OSCILLOPOLAROGRAPHIC TITRATIONS

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CONTENTS

INTRODUCTION

Oscillopolarographic titration include titrimetric methods using $\frac{dE}{dt} = f(E)$ curves to indicate the end-point of titrations.

The first paper dealing with oscillopolarographic titration was published in 1957 by Treindl who titrated In^{3+} and Cd^{2+} with EDTA. He called the method "oscillographic titration". /1/

Later Szyszko /2/ titrated HPO_3^{2-} with Pb^{2+}. From 1966 to 1968, Stefanovic published several papers /3-7/ on this subject. The present author and his co-workers have studied oscillopolarographic titration since 1963.

Oscillopolarographic titration has many advantages over other physico-chemical methods of titration e.g. simple apparatus and manipulation, visual end-point detection, less time-consuming procedure and wide range of applications.

The apparatus used in oscillopolarograhic titration is shown in Figs. 1 and 2. Thin film Hg electrodes and other solid electrodes are used as the polarized electrode and

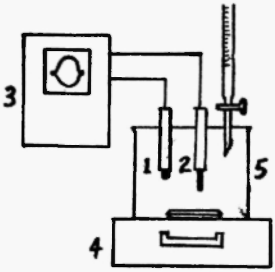

Fig. 1. Apparatus for oscillopolarographic titration

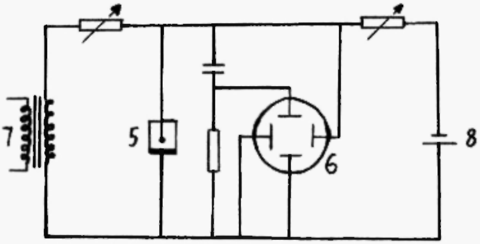

Fig. 2. End-point detecting device

1. Indicator Electrode (Thin film Hg Electrode)
2. Reference Electrode (Hg-coated Ag Electrode)
3. End-point detecting device
4. Magnetic stirrer
5. Electrolytic cell
6. Cathode-ray oscillograph
7. A.C. Source
8. D.C. Source

a Hg-coated Ag electrode or other solid electrode is used as the depolarized electrode. Because the dropping mercury electrode is replaced by solid electrodes and the titration is not upset by the presence of oxygen, the apparatus is much simpler in the case of oscillopolarographic titration than that used in ordinary amperometric titration.

Oscillopolarographic titrations utilize the appearance or disappearance of the incision of the $\frac{dE}{dt} = f(E)$ curve of the titrant or the titrate to indicate the end-point of the titration. The change of incision is watched visually just like the colour-change of an indicator. The graphic method ordinarily used in physico-chemical methods of titration for locating end-points is time-consuming and is unnecessary in oscillopolarographic titration. Furthermore, end-point detection in oscillopolarographic titrations is not interfered with by coloured substances or precipitates present in the titrate, which usually obscure the colour-change of an indicator. Ions that interfere with the titration can be precipitated beforehand and the coloured precipitates are allowed to remain in the titration vessel without filtration during the subsequent titration. This leads to quick analytical methods.

Oscillopolarographic titration has a wide range of applications including precipitation, neutralization, complex-formation and oxidation-reduction. The development of oscillopolarographic titration will greatly enlarge the field of titrimetric analysis by introducing a great many new chemical reactions that could not previously be used.

Precipitation Reactions

Owing to the lack of chemical indicators, ordinary visual titrimetric methods based on precipitation reactions are far fewer than those based on complex formation and oxidation-reduction. The use of oscillopolarographic technique will certainly change this situation and a great number of precipitation reactions will be used in titrimetric analysis.

Methods involving Potassium Chromate

In a solution of 0.IM NH_4Ac, K_2CrO_4 and $K_2Cr_2O_7$ give an oscillopolarogram with a distinct incision which can be used to indicate the end-point of titration (Fig. 3(c)).

Chromate ions can precipitate metal ions such as Pb^{2+}, which are also oscillopolarographically active at the polarized electrode (Fig. 3(a)).

