from the zero current mark was acceptable. All of the blanks showed that -0.12 volt, where the cupric wave was topped, was optimum for current measurements. A visible break denoting the top of the cupric wave was not necessary to obtain a straight-line titration plot, and this fact proved to be very useful in titrations at very low concentrations. The blanks were proof that the cupric ion itself could be determined polarographically in 0.05M 1:1 2-propanol-2,2,4-trimethylpentane solutions from zero to $8.0 \times 10^{-4}M$ concentrations. The drop time at zero current decreased with increased concentration of the cupric ion, but this did not seem to affect the linearity of the titration plots.

Eight titrations were made in which a full cathodic wave was obtained after each addition of titrant. These included one 10.0 mg.

sample, four 1.00 mg. samples and three 0.100 mg. samples. The results showed that Santolene J samples should be titrated as soon as possible after preparation to prevent reduction in titer of the Santolene J. The reasons for such loss were not established, but adsorption on the container walls and absorption of carbon dioxide from the air might have been important factors. Similar behavior of another amine additive had been observed by Gaylor, Conrad and Landerl (9). Some of the results were consistent enough so that it was decided to make sets of three titrations each, with the same burette filling used for each set. Three titrations from the same burette filling would indicate the variance to be expected with similar samples. The agreement between the averages of the sets would indicate success or the need for more work.

The solutions titrated were prepared from the same freshly prepared stock solution of distilled Santolene J in 2,2,4-trimethylpentane. The more dilute titrants were prepared by exact dilution of the 0.050M cupric chloride used as one titrant. The titration graphs of two 0.100 mg. titrations were perfectly straight lines, proving, together with past experience, that this concentration could not be titrated successfully. The other results are given in Table I. The parts of a mole which were present in a 20.0 mg. sample, a 10.0 mg. sample and a 1.00 mg. sample were 9.7×10^{-5} , 4.8×10^{-5} and 4.8×10^{-6} , respectively. A typical Santolene J titration curve is shown in Figure 9.

These results indicated several possibilities and conclusions. The probability of titrating successive 1.00 mg. samples with the same volume of titrant appeared very small. The differences in this particular case might be explained possibly by loss of sample due to adsorption on the surface of the titration cell. For the 10.0 and 20.0 mg. samples there

TABLE I

TITRATION OF DISTILLED SANTOLENE J IN 50 ML. OF 0.05M LITHIUM NITRATE IN
1:1 2-PROPANOL-2,2,4-TRIMETHYLPENTANE WITH CUPRIC
CHLORIDE IN 2-PROPANOL

Weight of Santolene J (mg.)		20.0	10.0	1.00
Titrant Concentration (mole/liter)		0.050	0.050	0.0050
	Sample			
	1	1.28	0.56	0.37
ML. of Titrant Required	2	1.18	0.55	0.47
	3	1.29	0.60	0.56
Mean		1.25	0.57	0.47
Average Deviation		0.05	0.02	0.06
Calculated End Point (ml.)*		0.97	0.48	0.48
<u>Actual End Point</u>				
Calculated End Point		1.29	1.19	0.98

*Based on the assumptions that one mole of cupric ions combined with two moles of Santolene J, that the reactive component of Santolene J had a molecular weight of 207 and that all of the Santolene J was reactive.

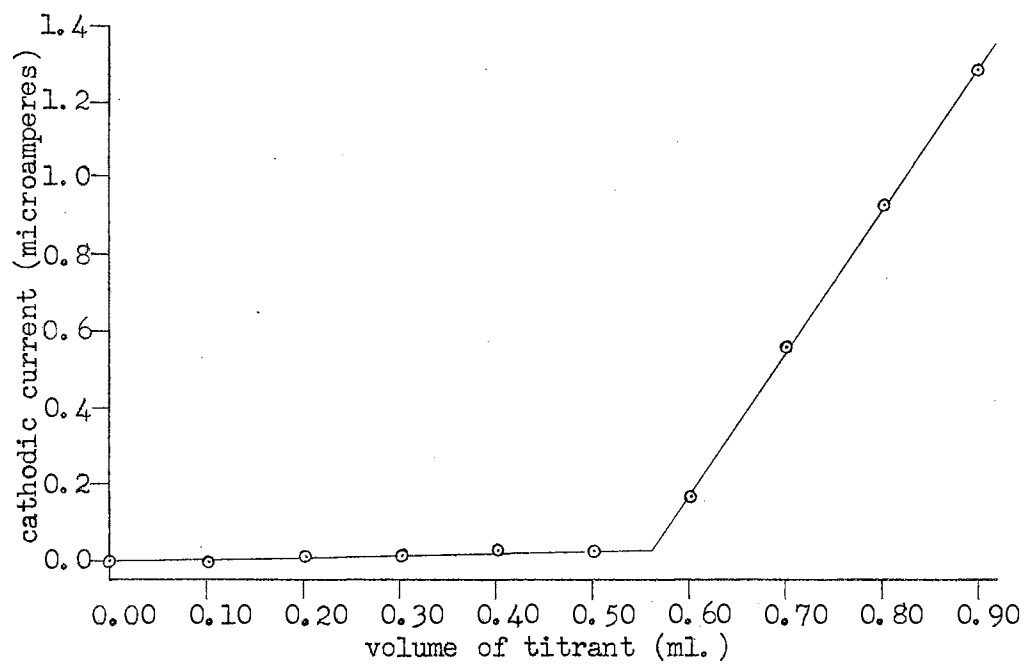


Figure 9. Titration Curve of 10.0 Mg. of Distilled Santolene J in 50 ML. of 0.05M Lithium Nitrate in 1:1 2-Propanol-2,2,4-Trimethylpentane With 0.050M Cupric Chloride in 2-Propanol.

were two possible explanations for the differences between calculated and actual end points. One explanation was occlusion of cupric ions in the precipitate, so that not all of the cupric ions were available for complexing the Santolene J. This explanation was given strength by the decrease of the ratio of actual end point to calculated end point with decreased size of Santolene J sample. The other explanation was that the titrants were not their nominal values. Standardized titrants would indicate the correct explanation.

In order to establish a better idea of the variance in end points to be expected, it was decided to make the titrations with standardized titrants in groups of five on sample sizes of 5.0 mg. and 20.0 mg. The 20.0 mg. samples were prepared by dissolving the appropriate weight of distilled Santolene J for ten samples in 250 ml. of 2,2,4-trimethylpentane and mixing with 250 ml. of 0.10M lithium nitrate in 2-propanol. Five samples were measured out into 50 ml. glass-stoppered volumetric flasks. The 5.0 mg. (2.4×10^{-5} mole) samples were prepared in the same manner. The titrants were prepared and degassed in polyethylene wash bottles and used with the burette assembly shown previously in Figure 8. Each titrant was standardized in an essentially aqueous medium against an aqueous solution of 0.0264N sodium thiosulfate by a method adapted from the iodometric method for copper presented by Pierce and Haenisch (41). The recommended pH range for the titration in aqueous solutions is 3-4. The proper quantity of acetic acid necessary to maintain this apparent pH in 2-propanol-water mixtures was determined by experiments with pHdrion indicator paper. Several solutions, each consisting of 10 ml. of water, 1.0 g. of potassium iodide, one to four ml. of 2-propanol and 0.10-0.16 ml. of glacial acetic acid, both with and without

TABLE II

TITRATION OF DISTILLED SANTOLENE J IN 50 ML. OF 0.05M LITHIUM NITRATE IN
1:1 2-PROPANOL-2,2,4-TRIMETHYLPENTANE WITH STANDARDIZED
CUPRIC CHLORIDE IN 2-PROPANOL

Titration of 20.0 mg. Samples with 0.0996M Cupric Chloride

Sample	End Point (ml.)	Deviation	Deviation ²
1	0.50	0.06	0.0036
2	0.58	0.02	0.0004
3	0.58	0.02	0.0004
4	0.53	0.03	0.0009
5	<u>0.62</u>	<u>0.06</u>	<u>0.0036</u>
Mean	0.56	0.04	0.0018

Standard Deviation, (5), = (Mean of Squared Deviations) ^{$\frac{1}{2}$} = 0.042

$\frac{\text{Standard Deviation}}{\text{Mean of End Points}} = 0.075 = 7.5\%$ Calculated End Point (ml.)* = 0.48

$\frac{\text{Actual End Point}}{\text{Calculated End Point}} = 1.17$

Titration of 5.0 mg. Samples with 0.0239M Cupric Chloride

Sample	End Point (ml.)	Deviation	Deviation ²
1	0.54	0.06	0.0036
2	0.53	0.05	0.0025
3	0.45	0.03	0.0009
4	0.44	0.04	0.0016
5	<u>0.45</u>	<u>0.03</u>	<u>0.0009</u>
Mean	0.48	0.04	0.0019

Standard Deviation = (Mean of Squared Deviations) ^{$\frac{1}{2}$} = 0.044

$\frac{\text{Standard Deviation}}{\text{Mean of End Points}} = 0.092 = 9.2\%$ Calculated End Point (ml.)* = 0.51

$\frac{\text{Actual End Point}}{\text{Calculated End Point}} = 0.94$

*Based on the assumptions that one mole of cupric ions combined with two moles of Santolene J, that the reactive component of Santolene J had a molecular weight of 207 and that all of the Santolene J was reactive.

