High Accuracy Titrimetry with Application to HCl

by
Richard Brown and Martin Milton COAM
and Paul Brewer (now Imperial College)

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National Physical Laboratory
Queens Road, Teddington, Middlesex, TW1 0LW

Approved on behalf of Managing Director, NPL
By D H Nettleton, Head of the Centre for Optical and Analytical Measurement

Executive Summary

Three independent methods of potentiometric titration using tris (hydroxymethyl) methylamine, potassium hydroxide and silver nitrate have been developed with full uncertainty budgets. We estimate the uncertainty of each of these methods to be approximately 0.1 % (relative to value) (k=2). These methods have been used for the accurate determination of the molality of HCl in solution as part of the international comparison CCQM-P19. The report also highlights the limitation imposed on the potentiometric titration method by the "dilution effect" which is particularly significant for volumetric methods operating at low concentrations.

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1. Introduction

This report was prepared as part of the Valid Analytical Measurement programme and reports results obtained by NPL in the CCQM-P19 HCl comparison study.

Titration is an important and commonly used technique for the determination of chemical concentration in solution. Titration techniques probe the total concentration of a species, and not just the free concentration, in solution. Furthermore, it has been proposed that titration has the potential to be a 'Primary Method' of measurement. In this report the method is applied to the determination of the amount content of a nominally 0.01 mol.kg^{-1} HCl solution using three independent titration methods. The molality determination of HCl solutions is a prerequisite for the use of a Harned cell, the accepted primary method for the determination of pH. Molality is defined as the amount ('number of moles') of solute per kilogram of solvent.

2. Methodology

2.1 Titration Methods

The three different titration methods developed for HCl content determination in the report are:

Method 1: Determination of the HCl content ($b_{HCl,1}$) by titration against tris(hydroxymethyl) methylamine (Tris buffer / $NH_2C(CH_2OH)_3$) according to:

$$NH_2C(CH_2OH)_3 + H_2O \leftrightarrow NH_3^+C(CH_2OH)_3 + OH^- \quad (1)$$

($\leftrightarrow$ represents an equilibrium) and then subsequently,

$$OH^- + H^+ \rightarrow H_2O$$

Method 2: Determination of HCl content ($b_{HCl,2}$), by titration of $COOHC_6H_4COOK$ against KOH, and subsequent titration of the KOH solution against HCl.

The equations for this method are:

$$HOOCC_6H_4COOK \rightarrow {}^-OOCC_6H_4COOK + H^+ \quad (2)$$

$$OH^- + H^+ \rightarrow H_2O$$

Both Methods 1 and 2 depend on a potentiometric determination of the endpoint using a glass electrode:

$$E = E^0 + \frac{RT}{F} \ln a_{H^+} \qquad \text{[For the Glass Electrode]} \qquad (3)$$

Method 3: Determination of HCl content ($b_{HCl,3}$) by titration against $AgNO_3$

The titration results in a white precipitate of AgCl:

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)} \qquad (4)$$

This method differs from the previous two as a glass electrode with a silver element is used to determine the titration endpoint instead of a simple glass electrode as in Methods 1 and 2. The endpoint of the titration in Method 3 was determined potentiometrically using a silver electrode:

$$E = E^0 - \frac{RT}{F} \ln a_{Cl^-} \qquad \text{[For the Silver Electrode]} \qquad (5)$$

Methods 1 and 2 are based on titration with respect to hydrogen ions. Method 3 is based on chloride ion titration.The relationship between the three titration methods is shown in Figure 1.

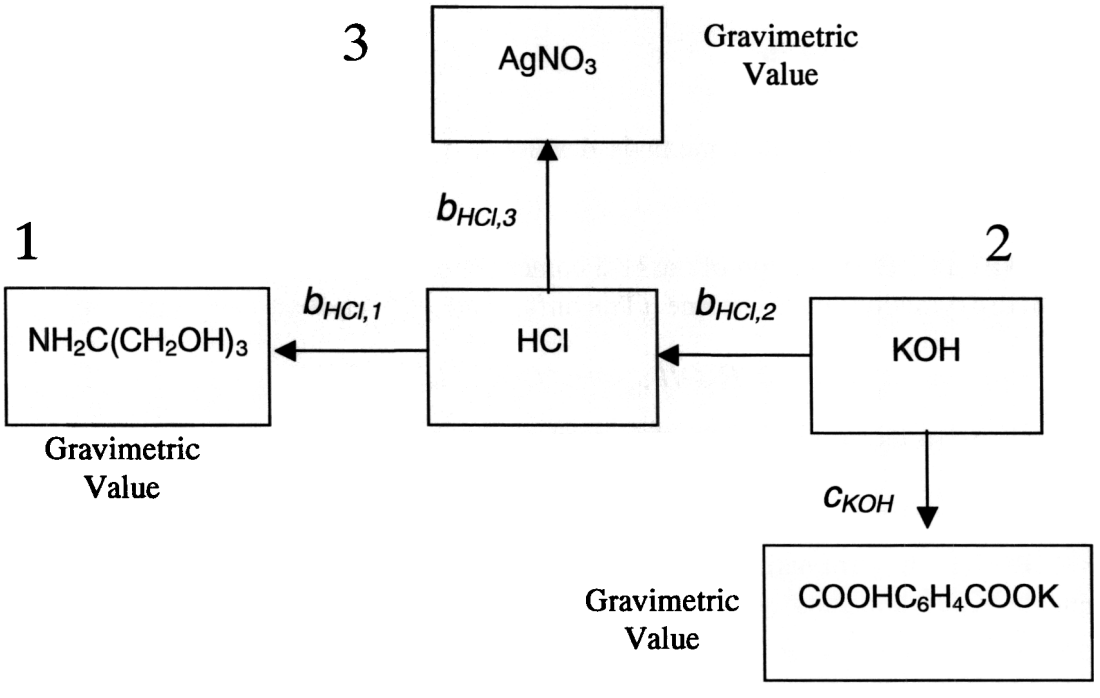

Figure 1 The proposed titration regimes to determine the HCl molality.

The experimental procedure for each of the titrations is described in detail in Appendix 1. The end point of the titration is taken to be the inflection point of the electrode potential verses volume titration curve, which is assumed to be the point of equivalence. The validity of this assumption is discussed in greater detail in section 6.5.

2.2 Gravimetric Preparation and Dilution of Solutions

To prepare the solutions a mass (m_{SM}) of starting material is added to a mass of water, m_{W1}, to yield a nominally 0.1 M solution. From this solution a mass, m_F, is removed which represents a mass fraction f_1 of the solution:

$$f_1 = \frac{m_F}{m_{SM} + m_{W1}}$$

When the aliquot m_F is added to a mass of water m_{W2}, the molality of the resulting solution is given by:

$$b = \frac{m_{SM} \times p \times f_1}{M_{SM} \times 100 \times (m_{W2} + f_1 \times m_{W1})}$$

Where p is the purity of the starting material (%) and M_{SM} is its molecular mass.

From this solution an aliquot of mass m_A, is used for the titration. This represents a mass fraction f_2 of the solution:

$$f_2 = \frac{m_A}{m_{W2} + f_1 \times m_{W1} + f_1 \times m_{SM}}$$

The amount of starting material in this aliquot is given by:

$$n = \frac{f_1 \times f_2 \times m_{SM} \times p}{100 \times M_{SM}} \qquad (7)$$

2.3 Measurement Equations

In Methods 1 and 3 and in the 'reverse' step of Method 2, HCl is used as the titrant. The mass of HCl titrated to the endpoint is given by:

$$m_{EP} = m_{HCL} + v_{HCL} \times S \times \rho_{HCL} \qquad (8)$$

where m_{EP} (g) is the mass of the HCl titrated, m_{HCL} (g) is the mass of HCl weighed out (approximately 40g) before the titration is commenced, v_{HCL} (cm^3) is the volume of HCl solution indicated by the titrator (approximately $10cm^3$), S is the calibration slope of the titrator unit and ρ_{HCl} ($g.dm^{-3}$) is the density of HCl. The HCl molality is then calculated from:

$$b_{HCl} = \frac{n}{m_{EP} - n \times M_{HCl}}$$

where n is given by equation (7) and M_{HCl} is the relative molecular mass of HCl

In Method 2, the amount of KHP titrated is determined from:

$$n_{HCl} = \frac{n_{KHP} \times v_{KOH2}}{v_{KOH1}}$$

where n_{HCl} is the amount of HCl in the solution, v_{KOH1} (cm^3) is the volume of KOH delivered by the titrator in the titration with potassium hydrogen phthalate, v_{KOH2} (cm^3) is the volume of KOH delivered in the titration with HCl and n_{KHP} is the amount of titrated potassium hydrogen phthalate. The molality of HCl is then given (for Method 2) by:

$$b_{HCl} = \frac{n_{HCl}}{m_{HCl} - n_{HCl} \times M_{HCl}}$$

where m_{HCl} (g) is the mass of HCl and M_{HCl} is the relative molecular mass of the HCl.

The detailed methods used for each of the titration regimes is given in Appendix 1 and the calculation of the uncertainty of the results in Appendix 2.