K_2CrO_4 and $K_2Cr_2O_7$ are valuable titrating reagents for metal ions that form insoluble metal chromates /8/.

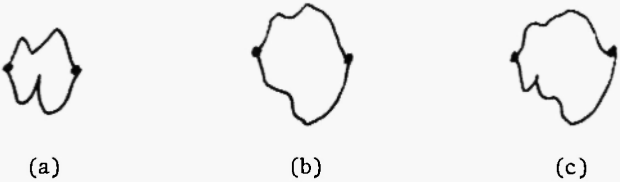
(a) (b) (c)

Fig. 3. Oscillopolarograms of 0.1M NH_4Ac solution during the titration of Pb^{2+} with K_2CrO_4: (a) Pb^{2+} in excess (b) Blank (c) K_2CrO_4 in excess

Titration of Pb^{2+} with K_2CrO_4. The titration of Pb^{2+} in 0.1M NH_4Ac with a 0.1M solution of K-chromate gives accurate results, with an average error of 0.2%. Ca, Mg, Zn, Cd, Ni, Co and Mn do not interfere. Cu, Al and Bi interfere when present in larger amounts than Pb^{2+}. Sb, Ba and Fe interfere (Table 1). The disappearance of the Pb^{2+} incision indicates the end point. A 0.1M K-chromate solution can be standardized against 0.1M Pb^{2+} solution which is standardized against a standard EDTA solution /8/.

Determination of Pb in White Metal. Pb in white metal can be determined by titration with K-chromate after separation from interfering ions by precipitating Pb^{2+} as $PbSO_4$, followed by extraction with NH_4Ac. Experimental results obtained in analysis of standard samples are shown in Table 2 /8/.

Table 1 Titration of Pb^{2+} with K_2CrO_4 in the presence of other ions

Ions Present	quantity (mg)	Pb (added) (mg)	Pb (found) (mg)	error (%)	Note
Mg^{2+}	100	20.92	20.83	-0.5	$Mg(NO_3)_2$
Ca^{2+}	200	20.92	20.88	-0.2	$CaCl_2$
Ba^{2+}	10	20.92	--	--	Interferes seriously
Zn^{2+}	120	16.73	16.69	-0.3	$ZnCl_2$
Co^{2+}	220	20.92	20.91	-0.1	$CoCl_2$
Cd^{2+}	224	16.73	16.79	+0.4	$Cd(NO_3)_2$
Ni^{2+}	200	20.92	20.89	-0.2	$NiCl_2$
Cu^{2+}	32	16.73	16.74	+0.1	$Cu(NO_3)_2$
	64	16.73	--		deformed oscillogram
Mn^{2+}	50	16.73	16.78	+0.3	$MnCl_2$
	100	16.73	16.85	+0.7	
Bi^{3+}	20	16.73	16.90	+0.1	$Bi(NO_3)_3$
	30	16.73	17.02	+1.7	
Al^{3+}	20	20.92	21.33	+2.0	$AlCl_3$
	40	20.92	--		deformed oscillogram

Table 2 Determination of Pb in White Metals and an Al-alloy

Sample	Wt. of sample	Pb content in Sample		Pb found		Pb found
	(mg)	(mg)	(%)	(mg)	(%)	ave.
	400.0	330.5	82.6	330.0	82.5	
White Metal	400.0	330.5	82.6	329.7	82.4	
"A" No. 177	400.0	330.5	82.6	330.7	82.7	82.6
	400.0	330.5	52.6	330.7	82.7	
	400.0	330.5	82.6	331.5	82.8	
Al-alloy No.181	1003	15.15	1.51	14.80	1.48	
	1003	15.15	1.51	14.90	1.49	1.49
	1000	15.10	1.51	14.90	1.49	

Determination of Pb in Al-alloys. Pb in Al-alloys can be determined in a similar way. /8/ Some data obtained in analysis of standard samples are shown in Table 2.