1.0-4.0 ml. of the sodium thiosulfate solution were employed, and the proper quantity of glacial acetic acid was found to be 0.10 ml. The starch indicator recommended by Pierce and Haensch (38) was employed.

The standardization of the cupric chloride in 2-propanol solutions within a short time before or after use was important, because it was found that these solutions in polyethylene bottles became less concentrated with time.

The results of the amperometric titrations are shown in Table II. These results and those in the previous table indicate that, for samples of about 5.0 mg. and less, the actual concentration of the Santolene J can be determined within the limits of precision as twice the quantity (in fractions of a mole) of the copper at the end point. For larger samples, a known sample of Santolene J of about the same size as the unknown probably could be used as a standard.

It was mentioned previously that the quantity of Santolene J in solutions prepared for titrations decreased upon standing. In some of the titrations in which complete polarographic curves were run, a very well-formed wave having a half-wave potential of about -0.50 volt appeared. The identity of the substance causing this wave was not discovered. The wave appeared both in Santolene J solutions and in blank solutions. Sometimes it was present in the first polarogram run on a solution, and other times it appeared after one or more waves had been run. Whenever this unknown wave was obtained from a solution containing Santolene J, the end point of the titration was always much lower than expected for the quantity of Santolene J originally in the sample, or the titration curve had no break and looked like a blank titration curve. When the unknown wave appeared in blank solutions or solutions already

containing Santolene J, the addition of Santolene J to such solutions caused the wave to disappear entirely. Obviously, the reaction between the unknown substance and Santolene J was rapid and complete. The unknown substance did not appear to affect the linearity of a blank titration curve, so if any reaction occurred between it and copper, the reaction had to be relatively slow.

Since this titration involved a precipitation, the length of time that elapsed between an addition of titrant and a current measurement would be expected to influence the size of the latter. Various intervals of time from about three minutes, which is close to the minimum time possible with the apparatus employed, to fifteen minutes were allowed to elapse between current measurements. The current readings before an end point became quite constant within five minutes, whereas the readings after the end point kept decreasing with time, rapidly in the first few minutes, then much less so. Neither the end point nor the quality of a titration curve appeared to be very dependent on the size of the time interval as long as it was kept constant and as long as the titration progressed at a steady pace with no long time lapse between a current measurement and the next addition.

Tenamene 60

Tenamene 60 was a transparent amber liquid, a product of Eastman Kodak. The label described it as "an Eastman copper deactivator, Disalicylal Propylene Di-imine, 80% solution in toluene". Accordingly, the formula of the active ingredient is $o\text{-HOC}_6\text{H}_4\text{CH:NCH(CH}_3\text{)CH}_2\text{N:CH-o-C}_6\text{H}_4\text{OH}$ (M.W. 282). All of the weights of Tenamene 60 reported in this research include both the active ingredient and the toluene.

A preliminary study was made with 2.8 mg. of Tenamene 60 in 26 ml. of 0.10M tetramethylammonium chloride. At first glance the resultant polarogram appeared to have a single, somewhat curved wave-front. However, after close examination the polarogram appeared to consist of two waves close together. The wave-fronts were not similar. The bottom wave-front was somewhat steeper than that of the top, and the bottom wave was about twice as high as the top wave. The decomposition potential was -1.26 volts and the half-wave potentials were -1.33 volts and -1.60 volts for the bottom and top wave-fronts, respectively.

According to the information supplied through the sponsor, the active ingredient of Tenamene 60 forms a chelate compound with copper, so several amperometric titrations were performed using cupric chloride in 2-propanol as titrant. The solutions of Tenamene 60 in 50 ml. of 0.10M lithium chloride in 1:1 2-propanol-2,2,4-trimethylpentane were not protected from the atmosphere. The current due to the cupric ion was measured from the zero current mark to the zero effective voltage line, as in the similar Santolene J titrations. These titrations, like their Santolene J counterparts, were unsuccessful. On the other hand, titrations of degassed solutions containing lithium nitrate as the supporting electrolyte yielded good titration curves. In the latter titrations the current was measured from the zero current mark to the top of the cupric ion wave at -0.12 volt, as in the successful Santolene J titrations.

A series of titrations was planned to evaluate the analysis of Tenamene 60 with cupric chloride. This series included one titration of 10.0 mg. of Tenamene 60 in 50 ml. of solution during which a complete polarogram was run before the addition of any titrant and then after each addition of titrant in order to determine for certain the best

voltage at which to measure the current.

An attempt to prepare a 25.0 ml. solution of 250 mg. of Tenamene 60 in 2,2,4-trimethylpentane failed due to limited solubility of the sample. A similar attempt with 2-propanol was successful. Another solution one-tenth as concentrated was prepared from part of this solution by exact dilution. These two solutions were used as stock solutions for preparation of the solutions to be titrated. One of the titrating solutions, 0.050M cupric chloride in 2-propanol, was used to prepare the others by exact dilution. The burette assembly previously shown in Figure 7 was employed. The same burette filling was used for all titrations of one concentration of Tenamene 60.

Several titration curves at different voltages were made from the titration in which complete polarograms were run. As in the Santolene J titrations, the top of the cupric wave at -0.12 volt was found to be most suitable. The Tenamene 60 itself yielded a wave which had a decomposition potential of -1.25 volts and which ran into the carrier decomposition curve of the lithium nitrate. After the first addition of titrant, the polarogram showed two new waves close together. The total height of these waves increased linearly with continued addition of titrant. These waves were probably due to the cupric ion in the complex which was formed during the titration. In the vicinity of the end point, where the waves were of maximum size and hence easiest to measure, the decomposition potential of the bottom wave was -0.29 volt, and the half-wave potentials for the lower and upper waves were -0.32 volt and -0.60 volt, respectively. The waves, as would be expected, were about the same height. The results of the complete set of titrations are shown in Table III, and a typical titration curve is shown in Figure 10.

TABLE III

TITRATION OF TENAMENE 60 IN 50 ML. OF 0.05M LITHIUM NITRATE
 IN 1:1 2-PROPANOL-2,2,4-TRIMETHYLPENTANE WITH
 CUPRIC CHLORIDE IN 2-PROPANOL

Weight of Tenamene 60 (mg.)		10.0	1.00	0.100
Titration Concentration (mole/liter)		0.050	0.0050	0.0025
	Sample			
ML. of Titration Required	1	0.51	0.58	0.11
	2	0.48	0.56	0.10
	3	0.45	0.58	0.10
	4	0.45	-	-
Mean		0.47	0.57	0.10
Average Deviation		0.02	0.01	0.01
Mg. of Tenamene 60 per mg. of Cu ⁺⁺		6.7	5.5	6.3
Mg. of active component of Tenamene 60 per mg. of Cu ⁺⁺ , assuming that the additive supplied was 80% by weight active ingredient.		5.4	4.4	5.0