3. Results and Discussion

3.1 Results

The methods described above were used to determine the molality of unknown samples of HCl as part of the pilot study CCQM-P19. The Pilot Laboratory (NIST) supplied six 'blue' and five 'red' ampoules, each containing approximately 55 dm^3 of HCl solution with a nominal molality of 0.01 $mol.kg^{-1}$. NIST stated that the molality of the red ampoules was known with a greater certainty than the blue ampoules and for this reason the blue ampoules were used for 'practice runs' for the titration methods using KOH and Tris. The scarcity of the supplied sample coupled with the practicality of our methodology meant that only two HCl molality determinations were made using each of

the three methods for the blue samples, whilst a further two titrations were carried out for both the KOH and Tris methods using the red samples. The $AgNO_3$ method was not used with the red ampoules. The experimental procedures used at NPL are described in full in Appendix 1. The results are displayed in Table 1.

	HCl Molality / mol.kg^{-1}			
Method / Ampoule	*Titration 1*	*Titration 2*	*Mean*	*Uncertainty (k=2)*
KOH / RED	0.009972	0.009983	**0.009978**	0.000009
KOH / BLUE	0.009988	0.009976	**0.009982**	0.000009
$AgNO_3$ / BLUE	0.010002	0.009990	**0.009996**	0.000009
TRIS / RED	0.009929	0.009923	**0.009926**	0.000008
TRIS / BLUE	0.009933	0.009935	**0.009934**	0.000009

k=2 representing a 95% confidence interval

Table 1 HCl molalities obtained by each of the three titration regimes for both the red and blue ampoule sets.

The best determination of the molality of the HCl samples supplied by NIST, by comparison with the CCQM-P19 accepted value, was obtained using the KOH method giving a value of 0.009978 mol.kg^{-1} with an uncertainty of 0.000009 mol.kg^{-1} (k=2) for the red ampoules and a value of 0.009982 mol.kg^{-1} with an uncertainty of 0.000009 mol.kg^{-1} (k=2) for the blue ampoules. The $AgNO_3$ method provides the best evaluation of the chloride content of the HCl at 0.009996 mol.kg^{-1} with an uncertainty of 0.000009 mol.kg^{-1} (k=2). The best attempt at evaluating the HCl molality using the TRIS method provided much lower results than the other two methods giving 0.009926 and 0.009934 mol.kg^{-1} for the red and blue ampoules respectively, with an uncertainty of 0.000009 mol.kg^{-1}. The uncertainties were estimated using the methods described in Appendix 2. The results in Table 1 are displayed graphically in Figure 2.

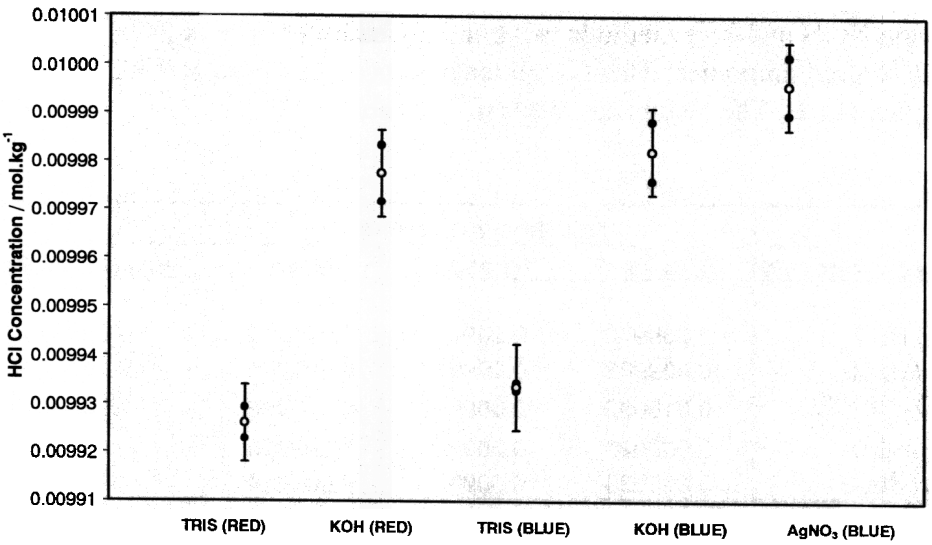

Figure 2. Comparison of HCl molalities obtained using the three methodologies for the red and blue ampoules. The mean of the results (•) for each method and ampoule set and the actual experimental determinations (•) are shown. The bars indicate the estimated uncertainty of the mean values representing a 95% confidence interval (with k=2).

3.2 Review of Results for Methods 1, 2 and 3

In the assessment of the discrepancy between the titration methods used to measure the NIST samples, it has been assumed that the HCl is of 100% purity and that the SRMs, prepared rigorously, are of the purity stated on the certificate. Differences between the results must be explained in terms of the different titration methodologies or different titration chemistry.

Titrations with $AgNO_3$ have consistently given higher molality values for the HCl solutions than the other two methods. The major difference in the methodology is that the $AgNO_3$ method represents a titration against chloride ions, rather than protons. Assuming a 1:1 stoichiometry of protons and chloride ions within the HCl solution the use of a chloride sensitive electrode should not impose any bias on the calculated molality. Other effects such as the photo-degradation of the $AgNO_3$ would lead to an overestimation of the HCl molality. Photo-degradation is a realistic problem since the $AgNO_3$ solid and solution are exposed to at least low levels of ambient light for extended periods. In terms of the chemistry of the process the existence of several complexation equilibria of the form,

$$\begin{aligned} AgCl_s + Cl^- &\rightarrow AgCl_2^- \\ AgCl_2^- + Cl^- &\rightarrow AgCl_3^{2-} \qquad etc., \end{aligned} \tag{17}$$

will also produce an over-estimation of the HCl molality. This effect will be most prevalent in more concentrated halide solutions. Practically the $AgNO_3$ titration is inhomogeneous as a solid precipitate is produced during the reaction process. The possibility of $AgNO_3$ becoming trapped, permanently or semi-permanently, within the solid AgCl precipitate might also lead to an over-estimation of the HCl molality. Additionally, the silver electrode becomes coated with the solid AgCl precipitate during the titration process leading to lower confidence in the voltage reading from the electrode.

The double titration methodology employed in the KOH titrations should lead to more accurate and more precise molality values for the HCl solutions as well as eliminating any dependence on the calibration of the titrator unit and the density of the HCl solution. This assumption is valid provided there is no further absorption of CO_2 by the KOH solution or, more importantly, no significant changes in ambient temperature between titrations. It is thought that changes during the experimental runs are indeed not significant. As a further safeguard the titrations were run in pairs, *i.e.* Phthalate 1, HCl 1 then Phthalate 2, HCl 2, to minimise the effect of any changes since it is the ratio of the volumes dispensed in the corresponding HCl and Phthalate titrations which is of primary importance. Because the endpoints of the two titrations occur at different pHs the effect of CO_2 in solution is not equal. For the strong acid-strong base titration the CO_2 endpoint is sufficiently far from the titration KOH-HCl equivalence pH to not affect the measured endpoint. However the CO_2 endpoint occurs very near to the KHP-KOH equivalence pH and serves to obfuscate the point of inflection in the titration curve by depressing and shifting the slope of the curve near equivalence.

For the NIST ampoules under study, the Tris titration method has produced HCl molality values below those obtained using the $AgNO_3$ and KOH methods. The explanation for the large discrepancy between the Tris method and the other two methods is not obvious but is thought to have a chemical basis. One possible reason is related to the purity of the SRMs. Whilst the purity of the $AgNO_3$ and KHP was sufficiently close to 100% that the effect of any impurities could be safely ignored, the certified purity of the Tris after preparation was only 99.9%. Thus far it has been assumed that impurities in SRMs are inert. However it is quite possible that the impurities may participate in the titration and be even more active than the pure compound, for example a by-product of Tris manufacture with two amine groupings. If the significant impurity in the Tris SRM is participating in the titration then the molality of the HCl solution will be under-estimated. However it is thought that the impurity in the Tris SRM is simply occluded mother liquor[1].

3.3 Discussion of sources of bias affecting all Methods

The major disadvantage of titrimetry over coulometry is the problem associated with dilution. This leads to shallower titration slopes and an equivalence point not coincident with the maximum $\frac{d(pH)}{dV}$ value even for strong acid – strong base titrations. This

effect is discussed, in full, in section 6.5 where we estimate its maximum value as 0.25 % (relative).

A major cause of the over estimation of the proton concentration is the absorption of atmospheric carbon dioxide and the formation of carbonic acid. However, more seriously, carbon dioxide has a differential effect on the KHP and HCl titrations. The KHP endpoint (nearer pH 7) is more adversely affected by the presence of the carbon dioxide producing an artificially high value for the KOH concentration. Therefore, instead of the KHP/KOH method being self-consistent it actually imposes a double error on the final HCl value. This is probably the main reason for our KHP value for the HCl determination being higher than the accepted value. It may be beneficial to rigorously degas solutions before and during use to eliminate carbon dioxide from them. Clearly this will not work for alkaline solutions where the carbon dioxide has been bound in as carbonate.

Other miscellaneous effects that may influence the HCl molality results include the possibility of chloride and other ions being semi-permanently attached to glass surfaces and the potential contamination caused by hydrocarbon residues in the purging/drying nitrogen gas stream. Additionally it has been stated[2] that for potentiometric titrations, the design and size of the titration cell and the relative positions of the stirrer, burette tip, and sensing pH electrode, in the cell are often dominant sources of lag and noise, especially in automated titrations. The dominant noise in the acid-base titration is due to incomplete mixing, and is maximal at the equivalence point. (The process of taking the derivative for endpoint determination will further enhance this noise).

