REVIEW METHODS OF END-POINT DETERMINATION FOR ACID BASE QUANTITATIVE VOLUMETRIC ANALYSIS

A PROJECT REPORT

PRESENTED BY

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D E C L A R A T I O N

I, hereby, declare that, except for reference to work of other researchers which have been duly cited, the work presented in this dissertation was carried out by me at the Food Research Institute under the supervision of Mrs. Nana T. Annan.

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S U M M A R Y

Some methods of end-point determination for acid-base quantitative volumetric analysis were reviewed. Three methods were considered. These include the Visual Indicator, Potentiometric and Conductometric methods.

Sodium Carbonate (Na_2C0_3) was titrated against Hydrochloric Acid (HCl) using each of the mentioned methods. Comparison of the methods in terms of advantages and disadvantages and estimation of the numerical uncertainty in the results was made. Using a concentration of 0.05004M of Na_2C0_3 the molarity of the Na_2C0_3 solution in the colour indicator was found to be between 0.05025 and 0.05015 with an error of between 0.22% and 0.42% as against 0.02%-0.14% for the potentiometric method. The conductometric method showed an error of between 0.12% and 0.18%.

The relative deviations of all three methods showed that they fell within acceptable limits. However, the potentiometric method was found to be more superior to the other methods as it gave the least error.

1.0 INTRODUCTION

1.1 Acid-base quantitative volumetric analyses are vital in the estimation of the concentration in test solutions. The use of acids/bases and buffers in scientific laboratories and industries calls for a concise review methods of end-point determination. End-point determination methods are practically dependent on the colour, degree of ionisation, strength of the acid/base and dilution. Hence, the need to use colour indicators and instrumental methods for locating the end-point.

The equivalence point is the stage in a titration when the reactants and products are present in equivalent amounts according to their stoichiometric equation. This is accompanied by a large and sudden change in the property employed by the method. The changes may be observed in colour indicators, pH, e.m.f., conductance, current, temperature, redox potential, etc. The analyst must therefore attempt to make the equivalence point and the experimental end-point coincide as closely as possible.

End-point detection techniques may be divided broadly into two classes; optical and electrical methods.

Optical Methods

i) Visual - this involves the use of colour indicators in neutralization reaction.

ii) Photometric/Spectrophotometric - a titration where the end-point is found by absorbance measurements.

Electrical Properties/Electrometic Techniques

iii) Potentiometric/pH titration - is one where the end-point is found by measuring the e.m.f. or pH of aqueous solutions.

iv) Amperometric titration - is one where the end-point is found by observing the effect of titrant addition upon a measured current.

v) Conductometric titration - is one where the end-point is found by measuring the electrical conductance of a solution.

vi) Voltammetric and amperometric titration - measurement of voltage and current as a function of the volume of the titrating solution.

1.2 AIM AND APPROACH

The aim of the project is to review some of the methods of end-point determination for acid-base quantitative volumetric analysis. In addition, comparison of the methods chosen in terms of advantages and disadvantages and estimation of the numerical uncertainty in the results.

Visual colour indicator, pH/potentiometric and conductometric titrations methods are specifically discussed because they are readily available in my place of work.

2.0 THEORY OF ACID-BASE NEUTRALIZATION REACTIONS

In water solution, according to Arrhenius acids dissociate into hydrogen ions (H^+) and anions, and bases dissociate into hydroxide ions (OH^-) and cations. HX and BOH being acid and base respectively.

Acid: $HX \longleftrightarrow H^+ + X^-$

Base: $BOH \longleftrightarrow OH^- + B^+$

An acid can only give up a proton if a base is presnt to accept it, hence two acids and two bases take part in any reaction involving proton transfer that is

$HA_1 + B_2 \longleftrightarrow HA_2 + B_1$

Acid Base Acid Base

The interaction of the two conjugate acid-base pairs (designated by subscripts 1 and 2) leads to an equilibrium in which some of the acid molecules have transferred their protons to the solvent. Since free protons do not exist in solution, the functioning of an acid depends on the presence of a base to which protons can be transferred. The solvent thus plays an important role in determining acidic and basic properties of a substance. A solvent, SH, capable of being both a proton donor and acceptor (ie. amphiprotic) can undergo autoprotolysis

$$SH + SH \longleftrightarrow SH_2^+ + S^-$$

Using water as example: $H_2O + H_2O \longleftrightarrow H_3O^+ + OH^-$

In such solvents, the strongest acid is the solvent cation SH_2^+ and the strongest base is the solvent anion S^-. Neutralization of strong acids and bases is simply the reverse of this self-dissociation or auto protolysis reaction.

$$H_2O + OH^- \longleftrightarrow 2H_2O$$

Titration of Polyprotic Acids and Bases

In general, acids which furnish two or more protons called polyprotic acid, eg. H_2SO_4, H_3PO_4, H_2CO_3, H_3BO_3 etc. Similarly, salts of the acids are capable of acting as bases and accepting two or more protons. They can undergo stepwise ionisation, eg. orthophosphoric acid:-

$$H_3PO_4 \longleftrightarrow H^+ + H_2PO_4^-; \quad K_1 = 7.5 \times 10^{-3}$$

$$H_2PO_4^- \longleftrightarrow H^+ + HPO_4^{2-}; \quad K_2 = 6.2 \times 10^{-8}$$

$$HPO_4^{2-} \longleftrightarrow H^+ + PO_4^{3-}; \quad K_3 = 4.8 \times 10^{-13}$$