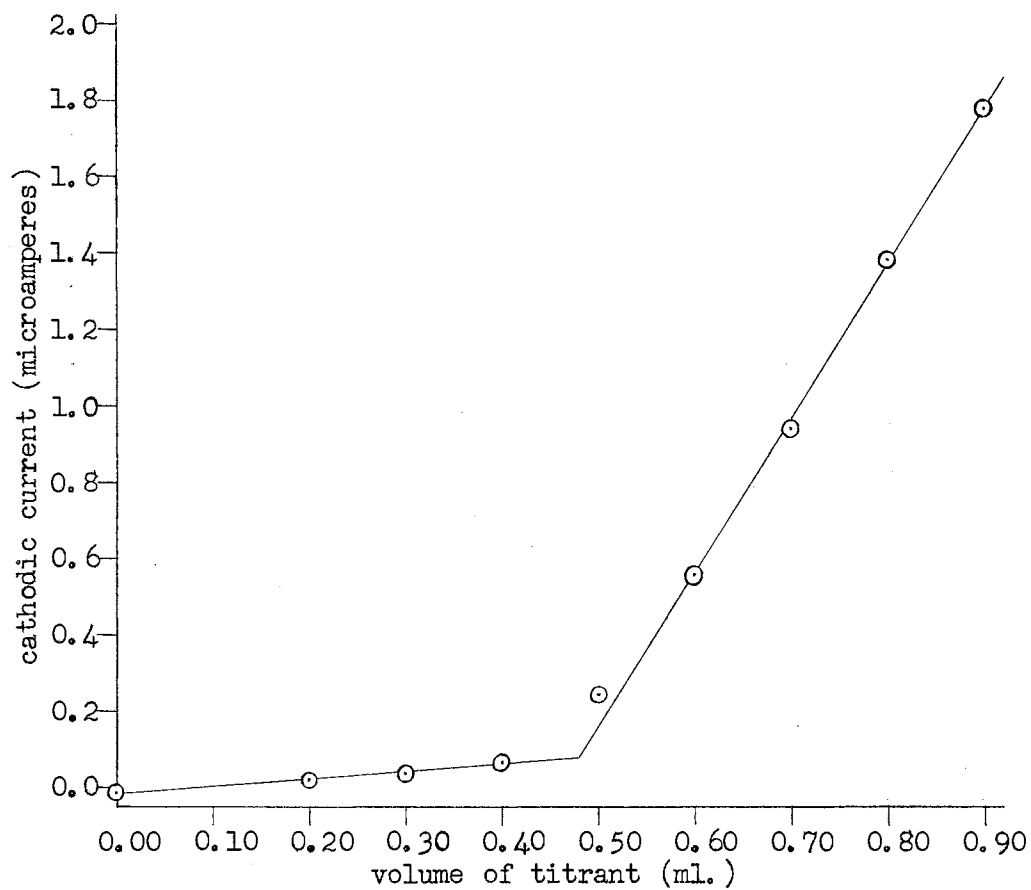


Figure 10. Titration Curve of 10.0 Mg. of Tenamene 60 in 50 ML. of 0.05M Lithium Nitrate in 1:1 2-Propanol-2,2,4-Trimethylpentane With 0.050M Cupric Chloride in 2-Propanol.

The results of these titrations, including the ease of obtaining good titration curves, indicated that this type of titration should be a good method of analysis. Apparently, the practical lower limit of concentration is dependent only on the accurate measurements of small currents and volumes. The agreement among the three sets of the number of milligrams of Tenamene 60 per milligram of cupric ion left something to be desired, and it was believed that the measurement of the volumes necessary to titrate the 0.100 mg. samples were too small for good accuracy, so another set of titrations was made using standardized titrants on 10.0 mg. and 0.30 mg. samples. The burette assembly previously shown in Figure 8 was employed, and the titrants were standardized in the same manner as described in the section on Santolene J. The results are shown in Table IV.

The results in Table IV indicate that the application of this method to routine analyses would involve only the standardization of titrants on known weights of Tenamene 60 or of its active component. Considering the coordination and stereochemical aspects involved, a mole-for-mole combination of cupric ions with the active component seems most likely. It is probably significant that the titration results indicate that the additive was 65% active instead of the stated 80%.

There was no noticeable effect on the titration curve caused by different time intervals between additions of titrant and measurements of current.

It may be possible to employ a colorimetric method for Tenamene 60. The solutions containing 10.0 mg. of Tenamene 60 became a deep lavender color and the solutions containing 1.00 mg. became pink upon addition of the cupric chloride solutions. The 0.100 mg. solutions apparently

TABLE IV

TITRATION OF TENAMENE 60 IN 50 ML. OF 0.05M LITHIUM NITRATE IN
1:1 2-PROPANOL-2,2,4-TRIMETHYLPENTANE WITH STANDARDIZED
CUPRIC CHLORIDE IN 2-PROPANOL

Titration of 10.0 mg. Samples with 0.0483M Cupric Chloride

Sample	End Point (ml.)	Deviation	Deviation ²
1	0.50	0.01	0.0001
2	0.52	0.03	0.0009
3	0.48	0.01	0.0001
4	0.45	0.04	0.0016
5	<u>0.49</u>	<u>0.00</u>	<u>0.0000</u>
Mean	0.49	0.02	0.00054

Standard Deviation = (Mean of Squared Deviations) ^{$\frac{1}{2}$} = 0.023

$\frac{\text{Standard Deviation}}{\text{Mean of End Points}} = 0.047 = 4.7\%$

Mg. of Tenamene 60 per mg. of Cu⁺⁺ 6.7

Mg. of active component of Tenamene 60 per mg. of Cu⁺⁺, assuming
that the additive supplied was 80% by weight active ingredient 5.4

Titration of 0.30 mg. Samples with 0.00215M Cupric Chloride

Sample	End Point (ml.)	Deviation	Deviation ²
1	0.33	0.01	0.0001
2	0.30	0.02	0.0004
3	0.32	0.00	0.0000
4	0.34	0.02	0.0004
5	<u>0.33</u>	<u>0.01</u>	<u>0.0001</u>
Mean	0.32	0.012	0.0002

Standard Deviation = (Mean of Squared Deviations) ^{$\frac{1}{2}$} = 0.014

$\frac{\text{Standard Deviation}}{\text{Mean of End Points}} = 0.044 = 4.4\%$

Mg. of Tenamene 60 per mg. of Cu⁺⁺ 6.9

Mg. of active component of Tenamene 60 per mg. of Cu⁺⁺, assuming
that the additive supplied was 80% by weight active ingredient 5.5

remained colorless.

Solubilities of Sulfonic Acids and Sulfonic Acid Salts

One of the great difficulties of working with sulfonic acids and their salts was that of getting them into solution. Many qualitative observations of the solubilities of sulfonic acids and salts were made during the course of the research. These observations are presented below as a guide for future research.

A solution of $6 \times 10^{-4}M$ benzenesulfonic acid in $0.10M$ tetramethylammonium chloride in 1-butanol resulted only after the acid had been in contact with the solution overnight, and an attempt to form a $6.3 \times 10^{-3}M$ solution of benzenesulfonic acid in petroleum ether was a failure.

Sodium benzenesulfonate exhibited decreasing solubility in absolute methanol, absolute ethanol and 1-propanol, being quite soluble in methanol and only slightly soluble in 1-propanol. It was impossible to form a $2 \times 10^{-3}M$ sodium benzenesulfonate solution in $0.10M$ tetramethylammonium chloride in 1-butanol, but after the sodium benzenesulfonate had been in contact with the solution for some time, a wave from sodium ion was obtained.

Solutions of $1.0 \times 10^{-3}M$ concentration of para-methylbenzenesulfonic acid, 2,5-dimethylbenzenesulfonic acid and 2-naphthalenesulfonic acid in $0.10M$ tetramethylammonium chloride in 1-butanol and a $1.0 \times 10^{-3}M$ solution of 2-naphthalenesulfonic acid in absolute methanol were prepared readily.

A solution of $2.0 \times 10^{-3}M$ 2-naphthalenesulfonic acid in 2,2,4-trimethylpentane could not be prepared. Much of the solid acid was still visible after five hours. Decanting the 2,2,4-trimethylpentane and

replacing it with an equal volume of 2-propanol caused the acid to dissolve almost immediately. In a mixture of the alcohol and 2,2,4-trimethylpentane, a $1.0 \times 10^{-3}M$ apparently true solution was obtained. This was put aside. When nineteen days later it was again observed, a somewhat flocculent precipitate was visible.

A solution of $2.0 \times 10^{-3}M$ sodium 2-naphthalenesulfonate in 2,2,4-trimethylpentane could not be formed. The salt was not soluble to any visible extent. A solution in an alcohol was not attempted.

An attempt to form a 0.0100M solution of sodium dinonylnaphthalenesulfonate in 2-propanol failed. The salt formed a cloudy dispersion, but vigorous shaking could not disperse the fine particles uniformly even for a short period of time. Enough sodium dinonylnaphthalenesulfonate in 2,2,4-trimethylpentane for $2.0 \times 10^{-3}M$ solution formed almost immediately what appeared to be a true solution. After standing about one-half hour the "solution" became somewhat cloudy in appearance. The next day the flask contained clear liquid and a quantity of flocculent precipitate at the bottom of the flask. Shaking the flask dispersed the precipitate throughout the liquid into an apparent suspension that was discernible with good lighting, and no visible separation occurred during the next four hours. Allowing it to stand overnight resulted in a visible precipitate again at the bottom of the flask. A $4.0 \times 10^{-4}M$ dispersion of the same salt in 2,2,4-trimethylpentane behaved similarly except that the quantity of solid that settled out was noticeably less. A milky dispersion was formed within five to ten minutes when 4.0×10^{-3} mole per liter of the salt was shaken with 2,2,4-trimethylpentane, but it was not allowed to stand for later observation.

