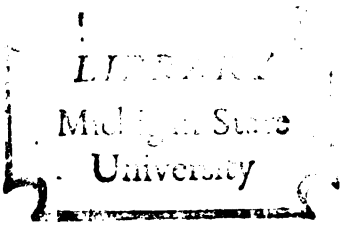
HIGH FREQUENCY TITRATION OF SOME WEAK ACIDS IN NON-AQUEOUS MEDIA

Thesis for the Degree of M. S.

MICHIGAN STATE UNIVERSITY

Ray Hooser

1956



HIGH FREQUENCY TITRATION OF SOME WEAK ACIDS IN NON-AQUEOUS MEDIA

By

Ray Hooser

A THESIS

Submitted in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

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HIGH FREQUENCY TITRATION OF SOME WEAK ACIDS IN NON-AQUEOUS MEDIA

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AN ABSTRACT

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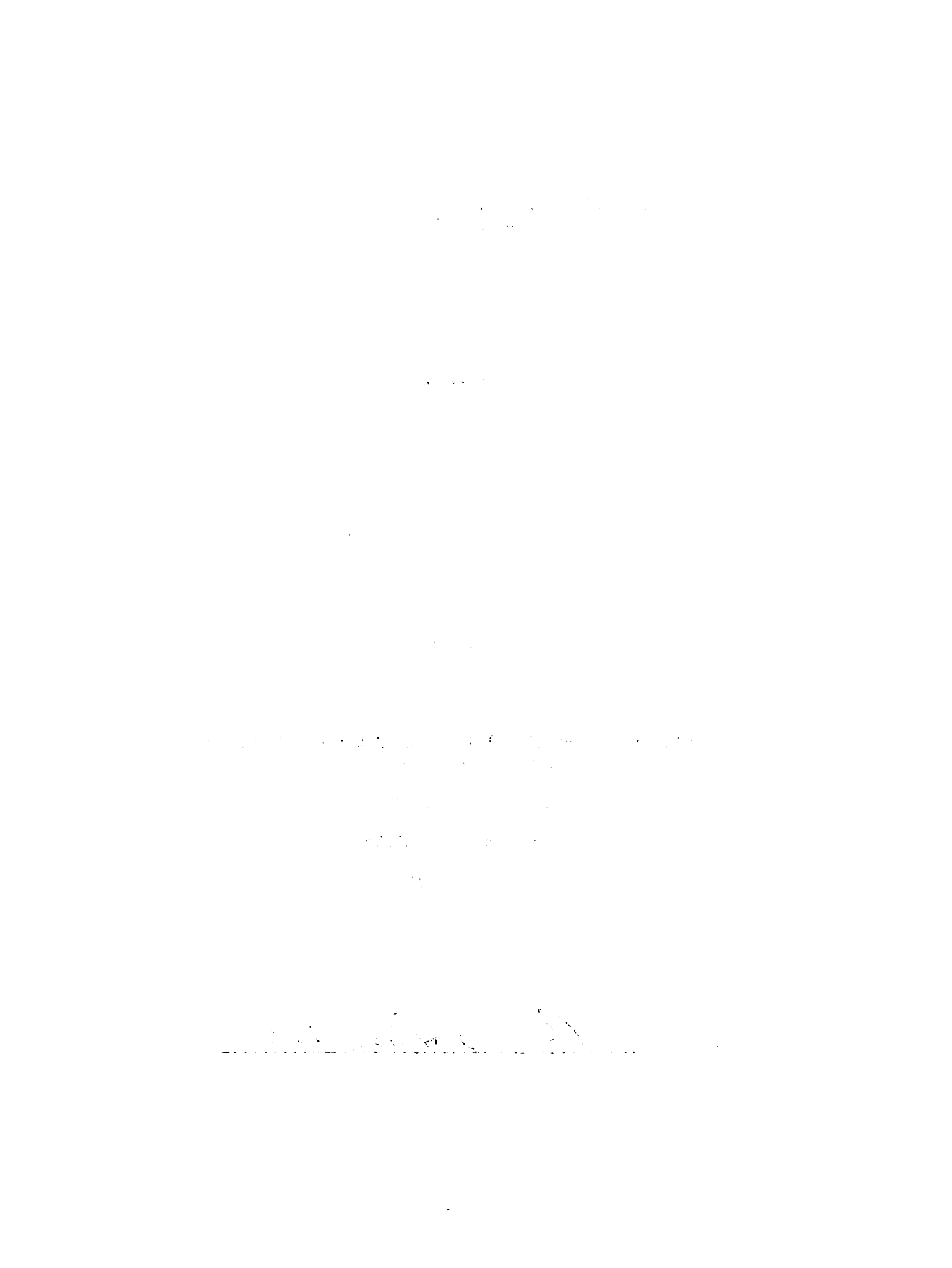

ABSTRACT

A grid-dip, capacitative type high frequency titration apparatus operating at 141 megacycles was used to determine whether high frequency titrations of weak acids in aprotic or basic solvents are practical and whether the method offers any advantages over potentiometric or indicator methods of analysis for these solvent systems.

Successful high frequency titrations of p-aminobenzoic, benzoic, malonic, m-nitrobenzoic, and salicylic acids were performed in benzene-methanol mixed solvent with potassium methoxide in benzene-methanol. No successful high frequency titrations of catechol, hydroquinone, phenol, or resorcinol were accomplished employing this solvent-titrant system.

Resacetophenone, 8-quinolinol, 2,4,6-trichlorophenol, or vanillin were successfully titrated in dimethylformamide with potassium methoxide in benzene-methanol. The end point breaks for benzoic acid, salicylic acid, or methyl salicylate ranged from poorly defined to indeterminate. No successful high frequency titrations of phenol or catechol were accomplished employing this solvent-titrant system.

High frequency titrations of very weak acids in dimethylformamide with alcoholic potassium hydroxide titrant proved successful for the monohydroxy phenols, p-benzylphenol, p-bromophenol, o-hydroxydiphenyl, 2-naphthol, and phenol. The end point breaks for p-tert-amylphenol were sharp but the results were very erratic. High frequency titration

of catechol or phloroglucinol were unsuccessful, possibly because of oxidation in excess basic titrant.

High frequency titrations of adipic acid, p-aminobenzoic, benzoic acid, malonic acid, methyl salicylate, m-nitrobenzoic acid, 8-quinolinol, resacetophenone, 2,4,6-trichlorophenol, or vanillin in dimethylformamide were performed successfully with alcoholic potassium hydroxide titrant.

Although comparable titration results were obtained for the dimethylformamide solvent system by high frequency and potentiometric methods, the high frequency method is more attractive since the electrodes do not come into contact with the solution being titrated. By the high frequency method very weak acids were titrated in dimethylformamide. Such titrations have not been carried out successfully by an indicator method.

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INTRODUCTION

High frequency titrations are purported to offer two distinct advantages over potentiometric titrations in non-aqueous systems: 1) the electrodes are not in contact with the solution, thereby eliminating the serious problems of electrode deactivation and liquid-junction irregularities and, 2) measurements near the equivalence point have no special significance. The end point is determined by the intersection of the extrapolated straight line portions of the titration curve on either side of the end point where the excess of the ion being titrated or the excess of the titrant will repress the hydrolysis, solubility, or dissociation of the reaction products.

A major factor for the limited acceptance of high frequency titration methods has been the lack of a stable, sensitive, relatively simple instrument capable of operating in the megacycle region. Within the last year, Dowdall, et al., (4) and Johnson and Timnick (23) have reported the development of simple, stable instruments which possess the desired sensitivity for both aqueous and non-aqueous titrimetry.

Lippincott and Timnick (26) have found that the instrument developed by Johnson and Timnick gave excellent results for the titration of weak, substituted anilines in glacial acetic acid solvent with perchloric acid in glacial acetic acid. Therefore, this investigation was undertaken to determine: 1) if high frequency titrations of weak acids in aprotic or basic solvents are practical and, 2) if the method offers any advantages over potentiometric or visual methods for these solvent systems.

HISTORICAL BACKGROUND

Non-aqueous Titrimetry

Folin and Wentworth (5) in 1910 carried out the first analytical non-aqueous titrations with the titration of some higher fatty acids in various aprotic solvents with sodium alcoholate, using phenolphthalein as the indicator.

Although some work was done after this, the field languished until Brønsted, Lowry, and Lewis formulated their acid-base theories, thus putting non-aqueous titrimetry on a more firm theorical basis.

The next major advancement was the study of "super acids" by Hall, Conant and Werner (1,16,17) in which they reported titrations of weak bases in glacial acetic acid medium with strong mineral acids.

The first non-aqueous acid-base titration to find wide acceptance was the procedure of Hadeau and Branchen (28) for the determination of amino acids in acetic acid with perchloric acid in glacial acetic acid.

Moss, Elliott, and Hall (27) reported the successful titration of phenol and other very weak acids in ethylenediamine with sodium aminoethoxide in the same solvent.

Non-aqueous titrimetry came into prominence with the recent, rapid expansion of the chemical and pharmaceutical industries. Numerous, rapid control procedures for many organic intermediate and final products which are too weak as acids and bases to be determined in aqueous medium had to be developed. A major share of the credit for developing this field must be given to Fritz (6-15), Riddick (34,35), Wollish and Pifer (30,31,32).

All four types of solvents, basic, acidic, amphiprotic, and aprotic, have been utilized in non-aqueous titrimetry (34,35). The properties of the compound to be titrated must be considered in the choice of a suitable solvent. Since a basic solvent will enhance the apparent acidity of weak acids dissolved in it, ethylenediamine would be a proper choice of solvent for titrations of compounds such as phenol, o-bromophenol, or catechol. Likewise, an acidic solvent such as glacial acetic acid which enhances the apparent basicity of any weak base dissolved in it would be chosen for aniline, m-chloroaniline, and pyridine. Since there is little or no leveling effect in aprotic and amphiprotic solvents, they are often selected when differential titrations of mixtures containing compounds of substantially different pK's are desired. An example of this would be the differential titration of a mixture of phenol, acetic acid, and hydrochloric acid dissolved in dimethylformamide with alcoholic potassium hydroxide titrant (2).

Among the many titrants suggested for use in non-aqueous titrimetry, perchloric acid in glacial acetic acid has been almost universally adopted for titration of weak bases. However, no one titrant has yet been found which satisfies all the requirements for a good titrant for weak acids. Deal and Wyld's suggestion of potassium hydroxide dissolved in isopropyl alcohol appears to the best developed thus far (2). Other titrants which have been tried are potassium methoxide, sodium methoxide, sodium aminoethoxide, and tetrabutylammonium hydroxide (6).

Workers in non-aqueous titrimetry have been plagued from the beginning with a lack of suitable means of end point detection.

Some specific indicators are available, but no series of indicators to cover the entire so-called "pH range" for each solvent system has yet been developed (6).

Instrumental methods of analysis which have been utilized to circumvent this difficulty are potentiometry (6), photometry (33), conductimetry (18,19), and high frequency titrimetry (3,20,21,25,26,37). Of these, potentiometric titrimetry has received the most attention. One problem which has not yet been completely solved is that of developing an electrode pair which will give stable response and not be easily deactivated in non-aqueous media. Of the many combinations suggested (6,2), the glass-calomel (sleeve type) electrode pair has given the best results of the pairs tried in this investigation.

The preceding discussion is only a brief sketch of the developments in non-aqueous titrimetry. For a more complete treatment, Riddick's reviews (34,35), Frita's booklet (6), and Palit's monograph (29) are excellent sources for information on this topic.

High Frequency Non-aqueous Titrimetry

Jensen and Parrack (21) who developed the first practical high frequency titration apparatus in this country were also the first to recognize the potential usefulness of high frequency titrimetry for non-aqueous systems. They reported in their original paper the successful titration of benzoic acid or o-phthalic acid dissolved in acetone with sodium methoxide titrant.

For the next few years the literature on high frequency oscillators was mainly devoted to improving instrumentation. Jankowski (20) has an excellent review covering this period.

The first successful high frequency titrations in glacial acetic acid with perchloric acid dissolved in glacial acetic acid were reported by Wagner and Kauffman (37). They compared potentiometric and high frequency results for aniline, p-toluidine, pyridine, and N,N'-bis (2-cyanoethyl)-2,5-dimethylpiperazine and expressed the view that results obtained from high frequency titrations for these bases compared very favorably with those obtained from potentiometric titrations. Unsuccessful titrations were reported for urea, p-nitroaniline, and o-nitroaniline.

Jankowski (20) titrated successfully 8-quinolinol, aniline, hexamethylenediamine, pyridine, diethylaniline, and β-alanine in glacial acetic acid with perchloric acid dissolved in glacial acetic acid. No satisfactory end point for urea was obtained.

Dean and Cain (3), using a Sargent "Oscillometer," reported good results for the titration of salicylic acid, potassium acid phthalate, benzoic acid, o-nitrophenol, boric acid, and ammonium ion. The samples were dissolved in dimethylformamide and titrated with sodium methoxide in benzene-methanol. The end point for phenol was unsatisfactory.

Lippincott and Timnick (26) titrated a series of weak, substituted anilines in glacial acetic acid with perchloric acid dissolved in the same solvent, reporting results which compared very favorably with data obtained by potentiometric and classical conductimetric titrations.

The compounds successfully titrated were:

Aniline	p-bromoaniline	m-nitroaniline
p-anisidine	p-aminoacetophenone	p-nitroaniline
p-toluidine	p-aminobenzoic acid	
p-chloroaniline	o-nitroaniline	

They also were able to carry out differential titrations, not possible by potentiometric or conductimetric methods, of some pairs of the substituted anilines listed above.

Lane (25), in order to evaluate the usefulness for non-aqueous titrimetry of a portable instrument designed by Dowdall, et al.(4), titrated some weak bases in glacial acetic acid and some weak acids in ethylenediamine. The compounds were:

In Glacial Acetic Acid*

Benzidine
Decamethylenebispyridinium nitrate
8-Hydroxyquinoline
o-Phenanthroline
Quinoxaline
Phenazine
p-Nitroaniline
Pyridine
Hexamethylenetetramine
2(2-Hydroxyphenyl)-benziminazole
Dianisyldimethylphosphonium iodide
Dianisylethylmethylphosphonium iodide
Dianisylmethylphosphine
Tetraethylammonium bromide
Tetraethylammonium iodide
Tetraethylammonium nitrate
Tetramethylammonium iodide
Ethyltrimethylammonium iodide
Phenyltrimethylammonium iodide
Hexamethylenebispyridinium nitrate
Tri (o-hydroxyphenyl)-sulphonium chloride

*The quaternary ammonium halides were determined by the mercuric acetate reagent method suggested by Pifer and Wollish (31).

In Ethylenediamine

Dimedone
p-Nitrophenol
8-Hydroxyquinoline
2 (2-Hydroxyphenyl)-benzoxazole
4-Hydroxy-1,2,3-benzselenadiazole
2,3-Dihydroxy-5-methoxyquinoxaline
5-Hydroxy-2,3-diphenylquinoxaline
5-Hydroxy-2,3-di (2-phridyl)-quinoxaline
5,8-Dihydroxy-2,3-tetramethylenequinoxaline
5,8-Dihydroxy-2-phenylquinoxaline
5,8-Dihydroxy-2-isopropylquinoxaline
5,8-Dihydroxy-2,3-pentamethylenequinoxaline
Tri (o-hydroxyphenyl)-phospine oxide

Ishidate and Masui (38) titrated a series of monobasic and dibasic carboxylic acids in benzene-methanol mixed solvent with sodium methoxide in benzene-methanol. They reported the titration of a series of alkaloids and acid salts of some organic weak bases dissolved in water or water-alcohol with perchloric acid in glacial acetic acid (39). In another paper (40) the titration of amino acids and organic bases dissolved in benzene-methanol solvent containing some acetic acid with perchloric acid in glacial acetic acid was reported.

EXPERIMENTAL

Reagents

No attempt to repurify the organic acids used in this investigation (except where noted below) was made since most were nominally "pure." A comparison for a given compound of results obtained by potentiometric, high frequency, and visual methods was deemed sufficient basis for judging the merits of high frequency titrimetry for weak acids. To check the purity of phenol by an independent method, the bromination procedure described by Siggia (36) was employed. Although Siggia states that resorcinol can be determined in the same manner, satisfactory results were unattainable.

The compounds titrated, source and labeled purity, are:

Weak Acids*

Adipic acid	Recrystallized from acetic acid
p-Aminobenzoic acid	Eastman White Label
Benzoic acid	Primary reagent grade (General Chemical Company)
Malonic acid	Dow Company
Methyl salicylate	Eastman White Label
m-Nitrobenzoic acid	Eastman White Label
8-Quinolinol	Eastman White Label
Resacetophenone	Eastman White Label
Salicylic acid	C.P. (Coleman & Bell)
2,4,6-Trichlorophenol	Unknown
Vanillin	U.S.P. (Retort Pharmaceutical Co.)

Very Weak Acids**

p-Benzylphenol	Eastman White Label
p-Bromophenol	Eastman White Label
Catechol	Recrystallized from toluene

*This classification will be used throughout the thesis to designate compounds similar to benzoic acid in their pK values.

**This classification will be used throughout the thesis to designate compounds similar to phenol in their pK values.

Hydroquinone	Eastman White Label
o-Hydroxydiphenyl	Eastman White Label
β-Naphthol	Matheson Company
Phenol	Eastman White Label
Phloroglucinol	Eastman White Label
Resorcinol	Eastman White Label
p-Tert-amylphenol	Eastman Yellow Label

Other chemicals used were:

Primary Standards: benzoic acid, potassium acid phthalate, National Bureau of Standards or primary reagent grade.

Other Chemicals: potassium metal, sodium metal, antimony metal, lithium chloride, potassium bromate, potassium bromide, potassium iodate, potassium iodide, and sodium thiosulfate, chemically pure.

Solvents: butylamine, Eastman White Label; ethylenediamine, Eastman, 95-100%; isopropyl alcohol, ethanol, methanol, and benzene, chemically pure grade; dimethylformamide, Matheson's technical grade.

Technical grade dimethylformamide required a blank correction of approximately 0.04 milli-equivalent per 150 milliliters. Dimethylformamide distilled at atmospheric pressure through a six foot long glass column packed with glass helices was found to have a larger blank correction than the charge (0.05 milli-equivalent per 150 milliliters solvent after distillation). Thus the dimethylformamide used in this investigation was used as purchased. The blank was determined by comparing the amount of titrant consumed with the theoretical amount of titrant required for a known weight of benzoic acid. Direct potentiometric determination of the blank was found to be unreliable. To prevent additional absorption of atmospheric carbon dioxide by the slightly

basic dimethylformamide, the solvent was stored in glass bottles and transferred to the titration cell by means of a 50 milliliter automatic buret provided with guard tubes filled with ascarite. "Oil pumped" nitrogen was used to force the solvent from the reservoir into the buret. The stopcock of the buret was not greased since any grease extracted by the dimethylformamide obscured high frequency end points.