In the titration of Na_2CO_3 with HCl which I have chosen as the reagents for the experiment, the following reactions take place:-

$$CO_3^{2-} + H_3O^+ \longleftrightarrow HCO_3^- + H_2O$$

$$HCO_3^- + H_3O^+ \longleftrightarrow H_2CO_3 + H_2O$$

2.1 VISUAL COLOUR INDICATORS

A visual acid-base indicator is a weak organic acid or base which shows different colours in the molecular and ionic forms, or when a change in the pH of the solution occurs. For an acid-base indicator, HIn_A

$$HIn_A + H_2O \longleftrightarrow In_B^- + H_3O^+$$

acid form colour A basic form colour B

and the equilibrium constant, K_{In}, as

$$K_{In} = \frac{[In^-_B]\,[H_3O^+]}{[HIn_A]}$$

This may be written in the logarithmic form:

$$pH = pK_{In} + \log \frac{C_{In^-,B}}{C_{HIn,A}}$$

where $pK_{In} = -\log K_{In}$, $C_{In^-,B}$ and $C_{HIn,A}$ are the concentrations of basic form and acid form respectively.

$$pH = pK_{In} + \log \frac{\text{intensity of colour B}}{\text{intensity of colour A}}$$

assuming that the concentration of the two forms are proportional to the intensities of light transmitted by solutions of colour A and colour B. Thus, provided that pK_{In} is known, the pH of a solution can be obtained from a measurement of the ratio of the intensities of the colours using a visual comparator or a spectrophotometer. Because of the difficulty of detecting a small intensity of one colour in the presence of another, the useful range of the indicator is limited to

$$pH = pK_{In} \pm 1$$

This enables the correct choice of indicator for a given solution. Acid-base indicators must exhibit colour changes as closely as possible to the pH of the equivalence point. A structural example of a visual indicator

Eg. Phenol red

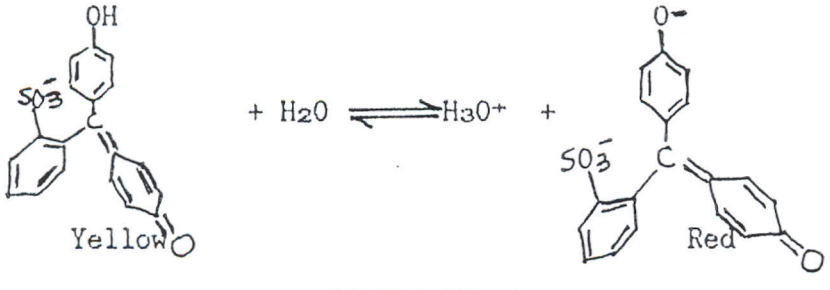

Fig. 1

$$K_1 = \frac{[H_3O^+]\,[In^-]}{[HIn]}$$

There is a natural limitation on the range of pH values in which a given indicator is useful. The eye can detect changes in colour only when the ratio of concentration of the coloured form falls in the range of 0.1 to 10.

TABLE 1: pH Range and Colour Changes of Certain Acid-Base Indicators

Indicator	pH Range	Colour in Acid Soln.	Colour in Basic Soln.	pK_{In}
Methyl Orange	3.1-4.4	Red	Orange	3.7
Bromothymol Blue	6.0-7.6	Yellow	Blue	6.3
Phenol Red	6.8-8.4	Yellow	Red	7.9
Phenolphthalein	8.3-10.0	Colourless	Red	9.6
4-nitrophenol	5.6-7.6	Colourless	Yellow	7.1

3.0 END-POINT INDICATION BY POTENTIOMETRIC TITRATION METHOD

The End-point of a neutralization reaction can be indicated by measuring change in the pH or the potential of the solution. To measure the hydrogen ion concentration of a solution the glass electrode must be combined with a reference electrode, for which purpose the saturated calomel electrode (SCE) is most commonly used, thus giving the cell:

$$\ominus\ Ag,AgCl_{(s)}/HCl(0.1M)/Glass/Test\ Solution//KCl\,sat'd,Hg_2Cl_2(s)/Hg\ \oplus$$

Glass electrode — S. C. E.

Owing to the high resistance of the glass membrane, a simple potentiometer cannot be employed for measuring the cell e.m.f. and specialized instrumentation must be used which is the pH meter. Since the potentials of the two reference electrodes remain constant, any change in the potential of the cell when test solution is changed must reflect a change in the potential developed across the glass membrane, provided that any change in the liquid junction potential between calomel electrode and test solution is quite small. It is found experimentally that the potential of this cell follows the relation

$$E = k + 0.0591\ pH$$

at 25°C and over a pH range of about 0 to 10 or 12, depending upon the composition of the glass and of the test solution.

3.1 pH METERS AND SCALE

pH Meters are classified as:
(a) direct reading or (b) potentiometric type meters.

In type (a) it is calibrated in millivolts so that the cell e.m.f. is recorded directly, and since in fact, the quantity measured is pH, the scale is also calibrated in pH units, a selector switch being provided to allow choice of scale reading.

