Checking anion-cation charge balance of water quality analyses: Limitations of the traditional method for non-potable waters

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Abstract

The factors affecting the sound application of an anion-cation balance check to water quality analyses are investigated. It is shown that the carbonate contribution to the total negative charge (in meq/ℓ) is satisfactorily calculated from the formula $[HCO_3]$ = (Total Alkalinity)/50 below about pH 10 in samples in which carbonate is the only titratable component. It is also shown that ignoring the presence of titratable organic components may significantly affect this. It is shown that the contributions of H^+ and OH^- to the total positive and negative charge respectively become important at an 0.1 meq/ℓ level below about pH 4 and above about pH 10. Examples are presented that highlight the importance of knowing detailed speciation of ligands that protonate and of metal ions that hydrolyse. In each case, the contribution to the total negative or positive charge is significantly altered from that of the deprotonated ligand or unhydrolysed metal cation because the effective average charge on the predominant species is modified. Furthermore, strong complex formation between protonated ligands and metal cations and between hydrolysed metal cations and strongly binding ligands can significantly alter the charge that might be deduced from simplistic equilibrium distributions that ignore this binding.

Introduction

Quality control in chemical analysis is a well-known and widely practised concept. For these reasons and for the purposes of this paper a precise definition of "quality" is not necessary. It is simply defined here as the value of a set of desired properties. It involves such features as the sampling method, the limit of detection, sensitivity, selectivity and specificity, safety, cost, precision and accuracy. These are discussed in detail by Kateman and Pijpers (1981). It has also been demonstrated that analytical laboratories with the strongest quality control procedures score significantly better in proficiency tests (Thompson and Lowthian, 1993).

Standard Methods (1992) suggests a number of procedures for checking the correctness of analyses of water samples. One of these methods, the anion-cation balance, is the subject of this paper. *Standard Methods* (1992) states that "the anion and cation sums, when expressed as milli-equivalents per litre, must balance because all potable waters are electrically neutral". It also correctly states that this check is applicable specifically to water samples for which relatively complete analyses are made.

This paper examines the assumptions upon which these statements are made in an attempt to raise awareness of them. It illustrates why the method should not, in general, be applied to non-potable waters. The paper also shows that taking account of detailed speciation of a water sample may allow the anion-cation balance check to be applied to a wider range of (non-potable) waters. Ultimately it is hoped that all involved will benefit from improved quality of the analytical data that should result if the anion-cation balance check is not only applied more widely but also more rigorously.

The "traditional" anion-cation balance method

Although not necessarily applicable to potable waters but certainly so to other waters, one of the implications of the *Standard Methods* (1992) statements above is that the sample is filtered. That is, there are no solid phases in contact with the sample other than the walls of the container. The anion-cation balance check should not be applied to samples which contain suspended solids because the contribution of solid phases to the total charge in the system is difficult to define.

The anion-cation balance check is based on a percentage difference between the total positive charge and the total negative charge, defined as follows.

$$\% \text{ difference} = 100(\Sigma\text{cations}-\Sigma\text{anions})/(\Sigma\text{cations}+\Sigma\text{anions}) \quad (1)$$

where contributions to charge are in units of meq/ℓ. Criteria have also been proposed for acceptance of the analytical data (Table 1).

TABLE 1
CRITERIA FOR ACCEPTANCE
(STANDARD METHODS, 1992)

Anion sum (meq/ℓ)	Acceptable difference
0-3.0	± 0.2 meq/ℓ
3.0-10.0	± 2 %
10.0-800	± 2-5 %

It can be noted here that some laboratories do not define the % difference according to Eq. (1). It has also been defined as follows:

$$\% \text{ difference} = 100(\Sigma\text{cations}-\Sigma\text{anions})/\min(\Sigma\text{cations},\Sigma\text{anions}) \quad (2)$$

The effect of this is that values calculated according to Eq. (2) will be about twice those using Eq. (1). Although alternative criteria for acceptance may exist for this method, this lack of standardisation is unfortunate. Clients who are presented with a calculated % difference in an analytical report cannot easily compare results from different laboratories. It is preferable that only a single formula is used and it could be recommended that Eq. (1) be the preferred one, simply on the basis of *Standard Methods* being the most widely-practised international standard.