Solutions are not de-oxygenated before titration. Although standard in most electrochemistry, deoxygenation and, more importantly, keeping them deoxygenated during titration is extremely awkward. The presence of oxygen in solution may have a small, and here unquantified, effect on the operation of the glass and silver electrodes. However it is predicted that this complication would not have any significant effect on the position of the titration endpoint. The presence of carbon dioxide in the solutions may have a more dramatic effect.

Towards the end of the study it was noted that the rate of evaporation of the HCl solution was potentially significant. The rate of mass loss was up to 12 $mg.min^{-1}$ (apparently greater than for other solutions used in the titration procedures) and was exacerbated by the weighing of the HCl solution in beakers with a large surface area to volume ratio. It was also noted that solution weight was lost on transferring the HCl solution from the ampoules to the beaker, again assumed to be due to evaporation. Such an effect would cause an over-estimation of the molality of the HCl. By weighing the acid immediately after decanting from the ampoules the weight loss was kept to a minimum and was not thought to be significant with respect to the overall uncertainty budget.

Ideally[3] the use of beakers for weighing and titration should be avoided as the larger surface area to volume ratio exacerbates the evaporation issue. A methodology based on a syringe arrangement with a Teflon proboscis, for dipping into the ampoules, could be used for weighing and dispensing.

4. Conclusions

The results from the three methods described here are given in Figure 2.

Molality values obtained for the $AgNO_3$ method are slightly greater than those obtained using the KOH method but are in agreement within the limits of uncertainty. For both the Tris and KOH methods the molality of the red samples is found to be slightly lower than that of the blue samples, perhaps surprisingly since the blue samples were thought to contain extra moisture. Again the agreement between the molality values for the red and blue samples is very good and well within the limits of uncertainty.

Potentiometric titration is limited by the error imposed by the dilution effect, which is most pronounced for weaker reagents and less concentrated solutions and might be as large as 0.25 %. Consequently, potentiometric titrations have the potential to operate as a Primary Measurement Method only when this source of uncertainty can be fully quantified [4]. Our results for CCQM-P19 indicate that KOH is the best method for potentiometric titration of HCl, followed by Tris, with silver nitrate being the least precise, mainly because of the large amount of precipitate formed during the reaction.

The Pilot Laboratory's report showed that the leaching of sodium ions from the glass ampoules over extended periods of time contributed to a lowering of the proton concentration in the acid. However it is not thought that this constitutes a serious issue over the timescale of titration and Harned cell work. Since the HCl contained only very low levels of anionic impurities[3] (bromide and nitrate) this is another reason why the chloride titrations produced higher values than the proton titrations.

Accurate Harned cell measurements require a good method for hydrogen (or chloride ion) determination in HCl. Since some aspersions have been cast over the accuracy of the KHP and Tris titrations for hydrogen ion concentration and titrimetry for the chloride ion is known to be inaccurate other materials to titrate against should be considered. Sodium carbonate has been suggested in this role[1] although its preparation would be more demanding.

5. Appendix 1 : Experimental Procedure

5.1 Experimental procedure for HCl titration

5.1.1 General Experimental

The water used for making up the solutions for titration and for final stage equipment washing was quadruply distilled (Millipore, Milli-Q gradient, with a UV light, organics removal regime). All glassware was cleaned thoroughly before use and dried in an oven (120°C) and subsequently with a stream of nitrogen.

5.1.2 Preparation of the HCl solution

The HCl solution was used as provided from NIST in approximately 55 cm^3 ampoules. The ampoules were washed (quadruply distilled water) and dried (N_2 stream) before use. The ampoules were then opened along the pre-scored joint immediately prior to use.

5.1.3 Preparation and Titration of $NH_2C(CH_2OH)_3$ solution

Approximately 10 g of $NH_2C(CH_2OH)_3$ (SRM 723a, NIST) was weighed out and desiccated over silica gel (reduced pressure) for 24 h. A 0.01 $mol.kg^{-1}$ solution of $NH_2C(CH_2OH)$ was then prepared gravimetrically. This was achieved by making a 0.1 $mol.kg^{-1}$ solution followed by a further dilution.

40cm^3 of the HCl provided by NIST was dosed out from the previously cleaned and fully dried 721 NET Titrino (Mettler Toledo) exchange unit into a clean, dried 250cm^3 beaker and its mass determined. 50cm^3 of the $NH_2C(CH_2OH)_3$ solution was pipetted into the same beaker and its mass measured. A stirrer bar was added to the beaker. The burette on the exchange unit was filled with the HCl solution and closely inspected for any air bubbles. The electrode and the pipette from the 721 NET Titrino were inserted into the beaker after being rinsed with distilled water. (The dispensing tip was in contact with the solution to ensure that the dispensed volume actually entered the solution and did not remain on the dispensing tip as a drop. The solution was stirred during the titration and the titration commenced.

5.1.4 Preparation and Titration of $AgNO_3$ solution

The method for $AgNO_3$ titration is that described in 5.1.3 except that a $AgNO_3$ solution is used. Approximately 7-8 g of $AgNO_3$ (Aldrich) was desiccated over silica gel (reduced pressure) for two hours, under low ambient light conditions, before use. A nominally 0.01 $mol.dm^{-3}$ solution of the $AgNO_3$ was then made up by dilution of an initially produced 0.1 $mol.dm^{-3}$ $AgNO_3$ solution.

5.1.5 Preparation and titration of KOH solution:

An approximately 1 mol.dm^{-3} solution of KOH (Fisher) was prepared in a 1 dm^3 class 'A' volumetric flask with water. This solution was used to wash out the exchange unit and the reagent flask was filled with the solution. A NaOH trap was put on the reagent flask to ensure that no additional CO_2 would be dissolved in the KOH whilst in the exchange unit. The potassium hydrogen phthalate, $COOHC_6H_4COOK$ (SRM 84k, NIST), was prepared for use by heating at 120°C (2 hrs). A solution of gravimetrically prepared $COOHC_6H_4COOK$ was titrated against the KOH. The titrator was used to titrate all 50cm^3 of the KOH. The determined concentration of the KOH was used to calculate the HCl molality by performing another titration as described above but between KOH and HCl.

5.2 Assigning a Density Value to the HCl Solution

The titration endpoint is determined and expressed as a volume and for this reason a density value for the nominally prepared 0.01 mol.kg^{-1} HCl solution is required for conversion to 'true' mass with minimum uncertainty. Three HCl solutions of nominal concentrations: 0.009, 0.010 and 0.011 mol.kg^{-1} were prepared. The concentration of each was later determined by titration with $AgNO_3$. A Paar DMA 55 density meter was employed to take measurements for each solution at 15 and 25°C. The system operates by measuring the vibrational frequency of the solution.

The results at both temperatures indicated a positive linear correlation between density and solution concentration. More importantly, the density change was fairly small for a change in solution concentration. Therefore for the purposes of the titration the density of the nominally prepared HCl solution will be insignificant between preparations. However, the variation in density between the 15°C and 25°C measurements was significant and for this reason it is important that the solution temperature is known with minimum uncertainty.

For simplicity it was decided that experimentally the HCl solution density would be determined by use of the density equation for water, with substitution of solution temperature, and addition of 0.2 g.dm^{-3}, which is an approximation of the variation from pure water density.

6. Appendix 2 : Uncertainty Evaluation

6.1 Uncertainty Budgets

In the following section the contribution of components of the titrimetry uncertainty budget, identified in the measurement equations, are evaluated.

6.1.1 Method

Table 1: Uncertainty in the HCl Molality determination ***[Equation 11]***

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / mol.kg^{-1}	
True HCl Solution Mass (g)	m_{HCl}	4.805E+01	-2.192E-04	3.043E-03	-6.672E-07	*(Table 2)*
Amount of HCl Titrated	n_{HCl}	5.058E-04	2.083E+01	2.124E-07	4.424E-06	*(Table 3)*
Mw HCl	M_{HCl}	3.646E+01	-			
u (molality) (mol.kg^{-1})	b_{HCl}	**1.053E-02**			**4.474E-06**	
				% (1.s.d.)	4.249E-02	

Table 2: Uncertainty in the True HCl Solution Mass ***[Equation 14]***

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / mol/Kg	
Uncorrected Mass of HCl Solution (g)	m'_{HCl}	4.800E+01	1.001E+00	3.000E-03	3.003E-03	
Air Density (g.dm^{-3})	ρ_A	1.183E+00	4.819E-02	9.597E-03	4.625E-04	*(Table 14)*
HCl Density (g.dm^{-3})	ρ_{HCl}	9.982E+02	-5.710E-05	3.000E+00	-1.713E-04	
u (True HCl Solution Mass) (g)	m_{HCl}	**4.805E+01**			**3.043E-03**	

Table 3: Uncertainty in Amount of HCl Titrated **[Equation 10]**

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / Amount	
Amount of KHP Titrated	n_{KHP}	5.297E-04	9.549E-01	1.613E-07	1.540E-07	*(Table 4)*
Measured Endpoint 1 (dm^3)	v_{KOH1}	5.006E-02	-1.010E-02	1.000E-05	-1.010E-07	*(Table 5)*
Measured Endpoint 2 (dm^3)	v_{KOH2}	4.781E-02	1.058E-02	1.000E-05	1.058E-07	*(Table 6)*
u (Amount of HCl Titrated)	n_{HCl}	**5.058E-04**			**2.124E-07**	