Because the solutions with which we deal most commonly are dilute, the concentration of hydrogen ion in them is often small. As a result, $[H^+]$ in moles/litre are often expressed as negative powers of 10. Eg. $[H^+]$ in a saturated solution of CO_2 is 1.2×10^{-4} M. To achieve compactness of notation and brevity of expression, it is convenient to give these concentrations in terms of their negative logarithms. Thus, pH is defined as

$$pH = -\log[H_3O^+]$$

The pH values of two solutions A and B determined by this cell is related to the e.m.f. values by

$$pH_A = pH_B + (E_A + E_B)F/2.303RT$$

in which E is the potential, R the gas constant, T the absolute temperature, and F the Faraday's constant.

3.2 APPLICATION OF POTENTIOMETRIC TITRATIONS

In potentiometric titrations, the change in the e.m.f. of a suitable cell (containing an indicating and a reference electrode) is dependent on the logarithm of the concentration of the species being titrated, and so it is important to obtain a large number of reading in the vicinity of the equivalence

point.

On the addition of the base, the e.m.f. or pH changes relatively slowly at first since this depends on the fraction of the particular ion removed. Towards the equivalence point the fraction of ion(H^+) removed by a constant amount of titrant (base) increases rapidly, and this is reflected by a rapid change in the e.m.f. (pH). Above the equivalence point, the curve flattens out see Fig.2(a). The exact location of the equivalence point is best achieved by plotting the first derivative curve (ie. $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ against V). Even better results are obtained by plotting the second derivative $\Delta^2 E/\Delta V^2$ or $\Delta^2 pH/\Delta pH^2$ versus V producing the graph shown in Fig 2(b).

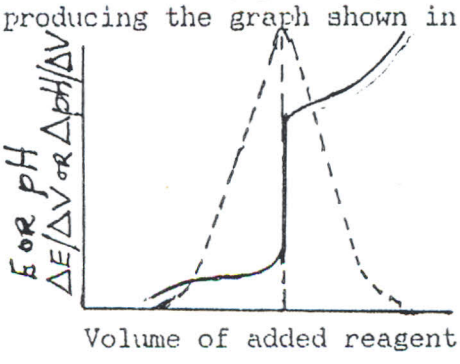

Fig.2(a): Typical potentiometric titration curve and first derivative plot (.....)

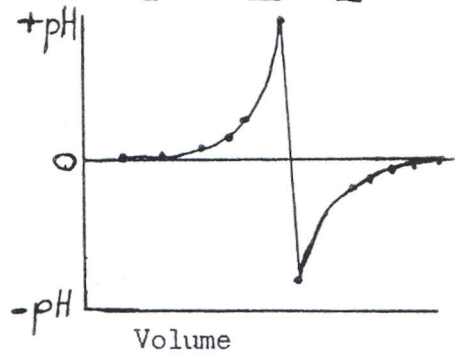

Fig.2(b): Second derivative plot.

Acid-Base Titrations (Potentiometric)

The shape and position of the titration curve (see Fig.3) depends on the strengths of the acid and the base. The curve for the titration of a strong acid with a strong base (I-II) is readily calculated since the concentration of hydrogen ions is equal to the concentration of unneutralized acid up to the equivalence point (B), at which point the concentration is 10^{-7} mol dm^{-3}. The curve for the titration of a weak acid with a strong base (III-II) can be traced up to the equivalence point (C). At the end-point, the solution is alkaline owing to the hydrolysis of the salt of the weak acid and strong base. Similarly for the titration of a weak base with a strong acid (I-IV), the equivalence point (A) falls on the acid side of neutrality. In the titration curve for a weak acid/ Weak Base (III-IV), there is only a gradual change with no marked at the equivalence point.

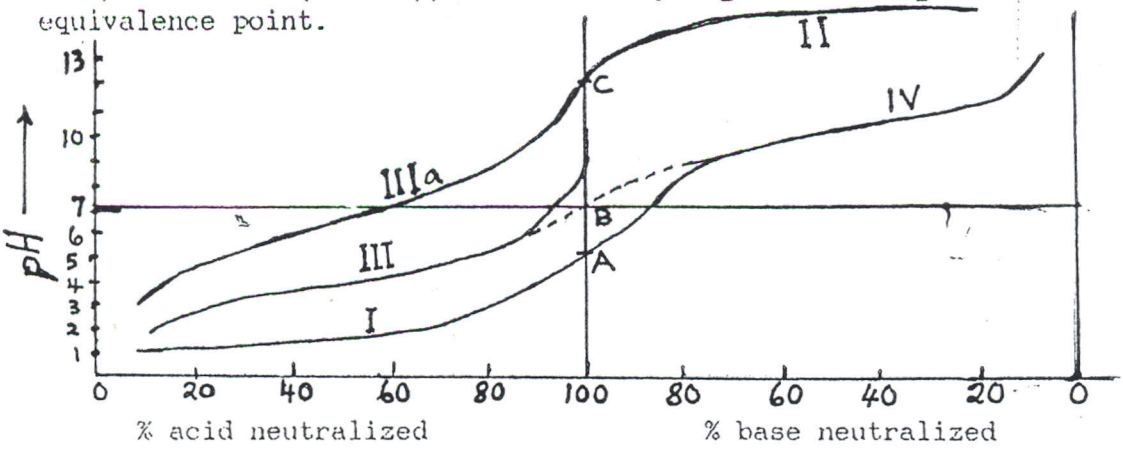

Fig. 3. Neutralization curves for acid and bases (all concentration 0.1 mol dm^{-3}): I, strong acid, II, strong base; III, weak acid; IIIa, very weak acid; IV, weak base. A is equivalence point for I-IV, B for I-II and C for II-III.