A portion of the above $2.0 \times 10^{-3}M$ sodium dinonylnaphthalenesulfonate

dispersion was diluted 1:1 with 0.20M lithium chloride in 2-propanol solution. There was no visible evidence of a suspension, but the next day a very fine precipitate was present. Shaking dispersed the precipitate throughout the liquid, which then appeared cloudy; the same observation of a fine precipitate was made after the suspension had been standing fourteen days.

Available data of the solubilities of sulfonic acids and their salts in water show that a given acid usually has many times greater solubility than its corresponding sodium salt.

Titration and Polarographic Behavior of Sulfonic Acids and Their Salts

Exploratory experiments showed that all of the sulfonic acids employed gave good polarographic waves in solutions of 0.10M tetramethylammonium chloride in 1-butanol. These waves looked alike and had similar decomposition potentials. The results are tabulated below in Table V. Cell temperature was not controlled and room temperature was approximately 35° C.

TABLE V

DECOMPOSITION AND HALF-WAVE POTENTIALS OF SOME SULFONIC ACIDS

Acid	Concentration	E_d (volt)	$E_{\frac{1}{2}}$ (volt)
Benzenesulfonic	$1 \times 10^{-3}M$	-0.87	-1.02
p-Toluenesulfonic	$1 \times 10^{-3}M$	-0.89	-1.00
2,5-Dimethylbenzenesulfonic	$5 \times 10^{-4}M$	-0.91	-1.04
2-Naphthalenesulfonic	$6 \times 10^{-4}M$	-0.88	-0.99

In this same carrier and solvent combination, sodium benzenesulfonate and sodium dinonylnaphthalenesulfonate each gave only small waves

characteristic of sodium ion. Since all of the sulfonic acids gave similar characteristic waves which were different from those of the two salts, a titration of the acid with a base appeared feasible. A $5 \times 10^{-4}M$ solution of *p*-toluenesulfonic acid in 0.10M tetramethylammonium chloride in 1-butanol was titrated with $9 \times 10^{-3}N$ potassium hydroxide in 0.10M tetramethylammonium chloride in 1-butanol. Each addition of titrant reduced the wave height linearly. The resultant titration curve of current vs. volume of titrant was as shown in Figure 5c. The establishment of this type of titration as a method for the quantitative estimation of sulfonic acids would result in not only a novel method for these acids, but also a method which might lend itself to the quantitative estimation of the sulfonic acid salts, if the latter could be suitably converted to the acids.

A solution of 1.00 ml. of aqueous 6N sulfuric acid plus 60 ml. of 1-butanol plus 60 ml. of 2,2,4-trimethylpentane was prepared. The addition of the acid to the butanol resulted in a single phase after shaking, and a single phase was still present after the 2,2,4-trimethylpentane was added and shaken. The theory behind this was that if a sulfonic acid salt were added to such a solution, the salt might be converted to the acid, which could then be estimated by wave height, the excess sulfuric acid acting as the supporting electrolyte. A polarogram was run on 50 ml. of the above solution. A curve which could not be topped was the result. Its decomposition potential was -0.94 volt. The temperature was about 35° C. This value is close to the decomposition potentials mentioned previously for the sulfonic acids in 0.10M tetramethylammonium chloride in 1-butanol. Sodium dinonylnaphthalenesulfonate was added to the solution despite the fact that a wave had already appeared. Enough

of the salt was added to make the solution $5.1 \times 10^{-4}M$. The curve of this solution coincided with the first. These studies were dropped for a time, and when they were resumed, 1-butanol was no longer used, 2-propanol being used exclusively. The use of tetramethylammonium chloride had also been suspended, the reasons for these changes being those given earlier. A curve of $1.0 \times 10^{-3}M$ 2-naphthalenesulfonic acid in a solution of 50 ml. of 1:1 2-propanol-2,2,4-trimethylpentane containing 1 ml. of aqueous concentrated hydrochloric acid was another which could not be topped; the decomposition potential was again -0.94 volt, and the temperature was $25.0^{\circ}C$. These experiments with sulfuric acid and hydrochloric acid indicated that the waves obtained with the sulfonic acids might not have been due to a particular property of the sulfonic acid group; in fact all of these waves might have been the result of solvated protons alone, so that the kind of wave observed was independent of the anion of the acid, if the acid were strong. Santolene C, mentioned earlier, which is a fatty-acid type additive, gave a more negative half-wave potential. A solution of $2.4N$ hydrochloric acid was prepared by diluting one volume of aqueous concentrated hydrochloric acid to five times its original volume with 2-propanol. This was added from a microburette into a 50 ml. solution of $0.10M$ lithium chloride in 1:1 2-propanol-2,2,4-trimethylpentane solution at $25.0^{\circ}C$. from which the residual current and carrier decomposition curve had been obtained. A total of 0.05 ml. hydrochloric acid was added to the solution in the cell, giving a concentration of $2 \times 10^{-3}M$ hydrochloric acid. This produced a wave similar to the sulfonic acid waves with a decomposition potential of -1.04 volts. One peculiarity of the hydrochloric acid wave-front was observed, this occurring also with 2-naphthalenesulfonic acid. When the

concentration of the acid was about $1 \times 10^{-3}M$ or less, there was usually a single wave-front. At a concentration of about $2 \times 10^{-3}M$ and greater, two wave-fronts appeared. When lines were drawn through each wave-front on the hydrochloric acid polarogram and extended past the junction of the waves, the two lines were found to be close together and almost parallel to one another. The space between them at the junction of the waves represented approximately 0.013 volt. The height of each wave was approximately one-half the total wave height. The half-wave potentials were -1.28 volts for the top wave and -1.12 volts for the bottom wave. When a single wave-front was taken as a line drawn between the two lines of the separate wave-fronts, the half-wave potential was -1.20 volts. The decomposition and half-wave potentials for a wave of approximately $1 \times 10^{-3}M$ hydrochloric acid were -1.04 volts and -1.15 volts, respectively.

All of these experiments indicated that the waves resulting from these acids by the reduction of the solvated proton (if that is what occurred) might be the basis for the quantitative determination of any kind of strong acid in this type of nonaqueous medium. It also might be used to determine salts of sulfonic acids, if these could be converted quantitatively into the sulfonic acids themselves. It was thought that dry hydrogen chloride might bring about this conversion in hydrocarbon solutions.

Anhydrous hydrogen chloride, therefore, was passed into a suspension of sodium dinonylnaphthalenesulfonate in 2,2,4-trimethylpentane. Soon a fine white solid appeared and settled. This precipitate showed the characteristic yellow color of sodium when subjected to a platinum wire flame test. This was evidence that the hydrogen chloride had converted at least part of the salt to the acid.

By employing the vessel shown in Figure 11, anhydrous hydrogen chloride saturated with 2,2,4-trimethylpentane was bubbled for fifteen minutes through 25 ml. of 2,2,4-trimethylpentane containing nothing else. The saturating vessel was disconnected from the supply of hydrogen chloride and connected to a supply of dry nitrogen saturated with 2,2,4-trimethylpentane. When white traces of ammonium chloride no longer appeared at the outlet on holding a bottle of concentrated ammonium hydroxide near it, the nitrogen was bubbled through about fifteen minutes longer. This total time was fifty-five minutes. The 2,2,4-trimethylpentane was diluted 1:1 with a solution of 0.20M lithium chloride in 2-propanol. Its polarographic curve showed no trace of the hydrogen chloride; only the curve due to the residual current and the carrier decomposition appeared. In this way it was shown that it was possible to introduce hydrogen chloride for converting the salt to the acid and to remove quantitatively the excess hydrogen chloride.

The next step was to try to develop a satisfactory titration procedure for a sulfonic acid. Unless this could be done, any conversion of a salt to its acid would have been to no avail. The most suitable acid available was 2-naphthalenesulfonic acid. This was a brown powder which appeared dry. It absorbed water from the atmosphere slowly compared with the lower molecular weight sulfonic acids and could be kept reasonably dry. It was, therefore, easily handled, and samples could be weighed with reasonable accuracy. Another advantage of 2-naphthalenesulfonic acid was its molecular weight, which was nearer to those of the acids whose salts are commonly used for petroleum additives than were the molecular weights of other available sulfonic acids.