Alcoholic potassium hydroxide* (0.1N and 0.26N) was prepared by dissolving, with gentle heating, sufficient potassium hydroxide in two liters of isopropyl alcohol. After allowing the solution to stand for twelve hours, it was filtered through a coarse sintered glass filter to remove the insoluble potassium carbonate. A nitrogen atmosphere was provided during the filtering operation to exclude atmospheric carbon dioxide. The filtered alcoholic potassium hydroxide was stored in glass bottles and dispensed from calibrated automatic burets. The burets were provided with guard tubes filled with ascarite. "Oil pumped" nitrogen was used to force the titrant from the reservoir into the burets. These precautions were taken to protect the titrant from atmospheric carbon dioxide. The alcoholic potassium hydroxide was standardized against potassium acid phthalate dissolved in carbon dioxide-free distilled water, using phenolphthalein as the indicator. A few of the standardization titrations were carried out by high frequency titrimetry.

One tenth normal potassium methoxide and 0.1N sodium methoxide were prepared and standardized against benzoic acid as described by Fritz (6).

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*The term alcoholic potassium hydroxide is used in this thesis to designate potassium hydroxide dissolved in isopropyl alcohol.

The non-aqueous indicators, thymol blue, azo violet, and o-nitroaniline, were prepared as suggested in Frits's booklet (6).

Potassium benzoate required for obtaining a high frequency response curve for potassium benzoate in dimethylformamide was prepared by adding potassium hydroxide dissolved in ethanol to an alcoholic solution of benzoic acid. The resulting precipitate was isolated by filtration, recrystallized from hot alcohol, and collected by filtration. The precipitate was then dried in a vacuum desiccator for 48 hours.

Apparatus

A Fisher "Titrimeter" was used for all potentiometric titrations. Various combinations of the electrodes listed below were used: 1) antimony, 2) Beckman #1190 glass, 3) Beckman #1170 fiber type calomel, and 4) Beckman #4970-71 sleeve type calomel.

A Serfass Model RCM 15 Conductivity Bridge, in conjunction with a platinized platinum immersion electrode pair (cell constant of 0.1), was used for the conductimetric titration.

The capacitative type high frequency instrument used in this investigation was a duplicate of the prototype designed and built by Johnson (22). The progress of a titration was followed by measuring the oscillator tube grid current changes with a Model XXI Sargent Polarograph.

By the use of various combinations of capacitative type cells and coils or co-axial half-wave line the operating frequency of the instrument could be altered. Two capacitative type cells were

constructed. One was a band type in which two one-half inch wide copper bands, mounted one above the other approximately one-half inch apart, encircled the titration vessel. The other consisted of two brass plates, one-half inch wide by one inch long, mounted against the titration cell at the same level, but three quarters of an inch apart. Other constructional details are identical with those presented by Johnson (22).

Operating frequencies were measured with a Signal Corps Net. Monitor-BC-1255-A frequency meter.

The frequencies for various combinations of cells and coils or half-wave line were:

Cell	Inductance	Frequency*
Band type	42 turn coil	11 MC
Band type	8 turn coil	36 MC
Plate type	42 turn coil	15 MC
Plate type	8 turn coil	49 MC
Plate type	Half-wave line (85 cm.)	141 MC

The automatic burets were calibrated using the titrant to be dispensed from them as the calibrating liquid. The coefficients of cubical expansion of the titrants were determined in a 25 milliliter dilatometer at five degree intervals from 20 to 35°C. The coefficient of cubical expansion for 0.1N potassium methoxide in benzene-methanol (10/1) was found to be 0.12% per degree centigrade; for 0.1N alcoholic potassium hydroxide, 0.11% per degree centigrade. All volumes of titrant recorded in this investigation were corrected to 20°C.

*Frequencies were measured with the titration vessel filled with 150 milliliters of dimethylformamide.

All analytical weighings were weighed to the nearest 0.1 milligram, employing weights calibrated against National Bureau of Standards calibrated weights, N.B.S. Test No. 87925.

Titration Procedures

Visual

The compounds listed on page 8 as weak acids were dissolved in 50 milliliters of dimethylformamide and titrated with 0.1N sodium methoxide to the first blue color of azo violet indicator (6). Before adding the sample the acid impurities in the dimethylformamide were neutralized with titrant to the same blue color.

The compounds listed on pages 8 and 9 as very weak acids were titrated in 50 milliliters of ethylenediamine to the orange-red color of o-nitroaniline with 0.1N sodium methoxide (6). As in the case of dimethylformamide the acid impurities were neutralized before the addition of the sample.

Potentiometric

Three electrode combinations were used in this investigation: 1) antimony-glass system for titrations of benzoic acid dissolved in dimethylformamide with potassium methoxide, 2) calomel (fiber)-glass system for titrations of weak acids dissolved in dimethylformamide with alcoholic potassium hydroxide, and 3) calomel (sleeve)-glass system for titrations of very weak acids dissolved in dimethylformamide with alcoholic potassium hydroxide.

The Fisher "Titrimeter" was balanced at 0.5 volts.

The samples were dissolved in 75 milliliters of dimethylformamide. A nitrogen atmosphere was provided to protect the titration solution from atmospheric carbon dioxide. Increments of 0.25 milliliter of titrant were added at the beginning of the titration. Near the end point the increments were reduced to 0.1 milliliter.

Conductimetric

The Serfass Conductivity Bridge was operated at 60 cycles. External capacitance compensation was not employed since it did not seem to improve instrument balance.

The sample of benzoic acid was dissolved in 100 milliliters of dimethylformamide. The titration vessel was provided with a cover to exclude atmospheric carbon dioxide.

High Frequency

The instrument was allowed to warm up for a minimum of two hours in order to stabilize its response.

The sample was weighed to the nearest 0.1 milligram and transferred to the polyethylene titration vessel. This vessel was then placed in the cell assembly and a polyethylene cover, containing openings for a nitrogen gas inlet, glass stirrer, and buret tip, was slipped over the mouth of the titration vessel. The motor driven glass stirrer was positioned so that the paddle blades were below the bands or plates.

One hundred and fifty milliliters of solvent was transferred to the titration vessel with a 50 milliliter automatic buret. After the nitrogen flow had been adjusted to a moderate rate and the opening for the buret tip plugged with a small cork, the solution was stirred

for approximately 15 minutes to establish temperature equilibrium in the solution.

While the solution was attaining temperature equilibrium, the Sargent Model XXI Polarograph was turned on, the span voltage set at one volt, and the proper sensitivity (usually 0.100 microampere per mm.) selected.

After the required waiting period the titrant buret was positioned with its tip below the surface of the solution in the titration vessel.

Unless a complete titration curve was desired, the bridge control of the polarograph was not adjusted to bring the scale pointer to the lower end of the scale until approximately all but five milliliters of the theoretical amount of titrant required had been added. This step was taken because the initial formation of the salt of many of the compounds titrated so "loaded" the instrument that either an extremely large compensation setting was required to bring the pointer onto the scale again or the instrument went out of oscillation for the particular bridge control setting.

Once the initial amount of titrant had been added and the final adjustments of the bridge control made, the titrant was added in increments of 0.25 or 0.50 milliliter. Recorder readings were taken 30 seconds after each addition of titrant. Timed readings were necessary because of recorder fluctuations. Usually, readings were made over a span of 10 milliliters, five milliliters before and five milliliters after the end point.

DISCUSSION OF RESULTS

Response Curves

Response curves are obtained by adding in known increments to pure solvent one of the substances removed, added or formed during an actual titration and recording the oscillator tube grid current changes produced. Semi-log paper is used to graph response against molarity because the concentration ranges involved in determining response curves extend through several powers of ten. There is no logarithmic relationship between response and molarity.

If response curves for the titrant, titrant diluent, the compound being titrated, and the salt formed during the titration were available for a given frequency, theoretical titration curves for a given solvent could possibly be constructed. Usually only the response curve for the addition of titrant to the solvent is obtained.

The response curves vary from bell to "S" shape, depending on the frequency, solvent, and titrant selected. Figure 1 shows the effect of frequency changes upon the shape of the response curves. The linear portions of the response curves indicate the optimum concentration level at which the response of the instrument is linear and large for changes in concentration. This information is used to select the proper sample size to obtain optimum linearity in the titration curve.

A rather complete survey at 11 megacycles of the response curves for the various elements involved in the titration of benzoic acid in dimethylformamide with potassium methoxide was made because of the

poorly defined end points obtained for this compound. From curve C of Figure 2 it is apparent that the response change due to the disappearance of benzoic acid during the course of the titration is small. The slopes of the potassium benzoate curve (curve A, Figure 1) and of the potassium methoxide curve (curve B, Figure 1) are similar. Little or no change of slope of the titration curve can be expected when potassium benzoate ceases to be formed and the first excess of potassium methoxide is added. Benzene, methanol, or a mixture of the two caused no response change when added to dimethylformamide.

The response curve for alcoholic potassium hydroxide was determined at 141 megacycles. (Figure 3).

Titrations in Benzene-Methanol Solvent (Potassium Methoxide as Titrant)

High Frequency

A ratio of one part benzene to one part methanol was found to be a satisfactory mixed solvent for the titration of p-aminobenzoic, benzoic, malonic, m-nitrobenzoic, or salicylic acids with potassium methoxide titrant. Smooth titration plots and distinct end point breaks were obtained for these weak acids, as shown in Figures 4 and 5. The titration results for these compounds are listed in Table II.

No end point breaks were obtained for the titrations of resorcinol, hydroquinone, catechol, or phenol. The acidity of methanol precluded the successful titration of these compounds in this solvent system. Pure benzene was also tried as a solvent for phenol but the instrument showed no response on adding titrant to this solvent, even when 0.2 gram of lithium chloride was added to provide some instrument loading.