Table 4: Uncertainty in the Calculated Amount of KHP Titrated **[Equation 7]**

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / Amount	
True Mass of KHP (g)	m_{SM}	1.021E+01	5.190E-05	3.026E-03	1.571E-07	*(Table 9)*
Dilution Factor 1	f_1	2.110E-01	2.510E-03	4.918E-06	1.234E-08	*(Table 8)*
Dilution Factor 2	f_2	5.023E-02	1.055E-02	3.122E-06	3.292E-08	*(Table 7)*
Purity (%)	p	1.000E+02	5.297E-06	2.000E-03	1.059E-08	
Mw KHP (g.mol^{-1})	M_{KHP}	2.042E+02	-	-		
u (Amount of KHP Titrated)	n_{KHP}	**5.297E-04**			**1.613E-07**	

Table 5: Uncertainty in Measured Endpoint 1

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / dm3
Titrator Uncertainty		-	1.000E+00	1.000E-05	1.000E-05
u (Measured Endpoint 1) (dm^3)	v_{KOH1}	**5.006E-02**			**1.000E-05**

Table 6: Uncertainty in Measured Endpoint 2

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / dm3	
Titrator Uncertainty		-	1.000E+00	1.000E-05	1.000E-05	
u (Measured Endpoint 2) (dm^3)	**v_{KOH2}**	**4.781E-02**			**1.000E-05**	

Table 7: Uncertainty in Dilution Factor 2 *[Equation 6]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
True Mass of KHP (g)	m_{SM}	1.021E+01	-1.059E-05	3.026E-03	-3.204E-08	*(Table 9)*
True Mass of the Aliquot (g)	m_A	5.028E+01	9.990E-04	3.047E-03	3.044E-06	*(Table 13)*
True Mass of Water 1 (g)	m_{W1}	9.385E+02	-1.059E-05	1.350E-02	-1.429E-07	*(Table 10)*
True Mass of Water 2 (g)	m_{W2}	8.008E+02	-5.017E-05	1.265E-02	-6.346E-07	*(Table 12)*
Dilution Factor 1	f_1	2.110E-01	-4.760E-02	4.918E-06	-2.341E-07	*(Table 8)*
u (Dilution Factor 2)	**f_2**	**5.023E-02**			**3.122E-06**	

Table 8: Uncertainty in Dilution Factor 1 *[Equation 6]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi)	
True Mass of Fraction (g)	m_F	2.002E+02	1.054E-03	3.639E-03	3.836E-06	*(Table 11)*
True Mass of KHP (g)	m_{SM}	1.021E+01	-2.224E-04	3.026E-03	-6.732E-07	*(Table 9)*
True Mass of Water 1 (g)	m_{W1}	9.385E+02	-2.224E-04	1.350E-02	-3.003E-06	*(Table 10)*
u (Dilution Factor 1)	**f_1**	**2.110E-01**			**4.918E-06**	

Table 9: Uncertainty in the KHP Mass *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of KHP (g)	m'_{SM}	1.020E+01	1.001E+00	3.000E-03	3.002E-03	
Air Density ($g.dm^{-3}$)	ρ_A	1.183E+00	6.242E-03	9.597E-03	5.990E-05	*(Table 14)*
KHP Density ($g.dm^{-3}$)	ρ_W	1.636E+03	-3.815E-06	1.000E+02	-3.815E-04	
u (True Mass of KHP) (g)	**m_{SM}**	**1.021E+01**			**3.026E-03**	

Table 10: Uncertainty in True Mass of Water 1 *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Water 1 (g)	m'_{W1}	9.375E+02	1.001E+00	1.000E-02	1.001E-02	
Air Density ($g.dm^{-3}$)	ρ_A	1.183E+00	9.412E-01	9.597E-03	9.032E-03	*(Table 14)*
Water Density ($g.dm^{-3}$)	ρ_W	9.982E+02	-1.115E-03	6.196E-01	-6.910E-04	*(Table 15)*
u (True Mass of Water 1) (g)	**m_{W1}**	**9.385E+02**			**1.350E-02**	

Table 11: Uncertainty in True Mass of Fraction *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Fraction (g)	m'_F	2.000E+02	1.001E+00	3.000E-03		
Air Density (g.dm^{-3})	ρ_A	1.183E+00	2.008E-01	9.597E-03		*(Table 14)*
0.1 mol/Kg Solution Density (g.dm^{-3})	$\rho_{0.1}$	9.980E+02	-2.380E-04	3.000E+00		
u (True Mass of Fraction) (g)	m_F	**2.002E+02**			**3.639E-03**	

Table 12: Uncertainty in the True Mass of Water 2 *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi)	
Uncorrected Mass of Water 2 (g)	m'_{W2}	8.000E+02	1.001E+00	1.000E-02	1.001E-02	
Air Density (g.dm^{-3})	ρ_A	1.183E+00	8.031E-01	9.597E-03	7.707E-03	*(Table 14)*
Water Density (g.dm^{-3})	ρ_W	9.982E+02	-9.517E-04	6.196E-01	-5.897E-04	*(Table 15)*
u (True Mass of Water 2) (g)	m_{W2}	**8.008E+02**			**1.265E-02**	

Table 13: Uncertainty in the True Mass of the Aliquot *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of the Aliquot (g)	m'_A	5.023E+01	1.001E+00	3.000E-03	3.003E-03	
Air Density (g.dm^{-3})	ρ_A	1.183E+00	5.043E-02	9.597E-03	4.840E-04	*(Table 14)*
0.01 mol.kg^{-1} Solution Density (g.dm^{-3})	$\rho_{0.01}$	9.980E+02	-5.977E-05	3.000E+00	-1.793E-04	
u (True Mass of the Aliquot) (g)	m_A	**5.028E+01**			**3.047E-03**	

Table 14: Uncertainty in the Air Density *[Equation 13]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(vi) / g.dm^{-3}
Temperature (°C)	T	2.000E+01	-3.199E-03	3.000E+00	-9.596E-03
Pressure (Pa)	P	1.001E+05	6.379E-07	2.500E+01	1.595E-05
RH (%)	H	7.070E+01	-5.607E-06	3.000E+01	-1.682E-04
u (Air Density) (g.dm^{-3})	ρ_A	**1.183E+00**			**9.597E-03**

Table 15: Uncertainty in the Water Density *[Equation 12]*

Quantity	Symbol	Estimate	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(vi) / g.dm^{-3}
Temperature (°C)	t	2.000E+01	-2.065E-01	3.000E+00	-6.196E-01
po (g.dm^{-3})		1.000E+03	-		
to (°C)		3.982E+00	-		
A (°C^{-1})		7.013E-08	-		
B (°C^{-2})		7.927E-06	-		
C (°C^{-3})		-7.576E-08	-		
D (°C^{-4})		7.315E-10	-		
E (°C^{-5})		-3.596E-12	-		
u (Water Density) (g.dm^{-3})	ρ_W	**9.982E+02**			**6.196E-01**

6.1.2 Method 2

Table 1: Uncertainty in the HCl Molality Determination *[Equation 9]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / mol.kg^{-1}	
Amount of the Silver Nitrate Titrated	n_{AGNO3}	3.901E-04	2.562E+01	1.716E-07	4.395E-06	*(Table 2)*
Total Mass of HCl Titrated (g)	m_{EP}	3.906E+01	-2.559E-04	1.097E-02	-2.806E-06	*(Table 3)*
Mw HCl	M_{HCl}	3.646E+01				
u (molality) (mol.kg^{-1})	b_{HCl}	9.990E-03		-	**5.215E-06**	
				% (1.s.d.)	**5.220E-02**	

Table 2: Uncertainty in the Calculated Amount of Silver Nitrate Titrated [Equation 7]

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / Amount	
True Mass of Silver Nitrate (g)	m_{SM}	7.927E+00	4.921E-05	3.001E-03	1.477E-07	*(Table 6)*
Dilution Factor 1	f_1	2.004E-01	1.947E-03	4.604E-06	8.964E-09	*(Table 5)*
Dilution Factor 2	f_2	4.172E-02	9.349E-03	3.098E-06	2.896E-08	*(Table 4)*
Purity (%)	p	1.000E+02	3.901E-06	2.100E-02	8.191E-08	
Mw Silver Nitrate (g.mol^{-1})	M_{AGNO3}	1.699E+02	-	-		
u (Amount)	n_{AGNO3}	**3.901E-04**			**1.716E-07**	

Table 3: Uncertainty in Total Mass of HCl Titrated *[Equation 8]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Calibration Slope	S	9.999E-01	1.380E+01	9.161E-05	1.264E-03	
True Mass of HCl Added (g)	m_{HCl}	2.526E+01	1.000E+00	3.017E-03	3.017E-03	*(Table 7)*
Measured Endpoint (dm^3)	v_{HCl}	1.382E-02	9.980E+02	1.000E-05	9.980E-03	*(Table 8)*
HCl Density (g.dm^{-3})	ρ_{HCl}	9.981E+02	1.382E-02	2.285E-01	3.159E-03	*(Table 9)*
u (Total Mass of HCl Titrated) (g)	m_{EP}	3.906E+01			**1.097E-02**	