Direct Titration of Ba^{2+} with $K_2Cr_2O_7$ Solution. The direct titration of Ba^{2+} with standard $K_2Cr_2O_7$ solution is carried out in 0.5 M HAc solution, containing 20% ethanol by volume, using the appearance of the K_2CrO_4 incision to indicate the end-point of the titration /9/. The method is very rapid and accurate and can be used to determine the Ba content of a mixture of pure carbonates of Ba, Sr and Ca.

Determination of Ba in a mixture of Pure carbonates of Ba, Sr and Ca. /9/ An accurately weighed sample of 0.1 g is dissolved in 0.5 ml. of acetic acid, and the acidity of the solution is adjusted to pH 7 with NH_4OH and then to pH 7 with HAc. 20 ml. of H_2O and 20 ml. of ethanol are added and the final volume of the solution is about 50 ml. The solution is titrated with standard $K_2Cr_2O_7$ solution which can be prepared directly by dissolving a known quantity of pure $K_2Cr_2O_7$ in water. The accuracy and precision of the method are quite satisfactory (Table 3).

Table 3 Determination of $BaCO_3$ in a mixture of $BaCO_3$, $SrCO_3$ and $CaCO_3$

Sample contents		$BaCO_3$ % found in 13 determinations				
$BaCO_3$	57.00%	56.91,	56.91,	56.91,	56.91,	57.06
$SrCO_3$	38.00%	57.06,	57.06,	57.06,	58.74,	58.74
$CaCO_3$	5.00%	57.24,	57.24,	56.91		

In contrast to oscillopolarographic titration, the original method used for determination of Ba in carbonate mixtures of Ba, Sr and Ca is time-consuming. The full procedure reads as follows:

Dissolve an accurately weighed sample of 2 g. in 20 ml. of H_2O and 7-10 ml. of 1 : 1 HNO_3 by heating the solution gently and boil for 5 minutes. Cool. Neutralize with NH_4OH until the solution is slightly alkaline. Add 2 ml. of HAc and 6 ml. of NH_4Ac. Heat to boiling. Cool. Transfer the solution to a 100 ml. volumetric flask. Add accurately 10 ml. of $(NH_4)_2Cr_2O_7$ solution (20%) and dilute the solution to the mark of the flask with water. Shake thoroughly, put the flask on the water-bath at 60°C for 1 hour, cool and filter through a dry filter paper. Repeat the above procedure with a blank solution. Pipette 10 ml. of the filtrate into a 300 ml. Erlenmeyer flask. Add 20 ml. of H_2O, 20 ml. of 30% HCl and 6 g. of KI. Shake thoroughly. Place the flask in a dark place for 10 minutes and titrate with standard $Na_2S_2O_3$ solution until the solution turns yellow. Add 5 ml. of starch indicator and continue the titration until a bright green colour appears.

Methods involving Pb^{2+} Ions

In NH_4Ac solution, Pb^{2+} has a distinct incision on its oscillopolarogram, which can be used to indicate the end-point of titration. Many anions such as CrO_4^{2-} , MoO_4^{2-}, WO_4^{2-} and PO_4^{3-} can be titrated directly with standard Pb^{2+} - solutions.

Direct titration of MoO_4^{2-} with Pb^{2+} /10/. With MoO_4^{2-},

Pb^{2+} forms an insoluble precipitate, $PbMoO_4$, in 1 M NH_4Ac solution. $MoO_4{}^{2-}$ can be directly titrated with standard Pb^{2+} solution in NH_4Ac solution (pH = 5 ~ 6). Small amounts of W can be masked by KF. Very small amounts of other elements present in the Mo sample do not interfere with the titration (Table 4). This procedure can be used to determine Mo in Mo Metal, Mo powder and molybdates.

To determine the Mo in a 1 : 1 Mo-W alloy, the sample is dissolved in H_2SO_4 solution containing $(NH_4)_2SO_4$ on heating and W is precipitated as H_2WO_4 on dilution with water. Part of the mixture is filtered through a dry filter paper and the $MoO_4{}^{2-}$ in the filtrate is titrated by the Pb^{2+} solution (Table 5).

