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Improved Methodology for High Accuracy Titration of HCl and Experimental Demonstration of Equivalence with Coulometry

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Improved Methodology for High Accuracy Titrimetry with Application to HCl – Equivalency with Coulometry

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Executive Summary

Potentiometric titration methods have been developed for HCl using tris (hydroxymethyl) methylamine (Tris) and silver nitrate. The Tris titration method includes the use of both 0.01 $mol.kg^{-1}$ and 0.1 $mol.kg^{-1}$ Tris and a 'reverse' titration using 0.01 $mol.kg^{-1}$ Tris. The uncertainty of these methods is estimated to be approximately 0.2 % (relative to value) (k=2). The methods have been used for the accurate determination of the amount of substance content of HCl in solution as part of the international study CCQM-P19.1.

This report also reviews the limitation imposed on potentiometric titration method by the "dilution effect" and provides both experimentally and mathematically determined corrections for the effect. When the correction is applied the results of potentiometric and coulometric titrations are comparable within their stated uncertainties. Best practice guidelines for the use of potentiometric titration in analytical chemistry are also detailed.

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High Accuracy Titrimetry with Application to HCl

by Richard Brown, Martin Milton and Paul Brewer

1. Introduction

This report was prepared as part of the Valid Analytical Measurement programme and reports the results obtained by NPL in the comparison study CCQM-P19.1 of HCl amount of substance content.

CCQM-P19.1 is the successor to the comparison study CCQM-P19, also on the determination of the amount of substance content of nominally 0.01 M HCl (NPL Report COAM 5). The comparison had been repeated owing to problems with impurity levels in the samples used in the initial 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 two independent titration methods. One of the methods can be implemented according to three different sub-procedures.

Numerically and experimentally evaluated corrections have been made to the experimentally determined values to account for the bias resulting from the dilution effect caused by the discrepancy between the inflection point of the titration curve and the actual end-point of the titration. In this way comparability of coulometry and potentiometric titration has been demonstrated.

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. Amount of substance content is defined as the amount ('number of moles') of solute per kilogram of solution.

2. Methodology

2.1 Titration Methods

The two titration methods for HCl content determination (b_{HCl}) described in this 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:

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

(↔ represents an equilibrium) and then subsequently

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

The 'reverse' Tris titration relies on exactly the same chemical equilibria with the only physical difference being that the Tris is titrated *into* the HCl and hence the shape of the titration curve is inverted.

Method 1 depends on a potentiometric determination of the endpoint using a glass electrode:

$$E = E^0 + \frac{RT}{F} \ln a_{H^+} \qquad \text{[For the Glass Electrode]} \qquad (2)$$

Method 2: Determination of HCl content ($b_{HCl,2}$) by titration against $AgNO_3$.

The titration results in a white precipitate of AgCl:

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)} \qquad (3)$$

This method differs from the Tris method as a glass electrode with a silver element is used to determine the titration endpoint in place of the simple glass electrode used in Methods 1 and 2. Hence the endpoint of the titration is determined by:

$$E = E^0 - \frac{RT}{F} \ln a_{Cl^-} \qquad \text{[For the Silver Electrode]} \qquad (4)$$

The relationship between the two titration methods is shown in Figure 1. Method 1 is based on titration with respect to hydrogen ions. The two-way arrows indicate the forward (1a) and reverse (1b) titration procedures that have been employed. Method 2 is based on chloride ion titration.

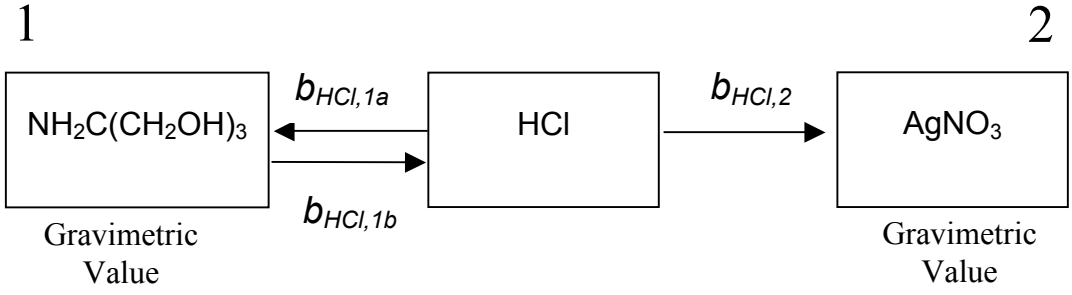

Figure 1 The proposed titration regimes to determine the HCl molality.

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 taken to be the point of

equivalence. The validity of this assumption and systematic biases resulting from it are discussed in greater detail below.

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:

$$f_1 = \frac{m_F}{m_{SM} + m_{W1}} \tag{5}$$

For situations where 0.1 M Tris was used for titration, the dilution factor f_1 is simply equal to unity with zero uncertainty. When the aliquot m_F is added to a mass of water m_{W2}, the molality of the resulting solution is given by:

$$b = \frac{m_{SM} \times p \times f_1}{M_{SM} \times 100 \times (m_{W2} + f_1 \times m_{W1})} \tag{6}$$

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:

$$f_2 = \frac{m_A}{m_{W2} + f_1 \times m_{W1} + f_1 \times m_{SM}} \tag{6c}$$

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

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

2.3 Measurement Equations

In Methods 1 and 2 (for the titration of the acid in the LDPE bottle), HCl is used as the titrant. The mass of HCl titrated to the endpoint is given by:

$$m_{EP} = m_{HCL} + v_{HCL} \times S \times \rho_{HCL} \tag{8}$$

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 (determined by weighing the metered fluid output of the dispensing syringe) and ρ_{HCl} (g.dm^{-3}) is the density of HCl. The HCl molality is then calculated from:

$$b_{HCl} = \frac{n}{m_{EP} - n \times M_{HCl}} \tag{9}$$

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

For the titration of HCl from the ampoules a reverse form of Method 2 was used where Tris was used as the titrant. In this case the mass of Tris titrated to the endpoint is determined from:

$$m_{EP} = m_{Tris} + v_{Tris} \times S \times \rho_{Tris} \tag{10}$$

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

$$b_{HCl} = \frac{b_{Tris} \times m_{EP}}{m_{HCl} - n_{HCl} \times M_{HCl}} \tag{11}$$

where b_{Tris} is the molality of the Tris solution, m_{HCl} (g) is the mass of HCl and M_{HCl} is the relative molecular mass of the HCl.

