Table II. Titration of Dyes

Dye	Titanous Ion, Coulometric Titration: % dye	No. of detns.	Standard deviation	Titration with 0.03N Titanous Chloride, % Dye
Orange II				
Direct titration	88.70	4	0.17	88.1
Indirect titration	88.96	4	0.20	88.5
Tartrazine, indirect titration	80.60	5	0.23	79.5
p-Aminoazobenzene HCl paste, indirect titration	44.4	1	..	44.4
Methyl violet, indirect titration	77.7	7	0.58	..

reagent, and the electric field can be evenly distributed directly above the mercury pool.

Titration of Dyes. Results of the coulometric titration of several (technical grade) dyes are shown in Table II along with the corresponding results obtained by ordinary standard titanous chloride titration (*5*) for some of these. A current of 260 ma. was used in order to obtain a 0.25-second visual sensitivity for the Orange II direct end point. Sample sizes were taken such that the titration required about 200 seconds. It was important to limit the time of titration, as the addition of too much titanium tetrachloride solution caused the titanium dioxide to precipitate, thus obscuring the end point.

The values in Table II indicate the kind of precision which can be obtained by the coulometric titration. In addition, there are given some values for these samples which were obtained in the authors' Control Laboratories under normal control laboratory conditions by titration with standard titanous chloride. In view of the generally accepted estimate of the accuracy and reproducibility of such determinations as given, for example, in Siggia (*9*), it may be concluded that there is no serious disagreement between the two methods.

The large excess of titanium chloride added by the coulometric method may have some effect on the buffer action. Evenson and Nagel (*4*) state that the function of the buffer (buffer catalyst) is not only to regulate the hydrogen ion concentration, but also to promote the reduction of the dye. The rate of reaction of titanous ion with the dye may be somewhat slower by the coulometric titration, as the titanic ion is about 20 times the titanous ion added—for example, the rate of reaction for the direct titration of tartrazine was slowed so that it was necessary to employ the indirect end point procedure. The titration of aminoazobenzene (oil-soluble) in alcohol-water solution was satisfactory; this dye is normally run by the indirect procedure.

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Titration of Acids in Dimethylformamide Using High Frequency

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The purpose of the investigation was to determine the applicability of a high frequency oscillator to the titration of acids in dimethylformamide. Sharp V-shaped titration curves are obtained for strong acids and the ammonium ion over the complete range of the sensitivity of the instrument which includes concentrations as small as 0.0001*M*. Less acute angles are obtained in the titration of acids of intermediate strength, although generally adequate end point discrimination is possible for acids whose pK_a values do not exceed 7 in water. The high frequency method should be a useful adjunct for titrations in dimethylformamide, particularly as only a very limited number of color indicators are available at present.

IT WAS the purpose of the present investigation to determine the applicability of a high frequency oscillometer to the titration of acids in dimethylformamide. Wagner and Kauffman (*6*) have reported a successful application of high frequency titrations to organic bases in glacial acetic acid, and Ishidate and Masui (*3*) have titrated a number of organic acids in a benzene-methanol mixture by high frequency.

Dimethylformamide has been used as a titration medium for a number of weak organic acids. Fritz (*2*) has recommended the use of the solvent for the titration of enols and imides and negatively substituted phenols. Vespe and Fritz (*5*) have determined many of the sulfa drugs as acids by titration in dimethylformamide. Fritz (*1*) has also suggested a procedure for the determination of salts of strong bases—i.e., their conjugate acids—in dimethylformamide.

The lack of a variety of suitable visual indicators, or adequate electrode systems for potentiometric titrations, is a major limitation to the use of dimethylformamide. The range of acid strengths which may be successfully titrated in the solvent has only been qualitatively estimated.