Determination of $WO_4{}^{2-}$ /10/. $WO_4{}^{2-}$ in NH_4Ac solution can be determined by precipitation as $PbWO_4$ with excess Pb^{2+} solution followed by titration of the excess Pb^{2+} by standard EDTA solution. Fe^{3+} forms $Fe(OH)_3$ in the NH_4Ac solution and does not interfere. This method can be used to determine W in W-Fe alloys (Table 6).

Determination of Cd^{2+} *and* $MoO_4{}^{2-}$ *by successive titrations* /10/. Cd^{2+} and $MoO_4{}^{2-}$ present in NH_4Ac solution can be easily determined by successive oscillopolarographic titrations. Cd^{2+} is titrated by standard EGTA solution using the disappearance of the Cd^{2+} incision to indicate the end-point of the titration; then titrate the $MoO_4{}^{2-}$ with standard Pb^{2+} solution using the appearance of the Pb^{2+} incision to indicate the end-point of the titration.

Dimethylglyoxime as a Titrimetric Reagent /11/

An alcoholic solution of dimethylglyoxime can be used as

Table 4 Very small amounts of elements present in pure Mo metal do not interfere with the Pb titration of MoO_4^{2-}

Mo added	Elements present (mg)								Mo found
(mg)	W	Cu	Sn	Ca	Mg	Fe	Si	P	(mg)
7.89	0.15	0.3	0.03	0.4	0.3	0.3	1.5	0.03	7.89
7.89	0.15	0.3	0.03	0.4	0.3	0.3	1.5	0.03	7.89
7.89	0.15	0.3	0.03	0.4	0.3	0.3	1.5	0.03	7.89
6.94	1.5	0.5	0.05	0.5	0.3	0.6	1.5	0.05	6.94

Table 5 Analysis of Standard Samples of 1:1 W-Mo alloy (by wt.)

Wt of sample (mg)	Standard Pb solution used (ml.)	Mo found (%)	Mo % of the standard sample
40.00	8.45	49.77	50.00
40.00	8.53	50.28	
40.00	8.55	50.40	
20.00	4.28	50.14	
20.00	4.27	50.14	
20.00	4.23	49.60	

Table 6 Determination of W in Standard Samples

% of W in Standard Samples	Results of 3 successive determinations	% of W found average	error
W-Fe alloy 81.28%	80.92 % 81.17 % 81.12 %	81.12 %	0.2%
Pure W powder 99.70%	99.77 % 99.31 % 100.2 %	99.76 %	0.1%

a standard solution to titrate Ni^{2+} in an ammoniacal solution, using the appearance of the incision of the reagent to indicate the end-point of the titration (Fig. 4).

Fig. 4. Oscillopolarogram of dimethylglyoxime in ammoniacal solution

The method can be used to determine Ni in steel. The method is accurate and rapid. /11/

Methods involving Na-TPB /12/

Sodium tetraphenylborate (Na-TPB) has a distinct incision on its oscillopolarogram which can be used as an end-point detector. Na-TPB forms insoluble precipitates with a great many ions, both organic and inorganic. Therefore, Na-TPB is a very useful titrating reagent in oscillopolarographic titration.

Determination of K.

The precipitation of K^+ as K-TPB with excess standard Na-TPB solution, followed by back titration of the excess with standard Tl^+ solution, using the disappearance of the incision of Na-TPB to indicate the end-point of the titration, is an accurate and rapid method for determination of K^+, free from interference of other metals.


(a) (b)

Fig. 5 $\frac{dE}{dt}$ = f(E) curves of Na-TPB (a)

For the determination of K^+ in aqueous solution, a measured volume of sample solution is transferred to a 100-ml volumetric flask, and 1 ml. of 25% NaOH and a measured volume of Na-TPB solution are added before dilution to the mark with distilled water. The flask is shaken thoroughly and set aside for 10 minutes. Part of the contents of the flask is filtered through a dry filter paper and 25.00 ml. of the filtrate transferred to a 100-ml. beaker. 0.5 g. of NaAc. and H_2O are added until the total volume of the solution is 40 - 50 ml. The excess of Na-TPB in the filtrate is titrated with standard Tl^+ solution. The average error of determination is 0.3%. Ions forming precipitates in a slightly alkaline medium do not interfere.