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

2.4 Methodological Improvements

The ‘dilution effect’ (see section 6.2) causes inaccuracies in potentiometric titrations because the point of inflection of the titration curve (taken as the end-point of the reaction) and the point of equivalence (the true end-point of the reaction) are not coincident. The discrepancy increases as the titration solutions become weaker and more dilute. To improve the accuracy of potentiometric titrations, especially for the determination of the nominally 0.01 M HCl in this study, the dilution effect must be fully understood and a bias correction applied.

2.4.1 An experimentally determined correction for the dilution effect

It is accepted that for the titration of 0.1 M HCl with 0.1 M Tris, the discrepancy between points of inflection and equivalence is taken to be negligible with respect to the magnitude of the measurement uncertainty of potentiometric titration. The actual discrepancy is expected to be less than 0.01%. The discrepancy between the inflection point and the equivalence point for the titration of 0.01 M HCl with 0.01 M Tris has not been determined in the literature but is known to be negative and thought to represent a significant bias with respect to the size of the measurement uncertainty of potentiometric titration. Additionally the literature fails to document whether increasing the concentration of just one of the components of titration causes a diminution of the dilution effect. Efforts have been made to resolve these issues experimentally.

A nominally 0.1 M HCl solution was made up and titrated against a 0.1 M Tris solution. The amount of substance content of the HCl was determined. A portion of the HCl was then diluted gravimetrically to produce a nominally 0.01 M HCl solution, whose amount of substance content was known within the measurement uncertainty of the 0.1 M HCl against 0.1 M Tris titration and of the gravimetric dilution procedure. The 0.01 M HCl was then titrated against 0.01 M Tris and subsequently against 0.1 M Tris and amount of substance contents calculated for the nominally 0.01 M HCl. The results are presented below in Figure 2.

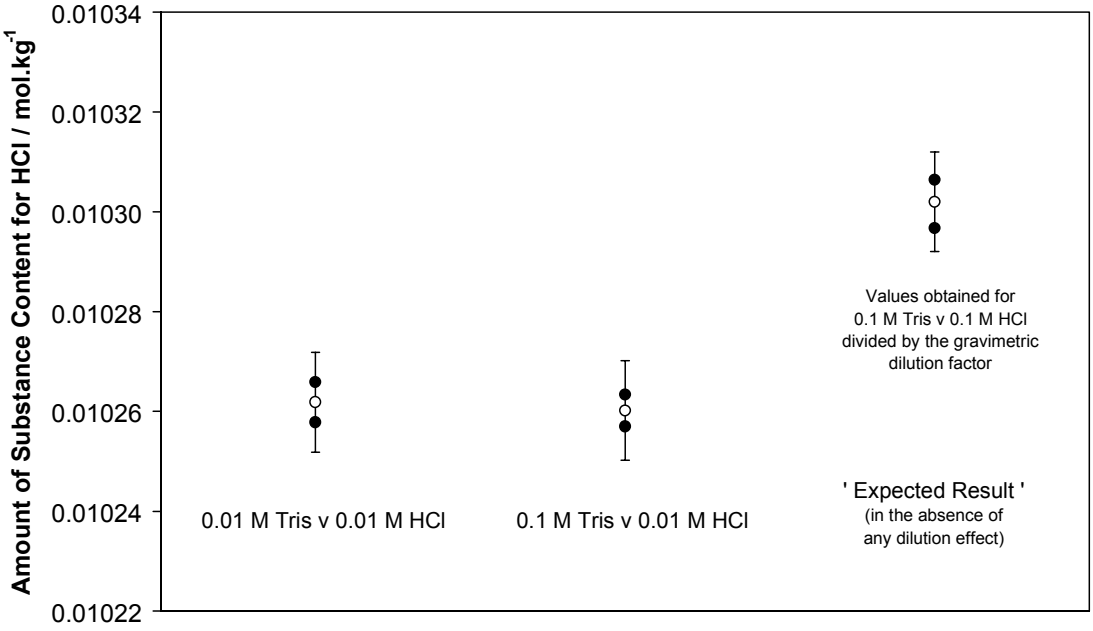

Figure 2 Comparison of amount of substance contents for test solutions of HCl, obtained using the Tris titration methodology involving different HCl and Tris concentrations. The results for 0.1 M HCl have been divided by the gravimetric dilution factor to provide an 'expected result' for the nominally 0.01 M HCl in the absence of the dilution effect. The mean of the results (○) for each method 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).

The results for the 0.01 M HCl are lower than the amount of substance content for the 0.1 M HCl solution divided by the subsequent dilution factor. Since it is assumed that the 0.1 M HCl against 0.1 M Tris titration exhibits a negligible dilution effect at the overall level of measurement uncertainty, the discrepancy between the two amount of substance contents on the left of Figure 2 and the value on the right of Figure 2 represents an experimentally determined value for the dilution effect for potentiometric titration of 0.01 M HCl. **The mean discrepancy for the 0.01 M and 0.1 M Tris sub-methods are –0.39% and –0.40% respectively.** This correction has been retrospectively applied to results obtained by the standard Tris method for the CCQM-P19.1 samples.

