A Survey of Charge-Balance Errors on Published Analyses of Potable Ground and Surface Waters

by Steven J. Fritz[a]

Abstract

Although the charge balance for a single chemical analysis of a water's electrolytes is not a reliable gauge for the accuracy of that analysis, the percent charge-balance error (%CBE) becomes more credible as a means for evaluating analytical technique when applied to groups of analyses.

Just how good are charge balances for chemical analyses of potable ground and stream waters in mainline geological journals? Starting with each journal's first volume, a search found 68 articles in six journals (*Appl. Geochem., Chem. Geol., Geochim. Cos. Acta., Ground Water, J. Hydrol.,* and *Water Resources Res.*) that had what was deemed to be "complete" analyses of individual samples' major ions. Analyses of brines and hydrothermal solutions were excluded as were "composite" averages. A total of 1,062 %CBEs were computed and tabulated, and the average was 3.99% ± 6.56 (1σ).

The average %CBE (by journals) ranges from 1.55% to 9.34%. Quality of %CBE is slightly better for articles published after 1970. Not surprisingly, low ionic strength samples are prone to charge-balance errors > 10%. Of the 1,062 charge balances calculated, 612 were positive and 450 were negative. Eight of the 68 articles had analyses that were evenly balanced between positive and negative CB errors. There are 21 articles in which the majority of analyses had negative charge-balance errors. Thus a clear majority (39) of articles had analyses in which there were more positive than negative charge-balance errors.

Systematic error is likely for situations where the analyses in an article are predominantly positive or predominantly negative. The likely reason for the former occurrence is lab determination of alkalinity from the nonacidified field aliquot. Failure to filter samples may cause the latter situation—especially in carbonate terranes. Systematic laboratory errors involving salt standards and dilutions can also yield charge-balance errors for a suite of analyses that are skewed to either positive or negative errors. The care with which the analyst did his/her job may also impact charge-balance errors.

Introduction

Suppose you read a scientific paper in which the author uses a rock's chemistry to fashion conclusions concerning petrogenesis. You notice in the table of his/her analyses that the sum of the 10 major oxides is 115%. Arguably, you would be much more likely to believe the author's conclusions if the oxide sum were near 100%. Let's further suppose that you immediately read another article on a similar topic, and the tabulated data for a granite's analysis show no analyses for $\%K_2O$, $\%TiO_2$, or %MgO. Instinctively, most of us in that situation would wish for a complete chemical analysis of that rock in order to apply the "mass-balance" yardstick for believability of the data.

In a *Ground Water* editorial entitled "Where Are the Rest of the Analyses?" Davis (1988) urged authors of reports and articles to include complete analyses for water samples. He defined "complete" as generally being those constituents found in potable waters at levels above 1 mg/l. Similar to the scenario described above with the missing oxide data, he argued that... "A 'complete' analysis is necessary before the cation-anion balance of the analysis can be calculated. This is the most fundamental item in the true quality control of chemical analyses. No matter what the certification of the laboratory is and what the amount of automation is, impossibly poor analyses are routinely detected by the simple procedure of calculating ion balances." Davis (1988, p. 4.)

According to Freeze and Cherry (1979), the percent charge-balance error (%CBE) is calculated as:

$$\%\text{CBE} = \frac{\Sigma z \cdot m_c - \Sigma z \cdot m_a}{(\Sigma z \cdot m_c + \Sigma z \cdot m_a)} \cdot 100\%. \qquad (1)$$

In this equation, z is the absolute value of the ion's charge, and m_c and m_a are molalities of the cationic and anionic species, respectively. A perfectly charged-balanced analysis for an electrolyte solution (zero charge-balance error) means that $\Sigma z \cdot m_c = \Sigma z \cdot m_a$. [It should be pointed out that there are adherents who prefer the denominator of equation (1) to be divided by 2 in order to relate the difference of cation and anion equivalents to the mean. For example, Ball and Nordstrom (1991) adopt this more logical usage. Either form of the charge-balance equation is acceptable; however, in this paper equation (1) is adopted simply because it presently enjoys a greater currency. Using the alternative equation results in doubling both the mean %CBE and the standard deviation for groups of analyses].