Calculating the total positive (Σcations) and total negative charge (Σanions) involves knowing two things for each component analysed. These are the concentration of the component and its

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charge. The concentration is usually what the analyst has measured. However, in the case of carbonate, even this is not measured directly. This is dealt with below. The real issues dealt with in this paper revolve around the assumed charge on the component.

Traditionally, the charges on many components are assumed to be that of some simple form of the component. Some typical examples are Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-}. For potable waters it is usually quite satisfactory to assume these charges for an anion-cation balance check. However, if concentrations increase, other components are present or if the sample approaches extremes of pH then these charges may not be satisfactory. The sections below illustrate why this is so.

Methods

The best way of establishing the charge on each component that should be used in an anion-cation balance check is to subject the analytical data to an equilibrium calculation. This calculates the detailed speciation of the system and allows one to establish the charges on the predominant forms of each component. All calculations were done using the software package JESS (Joint Expert Speciation System) (May and Murray, 1991a; b).

The JESS thermodynamic database has extensive data at multiple temperatures, ionic strengths and background electrolytes. Consistency checking of data is carried out as far as possible.

For each system under study, JESS extracts those reactions and data applicable to the system. Appropriate linear combinations of reactions are automatically constructed that optimise the accuracy of the equilibrium constants of the resultant reactions. These latter reactions are written in the forms required for the equilibrium calculation, i.e. in terms of an independent set of basis species. Constants are also corrected for ionic strength and temperature, when necessary, using customary methods. These have been described in detail elsewhere (May and Murray, 1993) and have been improved since then.

Carbonate concentration and charge

Figure 1 shows the distribution of carbonate species in a 1 mmol/ℓ $CaCO_3$ solution. The contribution of carbonate species to the total negative charge is usually obtained from the measured total alkalinity in units of mg/ℓ $CaCO_3$. The calculation is as follows:

$$[HCO_3] = \text{Alkalinity}(\text{mg}/\ell\ CaCO_3)/50 \quad (3)$$

The value obtained is assumed to refer to the bicarbonate species, HCO_3^-, which is assumed to be the predominant form of carbonate in solution. Accordingly the charge on the species is assumed to be -1. The contribution of all carbonate species to the total negative charge (Σanions) is therefore assumed to be -[HCO_3] meq/ℓ (or mmol/ℓ) as calculated by Eq. (3). The correctness of this can be examined as follows:

Alkalinity is obtained in the laboratory by titrating the sample with a strong acid (sulphuric or hydrochloric) to a certain endpoint. *Standard Methods* (1992) suggests that the pH of this endpoint should be 4.9 if the alkalinity is 30 mg/ℓ $CaCO_3$ or 4.6 if the alkalinity is 150. A 1 mmol/ℓ solution of $CaCO_3$ at a pH of about 8 will have an alkalinity of about 50. Therefore, for the purposes of this illustrative calculation, an endpoint pH of 4.9 will be assumed.

The total alkalinity can be calculated for any given pH as follows. The pH of the 1 mmol/ℓ $CaCO_3$ solution can be assumed to be decreased by addition of HCl. The total concentrations of Ca and CO_3 can be fixed at 1 mmol/ℓ. If the pH is fixed at, say, 8, the total concentration of chloride present can be calculated by invoking

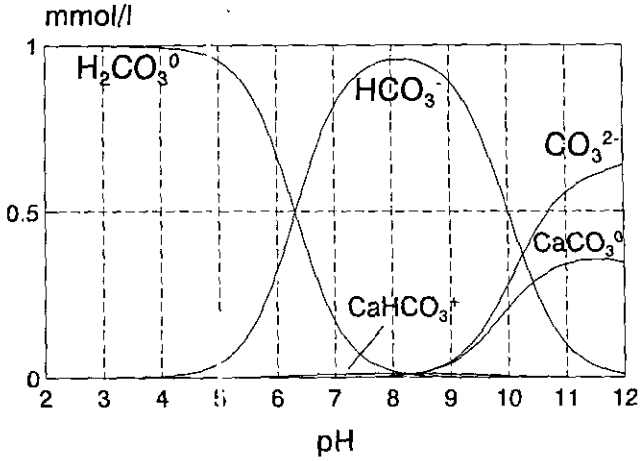

Figure 1
Carbonate species distribution in a 1 mmol/ℓ $CaCO_3$ solution

a charge balance equation. Having performed this equilibrium calculation, one can determine the total proton concentration in this solution, T_H^{obs}. (For a detailed discussion on the meaning of T_H see Morel, 1983.) One then performs the same calculation except that the pH is now fixed at the endpoint of the alkalinity titration, namely 4.9. The total proton concentration at the endpoint T_H^{end} is then determined in the same way. It can be assumed that the change in total proton concentration (from the observed pH 8 to the endpoint pH 4.9) is entirely due to the addition of the strong acid. The total alkalinity can then be calculated as follows:

$$\text{Alk} = (T_H^{end} - T_H^{obs}) \times 50000 \quad (4)$$

One can perform this calculation over the whole pH range from 4.9 to 10.4 (about the pH of the pure $CaCO_3$ solution). [HCO_3] can then be calculated from this alkalinity using Eq. (3). These values can be compared to the actual total carbonate concentration (which was fixed at 1 mmol/ℓ) by calculating the percentage error.

$$\%\ \text{error} = ([HCO_3^-] - 1) \times 100/1 \quad (5)$$

The results are shown as the dotted line in Fig. 2. A negative percentage error indicates that the calculated value is less then the actual value and a positive error indicates that it is greater.

Of course, this concentration needs to be multiplied by a charge. Strictly, this should be the average charge on the predominant protonated species ignoring binding with calcium. This was calculated as a function of pH. Comparing this with the traditionally assumed charge of -1, one obtains the series of percentage errors shown by the dashed line in Fig. 2. It is evident that over most of the range, these two errors almost cancel each other out (solid line) quite effectively, except above pH 10.

One can conclude from this that the use of Eq. (3) to estimate the contribution of carbonate species to the total negative charge is quite satisfactory, except above pH 10.

Calculating the contribution of carbonate to the total negative charge using Eq. (3) is significantly affected by the presence of other titratable components in solution. For example, the presence of organic acids will result in an alkalinity being measured that is higher than the alkalinity that would have been obtained in their absence. The following simple example serves to illustrate this.

Consider a solution containing 1 mmol/ℓ $CaCO_3$ and 0.5 mmol/ℓ sodium acetate (about 6 mg/ℓ C). If this solution is adjusted to pH 8 with HCl, the calculated alkalinity is 57.7 mg/ℓ $CaCO_3$ (using the same method as above). Without the acetate

present it is about 48.3. Therefore, the calculated contribution to the total negative charge would be assumed to be -1.15 meq/ℓ. However, the actual contribution to the total negative charge from both carbonate and acetate species (the latter being fully deprotonated at pH 8), is found to be about -1.48 meq/ℓ. Therefore using Eq. (3) to calculate the contribution to the total negative charge invokes an error of about 22% in this specific case. It is evident that not accounting for the presence of organic acids can have a significant effect on the calculated contribution of carbonate to the total negative charge.

Naturally, the real effect of this may be neglible to the overall charge balance if carbonate and organic acid concentrations are relatively small. However, if they are not, the effect could be significant.

Contribution from H^+ and OH^-

The lower the pH of the sample being analysed the greater the contribution of the proton is to the total positive charge (Σcations). Similarly, as the pH increases, the hydroxide ion becomes an increasingly important contributor to the total negative charge (Σanions). The activity of each (in mol/ℓ) can be estimated from the measured pH as follows:

$$\{H^+\} = 10^{-pH} \quad (6)$$

$$\{OH^-\} = K_w/\{H^+\} \quad (7)$$

where K_w is the ion product of water. In dilute solutions and at 25°C it is sufficiently accurate for the present purposes to assume a value for K_w of 10^{-14}.

For simplicity in indicating the approximate extent of the effect, the activity coefficient of each is assumed to be unity. Hence, the activities can be regarded as equal to the concentrations. Figure 3 illustrates the approximate contribution of H^+ and OH^- to the total positive and negative charge as a function of pH. It can be seen that their respective contributions only become significant (at a 0.1 meq/ℓ level) below about pH 4 and above pH 10. Their contributions should therefore be taken into account in an anion-cation balance check when the pH of the sample is outside the range 4 to 10.

Protonation of ligands

Figures 4 through 7 show the species distributions of 1mmol/ℓ solutions of the four common ligands sulphate, ammonia, silicate and phosphate. The plots were calculated by assuming that the 1mmol/ℓ solution was first brought down to pH 2 using HCl and then NaOH was used to raise the pH up to 12. All calculations were performed at 25°C using equilibrium constants corrected to the calculated ionic strength (over the whole pH range).