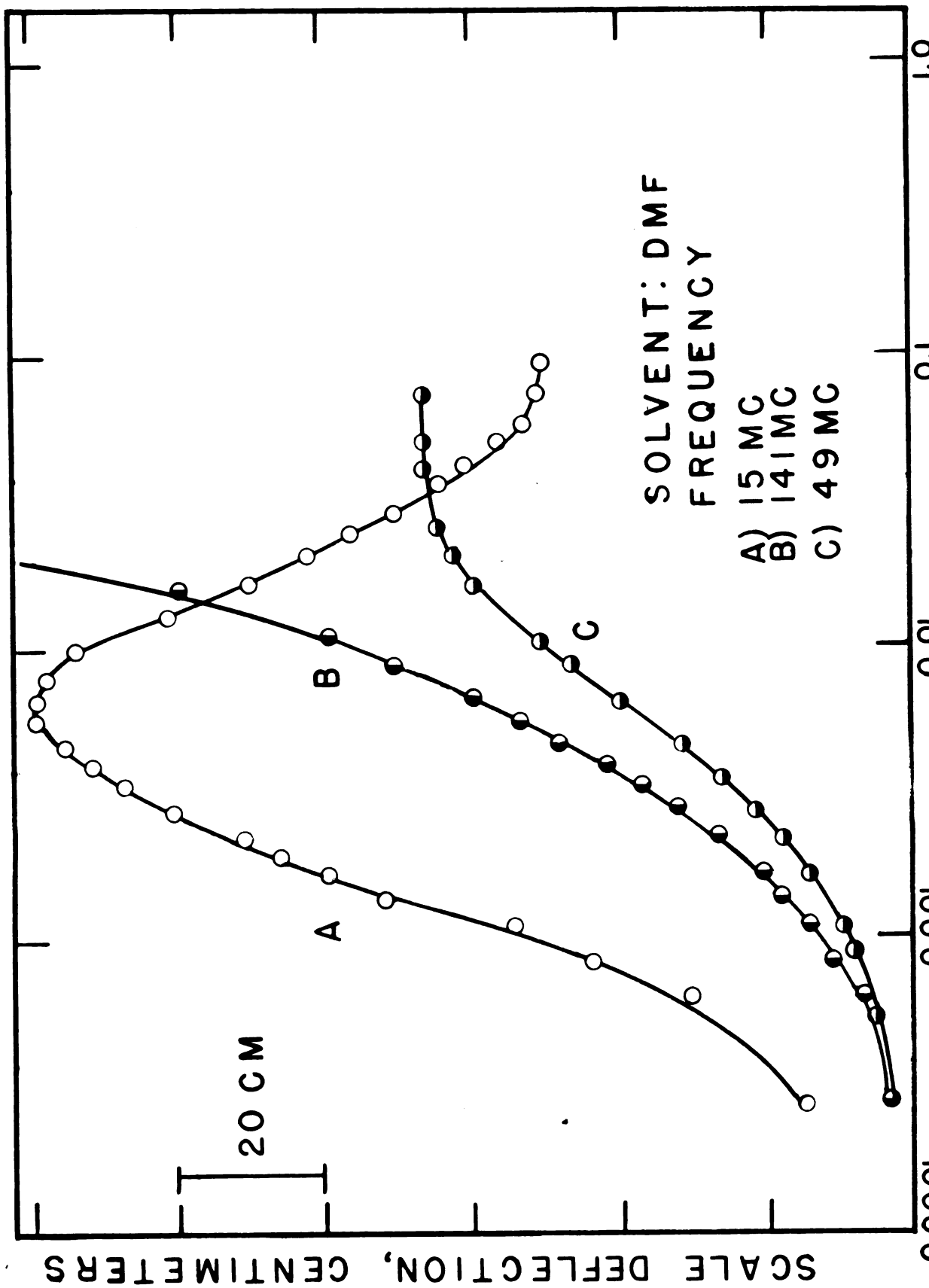

FIGURE I. RESPONSE CURVES FOR KOME, AT VARIOUS FREQUENCIES

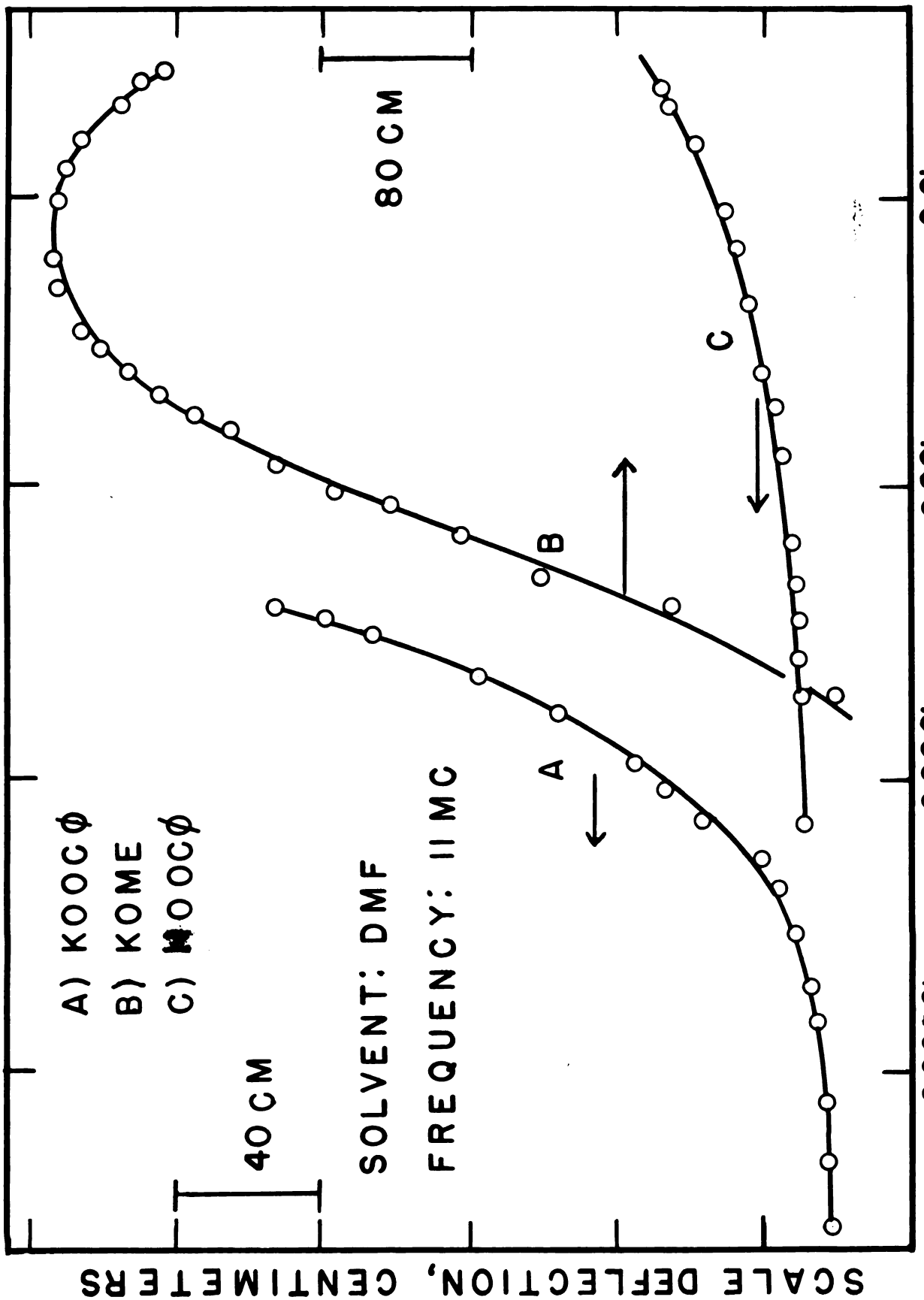

FIGURE 2. RESPONSE CURVE

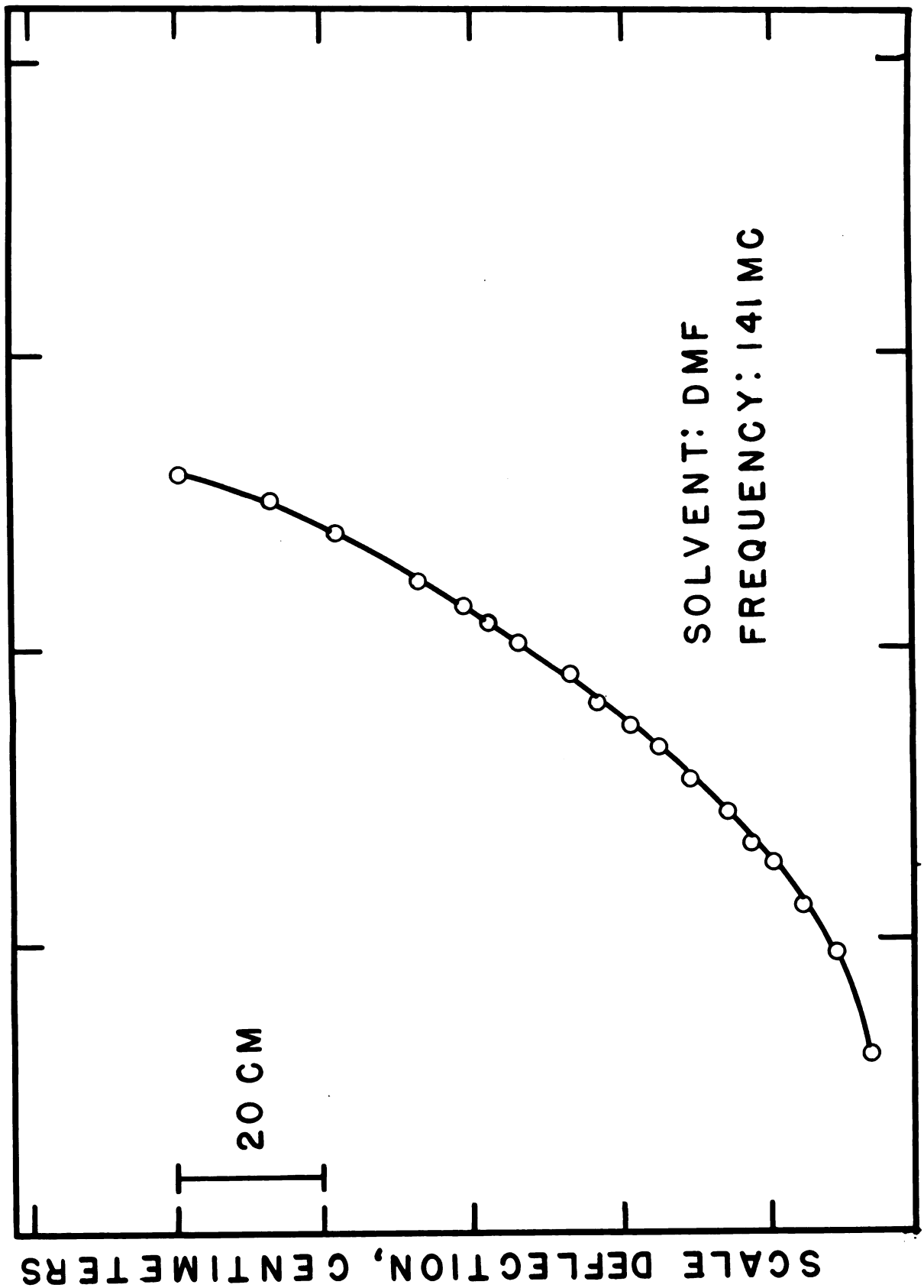

FIGURE 3. RESPONSE CURVE FOR ALC. KOH

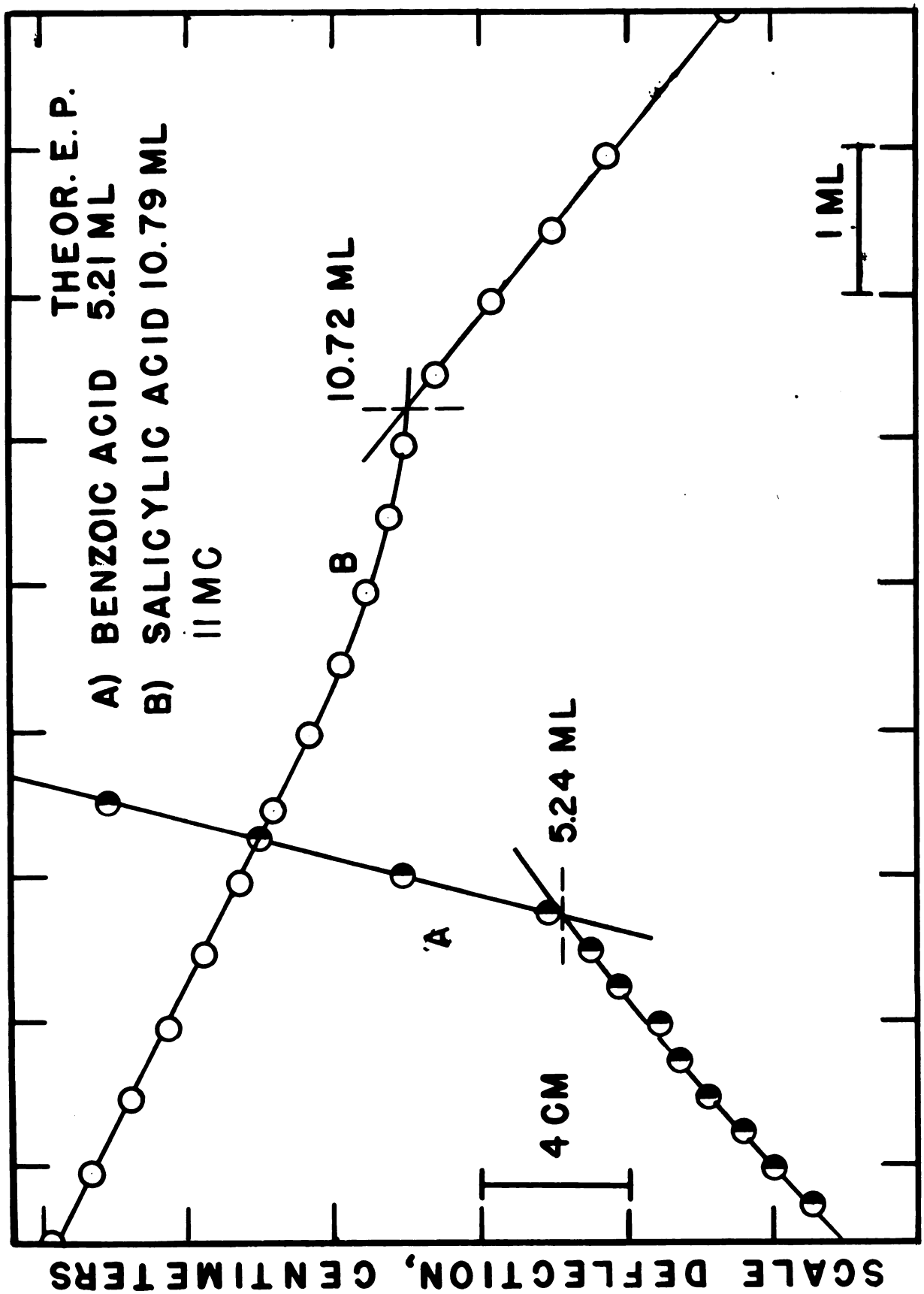

FIGURE 4. H.F. TITRATION CURVES FOR WEAK ACIDS IN BENZENE-METHANOL, KOME TITRANT.

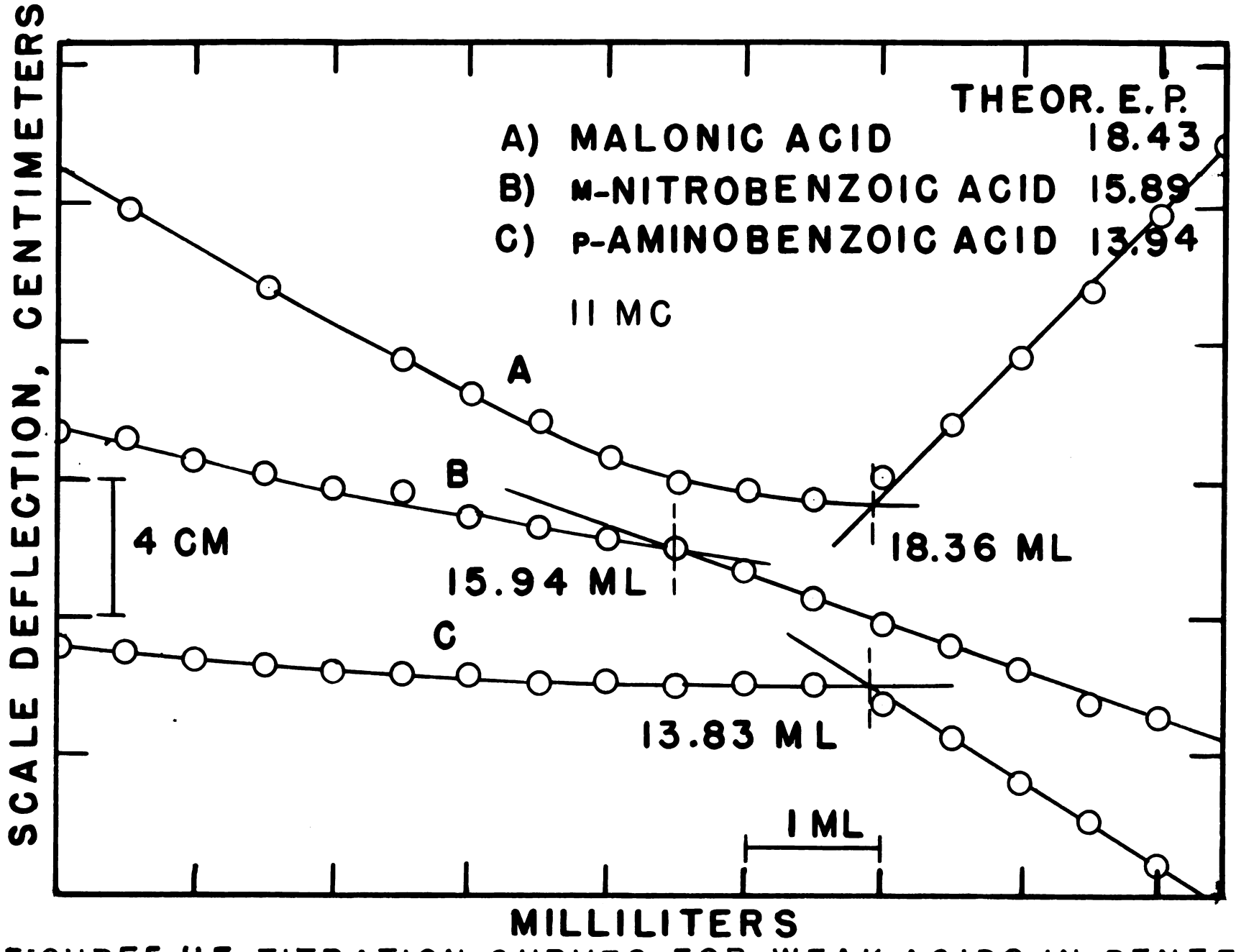

FIGURE 5. H.F. TITRATION CURVES FOR WEAK ACIDS IN BENZENE–METHANOL, KOME TITRANT.

Titrations in Dimethylformamide Solvent (Potassium Methoxide as Titrant)

Conductimetric

The titration of benzoic acid with potassium methoxide was the only conductimetric titration performed in this investigation. The conductimetric titration curve is very similar to that obtained by high frequency titrimetry for the same compound as is shown in Figure 6.

Potentiometric

An antimony-glass electrode pair was used in conjunction with the standardization of potassium methoxide with benzoic acid. No other compounds were titrated potentiometrically with potassium methoxide.

High Frequency

Phenol could not be titrated successfully with potassium methoxide because the acidity of the methanol present in the titrant solution masked the end point.

Either poorly defined or no end point breaks were obtained for the titration of benzoic acid, catechol, or methyl salicylate. Oxidation of catechol in the presence of excess titrant may have prevented its successful titration (24).

Vanillin, 2,4,6-trichlorophenol, resacetophenone, or 8-quinolinol were titrated satisfactorily. Typical titration curves for these compounds are shown in Figure 7. Results are listed in Table II.

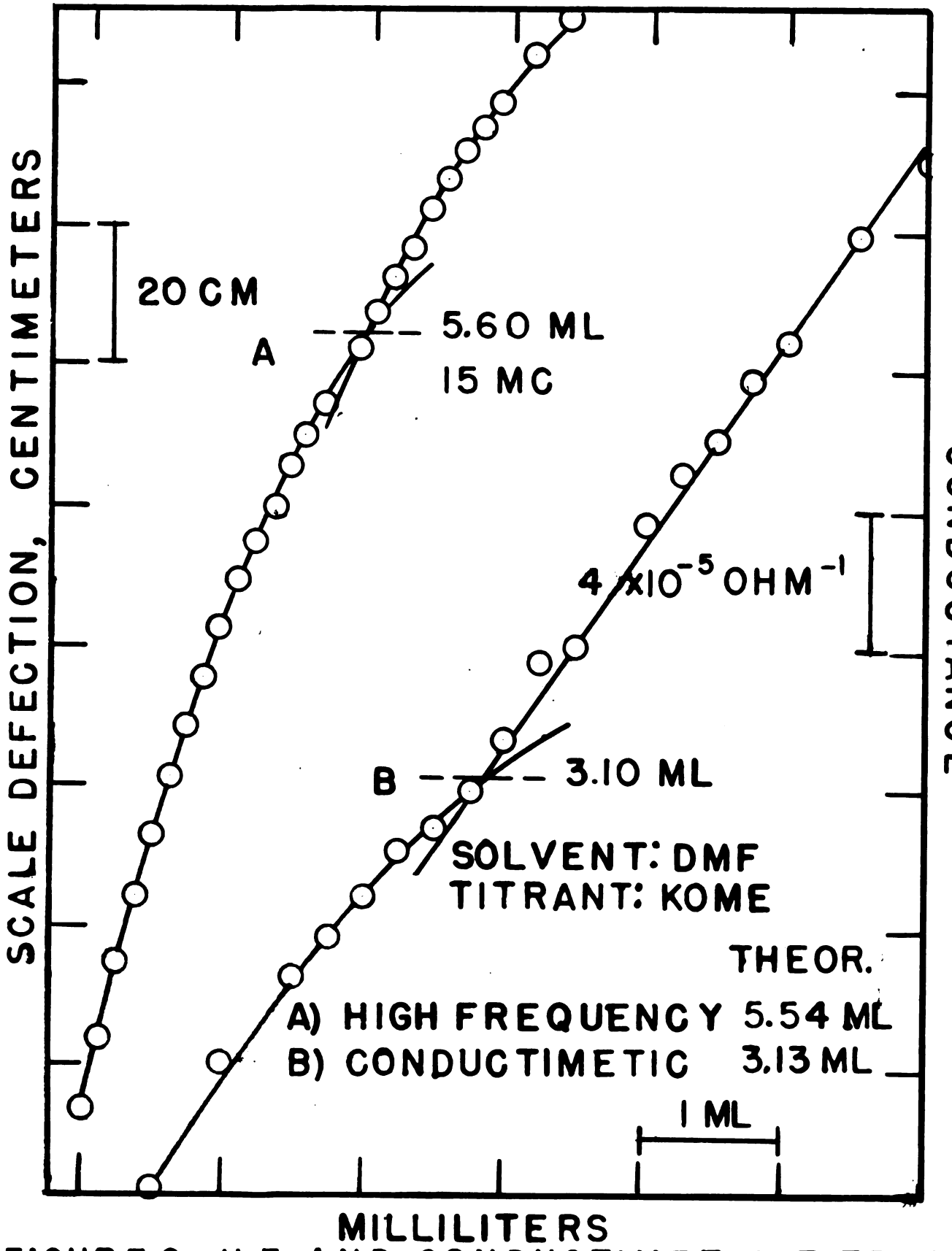

FIGURE 6. H.F. AND CONDUCTIMETIC TITRATION CURVES FOR BENZOIC ACID.

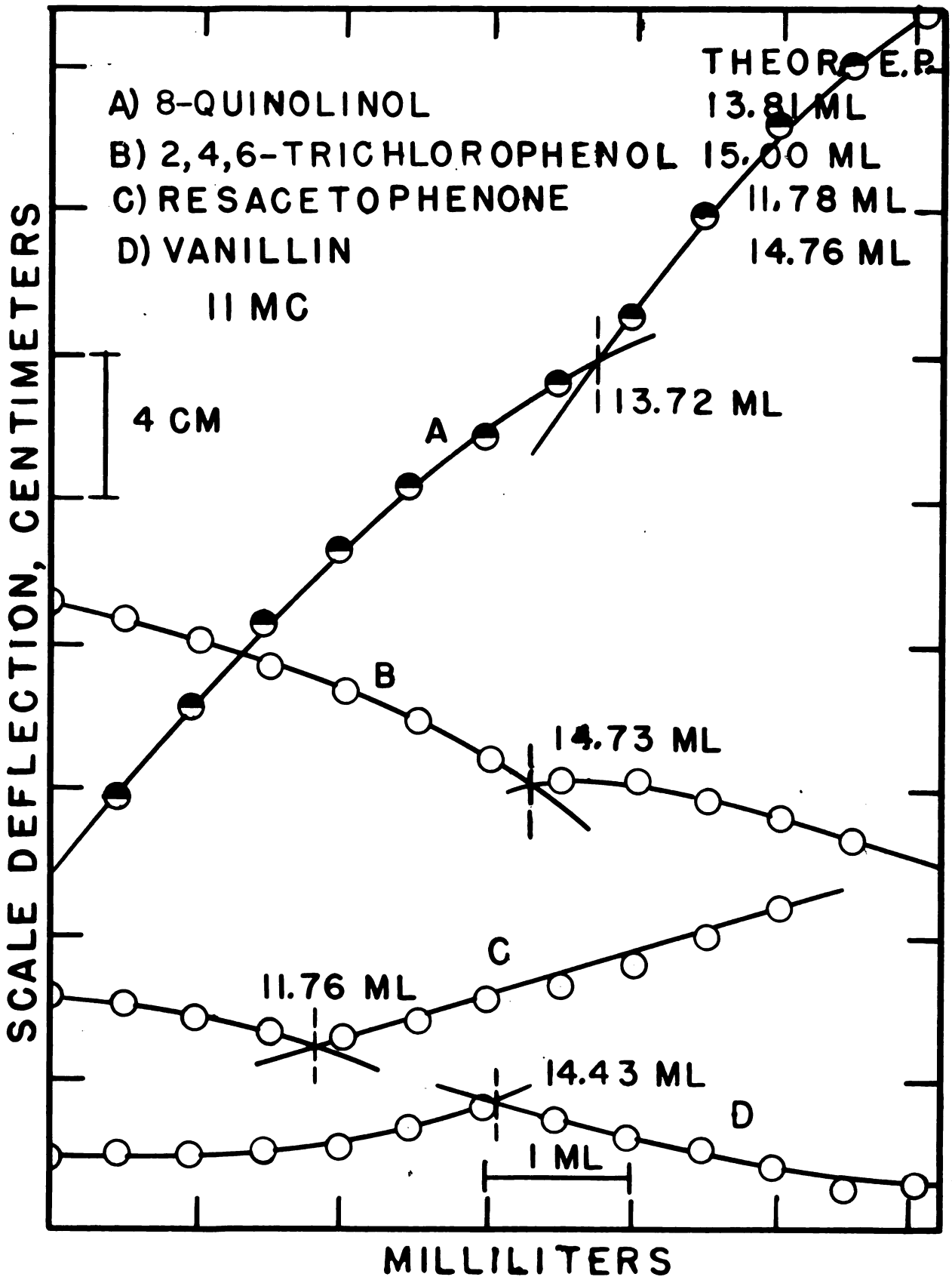

FIGURE 7. H.F. TITRATION CURVES FOR WEAK ACIDS IN DMF, KOME TITRANT.