4.0 END-POINT INDICATION BY CONDUCTOMETRIC TITRATION METHOD

Conductance is an additive property of a solution depending on all the ions present. Electrolyte solutions are ionic conductors and, except at very high electrical fields in excess of 1000 volts per cm, obeys Ohm's Law. The law

$$I = E/R$$

where I is the current in amperes, E is the e.m.f. in volts and R is the resistance (ohm) of the conductor. The reciprocal of the resistance is termed the conductance measured in ohm^{-1} (mho). The resistance of a sample of homogeneous material, length L, and cross-sectional area A is given by $R = \frac{\rho L}{A}$, where ρ is the specific resistance or resistivity. $\rho = \frac{RA}{L}$ is measured in ohm meter or ohm cm units. The reciprocal of resistivity is the conductivity, k measured in ohm^{-1} cm^{-1} or ohm^{-1} m^{-1}(Scm^{-1}).

When a solution of an electrolyte is diluted, the conductivity decreases, since fewer ions are present per cm^3 of solution carrying the current. If all the solution be placed between two electrodes 1 cm. apart and large enough to contain the whole of the solution, the conductance increases as the solution is diluted. This is largely due to a decrease in inter-ionic effects for strong electrolytes and to an increase in the degree of dissociation for weak electrolytes.

The molar conductivity (Λ) of an electrolyte defined as the conductivity due to one mole is given by:

$$\Lambda = 1000k/c = k.1000V,$$

where C is the concentration of the solution in moles per dm^3, and V is the dilution in dm^3. The units of Λ are $ohm^{-1}m^2mol^{-1}$ or $ohm^{-1}cm^2mol^{-1}$.
For strong electrolytes, the molar conductivity increases as the dilution is increased, but it appears to approach a limiting value known as the molar conductivity at infinite dilution, Λ_∞; this quantity is written as Λ_o when concentration, rather than dilution is considered. At infinite dilution the ions are independent of each other, and each contributes its part to the total conductivity, thus

$$\Lambda_o = \Lambda_o^+ + \Lambda_o^-$$

where Λ_o^+ and Λ_o^- are the ionic molar conductivities at infinite dilution of the cation and anion respectively.

Table 2: Limiting ionic molar conductivities at 25°C

Cation	Λ_o^+ mhocm²/g	Anion	Λ_o^- mho-cm²/g
H^+	349.8	OH^-	198.3
NH_4^+	73.5	Cl^-	76.3
Na^+	50.1	PO_4^{3-}	80.0
Ca^+	59.5	$CO_3^=$	69.3
K^+	73.5	CH_3COO^-	40.9

The addition of one electrolyte (A^+B^-) to another (C^+D^-) will result in a change of conductance on account of volume changes and possible ionic reactions. If the addition is made so that there is no appreciable change in volume and there is no chemical reaction, the conductance of CD will gradually increase on addition to AB. On the other hand, if there is an ionic reaction

$$A^+B^- + C^+D^- \longrightarrow A^+D^- + C^+B^-$$

in which one of the products (CB) is either only slightly ionised or insoluble, then a marked change of conductance occurs at the equivalence point. During the addition, the ions A^+ replace the ions C^+ and the conductance may increase or decrease depending on relative mobility values of A^+ and C^+.

4.1 APPLICATION OF CONDUCTOMETRIC TITRATION

1. **Strong Acid and Strong Base Titration:**

In this type of titration a sharp break in the conductivity occurs at the equivalence point. The conductance first falls, due to the replacement of the hydrogen ion conductivity 350, by the added cation (conductivity 40-80) and then after the equivalence point has been reached, rapidily rises with further additions of strong alkali due to the large conductivity of the hydroxyl ion (198). The two branches of the curve are straight lines provided by volume of the reagent added in negligible, and their intersection gives the end-point. Fig. 4(a).

2. **Strong Acid and Weak Base:**

The titration of a strong acid with a moderately weak base ($K_b \simeq 10^{-5}$) may be illustrated by the neutralization of dilute H_2SO_4 by dilute ammonia solution (Fig. 4(b). The first branch of the graph reflects the disappearance of the hydrogen ions during the neutralization, but after the end-point has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.

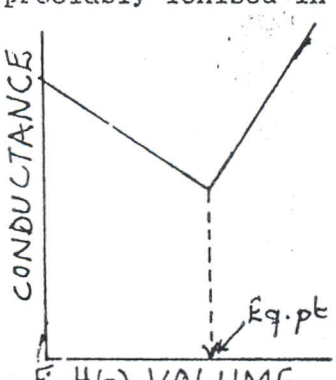

Fig.4(a)

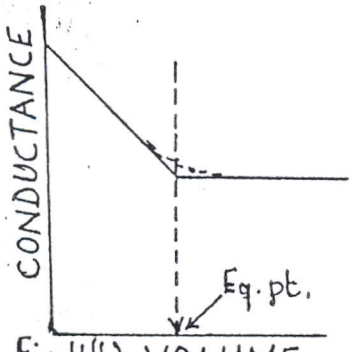

Fig.4(b)