As Freeze and Cherry (1979) so correctly point out, a zero percent charge-balance error does not insure that the analysis is accurate. An overestimation of a cation like Na^+

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[a] Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, Indiana 47907.

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can be compensated in the %CBE calculation of that sample's analysis by an equivalent underestimation of another cation like Mg^{2+}. Likewise, an underreporting of Ca^{2+} could be offset by an equivalent underreporting of an anion like Cl^-.

This logic, although sound for an analysis of an individual sample, becomes less defensible when assessing charge-balance errors of many samples. For example, if an analyst performs the major-ion chemistry of 10 different samples, and the %CBEs for each sample falls between -1% and +1%, then these excellent charge-balance errors are highly unlikely to be accounted for by a lucky cancelling-out of errors for the 7 or 8 components determined for each sample.

This paper has three objectives: (1) to examine the quality of %CBEs in selected journals deemed likely to publish articles including chemical analyses of ground and stream waters; (2) to identify several important factors (of the potentially many) that contribute to poor charge-balance errors; and (3) to recommend some commonsensical field/laboratory techniques that should insure decent %CBEs (arbitrarily defined here as being less than 2%). This 2% threshold is a reasonable goal. "Water analysis laboratories normally consider a charge-balance error of less than about 5% to be acceptable, although for some types of groundwater many laboratories consistently achieve results with errors that are much smaller than this." (Freeze and Cherry, 1979; p. 97.)

Results of the Compilation

I chose six journals which I thought would most likely have articles dealing with chemistry of natural waters and, in addition, include tables listing major-ion chemistry of individual samples. Those journals are: *Applied Geochemistry, Chemical Geology, Geochimica et Cosmochimica Acta, Ground Water, Journal of Hydrology,* and *Water Resources Research.* Any article having a "complete" analysis necessary to compute a charge balance (T° C, pH, Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, NO_3^-, SO_4^{-2}, HCO_3^-, and CO_3^{-2}) was referenced for tabulation and computation of %CBE for each analysis listed in that article. In those articles where HCO_3^- and CO_3^{-2} were not listed, these parameters were calculated from the pH and alkalinity of each analysis. Literally thousands of articles in these six journals were scanned to see if they contained data that could be tabulated for this study. In that process it's very likely that some articles were overlooked. Purposely overlooked were certain types of samples and formats of tabulated data. Chemical analyses of brines and hydrothermal solutions were not compiled because I wanted to focus on ground and stream waters that are sources for drinking water. Oftentimes an article reported a composite analysis of several (or many) water samples. These articles were excluded from the compilation because gross disparities of %CBE might have been thrown out by the author. Moreover, large variations in %CBE could be hidden by the single reporting of an average %CBE without an accompanying standard deviation.

This compilation was not meant to be exhaustive because other journals, books, and reports having such analyses are not included here. The main intent was to have sufficient data to make generalized statements concerning the caliber of charge-balance analyses in refereed journals. I also eschewed heavy use of statistics in favor of a straightforward presentation of the data. Hence the conclusions are qualitative, generally in the form of recommendations. As such the tenor of this article is primarily pedagogical.

Starting with each journal's first volume and ending with January 1993, the search encountered 68 articles in the six journals that had at least two complete chemical analyses of ground water or surface water. A total of 1,062 %CBEs were computed—an average of about 16 analyses per article. Of the 68 articles, 43 had 10 or more analyses, while three had 50 or more analyses.