In the pH range 2 through 12 each ligand is protonated to some extent. Even sulphate protonation becomes significant below pH 4. Below pH 7 the charge on ammonia should be regarded as +1. However, above this pH the presence of the neutral NH_3^0 species becomes significant and the charge on ammonia should ideally be less than 1. For example, at about pH 9.3 it should be taken as 0.5. The charge associated with silicate should be zero below about pH 8 but above that pH it should decrease to -0.5 at about pH 9.6 and tend to -1 at about pH 11. Over the pH range 2 to 12 the charge on phosphate can vary from -0.5 to -2.5. When choosing the charge for an anion-cation balance check on any of these ligands the protonation in solution must be taken into account. Ligands like Cl^- and NO_3^- are not significantly protonated in the pH range 2 to 12 so their charge can safely be assumed to be -1.

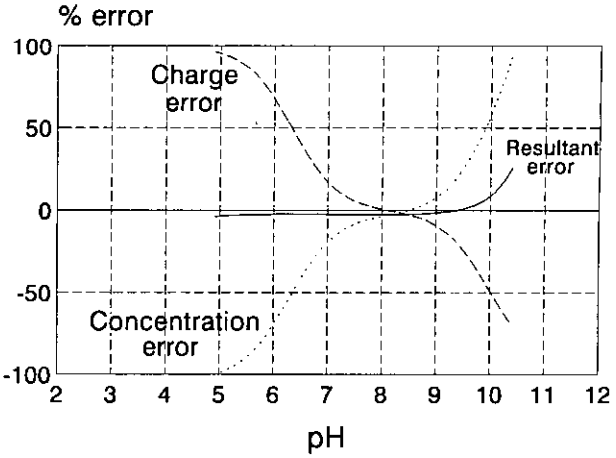

Figure 2
Cancellation of errors of the total concentration and charge of carbonate as a function of pH based on the calculation $[HCO_3] = Alk/50$ for a 1 mmol/ℓ $CaCO_3$ solution

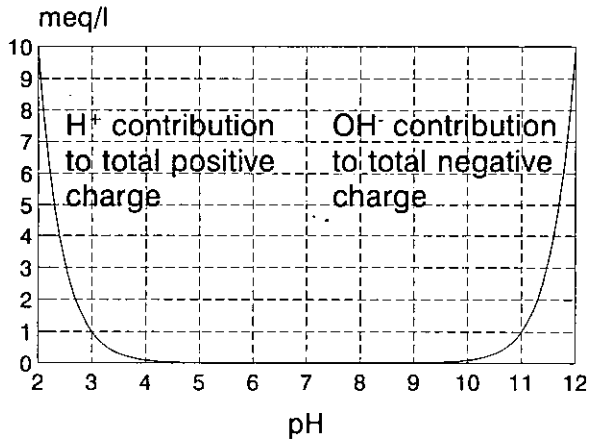

Figure 3
The contribution of the proton and hydroxide ion to the total positive and negative charge respectively as a function of pH

Unfortunately in more concentrated or more complex solutions it is not sufficient to simply use these guidelines to obtain a charge on a species. Strong binding between species may well alter the charge on the component of interest that should be used in anion-cation balance checks. Therefore, when the total concentration of any ligand is sufficiently high to significantly influence the overall total negative or positive charge, an equilibrium calculation may be necessary for optimum accuracy.

It should be noted that binding *per se* does not significantly affect the charge that should be chosen for an anion-cation balance check. For example, in a solution of Na^+ and SO_4^{2-}, the existence of a complex such as $NaSO_4^-$ does not mean that the charge on Na^+ should not be +1 nor that the charge assumed for SO_4^{2-} should not be -2. The total amount of sodium and sulphate that was analysed includes that bound in such complexes and charges should be +1 and -2. However, strong binding does affect the charge that should be chosen when the ligand is protonated and strong binding displaces these protons from the ligand.

It is clear from these figures that the protonation of many ligands needs to be known in some detail for one to choose the best charge on the component for anion-cation balance checks.