Determination of K in Diorite

An accurately weighed powder sample (heated to constant weight at 120°C) of 0.5 - 1.0 g. is placed in a platinum dish, 10 ml. of HF are added and the dish is heated gently until the sample dissolves completely. 2ml. of 1 : 1 H_2SO_4 are added and evaporated to fumes of sulphuric acid followed by 1 ml. of 1 : 1 HNO_3. The dish is rinsed with water and heated to dissolve the salts. The solution is transferred to a 100 ml. beaker, boiled for several minutes, cooled and transferred to a 100-ml. volumetric flask. The solution is neutralized with 50% NaOH until $Fe(OH)_3$ precipitates completely plus 1 ml. in excess. The pH of the solution should be *ca* 14. A measured volume of standard Na-TPB solution is added, diluted to the mark with H_2O and set aside for 10 minutes. Part of the mixture in the flask is then filtered through a dry filter paper and 25.00 ml. of the filtrate are transferred to a 100 ml. beaker. 0.5 g. of NaAc is added and the solution is diluted with H_2O to a volume of 40-50 ml. and titrated with standard Tl^+ solution until the incision of Na-TPB disappears.

Methods Involving Zn^{2+} Salts /13/

Owing to its distinct incision (Fig. 6), Zn^{2+} ion is a good reagent in oscillopolarographic titration. Standard Zn solution can be used to titrate EDTA, EGTA and $Fe(CN)_6^{4-}$. The reaction

Fig. 6 $\frac{dE}{dt}$ = f(E) curve

of Zn^{2+} in NH_4OH-NH_4Cl buffer
(pH = 10)

between Zn^{2+} and Fe $(CN)_6^{4}$:-

$$2\ Zn^{2+} + Fe(CN)_6^{4} \rightarrow Zn_2Fe(CN)_6 \downarrow \quad \text{(alkaline medium)}$$

is well-known to analysts,but it is used infrequently in titrimetric analysis because of a lack of internal indicators. However, in oscillopolarographic titration, $Fe(CN)_6^{4-}$ ions can be titrated by Zn^{2+} or *vice versa* using Zn^{2+} ion itself as the indicator. The method is simple and gives very satisfactory results. Because $K_3Fe(CN)_6$ is a good oxidizing agent, the above titration may have wide applications.

Chelometric Reactions

Titration of Ga with EDTA /14/

In $(NH_4)_2SO_4$ - NH_4OH (pH = 11) medium, Ga^{3+} has a distinct incision (Fig. 7) which can be used to indicate the end-point of the titration.

Fig. 7 $\frac{dE}{dt}$ = f(E) curve of Ga^{3+} in $(NH_4)_2SO_4$ - NH_4OH medium (upper part: anodic branch)

Procedure To 20 ml. of $1M(NH_4)_2SO_4$ in a 100 ml. beaker add 1 ml. of conc. NH_4OH and a measured volume of standard Ga^{3+} solution. Dilute with H_2O to a volume of 30 ml. and titrate with EDTA. The disappearance of the Ga incision indicates the end-point. Ions that precipitate in the medium such as Al^{3+}, Ti^{4+}, Bi^{3+} and Sb^{3+} do not interfere when present in small quantities.

Titration of Ca^{2+} with EGTA /15/

In 0.4 M NH_4Cl - NH_4OH buffer (pH = 10), the logarithms of the apparent stability constants between Ca^{2+}, Zn^{2+} Mg^{2+} and EGTA are respectively 10.9, 8.7 and 5.2. Therefore, when a solution containing Ca^{2+}, Mg^{2+} and a small amount of Zn^{2+} is titrated with EGTA, Ca^{2+} is titrated first followed by Zn^{2+}. The disappearance of the Zn incision on the $\frac{dE}{dt}$ = f(E) curve indicates the end-point of the titration. Thus Ca^{2+} can be titrated in the presence of Mg^{2+} oscillopolarographically. Ca^{2+} can be accurately determined in the presence of Mg^{2+} up to 40-50 times the quantity of Ca^{2+}.