Table 1 is a compilation of the survey. The entries are listed in chronological fashion for each journal. The *Journal of Hydrology* (JH) has the most listings (20) while *Applied Geochemistry* (AG), a relatively recent journal, has only two entries. The frequency of articles containing "complete" chemical analyses of ground/surface waters has averaged about two to three per year since the early 1970s. Because the plethora of numbers in Table 1 is somewhat overwhelming, a read-through example for an analysis should prove helpful. Analysis #1, published in 1987 in *Applied Geochemistry*, had 20 analyses of which 9 had positive %CBEs and 11 negative %CBEs. The %CBE ranged from a miminum of -3.55 to a maximum of +3.55, with the median being -0.13. The mean %CBE was 0.27 ± 1.83 (1σ), whereas the mean of the absolute values of the %CBE for all 20 samples is 1.48 ± 1.06. The average ionic strength is 0.0089. The mean milli-Normality of the cations for the 20 samples was 5.62, and 5.76 meq/l was the mean for the anions. Alkalinity was performed in the field (yes) as opposed to those articles where alkalinity was done in the lab (no) or not said (ns) as to whether alkalinity was done in the lab or in the field.

The average %CBE for all 1,062 analyses is a surprisingly good 0.83 ± 7.63 (1σ). Taken at face value, a 0.83% charge-balance error is of enviably high quality. However, this figure is misleading because large positive and negative errors for individual analyses can average to give a figure close to zero percent. If one adopts the attitude that "an error is an error," then one should treat these %CBEs in terms of the absolute value of the error. For example, if the CB errors for two analyses are -8% and +6%, then the mean of the absolute values of the errors is 7% as opposed to the simple mean of -1%. From this perspective, the average %CBE for all 1,062 analyses is 3.99 ± 6.56 (1σ). Hereafter the %CBE is computed as the absolute value of equation (1). Within that respect, the following are the average %CBEs for each journal, with integers in parenthesis referring to number of articles in that journal upon which the average was computed: AG (2) = 1.55 ± 0.10; CG (7) = 5.55 ± 4.33; GCA (15) = 4.26 ± 4.88; GW (10) = 4.17 ± 3.38; JH (20) = 3.66 ± 3.01; and WRR (14) = 9.34 ± 10.6.

A sensible assumption would be that the quality of charge-balance errors is better for more recent publications. The rationale is that improvements of instrumentation and increased automation leads to better quality analyses. Of the six papers listed in Table 1 having publication dates in the

1960s, three have CB errors below 2%. The other three have %CBEs in double figures. The average %CBE for all six papers is 10.0. Although there are double-digited averages for %CBEs of individual papers in each of the four decades represented in Table 1, the average %CBE per article appears to be better for papers published since 1970. Of the 19 papers published in the 1970s, the average %CBE is 5.3. The 35 papers in the 1980s have an average %CBE of 4.3, and the eight papers in the 1990s have an average of 5.2.

The quality of charge balance appears to be a function of ionic strength. There are nine articles in Table 1 whose average analysis has an ionic strength below 0.001. The average %CBE for these nine articles is 14.7, much greater than the average of 3.99 for all 68 articles. As anyone analyzing rain-water chemistry can testify, it is very difficult to achieve decent charge balances when dealing with dilute samples. For example, #4's %CBE is 10.8 for seven analyses whose average ionic strength is 0.0005; yet the difference between the mean $mN_{cations}$ and mN_{anions} is only 0.02 meq/l (Table 1). In contrast, article #29 has the best %CBE (0.37) of all 68 articles; yet $[mN_{cations} - mN_{anions}]$ is 0.05—a difference that is more than twice that of #4. This example points out the problem of using charge-balance analyses as a criterion for quality control. Clearly, a truer gauge of the quality of an analysis should be an absolute measure like $|mN_{cations} - mN_{anions}|$ rather than presenting CB data as a normalized percentage.

Of the 1,062 charge balances calculated, 612 were positive and the remaining 450 had $\Sigma z \cdot m_c < \Sigma z \cdot m_a$. Eight of the 68 articles had analyses that were evenly balanced between positive and negative CB errors. There are 21 articles in which the majority of analyses had negative charge-balance errors. Thus a clear majority (39) of articles had analyses in which there were more positive than negative charge-balance errors.