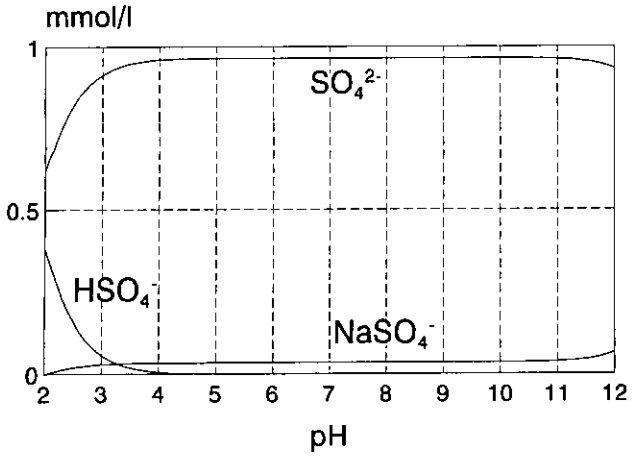

Figure 4
Sulphate species distribution

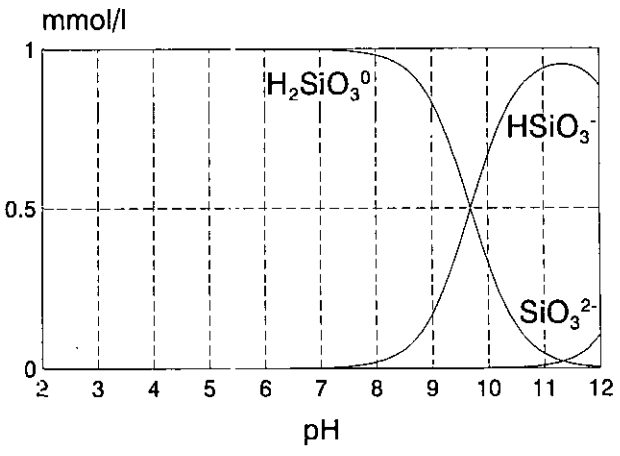

Figure 6
Silicon species distribution

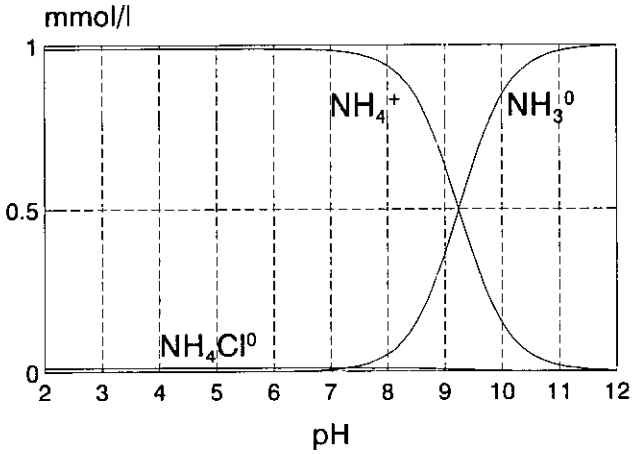

Figure 5
Ammonia species distribution

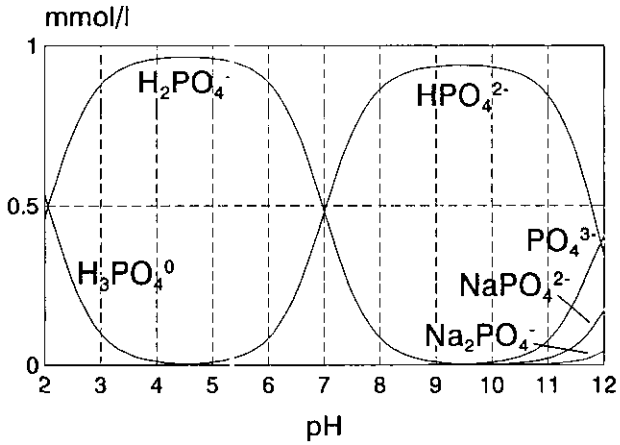

Figure 7
Phosphate species distribution

Hydrolysis of metal ions

Figures 8 through 11 show the predominant species of 1 mmol/ℓ solutions of magnesium, calcium and aluminium chlorides. As above, the plots were calculated by assuming each solution was first brought down to pH 2 using HCl and then raised up to pH 12 using NaOH. All calculations were performed at 25°C at the calculated ionic strength.