Titrations in Dimethylformamide Solvent (Alcoholic Potassium Hydroxide as Titrant)

Potentiometric

During the preliminary investigation of alcoholic potassium hydroxide as a titrant for weak and very weak acids a sleeve type calomel electrode was not available, so a fiber tip type was tried. The fiber tip type calomel electrode was usable with the weak acid class even though it was less stable than the sleeve type. A serious draw-back to the utilization of the fiber tip type calomel electrode in dimethylformamide is the deposition of potassium salts on the fiber tip (2). It was observed that the electrode became sensitive to body capacitance upon prolonged use. To mitigate this effect somewhat, the electrode was soaked in water for a short period after a series of seven or eight titrations. A very erratic titration curve was obtained for phenol, Figure 8, curve B, when a fiber tip calomel electrode was used. The titration curve for 2,4,6-trichlorophenol, Figure 9, curve A, shows a large drop in potential immediately after the end point inflection.

The calomel (sleeve type)-glass electrode system proved to be responsive and stable for titrations of most of the very weak acids. Curve B of Figure 9 and curve A of Figure 8 are typical for these compounds. The end point inflections were small but sharp, except in the case of o-hydroxydiphenyl. For this compound almost a milliliter of titrant was required before the potential leveled off after the initial sharp rise at the inflection point. A representative titration curve for this compound is curve C, Figure 9.

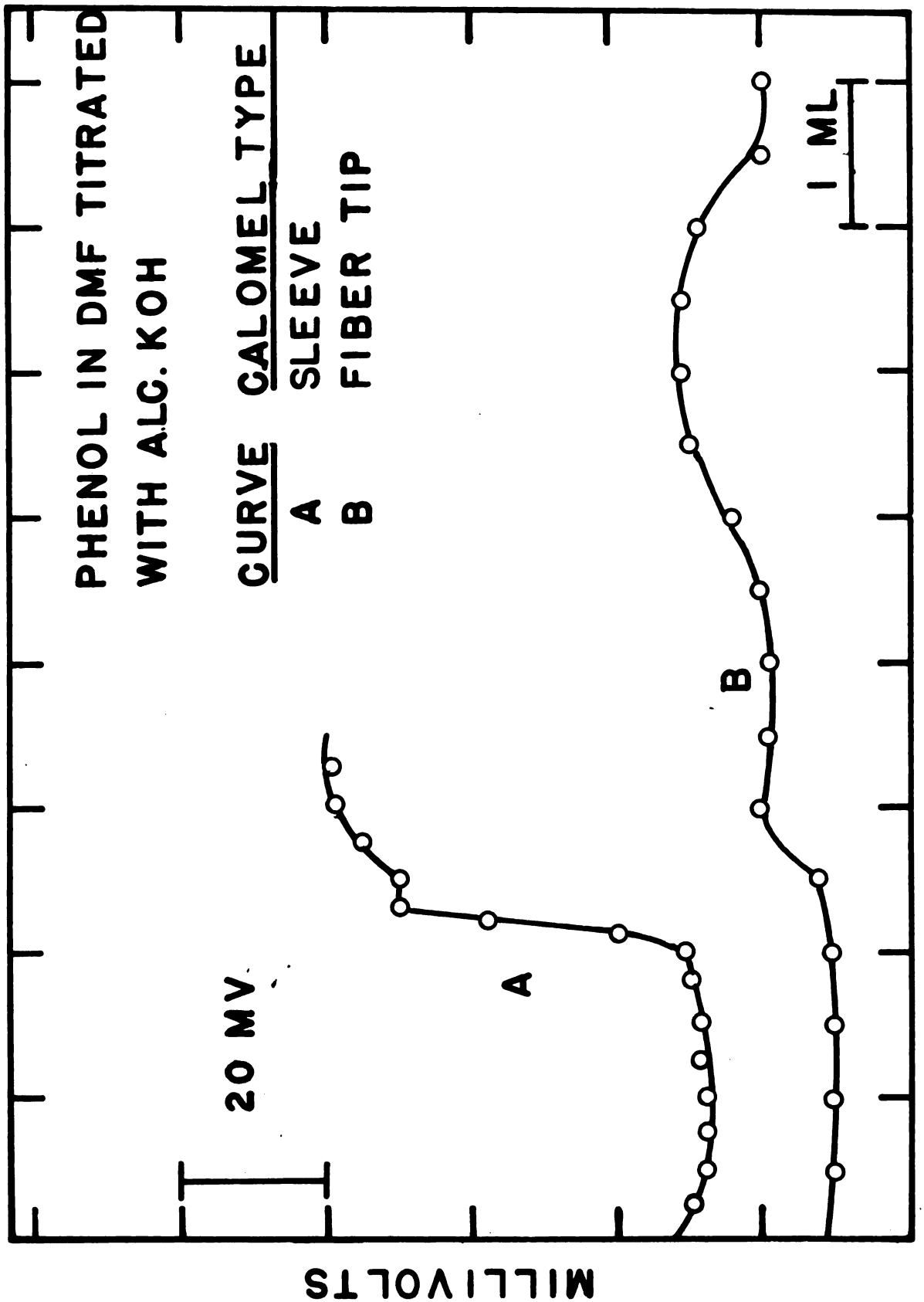

FIGURE 8. CALOMEL ELECTRODE PERFORMANCE

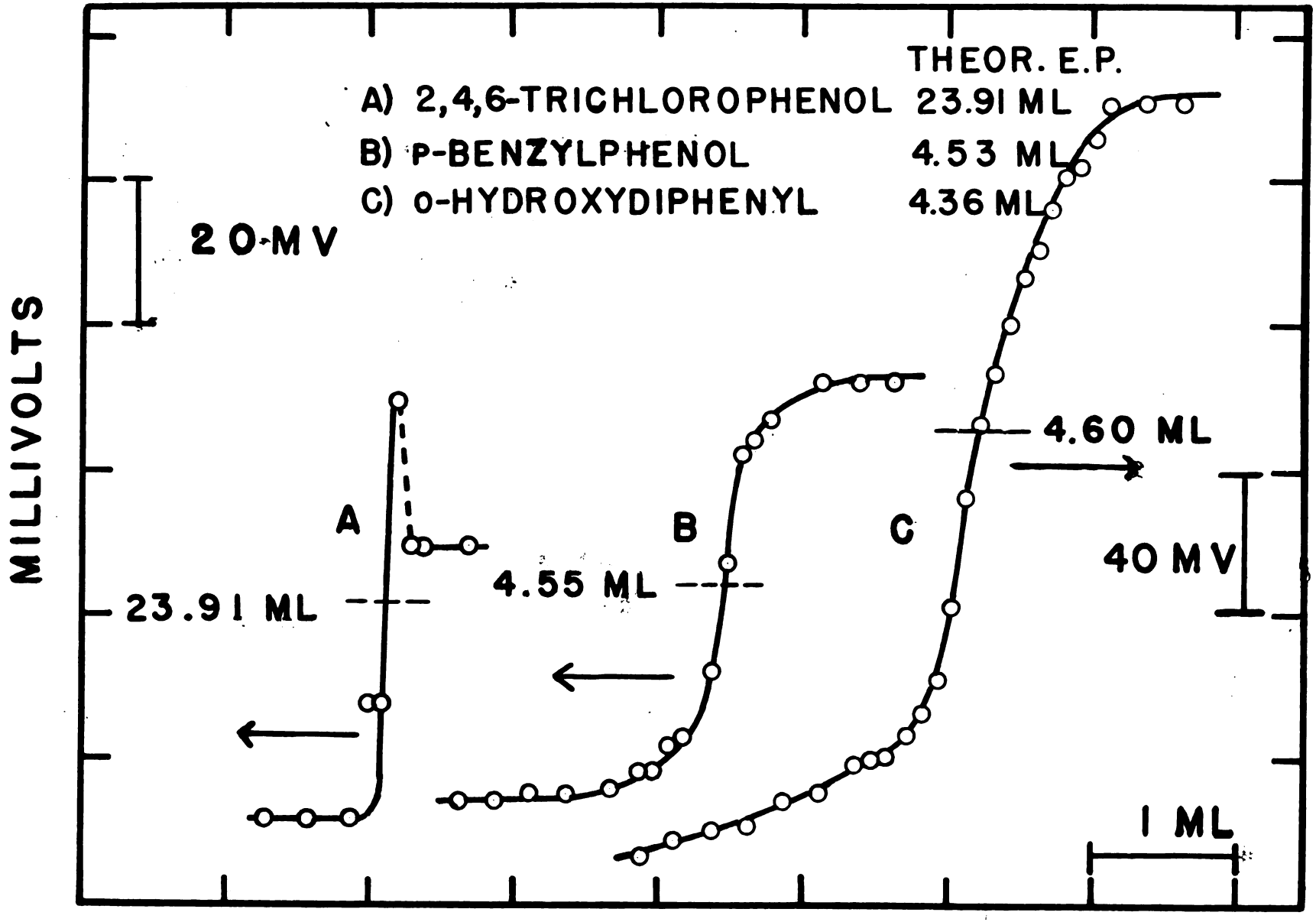

FIGURE 9. POTENTIOMETRIC TITRATION CURVES FOR VARIOUS PHENOLS IN DMF TITRATED WITH ALC. KOH

Titration results for the very weak acids are listed in Table I. Titration results for the weak acids are listed in Table II.

High Frequency

Distinct end point breaks were obtained for titrations of phenol, p-benzylphenol, p-bromophenol, o-hydroxydiphenyl, or β-naphthol, all very weak acids. Figures 10 and 11 are representative of the type of titration curves obtained for these compounds. Titration results are listed in Table I.

Para-tert-amylphenol failed to yield stoichiometric results even though the end point breaks were sharp and well defined as shown by curve C in Figure 10.

Stoichiometric results were unattainable for catechol or phloroglucinol. Black discoloration of the solutions after titration indicated oxidation of the compounds in an excess of titrant. No attempt was made to titrate resorcinol or hydroquinone. A possible solution to this oxidation problem would be to bubble nitrogen through the solvent to remove any dissolved oxygen before adding the sample.

The titration curves for benzoic or salicylic acids were unsatisfactory. At best, the scattering of individual points made the selection of the end point difficult.

Titration plots, Figures 12, 13 and 14, for adipic acid, 8-quinolinol, p-aminobenzoic acid, methyl salicylate, malonic acid, resacetophenone, m-nitrobenzoic acid, 2,4,6-trichlorophenol, or vanillin ranged from fair to good. Titration results are listed in Table II.

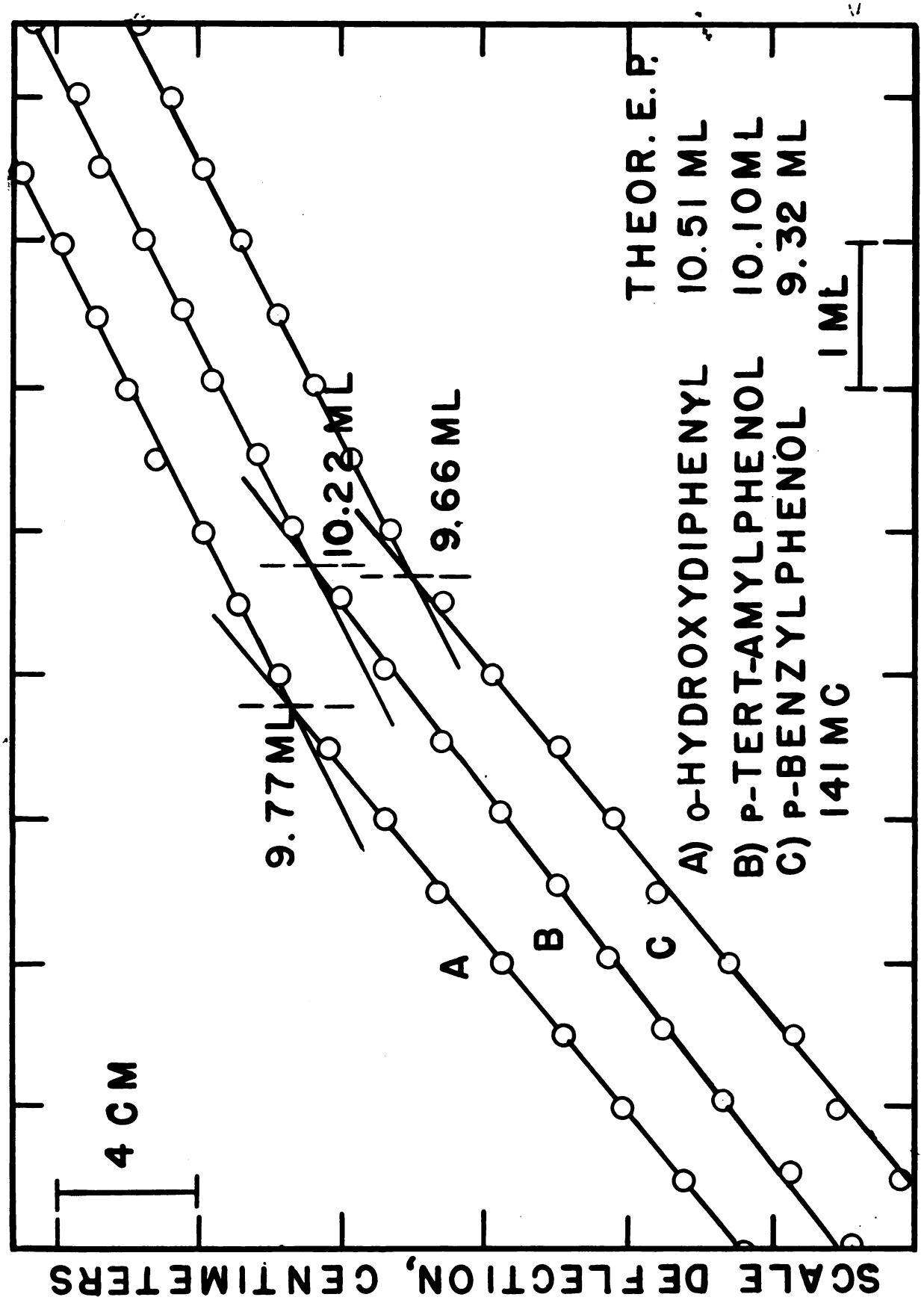

FIGURE 10. H.F. TITRATION CURVES FOR VERY WEAK ACIDS IN DMF, ALC. KOH TITRANT.

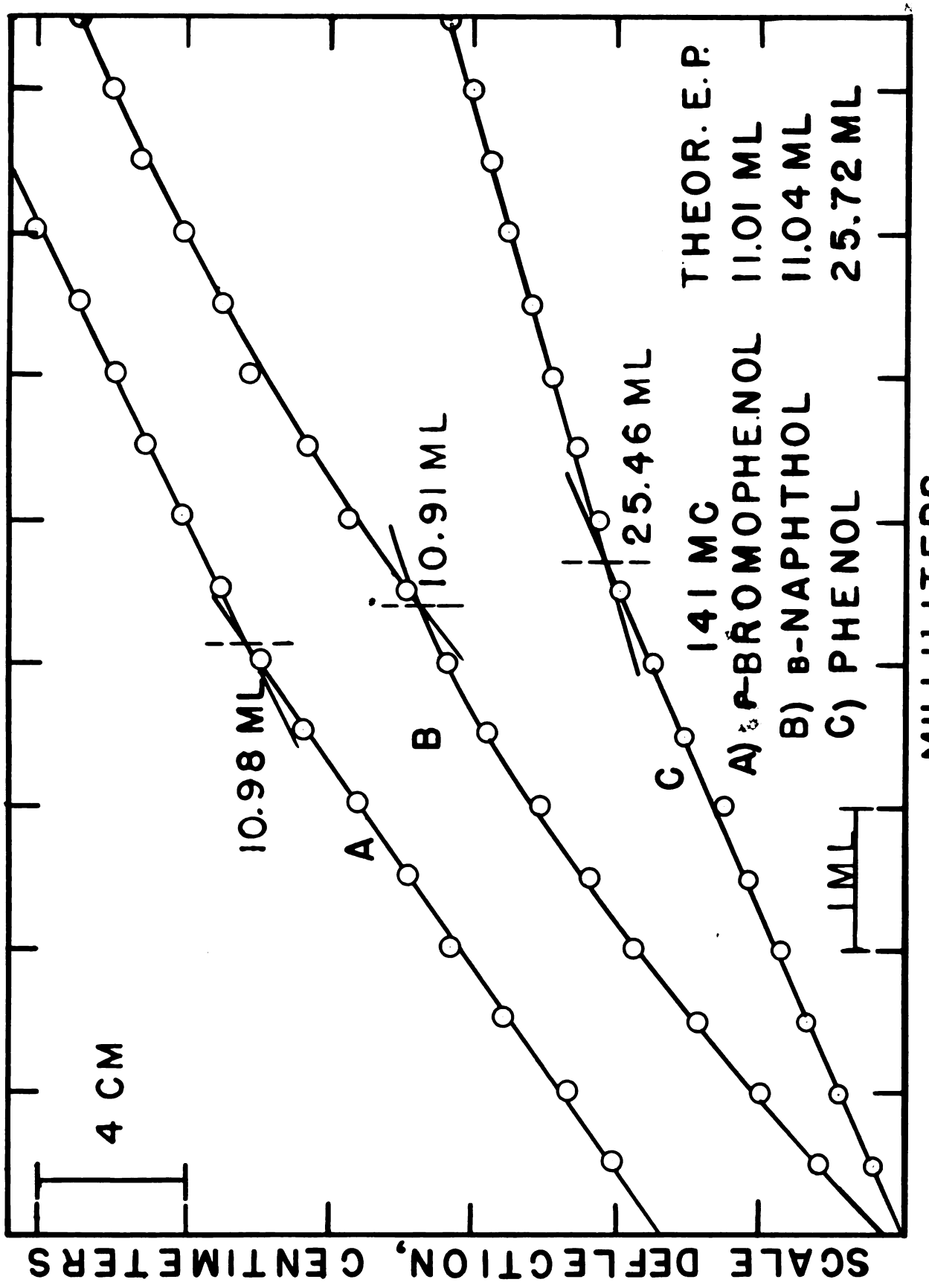

FIGURE II. H.F. TITRATION CURVES FOR VERY WEAK ACIDS IN DMF, ALC. KOH TITRANT.