2.4.2 A mathematically determined correction for the dilution effect†

The second order differential equations detailed in Meites's publication[1] and reproduced in Section 6.2 have been solved numerically for a variety of initial conditions[2]. The differential equation describes the titration of a weak monobasic acid (with a dissociation constant K_a and an initial concentration of C_a^0) against a completely dissociated monobasic base (with concentration C_b) but the results obtained from the numerical solutions are generally applicable to all potentiometric titrations. The relationship between the negative percentage error caused by dilution, and the dissociation constant K_a, for four different concentrations of the acid and base solutions, are shown in Figure 3.

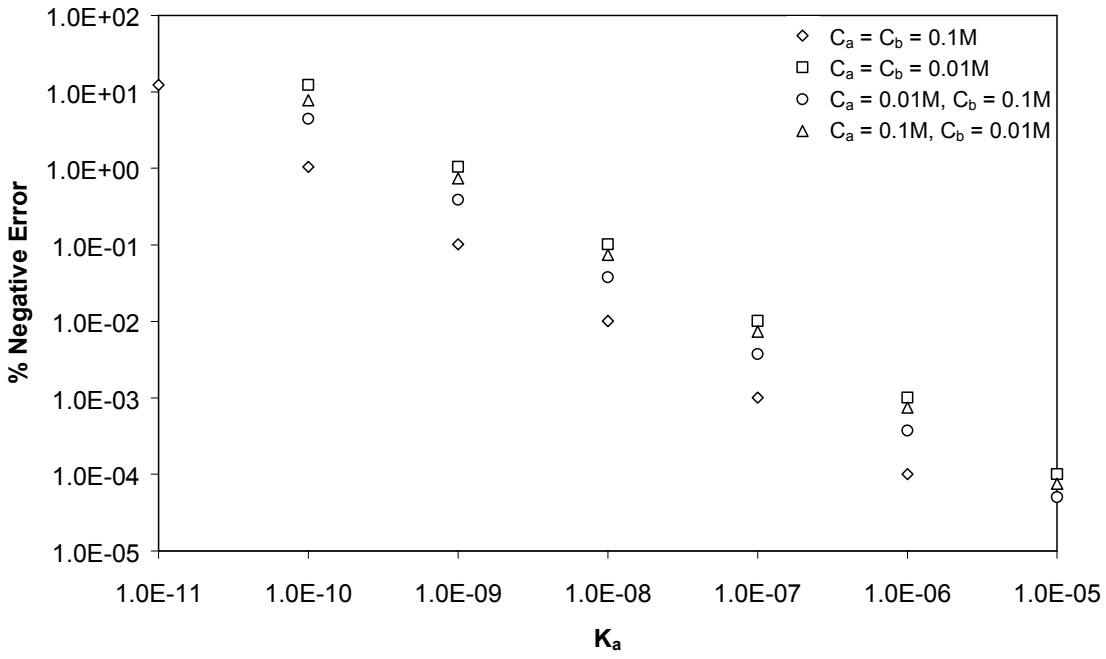

Figure 3 The negative percentage error caused by dilution, against the dissociation constant K_a, for four different concentrations of a weak acid (C_a) and a strong base (C_b) undergoing potentiometric titration.

† Grateful thanks are proffered to Louise Wright (CMSC, NPL) for performing all the numerical calculations on the titration equations.

Clearly the negative discrepancy caused by the dilution effect is increasing as the value of K_a increases, i.e. as the acid becomes weaker. The negative discrepancy in the potentiometric titration is also seen to increase as the components of titration become more dilute. The difference between the percentage error for the situation where both components are of 0.1 M concentration and the situation where both components are of 0.01 M concentration is an order of magnitude over all values of K_a. This is clearly a significant difference. Additionally the percentage error for any given acid/base concentration increases by an order on magnitude for every order of magnitude decrease in K_a. Significantly this shows that the KOH/KHP (pK_a = 10.36) titration, which was used as the first part of one of the methods employed for the previous CCQM-P19 comparison, has a large error at the 0.01 M concentration level. This corresponds with the biases exposed in the CCQM-P19 results. **At the value of K_a corresponding to a strong acid / weak base type titration as used in the Tris methodology we observe an error of approximately 0.5% which is in good agreement with the experimental determination.** It is also important to note that the largest discrepancies occur when the strong component of the titration is at low concentration. This relationship is displayed graphically in Figure 4.