Figure 8 shows that the assumption that magnesium has a charge of +2 is only valid below about pH 10. Above this pH the species $MgOH^+$ begins to form and therefore the charge that should be used should be less than +2. Figure 9 suggests that the assumption that calcium has a charge of +2 is satisfactory below a pH of about 11.

Figures 10 and 11 show how the species distribution of a strongly hydrolysed cation like aluminium changes when in the presence of a relatively high concentration of sulphate. The concentration chosen for sulphate was 30 mmol/ℓ (about 2 880 mg/ℓ), which is typical of acid mine drainage. In an attempt to make these diagrams as realistic as possible, the solid phase amorphous $Al(OH)_3$ was allowed to precipitate when its solubility product was exceeded.

These two figures illustrate a number of points. First, because aluminium is hydrolysed to some extent above pH 3, a charge of +3 for aluminium is only strictly valid below pH 3. Above this pH the charge varies according to the extent of hydrolysis. Secondly, binding between aluminium and sulphate (or any ligand) changes the species distribution in a way that affects the optimum charge that should be used for an anion-cation balance check. For aluminium and sulphate, these effects are evident below a pH of about 6. This occurs primarily because the ligand displaces OH^- from the aluminium. (This effect is equivalent to the effect of metal cations displacing protons from a protonated ligand, mentioned above). Finally, the presence of a relatively high concentration of sulphate changes the ionic strength of the solution. This also affects the species distribution and therefore the charge that should be assumed for aluminium. This effect is largely responsible for the differences in the total amount of aluminium remaining in solution (in the presence and absence of sulphate) at high pH (Fig. 12).

The general conclusion is therefore that a detailed knowledge of the speciation of metal cations is sometimes necessary if the correct charge is to be obtained for anion-cation balance checks. The traditional assumptions of charges on cations may not be valid if the cation is significantly hydrolysed. For cations such as Na^+ and K^+ this is not a problem.

It should be reiterated that the figures presented here should not be used in a general way to determine the correct charge on a metal cation because the speciation will vary from sample to sample.