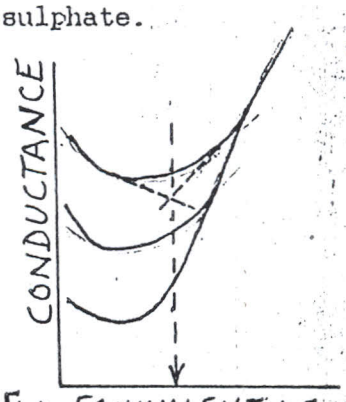

Fig.4(c)

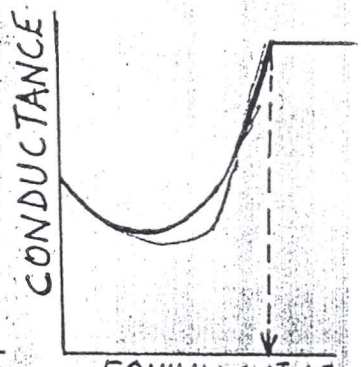

Fig.4(d)

3. **Weak acid with a Strong Base:**

Acetic acid, for example, is present partly in the form of H^+ and CH_3COO^- but largely as non-ionized molecules. Initially the solution has a low conductance. As neutralisation proceeds, the common-ion formed, eg. the acetate ion, represses the dissociation of the acetic acid so that an initial fall in conductance may occur. With further addition of NaOH the conductance of the sodium and acetate ion soon exceeds that of the acetic acid which they replace, and so the curve passes through a minimum and thereafter the conductance of the solution increases. The shape of the initial portion of these conductance curves will vary with the strength of the weak acid and its concentration, as indicated in Fig.4(c).

4. **Weak Acids with Weak Bases:**

When a weak acid is titrated with a weak base, the initial portion of the conductance titration curve follows the pattern described above. (Fig.4(d).

Beyond the equivalence point, there is no change in the conductance because of very small conductance of the excess free base. The intersection of the two branches is sharper than for a corresponding titration of a weak acid with a strong base.

5. Polybasic Acids:

Separate end-points from the stepwise neutralization of polybasic acids are rarely observed in conductometric titrations. The reason is that the various branches of the conductance titration curve have very nearly the same slope. The curve for H_3PO_4 vrs. NaOH (see Fig.5(a) and Na_2CO_3 and HCl (see Fig 5(b).

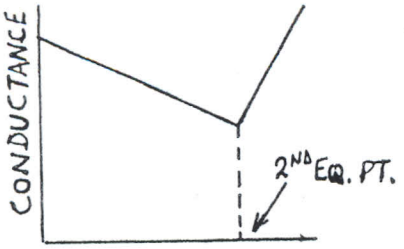

Fig. 5(a) Volume of NaOH
H_3PO_4 with NaOH

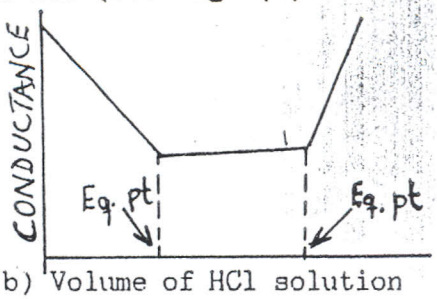

Fig. 5(b) Volume of HCl solution
Na_2CO_3 with HCl

5.0 COMPARATIVE DISCUSSION OF THE METHODS

5.1 ADVANTAGES AND DISADVANTAGES OF THE METHODS DESCRIBED

Advantages of Visual Indicator Method

It needs simpler apparatus, whenever applicable, and is generally quickly performed. Easy to handle, less expensive and no need for curves/graphs to be plotted. Generally, visual end-points give quite precise (c.a. 0.1%) results when macro quantities are titrated.

Disadvantages

Visual indicator method fails to give good results when the solution has a dark colour. End-point error is significant, ie. difference between experimental end-point and theoretical equivalence point. The eye can wrongly detect changes in colour due to colour blindness.

POTENTIOMETRIC METHOD

Advantages

Chief advantages of the method are applicability to turbid, fluorescent, opaque or coloured solutions when suitable visual indicators are unavailable or inapplicable. As compared with colour indicators, the end-point can be located precisely, even with dilute solutions. The technique allows the recording of complete curves of mixtures of acids or bases in either aqueous or non aqueous solvents. This method is exceptionally versatile because electrodes for almost every type of acid-base reactions have been developed.

Disadvantages

Potentiometric titration method is time consuming unless automated. The glass electrode is somewhat fragile, but this is not a serious disadvantage. One effect that can lead to a serious error, however, is the response of the electrode to ions other than hydrogen in solutions of high pH. In a sodium hydroxide solution of about pH 12, where $[H^+]$ is about $10^{-12}M$ and $[Na^+]$ about $10^{-2}M$, the potential of the glass electrode depends somewhat upon the activity of Na^+ and hence may yield an error in pH despite a high inherent selectivity in

responding to H^+ rather than to other ions.

CONDUCTOMETRIC METHOD

Advantages

Conductometric titrations are potentially useful in any reaction where the ionic content is markedly less at the equivalence point than either before or after it. Another advantage of the method is that it is applicable to very dilute solutions with relatively little loss in precision or accuracy. It has practical significance when the solution has a dark colour. The shape of the conductivity line is practically independent of the dilution. Extremely dilute solutions of strong acids or strong bases, of the order of 0.0001N, can be titrated with the same accuracy as more concentrated solutions, if care is taken to exclude CO_2.

