# HIGH FREQUENCY TITRATION OF SOME MONOBASIC AND DIBASIC ACIDS IN NON-AQUEOUS MEDIA

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Lawrence LaRoy Fleck
1958

# HIGH FREQUENCY TITRATION OF SOME MONOBASIC AND DIBASIC ACIDS IN NON-AQUEOUS MEDIA

By

**Lawrence LaRoy Fleck**

A THESIS

Submitted to the College of Science and Arts of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1958

# ACKNOWLEDGMENTS

The author is deeply indebted to Dr. Andrew Timnick for his guidance and his help given throughout the entire investigation and preparation of this thesis.

Acknowledgment is also extended to Mr. Dante A. Constanzo for his helpful suggestions in the construction of the high frequency titration apparatus.

* * *

# VITA

Name: Lawrence LaRoy Fleck

Born: February 24, 1931 in Kalamazoo, Michigan

Academic Career: St. Augustine High School, Kalamazoo, Michigan (1945-1949)

Western Michigan College, Kalamazoo, Michigan (1951-1955)

Michigan State University, East Lansing, Michigan (1955- )

Degrees Held: B. S. Western Michigan College (1955)

# HIGH FREQUENCY TITRATION OF SOME MONOBASIC AND DIBASIC ACIDS IN NON-AQUEOUS MEDIA

By

**Lawrence LaRoy Fleck**

AN ABSTRACT

Submitted to the College of Science and Arts of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

Year 1958

Approved Andrew Timnick

# ABSTRACT

A stable high frequency titration apparatus was constructed. This instrument, utilizing a plate type capacitance cell, was employed for all high frequency titrations conducted in this investigation.

The high frequency titration results obtained in this investigation were evaluated by comparing these results with those obtained by conductimetric and potentiometric methods. The shape of the high frequency and conductimetric titration curves were similar for all acids titrated.

Tetrabutylammonium hydroxide was tested as a titrant for the high frequency titration of some monobasic and dibasic acids dissolved in non-aqueous solvents. The best over-all titration results were obtained for acids dissolved in 80% benzene-20% methanol. Other solvents examined were dimethyl formamide, methyl isobutyl ketone, 90% benzene-10% methanol, and 50% benzene-50% methanol.

The high frequency titrations of benzoic and salicylic acid dissolved in methyl isobutyl ketone were unsuccessful due to poorly defined titration end points. Phenol, however, was successfully titrated in methyl isobutyl ketone with tetrabutylammonium hydroxide.

The following monobasic and polybasic acids dissolved in 80% benzene-20% methanol were successfully titrated with tetrabutylammonium hydroxide: adipic, benzoic, citric, fumaric, maleic, malonic, oxalic, salicylic, sebacic, and succinic acids and vanillin. Two end points in the titration curves, corresponding to the neutralization of both carboxyl groups, were obtained for the dibasic acids. The second titration end point for these acids was sharper than the first. Citric acid, a tricarboxylic acid, gave two good end points. The third end point for citric acid was poorly defined.

The titration of fumaric and maleic acid mixtures dissolved in 80% benzene-20% methanol with tetrabutylammonium hydroxide resulted in four distinct end points. The mean percentage purity value for the total acid content was found to be 96.3 ± 2.5% for four trials.

## TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# INTRODUCTION

Jensen and Parrack (34), who pioneered high frequency titrations in the United States, greatly enlarged the scope of high frequency titrimetry by conducting titrations in non-aqueous media.

High frequency titrations conducted in non-aqueous solvents offer several advantages over those conducted in aqueous solutions. The main advantages are: 1) non-aqueous solvents can be chosen which increase the apparent acidity or basicity of weak acids or bases dissolved in them and, 2) these solvents dissolve many organic acids or bases which are not ordinarily soluble in water.

The choice of titrant depends on the characteristics of the solvent, the apparent acidity or basicity of the material being titrated, and the strength of the titrant. These are the main factors that are considered when choosing a suitable titrant-solvent system for non-aqueous high frequency titrimetry.

Several investigators (7,11,12,23,25,26) have shown that tetrabutylammonium hydroxide in non-aqueous solvents is a good basic titrant for potentiometric titration and differentiation of strong, weak, and very weak* acids in non-aqueous media. These workers used tetrabutylammonium hydroxide successfully as a titrant for acids dissolved in a variety of solvents including methyl isobutyl ketone, dimethyl formamide, ethylenediamine, 1:1 benzene-isopropyl alcohol, benzene-methanol, acetonitrile, pyridine and others.

Wyld, _et al._ (23) found that tetrabutylammonium hydroxide dissolved in isopropyl alcohol compared favorably in performance with alcoholic potassium hydroxide for the potentiometric titration of phenol in several non-aqueous solvents. In view of this work a study was undertaken to test the performance of tetrabutylammonium hydroxide as the titrant for non-aqueous high frequency titrations of some monobasic and dibasic acids.

---

*Throughout this thesis acids similar in strength to mineral acids are designated as "strong acids", those similar in strength to unsubstituted carboxylic acids are designated as "weak acids", and those similar in strength to phenol are designated as "very weak acids".

# HISTORICAL BACKGROUND

Several reviews (18,20,54,61) of fundamental developments in non-aqueous analysis have appeared in the recent literature. Skolik (58) reviewed the roles of solvents and standard solutions, the determinations of endpoints, applications and sources of errors in non-aqueous titrimetry. Higuchi, et al. (28) discussed the results of spectrophotometric and potentiometric studies on 13 indicators in anhydrous acetic acid. Van der Heijde and Dahmen (60) determined an empirical acidity potential scale of 12 solvents by potentiometric titrations of strong acids with strong bases. Kilpatrick (41) discussed the theoretical and practical problems of acidity measurements in non-aqueous media. Hooser (31) included a brief review of non-aqueous titrations and listed a complete bibliography of non-aqueous high frequency titrations reported through 1954.

The following extensive review is for the period from 1954 through the November 10, 1957 issue of Chemical Abstracts.

## Non-aqueous Titrimetry

Perchloric acid in glacial acetic acid has been used extensively for potentiometric titrations (4,9,15,16,17, 30,39,40,45,47) and for photometric titrations (17,28) of a large variety of organic bases dissolved in glacial acetic acid. Titration of some organic bases using dioxane (29,53), acetonitrile, and nitromethane (9), and chloroform (10) as solvents have been performed potentiometrically with a standard perchloric acid solution. Blake (5) back titrated a measured excess of perchloric acid in glacial acetic acid with sodium acetate for the determination of some organic bases. Two different types of electrode systems (33,57) were characterized by neutralization titrations with perchloric acid. Kolthoff (42) interpreted acid-base titrations in glacial acetic acid. Palit and Singh (51) investigated phenol as a cosolvent with glycols for organic bases titrated with standard perchloric acid.

Mizukami and Hirai (50) titrated 5-acetamidomethyl-4-amino-2-methylpyrimidine in glacial acetic acid with standard periodic acid using a mixed indicator composed of methyl violet and bromophenol blue.

Numerous titrations of acids dissolved in dimethyl formamide (4,14,45) benzene-methanol (3,4,47) ethylenediamine (14) or pyridine with sodium methoxide have been performed.

Streuli (59) titrated heterocyclic amine salts of polymers dissolved in dimethyl formamide with 1,3-di-o-tolylguanidine in 1:9 methanol-chloroform.

Chatten (8) titrated p-aminosalicylic acid and its sodium salt with alcoholic potassium hydroxide in methanol using acetone as the non-aqueous medium. Deal and Wyld (12) used alcoholic potassium hydroxide as a basic titrant for the titration of very weak acids using ethylenediamine and dimethyl formamide as solvents.

Martin (48) titrated peracids, hydrogen peroxide and hydroperoxides as weak acids in anhydrous ethylenediamine with sodium aminoethoxide using antimony electrodes in a potentiometric titration procedure.

Karchmer (37) determined mercaptans in the presence of elemental sulfur by titration with an alcoholic silver nitrate solution. Two types of solvents were employed in this study. One, a "regular" solvent, contained sodium acetate trihydrate in a small amount of water, benzene and isopropyl alcohol, and the other, an "acidic" solvent contained sodium acetate trihydrate, glacial acetic acid, methanol and benzene.

Brummet and Hollweg (6) demonstrated the applicability of using chelating agents in non-aqueous titrimetry. They determined the concentrations of several metal ions in benzene-methanol by adding a chelating agent and titrating the liberated hydrogen ions with sodium methoxide.

Wyld, et al. (24) compared the performance of polarized platinum-calomel electrodes with glass-calomel electrodes in titrations in which potassium hydroxide or sodium aminoethoxide in isopropyl alcohol was the titrant.

Henry, et al. (27) titrated organic bases conductimetrically with boron tribromide in aprotic solvents.

Several recent articles (7,11,12,19,23,25,26) reported the titrations of acids using tetraalkylammonium hydroxides as the basic titrants. Wyld and Bruss (7) found that methyl isobutyl ketone was a good differentiating solvent for the titration of acids.

## Non-aqueous High Frequency Titrimetry

Hooser (31) compared high frequency titration results with corresponding conductimetric and potentiometric titrations. He successfully titrated weak acids dissolved in dimethyl formamide or benzene-methanol with alcoholic potassium hydroxide. Excellent results were reported for high frequency titrations of some very weak acids such as o-hydroxydiphenyl, phenol, p-bromophenol, β-naphthol and for weak dicarboxylic acids such as adipic acid. Only one endpoint was reported in the titration of the dicarboxylic acids.

Hall, et al. (21) successfully titrated boric acid in methanol in the presence of glycerol with sodium hydroxide in methanol.

Ishidate and Masui (32) titrated some salts of organic acids with perchloric acid or sodium acetate in acetic acid.

Dean and Cain (13) titrated salicylic acid, potassium acid phthalate, benzoic acid, o-nitrophenol, boric acid, ammonium bromide and ammonium iodide in dimethyl formamide with sodium methoxide. They also reported that n-butylamine was a suitable non-aqueous titrant for "stronger acids".