A 250 ml. dispersion of 2.00×10^{-3} M sulfonic acid in 0.10M lithium

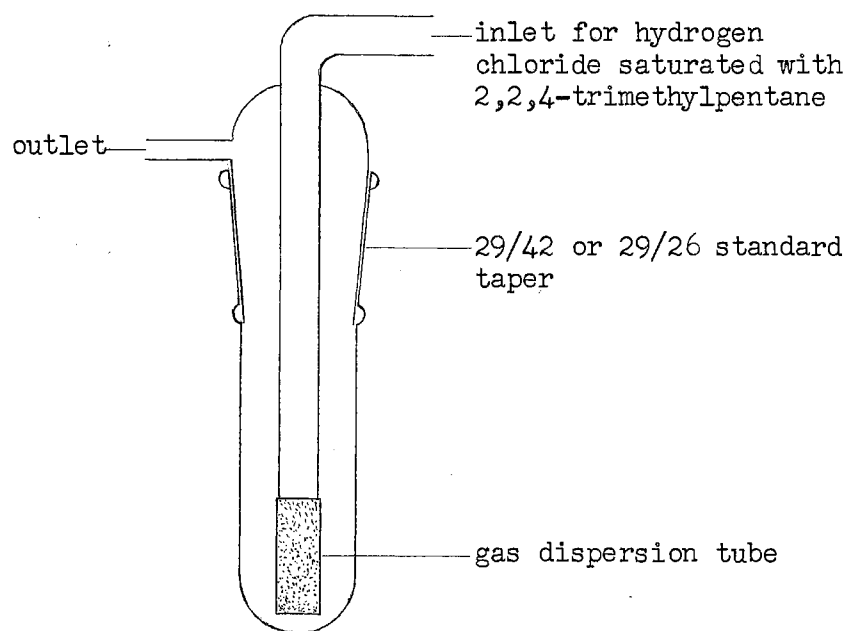


Figure 11. Cutaway View of Vessel for Saturating Hydrocarbon Solutions With Anhydrous Hydrogen Chloride.

chloride in 1:1 2-propanol-2,2,4-trimethylpentane was prepared. Samples were measured into 50 ml. glass-stoppered volumetric flasks. A titrant of potassium hydroxide in 2-propanol was prepared by adding a weighed quantity of potassium hydroxide pellets to 250 ml. of the alcohol in a 500 ml. polyethylene wash bottle. The concentration of the potassium hydroxide solution was such that five amperometric titrations could be performed with one filling of the burette. The 2-propanol previously had been degassed in the wash bottle with nitrogen saturated with 2-propanol. After the addition of the potassium hydroxide, the bubbling of the nitrogen through the solution was continued, with occasional shaking, until the potassium hydroxide had dissolved. The potassium hydroxide solution was then ready for use. At a convenient time after the filling of the burette used for the amperometric titrations, the potassium hydroxide solution was standardized against a less concentrated standard aqueous solution of hydrochloric acid. The water-to-alcohol ratio was greater than one at the equivalence point, so the titration was essentially aqueous. Phenolphthalein was the indicator. The concentration of the potassium hydroxide solution in the polyethylene bottle was the same when analyzed a week later.

The contents of each of the five 50 ml. volumetric flasks were in turn emptied into the electrolysis cell, degassed, and titrated with the potassium hydroxide solution. A full polarogram, which for each sample consisted of two waves closely spaced, was obtained before any titrant was added. Each drop of titrant formed a single piece of white solid, presumably the potassium salt of 2-naphthalenesulfonic acid, as it came into contact with the unstirred solution in the cell. The solid sank rapidly to the bottom. The solution was stirred by moving the gas

dispersion tube to break up the lumps in order to free unreacted potassium hydroxide which might have been occluded in the solid, the action of the nitrogen bubbles themselves not being enough to move the solid. This hand stirring was obviated considerably by submerging the gas dispersion tube prior to an addition of titrant, the copious nitrogen bubbles in the solution and breaking its surface preventing the formation of a single lump of precipitate from each drop. After each addition of titrant the applied voltage was decreased until the recorder pen registered a current slightly less than the top of the wave of the remaining sulfonic acid. The motor driven bridge then was set in operation, and the top part of the polarographic wave and a bit of the carrier decomposition curve were recorded. The current was measured at -1.49 volts for each addition of titrant. Table VI gives the results of the titrations. One of the titration curves is shown in Figure 12.

The mean of the end points of five titrations represented slightly less than 94% of the acid, if the weight of solid acid used to prepare the samples was assumed to be 100% acid. Since this was doubtful, three samples of 2-naphthalenesulfonic acid were titrated with the same 0.1644N solution of potassium hydroxide in 2-propanol in order to determine the quantity of acid in the solid. Each sample of about 0.6 g. was weighed accurately, dissolved in about 35 ml. of distilled water, and titrated with the base. Phenolphthalein was the indicator. The average of the three samples showed 98.4% acid with a mean deviation of 0.3%. The mean of the end points of the amperometric titrations represented slightly more than 95% of the acid supposed to be present; this is the value given with Table VI.

In an effort to improve the above accuracy of 95%, another group of

TABLE VI

TITRATION OF $1.97 \times 10^{-3}M$ 2-NAPHTHALENESULFONIC ACID IN 0.10M LITHIUM CHLORIDE IN 1:1
2-PROPANOL-2,2,4-TRIMETHYLPENTANE WITH 0.1644N POTASSIUM HYDROXIDE IN 2-PROPANOL

Sample (50 ml.)	1	2	3	4	5	Mean
End Point (ml.)	0.55	0.60	0.57	0.57	0.58	0.57
Deviation	0.02	0.03	0.00	0.00	0.01	0.012
Deviation ²	0.0004	0.0009	0.0000	0.0000	0.0001	0.00028
E_d (-volt)	1.05	1.04	1.05	1.03	1.05	1.04
$E_{1/2}$ of Waves (-volt)						
Lower	1.12	1.12	1.12	1.11	1.12	1.12
Upper	1.28	1.28	1.29	1.28	1.32	1.29
Average of Upper & Lower	1.20	1.20	1.20	1.20	1.22	1.20
Total Wave	1.20	1.21	1.19	1.20	1.23	1.21
One Wave Height Divided by Total Wave Height						
Lower	0.444	0.458	0.540	0.487	0.413	0.468
Upper	0.556	0.542	0.460	0.513	0.587	0.532
E.M.F. Difference at Junction of Waves	0.016	0.020	0.027	0.012	0.027	0.020