APPARATUS AND REAGENTS

The high frequency measurements were made with the Sargent Chemical oscillometer, Model V. The frequency of the instrument was approximately 4.89 megacycles. After the addition of each titration increment the instrument was brought back into resonance by adjusting appropriate capacitances in parallel with the titration cell (*4*). All subsequent references to capacitance readings or measurements in this paper refer to the high frequency capacitances as measured by this instrument.

The titrations were carried out in a standard cell supplied with the instrument. The annular space between the condenser

plates had a volume of 50 ml. In all the titrations a volume considerably in excess of this amount was employed, making it possible to perform the titration without changing the volume of solution between the plates of the condenser.

A stirring motor was in position to be raised or lowered into the titration cell, which was fitted with a polyethylene cover through which the stirrer, inlet tube for nitrogen gas, and buret tip were inserted. Carbon dioxide was excluded from the system by directing a stream of nitrogen over the surface of the solution. A 10-ml. microburet, which could be read to the nearest 0.01 ml., was used for all titrations.

Dimethylformamide, technical grade, obtained from E. I. du Pont de Nemours & Co. was used without further purification. It contained approximately 0.03 meq. of acid impurity (presumably formic acid) per 100 ml. The presence of this impurity necessitated the neutralization of the solvent, or a blank correction.

All acids were C.P. grade, and when possible, those meeting ACS specifications were employed.

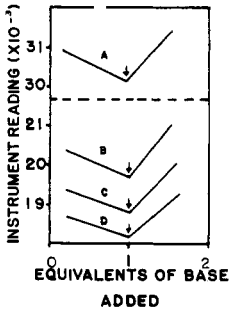

Figure 1. Effect of dilution on titration of strong acids

A. 0.006*M*
B. 0.0009*M*
C. 0.0005*M*
D. 0.00025*M*

EXPERIMENTAL

The following procedure was used for all high frequency titrations.

The instrument was allowed to warm up for 1 hour. Ninety-five milliliters of dimethylformamide were placed in the titration cell, followed by 5 ml. of the sample solution. An indicator was added, the titration assembly was lowered into place, and the nitrogen gas flow was adjusted. With the stirring motor running, resonance was established by adjustment of the calibrated condensers. The titration was carried out by adding approximately 0.5-ml. increments of the titrant, and recording the condenser reading required to re-establish resonance after each addition. Addition of the titrant was continued until the end point was reached, and seven or eight readings were obtained beyond it. The condenser readings were plotted against volume of titrant added; the intersection of the extrapolated straight-line portions of the plot was taken as the end point of the titration.

Standardization of Sodium Methoxide Solution. A sodium methoxide solution, approximately 0.1*N*, was prepared by dissolving 3 grams of sodium, previously washed in absolute methanol, in 50 ml. of absolute methanol, then diluting to 1 liter with a 4 to 1 mixture of benzene-methanol. The solution was standardized against benzoic acid, using thymol blue indicator, according to the procedure of Fritz (*1*). Standard 0.01*N* solution was prepared by proper dilution of the 0.1*N* solution. Standardization was also carried out in a benzene-methanol solvent mixture by high frequency titration (*3*). The 0.01*N* solution was used as the titrant in this investigation.

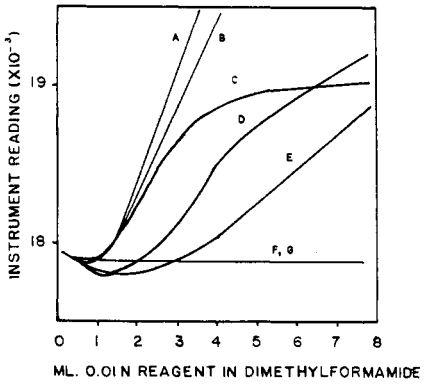

Figure 2. Instrument response curves

A. Perchloric acid
B. *p*-Toluenesulfonic acid
C. Salicylic acid
D. Sodium methoxide
E. Sulfuric acid
F, G. Formic acid, *n*-butylamine