Lane (43) determined the equivalent weights of a large number of organic bases dissolved in glacial acetic acid with perchloric acid. Lane (44) also reported the determination of mercury (II) by the precipitation of copper dipropylenediamine mercuric iodide. The precipitate was dissolved in glacial acetic acid and mercuric acetate and titrated with perchloric acid in glacial acetic acid. In the same report Lane also describes the determinations of some metal ions by chelation and subsequent titration of the liberated hydrogen ions with a standard solution of potassium methoxide.

Young (62) titrated lithium halides and other salts with a standard solution of silver nitrate in a pyridine solution. He also reported that high frequency methods can be used to determine alkali metal acetates by titration with perchloric acid.

Lippincott and Timnick (46) determined aniline, substituted anilines, and mixtures of substituted anilines in glacial acetic acid with a standard perchloric acid titrant.

Karrman and Johansson (38) used potassium methoxide in 10:1 benzene-methanol for the titration of monohydroxy-, dihydroxy - and trihydroxy phenols dissolved in benzene-methanol or benzene-dimethyl formamide. They also reported that when mixtures of phenols were titrated, each component gave a titration break in the order of decreasing dissociation constant.

Riolo and Marcon (55) reported that titrations of dihydrophenazine with potassium dichromate in glacial acetic acid gave sharp high frequency endpoints. They also titrated organic bases dissolved in glacial acetic acid with a standard perchloric acid solution (56).

Allen and co-workers (1) employed a Q-Meter for non-aqueous titration of sulfonamides and the sodium and potassium salts of organic acids.

Hara and West (22) successfully titrated a number of organic acids, bases, and chelating groups in non-aqueous solvents. Titrations of lactic, tartaric, succinic, citric, formic, or propionic acids dissolved in pyridine with alcoholic potassium hydroxide were carried out. The bases dissolved in glacial acetic acid were titrated with perchloric acid.

## EXPERIMENTAL

### Reagents

The chemicals used in this investigation were not repurified unless otherwise noted. Repurification of the organic acids was not considered necessary, since the high frequency titrations were evaluated by comparing these results with those obtained by conductimetric and potentiometric titrations.

The compounds titrated, labeled purity, and source are:

Organic Acids:

| | |
|---|---|
| Adipic acid | Recrystallized from acetic acid |
| Citric acid | Fisher, Certified Reagent |
| Fumaric acid | Practical |
| Maleic acid | Eastman, practical |
| Malonic acid | Dow Company |
| Oxalic acid | Reagent grade |
| Phenol | Eastman White Label |
| Salicylic acid | Coleman and Bell, C.P. |
| Sebacic acid | Eastman, Practical |
| Succinic acid | Baker's Analyzed Reagent |
| Vanillin | Retort Pharmaceutical, U.S.P. |

Other chemicals used were:

Primary Standards:

| | |
|---|---|
| Benzoic acid | dried over sulfuric acid |
| Potassium acid phthalate | ovendried for two hours at 105° |

Other Chemicals:

| | |
|---|---|
| Amberlite I.R.A.-400 resin | analytical grade |
| Tetrabutylammonium iodide | Matheson, Coleman and Bell or Eastman Kodak |

**Solvents:** Benzene, C. P. and methanol, Merck, absolute were used as received. Methyl isobutyl ketone was freed of acid by passing it through an activated alumina column. Anhydrous isopropyl alcohol was prepared by distillation from calcium metal turnings. An 82-83° boiling point fraction was collected. Dimethyl formamide was purified by distillation.

Tetrabutylammonium hydroxide in isopropyl alcohol was prepared by the method of Wyld and co-workers (23). In this method an Amberlite I.R.A. ion exchange resin was used to convert the tetrabutylammonium iodide to tetrabutylammonium hydroxide. The ion exchange column, 62 centimeters long, was made from 4 centimeter glass tubing. The column was conditioned by passing slowly 10 liters of 1 N potassium hydroxide through the column. The column was then washed with 6 liters of distilled water followed by 5 liters of anhydrous isopropyl alcohol. Seven hundred milliliters of isopropyl alcohol containing 100 grams of tetrabutylammonium iodide were passed through the column. The throughput was kept at a rate less than 5 milliliters per minute to insure maximum conversion to the hydroxide form. Seven hundred milliliters of anhydrous isopropyl alcohol were then passed through the column and these washings were combined with the reagent.

The 1400 milliliters of tetrabutylammonium hydroxide were stored in a 2 liter pyrex bottle equipped with an ascarite-anhydrone absorption bulb to insure maximum reagent stability. Reagent solution was withdrawn from this bottle through an all-glass siphon.

The tetrabutylammonium hydroxide was standardized against primary standard benzoic acid by a visual titration procedure. Five drops of thymol blue dissolved in isopropyl alcohol was used as the indicator. Methyl isobutyl ketone or 80% benzene-20% methanol was used as the solvent for the standardization. The indicator blank for 50 milliliters of the solvents was less than 0.06 milliliters. To check the adequacy of thymol blue as the standardization indicator, several potentiometric standardization titrations were performed. Good agreement between the two standardization methods was observed.

## Apparatus

A Beckman Model H-2 pH Meter, equipped with a glass electrode and a sleeve type saturated calomel electrode pair, was used for the potentiometric titrations.

The conductance titrations were performed with a Serfass Model RCM 15 Conductivity Bridge. Platinized platinum immersion electrodes (cell constant of 0.1) were employed.

Preliminary high frequency titrations were conducted with the high frequency titration apparatus designed and constructed by Johnson and Timnick (36). It was found, however, in the course of the preliminary titrations carried out, that the apparatus was affected at times by line voltage fluctuations which resulted in erratic instrument response. To eliminate or greatly reduce this erratic behavior a second stage voltage regulator unit was incorporated in the circuit.

Figure 1 shows the circuit diagram of the modified high frequency titration apparatus utilizing a R.C.A. voltage regulator circuit. This voltage regulator circuit (52) includes a 5651 voltage reference tube. Only two major modifications were required for the adaption of the voltage regulator circuit. Two voltage reference tubes (type OD3) in series were required to supply the 300 volt operation level of the second stage voltage regulator. A potential divider at the output of the regulated power supply was added to provide 150 volts to the 955 oscillator tube.

A new instrument, including the second stage voltage regulator circuit, was constructed. Very stable instrument operation was attained. By tests in which line voltage to the instrument was varied from 120 to 60 volts, only very small changes in instrument response were observed. The real test of satisfactory stable performance was made during titrations. Very little scattering of points in the titration curves was detected.

## High Frequency Circuit Diagram Code
(For Figure 1)

$C_s$. Cell assembly

$C_1$, $C_2$, $C_3$, $C_4$. 100 micromicrofarads, mica

$C_5$, $C_6$. 20 microfarads, 450 volts

$C_7$. 0.1 microfarads, 400 volts

$L_1$. RG 8/U coaxial half-wave line, approximately 85 centimeters total length

$L_2$. 10 turns No. 22 wire wound around $R_4$

$L_3$. Filter choke, Stancor C-1709, 8Hy, 85ma. DC.