Determination of CaO in Limestone. An accurately weighed sample of 0.2 g. is put in a porcelain crucible and heated at 1000°C in a muffle furnace for 1 hr. The sample is dissolved in conc. HCl, transferred to a 250-ml. volumetric flask and diluted with H_2O to the mark. 10 ml. of the solution are transferred to a beaker and 0.50 ml. of Zn^{2+} solution added. The solution is neutralised with NH_4OH until the solution is neutral to litmus paper and 30 ml. of NH_4Cl - NH_4OH buffer solution are added followed by H_2O until the volume of the solution is about 60 ml. The Ca^{2+} is then titrated with EGTA to the disappearance of the Zn incision on the $\frac{dE}{dt} = f(E)$ curve. The results of some determinations are shown in Table 7.

Determination of Ca in a mixture of pure carbonates of Ba, Sr and Ca /16/

A sample of 5 g. is mixed with 20 ml. of H_2O and 10 ml. of 1 : 1 HNO_3 are added from a dropper to dissolve the sample. The solution is boiled to expel the CO_2 amd then cooled, transferred to a 250-ml. volumetric flask and diluted with H_2O to the mark.

50 ml. of the solution are transferred to a 250 ml. beaker, heated to 70-80°C, and 8 ml. of 10% $(NH_4)_2SO_4$ added from a dropper to the stirred solution. The solution is heated to 60° - 80°C on a water-bath for 30 minutes, cooled, transferred to a 100 ml. volumetric flask and diluted with H_2O to the mark. Part of the mixture was filtered through a dry filter paper, and 50 ml. of the filtrate transferred to a 100 ml. beaker, neutralized with NH_4OH, and 15 ml. of NH_4Cl-NH_4OH buffer (pH = 10) and 0.50 ml. of Zn^{2+} solution.

Table 7 Determination of CaO in limestone samples

Sample No.	CaO content %	Other constituents (%)						CaO found (%)
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Cr_2O_3	MgO	
Limestone No. 1	51.08	4.62	0.78	0.36	0.03	--	1.03	51.13 51.07
Limestone No. 2	51.42	4.75	0.74	0.40	0.03	--	1.25	51.53
Ultrabasic rock	1.80	37.75	0.21	7.04	6.90	0.42	38.35	1.83

The solution was titrated with EGTA to the disappearance of the Zn incision.

5% $CaCO_3$ can be accurately determined in the presence of 57% of $BaCO_3$ and 38% of $SrCO_3$.

Titration of Zn^{2+} *with EDTA* /13/

One of the advantages of oscillopolarographic titration over ordinary methods using chemical indicators is that the end-point detection is not obscured by coloured precipitates present in the titrate. Interfering ions present in the solution can be precipitated and the ions to be determined titrated in the presence of the pricipitates; filtration is unnecessary. This leads to simple and rapid procedures. For example, in the determination of Zn in Zn ores, titration of Zn by EDTA is interfered with by many metals, existing in the ores, such as Fe, Mn, Al, Pb, Cu and Cd. These metals must be removed by precipitation in an ammoniacal solution before Zn is titrated. The procedure used in the ordinary indicator method is thus time-consuming. But in the case of oscillopolarographic titrations, the procedure is quite simple, as shown in the following.

