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

K Murray* and P Wade

Division of Water Technology, CSIR, PO Box 395, Pretoria 0001, South Africa

Abstract

The factors affecting the sound application of an anion-cation balance check to water quality analyses are investigated. ft is shown that the carbonate contribution to the total negative charge (in meq/l) is satisfactorily calculated *from* the formula [HCO3] = (Total Alkalinity)/50 below about pH l0 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 importanl *at an* 0.) *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 deprolonateii ligand or unhydrolyseti 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-potabie) 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

---

* To whom all correspondence should be addressed.

(012) 841-2647; Fax (012) 841-2506: E-mail: kmurray@csir.co.za

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.

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

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. (I). It has also been defined as follows:

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

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. (I) 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 tilings for each component analysed. These are the concentration of the component and its