$R_1$, $R_4$. 15,000-ohm, 1-watt

$R_2$. 1000-ohm, 1-watt

$R_3$. 100-ohm, 2-watts

$R_5$. 12,000-ohm, 2-watts

$R_6$, $R_7$. 47,000-ohm, 0.5-watts

$R_8$. 12,000-ohm, 2-watts

$R_9$. 68,000-ohm, 2-watts

$R_{10}$. 1,000,000-ohm, 0.5-watts

$R_{11}$. 15,000-ohm, 2-watts

$R_{12}$. 10,000-ohm output voltage-control potentiometer

$R_{13}$. 5000-ohm, wire wound

$R_{14}$. 160-ohm, 10-watts, plate current balancing potentiometer

T. 350-0-350, 90ma.; 5 volts, 3a; 6.3 volts, 3a.

$V_1$. 955

$V_2$. 5Y3

$V_3$, $V_4$. OD3, VR 150/30

$V_5$. 6AS7-GT

$V_6$. 6SL7-GT

$V_7$. 5651

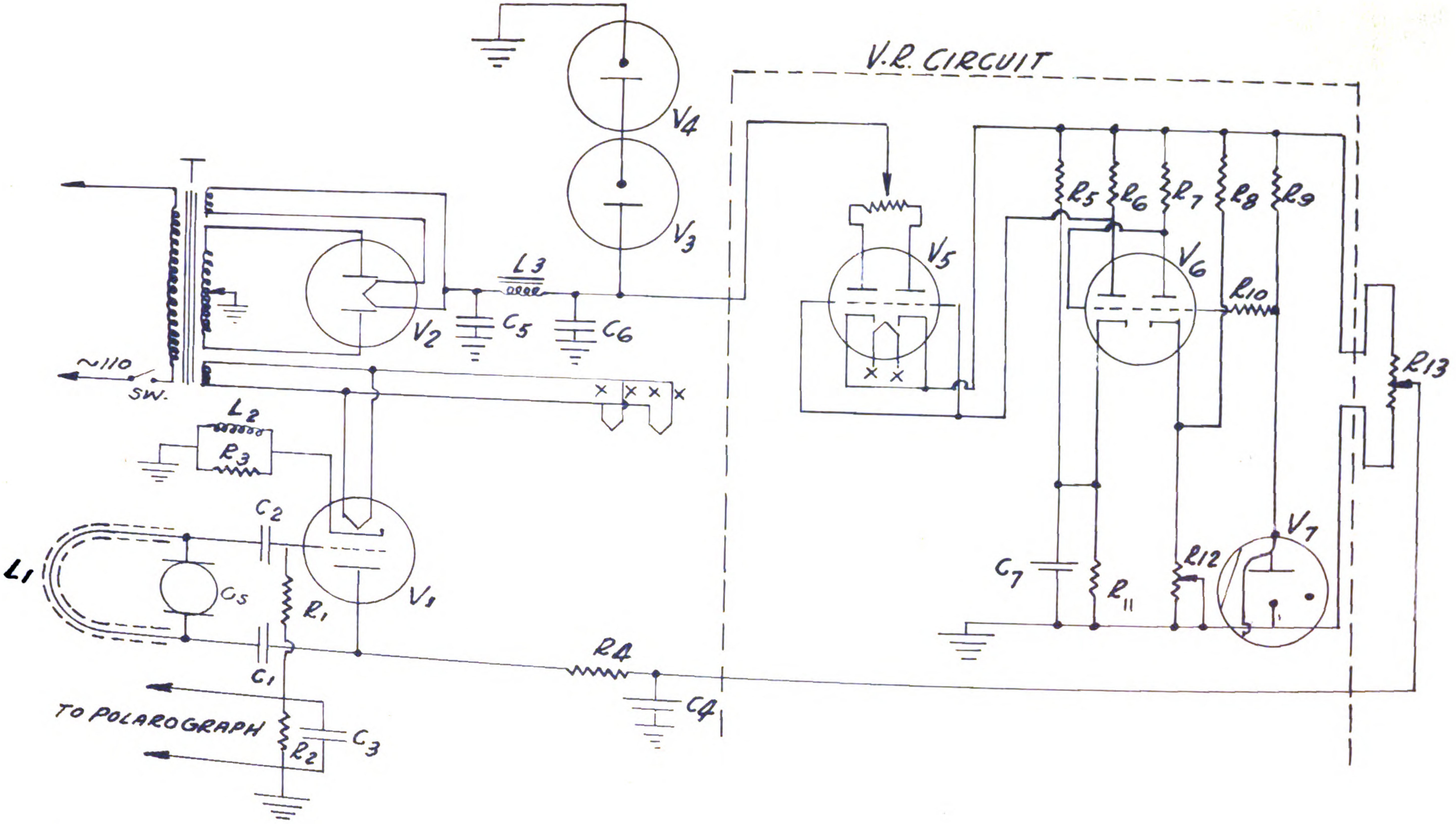

FIGURE 1 SCHEMATIC DIAGRAM OF MODIFIED HIGH FREQUENCY TITRATION APPARATUS

The operating frequency of the titration apparatus was measured with a Signal Corps Signal Generator Model 1-222-A and Signal Corps Heterodyne Monitor Model-BC-1755-A. The operating frequency employed throughout this study was 142.5 mc.

A Sargent Model XXI Polarograph, connected across a fixed resistor in series with the grid leak resistor of the oscillator tube, was used to detect grid current changes (36).

The half-wave coaxial line and the plate type capacitative cell employed were those constructed by Hooser (31).

A 250 milliliter polyethylene bottle was employed as a titration vessel. A motor driven glass stirring paddle extended through a small hole in the cap of the bottle. Continuous stirring was used throughout the titration. The tip of a semi-micro buret, extending through a small hole in the shoulder of the bottle, was immersed in the solution being titrated. Through appropriate ports a nitrogen atmosphere could be maintained in the bottle.

The response curve for tetrabutylammonium hydroxide in the relatively basic dimethyl formamide was obtained with the solution in the vessel under a nitrogen atmosphere. A nitrogen atmosphere was not maintained while titrations in which methyl isobutyl ketone or benzene-methanol served as solvents.

## Titration Procedures

### Potentiometric Titrations

The weighed samples were dissolved in 50 milliliters of either 80% benzene-20% methanol or methyl isobutyl ketone. The choice of the solvent depended on the apparent acidity of the acid.

The standardization control on the pH meter was adjusted until the lowest pH value, usually one, was indicated on the meter. Titrant was added in 0.5 milliliter increments to the stirred solution. Near the endpoint the increments were reduced to 0.05 milliliter.

Some of the stronger dibasic acids could not be titrated in methyl isobutyl ketone using the Model H-2 pH Meter, because the meter needle went off scale before the titration was completed.

### Conductimetric Titrations

The weighed samples were dissolved in 50 milliliters of solvent. Titrant was added through the buret tip which was immersed in the solution being titrated. Conductance values were measured during the course of the titration with the oscillator of the conductivity bridge operating at 60 cycles per second.

A nitrogen atmosphere was maintained in the titration vessel only while the response curve was being obtained for the dimethyl formamide system.

## High Frequency Titrations

The high frequency titration apparatus and the polarograph were allowed to warm up for at least 15 minutes prior to titrations.

Weighed samples were introduced into the titration vessel and dissolved in 150 milliliters of solvent.

Polarograph adjustments were made so that the recorder indicator assumed some desirable initial value. This was attained by selecting a 1.0 volt span, a 20% bridge setting and a sensitivity of 0.06 microamperes per millimeter. Downscale compensation was employed for the final adjustment. When the indicator moved too far upscale during a titration, it was returned to the initial value by adjusting the downscale compensator.

The reagent buret tip extended below the surface of the solution being titrated. Reagent was added in 0.25 to 0.50 milliliter measured portions. Instrument readings were made 30 seconds after each portion of reagent had been added.

# DISCUSSION OF RESULTS

## Instrument Response Curves

To obtain the information for constructing response curves, measured increments of titrant were added to a known volume of solvent contained in the titration vessel of the instrument being used. Instrument readings for various concentrations were recorded.

High frequency and conductimetric response curves were constructed by plotting the molar concentration of the titrant in the solvent being studied against the instrument readings. These curves served as useful guides in the selection of suitable solvent-titrant systems and of the optimum concentration level in the solution to be titrated. The best solvent-titrant system is one which yields relatively high and linear instrument response for slight changes in concentration. The optimum concentration level in the solution being titrated is that which yields linear and relatively high instrument response when the concentration changes in the solution.

Figure 2 shows the high frequency response curves for tetrabutylammonium hydroxide in 80% benzene-20% methanol, methyl isobutyl ketone, and dimethyl formamide. The greatest instrument response was obtained when the

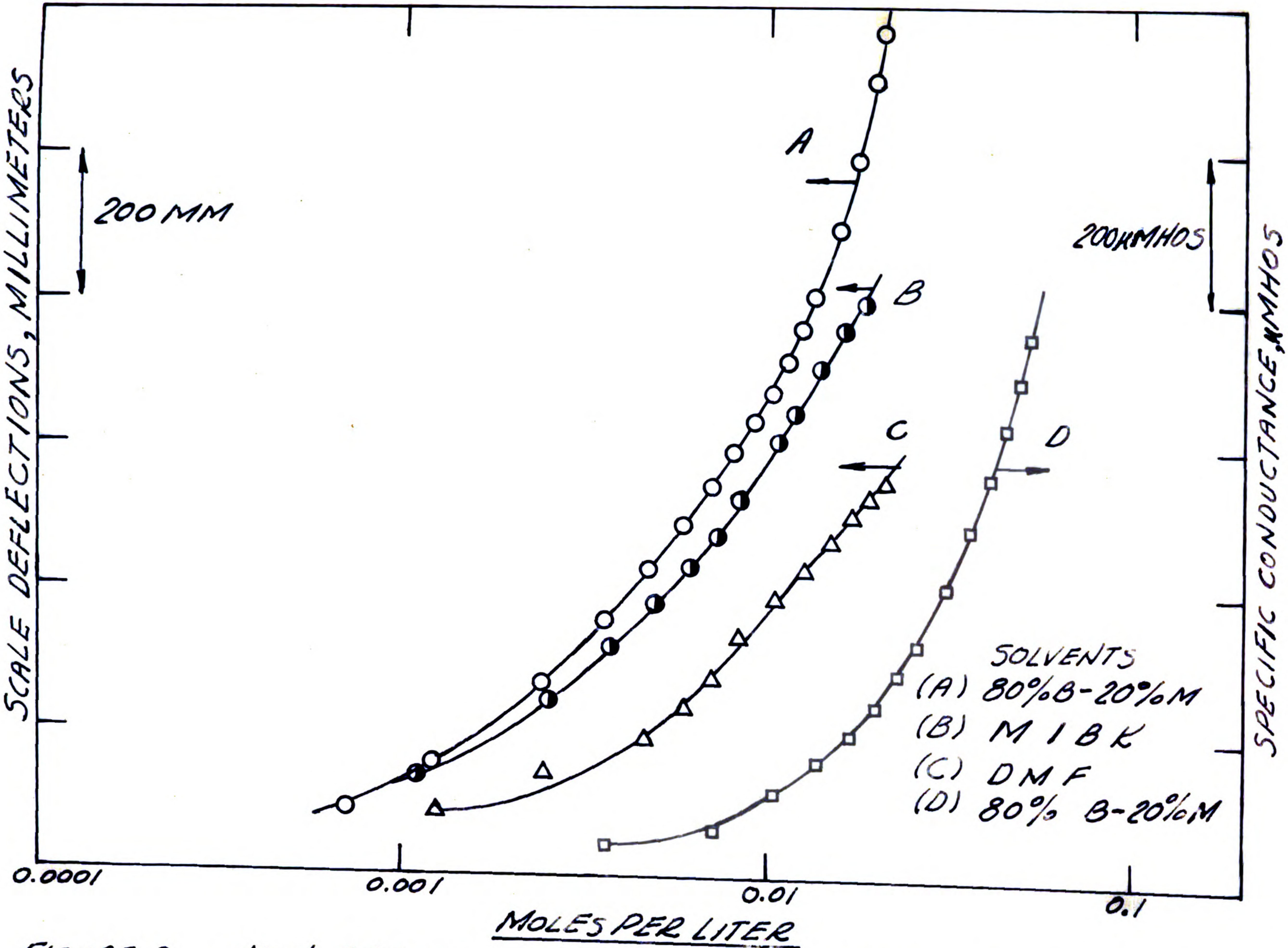

FIGURE 2 HIGH-FREQUENCY AND CONDUCTIMETRIC RESPONSE CURVES FOR TBAH

tetrabutylammonium hydroxide concentration was varied in 80% benzene-20% methanol. Dimethyl formamide as the solvent gave the least instrument response, and thus was not considered an adequate solvent for titrations with tetrabutylammonium hydroxide.