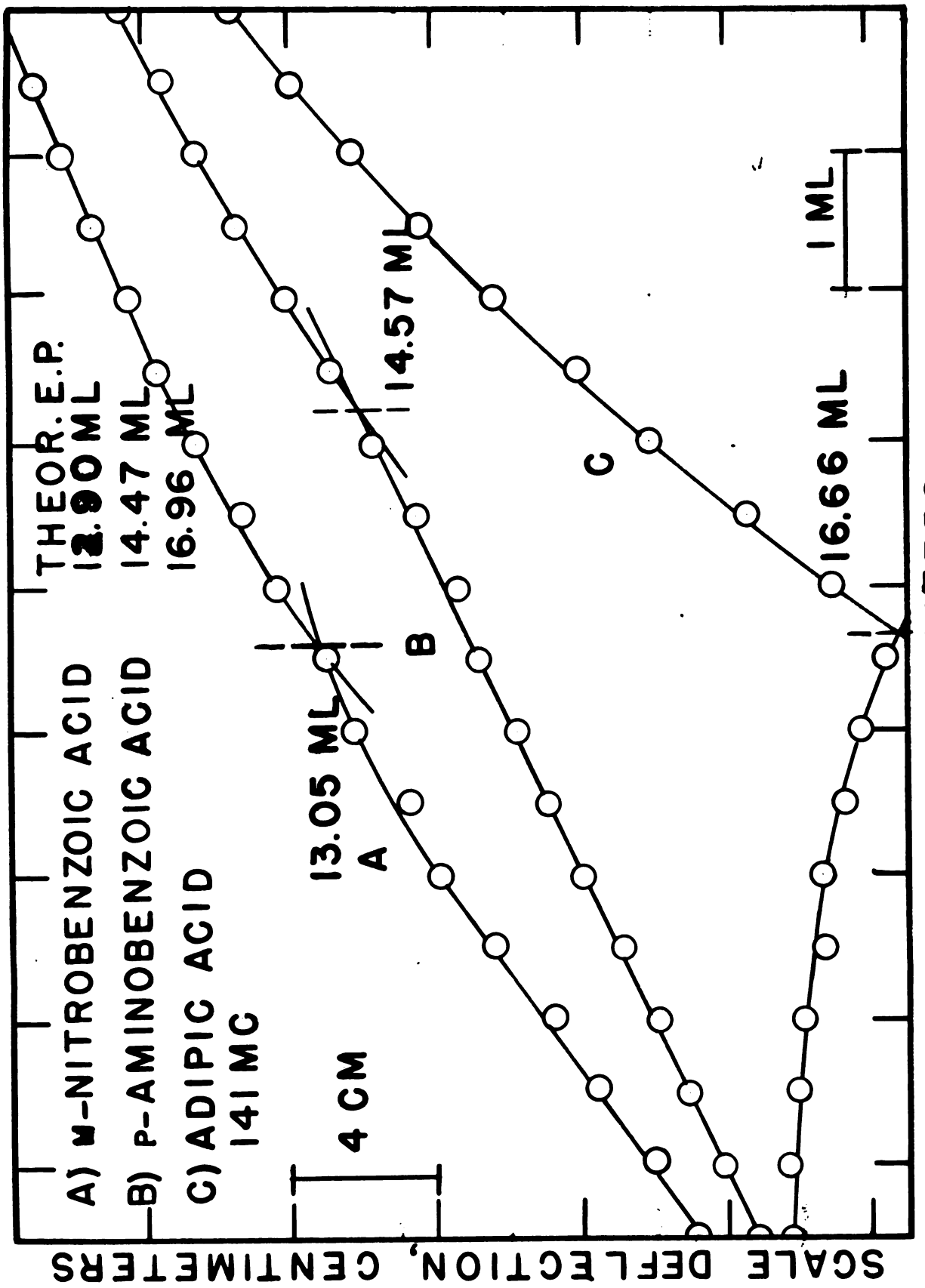

FIGURE 12. H.F. TITRATION CURVES FOR WEAK ACIDS IN DMF, ALC. KOH TITRANT.

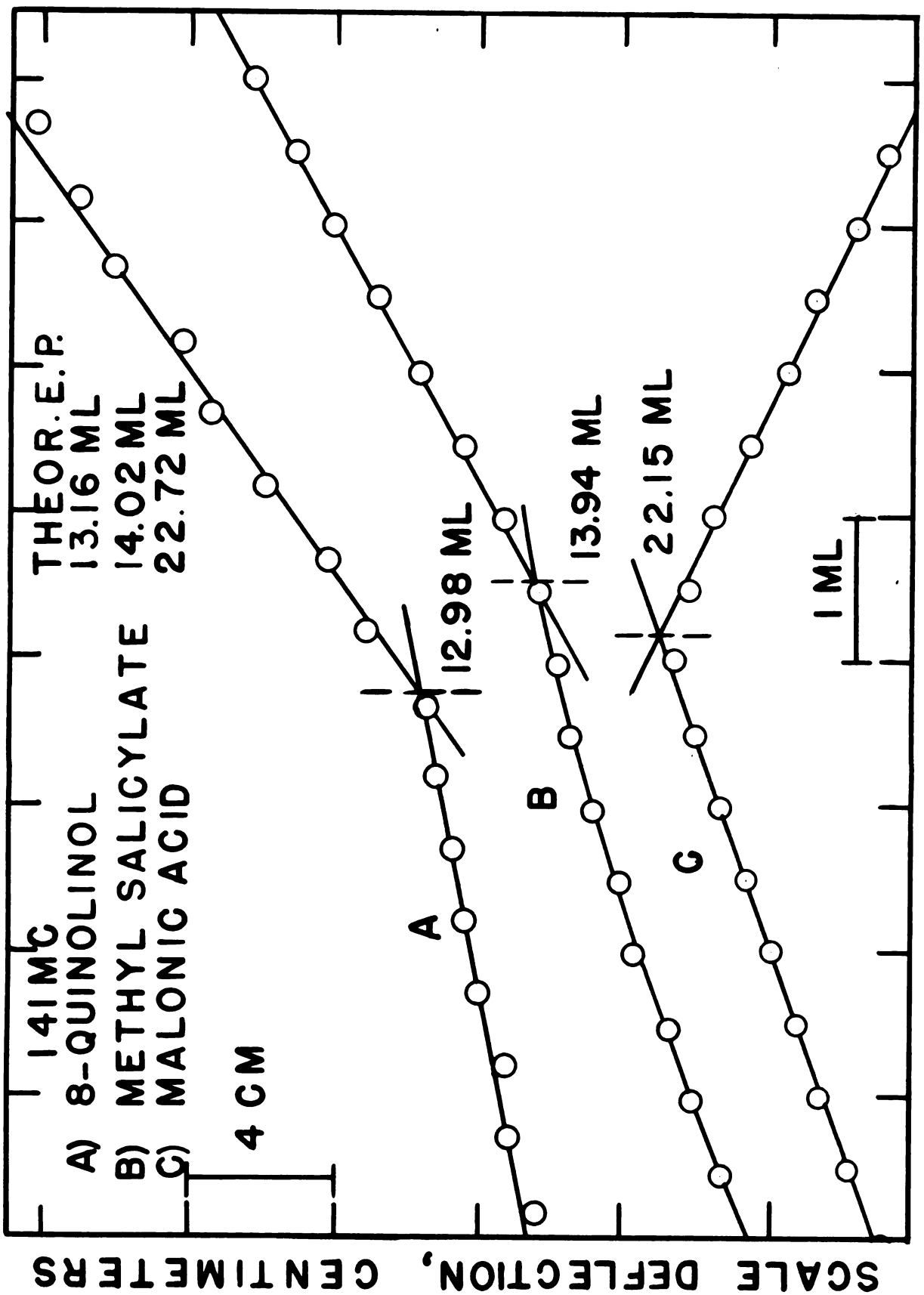

FIGURE 13. H.F. TITRATION CURVES FOR WEAK ACIDS IN DMF, ALC. KOH TITRANT.

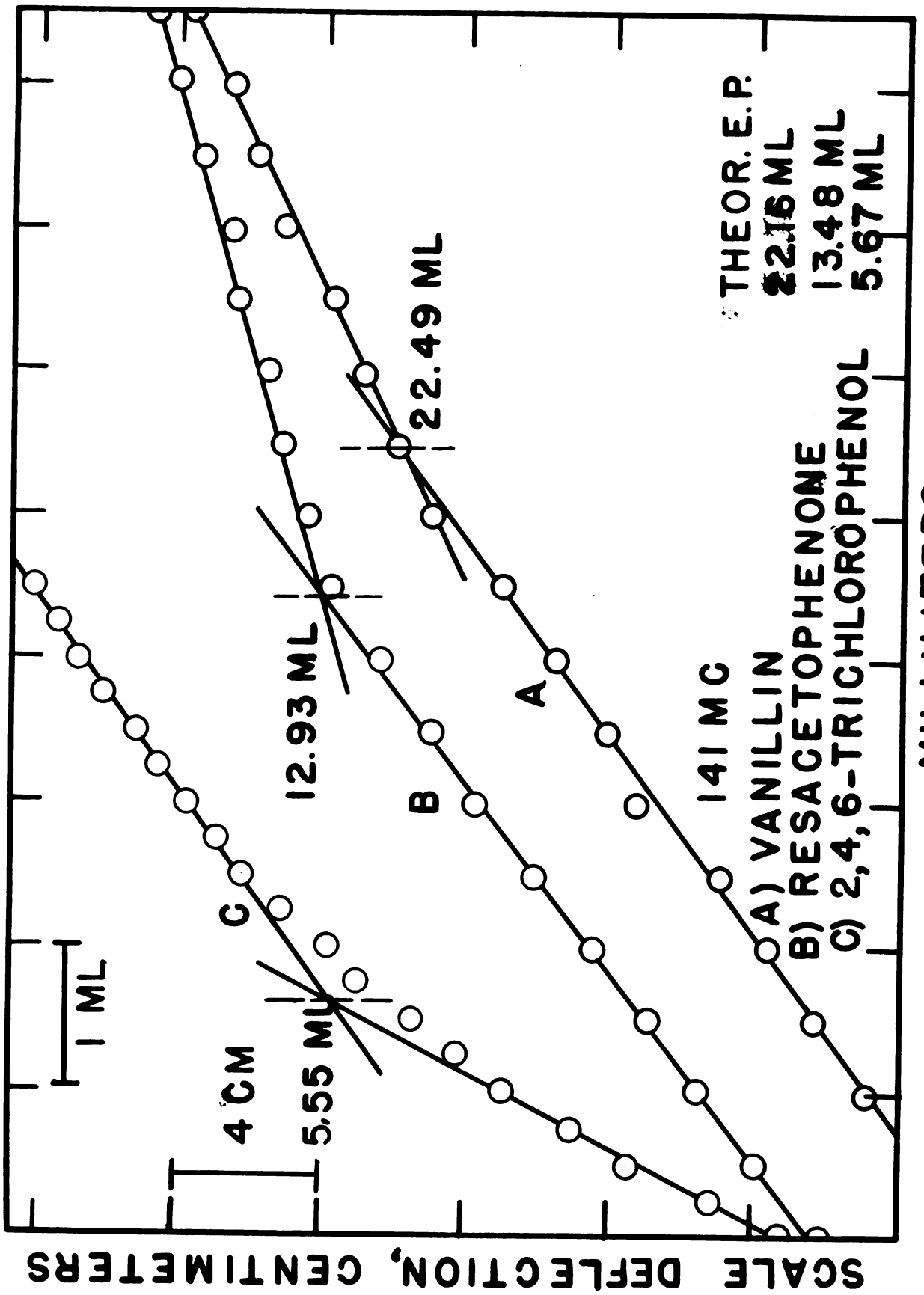

FIGURE 14. H.F. TITRATION CURVES FOR WEAK ACIDS IN DMF, ALC. KOH TITRANT.

As might be expected from pK values, the end point breaks for adipic or malonic acids were very well defined. The titration plots for p-aminobenzoic or m-nitrobenzoic acids, which have pK's similar to adipic and malonic acids, did not exhibit sharply defined end points. There was much scattering of individual points of the plots for these acids. The whole weak acid group, except for adipic and malonic acids, showed this tendency for scattered individual points of the titration plot, but not to such a marked degree.

Differential titrations of mixtures of phenol and 2,4,6-trichlorophenol were attempted. The data from the two titrations performed, although not conclusive, indicate the feasibility of the simultaneous titration of weak acids of different pK values by high frequency titrimetry. The results are:

	Run I	Run II
Total acid.....	100.6%	96.4%
2,4,6-Trichlorophenol.....	97.9	112.8
Phenol.....	103.2	82.3

Figure 15 shows the titration curve for Run I.

Titrations in Dimethylformamide Solvent (Sodium Methoxide as Titrant)

Visual

Only two weak acids did not give entirely satisfactory titrations with azo violet indicator. The end point for adipic acid was obscured by precipitation of its potassium salt. Fading of the end point was observed when malonic acid was titrated. Titration results are listed in Table II.

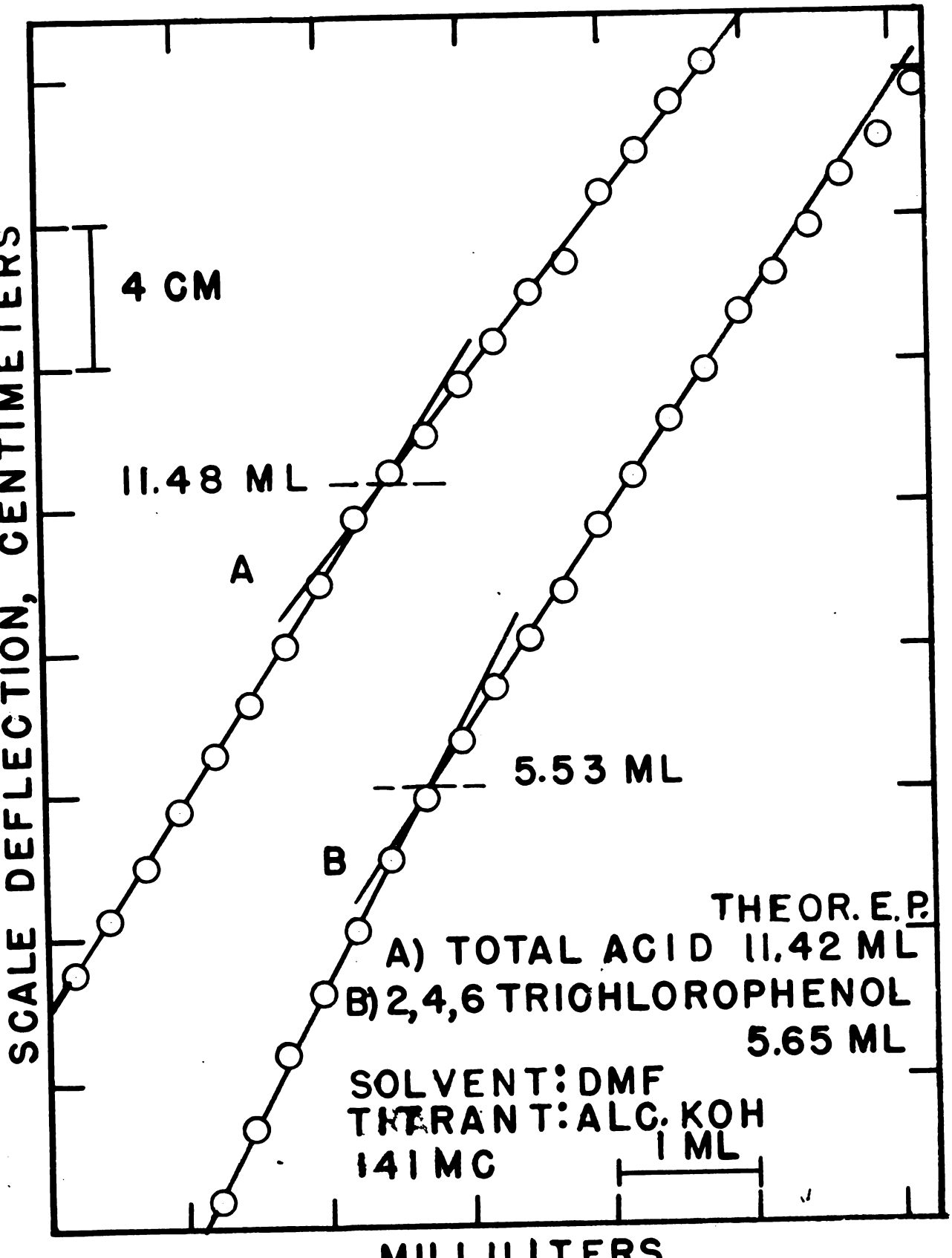

FIGURE 15. H.F. TITRATION FOR A MIXTURE OF PHENOL AND 2,4,6-TRICHLOROPHENOL.

Titrations in Ethylenediamine Solvent (Sodium Methoxide as Titrant)

Visual

The color change from yellow to orange-red for o-nitroaniline indicator used for titrations in ethylenediamine with sodium methoxide is not as distinct as the change to blue of azo violet in dimethylformamide. Little difficulty was encountered in determining the end point. Titration results for the very weak acids are listed in Table I.

Tabulation of Titration Results

The compounds titrated in this investigation were divided into two groups, weak acids and very weak acids. This division is based upon relative strengths. The tables of experimental results were therefore organized on this basis.

The titration results obtained from high frequency, potentiometric, and visual procedures for individual compounds are grouped together under the name of the compound in order to facilitate comparison.

The size of the circles used in the titration plots is not proportional to error because of uncertainty as to the magnitude of error introduced by fluctuations of the recorder.

TABLE I

TITRATIONS OF VERY WEAK ACIDS

Method	Solvent	Sample Wt. (grams)	Titrant	Normality	Ml. Used[a]	Ml. Theor.	Percent Purity
			p Tert-amylphenol				
HF[b](1µl mc)	DMF[c]	0.2045	Alc. KOH	0.0961	11.47	12.96	88.5
HF(1µlmc)	DMF	0.1564	Alc. KOH	0.0961	8.96	9.91	90.5
HF(1µl mc)	DMF	0.1537	Alc. KOH	0.0961	9.86	9.74	101.3
Pot[d]	DMF	0.2010	Alc. KOH	0.2677	4.55	4.57	99.5
Pot	DMF	0.2021	Alc. KOH	0.2677	4.56	4.60	99.2
Visual	EDA[e]	0.1975	NaOMe	0.1609	7.52	7.47	100.6
Visual	EDA	0.2029	NaOMe	0.1609	7.70	7.68	100.3
			p-Benzylphenol				
HF(1µl mc)	DMF	0.2237	Alc. KOH	0.0961	12.58	12.63	99.6
HF(1µl mc)	DMF	0.1792	Alc. KOH	0.0961	10.09	10.12	99.7
HF(1µl mc)	DMF	0.1579	Alc. KOH	0.0961	9.26	8.92	103.8
Pot	DMF	0.2093	Alc. KOH	0.2677	4.27	4.24	100.6
Pot	DMF	0.2190	Alc. KOH	0.2677	4.46	4.44	100.4
Visual	EDA	0.2029	NaOMe	0.1609	6.84	6.84	99.9
Visual	EDA	0.2147	NaOMe	0.1609	7.20	7.24	99.4

[a] Corrected for blank, if necessary.
[b] High frequency method.
[c] Dimethylformamide.
[d] Potentiometric Method.
[e] Ethylenediamine.