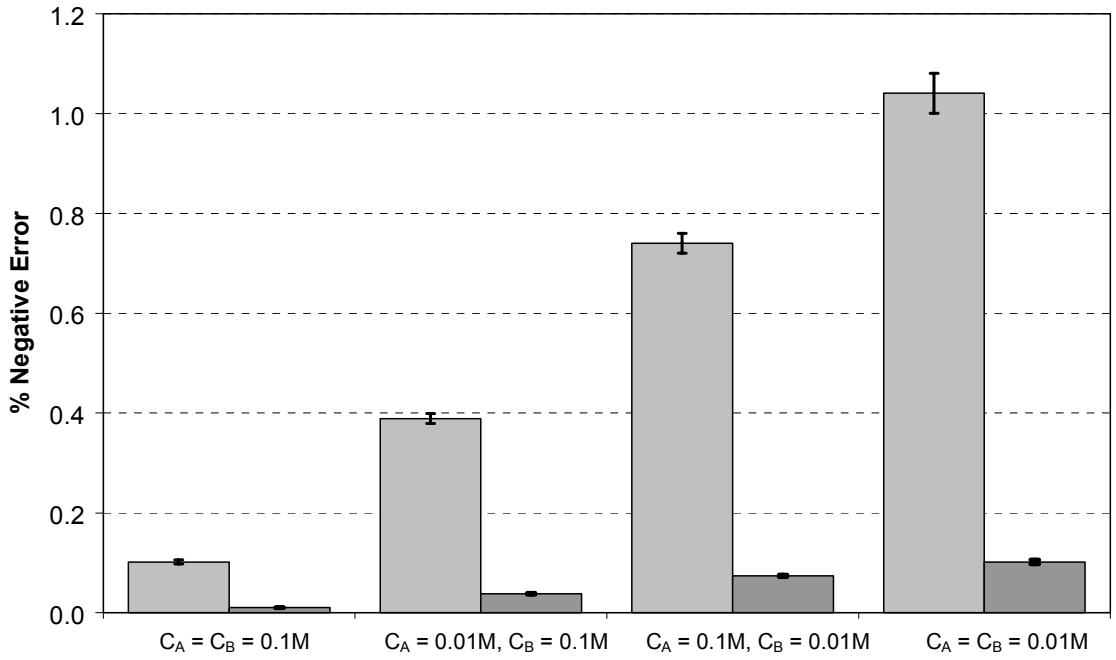

Figure 4 The negative % error caused by dilution against the acid/base solution concentration for a weak acid (A, $K_a = 1x10^{-9}$ [left-hand bars] and $1x10^{-8}$ [right-hand bars]) / strong base (B) titration. The error bars represent the uncertainty in the numerical result when experimental uncertainties (0.1% for C_A, C_B and K_a) are included in the initial input parameters.

In terms of the titrations used in this study, for the CCQM-P19.1 comparison, Figure 4 shows that since the acid to be titrated is nominally 0.01 M, there is little advantage from increasing the concentration of the titre, here the Tris or silver nitrate. Figure 4 shows that the decrease in the % error on moving from 0.01 M titre to 0.1 M titre is only

0.2% (absolute, for $K_a = 10^{-8}$). The experimental determination found no improvement at all on moving from 0.01 M to 0.1 M Tris. However if 0.1 M acid were to be used with 0.01 M and 0.1 M Tris the decrease in the observed error would be 0.6% and 0.9% respectively. The uncertainties in the mathematically determined dilution effect correction, shown as error bars on the bar graphs in Figure 4, have been calculated by using input parameters with suitable mathematical distributions to represent the experimental uncertainty in the concentration of both the acid and base components and the dissociation constant. These uncertainties are of the same order of magnitude as the uncertainty in the experimentally determined dilution effect correction.

2.4.3 Experimental Improvements and modifications

Additionally, some improvements have been made to the experimental procedure used in CCQM-P19 [3].

2.4.3.1 Reference material preparation

Before use, the $AgNO_3$ (Aldrich) and the Tris CRM (NIST), spent 120 hours in a vacuum desiccator rather than the 24 hours (for Tris) and 2 hours (for silver nitrate) previously used for CCQM-P19. It is known that Tris can accumulate occluded mother liquor and a prolonged period of drying is more effective in removing this water. Longer drying periods for the silver nitrate must also be beneficial.

2.4.3.2 Improvements in titration procedure

Several improvements were made to the titration procedure.

The beaker previously used as a titration vessel was replaced with a smaller volume narrow-necked conical flask with just enough room to insert the measuring electrode and the dispensing tip. This minimises evaporation during the pre-titration solution weighing steps of the procedure. The shape of the conical flask also allowed the contents to be stirred more efficiently and more completely during titration.

Additionally, evaporation of HCl is known to be a particular problem during weighing. To minimise this, the order of solution weighing before titration has been altered. Under the new procedure Tris buffer is pipetted into the titration vessel and weighed and subsequently HCl is dosed out from the titrator unit into the titration vessel and the vessel weighed again. The weighing of solutions in this order means that the dosed out HCl is already totally neutralised before weighing and the chances of evaporation are minimised.

The standard Tris titration method has been expanded to also use 0.1 M Tris as well as 0.01 M Tris. This allows easier solution handling during the titration owing to the decreased volumes and a slightly lower overall measurement uncertainty, compared to the 0.01 M Tris method, because of a lower uncertainty in the concentration of the Tris solution (although the relative uncertainty in the amount of Tris weighed out is slightly increased).

In order to deal with the low volume (approximately 35 ml) quartz ampoules supplied for the intercomparison a new Tris methodology has also been introduced, referred to as the 'reverse' Tris titration. This involves the HCl being transferred directly into the titration vessel and the Tris being dosed out from the titration unit, the reverse procedure to a standard Tris titration. In order to extract the HCl from the ampoule and place it in the titration vessel with a minimum of evaporation and with no splashing a proboscis device was employed. The proboscis device and an opened ampoule are shown in Figure 3.

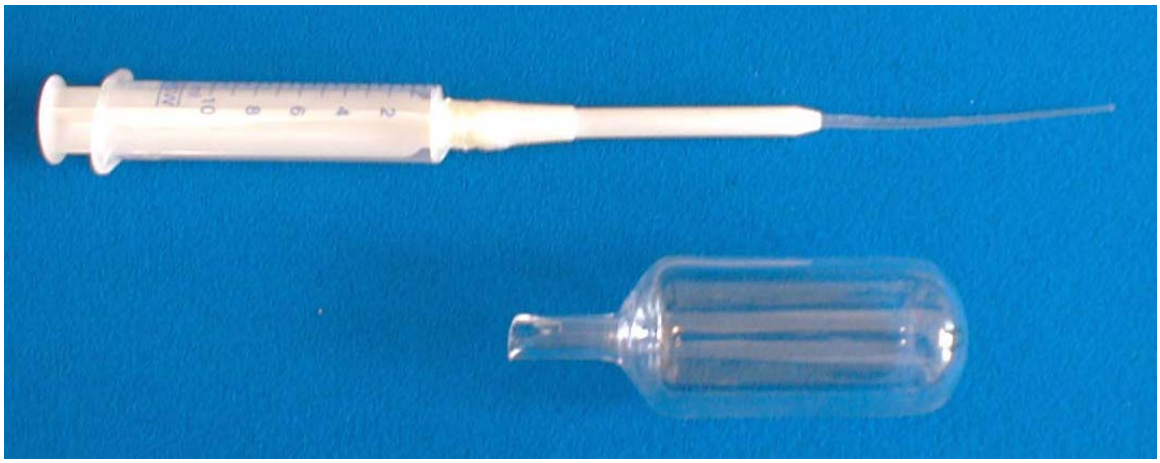

Figure 3 The proboscis device (top) used to transferring acid from a quartz ampoule (below) during a reverse Tris titration.