For comparison purposes a conductimetric response curve for tetrabutylammonium hydroxide in 80% benzene-20% methanol is included in Figure 2. The shapes of the curves are similar. This is to be expected since high frequency response is related to specific conductance. Greater relative response was obtained with the high frequency apparatus than with the conductimetric apparatus in the concentration range 0.001 to 0.01 molar tetrabutylammonium hydroxide.

## High Frequency And Conductimetric Titrations

### Monobasic Acids in Methyl Isobutyl Ketone

Titration of several weak and very weak acids dissolved in methyl isobutyl ketone with tetrabutylammonium hydroxide were performed by high frequency titrimetric procedures. Very little change in slope at the endpoint was observed for these acids. The acids titrated were benzoic, salicylic, and phenol.

Several conductimetric titrations of benzoic acid in methyl isobutyl ketone with tetrabutylammonium hydroxide resulted in titration curves which were comparable in shape to those obtained by high frequency methods.

The results of these titrations indicate the unsuitability of using tetrabutylammonium hydroxide as the basic titrant for high frequency titrations of weak and very weak monobasic acids in methyl isobutyl ketone.

## Monobasic Acids in Benzene-Methanol

High frequency and conductimetric titrations of benzoic acid in three different benzene-methanol mixed solvents indicate that 80% benzene-20% methanol is the best solvent for titrations conducted with tetrabutylammonium hydroxide. Figure 3 shows the high frequency titration curves obtained for benzoic acid dissolved in 50% benzene-50% methanol, 80% benzene-20% methanol, or 90% benzene-10% methanol. The titration curve A, Figure 3, indicates that relatively high instrument response was obtained when 50% benzene-50% methanol was employed as the solvent. Conductimetric titrations of benzoic acid conducted in these solvents clearly show that the best defined endpoints were obtained for the 80% benzene-20% methanol solvent. The 80% benzene-20%methanol, therefore, was chosen as the solvent for all high frequency and conductimetric titrations conducted in the remainder of this investigation.

Benzoic acid, salicylic acid, and vanillin dissolved in benzene-methanol* were successfully titrated with

---

*Throughout the remainder of this thesis the term benzene-methanol refers to 80% benzene-20% methanol solvent unless otherwise stated.

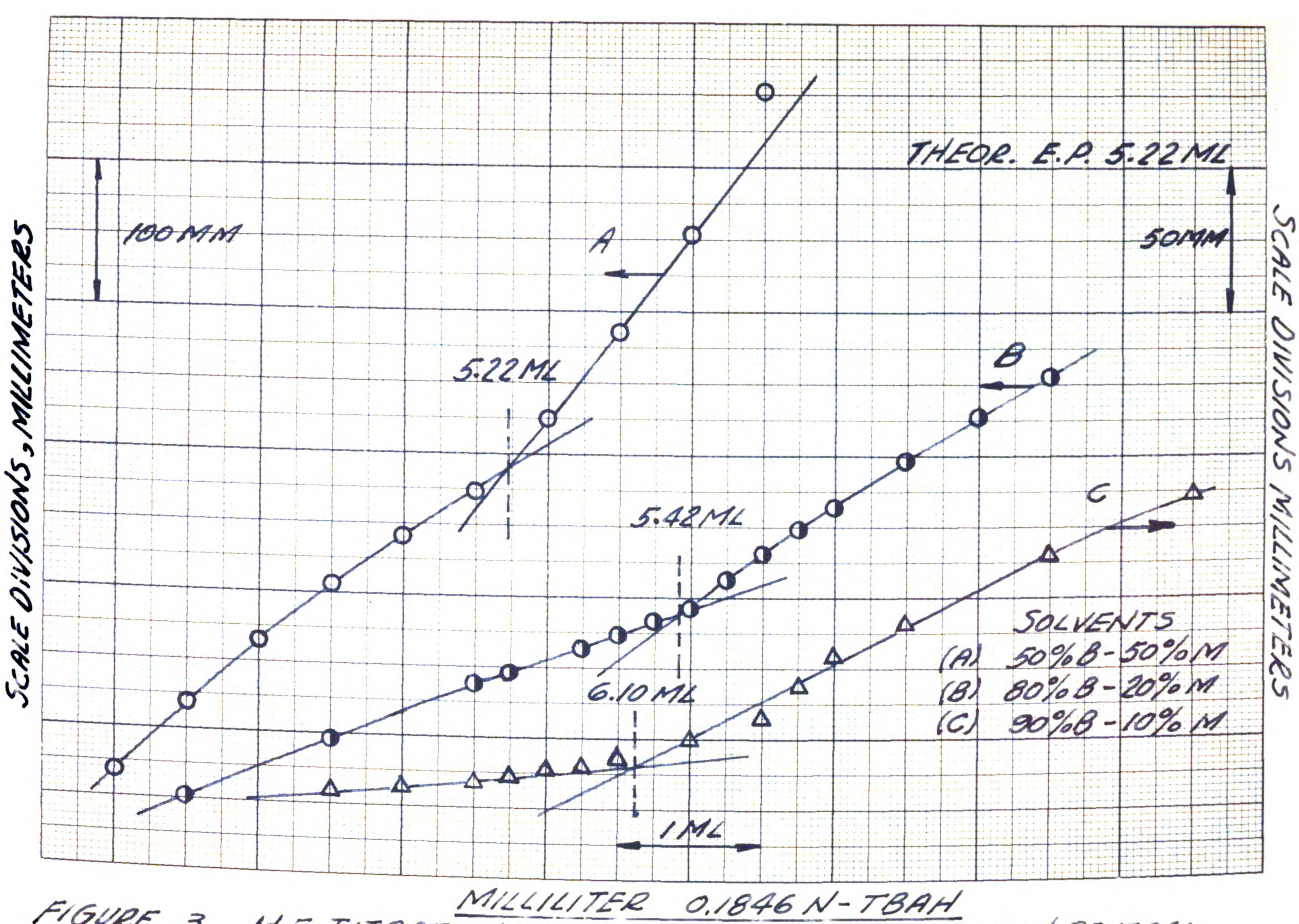

FIGURE 3 H.F. TITRATIONS OF 0.1221 GRAMS BENZOIC ACID IN SEVERAL BENZENE-METHANOL MIXED SOLVENTS

tetrabutylammonium hydroxide by high frequency and conductimetric titration methods. Figure 4, curve C, shows the high frequency titration results obtained for salicylic acid in this solvent.

A single conductance titration of phenol dissolved in benzene-methanol with tetrabutylammonium hydroxide resulted in a poorly defined titration endpoint.

## Polybasic Acids in Benzene-Methanol

Several dicarboxylic acids were successfully titrated in benzene-methanol with tetrabutylammonium hydroxide. The saturated dibasic acids titrated were adipic, malonic, oxalic, sebacic, and succinic acids. The unsaturated dibasic acids titrated were fumaric and maleic acids.

The titration of dicarboxylic acids with tetrabutylammonium hydroxide resulted in distinct endpoints for each carboxyl group present. Titration curves A and B of Figure 4 show the results obtained for succinic and sebacic acid respectively. Much sharper endpoints were obtained for the shorter chain dicarboxylic acids than for the longer chain members. An exception was maleic acid. Very little change in the slope of the successive titration curve segments was observed for this acid.

Excellent first and second endpoints were obtained in the high frequency titration of the tricarboxylic citric acid. A slight indication of a third endpoint was observed. Curve B of Figure 5 shows the complete titration curve.