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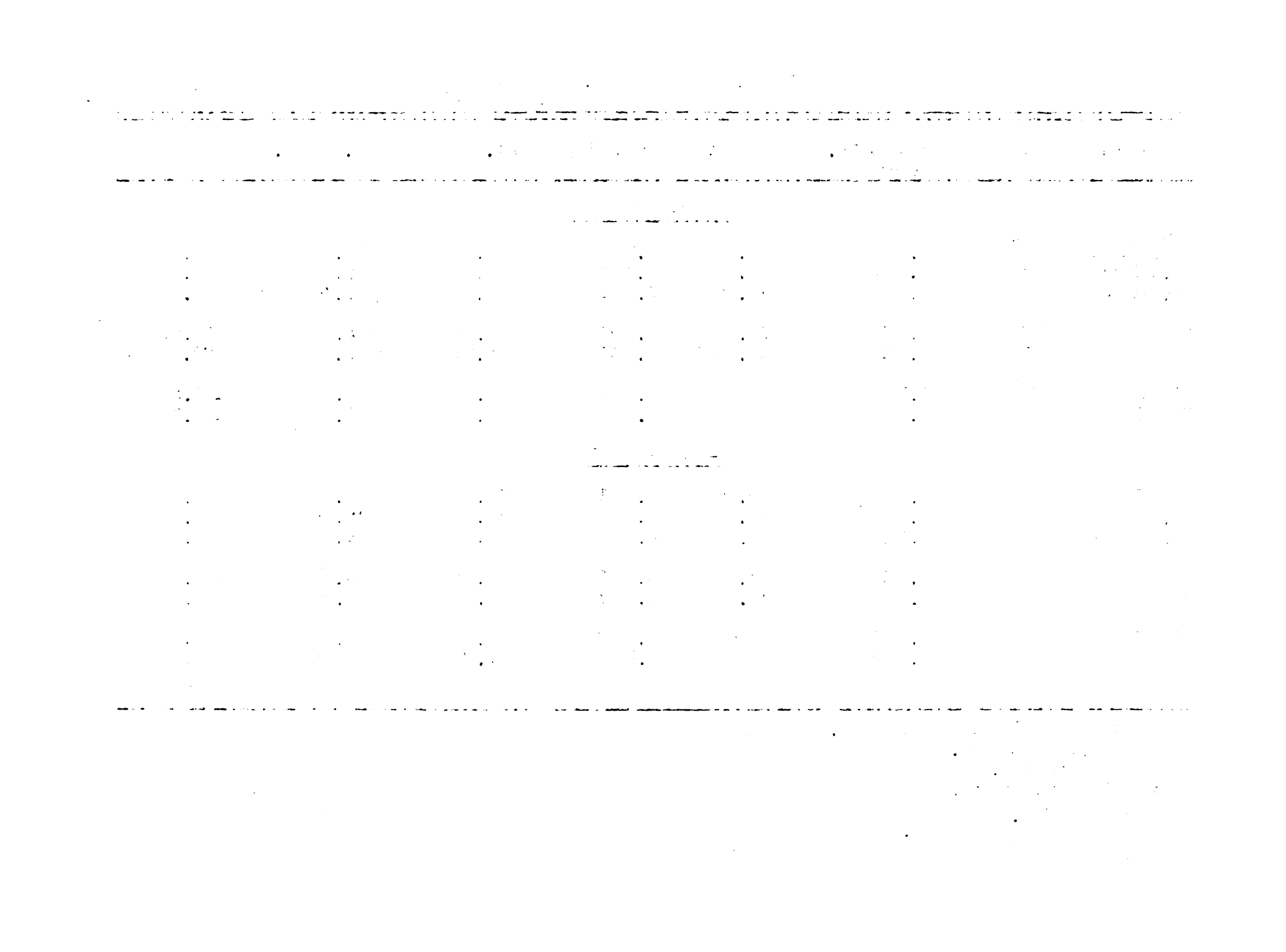

TABLE I - Continued

Method	Solvent	Sample Wt. (grams)	Titrant	Normality	Ml. Used[a]	Ml. Theor.	Percent Purity
			p-Bromophenol				
HF(141 mc)	DMF	0.1771	Alc. KOH	0.0961	10.62	10.65	99.7
HF(141 Mc)	DMF	0.1998	Alc. KOH	0.0961	11.97	12.02	99.6
Pot	DMF	0.1986	Alc. KOH	0.2677	4.36	4.29	101.7
Pot	DMF	0.1973	Alc. KOH	0.2677	4.31	4.26	101.2
Visual	EDA	0.1782	NaOMe	0.1609	6.45	6.40	100.8
Visual	EDA	0.1296	NaOMe	0.1609	4.67	4.66	100.4
			o-Hydroxydiphenyl				
HF(141 mc)	DMF	0.1471	Alc. KOH	0.0961	9.02	9.00	100.3
HF(141 mc)	DMF	0.1658	Alc. KOH	0.0961	9.41	10.15	92.8
HF(141 mc)	DMF	0.1575	Alc. KOH	0.0961	9.74	9.64	101.1
Pot	DMF	0.1946	Alc. KOH	0.2677	NG	4.28	
Pot	DMF	0.2041	Alc. KOH	0.2677	4.54	4.48	101.4
Visual	EDA	0.1949	NaOMe	0.1609	7.14	7.12	100.3
Visual	EDA	0.1869	NaOMe	0.1609	6.77	6.83	99.2
Visual	EDA	0.1805	NaOMe	0.1609	6.63	6.60	100.6
			β Naphthol				
HF(141 mc)	DMF	0.1643	Alc. KOH	0.0961	11.80	11.86	99.4
HF(141 mc)	DMF	0.1474	Alc. KOH	0.0961	10.51	10.64	98.8
HF(141 mc)	DMF	0.0988	Alc. KOH	0.0961	7.11	7.13	99.7
Pot	DMF	0.2015	Alc. KOH	0.2677	5.24	5.22	100.4
Pot	DMF	0.2013	Alc. KOH	0.2677	5.30	5.22	100.7
Visual	EDA	0.2140	NaOMe	0.1609	9.29	9.23	100.7
Visual	EDA	0.2124	NaOMe	0.1609	9.16	9.16	100.0

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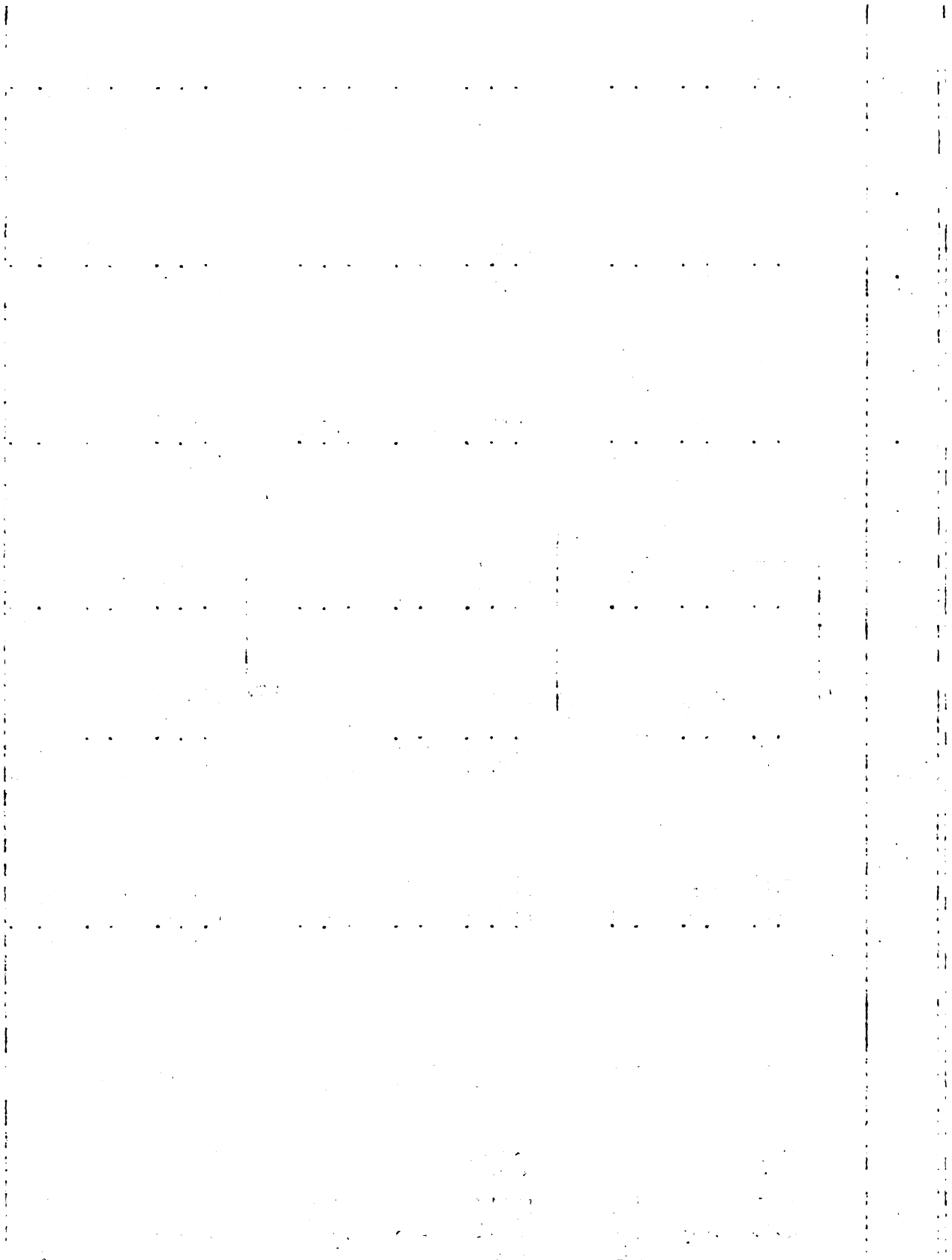

TABLE I - Continued

Method	Solvent	Sample Wt. (grams)	Titrant	Normality	Ml. Used[a]	Ml. Theor.	Percent Purity
			Phenol-(pK-9.9)				
HF(11 mc)	DMF	0.1562	Alc KOH	0.1006	16.32	16.50	98.9
HF(11 mc)	DMF	0.1222	Alc KOH	0.1006	11.98	12.91	92.8
HF(11 mc)	DMF	0.2012	Alc KOH	0.1006	21.12	21.25	99.4
HF(141 mc)	DMF	0.2832	Alc KOH	0.1021	28.99	29.47	98.4
HF(141 mc)	DMF	0.2709	Alc KOH	0.1021	27.69	28.19	98.2
HF(141 mc)	DMF	0.2374	Alc KOH	0.1021	24.44	24.70	98.9
HF(141 mc)	DMF	0.2585	Alc KOH	0.1021	27.51	26.90	102.3
HF(141 mc)	DMF	0.1950	Alc KOH	0.0997	21.21	20.78	102.1
HF(141 mc)	DMF	0.1876	Alc KOH	0.0997	18.88	19.98	94.4
HF(141 mc)	DMF	0.2137	Alc KOH	0.0997	23.33	22.76	102.4
HF(141 mc)	DMF	0.2127	Alc KOH	0.0961	23.14	23.52	98.4
HF(141 mc)	DMF	0.1031	Alc KOH	0.0961	11.09	11.40	97.3
HF(141 mc)	DMF	0.1243	Alc KOH	0.2697	4.83	4.90	98.6
HF(141 mc)	DMF	0.2310	Alc KOH	0.2697	9.00	9.10	98.9
Pot	DMF	0.1774	Alc KOH	0.2677	7.05	7.04	100.1
Pot	DMF	0.1878	Alc KOH	0.2677	7.46	7.45	100.1
Visual	EDA	0.1287	NaOMe	0.1609	8.51	8.50	100.1
Visual	EDA	0.1228	NaOMe	0.1609	8.08	8.11	99.6

Phenol by Bromination

Solvent	Sample Wt. (grams)	Aliquot	Blank Average)	Titrant	Normality[a] $Na_2S_2O_3$	Ml. Used	Ml. Theor.	Percent Purity
1000 ml. H_2O	0.3108	A) 100 ml.	47.82 ml.	$Na_2S_2O_3$	0.1008	28.23	28.13	99.7
		B) 100 ml.	47.82 ml.	$Na_2S_2O_3$	0.1008	28.41	28.13	98.7
		C) 100 ml.	47.82 ml.	$Na_2S_2O_3$	0.1008	28.40	28.13	98.8

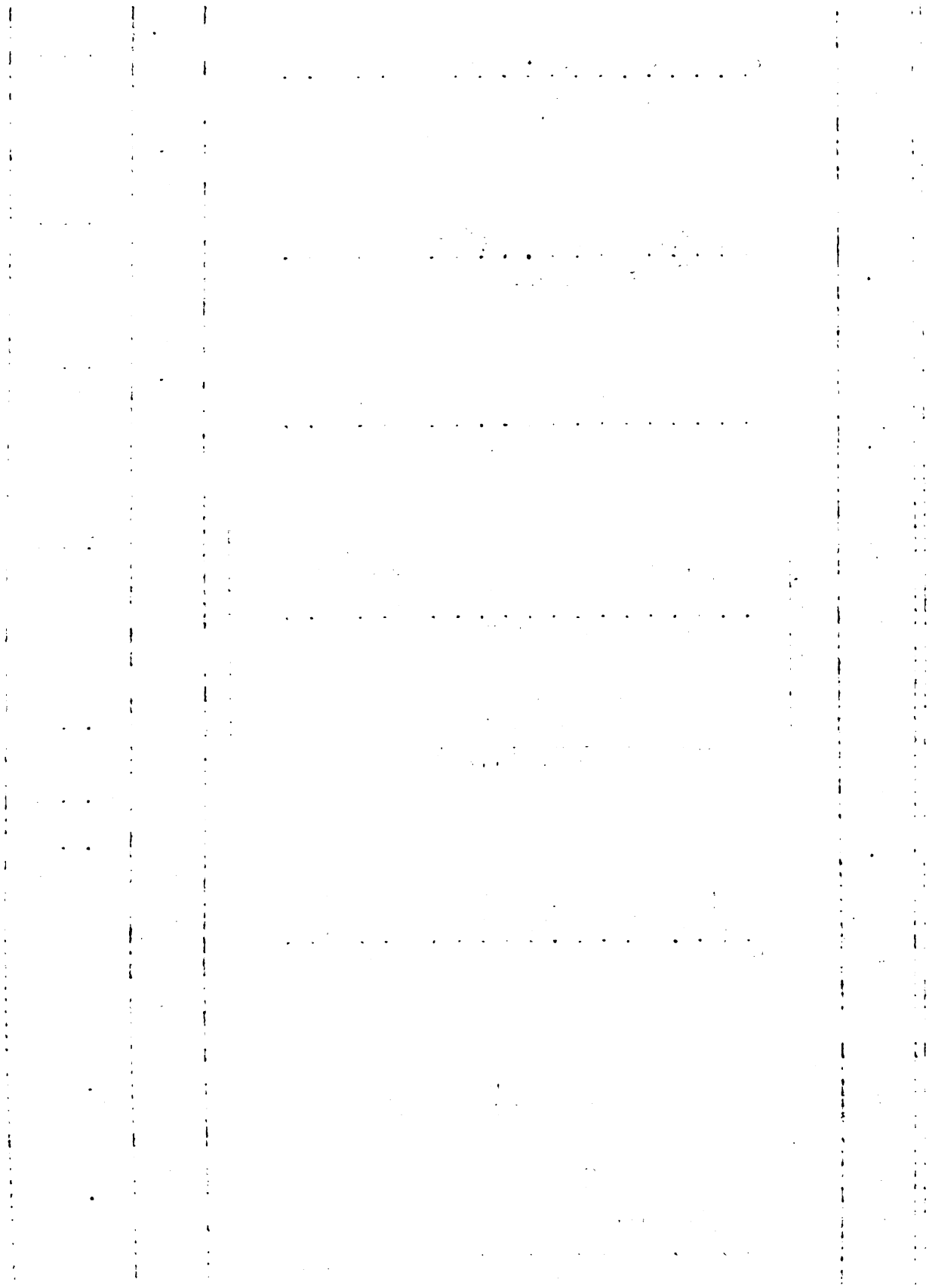

TABLE II

TITRATIONS OF WEAK ACIDS

Method	Solvent	Sample Wt. (grams)	Titrant	Normality	Ml. Used[a]	Ml. Theory	Percent Purity
			Adipic Acid (pK-4.4)				
HF[b](141 mc)	DMF[c]	0.1657	Alc KOH	0.0961	23.12	23.59	98.0
HF(141 mc)	DMF	0.1936	Alc KOH	0.0961	27.27	27.57	99.9
HF(141 mc)	DMF	0.1165	Alc KOH	0.0961	16.29	16.59	98.2
HF(141 mc)	DMF	0.0930	Alc KOH	0.2697	4.64	4.72	98.3
HF(141 mc)	DMF	0.1000	Alc KOH	0.2697	5.05	5.07	99.5
Pot[d]	DMF	0.1991	Alc KOH	0.0979	26.35	27.27	94.8
Pot	DMF	0.1854	Alc KOH	0.1095	22.90	23.17	98.8
Pot	DMF	0.0988	Alc KOH	0.2677	4.94	5.05	98.2
Visual	DMF	0.0817	NaOMe	0.1609	6.99	6.95	100.6
Visual	DMF	0.0774	NaOMe	0.1609	6.61	6.58	100.4
			p-Aminobenzoic Acid (pK 4.9)				
HF(11 mc)	Benzene-Methanol	0.2019	KOMe	0.1056	13.83	13.94	99.2
HF(141 mc)	DMF	0.2945	Alc KOH	0.1091	19.83	19.68	100.7
HF(141 mc)	DMF	0.2044	Alc KOH	0.1091	13.69	13.66	100.2
HF(141 mc)	DMF	0.1855	Alc KOH	0.0961	14.17	14.07	100.7
Pot	DMF	0.3145	Alc KOH	0.0979	23.65	23.43	101.1
Pot	DMF	0.4008	Alc KOH	0.1095	26.89	26.69	100.7
Visual	DMF	0.1422	NaOMe	0.1609	6.45	6.44	100.1
Visual	DMF	0.1199	NaOMe	0.1609	5.44	5.43	100.1