The proboscis device is based on a 10 ml syringe and a dispensing tip from the titration system.

3. Results and Discussion

3.1 Results

The various titration methods detailed above were used to determine the amount of substance content of unknown samples of HCl as part of the pilot study CCQM-P19.1. The Pilot Laboratory (NIST) supplied each participant with two quartz ampoules, each containing 42 ± 2g of the HCl solution and one low-density polyethylene (LDPE) bottle containing 496 ± 3 g of the HCl solution with a nominal amount of substance content of 0.01 mol.kg^{-1}. NIST stated that amount of substance content of the ampoules was expected to be nearer to the amount content of the original batch of HCl solution as the bottle was expected to transpire HCl and/or water over a period of time, whereas the ampoules were expected not to transpire fluid and not contaminate the HCl (as had previously been the problem with the glass vessels in CCQM-P19). The volume of sample in the bottle allowed seven titrations to be conducted, whilst the low volume contained within each ampoule meant that only one titration was carried out on each ampoule using the 'reverse' Tris method. The experimental procedures used at NPL are described in full in Appendix 1. The results are displayed in Table 1.

	HCl Amount of Substance Content / mol.kg^{-1}				
Method (Sample)	***Titration 1***	***Titration 2***	***Titration 3***	***Mean***	***Uncertainty (k=2)***
Tris [0.01 M] (*Bottle*)	0.010003	0.010016	0.009999	**0.010009**	0.000022
Tris [0.1 M] (*Bottle*)	0.010017	0.010012	-		
$AgNO_3$ (*Bottle*)	0.010002	0.010005	-	**0.010004**	0.000022
Reverse Tris (*Ampoules*)	0.010004	0.010009	-	**0.010006**	0.000022

Table 1 HCl amount of substance contents obtained by each of the titration regimes for both the bottle and ampoules supplied by the pilot laboratory for CCQM-P19.1.

The results in Table 1 are displayed graphically in Figure 4.

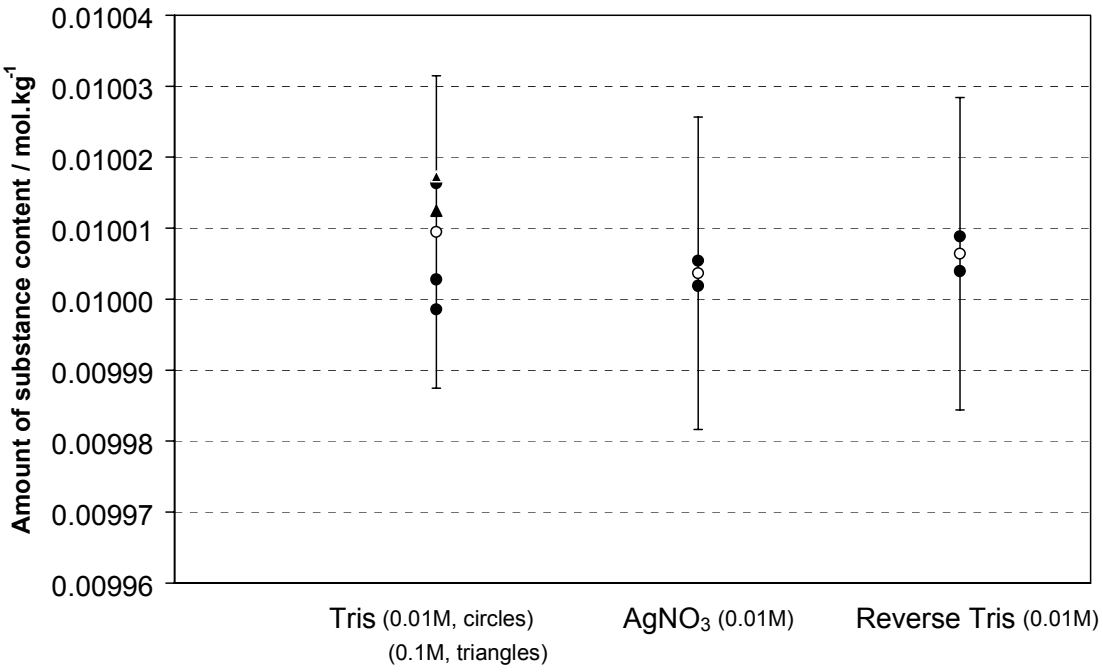

Figure 4. Comparison of amount of substance contents obtained using the different methodologies for HCl amount of substance content determination in the LDPE bottle (Tris and $AgNO_3$) and the ampoules (reverse Tris) supplied for CCQM-P19.1. The mean of the results (○) for each method and the actual experimental determinations (● and ▲) are shown. The bars indicate the estimated uncertainty of the mean values representing a 95% confidence interval (with k=2).

The NPL results in Figure 4 are also displayed in Figures 5a and 5b as part of the combined CCQM-P19.1 results including the amount of substance content results for other participating NMIs.