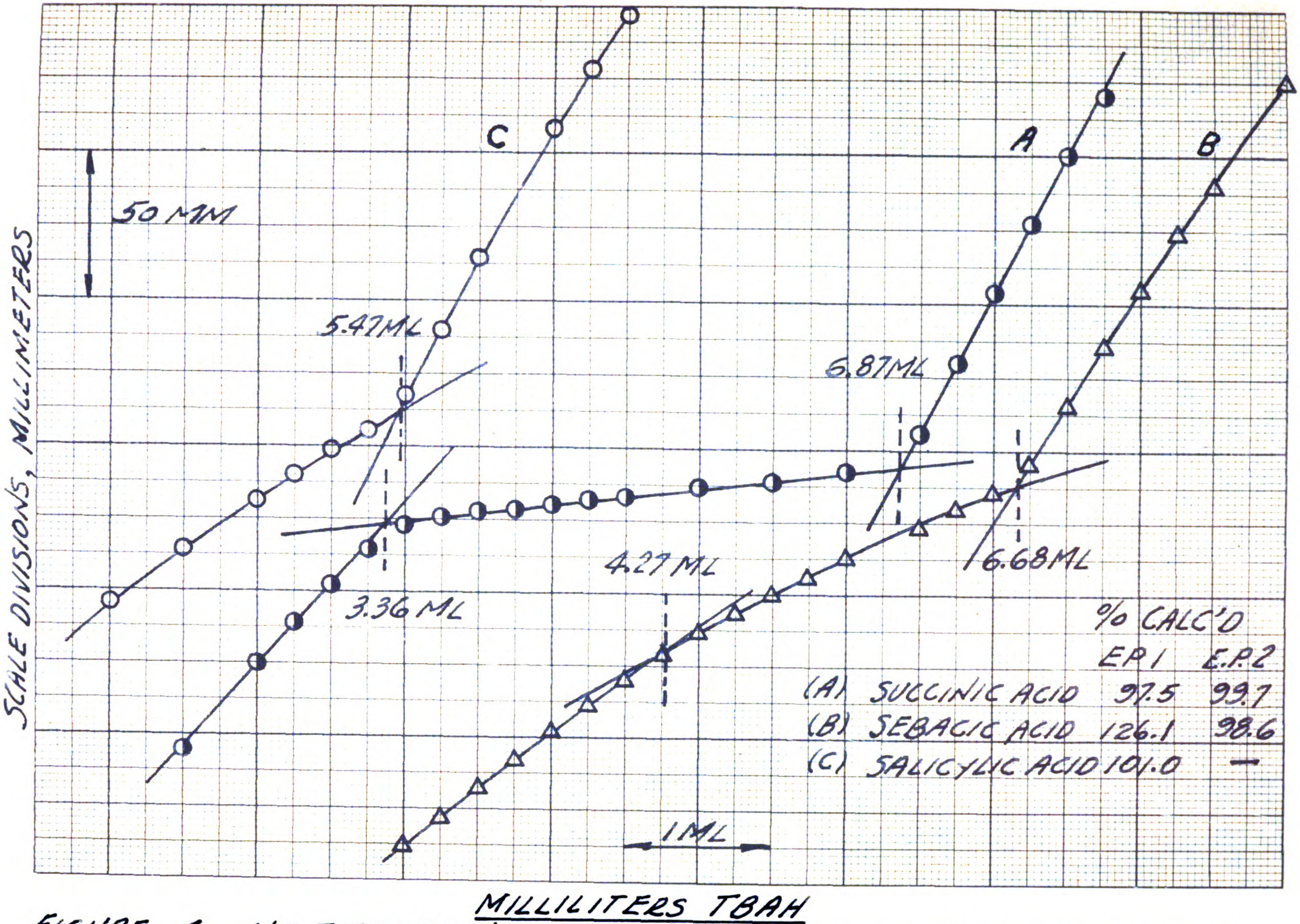

FIGURE 4 H.F. TITRATION CURVES FOR SALICYLIC ACID AND SOME DI-CARBOXYLIC ACIDS IN BENZENE-METHANOL

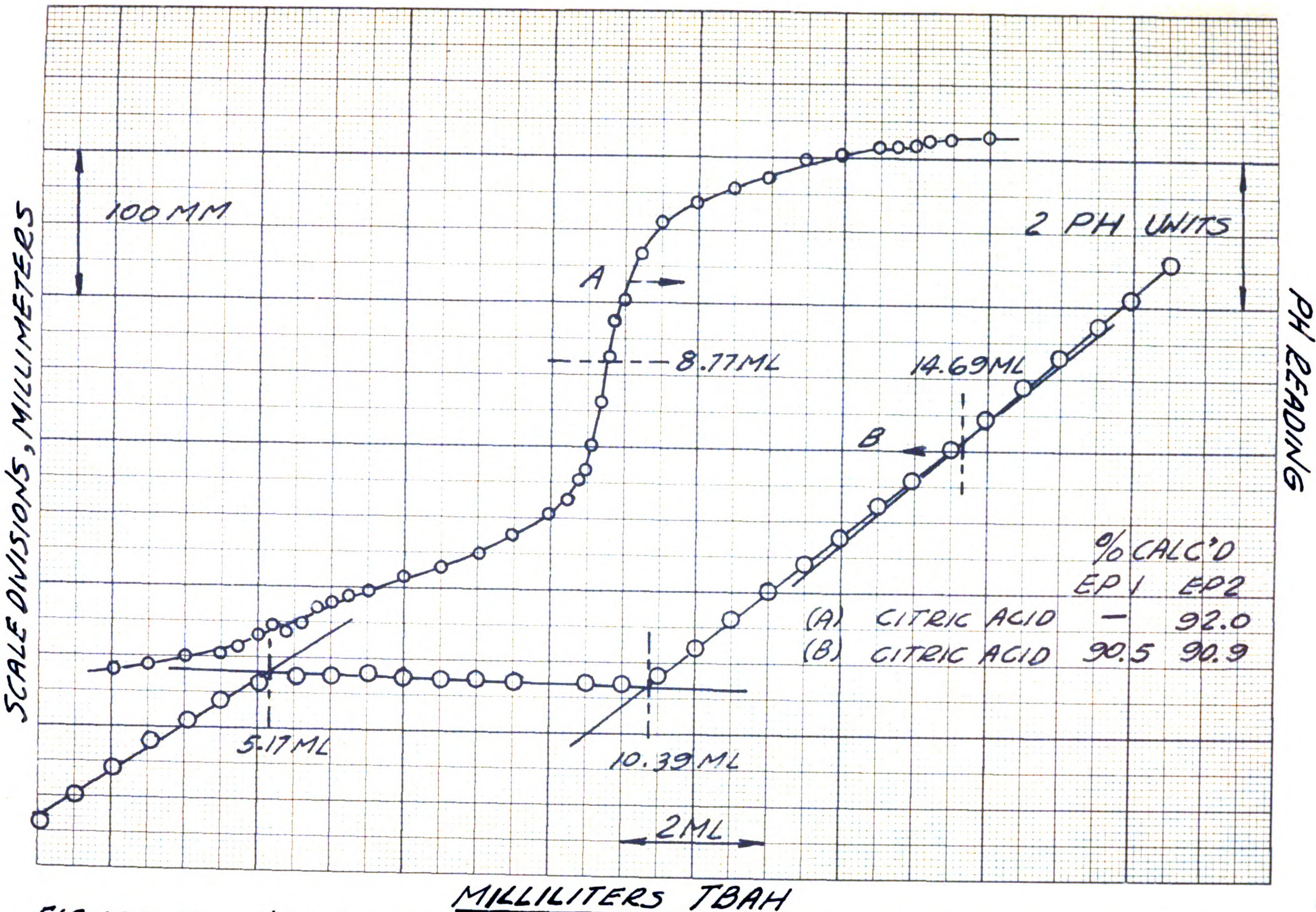

FIGURE 5 H.F. AND PH TITRATIONS OF CITRIC ACID IN BENZENE-METHANOL, TBAH TITRANT

Of all the monobasic and polybasic acids titrated with tetrabutylammonium hydroxide, adipic acid was the only acid which gave a precipitate during the titration. The precipitate, which formed before the first endpoint, completely dissolved before the second endpoint was reached.

The shapes of the conductimetric titration curves for all of the polybasic acids titrated were similar to those obtained by the high frequency titration methods.

## Potentiometric Titrations

Potentiometric and conductimetric titrations were performed to compare the results obtained by these methods with those obtained by the high frequency method.

By the potentiometric titration method the following acids dissolved in methyl isobutyl ketone or benzene-methanol were successfully titrated with tetrabutylammonium hydroxide: adipic, benzoic, citric, fumaric, maleic, malonic, oxalic, salicylic, sebacic, succinic, and vanillin. Figure 6 shows the titration curves obtained for adipic acid and malonic acid dissolved in methyl isobutyl ketone and benzene-methanol respectively. The potentiometric titration curve for citric acid is shown by curve A of Figure 5. Only one good endpoint, corresponding to the neutralization of 2 equivalents of citric acid, was obtained.

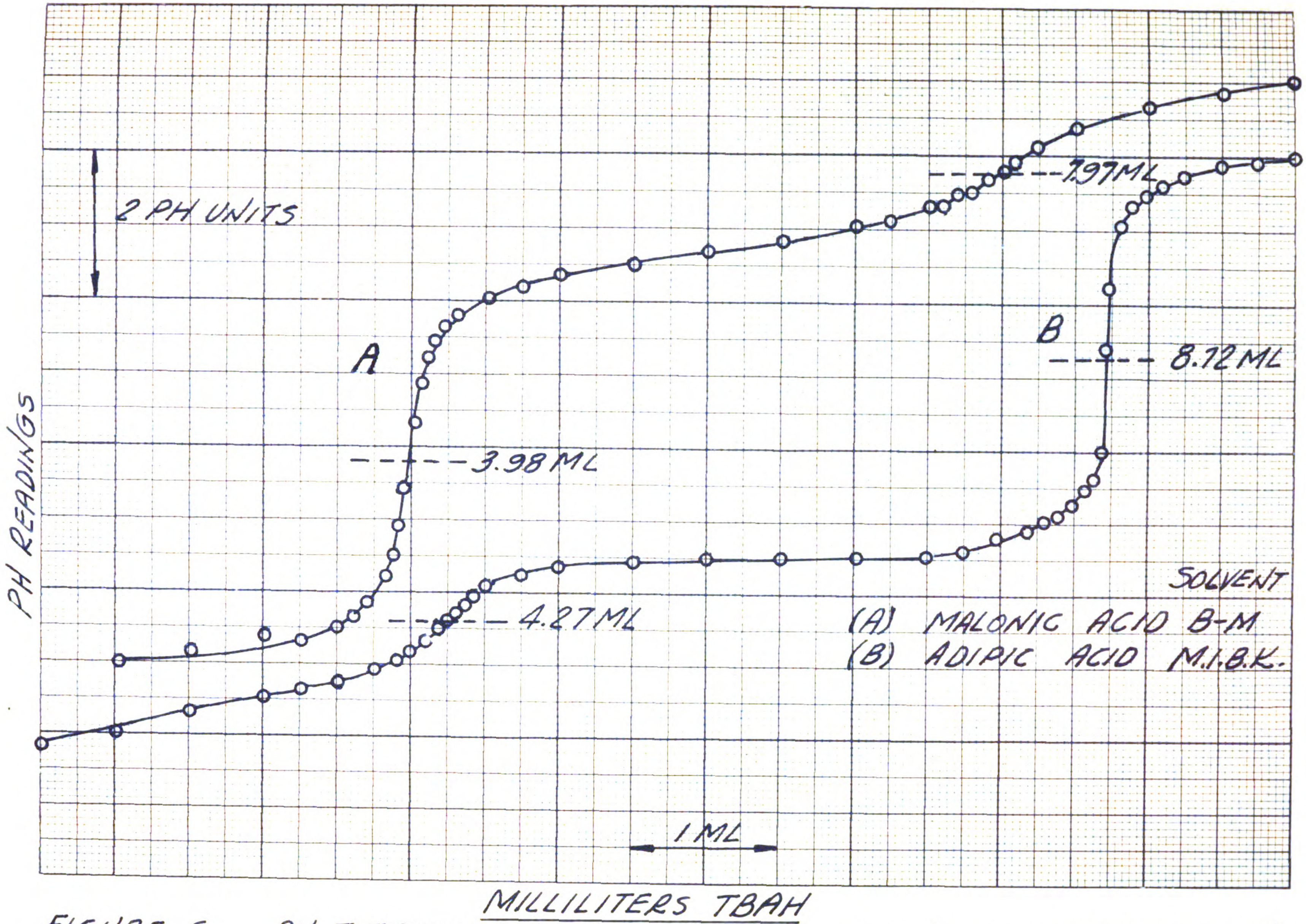

FIGURE 6 PH TITRATION OF MALONIC ACID IN BENZENE-METHANOL AND ADIPIC ACID IN METHYL ISOBUTYL KETONE, TBAH TITRANT

## Comparison of Titration Results

To facilitate the intercomparison of titration results obtained by high frequency, conductimetric, and potentiometric titration methods, the titration results for monobasic acids are tabulated in Table I and results for the polybasic acids are tabulated in Table II.