Disadvantages

The method is not conveniently applicable where the total ionic content is large, and changes only slightly at the equivalence point. Hydrolysis of reactants or products or partial solubility of a precipitated product may cause departures from linearity.

5.2 CHOICE OF METHODS

Choice of end-point detection methods are practically dependent on the colour, degree of ionization, strength and dilution of the acid and base. Satisfactory results are obtained in most acid-base titrations using potentiometry except (a) those in which either the acid or the base is very weak (K 10^{-8}) and (b) those in which both the acid and base are weak. Conductometric titrations are preferred to potentiometric titrations in the above exceptions (a) and (b). Such very weak acids as boric acid, phenol, citric acid and hydroquinone which cannot be titrated potentiometically can be titrated relatively with ease conductometrically.

Mixtures of certain acids or bases which differ greatly in their strengths, eg. of mixtures of HCl and acetic acid can be titrated more accurately by the conductometric than by pH methods.

Conductometric titration is very useful where such factors as hydrolysis, solubility and dissociation of the reaction product may cause inaccuracies in potentiometric titration.

Sea water which contain large amounts of electrolytes like Na^+, Ca^{2+}, K^+, Cl^-, etc. which take no part in the reaction do affect the conductivity of the solution. However, in this case, potentiometric or colour indicator titrations are to be preferred.

Considerable difficulty is experienced in the determination of the acid values of oils and acidity in coloured fruit juices and wines. This difficulty arises because the dark colour obscures the end point of the titration if phenolphthalein is used as the indicator. Conductometric and potentiometric methods are preferable. The titration of weak acids with weak bases is complicated by the difficulty in judging the end-point as the change in pH may be very slight. Conductivity titration overcomes this difficulty.

5.3 NUMERICAL UNCERTAINTIES

Na_2CO_3 is a diprotic base and as such two end-points were detected for all the three methods. Numerical uncertainties in the results are achieved from the use of pipettes, burettes and graduated flask because of their tolerance levels.

1. Acid-Base Indicator

Uncertainty in the result of the visual indicator method may be from the type of indicator used. Eg. thymol blue-cresol red mixture gives better result than phenolphthalein for the 1st end-point. One error occurs when the indicator employed does not change at the proper pH. Another error occurs in the case of weak acids (or bases) where the colour change at the end-point is not sharp. In the titration of Na_2CO_3, the CO_2 so formed shifts the 2nd equivalence point to higher values. The uncertainty is reduced by boiling off the gas.

2. Potentiometric Method

As the acid or base becomes progressively weaker, the distinctness of the inflection point diminishes, hence the precision with which an end-point may be reproduced becomes poorer by inspection. For a reaction which goes well to completion, the titration curve is so steep near the equivalence point that the uncertainty is small. For an uncertainty of 0.1% or less, and in aqueous solution, the product $K_a[HA]$ or $K_b[B]$ should exceed 10^{-3}, assuming that the titrant is completely dissociated and 0.1N in strength.

3. Conductometric Method

In favourable conditions, titrations should give an error of ±1%. The uncertainty in the result may arise because the titrant (0.1M HCl) is not 20 to 100 times more concentrated than the Na_2CO_3 solution (0.05M) being titrated. The accuracy of the method is greater the more acute the angle of intersection and the more nearly the points of the graph lie on a straight line.

6.0 EXPERIMENTAL

5.305g of dried anhydrous Na_2CO_3 was weighed and dissolved and made into 1 litre solution. 50ml of this solution is titrated with the standard HCl in all the three methods. Magnetic stirrer is also used in each method. Phenolphthalein and methyl orange are the indicators in the visual method.

CRISON pH/mV meter Model 501(digital) and TOA Conductivity Meter Model CM-20S (digital) were used for the potentiometric and conductometric titrations respectively. Room temperature was 27.7°C and Conductivity Constant is 0.958. Results are in the Appendix.

Table 3: Titre values, concentrations and relative deviations of Na_2CO_3 titrations

Method	Stage	Titre(ml)	Molarity	Relative Deviation(%)
Colour Indicator	1st Stage Phenolphthalein	25.05	0.05025	0.42
	2nd Stage Methyl orange	50.00	0.05015	0.22
Potentiometric	1st Stage	24.95	0.05005	0.02
	2nd Stage	49.96	0.05011	0.14
Conductometric	1st Stage	24.90	0.04995	0.18
	2nd Stage	49.95	0.05010	0.12

7.0 CONCLUSION

The concentration of the Na_2CO_3 prepared was 0.05004M. The molarity of the Na_2CO_3 solution in the colour indicator method is 0.05025 and 0.05015. The error in the colour indicator method is between 0.22% and 0.42% as against 0.02%-0.14% for potentiometric method, while the error for conductometric method fell between 0.12%-0.18%. From their relative deviation above, all the three methods could be employed successfully. However, the potentiometric method gave the least error, demonstrating its superiority over the others.