[a] Corrected for blank, if necessary
[b] High frequency method
[c] Dimethylformamide
[d] Potentiometric method

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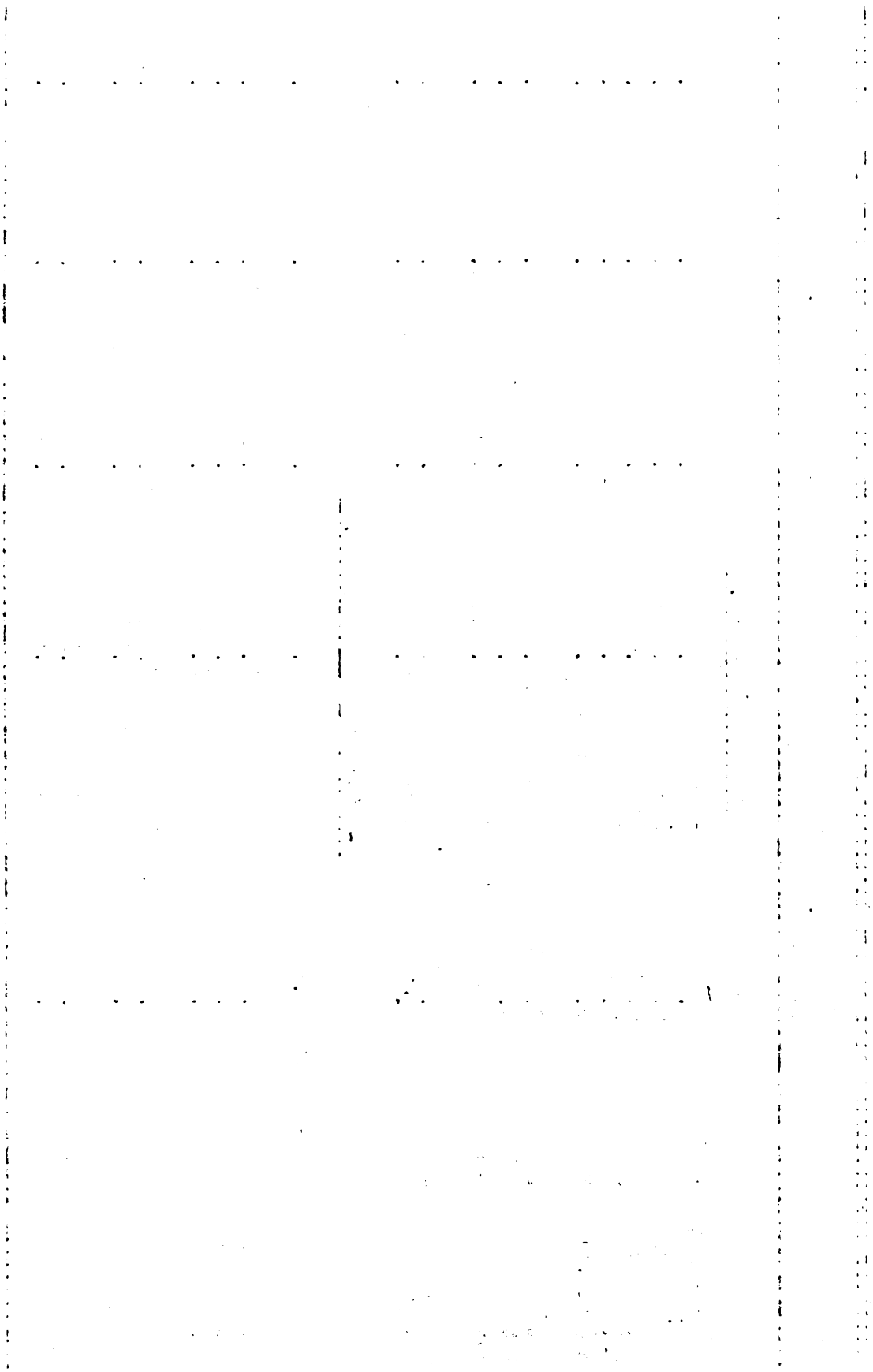

TABLE II - Continued

Method	Solvent	Sample Wt. (grams)	Titrant	Normality	Ml. Used[a]	Ml. Theory	Percent Purity
			Benzoic Acid (pK-4.2)				
HF(11 mc)	Benzene-Methanol	0.0681	KOMe	0.1056	5.24	5.28	99.2
HF(11 mc)	Benzene-Methanol	0.0835	KOMe	0.1056	6.34	6.47	98.0
HF(11 mc)	Benzene-Methanol	0.0529	KOMe	0.1056	4.09	4.10	99.8
HF(141 mc)	DMF	0.1386	Alc. KOH	0.0961	11.59	11.81	98.1
HF(141 mc)	DMF	0.1883	Alc. KOH	0.2697	5.60	5.72	98.0
HF(141 mc)	DMF	0.1633	Alc. KOH	0.2697	4.94	4.96	99.6
HF(141 mc)	DMF	0.1391	Alc. KOH	0.2697	4.17	4.22	98.7
Conductivity	DMF	0.0405	KOMe	0.1084	3.06	3.09	99.0
			Malonic Acid (pK's-2.9,6.1)				
HF(11 mc)	Benzene-Methanol	0.2025	KOMe	0.1056	18.36	18.43	99.6
HF(141 mc)	DMF	0.2539	Alc. KOH	0.1091	21.79	22.36	97.4
HF(141 mc)	DMF	0.2537	Alc. KOH	0.1091	21.75	22.35	97.3
Pot	DMF	0.2578	Alc. KOH	0.0979	24.60	25.31	97.4
Pot	DMF	0.2576	Alc. KOH	0.1095	22.20	22.61	98.2
Pot	DMF	0.1421	Alc. KOH	0.2677	4.90	5.10	96.3
Visual	DMF	0.0905	NaOMe	0.1609	10.92	10.81	101.1
Visual	DMF	0.0707	NaOMe	0.1609	8.45	8.40	100.7
			Methyl Salicylate				
HF(141 mc)	DMF	0.1775	Alc. KOH	0.0961	11.97	12.14	98.6
HF(141 mc)	DMF	0.1996	Alc. KOH	0.0961	13.57	13.65	99.4
HF(141 mc)	DMF	0.2054	Alc. KOH	0.0961	13.75	14.05	97.9

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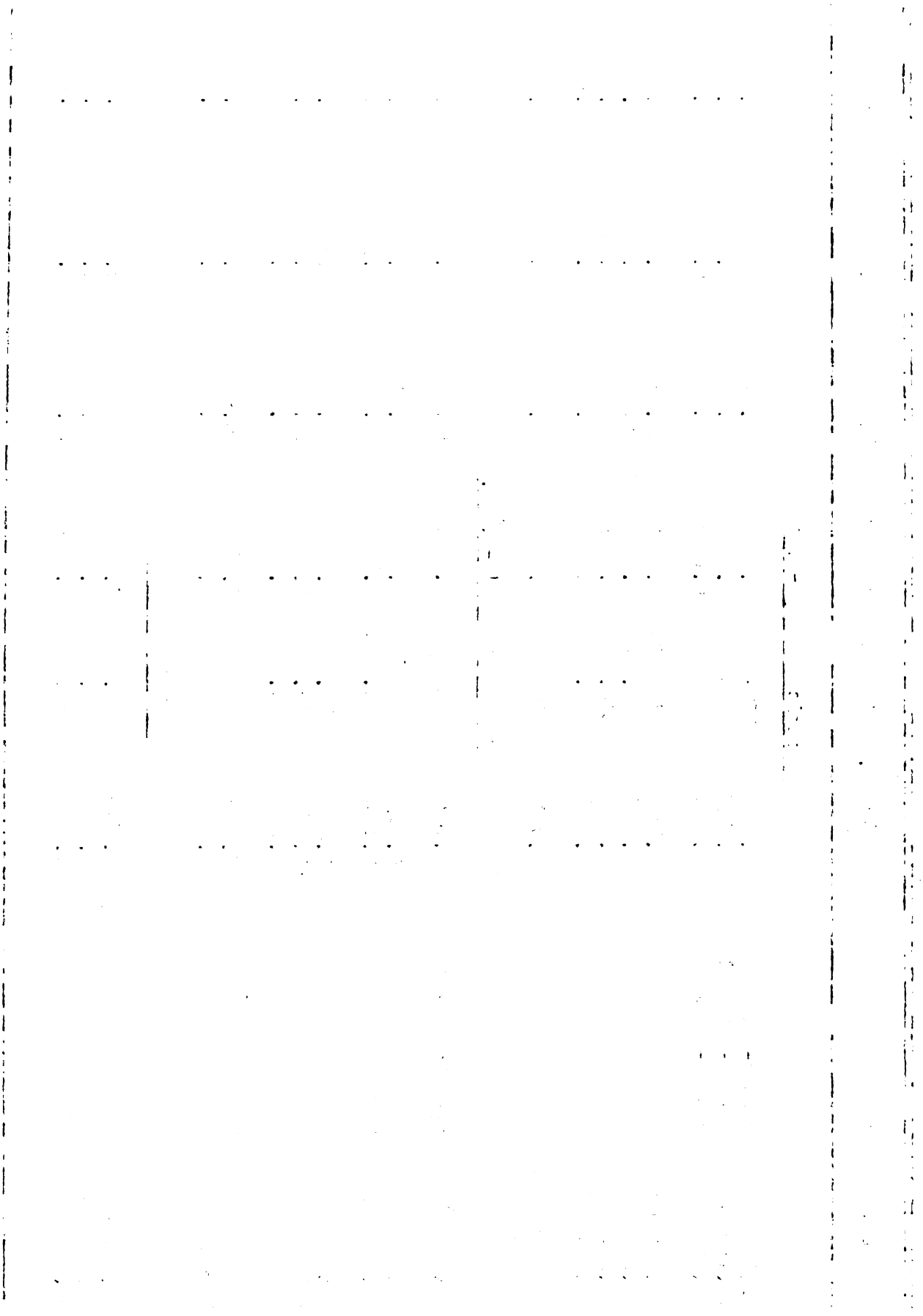

TABLE II - Continued

Method	Solvent	Sample Wt. (grams)	Titrant	Normality	Ml. Used[a]	Ml. Theory	Percent Purity
			Methyl Salicylate (Continued)				
Pot	DMF	0.3229	Alc. KOH	0.0979	21.45	21.68	99.2
Pot	DMF	0.2465	Alc. KOH	0.1095	14.50	14.80	98.0
Pot	DMF	0.2940	Alc. KOH	0.2677	7.18	7.22	99.6
Visual	DMF	0.1310	NaOMe	0.1609	5.29	5.35	98.9
Visual	DMF	0.1356	NaOMe	0.1609	5.55	5.54	100.2
Visual	DMF	0.1206	NaOMe	0.1609	4.88	4.93	99.1
			m-Nitrobenzoic Acid (pK-3.5)				
HF(11 mc)	Benzene-Methanol	0.2805	KOMe	0.1056	15.94	15.89	100.3
HF(141 mc)	DMF	0.2029	Alc. KOH	0.096	12.57	12.63	99.5
HF(141 mc)	DMF	0.2008	Alc. KOH	0.0961	12.65	12.50	101.2
HF(141 mc)	DMF	0.1448	Alc. KOH	0.0961	9.00	9.02	99.8
Pot	DMF	0.3763	Alc. KOH	0.0979	22.82	23.00	99.4
Pot	DMF	0.3873	Alc. KOH	0.1095	21.20	21.16	100.1
Visual	DMF	0.1330	NaOMe	0.1609	4.92	4.95	99.5
Visual	DMF	0.1473	NaOMe	0.1609	5.44	5.48	99.3
			8-Quinolinol				
HF(11 mc)	DMF	0.2095	KOMe	0.1056	13.64	13.73	99.8
HF(141 mc)	DMF	0.3474	Alc. KOH	0.1091	21.57	21.94	98.3
HF(141 mc)	DMF	0.2027	Alc. KOH	0.1091	12.62	12.80	98.6
Pot	DMF	0.3278	Alc. KOH	0.0979	23.25	23.07	101.0
Pot	DMF	0.3687	Alc. KOH	0.1095	23.55	23.20	101.5
Visual	DMF	0.1411	NaOMe	0.1609	6.04	6.04	100.0
Visual	DMF	0.1479	NaOMe	0.1609	6.34	6.33	100.1

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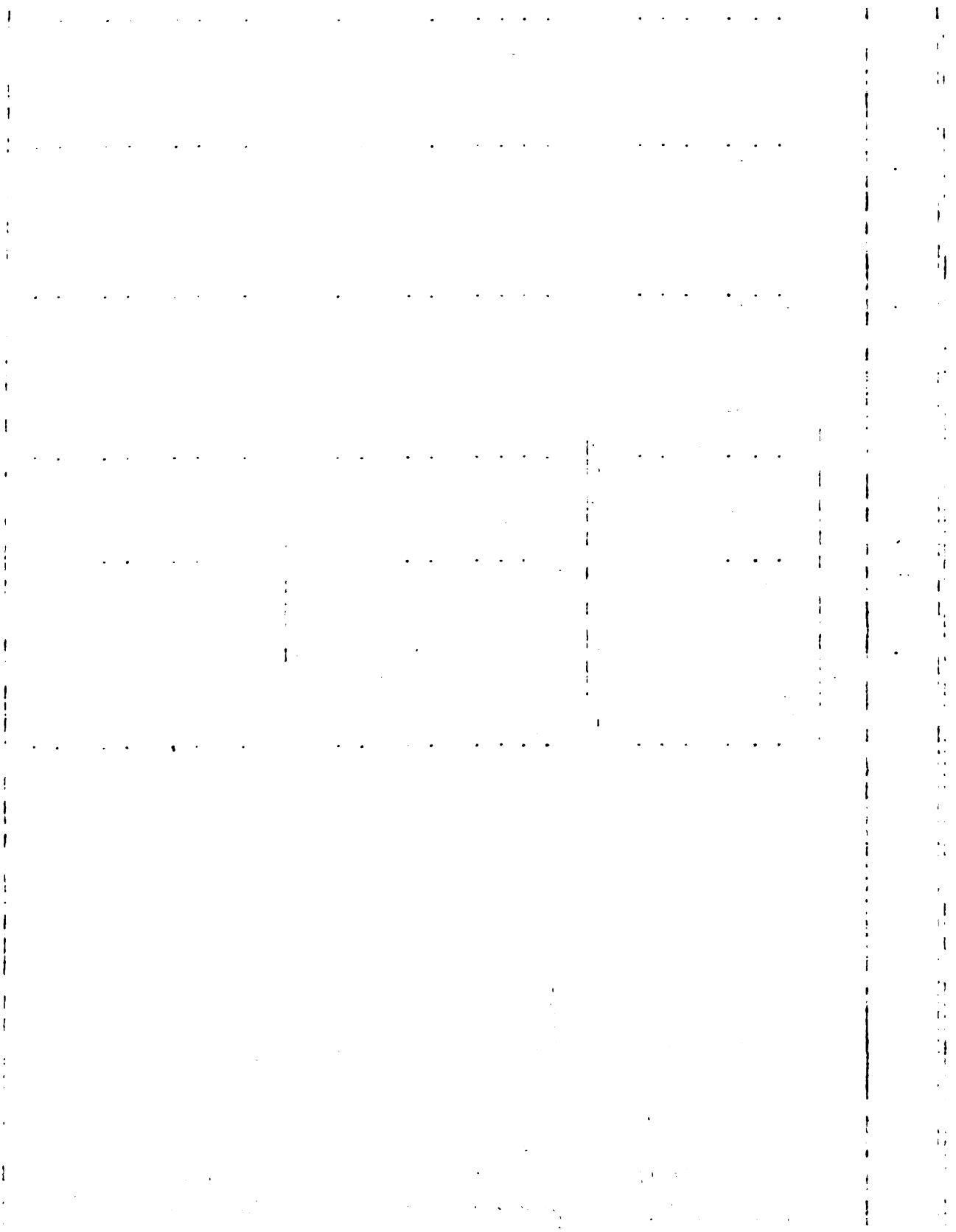

TABLE II - Continued

Method	Solvent	Sample Wt. (grams)	Titrant	Normality	Ml. Used[a]	Ml. Theory	Percent Purity
			Resacetophenone				
HF(11 mc)	DMF	0.2230	KOMe	0.1056	13.27	13.88	95.6
HF(11 mc)	DMF	0.1879	KOMe	0.1056	11.68	11.70	99.9
HF(141 mc)	DMF	0.1971	Alc. KOH	0.0961	13.59	13.48	100.8
HF(141 mc)	DMF	0.1913	Alc. KOH	0.0961	12.53	13.08	95.7
HF(141 mc)	DMF	0.1593	Alc. KOH	0.0961	10.91	10.90	100.1
Pot	DMF	0.3500	Alc. KOH	0.0979	23.35	23.50	99.6
Pot	DMF	0.3613	Alc. KOH	0.1095	21.71	21.69	100.1
			Salicylic Acid (pK's-3.0,13.4)				
HF(11 mc)	Benzene-Methanol	0.1574	KOMe	0.1056	10.72	10.79	99.3
HF(11 mc)	Benzene-Methanol	0.2355	KOMe	0.1056	16.22	16.15	100.5
HF(141 mc)	DMF	0.1449	Alc. KOH	0.0961	9.96	10.92	91.2
HF(141 mc)	DMF	0.1156	Alc. KOH	0.0961	8.77	8.72	100.7
HF(141 mc)	DMF	0.0990	Alc. KOH	0.0961	7.58	7.46	101.6
Pot	DMF	0.3069	Alc. KOH	0.0979	22.35	22.70	98.7
Pot	DMF	0.3553	Alc. KOH	0.1095	23.50	23.49	100.0
Pot	DMF	0.2043	Alc. KOH	0.2677	5.47	5.53	99.2
Visual	DMF	0.1574	NaOMe	0.1609	7.11	7.08	100.4
Visual	DMF	0.1543	NaOMe	0.1609	7.01	6.94	100.9