In the discussion which follows, results obtained by the high frequency or the conductimetric methods agreeing within ±2% of the purity values obtained by potentiometric titrations will be designated as good or satisfactory results.

Very good high frequency titrations were obtained for benzoic acid, salicylic acid, and vanillin in benzene-methanol and for phenol in methyl isobutyl ketone. Methyl isobutyl ketone and benzene-methanol mixtures other than the 80% benzene-20% methanol are not satisfactory solvents for the titration of benzoic acid.

Methyl isobutyl ketone appears to be a satisfactory solvent for the conductimetric titrations of benzoic acid. The titration results for 3 trials using the benzene-methanol solvent were not in as good agreement as those obtained by the high frequency method.

For all of the polybasic acids titrated by the high frequency and conductimetric methods, the second break in the titration curve was more pronounced than the first one. The difference in the sharpness between the first

## TABLE I
## TITRATIONS OF MONOBASIC ACIDS WITH TETRABUTYLAMMONIUM HYDROXIDE

| Method | Solvent | TBAH (Normality) | Sample Wt. (grams) | Ml. Used | Percent Purity |
|---|---|---|---|---|---|
| | | Benzoic Acid (pK-4.20) | | | |
| HF[a] | MIBK[d] | 0.1867 | 0.1221 | 5.65 | 105.5 |
| HF | MIBK | 0.1867 | 0.1221 | 6.30 | 117.6 |
| HF | MIBK | 0.1867 | 0.2442 | 10.66 | 99.5 |
| HF | 50%B-50%M[e] | 0.1846 | 0.1221 | 5.22 | 96.4 |
| HF | 90%B-10%M | 0.1846 | 0.1221 | 4.76 | 87.9 |
| HF | 90%B-10%M | 0.1846 | 0.1221 | 6.10 | 112.6 |
| HF | 80%B-20%M | 0.1846 | 0.1221 | 5.42 | 100.0 |
| HF | 80%B-20%M | 0.1846 | 0.1221 | 5.47 | 101.0 |
| HF | 80%B-20%M | 0.1846 | 0.1221 | 5.46 | 100.8 |
| HF | 80%B-20%M | 0.1846 | 0.1221 | 5.50 | 101.5 |
| HF | 80%B-20%M | 0.1846 | 0.0610 | 2.72 | 100.5 |
| HF | 80%B-20%M | 0.1846 | 0.1496 | 6.70 | 101.0 |
| Cond[b] | MIBK | 0.1867 | 0.1221 | 5.25 | 98.0 |
| Cond | MIBK | 0.1856 | 0.2442 | 10.72 | 99.5 |
| Cond | 50%B-50%M | 0.1846 | 0.1221 | 5.46 | 100.8 |
| Cond | 90%B-10%M | 0.1846 | 0.1221 | 5.70 | 105.2 |
| Cond | 80%B-20%M | 0.1846 | 0.1221 | 5.76 | 105.6 |
| Cond | 80%B-20%M | 0.1846 | 0.1221 | 5.59 | 103.2 |
| Cond | 80%B-20%M | 0.1846 | 0.0650 | 2.87 | 99.5 |
| | | Phenol (pK-9.89) | | | |
| HF | MIBK | 0.1867 | 0.1866 | 10.53 | 99.2 |
| HF | MIBK | 0.1856 | 0.1407 | 8.00 | 99.3 |
| HF | MIBK | 0.1856 | 0.1872 | 10.88 | 101.0 |
| Cond | 80%B-20%M | 0.1846 | 0.0930 | 5.82 | 108.7 |

Continued next page

TABLE I - Continued

| Method | Solvent | TBAH (Normality) | Sample Wt. (grams) | Ml. Used | Percent Purity |
|---|---|---|---|---|---|
| | | Salicylic Acid (pK's-2.97,13.44) | | | |
| HF | MIBK | 0.1867 | 0.1380 | 5.50 | 102.8 |
| HF | 80%B-20%M | 0.1846 | 0.0703 | 2.73 | 99.0 |
| HF | 80%B-20%M | 0.1846 | 0.1381 | 5.47 | 101.0 |
| Pot[c] | 80%B-20%M | 0.1814 | 0.1594 | 6.28 | 98.7 |
| Pot | 80%B-20%M | 0.1814 | 0.1443 | 5.65 | 98.1 |
| | | Vanillin | | | |
| HF | 80%B-20%M | 0.1846 | 0.0764 | 2.77 | 101.8 |
| HF | 90%B-10%M | 0.1846 | 0.1524 | 5.15 | 94.9 |
| Cond | 80%B-20%M | 0.1812 | 0.1419 | 5.11 | 99.3 |
| Pot | 80%B-20%M | 0.1814 | 0.1692 | 6.18 | 100.8 |
| Pot | 80%B-20%M | 0.1814 | 0.1820 | 6.63 | 100.5 |

[a] High frequency method

[b] Conductimetric method

[c] Potentiometric method

[d] Methyl isobutyl ketone

[e] 50% benzene-50% methanol

## TABLE II
## TITRATIONS OF POLYBASIC ACIDS WITH TETRABUTYLAMMONIUM HYDROXIDE

| Method | Solvent | TBAH (Normality) | Sample Wt. (grams) | Ml. Used $EP_1$ | Ml. Used $EP_2$ | Percent Purity $EP_1$ | Percent Purity $EP_2$ |
|---|---|---|---|---|---|---|---|
| | | | <u>Adipic Acid</u> | <u>(pK-4.43)</u> | | | |
| HP$^a$ | 80%B-20%M$^d$ | 0.1846 | 0.0915 | 3.30 | 6.77 | 97.3 | 99.9 |
| HP | 80%B-20%M | 0.1846 | 0.1162 | 3.89 | 8.61 | 90.3 | 100.0 |
| Cond$^b$ | 80%B-20%M | 0.1814 | 0.1008 | 3.84 | 7.76 | 101.0 | 102.1 |
| Cond | 80%B-20%M | 0.1814 | 0.0834 | 3.30 | 6.20 | 104.9 | 99.8 |
| Pot$^c$ | MIBK$^e$ | 0.1814 | 0.1156 | 4.32 | 8.45 | 99.1 | 96.9 |
| Pot | MIBK | 0.1814 | 0.1156 | 4.40 | 8.73 | 100.9 | 100.1 |
| Pot | MIBK | 0.1814 | 0.1156 | 4.27 | 8.72 | 97.9 | 100.0 |
| | | | <u>Citric Acid</u> | <u>(pK's-3.06,4.74,5.40)</u> | | | |
| HP | 80%B-20%M | 0.1835 | 0.1013 | 2.60 | 5.28 | 90.5 | 91.9 |
| HP | 80%B-20%M | 0.1833 | 0.2012 | 5.17 | 10.39 | 90.5 | 90.9 |
| Cond | 80%B-20%M | 0.1814 | 0.1109 | 2.85 | 5.78 | 89.6 | 90.9 |
| Pot | 80%B-20%M | 0.1814 | 0.1659 | - | 8.77 | - | 92.0 |
| | | | <u>Fumaric Acid</u> | <u>(pK's-3.03,4.47)</u> | | | |
| HP | 80%B-20%M | 0.1833 | 0.0649 | 3.03 | 6.10 | 99.3 | 99.9 |
| Cond | 80%B-20%M | 0.1814 | 0.0662 | 3.12 | 6.31 | 99.2 | 100.3 |
| Pot | MIBK | 0.1814 | 0.0957 | - | 9.02 | - | 99.2 |
| Pot | MIBK | 0.1814 | 0.0956 | - | 9.02 | - | 99.8 |

continued next page

TABLE II - Continued

| Method | Solvent | TBAH (Normality) | Sample Wt. (grams) | Ml. Used $EP_1$ | Ml. Used $EP_2$ | Percent Purity $EP_1$ | Percent Purity $EP_2$ |
|---|---|---|---|---|---|---|---|
| | | | Maleic Acid | (pK's 2.00,6.26) | | | |
| HF | 80%B-20%M | 0.1833 | 0.0654 | 3.08 | 5.10 | 100.2 | 83.9 |
| Cond | 80%B-20%M | 0.1814 | 0.0709 | 3.29 | 6.05 | 97.7 | 89.8 |
| Cond | 80%B-20%M | 0.1814 | 0.0845 | 4.10 | 7.80 | 97.2 | 102.2 |
| Pot | MIBK | 0.1814 | 0.0925 | 4.36 | - | 99.2 | - |
| Pot | 80%B-20%M | 0.1814 | 0.0927 | 4.35 | - | 98.8 | - |
| Pot | 80%B-20%M | 0.1814 | 0.0925 | 4.35 | - | 98.0 | - |
| | | | Malonic Acid | (pK's-2.85,6.10) | | | |
| HF | 80%B-20%M | 0.1846 | 0.0695 | 3.57 | 7.16 | 98.7 | 98.0 |
| HF | 80%B-20%M | 0.1846 | 0.0903 | 4.60 | 9.32 | 97.9 | 99.1 |
| Cond | 80%B-20%M | 0.1812 | 0.0699 | 3.68 | 7.42 | 99.3 | 100.1 |
| Pot | 80%B-20%M | 0.1814 | 0.1247 | 6.55 | 13.08 | 99.2 | 99.0 |
| Pot | 80%B-20%M | 0.1814 | 0.0758 | 3.98 | 7.97 | 99.1 | 99.2 |
| | | | Oxalic Acid | (pK's-1.19,4.21) | | | |
| HF | 80%B-20%M | 0.1835 | 0.0702 | 2.93 | 6.02 | 69.0 | 70.8 |
| HF | 80%B-20%M | 0.1835 | 0.1215 | 5.40 | 10.48 | 73.4 | 71.3 |
| Cond | 80%B-20%M | 0.1814 | 0.0744 | 3.15 | 6.56 | 69.2 | 72.0 |
| Pot | 80%B-20%M | 0.1814 | 0.0817 | - | 7.06 | - | 70.6 |
| Pot | 80%B-20%M | 0.1814 | 0.1009 | 4.27 | 8.81 | 69.1 | 71.3 |
| Pot | 80%B-20%M | 0.1814 | 0.1009 | 4.30 | 8.80 | 69.6 | 71.2 |