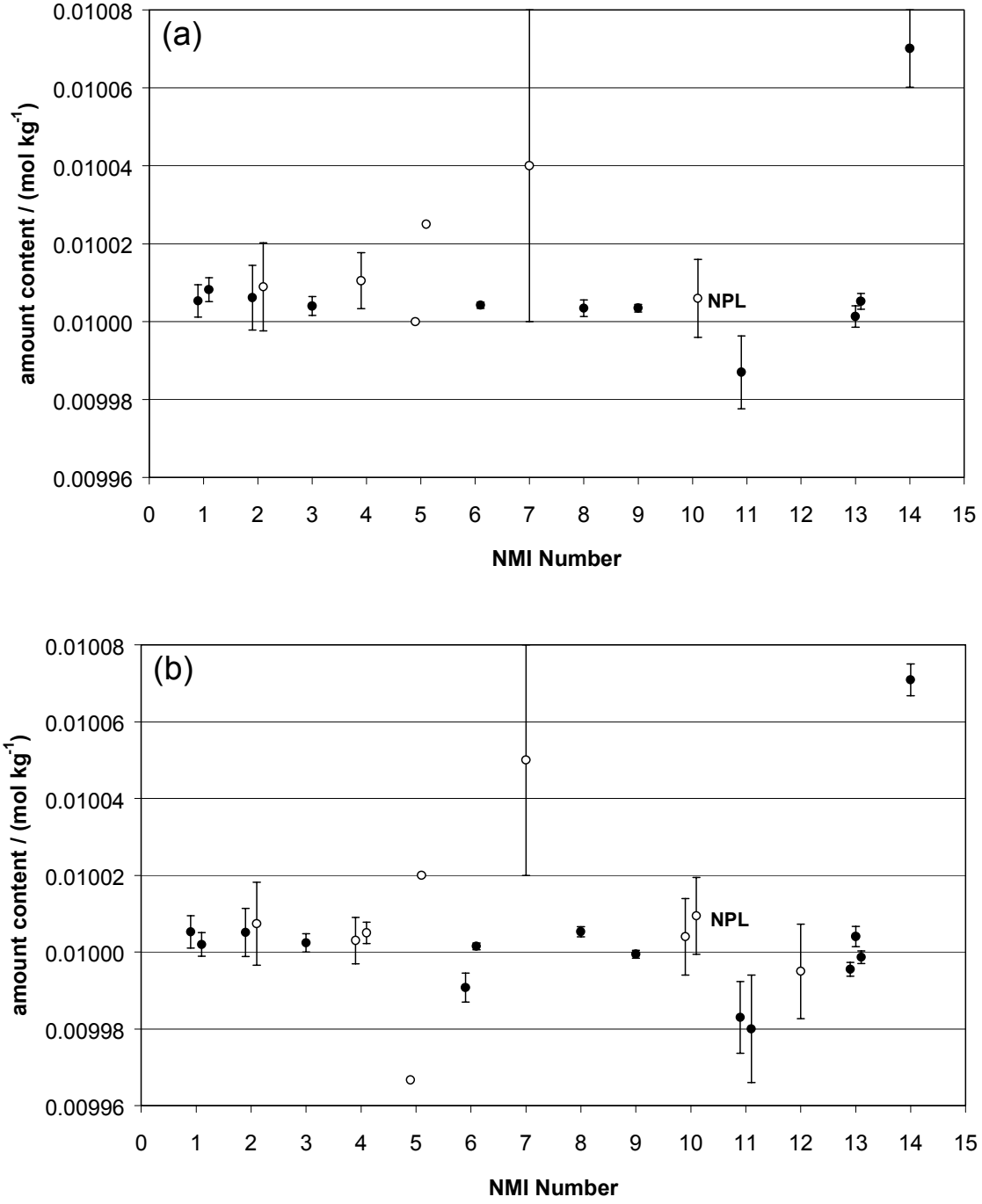

Figure 5. CCQM P19.1 ampoules (a) and bottle (b) results for the HCl amount of substance content determination. NPL is NMI number 10. The determinations made using coulometry (●) and titrimetry (○) are indicated. The bars indicate the estimated uncertainty of the mean values representing a 95% confidence interval (with k=2).

As a comparison the results of the previous CCQM-P19 intercomparsion are shown in Figure 6.

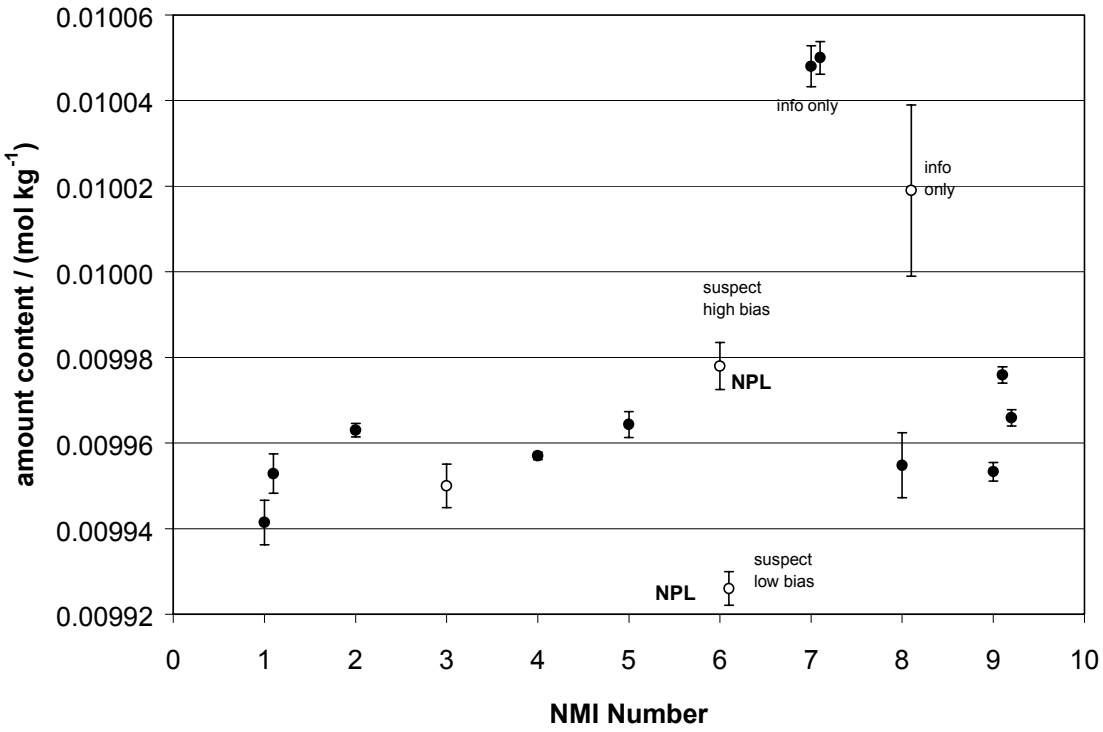

Figure 6. CCQM P19 ampoule results for the amount of substance content of HCl determination. NPL is NMI number 6. The determinations made using coulometry (●) and titrimetry (○) are indicated. The bars indicate the estimated uncertainty of the mean values representing a 95% confidence interval (with k=2).