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.0 APPENDICES

EXPERIMENTAL RESULTS (I)

VISUAL COLOUR INDICATOR TITRATION

1st Step-Wise Titration - Phenolphthalein indicator

Burette readings (ml)	Trial	1	2	3
Final	25.20	25.10	25.05	25.05
Initial	0.00	0.00	0.00	0.00
Titre Value	25.20	25.10	25.05	25.05

Average Titre Value = 25.05ml

2nd Step-Wise Titration - Methyl Orange Indicator

Burette reading (ml)	Trial	1	2	3
Final	50.10	50.00	50.00	50.00
Initial	0.00	0.00	0.00	0.00
Titre Value	50.10	50.00	50.00	50.00

Average Titre Value = 50.00ml

CONDUCTOMETRIC TITRATION READINGS

Volume of acid (ml)	Conductance (Λ) mS/cm
0.0	7.79
5.0	7.34
10.0	6.98
15.0	6.65
20.0	6.29
23.0	6.10
24.0	6.04
24.5	6.02
25.0	6.00
25.5	5.97
28.0	5.89
30.0	5.83
35.0	5.70
40.0	5.55
45.0	5.45
48.0	5.39
50.0	5.41
52.0	6.01
55.0	6.87
60.0	8.24

pH (POTENTIOMETRIC) TITRATION

Vol. of acid (ml)	pH	pH/ ΔV
0	10.80	
5	10.18	
10	9.81	
15	9.49	
20	9.09	0.18
24	8.39}	
24.2	8.28}	0.53
24.4	8.18}	
24.7	8.03}	0.60
24.8	7.97}	
24.9	7.93	0.40
25.0	7.89	0.40
25.1	7.85	0.40
25.2	7.81	0.40
25.4	7.74}	0.35
25.7	7.66}	0.26
27.0	7.33}	
35.0	6.54}	0.10
40.0	6.33}	
45.0	5.81}	0.07
49.0	4.98}	
49.4	4.64}	0.27
49.6	4.36}	1.40
49.8	3.88}	2.40
49.9	3.72	1.6
50.0	3.57	1.5
50.2	3.55	1.1
50.5	3.18	0.57
51.0	3.02	0.32
55.0	2.61	
60.0	2.32	

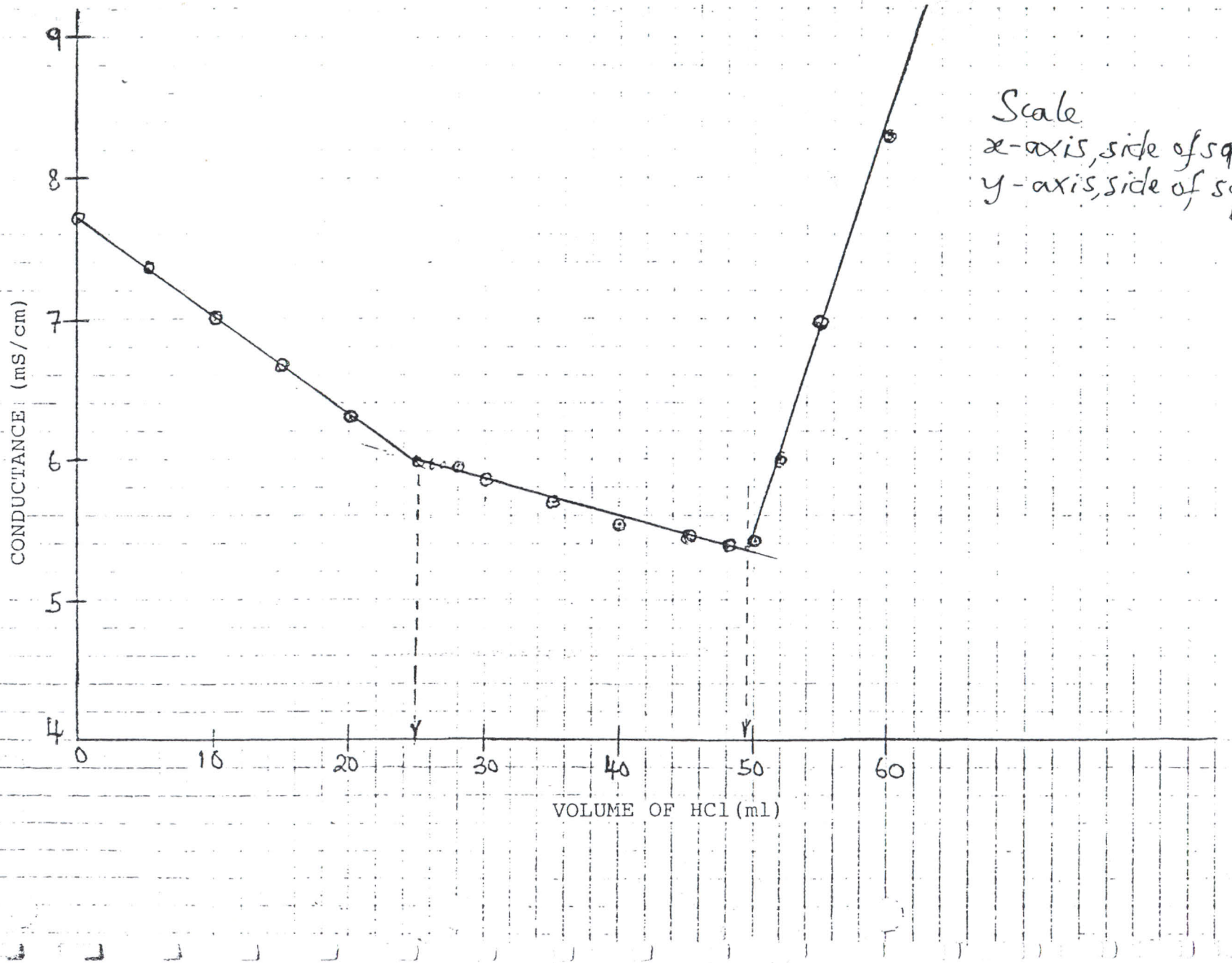
1st Stage

Vol. of HCl	pH	pH/ΔV
24.0	8.39	0.18
24.4	8.18	0.52
24.8	7.97	0.60
25.2	7.81	0.40
25.4	7.74	0.35
25.7	7.66	0.27
26.0	7.60	0.20