Determination of Zn in Zn-Ores. 0.2- 0.3 g. of powdered ore sample is introduced to a 150 ml. beaker and heated to boiling with 10 ml. of HCl. 3 ml. of HNO_3 are then added until the sample dissolves completely. Part of the acids is expelled and the solution is transferred to a 100 ml. volumetric flask and diluted to the mark with H_2O. 10 ml. of the above solution is transferred to a 100 ml. beaker and neutralized with conc. NH_3 until alkaline. 5 - 7 drops of 30% H_2O_2 are added and the solution is heated to boiling. 5 ml. of 0.1% sodium diethyl-dithio-carbamate and 20 ml. of NH_4Cl-NH_4OH buffer are added and the Zn^{2+} is titrated as before with EDTA. Some results are shown in Table 8.

Titration of Al with EDTA /17/

In the oscillopolarographic titration of Al with EDTA the ordinary procedure used in the indicator method is followed and Zn^{2+} is used for back-titration, the appearance of the Zn^{2+} incision being used to indicate the end-point.

Neutralization Reactions /18/

Neutralization oscillopolarographic titrations have unique advantages over indicator methods, e.g. the titration can be carried out in coloured solution, the titration of weak base with weak acid is possible, very weak acids such as boric acid, can be titrated directly; metal ions such as Zn^{2+}, Ga^{3+}, Eu^{3+} and In^{3+} can be used as neutralization indicators.

Titration of Coloured Titrates

Titration of Na-fluorescein with standard HCl.

The orange-coloured powder of Na-fluorescein is the Na-salt of a weak acid with the following structure:

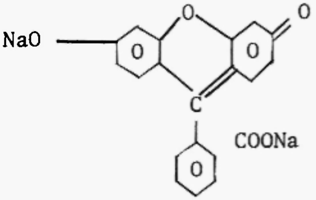

Table 8 Determination of Zn in Zn-ores

Sample No.	Indicator titration method Zn %	Atomic Absorption Zn %	Oscillopolarographic titration Zn %
1	24.29	24.14	24.32
			24.33
			24.32
2	26.62	26.64	26.66
			26.66
			26.72

In a KCl solution, Na-fluorescein shows a distinct incision which can be used to indicate the end-point of the titration of Na-fluorescein itself by HCl.

Titration of Weak Bases with a Weak Acid and vice versa

The titration of a weak base with a weak acid and vice versa cannot be carried out with visual indicators, because the pH jump at the end-point is not large enough to cause a distinct colour change with an indicator. A change of 2 pH units is necessary to cause a reasonable visual colour change. But, a change of 0.2 pH unit is enough to effect a distinct change in the oscillopolarogram of an indicator. In a solution containing 0.6-1g. of NH_4Ac and 1 g. of KCl in 40 ml. of solution, Congo red has a distinct incision (Fig. 8) which disappears at pH6.95. Thus Congo red can be used to indicate the end-point of a

Fig. 8. $\frac{dE}{dt}$ = f(E) curve of Congo Red indicator at the end point of the titration of NH_3 with HAc(a) just before and (b) at the end-point.

titration of 0.2M NH_4OH with 0.2MHAc. The theoretical end-point pH of this titration is 7.00. Similarly, Brilliant Yellow can be used to indicate the titration of HAc with NH_4OH.

Titration of Boric Acid with KOH Solution

Similarly, a very weak acid, such as boric acid with $K_1 = 5.9 \times 10^{-10}$, which cannot be titrated directly by a base without the addition of mannitol in the ordinary indicator method, can be directly titrated oscillopolarographically with a 0.1M KOH solution using aniline as the indicator. At the end-point of the titration (pH - 11.4) a distinct incision appears in the aniline oscillogram.

Titration of Na_2CO_3 with HCl Solution

Na-carbonate can be titrated in two stages with the 1st end-point at pH = 8.3, corresponding to sodium bicarbonate and the 2nd end point at pH = 3.89, corresponding to carbonic acid. The colour change of indicators at both end-points is not sharp. The oscillopolarographic titration gives sharp end-point detection in both cases. The first end point is indicated by the appearance of the Zn^{2+} incision in the solution containing Na_2CO_3, KCl and alcohol. The 2nd end point is indicated by the disappearance of the Congo Red incision (pH = 3.50) or by the appearance of the Ga^{3+} incision (pH = 3.70).

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