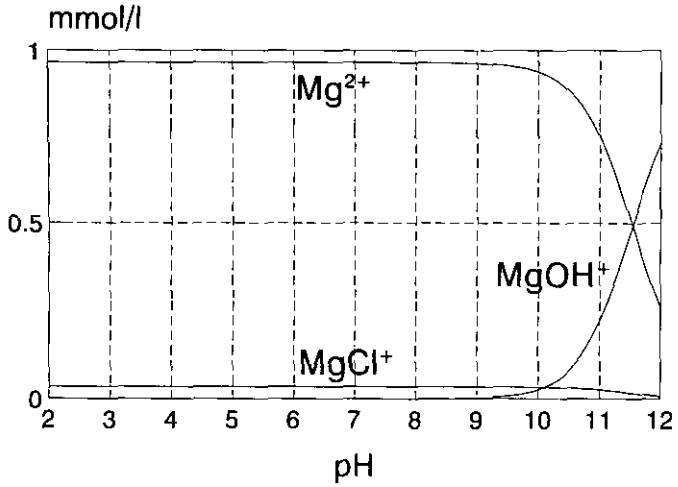

Figure 8
Magnesium species distribution in a 1 mmol/ℓ solution of $MgCl_2$

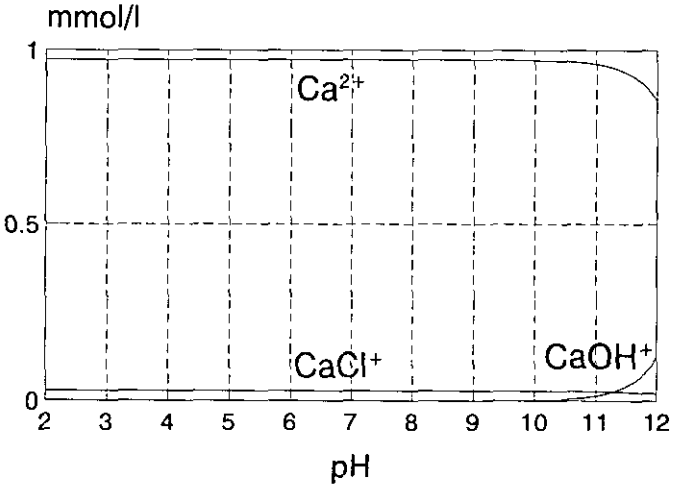

Figure 9
Calcium species distribution in a 1 mmol/ℓ solution of $CaCl_2$

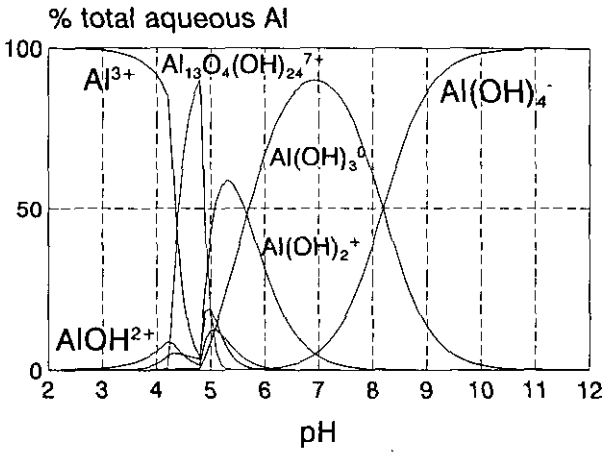

Figure 10
Aluminium species distribution in a 1 mmol/ℓ solution of $AlCl_3$ taking $Al(OH)_3$ precipitation into account

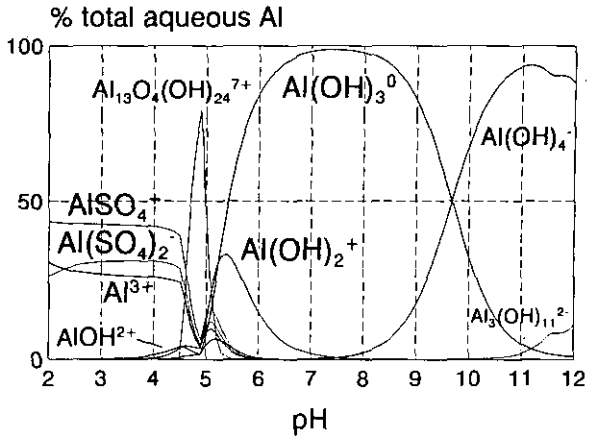

Figure 11
Aluminium species distribution in a 1 mmol/ℓ solution of $AlCl_3$ with 30 mmol/ℓ Na_2SO_4 taking $Al(OH)_3$ precipitation into account

Effect of oxidation potential

There are many components whose speciation depends as much on oxidation potential as on pH. As one of many examples, Fig. 13 shows the predominant aqueous Fe species in a 1 mmol/ℓ $FeCl_3$ (about 56 mg/ℓ Fe) system. The solid phase $Fe(OH)_3$ was allowed to precipitate in the calculations when its solubility product was exceeded. It is evident from the figure that the charge on Fe that should be used in an anion-cation balance calculation varies not only with pH (particularly because it is strongly hydrolysed like Al) but also with oxidation potential. If one has only analysed for total Fe then one is faced with the choice of either a 2+ or 3+ oxidation state. The most desirable situation is to have analyses for both Fe^{2+} and Fe^{3+}. Alternatively one can measure the oxidation potential. However, not many laboratories are equipped to perform this analysis and, even if they are, few requests are received that require it to be measured. However, because redox reactions are often relatively slow, even knowing the oxidation potential is not a good guarantee of being able to choose between 2+ and 3+. Indeed, both can be present in significant amounts.

Nevertheless, if concentrations are low (a few mg/ℓ) and the sample is likely to be oxidising, one can usually assume that the Fe exists in the 3+ oxidation state. However, even then, the charge that should be assumed for an anion-cation balance check can vary from +2 to 0, depending on pH. If concentrations are high the Fe is likely to be in the 2+ oxidation state. In this state, the charge needs to be closer to +1 than +2 above a pH of about 7.

These principles apply to many other metals. A few of the more commonly encountered metals include Cr, Cu and Hg. Again, the speciation is altered, sometimes very significantly, if strongly binding ligands are present. So, ideally, an equilibrium calculation is required for each sample if the concentrations of these metals are relatively high and good accuracy is required.