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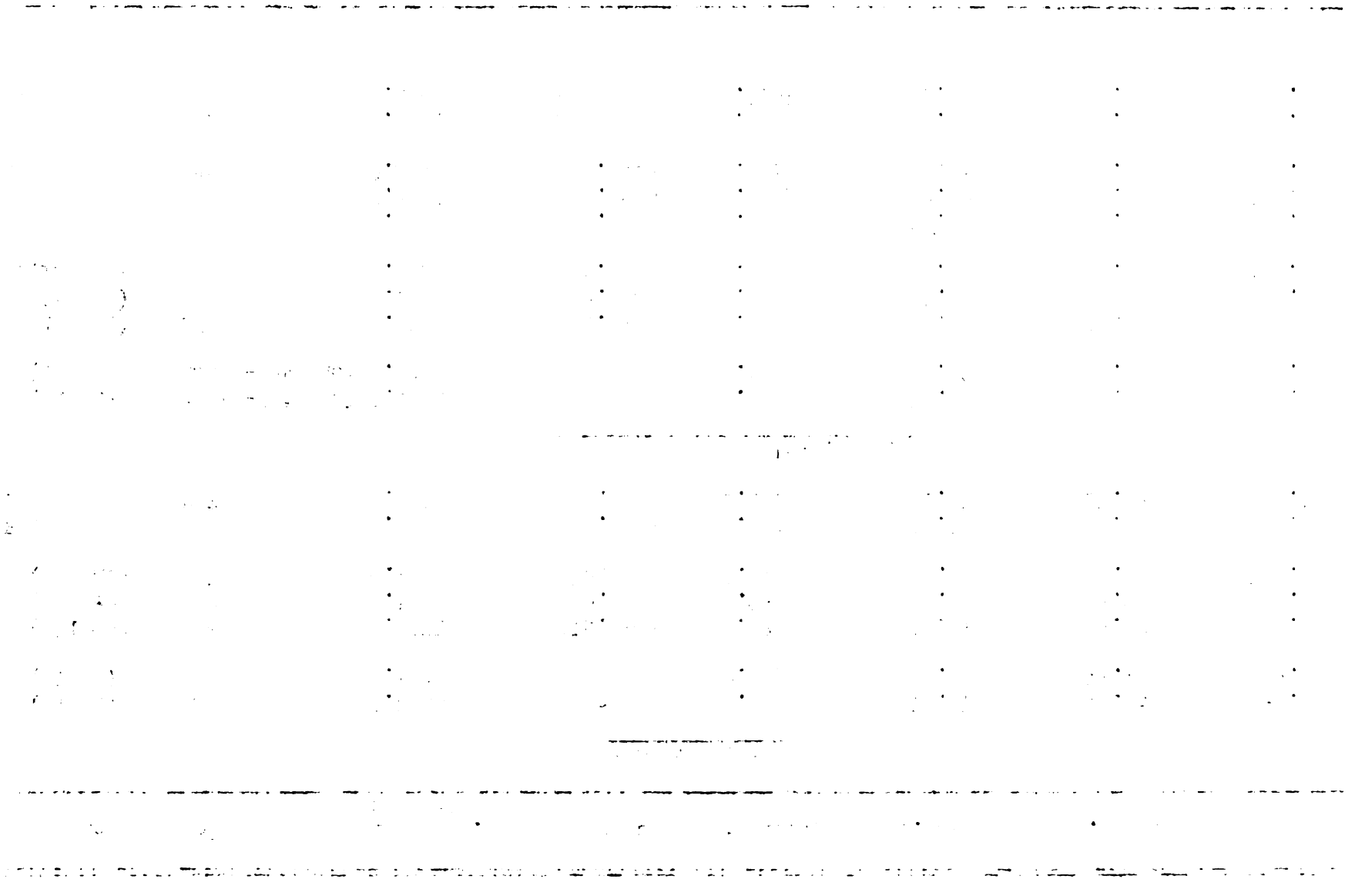
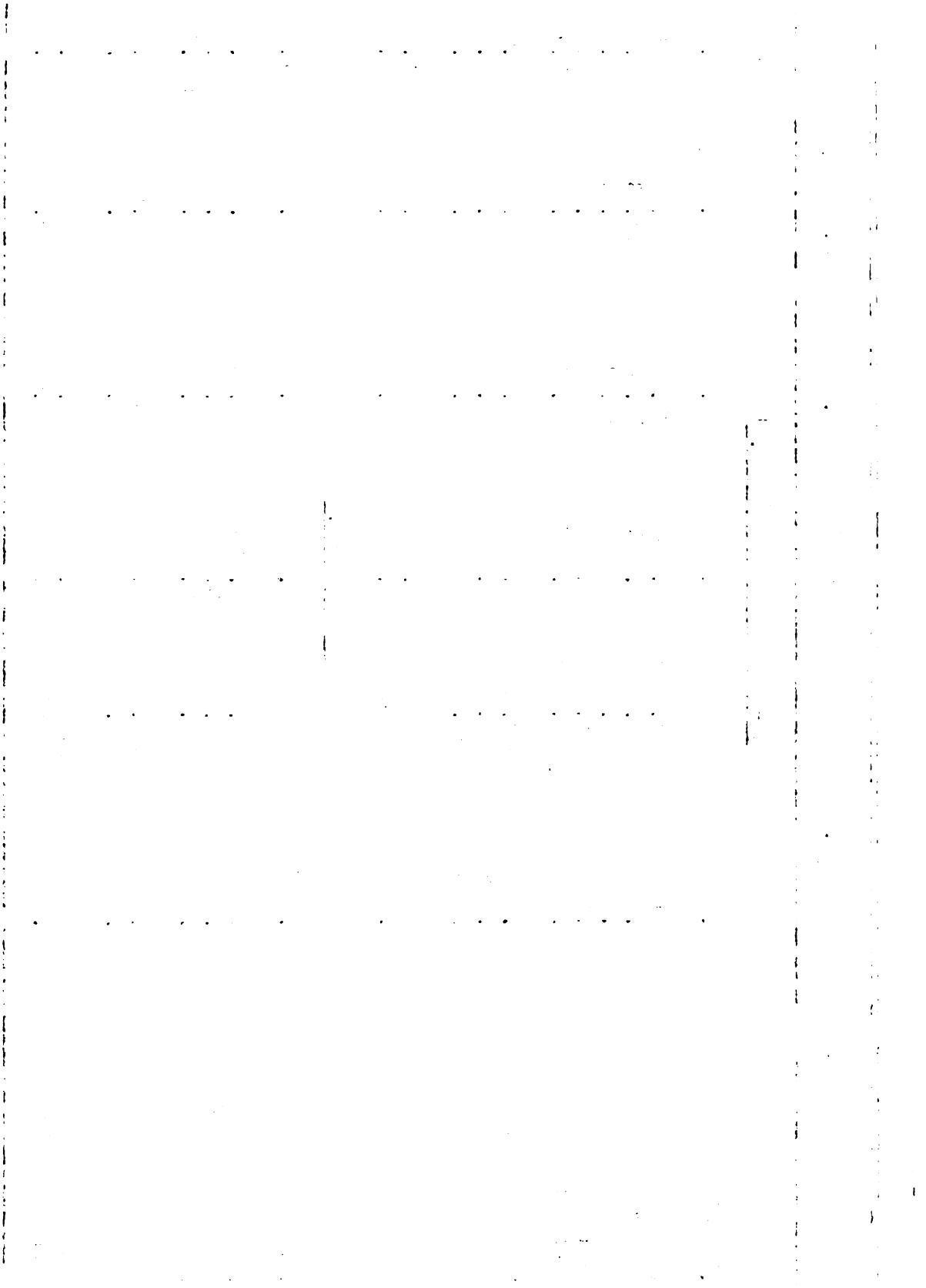


TABLE II - Continued

Method	Solvent	Sample Wt. (grams)	Titrant	Normality	Ml. Used[a]	Ml. Theory	Percent Purity
			2,4,6-Trichlorophenol (pK-7.6)				
HF(11 mc)	DMF	0.3112	KOMe	0.1056	14.65	14.92	98.2
HF(141 mc)	DMF	0.4659	Alc. KOH	0.1091	21.43	21.62	99.1
HF(141 mc)	DMF	0.2441	Alc. KOH	0.1091	11.12	11.33	98.1
HF(141 mc)	DMF	0.2437	Alc. KOH	0.0961	12.82	12.84	99.8
HF(141 mc)	DMF	0.2925	Alc. KOH	0.2697	5.41	5.49	98.5
HF(141 mc)	DMF	0.2938	Alc. KOH	0.2697	5.40	5.52	97.9
Pot	DMF	0.4552	Alc. KOH	0.0979	23.55	23.55	100.0
Pot	DMF	0.4634	Alc. KOH	0.1095	20.99	21.43	97.9
Pot	DMF	0.2447	Alc. KOH	0.2677	4.48	4.63	98.1
Visual	DMF	0.1519	NaOMe	0.1609	4.72	4.78	98.7
Visual	DMF	0.1487	NaOMe	0.1609	4.60	4.68	98.3
			Vanillin (pK-5.3)				
HF(11 mc)	DMF	0.2358	KOMe	0.1056	14.35	14.68	97.8
HF(141 mc)	DMF	0.3619	Alc. KOH	0.1091	22.13	21.80	101.5
HF(141 mc)	DMF	0.3661	Alc. KOH	0.1091	21.98	22.06	99.7
HF(141 mc)	DMF	0.2409	Alc. KOH	0.0961	16.75	16.48	101.7
Pot	DMF	0.3449	Alc. KOH	0.0979	23.10	23.16	99.9
Pot	DMF	0.3454	Alc. KOH	0.0979	23.10	23.20	99.8
Visual	DMF	0.1441	NaOMe	0.1609	5.85	5.89	99.4
Visual	DMF	0.1438	NaOME	0.1609	5.85	5.84	99.6



Unsatisfactory Solvent Systems for High Frequency Titrimetry

Titration of phenol in butylamine with potassium methoxide was attempted, but the instrument would not respond to addition of titrant. The same phenomenon occurred when titration of benzoic acid or phenol were attempted in benzene with potassium methoxide. Even the addition of lithium chloride had no effect. Benzene-isopropyl alcohol (9/1 or 1/1) mixed solvent likewise gave no instrument response when the titration of phenol with alcoholic potassium hydroxide was attempted.

SUMMARY AND CONCLUSION

Without knowledge of the accuracy of the comparison methods it is impossible to appraise the accuracy of high frequency titrimetry for weak and very weak acids. This study was intended as a survey to determine whether such acids could be titrated by the high frequency method, therefore, no special effort was put forth to study factors which affect the precision of the method. To provide some basis for comparison, mean values for the respective methods have been computed and these values tabulated below. Only those values agreeing within two per cent were included in computing mean values.

Although only relatively few high frequency titrations were performed in benzene-methanol, this solvent system, in conjunction with potassium methoxide titrant, seems to offer many advantages for high frequency titrimetry of weak acids. These advantages are smoothness of titration plots, sharpness of the end point breaks, availability and relatively low cost of the solvents, lack of blank correction, and lack of objectionable odor. Successful titration of very weak acids is not possible because the end point is masked by the acidity of the methanol present.

Successful high frequency titrations of p-aminobenzoic, benzoic, malonic, m-nitrobenzoic, and salicylic acids were performed in benzene-methanol mixed solvent with potassium methoxide. The end point breaks for benzoic acid were sharp and well defined, but no comparison can be made with results obtained by potentiometric or visual methods since

the titrant was standardized against benzoic acid employing these methods. The titration results for the others are:

	High Frequency*	Potentiometric	Visual
p-Aminobenzoic acid	99.2%	101.4%	100.9%
Malonic	99.6	erratic	100.4
m-Nitrobenzoic acid	100.3	99.8	99.4
Salicylic acid	99.9	99.0	100.7

No successful high frequency titrations of phenol, catechol, hydroquinone, or resorcinol were accomplished employing this solvent-titrant system.

Only a few compounds were titrated in dimethylformamide with potassium methoxide since alcoholic potassium hydroxide proved to be a far superior titrant for very weak acids. Compounds which were successfully titrated by the high frequency method were 8-quinolinol, resacetophenone, 2,4,6-trichlorophenol, and vanillin. The titration plots were smooth with little or no scattering of individual points. The titration results are:

	High Frequency**	Potentiometric	Visual
8-Quinolinol	99.8%	101.3%	101.1%
Resacetophenone	99.9	99.9	--
2,4,6-Trichlorophenol	98.2	98.0	98.5
Vanillin	97.8	99.9	99.5

No visual titrations of resacetophenone were performed because of insufficient sample. The end point breaks for benzoic acid, salicylic acid, or methyl salicylate ranged from poorly defined to indeterminate. The acidity of the methanol present in the titrant solution masked the end point break for phenol or catechol.

*Except for salicylic acid these high frequency titration values represent only one titration.

**Only one high frequency titration was performed for each of the compounds listed in the table.

High frequency titrations of very weak acids in dimethylformamide with alcoholic potassium hydroxide titrant proved successful for the monohydroxy phenols, p-benzylphenol, p-bromophenol, o-hydroxydiphenyl, β-naphthol, and phenol. Some scattering of individual points of the titration plots was observed but this phenomenon did not interfere with selection of the end point. The titration results are:

	High Frequency	Potentiometric	Visual
p-Benzylphenol	99.7%	100.5%	99.7%
p-Bromophenol	99.7	101.5	100.6
o-Hydroxydiphenyl	100.7	101.4	100.0
β-Naphthol	99.3	100.6	100.4
Phenol*	98.6	100.1	99.9

A result of 99.1 per cent was obtained for phenol by the standard bromination method. The end point breaks for p-tert-amylphenol were sharp but the results were very erratic. High frequency titrations of catechol or phloroglucinol were unsuccessful, possibly because of oxidation in excess basic titrant. The titration solutions were black after the titrations.

High frequency titrations of adipic acid, p-aminobenzoic, benzoic acid, malonic acid, methyl salicylate, m-nitrobenzoic acid, 8-quinolinol, resacetophenone, 2,4,6-trichlorophenol, or vanillin were performed successfully in dimethylformamide with alcoholic potassium hydroxide titrant. The titration results are:

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*The value listed under "High Frequency" results is the mean of nine titrations values obtained from three series of titrations. Two other values were discarded because of a large deviation from the mean. Another series of titrations, 102.1%, 94.4% and 102.4%, also was omitted.

	High Frequency	Potentiometric	Visual
Adipic acid	98.8%	98.5%	100.5%
p-Aminobenzoic acid	100.5	101.4	100.9
Malonic acid	97.4	erratic	100.4
Methyl salicylate	98.6	98.9	99.4
m-Nitrobenzoic acid	100.2	99.8	99.4
8-quinolinol	98.5	101.3	101.1
Resacetophenone	100.5	99.9	
2,4,6-Trichlorophenol	98.7	98.0	98.5
Vanillin	100.9	99.9	99.5
Salicylic acid	101.2	99.0	100.7

No visual titrations of resacetophenone were performed because of insufficient sample. Since benzoic acid was used as the standard or for determining the blank for the potentiometric or visual methods, no comparison was made. High titration results by the visual method for adipic acid may be due to the obscuring of the end point by the precipitation of potassium adipate during the titration. The individual points of the titration plots for all the weak acids, except adipic and malonic, showed some scattering. The scattering was largest for benzoic and salicylic acids. This scattering made selection of the end point somewhat difficult.

High frequency titrimetry for weak and very weak acids proved to be reasonably accurate. Of the three solvent-titrant systems used, benzene-methanol—potassium methoxide, dimethylformamide-potassium methoxide, and dimethylformamide-alcoholic potassium hydroxide, the last named system yielded the most erratic titration plots. The scattering of individual points of titration plots and small change of slope at the end point gave rise to difficulties in selecting the end point for some weak acids. This solvent-titrant system, however, was the only one with which successful titrations of very weak acids could

be performed. Benzene-methanol mixed solvent appears to be the better solvent for the titration of benzoic, salicylic, and other weak acids. There is little or no scattering of individual points of the titration plots and the end point breaks are distinct.

Although comparable titration results were obtained for the dimethylformamide solvent system by high frequency and potentiometric methods, the high frequency method is more attractive since the electrodes do not come into contact with the solution being titrated. By the high frequency method very weak acids were titrated in dimethylformamide. Such titrations have not been carried out successfully by an indicator method.

A possible solution to the problem of end point detection due to point scattering when the dimethylformamide-alcoholic potassium hydroxide system is employed would be to utilize an automatic recorder in conjunction with a constant delivery buret. Smoother titration curves would possibly be obtained.

Since any inherent instability of the electronic and mechanical systems of the Sargent Model XXI Polarograph is incorporated into the response values of the high frequency instrument, the substitution of a potentiometer type "nulling" arrangement employing calibrated "helipot," for the polarograph might improve the stability of the response of the instrument.

The titrations were almost exclusively carried out at 141 megacycles. Possibly operation at a lower frequency would yield smoother titration plots for some of the systems studied.

There was some difficulty defining the end point because of a slight curvature of the branches of the titration plots for some of the compounds and a lack of a large change of slope at the end point. Most of the titrations performed in this investigation were done with 0.1 N titrant, approximately 10 times the concentration of the sample solution. Increasing the titrant concentration to 0.2N might produce more linear plots and larger change of slope at the end point.

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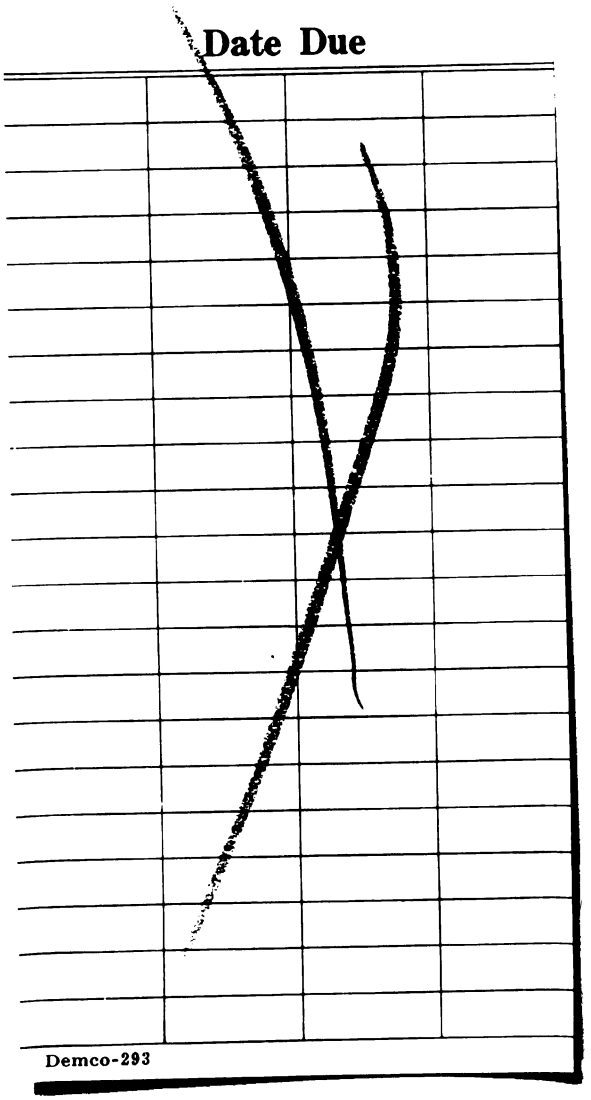
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