Table 4: Uncertainty in Dilution Factor 2 *[Equation 6]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi)	
True Mass of Silver Nitrate (g)	m_{SM}	7.927E+00	-8.340E-06	3.001E-03	-2.503E-08	*(Table 6)*
True Mass of the Aliquot (g)	m_A	4.181E+01	9.978E-04	3.044E-03	3.038E-06	*(Table 13)*
True Mass of Water 1 (g)	m_{W1}	9.013E+02	-8.340E-06	1.433E-02	-1.196E-07	*(Table 10)*
True Mass of Water 2 (g)	m_{W2}	8.201E+02	-4.163E-05	1.369E-02	-5.698E-07	*(Table 12)*
Dilution Factor 1	f_1	2.004E-01	-3.785E-02	4.604E-06	-1.743E-07	*(Table 5)*
u (Dilution Factor 2)	f_2	**4.172E-02**			**3.098E-06**	

Table 5: Uncertainty in Dilution Factor 1 *[Equation 6]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi)	
True Mass of Fraction (g)	m_F	1.822E+02	1.100E-03	2.985E-03	3.284E-06	*(Table 11)*
True Mass of Silver Nitrate (g)	m_{SM}	7.927E+00	-2.204E-04	3.001E-03	-6.612E-07	*(Table 6)*
True Mass of Water 1 (g)	m_{W1}	9.013E+02	-2.204E-04	1.433E-02	-3.159E-06	*(Table 10)*
u (Dilution Factor 1)	f_1	**2.004E-01**			**4.604E-06**	

Table 6: Uncertainty in the Silver Nitrate Mass *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Silver Nitrate (g)	m'_{SM}	7.926E+00	1.000E+00	3.000E-03	3.000E-03	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	1.822E-03	1.133E-02	2.065E-05	*(Table 14)*
Silver Nitrate Density (g.dm^{-3})	ρ_{AGNO3}	4.352E+03	-4.186E-07	1.000E+02	-4.186E-05	
u (True Mass of Silver Nitrate) (g)	m_{SM}	**7.927E+00**			**3.001E-03**	

Table 7: Uncertainty in True Mass of HCl Added *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of HCl (g)	m'_{HCl}	2.524E+01	1.001E+00	3.000E-03	3.003E-03	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	2.534E-02	1.133E-02	2.872E-04	*(Table 14)*
HCl Density (g.dm^{-3})	ρ_{HCl}	9.981E+02	-3.055E-05	2.285E-01	-6.981E-06	*(Table 9)*
u (True Mass of HCl Added) (g)	m_{HCl}	**2.526E+01**			**3.017E-03**	

Table 8: Uncertainty in the Measured Endpoint

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(vi) / dm^3
Titrator Uncertainty			1.000E+00	1.000E-05	1.000E-05
u (Measured Endpoint) (dm^3)	v_{HCl}	**1.382E-02**			**1.000E-05**

Table 9: Uncertainty in the Density Measurement

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(vi) / g.dm^{-3}
Temperature of HCl ($^\circ$C)	t	2.140E+01	-2.210E-01	5.000E-01	-1.105E-01
HCl Correction (g.dm^{-3})	x	2.000E-01	1.000E+00	2.000E-01	2.000E-01
u (HCl Density) (g.dm^{-3})	ρ_{HCl}	**9.981E+02**			**2.285E-01**

Table 10: Uncertainty in True Mass of Water 1 *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Water 1 (g)	m'_{W1}	9.003E+02	1.001E+00	1.000E-02	1.001E-02	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	9.036E-01	1.133E-02	1.024E-02	*(Table 14)*
Water Density (g.dm^{-3})	ρ_W	9.985E+02	-1.089E-03	5.714E-01	-6.223E-04	*(Table 15)*
u (True Mass of Water 1) (g)	m_{W1}	**9.013E+02**			**1.433E-02**	

Table 11: Uncertainty in True Mass of Fraction *[Equation 14]*

Quantity	Symbol	Estimate	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Fraction (g)	m'_F	1.820E+02	1.001E+00	2.044E-03	2.046E-03	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	1.827E-01	1.133E-02	2.071E-03	*(Table 14)*
0.1 mol.kg^{-1} Solution Density (g.dm^{-3})	$\rho_{0.1}$	9.980E+02	-2.204E-04	3.000E+00	-6.611E-04	
u (True Mass of Fraction) (g)	m_F	**1.822E+02**			**2.985E-03**	

Table 12: Uncertainty in the True Mass of Water 2 *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Water 2 (g)	m'_{W2}	8.192E+02	1.001E+00	1.000E-02	1.001E-02	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	8.222E-01	1.133E-02	9.319E-03	*(Table 14)*
Water Density (g.dm^{-3})	ρ_W	9.985E+02	-9.910E-04	5.714E-01	-5.663E-04	
u (True Mass of Water 2) (g)	m_{W2}	**8.201E+02**			**1.369E-02**	

Table 13: Uncertainty in the True Mass of the Aliquot *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of the Aliquot (g)	m'_A	4.177E+01	1.001E+00	3.000E-03	3.003E-03	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	4.194E-02	1.133E-02	4.754E-04	*(Table 14)*
0.01 mol.kg^{-1} Solution Density (g.dm^{-1})	$\rho_{0.01}$	9.980E+02	-5.058E-05	3.000E+00	-1.517E-04	
u (True Mass of the Aliquot) (g)	m_A	**4.181E+01**			**3.044E-03**	

Table 14: Uncertainty in the Air Density *[Equation 13]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g.dm^{-3}
Temperature (°C)	T	1.850E+01	-3.778E-03	3.000E+00	-1.133E-02
Pressure (Pa)	P	1.013E+05	6.896E-07	2.500E+01	1.724E-05
RH (%)	H	6.700E+01	-5.521E-06	3.000E+01	-1.656E-04
u (Air Density) (g.dm^{-3})	ρ_A	1.204E+00			**1.133E-02**

Table 15: Uncertainty in the Water Density *[Equation 12]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g.dm^{-3}
Temperature (°C)	t	1.850E+01	-1.905E-01	3.000E+00	-5.714E-01
po (g.dm^{-3})		1.000E+03			
to (°C)		3.982E+00			
A (°C^{-1})		7.013E-08			
B (°C^{-2})		7.927E-06			
C (°C^{-3})		-7.576E-08			
D (°C^{-4})		7.315E-10			
E (°C^{-5})		-3.596E-12			
u (Water Density) (g.dm^{-3})	ρ_W	**9.985E+02**			**5.714E-01**

6.1.3 Method 3

Table 1: Uncertainty in the HCl Molality Determination *[Equation 9]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / mol.kg^{-1}	
Amount of the Tris Buffer Titrated	n_{TRIS}	3.748E-04	2.648E+01	1.308E-07	3.463E-06	*(Table 2)*
Total Mass of HCl Titrated (g)	m_{EP}	3.779E+01	-2.627E-04	1.098E-02	-2.885E-06	*(Table 3)*
Mw HCl	M_{HCl}	3.646E+01	-	-		
u (molality) (mol.kg^{-1})	b_{HCl}	**9.923E-03**		-	**4.508E-06**	
				% (1.s.d.)	**4.543E-02**	

Table 2: Uncertainty in the Calculated Amount of Tris Buffer Titrated [Equation 7]

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / Amount	
True Mass of Tris Buffer (g)	m_{SM}	1.162E+01	3.227E-05	3.071E-03	9.908E-08	*(Table 6)*
Dilution Factor 1	f_1	9.839E-02	3.809E-03	2.831E-06	1.079E-08	*(Table 5)*
Dilution Factor 2	f_2	3.977E-02	9.425E-03	3.280E-06	3.092E-08	*(Table 4)*
Purity (%)	p	9.990E+01	3.752E-06	2.100E-02	7.879E-08	
Mw Tris Buffer (g.mol^{-1})	M_{TRIS}	1.211E+02	-	-		
u (Amount)	n_{TRIS}	**3.748E-04**			**1.308E-07**	

Table 3: Uncertainty in Total Mass of HCl Titrated *[Equation 8]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Calibration Slope	S	9.999E-01	1.397E+01	9.161E-05	1.279E-03	
True Mass of HCl Added (g)	m_{HCl}	2.382E+01	1.000E+00	3.014E-03	3.014E-03	*(Table 7)*
Measured Endpoint (dm^3)	v_{HCl}	1.399E-02	9.979E+02	1.000E-05	9.979E-03	*(Table 8)*
HCl Density (g.dm^{-3})	ρ_{HCl}	9.980E+02	1.399E-02	2.300E-01	3.218E-03	*(Table 9)*
u (Total Mass of HCl Titrated) (g)	m_{EP}	**3.779E+01**			1.098E-02	

Table 4: Uncertainty in Dilution Factor 2 *[Equation 6]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi)	
True Mass of Tris Buffer (g)	m_{SM}	1.162E+01	-4.164E-06	3.071E-03	-1.279E-08	*(Table 6)*
True Mass of the Aliquot (g)	m_A	3.737E+01	1.064E-03	3.033E-03	3.227E-06	*(Table 13)*
True Mass of Water 1 (g)	m_{W1}	9.477E+02	-4.164E-06	1.425E-02	-5.934E-08	*(Table 10)*
True Mass of Water 2 (g)	m_{W2}	8.452E+02	-4.232E-05	1.349E-02	-5.710E-07	*(Table 12)*
Dilution Factor 1	f_1	9.839E-02	-4.060E-02	2.831E-06	-1.150E-07	*(Table 5)*
u (Dilution Factor 2)	f_2	**3.977E-02**			**3.280E-06**	