2nd Stage

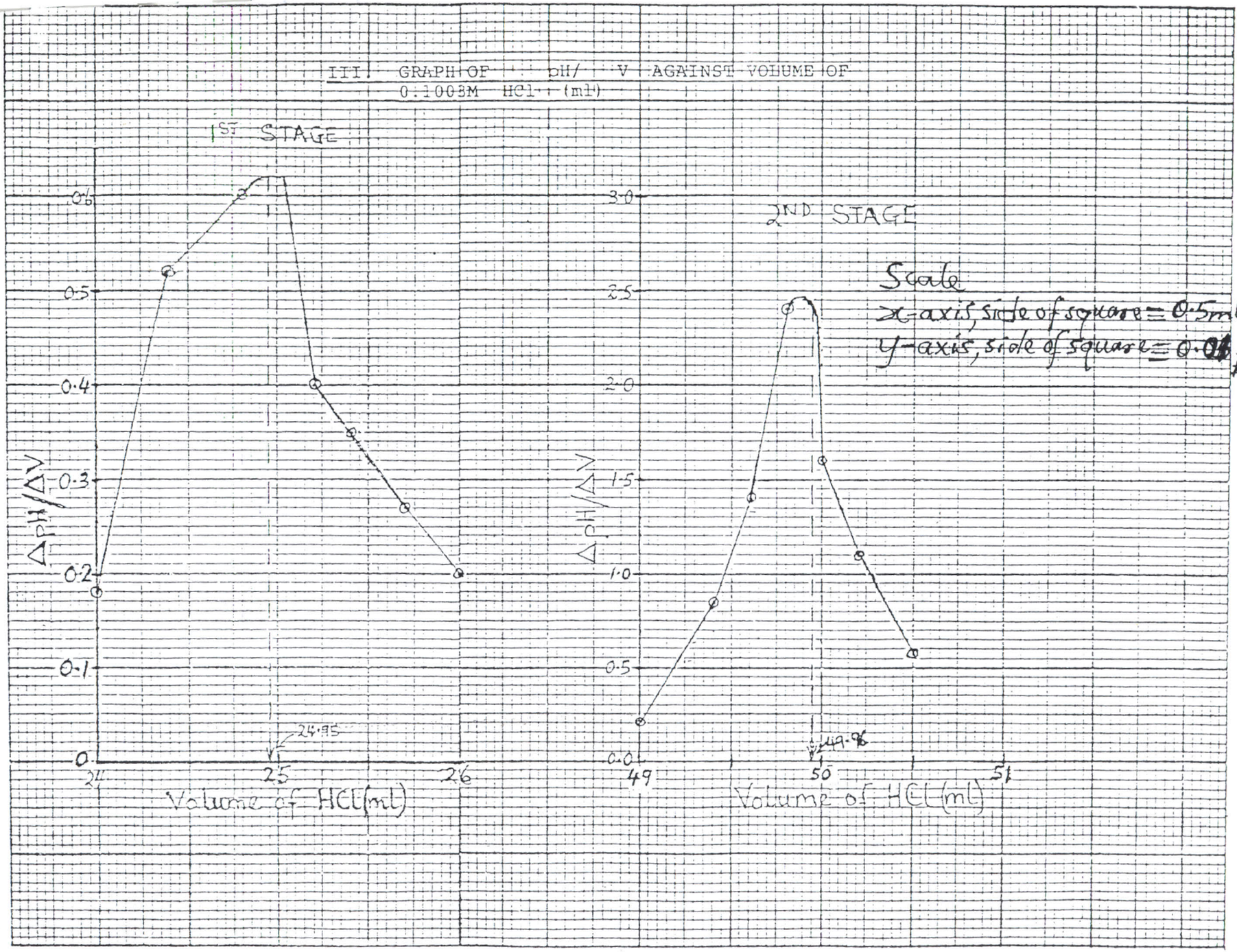
Vol. of HCl	pH	pH/ΔV
49.0	4.98	0.21
49.4	4.64	0.85
49.6	4.36	1.40
49.8	3.88	2.40
50.0	3.57	1.60
50.2	3.35	1.1
50.5	3.18	0.57

(II) GRAPH OF CONDUCTANCE (Λ) AGAINST VOLUME OF 0.1003M HCl (ml)



Scale
x-axis, side of square ≡ 2ml
y-axis, side of square ≡ 0.2ms/cm

III GRAPH OF ΔpH/ΔV AGAINST VOLUME OF 0.1003M HCl (ml)



IV. GRAPH OF pH AGAINST VOLUME OF 0.1003M HCl (ml)