Comparison of Figures 5 and 6 show a marked improvement in NPL's amount of substance content results between CCQM-P19 and CCQM-P19.1. All of NPL's results are now comparable with the pilot laboratory's stated amount of substance content values in Figure 5 (ampoules : 0.0100035 ± 0.0000003 mol.kg^{-1}, bottle : 0.0099994 ± 0.0000004 mol.kg^{-1}) within the quoted measurement uncertainty. Arguably, NPL is currently the most accurate exponent of potentiometric titration.

The improvement in NPL's results are, in part, due to an improved and more rigorous experimental methodology. However, the primary reason for the improved comparability of NPL with other NMIs, most of whom use coulometry, is due to numerical and experimental based solutions of the dilution effect for potentiometric titration, and the subsequent imposition of a correction on experimental data obtained by potentiometric titration.

NPL has now shown equivalency with coulometry for a dilution effect-corrected potentiometric titration methodology.

4. Conclusions

NPL has participated successfully in CCQM-P19.1, an international comparison of HCl amount of substance content. The results were comparable with the pilot laboratory within the quoted measurement uncertainties.

The pilot laboratory (NIST) provided nominally 0.01 $mol.kg^{-1}$ HCl samples in quartz ampoules and in a low-density polyethylene bottle. HCl amount of substance contents have been determined by potentiometric titration. The dilution effect for potentiometric titration under these experimental conditions has been solved both experimentally and numerically, with both solutions in good agreement. Corrections have been imposed on experimentally determined data for the discrepancy caused by the dilution effect and results for potentiometric titration now show equivalence with NMIs using coulometry.

Two distinct potentiometric titration methodologies were employed to determine HCl amount of substance contents. Chloride determinations were performed using 0.1 $mol.kg^{-1}$ silver nitrate solutions and a glass electrode with a silver element. Hydrogen ion determinations were performed using Tris (hydroxymethyl) methylamine solutions and a glass electrode. Three sub-methodologies were used for the tris-based potentiometric titrations including the use of 0.1 and 0.01 $mol.kg^{-1}$ tris solutions and the additional use of a reverse titration methodology for dealing with the small sample volumes afforded by the samples presented in ampoules. All the titration methodologies employed were comparable within the stated measurement uncertainty.

Comparability of coulometric and potentiometric techniques is of particular significance since potentiometric titration has long been, and continues to be, amongst the most frequently applied quantitative analysis methods. Owing to its low cost and relative ease-of-use, potentiometric titration is far more widely used than its coulometric counterpart, particularly in analytical laboratories, although coulometry is a routinely more accurate technique. Previous lack of comparability at the highest level between coulometry and potentiometric titration is therefore a matter of concern. Reconciliation of the systematic bias which potentiometric titration imposes owing to the dilution effect, in order to allow equivalence to be shown with coulometric techniques, has important implications for the improved comparability of potentiometric titration in general.

A number of additional methodological improvements have been made to the experimental procedure that have also helped improve the quality and comparability of potentiometric titration. Some of these improvements have been included in a ‘best-practice’ section below.

4.1 Best practice suggestions for potentiometric titration

Several improvements were made to the experimental methodology previously used for CCQM-P19 (detailed in NPL Report COAM 5). In addition, some general conclusions may be drawn about the best practice use of potentiometric titration for high accuracy amount of substance content analysis. A number of salient issues are listed below:

- Tris (hydroxymethyl) methylamine and silver nitrate reference materials for use in potentiometric titration should be prepared by storage in a vacuum desiccator for a minimum of 72 hours. (Other reference materials may need other preparation procedures).
- The titration vessel should have as narrow a neck as possible to minimise evaporation during solution handling and titration. It should also be as small as possible consistent with dealing with the solution volumes used. This allows more complete and efficient mixing during titration.
- When possible, the more volatile of the titration solutions (here HCl) should form the titrant and be contained within the titrator/dispensing unit to minimise evaporation. During pre-titration weighing procedures the more volatile solution should be weighed out into the titration vessel second.
- In cases where the more volatile solution is used as the titre (perhaps because of low solution volume) a proboscis-syringe style device can aid efficient transfer of liquid to the titration vessel and help to minimise evaporation / splashing.
- The bias imposed by the dilution effect decreases as the concentration of the titrant/titre increases. This is offset slightly by increased uncertainty of the amount of substance dispensed / weighed out, which may become significant at very high titrant concentrations.
- Experimental and theoretical corrections for the bias imposed on potentiometric titration by the dilution effect are possible for any given set of experimental conditions. Potentiometric titration may then yield results that are equivalent with coulometry.
- As a general principle, the most concentrated and strong solution possible should be used for potentiometric titration, consistent with sample handling or increased uncertainty issues, which may occur at very high concentrations or very low solution volumes.
- The major factor limiting the accuracy of potentiometric titration is the concentration of the stronger titration component.

5. Appendix 1 : Experimental Procedure

5.1 Experimental procedure for HCl titration

- **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^{o}C) and subsequently with a stream of nitrogen.

- **Preparation of the HCl solution**

The HCl solution was used as provided from The Pilot Laboratory (NIST) who supplied each participant with two quartz ampoules, each containing 42 ± 2g of the HCl solution and one low-density polyethylene (LDPE) bottle containing 496 ± 3 g of the HCl solution with a nominal molality of 0.01 mol.kg^{-1}.