Standard Deviation = (Mean of Squared Deviations)^{1/2} = 0.017

$\frac{\text{Standard Deviation}}{\text{Mean of End Points}} = 0.030 = 3.0\%$

Mean of End Points = 95% of Acid Present

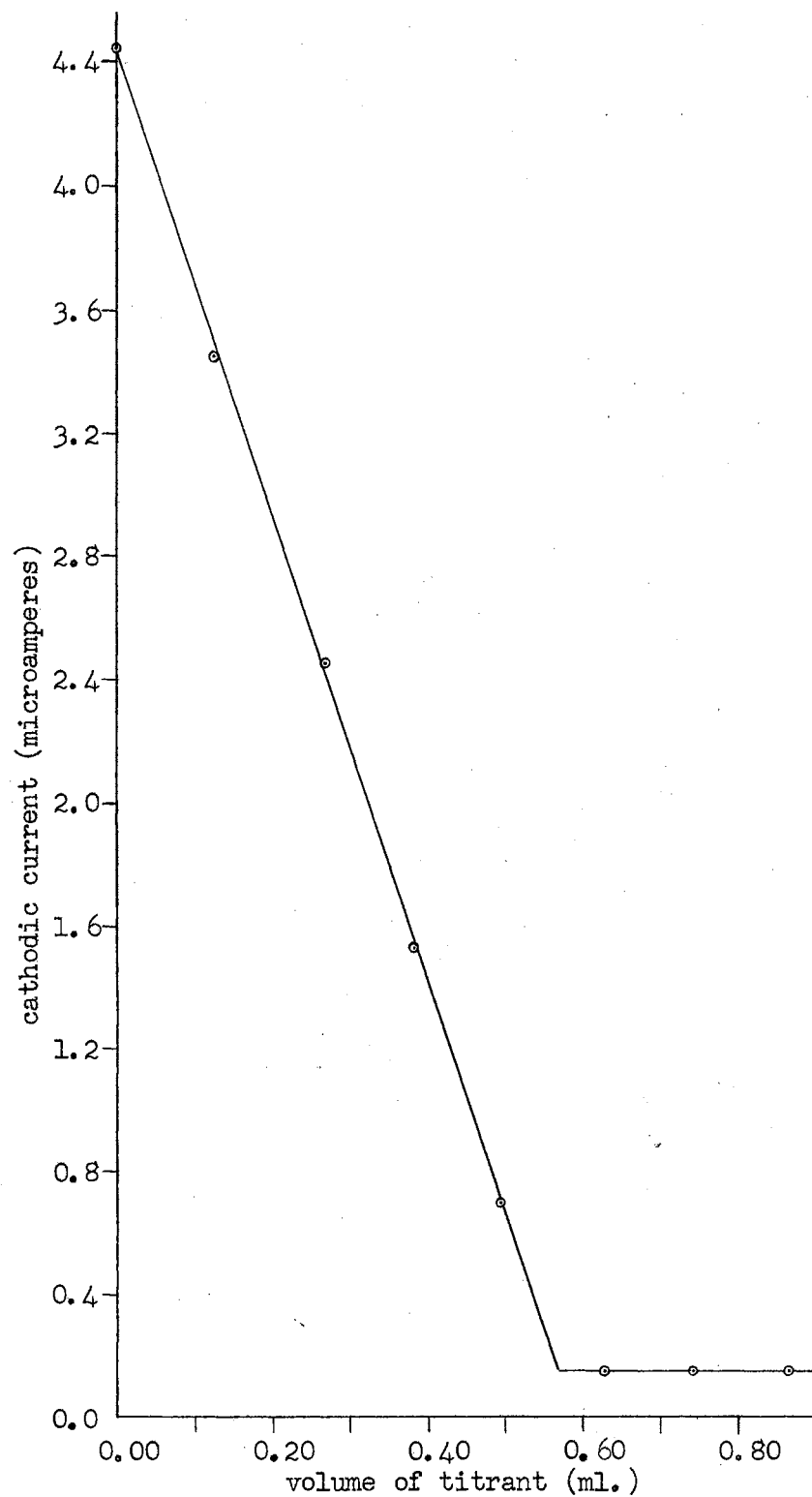


Figure 12. Titration Curve of 50 ML. of 1.97×10^{-3} M 2-Naphthalenesulfonic Acid in 0.10M Lithium Chloride in 1:1 2-Propanol-2,2,4-Trimethylpentane With 0.1644N Potassium Hydroxide in 2-Propanol.

titrations was performed. These titrations differed from those above in that each volumetric flask was rinsed after its contents were poured into the cell, and the rinses were added to the solution in the cell.

A 500 ml. dispersion of 2-naphthalenesulfonic acid in 2-propanol was prepared. Its concentration was $4.00 \times 10^{-3}M$ based on the weight of solid and $3.94 \times 10^{-3}M$ based on the solid as 98.4% acid. The 500 ml. dispersion was divided into two 250 ml. parts. To one part was added the quantity of lithium chloride necessary to make a 0.20M solution, and then it was diluted to 500 ml. with 2,2,4-trimethylpentane to yield a dispersion of $1.97 \times 10^{-3}M$ 2-naphthalenesulfonic acid in 0.10M lithium chloride in 1:1 2-propanol-2,2,4-trimethylpentane solution. Five samples were measured into 50 ml. glass-stoppered volumetric flasks. After the contents of a flask were added to the titration cell, the flask was rinsed with two successive 3.0 ml. portions of 0.10M lithium chloride in 1:1 2-propanol-2,2,4-trimethylpentane solution, and these in turn were poured into the titration cell. The results, shown in Table VII, indicate that the accuracy and standard deviation approached that which could be expected with the type of equipment used.

In order to compare the amperometric titration with the ordinary aqueous indicator method, the other half of the original dispersion, the 250 ml. of $3.94 \times 10^{-3}M$ 2-naphthalenesulfonic acid in 2-propanol, was titrated with the same 0.1579N potassium hydroxide in 2-propanol solution used for the amperometric titrations.

The samples of acid dispersion, 20-25 ml., were delivered from a burette into 25 ml. of distilled water in order to maintain an essentially aqueous titration. Phenolphthalein was used as indicator. Since the volumes of the samples varied, it is easier to present the data in

TABLE VII

TITRATION OF $1.97 \times 10^{-3}M$ 2-NAPHTHALENESULFONIC ACID IN 0.10M LITHIUM CHLORIDE IN 1:1
2-PROPANOL-2,2,4-TRIMETHYLPENTANE WITH 0.1579N POTASSIUM HYDROXIDE IN 2-PROPANOL

Sample (50.0 ml.)	1	2	3	4	5	Mean
End Point (ml.)	0.62	0.62	0.61	0.61	0.63	0.62
Deviation	0.00	0.00	0.01	0.01	0.01	0.006
Deviation ²	0.0000	0.0000	0.0001	0.0001	0.0001	0.00006
E_d (-volt)	1.01	1.02	1.04	1.02	1.02	1.02
$E_{1/2}$ of Waves (-volt)						
Lower	1.11	1.10	1.10	1.09	1.09	1.10
Upper	1.29	1.26	1.26	1.25	1.24	1.26
Average of Upper & Lower	1.20	1.18	1.18	1.17	1.16	1.18
Total Wave	1.20	1.19	1.19	1.18	1.16	1.18
One Wave Height Divided by Total Wave Height						
Lower	0.461	0.453	0.478	0.522	0.501	0.483
Upper	0.539	0.547	0.522	0.478	0.499	0.517
E.M.F. Difference at Junction of Waves	0.012	0.016	0.016	0.016	0.020	0.016

Standard Deviation = (Mean of Squared Deviations)^{1/2} = 0.008

$\frac{\text{Standard Deviation}}{\text{Mean of End Points}} = 0.013 = 1.3\%$

Mean of End Points = 99.5% of Acid Present

terms of molarity of the acid calculated from the volume of base used.

The results are presented in Table VIII.

TABLE VIII

TITRATION OF $3.94 \times 10^{-3}M$ 2-NAPHTHALENESULFONIC ACID IN APPROXIMATELY
50% 2-PROPANOL-50% WATER MIXTURE WITH 0.1579N
POTASSIUM HYDROXIDE IN 2-PROPANOL

M of Acid $\times 10^3$	Deviation $\times 10^5$	Deviation ² $\times 10^{10}$
4.20	1	1
4.16	3	9
4.25	6	36
4.09	10	100
4.18	1	1
4.15	4	16
4.29	10	100
4.18	1	1
<u>4.20</u>	<u>1</u>	<u>1</u>
Mean 4.19	4	29

$$\text{Standard Deviation} = (\text{Mean of Deviation}^2)^{\frac{1}{2}} = 5.4 \times 10^{-5}$$

$$\frac{\text{Standard Deviation}}{\text{Mean of M of Acid}} = 0.013 = 1.3\%$$

$$\text{Mean of End Points} = 106\% \text{ of Acid Present}$$

The high mean of the end points was due probably to the presence of carbon dioxide. The usual procedure in aqueous acid titrations is to boil the solution to expel carbon dioxide. This was impractical due to the volatile nature of 2-propanol. Also, the solubility of air in organic solvents is greater than in water, so that boiling may be impractical from this viewpoint also.

The sulfonic acid titration was next applied to sodium dinonylnaphthalenesulfonate after conversion to the acid. A 250 ml. dispersion of $4.00 \times 10^{-3}M$ sodium dinonylnaphthalenesulfonate in 2,2,4-trimethylpentane was prepared. Samples were measured out into 25 ml. glass-stoppered

volumetric flasks. In its turn each sample was poured into the hydrogen chloride saturator previously shown in Figure 11. A few ml. of 2,2,4-trimethylpentane were used to rinse the volumetric flask. The rinse was added to the rest of the sample. Anhydrous hydrogen chloride was bubbled first through 2,2,4-trimethylpentane and then through the salt dispersion for at least one-half hour. This length of time might not have been necessary, because a white cloud of sodium chloride appeared within less than a minute after the hydrogen chloride was started through the sample. The solution was then degassed with nitrogen for one hour to remove unused hydrogen chloride. Finally, the solution and as much precipitate as possible were transferred to the original 25 ml. volumetric flask. Usually the volume was within a milliliter or two of the 25 ml. mark. Some of the solution evaporated during the hydrogen chloride saturation treatment, because a gas dispersion tube was not used in the tower containing 2,2,4-trimethylpentane preceding the sample saturator. If the volume of the sample was less than 25 ml., it was brought up to the mark with 2,2,4-trimethylpentane, and poured into a 50 ml. glass-stoppered volumetric flask. The saturator and the 25 ml. flask were rinsed twice with 0.2M lithium chloride in 2-propanol, the rinses being added to the contents of the 50 ml. flask. At all times as much of the sodium chloride precipitate as possible was transferred to the 50 ml. flask. The flask was then filled to the mark. If the volume of the sample was more than 25 ml. after the hydrogen chloride treatment, the distance of the meniscus above the mark was noted, and since the neck sizes of the 25 and 50 ml. flasks were very similar, the 50 ml. flask was filled to approximately twice this distance above its mark. The contents of the flask were shaken well and emptied into the titration cell. Three

samples were titrated. Table IX shows the titration results and polarographic data. It is interesting to note that just one wave-front appeared in each of the polarograms recorded before the addition of titrant.