Conclusions

It has been shown that calculating the contribution of carbonate species to the total negative charge using Eq. (3) is satisfactory below about pH 10 in samples in which carbonate is the only significant titratable component. The presence of other titratable components such as organic acids not analysed for can result in significant errors. The presence of high concentrations of H^+ or

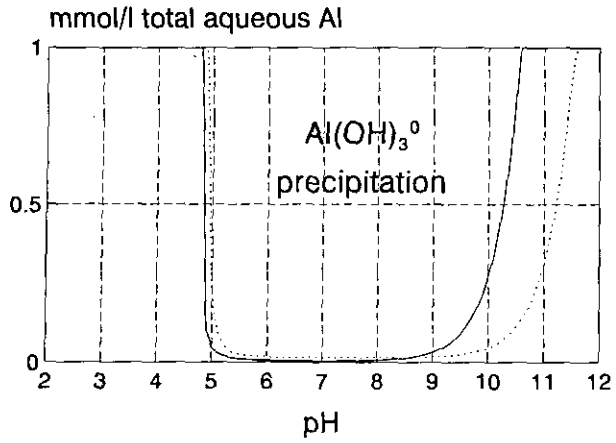

Figure 12
The total aqueous concentration of aluminium in a 1 mmol/ℓ system of $AlCl_3$ with sulphate (dotted line) and without sulphate (full line) taking $Al(OH)_3$ precipitation into account

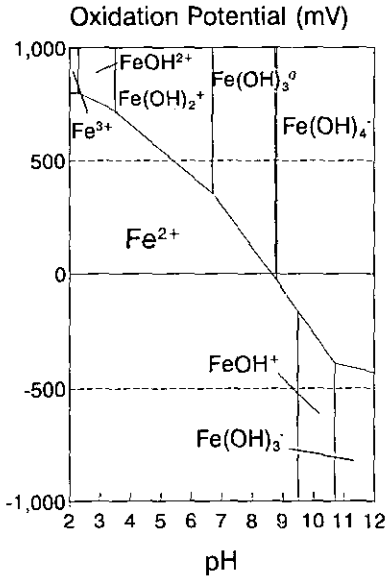

Figure 13
Predominant aqueous iron species in a 1 mmol/ℓ system of $FeCl_3$ taking precipitation of $Fe(OH)_3$ into account

OH^- in low and high pH samples, protonation of ligands and hydrolysis of metals can significantly affect the calculation of an anion-cation balance. Figure 14 summarises these trends.

Furthermore, complex formation between protonated ligands and metal cations and between hydrolysed metal cations and strongly binding ligands can significantly affect the charge that should be used in an anion-cation balance check. This makes it very difficult to generalise from the speciation distributions presented here for what are very simple solutions.

It is recommended above that under certain circumstances an equilibrium calculation is called for if optimum accuracy is to be

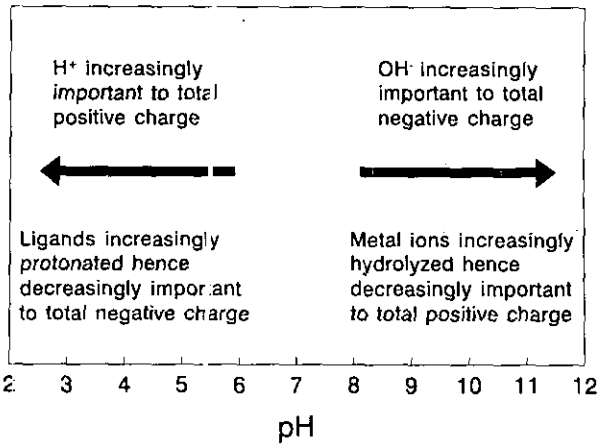

Figure 14
Some general trends that should be borne in mind when calculating an anion-cation balance

obtained in an anion-cation balance check. This is not a trivial task for the typical analytical chemist. Equilibrium calculation software packages have been traditionally designed with generalised interfaces and not particularly user-friendly ones at that. They are all likely to be singularly unsuitable for the fast-turnaround environment of the typical analytical laboratory. If access is not available to such facilities and if it is thought that traditional charges are not appropriate for any of the reasons mentioned above, then it is strongly recommended that the anion-cation balance check is not done. If assumptions are invalid a value may be calculated that indicates that a problem (i.e. an imbalance) exists when there is not or *vice versa*. Work is being continued at the CSIR with the aim of producing a standardised software package with an interface specifically designed for this application. It will address the problems highlighted in this paper by taking speciation into account and hence extend the application of anion-cation checks to certain non-potable waters.

Acknowledgements

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