- **Preparation and Titration of $NH_2C(CH_2OH)_3$ solution**

Approximately 10 g of $NH_2C(CH_2OH)_3$ (SRM 723c, NIST) was weighed out and desiccated over silica gel (reduced pressure) for 5 days. A 0.1 mol.kg^{-1} and a 0.01 mol.kg^{-1} solution of $NH_2C(CH_2OH)$ was then prepared gravimetrically. This was achieved by first making the 0.1 mol.kg^{-1} solution followed by a further dilution to make the 0.01 mol.kg^{-1} solution.

- **Procedure for the LDPE bottle sample**

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 150cm^3 conical flask and its mass determined. 50cm^3 of the 0.01 mol.kg^{-1} $NH_2C(CH_2OH)_3$ solution, or 5cm^3 of the 0.1 mol.kg^{-1} $NH_2C(CH_2OH)_3$ solution, depending on the sub-procedure being used, was pipetted into the same flask and its mass measured. A stirrer bar was added to the flask. 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 flask 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.

- **Procedure for the ampoules – reverse titration**

40cm^3 of the 0.01 mol.kg^{-1} Tris solution was dosed out from the previously cleaned and fully dried 721 NET Titrino (Mettler Toledo) exchange unit into a clean, dried 150cm^3 conical flask and its mass determined. A quartz ampoule supplied by NIST (see bottom of Figure 3) was then scored around the top and snapped open. The contents of the ampoule were then removed carefully using the proboscis and syringe arrangement (shown at the top of Figure 3) and placed carefully in the conical flask and its mass determined. A stirrer bar was added to the flask. The burette on the exchange unit was filled with the Tris solution and closely inspected for any air bubbles. The electrode and the pipette from the 721 NET Titrino were inserted into the flask 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.

- **Preparation and Titration of $AgNO_3$ solution**

The method for Tris titration is that described above is employed except that a $AgNO_3$ solution is used for titration against the HCl. Approximately 7-8 g of $AgNO_3$ (Aldrich) was desiccated over silica gel (reduced pressure) for 5 days, 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.

- **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. Density values for 0.1 M HCl at various temperatures were obtained from the literature.

6. Appendix 2 : Uncertainty Evaluation

6.1 Uncertainty Budgets

The uncertainty budgets used are almost the same as those developed in NPL Report COAM 5 "High Accuracy Titrimetry with application to HCl", with two exceptions:

- The uncertainty in the measured end-point has been increased from 0.01 ml to 0.035 ml, which represents a more realistic evaluation of the uncertainty of the Metrohm Titrino's determination of the point of inflection, especially for titrations involving weak components and thus shallow titration slopes.

- The correction imposed on the final amount of substance content value by the dilution effect has been included. This correction is added to the final amount of substance content value as a final step. The uncertainty associated with this correction is discussed in detail in the next section and is added in quadrature to the other contributions to the measurement uncertainty of the potentiometric titration.

6.2 Dilution Effect

The major disadvantage of titrimetry over coulometry is the problem of dilution[‡], which leads to shallower titration slopes and an equivalence point not coincident with the maximum value of $\frac{d(pH)}{dV}$. This effect increases as the reactants become more dilute, the extent of dilution increases and the reaction becomes weaker. Additionally, the last of these 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 has been estimated[4] 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,

$$c \geq 100K_s \tag{12}$$

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[5], precipitation[6] or chelometric[7] titrations the discrepancy is significant for the levels of precision and accuracy we are currently working to.

Meites[8] and Goldman[7] have provided a rigorous mathematical description of a titration involving at least one component considered to be 'weak'.

[‡] 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.

For the titration of V_a^0 (cm^3) of a C_a^0 ($mol.dm^{-3}$) solution of a weak monobasic acid with a C_b solution of a completely dissociated monobasic base, one has:

$$[H^+] = \frac{(1-f)\varsigma C_a^0 - [H^+] + [OH^-]}{f\varsigma C_a^0 + [H^+] - [OH^-]} K_a \tag{13}$$

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

Near the point of equivalence for the titration of any solution except a very strong acid, the hydrogen ion concentration is negligible in both the numerator and denominator of equation (13). If one ignores $[H^+]$ on the right hand side of equation (13), solving the resulting quadratic and transforming the solution into an equation explicit in $p[H^+]$, and differentiating twice with respect to f, one obtains:

$$\frac{d^2(p[H^+])}{df^2} = 0.434\left\{\frac{1}{D}\left(\frac{d^2D}{df^2}\right) - \frac{1}{D^2}\left(\frac{dD}{df}\right)^2 - \frac{1}{\sqrt{G^2+4D}}\left(\frac{d^2G}{df^2}\right)\right.$$
$$+ \frac{1}{(G^2+4D)^{3/2}}\left(\frac{dG}{df}\right)\left[G\left(\frac{dG}{df}\right) + 2\left(\frac{dD}{df}\right)\right] - \frac{2}{\sqrt{G^2+4D}(G+\sqrt{G^2+4D})}\left(\frac{d^2D}{df^2}\right)$$
$$\left. + \frac{4}{(G^2+4D)(G+\sqrt{G^2+4D})^2}\left(\frac{dD}{df}\right)\left[\left(G + \frac{G^2+2D}{\sqrt{G^2+2D}}\right)\left(\frac{dG}{df}\right) + \left(2 + \frac{G}{\sqrt{G^2+4D}}\right)\left(\frac{dD}{df}\right)\right]\right\} \tag{14}$$

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 (14) 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 ($f_{\max}$), often wrongly assumed to be the equivalence point. The difference between the value of f at the point of maximum slope ($f_{\max}$) and the *actual* equivalence point ($f = 1$) represents the error in the potentiometric titration.

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[9]. 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

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