Continued next page

TABLE II - Continued

| Method | Solvent | TBAH (Normality) | Sample Wt. (grams) | Ml. Used EP$_1$ | Ml. Used EP$_2$ | Percent Purity EP$_1$ | Percent Purity EP$_2$ |
|---|---|---|---|---|---|---|---|
| | | | Sebacic Acid (pK-4.5[illegible]) | | | | |
| HF[a] | 80%B-20%M[d] | 0.1835 | 0.1257 | 4.27 | 6.63 | 126.1 | 99.6 |
| HF | 80%B-20%M | 0.1835 | 0.2027 | 5.90 | 10.72 | 107.9 | 99.0 |
| Cond[b] | 80%B-20%M | 0.1814 | 0.1237 | 3.25 | 6.83 | 96.4 | 102.2 |
| Cond | 80%B-20%M | 0.1814 | 0.0981 | 3.07 | 5.49 | 114.9 | 102.7 |
| Pot[c] | MIBK[e] | 0.1814 | 0.1616 | - | 8.63 | - | 92.0 |
| Pot | MIBK | 0.1814 | 0.1616 | - | 8.62 | - | 97.8 |
| | | | Succinic Acid (pK's-4.19,5.57) | | | | |
| HF | 80%B-20%M | 0.1846 | 0.0751 | 3.36 | 6.87 | 97.5 | 99.7 |
| HF | 80%B-20%M | 0.1812 | 0.1085 | 4.97 | 10.02 | 96.0 | 98.8 |
| HF | 80%B-20%M | 0.1812 | 0.0549 | 2.55 | 5.15 | 99.4 | 100.4 |
| HF | 80%B-20%M | 0.1812 | 0.1478 | 6.88 | 13.77 | 99.6 | 99.7 |
| Cond | 80%B-20%M | 0.1846 | 0.0627 | 2.85 | 5.68 | 99.1 | 98.7 |
| Pot | 80%B-20%M | 0.1814 | 0.0865 | 3.89 | 7.97 | 96.3 | 98.7 |
| Pot | 80%B-20%M | 0.1814 | 0.0953 | 4.44 | 8.87 | 99.8 | 99.7 |
| Pot | MIBK | 0.1814 | 0.0906 | 4.15 | - | 99.2 | - |

[a] High frequency method
[b] Conductimetric method
[c] Potentiometric method
[d] 80% benzene-20% methanol
[e] Methyl isobutyl ketone

and second breaks in the titration curves is much greater for the longer chain adipic and sebacic acids. This fact is demonstrated by comparing the percentage purity values shown in Table II for each of these acids.

Satisfactory results, calculated on the basis of the second neutralization endpoint, were obtained for adipic, citric, fumaric, malonic, oxalic, sebacic, and succinic acids. In nearly all cases, the conductimetric titration results obtained for these acids were in good agreement with those obtained by the high frequency and potentiometric methods.

With the exception of the results obtained for the longer chain adipic and sebacic acids, the titration results evaluated on the basis of the first titration endpoint for high frequency and conductimetric titrations were satisfactory.

## Titration of Acid Mixtures

Very little change in the slope of the successive high frequency titration curve segments was observed for maleic acid. Much sharper endpoints were obtained for fumaric acid than for maleic acid. These results suggested the possibility of resolving a mixture of these acids. Figure 7 shows a typical high frequency titration curve obtained for a titration of fumaric and maleic acid mixture with tetrabutylammonium hydroxide. The results are summarized in Table III.

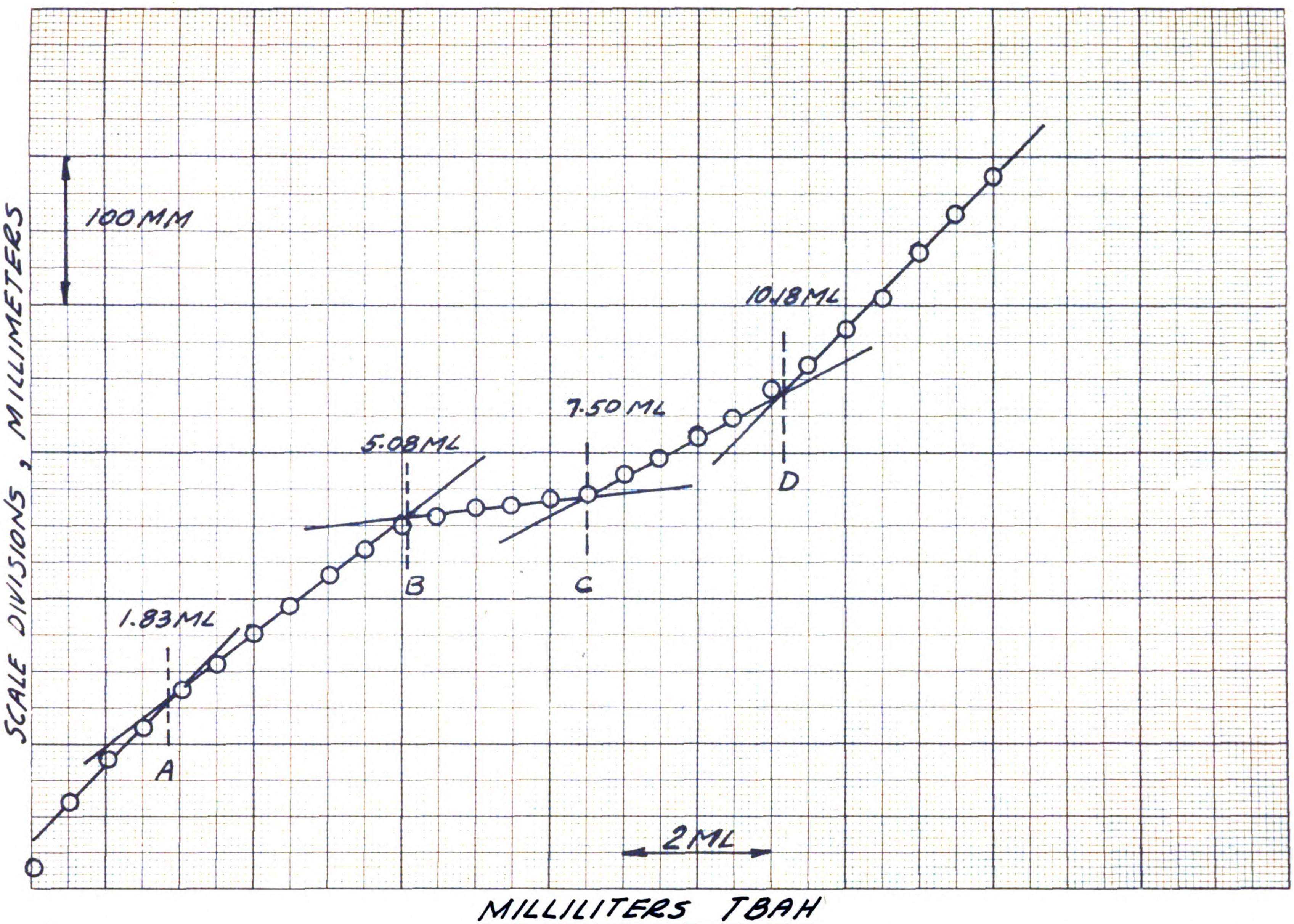

FIGURE 7 H.F. TITRATION OF 0.0496 GRAMS FUMARIC ACID AND 0.0649 GRAMS MALEIC ACID MIXTURE IN BENZENE-METHANOL, 0.1833 N-TBAH TITRANT

## TABLE III
## HIGH FREQUENCY TITRATION RESULTS FOR FUMARIC AND MALEIC ACID MIXTURES

| Trials | Meq. Acid Added | | Total Meq. Acid | | % Acid Found | |
|---|---|---|---|---|---|---|
| | Fumaric | Maleic | Added | Found[a] | Fumaric[b] | Maleic[c] |
| 1 | 1.032 | 0.513 | 1.545 | 1.526 | 104.6 | 75.5 |
| 2 | 0.855 | 1.118 | 1.973 | 1.866 | 103.8 | 87.2 |
| 3 | 0.836 | 1.640 | 2.476 | 2.325 | 94.6 | 79.3 |
| 4 | 1.758 | 0.915 | 2.673 | 2.606 | - | - |

a Volume of titrant corresponding to point D

b % Fumaric acid = $\frac{\text{(C-B)ml x N x meq.wt. x 100}}{\text{grams of fumaric acid in mixture}}$

c % Maleic acid = $\frac{\text{C-2(C-B)ml x N x meq.wt. x 100}}{\text{grams of maleic acid in mixture}}$

The volume of titrant added to attain the four successive endpoints in the titration of the fumaric and maleic acid mixture are designated by the letters A, B, C, and D as shown in Figure 7. Considering sample size and shape of titration curves obtained for the individual acids, the titration stage B-C should correspond to the neutralization of 1 equivalent of fumaric acid. Then the volume of titrant required to neutralize the first equivalent of maleic acid would be represented by C-2(C-B) milliliters. On the basis of relative strengths of fumaric and maleic acids in the aqueous system, it was concluded that points A and D correspond to neutralization of the first and second carboxyl groups of maleic acid and points B and C correspond to neutralization of the first and second carboxyl groups of fumaric acid.