Table 5: Uncertainty in Dilution Factor 1 *[Equation 6]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi)	
True Mass of Fraction (g)	m_F	9.439E+01	1.042E-03	2.307E-03	2.404E-06	*(Table 11)*
True Mass of Tris Buffer (g)	m_{SM}	1.162E+01	-1.026E-04	3.071E-03	-3.150E-07	*(Table 6)*
True Mass of Water 1 (g)	m_{W1}	9.477E+02	-1.026E-04	1.425E-02	-1.462E-06	*(Table 10)*
u (Dilution Factor 1)	f_1	**9.839E-02**			**2.831E-06**	

Table 6: Uncertainty in the Tris Buffer Mass *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Tris Buffer (g)	m'_{SM}	1.161E+01	1.001E+00	3.000E-03	3.002E-03	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	8.611E-03	1.065E-02	9.168E-05	*(Table 14)*
Tris Buffer Density (g.dm^{-3})	ρ_{TRIS}	1.350E+03	-6.378E-06	1.000E+02	-6.378E-04	
u (True Mass of Tris Buffer) (g)	m_{SM}	**1.162E+01**			**3.071E-03**	

Table 7: Uncertainty in True Mass of HCl Added *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of HCl (g)	m'_{HCl}	2.380E+01	1.001E+00	3.000E-03	3.003E-03	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	2.390E-02	1.065E-02	2.545E-04	*(Table 14)*
HCl Density (g.dm^{-3})	ρ_{HCl}	9.980E+02	-2.882E-05	2.300E-01	-6.628E-06	*(Table 9)*
u (True Mass of HCl Added) (g)	m_{HCl}	**2.382E+01**			**3.014E-03**	

Table 8: Uncertainty in the Measured Endpoint

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / dm^3
Titrator Uncertainty		-	1.000E+00	1.000E-05	1.000E-05
u (Measured Endpoint) (dm^3)	v_{HCl}	**1.399E-02**			**1.000E-05**

Table 9: Uncertainty in the Density Measurement

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g.dm^{-3}
Temperature of HCl (°C)	t	2.200E+01	-2.271E-01	5.000E-01	-1.136E-01
HCl Correction (g.dm^{-3})	x	2.000E-01	1.000E+00	2.000E-01	2.000E-01
u (HCl Density) (g.dm^{-3})	ρ_{HCl}	9.980E+02			**2.300E-01**

Table 10: Uncertainty in True Mass of Water 1 *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Water 1 (g)	m'_{W1}	9.467E+02	1.001E+00	1.000E-02	1.001E-02	
Air Density (g.dm^{-3})	ρ_A	1.204E+00	9.502E-01	1.065E-02	1.012E-02	*(Table 14)*
Water Density (g.dm^{-3})	ρ_W	9.984E+02	-1.145E-03	5.909E-01	-6.768E-04	*(Table 15)*
u (True Mass of Water 1) (g)	m_{W1}	**9.477E+02**			**1.425E-02**	

Table 11: Uncertainty in True Mass of Fraction *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Fraction (g)	m'_F	9.429E+01	1.001E+00	2.044E-03	2.046E-03	
Air Density ($g.dm^{-3}$)	ρ_A	1.204E+00	9.468E-02	1.065E-02	1.008E-03	*(Table 14)*
0.1 $mol.kg^{-1}$ Solution Density ($g.dm^{-3}$)	$\rho_{0.1}$	9.980E+02	-1.142E-04	3.000E+00	-3.425E-04	
u (True Mass of Fraction) (g)	m_F	**9.439E+01**			**2.307E-03**	

Table 12: Uncertainty in the True Mass of Water 2 *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of Water 2 (g)	m'_{W2}	8.444E+02	1.001E+00	1.000E-02	1.001E-02	
Air Density ($g.dm^{-3}$)	ρ_A	1.204E+00	8.475E-01	1.065E-02	9.024E-03	*(Table 14)*
Water Density ($g.dm^{-3}$)	ρ_W	9.984E+02	-1.022E-03	5.909E-01	-6.037E-04	*(Table 15)*
u (True Mass of Water 2) (g)	m_{W2}	**8.452E+02**			**1.349E-02**	

Table 13: Uncertainty in the True Mass of the Aliquot *[Equation 14]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / g	
Uncorrected Mass of the Aliquot (g)	m'_A	3.733E+01	1.001E+00	3.000E-03	3.003E-03	
Air Density ($g.dm^{-3}$)	ρ_A	1.204E+00	3.748E-02	1.065E-02	3.991E-04	*(Table 14)*
0.01 $mol.kg^{-1}$ Solution Density ($g.dm^{-1}$)	$\rho_{0.01}$	9.980E+02	-4.520E-05	3.000E+00	-1.356E-04	
u (True Mass of the Aliquot) (g)	m_A	**3.737E+01**			**3.033E-03**	

Table 14: Uncertainty in the Air Density *[Equation 13]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / $g.dm^{-3}$
Temperature (°C)	T	1.910E+01	-3.549E-03	3.000E+00	-1.065E-02
Pressure (Pa)	P	1.014E+05	6.680E-07	2.500E+01	1.670E-05
RH (%)	H	5.500E+01	-5.552E-06	3.000E+01	-1.665E-04
u (Air Density) ($g.dm^{-3}$)	ρ_A	1.204E+00			**1.065E-02**

Table 15: Uncertainty in the Water Density *[Equation 12]*

Quantity	Symbol	Estimate xi	Sensitivity Coefficient dy/dxi	u(xi)	Contribution to Standard Uncertainty u(yi) / $g.dm^{-3}$
Temperature (°C)	t	1.910E+01	-1.970E-01	3.000E+00	-5.909E-01
po ($g.dm^{-3}$)		1.000E+03	-	-	
to (°C)		3.982E+00	-	-	
A ($°C^{-1}$)		7.013E-08	-	-	
B ($°C^{-2}$)		7.927E-06	-	-	
C ($°C^{-3}$)		-7.576E-08	-	-	
D ($°C^{-4}$)		7.315E-10	-	-	
E ($°C^{-5}$)		-3.596E-12	-	-	
u (Water Density) ($g.dm^{-3}$)	ρ_W	**9.984E+02**			**5.909E-01**

6.1.4 General considerations

For Type A components, the experimentally determined values are presented. In the case of type B uncertainty components, a description and justification of the values used is given.

- **Air Density**

A room temperature of (20±3) °C was used as frequent temperature measurements stayed inside this range. Uncertainties of 25 Pa and 30% were approximated and assigned to atmospheric pressure and room humidity respectively.

- **Water Density**

The temperature uncertainty in the air density calculation was adopted for the water temperature variability. Water was allowed to equilibrate to room temperature.

- **Gravimetric Solution Preparations**

A type A uncertainty was determined for the balance (Mettler Toledo PR2003 Delta Range). Table 2 shows results of the repeated weighing of 2 items of glassware.

Experiment No.	Mass of flask (g)	Mass of flask (g)
1	731.22	4.908
2	731.23	4.912
3	731.23	4.909
4	731.23	4.908
5	731.23	4.908
6	731.22	4.907
7	731.23	4.908
8	731.23	4.908
9	731.23	4.904
10	731.23	4.907
σ	0.004216	0.002044

Table 2 Determination of the Gravimetric Uncertainty

It was assumed from Table 2 that the uncertainty of weighing in the 2 d.p. accuracy range of the balance was ± 0.01g whilst the uncertainty in the 3 d.p. range was ± 0.003 g.

Amount of Starting Material Titrated

The measurement equation involved various masses and the purity of the starting material.

The purities for the three compounds used in making up the solutions used during titration were all included in the respective uncertainty budgets. For the KHP and the $AgNO_3$ the purities are very close to 100%. However for the Tris method, purity is an important factor in the uncertainty as the stated minimum purity for $NH_2(CH_2OH)_3$ is 99.9%. The purity factor has been incorporated into the uncertainty budget by assuming a triangular distribution of the value stated on the products. A purity of 99.9% was taken

for $NH_2(CH_2OH)_3$ as this value is the mean of the minimum and maximum compound assays. The values for purity are tabulated below in Table 3:

Compound	Stated Minimum Purity / %	Mean Purity / %	Purity Uncertainty u(purity) / %
$COOHC_6H_4COOK$	99.99	99.996	2×10^{-3}
$NH_2(CH_2OH)_3$	99.880	99.901	0.021
$AgNO_3$	99.9999	99.99995	2×10^{-5}

Table 3 Compound Purity Data

6.2 Optimisation and Uncertainty of the Titration Endpoint

Two methods are offered by the TiNet 2.3 (Mettler Toledo) programme that supports the titration instrument: Monotonic Equivalence-point Titration (MET) and Dynamic Equivalence-point Titration (DET). With the former type of titration the titrant is added in constant volume increments. The latter method allows the titrant to be added in varying increments. Along the flat part of the titration curve, the increments are large, whereas in the steep part, near the equivalence point, small increments are added. The software determines the titration endpoint as the point of inflection of the curve. There are various parameters that can be changed within the program which alter the way in which the titration is operated. A brief description of each is given below:

Volume Step - This determines the size of the volume increment added to the vessel each time for the MET mode. Increments that are too small can cause incorrect endpoints. An addition range of 0.05 cm^3 - 0.10 cm^3 has been used in the titration methods.