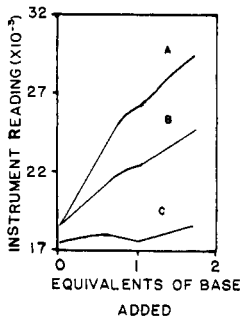

Figure 3. Effect of dilution on titration of intermediate strength acids

A. 0.0036*M*
B. 0.0022*M*
C. 0.0004*M*

TITRATION OF DISSOLVED ACIDS

High frequency titrations of acids of widely different pK_a values were attempted. The titration of strong acids with sodium methoxide solution produces in dimethylformamide curves which resemble the low frequency conductance curves for strong acids in water (Figure 1). The negative slope of the curve prior to the end point indicates the removal from solution of a highly capacitative ion, the protonated solvent ion, $DMF.H^+$. The removal of this ion decreases the capacitance and consequently the frequency of the oscillometer. A minimum was reached at the point in the titration curve where the $DMF.H^+$ ion was completely removed. Subsequent addition of sodium methoxide titrant produced an increase in the capacitance of the titration cell. The intersection obtained by extrapolation of the two branches of the titration curve results in a very acute angle at the end point. The difference in capacitance between the $DMF.H^+$ ion and the methoxide ion is small, as shown by the similar slopes of the two branches of the titration curve, and consequently, the indicated end point essentially coincides with the stoichiometric end point.

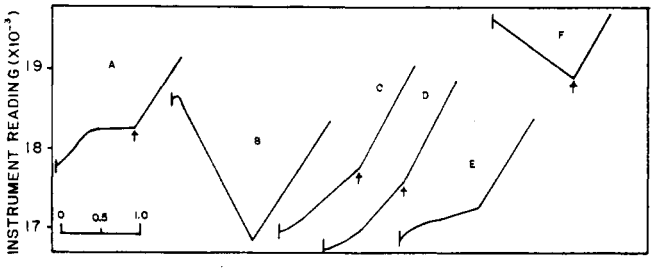

Figure 4. Titration curves of various acids

A. Salicylic acid
B. Potassium hydrogen phthalate
C. Benzoic acid
D. *o*-Nitrophenol
E. Boric acid
F. Ammonium ion

The instrument response curves for the $DMF.H^+$ ion and the methoxide ion (Figure 2) indicate that a maximum response would be obtained for the titration of strong acids over the complete range of the instrument's sensitivity, with the exception of concentrations less than 0.0001*M*. The curves obtained for the titration of very dilute solutions thus contain a break of the same magnitude as those obtained with the more concentrated solutions (Figure 1). These observations are contrary to the response observed with low frequency titration curves.

The response curve for salicylic acid (Figure 2) indicates that in low concentrations the proton exchange is virtually complete from acid to solvent, while in concentrations above 0.0005*M* its behavior is that of a slightly dissociated acid. This effect is shown by the titration curves in Figure 3.

In the titration of acids of intermediate strength, less acute angles were obtained from the intersection of the two branches of the titration curve. The results for salicylic acid (pK_a = 2.9), potassium acid phthalate (pK_a = 3.24), benzoic acid (pK_a = 4.20), *o*-nitrophenol (pK_a = 7.21), boric acid (pK_a = 9.24), and ammonium ion (pK_a = 9.24) are summarized in Figure 4. The small arrows appearing on the curves indicate the point at which thymol blue indicator (pK = 8.9) changed from yellow to blue. The horizontal scales (equivalents of base added) are the same, but the zero is shifted in each case to the right. Acids whose pK_a values in water exceed 4 are essentially nonionized in dimethylformamide, as is shown by their initially low capacitance and the nonexistence of any appreciable response curve (see curve *F* for formic acid in Figure 2). Except for concentrations less than 0.001*M*, the titration curves for these intermediate strength acids show increasing capacitance throughout the course of the titration. Prior to the end point of the titration the shape of the curve is determined by the capacitance of the sodium ion (from the sodium methoxide used as titrant) and the conjugate base ion of the respective acid. Following the end point, the increased slope of the titration curve is a result of the addition of excess sodium methoxide to the solution, exactly as for the titration of strong acids.