One of the 25 ml. samples of the above dispersion of $4.00 \times 10^{-3}M$ sodium dinonylnaphthalenesulfonate in 2,2,4-trimethylpentane was transferred quantitatively to a 100 ml. volumetric flask, diluted to the mark, shaken well, and portions were measured out into 25 ml. glass-stoppered volumetric flasks to yield $1.00 \times 10^{-3}M$ samples. Three samples were treated like the $4.00 \times 10^{-3}M$ samples and titrated with potassium hydroxide in 2-propanol. The results are also given in Table IX.

The tubing carrying hydrogen chloride to the saturating vessel was left exposed to the air when not used. The hydrogen chloride in the tubing collected moisture from the air and also acted upon the tubing itself. Moisture alone or a combination of moisture and plasticizer from the tubing collected inside the tubing. If this was not cleaned from the tubing before it was attached to the saturating vessel, and some of it entered the sample within, the sample was ruined, because the hydrogen chloride in this liquid could not be removed with nitrogen. The problem was avoided by wiping the inside of the tubing before each use with a pipe cleaner of large size.

Table IX shows that for each concentration of salt, the quantity of titrated acid represented less than the original concentration of salt. If the factor were constant in each case, an analytical method could be based on this percentage conversion and the titration could be used. However, the percentage conversion of salt to acid apparently decreased with decreased concentration of salt in a sample; consequently, this

TABLE IX

TITRATION WITH POTASSIUM HYDROXIDE IN 2-PROPANOL OF SODIUM DINONYL-
NAPHTHALENESULFONATE CONVERTED IN 2,2,4-TRIMETHYLPENTANE BY
DRY HYDROGEN CHLORIDE TO DINONYLNAPHTHALENESULFONIC
ACID AND MIXED WITH EQUAL VOLUME OF 0.20M
LITHIUM CHLORIDE IN 2-PROPANOL

$4.00 \times 10^{-3}M$ Salt; 0.1644N Potassium Hydroxide

Sample	End Point (ml.)	Deviation	E_d (-volt)	$E_{\frac{1}{2}}$ (-volt)
1	0.45	0.01	1.05	1.20
2	0.46	0.00	1.09	1.26
3	<u>0.46</u>	<u>0.00</u>	<u>1.04</u>	<u>1.20</u>
Mean	0.46	0.003	1.06	1.22

Mean of End Points = 76% of Original Salt in 2,2,4-Trimethylpentane

$1.00 \times 10^{-3}M$ Salt; 0.0382N Potassium Hydroxide

Sample	End Point (ml.)	Deviation	E_d (-volt)	$E_{\frac{1}{2}}$ (-volt)
1	0.36	0.01	1.02	1.17*
2	0.39	0.02	1.03	1.15
3	<u>0.37</u>	<u>0.00</u>	<u>1.02</u>	<u>1.14</u>
Mean	0.37	0.01	1.02	1.15

Mean of End Points = 57% of Original Salt in 2,2,4-Trimethylpentane

*Two waves appeared. The value given above was taken from a line drawn between the extended lines at the two wave fronts. The $E_{\frac{1}{2}}$ s of the lower and upper waves were -1.25 volts and -1.09 volts, respectively. The average of these is -1.17 volts.

method of conversion needs further study. It is important to note that the ranges of the end points of the data in Table IX were good enough so that with a 100% conversion of salt to acid the accuracy of this type of analysis would be extremely good.

CHAPTER VII

SUMMARY AND CONCLUSIONS

As was mentioned previously, the objective of this research was to study several additives and to develop quantitative analytical methods for a few of those selected as characteristic types. This objective was accomplished for the most part, and in addition a number of interesting and important facts were discovered.

Only preliminary experiments were performed with the majority of the additives. Several of them, Paradyne HO-2 Enjay, Oronite Dispersant FO, Nasul EDS, Santolene H, Gulf 178 and Santolene C, gave waves which could be expected to serve for quantitative determinations, if concentrations were sufficiently great or if interferences were not present. Applications could be made to problems such as the checking of the uniformity of different lots from the suppliers.

A method of analysis with an accuracy that may be acceptable for blending and control purposes was developed for the amine additive, Santolene J. More generally, this analysis gives a method of approach to the determination of any amine-type additive.

The method for titration of the chelating agent, Tenamene 60, is precise and quite sensitive, and the accuracy as determined by the comparison of the results of the different weights titrated is excellent. The Tenamene 60 also gave a polarographic wave upon which a fairly sensitive polarographic method could be based if there were no interfering

waves present.

The sulfonic acid amperometric titration and the polarographic behavior of hydrochloric and sulfuric acids present a new method of titrating very low concentrations of acids and bases in nonaqueous media. If suitable methods for converting the salts of sulfonic acids to the acids themselves could be developed, these salts certainly could be determined by amperometric titrations. From the experimental information obtained, it seems highly probable that usual polarographic methods could be employed for the determination of strong acids, if a nonaqueous polarograph were employed.

Perhaps amine additives could be titrated with sulfonic acids giving products which would be soluble, so that the disadvantages of a precipitation reaction would not be present as with cupric chloride. However, the sulfonic acid may react with total amine present, including that already expended in its role as additive. The utility of this proposal could be determined only by further experiments.

Because the dropping mercury electrode was used in this research, one advantage of amperometric titrations for additive analysis became quite evident. Many of these additives act as surface active agents, and the alcohols and hydrocarbons employed have considerably lower surface tensions than that of water. Either of these factors leads to greater ease of wetting the inside of a capillary and frequently results in erratic behavior of the dropping mercury electrode. Although some electrodes lasted for dozens of runs, other electrodes became erratic after only a few runs. It was a simple matter to replace a capillary with a new one and be ready immediately for another run without the need for calibrating the electrode.

It became very evident during this work that the cell employed was poorly suited to rapid work. The main problem was the time required to ready the cell for each run. The author's conception of a cell for rapid work is shown in Figure 13. The use of aqueous reference electrodes would greatly simplify preparations. The probes projecting from the reference electrodes into the electrolysis cell could be filled with agar gel and could be capped on the ends with an inert film. The method of capping would depend on the type of film, but a flexible film, "Saran" wrap for example, could be held in place by a tightly wrapped strip or twisted cord of the same film. This cell could rest on the bottom of a shallow constant-temperature bath, so that a bar magnet inside the cell could be rotated by a magnetic stirrer beneath the bath. With this type of cell design it would be possible to position the probes very close to the dropping mercury electrode, so that the cell resistances, even through the membrane, may well be no greater than with the cell used in this research.

Perhaps ultimately a tetra-alkyl or tetra-aryl ammonium compound which would dissolve readily and sufficiently in a hydrocarbon alone could be prepared, so that an analysis could be run without mixing the hydrocarbon with an alcohol.

The high resistance polarograph does not lend itself to rapid, routine amperometric analyses because of the necessity of running a small part of the polarogram for each current measurement. It is impossible to set the applied voltage to give a constant effective voltage for more than one point on a titration curve, because the iR -drop changes when the current through the cell changes, and hence the effective e.m.f. changes. This problem has been anticipated, however,