Titration Rate - This controls the dispensing rate for the volume increments. The available range is between 0.01-150 $cm^3.min^{-1}$ with a default value of 10 $cm^3.min^{-1}$.

Signal drift - A drift threshold is specified in $mV.min^{-1}$. When the measured potential difference drifts less than the set threshold rate, the data is transferred and the titrator continues with the next volume increment.

- *Equilibration time* - This is an alternative to using the signal drift parameter for determining when the next volume increment is added. A measured value can only be transferred when the equilibration time has elapsed. If both the signal drift and the equilibration time have been set, the value will be transferred when one of the two parameters has been satisfied. Throughout this work, the signal drift parameter has been used to determine the titration potential.

- *Measuring point density* - This is a factor that is set in the DET mode that corresponds to the duration of the titration. The value can be set between 0 and 9

inclusive, where 0 indicates small volume increments and a relatively slow titration. A value of 4 is suitable to achieve good precision.

Minimum increment - Determines the smallest volume increment for the entire titration in the DET mode. This smallest increment is dispensed at the start of the titration and, with steep curves, in the region of the endpoint.

Endpoint Criteria - This setting determines the change in potential required for an endpoint to be determined. A low EPC value, with zero being the lowest, corresponds to a lower potential change required for an endpoint to be recognised.

Studies to optimise the titration procedure have been performed. This was achieved by investigating the variables within the TiNet software and selecting the parameters that provided the optimum operation with the smallest variability of the measurement result.

Volume Step	0.05 cm^3	**Drift Speed**	30 $mV.min^{-1}$
Titration Rate	10 $cm^3.min^{-1}$	**Equilibrium Speed**	34 s
EPC	20 mV	**Method**	MET
Volume	20 cm^3 of each Reagent	**Pipette Tip**	Needle
Minimum Increment	0.01 cm^3	**Meas. Point Density**	4

Table 4 Preset Parameters for Metrohm TiNet 2.3

The MET method was used in most of the titrations and the other parameter default values listed in Table 4 (above) were adopted. In the following measurements a nominally 0.01 $mol.kg^{-1}$ HCl solution is titrated against a nominally 0.01 $mol.kg^{-1}$ Tris(hydroxymethyl) methylamine solution.

In order to simplify the assessment of uncertainty, the ratio (R_t) of the mass of Tris buffer in the titration vessel to the indicated volume of HCl dispensed to reach the endpoint is quoted. This calculated ratio is adequate to monitor and optimise the titration process.

$$Ratio(R_t) = \frac{Mass \cdot of \cdot TrisBuffer \cdot [kg]}{Indicated \cdot Volume \cdot of \cdot HCl \cdot Dispensed \cdot [dm^3]} \qquad (18)$$

Dispensing Tip effects

The effect of two different titration tips, a needle tip and a spraying tip, on the repeatability of the value of the titration ratio (R_t) was determined. The results are shown in Table 5:

Test No.	R_t / kg dm^{-3} Using Needle Tip	R_t / kg dm^{-3} Using Spraying Tip
1	1.044	1.040
2	1.045	1.038
3	1.044	1.034
4	1.037	1.040
5	1.041	1.043
6	1.041	1.039
mean	1.042	1.039
σ	0.003	0.003
σ/mean	0.00285	0.00286

Table 5 Dispensing Tip Effects

The results in Table 5 show that the choice of titration tip has little effect on the titration results. This is consistent with the fact that the solution is being stirred and therefore the variation in distribution from the tip will not be significant. Secondly, no significant evaporation from either tip occurs as they were both under the surface of the solution (see experimental). The spraying tip was used in all further titrations.

Optimisation of Volume Step for Titration

An investigation of the effect of the volume step parameter on end point variability was performed. R_t values have been determined for a titration of 10 cm^3 of a nominally 0.01 $mol.kg^{-1}$ HCl solution against nominally the same content of Tris solution. The results are shown in Table 6.

Test No.	R_t / kg dm^{-3} (0.05 cm^3 Volume Step)	R_t / kg dm^{-3} (0.07 cm^3 Volume Step)
1	1.004	1.040
2	1.002	1.038
3	1.014	1.034
4	1.012	1.040
5	1.011	1.043
6	1.010	1.039
mean	1.009	1.039
σ	0.005	0.003
σ/mean	0.00471	0.00286

Table 6 Effect of Volume Step

A volume step of 0.07 cm^3 provides the optimum precision for the endpoint determination for this titration system.

Optimisation of Drift Speed and Equilibration Time

The optimum values for the equilibrium time and drift speed parameters were investigated. A set of data was kept at the preset values for comparison. The equilibration time option was switched off and 3 sets of results were taken for varying drift speeds. As a final test, the drift speed was switched off and the equilibration time set to 10 seconds. Table 7 shows the data obtained. A 10 cm^3 aliquot of a nominally 0.01 mol kg^{-1} HCl solution has been titrated.

Test	R_t / kg dm^{-3} (15mV/min Drift speed)	R_t / kg dm^{-3} (30 mV/min Drift Speed)	R_t / kg dm^{-3} (45mV/min Drift speed)	R_t / kg dm^{-3} (10 seconds Equilibration time)
1	0.9790	0.9779	0.9784	0.9786
2	0.9788	0.9770	0.9782	0.9786
3	0.9786	0.9776	0.9766	0.9778
4	0.9781	0.9781	0.9777	0.9785
5	0.9785	0.9778	0.9774	0.9777
6	0.9778	0.9778	0.9793	0.9767
mean	0.9779	0.9777	0.9785	0.9780
σ	0.0009	0.0004	0.0004	0.0007
σ/mean	0.000945	0.000388	0.000456	0.000763

Table 7 Effect of Drift Speed and Equilibration Time

The results indicate that the drift speed that minimises the relative standard deviation is 30 mV/min. The uncertainty was not reduced for longer equilibration intervals.

Optimisation of Titration Rate

The effect of titration rate on end point repeatability has been tested and results are shown in Table 8.

Test	R_t / kg dm^{-3} (5 cm^3/min Titration rate)	R_t / kg dm^{-3} (10 cm^3/min Titration rate)	R_t / kg dm^{-3} (15 cm^3/min Titration rate)
1	0.9688	0.9779	0.9690
2	0.9677	0.9770	0.9688
3	0.9691	0.9776	0.9685
4	0.9679	0.9781	0.9664
5	0.9683	0.9778	0.9684
6	0.9674	0.9778	0.9672
mean	0.9682	0.9777	0.9681
σ	0.0007	0.0004	0.0010
σ/mean	0.000679	0.000388	0.001057

Table 8 Investigating the Effect of the Titration Rate

The fastest titration rate of 15cm^3.min^{-1} produced results with the largest deviation in endpoint. The results also indicate that at very slow titration rates the variation in endpoint is also high. This is explained by back diffusion of the contents of the titration vessel into the dispensing tip. From these results, the optimum titration rate would appear to be in the region of 10 cm^3.min^{-1}.

- **Comparison of MET and DET Titration Methods**

The repeatability of the MET and DET methods were compared. For each method 6 titration experiments were carried out. All parameters were kept at their preset values. The DET parameters required a minimum increment to be entered, for which the preset value of $0.01cm^3$ was chosen. Volumes of $20cm^3$ of the $NH_2C(CH_2OH)_3$ solution were titrated against $20cm^3$ of HCl solution. The results are shown below in Table 9:

Test No.	R_t / kg dm^{-3} (DET)	R_t / kg dm^{-3} (MET)
1	0.9758	0.9779
2	0.9783	0.9770
3	0.9794	0.9776
4	0.9782	0.9781
5	0.9791	0.9778
6	0.9770	0.9778
mean	0.9780	0.9777
σ	0.0014	0.0004
σ/mean	0.001382	0.000388

Table 9 Comparison of MET and DET Methods

The calculated standard deviation shows that MET gives a lower relative standard deviation than the DET. No bias between the two titration methods is observed in this case.

Summary of Optimum Titration Parameters

Table 10 lists all optimum parameters obtained from these experiments. These values were set in TiNet and used throughout all further work. However the volume step parameter was altered for different titration systems.

Volume Step	0.07 cm^3	**Drift Speed**	30 mV/min
Titration Rate	10 cm^3/min	**Equilibrium Speed**	OFF
EPC	20 mV	**Method**	MET
Volume	$20cm^3$ of each reagent	**Pipette Tip**	No Preference

Table 10 Optimum Experimental Parameters

Using these optimised titration conditions, the contributions to the total uncertainty arising from endpoint determination of a nominally 0.01 mol.kg^{-1} HCl solution was estimated to be $\pm 1 \times 10^{-5}$ dm^3 (k=1).