The difference in slope of the two branches of the titration curve is a measure of the difference in capacitance of the conjugate base ion and of the methoxide ion. This difference will determine whether or not a satisfactory end point can be secured upon extrapolation of the two branches. For example, in the titration of benzoic acid the capacitance of the benzoate ion and that of the methoxide ion are approximately equal. The change in capacitance during the release of the benzoate ion practically equals the change resulting from the addition of excess methoxide ion to the solution, and consequently, the titration curve exhibits only a small break at the end point.

Removal of ionic species from solution by precipitation or the formation of a volatile product improves the recognition of the end point considerably. The removal of high capacitance ions through evolution of gaseous ammonia during the neutralization of NH_4^+ effectively lowered the capacitance of the solution until the end point was attained, after which the addition of excess methoxide caused a sudden rise. The resulting titration curve resembles those obtained for the titration of strong acids. Similarly, the precipitation of sodium potassium phthalate during the titration of potassium acid phthalate is an advantage, although equilibrium was established very slowly after each addition of titrant.

The titration of phenol (pK_a = 9.9) was attempted but no satisfactory end point was achieved.

DISCUSSION

Results obtained from the investigation of the stoichiometry of the titrations indicates sufficient accuracy for the application of the high frequency method to titration of acids in dimethylformamide. Table I shows that the results of separate determinations are consistent within the limits of precision with which the titrations were performed. Proper calibration of volumetric ware and the control of temperature would considerably enhance the accuracy of the determinations.

In the use of thymol blue indicator, the solvent was neutralized to the base color of the indicator before the addition of the acid sample. A blank correction was obtained from the high frequency determinations from a graph of the end points obtained from the titration of a series of acid sample dilutions. These were extrapolated to zero concentration.

Only in the case of the strong acids, acids whose pK_a values are less than 3 in water, and the ammonium ion, are the indicator and instrument end points in agreement. For the other strength acids the indicator color change occurred after the instrument end point, indeed if a color change was observed at all. In the titration of boric acid, thymol blue exhibited its base color throughout the titration. Since a range of suitable indicators is presently not available for dimethylformamide, the high frequency method becomes a useful adjunct to the titration of acids in dimethylformamide.

Table I. Analysis of Acids

Acid	Type	Purity, %
Ammonium bromide	High frequency	99.7
		99.2
		101.3
	Indicator	100.4
		100.7
		100.7
Ammonium iodide	High frequency	100.6
		100.3
		99.2
	Indicator	99.2
		100.0
		100.2
Salicylic acid	High frequency	101.0
		100.2
	Indicator	99.7
		101.0
		100.2
o-Nitrophenol	High frequency	97.9
	Indicator	97.9

The use of dimethylformamide as a solvent appears to increase to a slight degree the acid strength of compounds which are incompletely ionized in water. However, the principal usefulness of the solvent is in the dissolution of materials which are only slightly soluble in water. With sodium methoxide as titrant the minimum acid strength which gives a distinguishable break at the end point appears to be an acid with a pK_a value of approximately 7, unless one of the titration products is removed from the reaction theater. *n*-Butylamine is also a suitable titrant for the stronger acids. Extensive solvolysis in the vicinity of the end point precludes its use for acids weaker than formic acid or benzoic acid.

Acids of differing strengths sometimes may be determined by means of successive titrations whereby two breaks are obtained in the titration curve. Often special procedures are necessary.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the E. H. Sargent and Co. for the loan of the high frequency oscillometer used in this work.

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Wet Carbon Combustion—Correction

In the article on "Wet Carbon Combustion and Some of Its Applications" [ANAL. CHEM., **26**, 1707 (1954)] footnotes [b] and [c] of Table I should refer to potassium iodate instead of potassium chlorate.

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