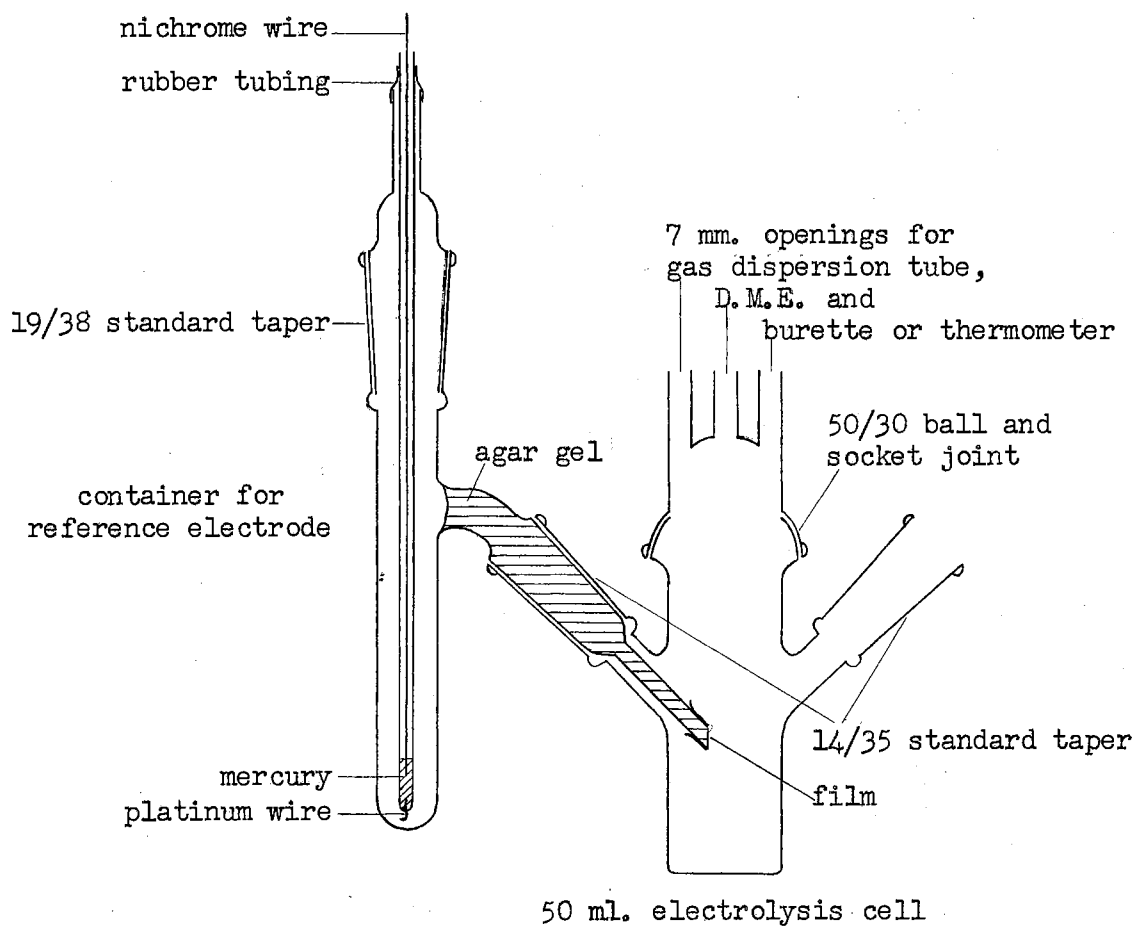


Figure 13. Cutaway View of Proposed Electrolysis Cell Assembly for Rapid Work.

and the solution is the result of other work by the author's adviser.

CHAPTER VIII

A SELECTED BIBLIOGRAPHY

- (1) Adams, R. N., and Voorhies, J. D., *Anal. Chem.* 29, 1690 (1957).
- (2) Altieri, V. J., "Gas Analysis and Testing of Gaseous Materials," p. 103, American Gas Association, New York, 1945.
- (3) Arthur, P., Lewis, P. A., and Lloyd, N. A., *Anal. Chem.* 26, 1853 (1954).
- (4) Arthur, P., and Lyons, H., *Ibid.*, 24, 1422 (1952).
- (5) Burr, I., "Engineering Statistics and Quality Control," p. 45, McGraw-Hill, New York, 1953.
- (6) Deschamps, P. M., *Bull. soc. chim. France* 1956, 126.
- (7) Detty, W. E., Heston, B. O., and Wender, S. H., *J. Am. Chem. Soc.* 77, 162 (1955).
- (8) Freedman, R. W., *Anal. Chem.* 28, 247 (1956).
- (9) Gaylor, V. F., Conrad, A. L., and Landerl, J. H., *Ibid.*, 29, 228 (1957).
- (10) Gordon, B. E. and Urner, R. S., *Ibid.*, 25, 897 (1953).
- (11) Grimes, M. D., Puckett, J. E., Newby, B. J. and Heinrich, B. J., *Ibid.*, 27, 152 (1955).
- (12) Gucker, F. T. Jr., and Peterson, A. H., *Ibid.*, 25, 1577 (1953).
- (13) Heilbron, I. M., "Dictionary of Organic Compounds," Vol. IV, p. 429, Oxford University Press, 1953.
- (14) Heyrovsky, J., *Chem. Listy.* 16, 256 (1922).
- (15) Heyrovsky, J., *Phil. Mag.* 45, 303 (1923).
- (16) Heyrovsky, J., "Polarographie," Vienna, Springer Verlag, 1941.
- (17) Heyrovsky, J., and Ilkovic, D., *Coll. Czech. Chem. Commun.* 7, 198 (1935).

- (18) Heyrovsky, J., and Shikata, M., *Rec. trav. chim.* 44, 496 (1925).
- (19) Hinsvark, O. N., and Stone, K. G., *Anal. Chem.* 28, 334 (1956).
- (20) Horning, E. C., "Organic Synthesis," Collective Vol. III, p. 72, Wiley and Sons, New York, 1955.
- (21) Ilkovic, D., *Coll. Czech. Commun.* 6, 498 (1934).
- (22) Ilkovic, D., *J. chim. phys.* 35, 129 (1938).
- (23) Ilkovic, D., Congress of Practical Polarography, Bratislava, Slovakia, February 1952; *Anal. Chem.* 24, 917 (1952) (by title).
- (24) Jackson, W., Jr., and Elving, P. J., *Anal. Chem.* 28, 378 (1956).
- (25) Kolthoff, I. M., and Harris, W. E., *Ind. Eng. Chem., Anal. Ed.* 18, 161 (1946).
- (26) Kolthoff, I. M., and Harris, W. E., *Anal. Chem.* 21, 963 (1949).
- (27) Kolthoff, I. M., and Lingane, J. J., "Polarography," Vol. II, 2nd ed., p. 952, Interscience, New York, 1952.
- (28) Kolthoff, I. M., and Pan, Y., *J. Am. Chem. Soc.* 61, 3402 (1939).
- (29) Kucera, G., *Ann. Physik.* 11, 529 (1903).
- (30) Laitinen, H. A., Jennings, W. P., and Parks, T. D., *Ind. Eng. Chem., Anal. Ed.* 18, 355 (1946).
- (31) Liberti, A. and Cervone, E., *Atti accad. Nazl. Lincei, Rend. classe sci. fis., mat. e nat.* 8, 613 (1950).
- (32) Lingane, J. J., and Loveridge, B. A., *J. Am. Chem. Soc.* 72, 438 (1950).
- (33) Lloyd, N. A., "A New Polarograph For Use With High Resistance Nonaqueous Solutions," Ph.D. thesis, Oklahoma State University, 1955.
- (34) Mann, G., *Magyar Kem. Folyoirat* 61, 26 (1955).
- (35) Meites, L., "Polarographic Techniques," p. 45, Interscience, New York, 1955.
- (36) Nicholson, M. M., *Anal. Chem.* 27, 1364 (1955).
- (37) Pickard, P. L., and Neptune, W. E., *Ibid.*, 27, 1358 (1955).
- (38) Pierce, W. G., and Haenisch, E. L., "Quantitative Analysis," 3rd ed., p. 237, Wiley and Sons, New York, 1948.
- (39) *Ibid.*, p. 241.

- (40) Ibid. , p. 241.
- (41) Ibid. , p. 247.
- (42) Rosenberg, S. , Perrone, J. D. and Kirk, P. L. , Anal. Chem. 22, 1186 (1950).
- (43) Salomon, E. , Z. physik. Chem. 24, 55 (1897).
- (44) Salomon, E. , Z. Electrochem. 4, 71 (1897).
- (45) Sawyer, D. T. , Pecsok, R. L. , and Jensen, K. K. , Anal. Chem. 30, 481 (1958).
- (46) Strehlow, H. , and von Stackelberg, M. , Z. Elektrochem. 54, 51 (1950).
- (47) Stromberg, A. G. , and Zelyanskaya, A. I. , Zhur. Anal. Khim. 4, 286 (1949).
- (48) Tomicek, O. , Blazek, A. and Roubal, Z. , Chem. Zvesti 4, 479 (1950).
- (49) Ulrich, F. , "Polarographic Behavior of Certain Organo-Boron Compounds in Nonaqueous Solutions," unpublished Ph.D. thesis, Oklahoma State University, 1956.
- (50) Zhdanov, A. K. , Tseitlin, R. I. , and Yakubov, A. M. , Zavodskaya Lab. 21, 7 (1955).
- (51) Zyká, J. , Chem. Listy. 48, 1864 (1954).

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*Trademark for DuPont acrylic fiber.