From the limited number of trials, it appears that fumaric acid can be determined to ±5% if approximately 1 milliequivalent of this acid is present in the mixture. In trial 4, poorly defined breaks were obtained so that no resolution was possible. The excessive curvature probably resulted from the high concentration of fumaric acid in the sample.

The total acid content, calculated for point D, in the samples titrated for trials 1 to 4 were 98.8, 94.6, 94.0, and 97.8% respectively.

A single high frequency titration of a mixture of salicylic and succinic acid with tetrabutylammonium hydroxide resulted in an unsuccessful attempt at resolving this mixture.

## SUMMARY AND CONCLUSION

The high frequency titration apparatus developed by Johnson and Timnick (36) was modified by introducing a second stage voltage regulation unit to the instrument power supply. Extremely stable performance with the instrument operating at 148.5 mc was attained.

Tetrabutylammonium was tested as a suitable titrant for high frequency titrations of acids dissolved in non-aqueous solvents. Of the solvents tested, methyl isobutyl ketone, dimethyl formamide, 50% benzene-50% methanol, 80% benzene-20% methanol, and 90% benzene-10% methanol, the 80% benzene-20% methanol was the most satisfactory.

The high frequency titration results were compared with conductimetric and potentiometric titration results. Titration results and shapes of titration curves were quite similar for the high frequency and the conductimetric methods.

High frequency titration results, agreeing to ±2% with corresponding potentiometric results, were obtained for the following monobasic acids dissolved in 80% benzene-20% methanol: benzoic acid, salicylic acid, and vanillin.

Three high frequency titrations were performed for phenol dissolved in methyl isobutyl ketone. The mean value of 99.5% purity obtained in this study is in excellent agreement with the mean 99.1% purity value obtained by the bromination method used by Hooser (31) for the same phenol supply.

High frequency titration results, agreeing to ±2% with the purity values obtained by potentiometric titration of acids dissolved in methyl isobutyl ketone or 80% benzene-20% methanol, were obtained for the following polybasic acids dissolved in 80% benzene-20% methanol: adipic, citric, fumaric, maleic, malonic, oxalic, sebacic, and succinic acids. Two breaks in the titration curves were obtained for all of the dibasic acids titrated. Only two sharp breaks were obtained for the tricarboxcylic citric acid. The third break was very poorly defined.

The two breaks in the titration curve for maleic acid were not as sharp as those obtained for fumaric acid. When a mixture of these two acids was titrated, four breaks in the titration curves were obtained. Fumaric acid content in a mixture was resolved in three trials to ±5% purity. A fourth trial was unsuccessful. Total acid content in the four mixtures was found to be 96.3 ±2.5%.

A mixture of succinic and salicylic acids could not be resolved.

## LITERATURE CITED

1. Allen, J., Geddes, E. T., and Stuckey, R. E., J. Pharm. Pharmacol., 8, 956 (1956). A. A. 4, 1316 (1957).

2. Anastasi, A., Gallo, U., and Mecarelli, E., Mikrochim. Acta, 252 (1956).

3. Ballard, D. G. H., Bamford, C. H., and Weymouth, F. J., Analyst, 81, 305 (1956).

4. Bergamini, C., and Mattei, G., Sperimentale, Sez. Chim. biol., 6, 13 (1955). C. A. 50, 9941 (1956).

5. Blake, M. I., J. Am. Pharm. Assoc., 46, 163 (1957).

6. Brummet, B. D., and Hollweg, R. M., Anal. Chem., 28, 448 (1956).

7. Bruss, D. B., and Wyld, G. E. A., Ibid., 29, 232 (1957).

8. Chatten, L. G., J. Am. Pharm. Assoc., 45, 556 (1956).

9. Ciaccio, L. L., Missan, S. R., McMullen, W. H., and Grenfell, T. C., Anal. Chem., 29, 1670 (1957).

10. Critchfield, F. E., and Johnson, J. B., Ibid., 29, 957 (1957).

11. Cundiff, R. H., and Markunas, P. C., Ibid., 28, 792 (1956).

12. Deal, V. Z., and Wyld, G. E. A., Ibid., 27, 47 (1955).

13. Dean, J. A., and Cain, C. Jr., Ibid., 27, 212 (1955).

14. DeVries, J. E., Schiff, S., and Gantz, E. S., Ibid., 27, 1814 (1955).

15. Durbetaki, A. J., J. Am. Oil Chemist's Soc., 33, 221 (1956).

16. Ellerington, T., Nicholls, J. J., Analyst, 82, 233 (1957).

17. Ficken, G. E., and Lane, E. S., Anal. Chim. Acta, 16, 207 (1957).

18. Fix, D. D., Org. Chem. Bull., Kodak Research Labs., 28, 3 (1956). C. A. 51, 123 (1957).

19. Fritz, J. S., and Yamamura, S. S., Anal. Chem., 29, 1079 (1957).

20. Gallo, U., and Mecarelli, E., Mikrochim. Acta, 1518 (1956).

21. Hall, J. L., Gibson, J. A. Jr., Phillips, H. O., and Critchfield, F. E., Anal. Chem., 26, 1539 (1954).

22. Hara, R., and West, P. W., Anal. Chim. Acta, 15, 193 (1956).

23. Harlow, G. A., Noble, C. M., and Wyld, G. E. A., Anal. Chem., 28, 787 (1956).

24. Ibid., 28, 784 (1956).

25. Harlow, G. A., and Wyld, G. E. A., Ibid., 30, 69 (1958).

26. Ibid., 30, 73 (1958).

27. Henry, M. C., Hazel, J. F., and McNabb, Anal. Chim. Acta, 15, 187 (1956).

28. Higuchi, T., Feldman, J., and Rehm, C. R., Anal. Chem., 28, 1120 (1956).

29. Higuchi, T., Rehm, C., and Barnstein, C., Ibid., 28, 1506 (1956).

30. Hill, C. H., Tai, H., Underwood, A. L., and Day, R. A. Jr., Ibid., 28, 1688 (1956).

31. Hooser, R., Unpublished Master's Thesis, Michigan State University of Agriculture and Applied Science, (1956).

32. Ishidate, M., and Masui, M., Pharm. Bull. (Japan), 2, 50 (1954). C. A. 49, 10129 (1955).

33. Jander, V. G., and Klaus, H., J. Inorg. and Nuclear Chem., 1, 126 (1955).

34. Jensen, F. W., and Parrack, A. L., Ind. Eng. Chem., Anal. Ed., 18, 595 (1946).

35. Johnson, J. B., and Funk, G. L., Anal. Chem., 28, 1977 (1956).

36. Johnson, A. H., and Timnick, A., Ibid., 28, 889 (1956).

37. Karchmer, J. H., Ibid., 29, 425 (1957).

38. Karrman, K. J., and Johansson, G., Mikrochim. Acta, 1573 (1956).

39. Kashima, T., Asahina, H., and Shiuchi, Y., J. Pharm. Soc. Japan, 75, 329 (1955). C. A. 49, 9885 (1955).

40. Ibid., 75, 586 (1955). C. A. 49, 12778 (1955).

41. Kilpatrick, M., Am. Soc. Testing Materials, Spec. Tech. Publ., 190, 73 (1956). C. A. 51, 9268 (1957).

42. Kolthoff, I. M., Experientia, Suppl. No. 5, 33 (1956). C. A. 51, 7222 (1957).

43. Lane, E. S., Analyst, 80, 675 (1955).

44. Ibid., 82, 406 (1957).

45. Lieber, E., Rao, C. N. R., and Chao, T. S., Anal. Chem., 29, 932 (1957).

46. Lippincott, W. T., and Timnick, A., Ibid., 28, 1690 (1956).

47. Malmstadt, H. V., Fett, E. R., Ibid., 27, 1757 (1955).

48. Martin, A. J., Ibid., 29, 79 (1957).

49. Mizukami, S., and Hirai, E., Ann. Rept. Shionogi Research Lab., 6, 68 (1956). C.A. 51, 4214 (1957).

50. Mizukami, S., and Hirai, E., Yakugaku Zasshi, 77, 165 (1957). C. A. 51, 7951 (1957).

51. Palit, S. R., and Singh, U. N., J. Indian Chem. Soc., 33, 507 (1956).

52. "Radiotron Designer's Handbook," Fourth Edition, p. 1221, Radio Corporation of America, Harrison, N.J., 1952.

53. Rehm, C., and Higuchi, T., Anal. Chem., 29, 367 (1957).

54. Riddick, J. A., Ibid., 28, 673 (1956).

55. Riolo, C. B., and Marcon, E., Ann. Chim., Roma, 46, 1121 (1956). C. A. 51, 7241 (1957).

56. Ibid., 46, 528 (1956). A. A. 4, 952 (1957).

57. Scarano, E., and Ceglie, A., Anal. Chim. Acta, 12, 293 (1955).

58. Skolik, J., Wiadomosci Chem., 10, 390 (1956). C. A. 51, 10295 (1957).

59. Streuli, C. A., Anal. Chem., 27, 1827 (1955).

60. Van der Heijde, H. B., and Dahmen, E. A. M. F. Anal. Chim. Acta, 16, 378 (1957).

61. West, T. S., Chem. Age, 72, 1143 (1955).

62. Young, J. P., Dessert. Abstr., 15, 1302 (1955).

---

Note: A. A. - Analytical Abstracts

Fleck,

High frequency titration of some monobasic and dibasic acids in non-aqueous media.
M.S. 1958

Thesis
c.1 CHEMISTRY LIBRARY
Fleck,

High frequency titration of some monobasic and dibasic acids in non-aqueous media. M.S. 1958

| Date Due. DATE DUE | Name. ISSUED TO |
|---|---|
| JUL 2 '59 | Keller |
| | |
| | |
| | |