6.3 Calibration of the Dispensing Syringe

The Dosing Test Software Version 1.3 was used to make a volume calibration of the titrator exchange unit. For each test, ten measurements were made of the actual dispensed volume and these results are plotted against the stated volume to be delivered. The actual volume is calculated by weighing (Sartorius LA 230S balance) the dispensed water according to equation 19:

$$v_A = \frac{m_{MEASURED}}{(\rho_{WATER} - \rho_{AIR})} \tag{19}$$

where

ρ_{AIR} = actual dispensed volume [m^3]

$m_{MEASURED}$ = measured mass [kg]

Two exchange units with a burette capacity of 20cm^3 were calibrated with respect to volume delivery. In each case the exchange unit was prepared by cleaning and filling with 4 times distilled water. A 100cm^3 volumetric flask was placed on the balance. The vessel had a small opening to minimise evaporation of the water. The titration tip was attached so that it was just inside the top of the flask, but not touching it, and on the same plane as the surface of the water level in the exchange unit. Before the start of the calibration procedure, the titration tip was purged with water and a drop was left hanging on the end of the tip. The programme was initiated and the 10 values of the nominal volume and mass of water dispensed were recorded, and the actual volume dispensed calculated. The ratio of these two values defines the calibration slope (S, equation 13) of the exchange unit. The experiment was run over three days to test the reproducibility and eight experiments were run per day to test the repeatability.

Table 11 shows the volume calibration slopes (S) taken from each test that involves ten readings. The value of (S) provides a ratio that can be multiplied by the stated volume to give the actual volume delivered.

	Calibration Slope (S)			
	Unit 1			Unit 2
	Day 1	Day 2	Day 3	Day 1
Test 1	0.9996	0.9996	0.9997	1.0003
Test 2	0.9999	0.9997	0.9998	1.0005
Test 3	0.9998	0.9997	0.9999	1.0007
Test 4	0.9997	0.9999	0.9996	1.0005
Test 5	0.9994	0.9995	0.9995	1.0005
Test 6	-	0.9998	0.9999	1.0008
Test 7	-	0.9997	0.9999	1.0006
Test 8	-	0.9997	0.9997	1.0006
Mean	0.99968	0.9997	0.99975	1.0005625

Table 11 Calibration Gradients for Exchange Units 1 and 2

The calibration slopes for exchange units 1 and 2 were 0.9999 ± 0.0001 (k=1) and 1.0005 ± 0.0001 (k=1) respectively. The values differ due to non-uniformity of the titration syringe cylinders. The Unit 2 calibration turns out not to be necessary since its effect is cancelled out in the measurement equations for the KOH titration.

6.4 Corrections for air buoyancy in weighing procedure

All mass measurements made are corrected for buoyancy. Values for water and air density were obtained respectively using the following equations:

$$\rho_w = \rho_0 - \rho_0[A(t-t_0) + B(t-t_0)^2 + C(t-t_0)^3 + D(t-t_0)^4 + E(t-t_0)^5] \quad [5]$$

where ρ_w is the water density, t is the water temperature (°C), t_0 is the temperature which water attains maximum density (°C), p_0 is the maximum density of water (g.dm^{-3}) . A, B, C, D and E are coefficients with values 7.0134 x 10^{-8} °C^{-1}, 7.926504 x 10^{-6} °C^{-2}, -7.575677 x 10^{-8} °C^{-3}, 7.314894 x 10^{-10} °C^{-4} and -3.596458 x 10^{-12} °C^{-5} respectively.

$$\rho_{AIR} = \frac{((3.48488 \times P) - ((8.0837) + (0.7374 \times T) + (0.00097525 \times T^3) \times H)}{1000(273.15 + T)} \quad [6]$$

where: ρ_{AIR} is the air density, P is atmospheric pressure (Pa), T is temperature (°C) and H is humidity (%).

Every mass measurement has been corrected for buoyancy and for the calibration of the balance in terms of "conventional mass" using:

$$m = \frac{m'}{(1 + \frac{1.2}{8000} - \frac{\rho_{AIR}}{\rho_M})}$$

where m' (g) is the balance reading, ρ_{AIR} is the air density (g.dm^{-3}), ρ_M (g.dm^{-3}) is the density of the substance of which the mass measurement is being determined and m (g) is the mass, corrected for buoyancy.

6.5 Dilution Effect

The major disadvantage of titrimetry over coulometry is the problem associated with dilution[‡]. This leads to shallower titration slopes and an equivalence point not coincident with the maximum $\frac{d(pH)}{dV}$ value even for strong acid – strong base titrations. This error increases as the reactants become more dilute, the extent of dilution increases and the reaction becomes weaker. This last effect has the added complication of making the point of maximum gradient harder to determine.

In fact the equivalence point precedes the point of maximum slope in all acid-base titrations. It is stated[7] that the error caused by taking the endpoint of the titration to be the maximum gradient of the titration curve is less than 0.1% providing that,

$$c \geq 100K_s$$

where c is the concentration of the determinand and K_s is the solubility product. For strong acid-strong base titrations the discrepancy should be negligible. However for weak acid-strong base[8], precipitation[9] or chelometric[10] titrations the discrepancy is significant for the levels of precision and accuracy we are currently working to. Meites and Goldman[7] have provided a rigorous mathematical description of a titration involving at least one component considered to be 'weak':

For the titration of V_a^0 cm^3 of a C_a^0 solution of a weak monobasic acid with a C_b solution of a completely dissociated monobasic base, one has:

$$[H^+] = \frac{(1-f)\varsigma C_a^0 - [H^+] + [OH^-]}{f\varsigma C_a^0 + [H^+] - [OH^-]} K_a \qquad (18)$$

where $\varsigma = \frac{V_a^0}{V^0 + V_b} = \frac{C_b}{C_b + fC_a^0}$ and $f = \frac{V_b C_b}{V_a^0 C_a^0}$ so that the equivalence point corresponds to $f = 1$.

Near the point of equivalence for the titration of anything but a very strong acid, the hydrogen ion concentration is negligible in both the numerator and denominator of equation (18). If one ignores $[H^+]$ on the right hand side of equation (18), solving the resulting quadratic and transforming the solution into an equation explicit in $p[H^+]$, and differentiating twice with respect to f, one obtains:

$$\frac{d^2(p[H^+])}{df^2} = 0.434\left\{\frac{1}{D}\left(\frac{d^2D}{df^2}\right) - \frac{1}{D^2}\left(\frac{dD}{}\right)^2 - \frac{1}{\sqrt{G^2+4D}}\left(\frac{d^2G}{df^2}\right)\right.$$

[‡] It is generally accepted that there is no volume change in a coulometric titration with an internally generated reagent. Although not rigorously true this assumption is valid to a first approximation.

$$+\frac{1}{(G^2+4D)^{3/2}}\left(\frac{dG}{df}\right)\left[G\left(\frac{dG}{df}\right)+2\left(\frac{dD}{df}\right)\right]-\frac{2}{\sqrt{G^2+4D}(G+\sqrt{G^2+4D})}\left(\frac{d^2D}{df^2}\right)$$
$$+\frac{4}{(G^2+4D)(G+\sqrt{G^2+4D})^2}\left(\frac{dD}{df}\right)\left[\left(G+\frac{G^2+2D}{\sqrt{G^2+2D}}\right)\left(\frac{dG}{df}\right)+\left(2+\frac{G}{\sqrt{G^2+4D}}\right)\left(\frac{dD}{df}\right)\right]\Bigg\} \quad (19)$$

where $D = f\varsigma K_W K_a$ and $G = K_W + (1-f)\varsigma K_W K_a$.

There are two values of f for which the right hand side of equation (19) vanishes, one corresponds to the point of minimum slope (the point of largest buffer capacity) and the other corresponds to the point of maximum slope, often wrongly assumed to be the equivalence point. The difference between the value of f at the point of maximum slope and the *actual* equivalence point ($f = 1$) represents the error in the potentiometric titration. The error in potentiometric titration is often significant at the levels of accuracy being worked at in this study. Indeed for a strong base-weak acid titration with 0.01M components, the weak acid having $pK_a = 9$, the titration error would be 1%.

Although equation (19) has not been definitively solved for the titrations described in this report, calculations on similar titrations [11] have lead us to estimate that, given the pKa values and the concentrations of the solutions being titrated in this study, the Tris value of the HCl molality will be approximately 0.25% too low whereas the KOH/KHP value will be approximately 0.25% too high.

Dilution effects can be minimised by using a titrant that is much more concentrated than the sample. Titration steepness may be estimated from logarithmic titration diagrams[2]. The steepness is defined as $S_t = \frac{C}{[H^+]_e}$, where $[H^+]_e$ is the value of $[H^+]$ at the equivalent point. In general values of the steepness above 10^3 indicate the possibility of an accurate titration, values between 10^2-10^3 show that a titration of limited accuracy can be attained whilst titrations with values below 10^2 should be avoided.

7. References

[1] K. W. Pratt, Personal Communication.

[2] R. de Levie, Aqueous Acid-Base Equilibria and Titrations, OUP, Oxford, 1999.

[3] K. W. Pratt, CCQM-P19 'Assay of 0.01 mol.kg-1 hydrochloric acid. Report of results and conclusions', November 2000.

[4] B. King, *Metrologia*, 1997, **34**, 77.

[5] J. Patterson and E. Morris, *Metrologia*, 1994, **31**, 277.

[6] ISO/DIS 6142

[7] D. Midgley and K. Torrance, Potentiometric Water Analysis, Wiley, London, 1978.

[8] L. Meites and J. A. Goldman, *Anal. Chimica Acta*, 1963, **29**, 472.

[9] L. Meites and J. A. Goldman, *Anal. Chimica Acta*, 1964, **30**, 18.

[10] L. Meites and T. Meites, *Anal. Chimica Acta*, 1967, **37**, 1

[11] L. M. Aleixo, O. E. S. Godinho and W. F. daCoasta, *Microchemical Journal*, 1987, **35**, 153.