The frequency of positive versus negative errors is quite informative about the presence of systematic errors. If indeed the errors involved in chemically analyzing the components comprising a charge balance are randomly distributed, then one should see close to a 50/50 split of negative vs. positive CB errors for analyses listed in an article. Thus a suite of analyses having either all positive or all negative charge-balance errors points to systematic error. Article numbers 14, 15, 43, and 65 are examples of studies having either all positive or all negative charge balances for an analysis population greater than 10 samples. Of these, all but #65 are wholly positive CB errors. An even more striking example of bias toward positive CB error is given by articles #51 and #64. The positive-to-negative split is 48-to-3 for #51 and 44-to-12 for #64 (Table 1). All of these articles have one thing in common: their methods section did not specifically state that alkalinity was performed in the field.

Discussion and Recommendations

Field vs. Laboratory Determined Alkalinity

Positive charge-balance errors are commonly related to alkalinity measurements. In potable water sampled in carbonate terrains, alkalinity (consisting almost entirely of bicarbonate) commonly comprises 80% of the anion equivalents, or 40% of the equivalents of the solution's electrolytes. In the field the sampler typically pours half of the filtered sample into a bottle containing a few drops of concentrated nitric acid and the remaining portion into an untreated bottle. The former bottle is reserved for cation analysis and the other bottle is saved for analysis of anions. If the sampled water is supersaturated with respect to calcite and/or dolomite, then it's highly likely that if alkalinity is performed in the laboratory a portion of that sample's alkalinity lies in the bottom of the bottle in the form of a precipitated carbonate mineral. Being acidified, the water in the cation bottle will not precipitate calcite or dolomite; hence, analysis of Ca and Mg should accurately reflect these ions' concentration in the sample. However, the alkalinity will be underreported. The result usually incurs a positive charge-balance error.

Of the 13 articles where alkalinity was reported to have been performed in the field, six had more positive %CBEs than negative %CBEs, six articles had the reverse, and one article had analyses evenly split between positive/negative CB errors. Moreover, the 212 analyses within the 13 articles comprising this category are evenly divided between the positive and negative errors. For the 30 articles in which it is unclear as to where alkalinity was performed, 16 had analyses that were biased toward positive charge balance errors, 10 had the opposite result, and four articles had analyses evenly split between negative and positive errors. Of the 483 analyses within these 30 articles, 277 had positive charge balances. If laboratory-determined alkalinity is a major source of reporting positive charge-balance errors, then one should expect such articles to have a high proportion of positive charge balances. Seventeen of the 25 articles in this category have analyses in which there are more positive than negative charge balances. Only five articles had the reverse trend, while three articles had analyses whose negative/positive errors were equally divided. Of the 367 analyses contained within this category, almost two-thirds (227) had positive charge-balance errors.

Under certain conditions alkalinity can also be a cause for a substantial bias towards negative CB errors. If alkalinity *is* performed in the field but the sampler and/or analyst titrates an unfiltered sample, then the reported results will be overrreported if there are suspended particles of calcite in the titration flask.

Errors Involving Salt Standards and Dilutions

Apart from alkalinity and pH measurements (leading to calculations of the hydronium, hydroxyl, bicarbonate, and carbonate concentrations), all other major ions are determined in the laboratory. Two common laboratory mistakes that even a conscientious analyst can make that create charge-balance errors are: (1) improperly characterized salt standards; and (2) dilution errors.

Although gravimetry, turbidimetry, and colorimetry can be used to analyze water chemistry, the three most common techniques used to routinely analyze the major ions of aqueous solutions are: titrimetry, atomic absorption spectrophotometry (AAS), and ion chromatography (IC). The accuracy of an analysis is constrained by the accuracy of the standard and adequate understanding and control of

Table 1. Compilation of Charge-Balance Data

Jour.	*Year*	+	–	*Error range*		*Median*	*Mean (±1σ)*	*Absolute value mean (±1σ)*	*I.S.*	*Mean meq/l*		*Field alk?*
										cat.	*an.*	
1. AG	1987	9	11	-3.55	3.55	-0.13	0.27 (± 1.83)	1.48 (± 1.06)	0.0089	5.62	5.76	yes
2.	1991	22	9	-3.00	9.38	0.50	0.98 (± 2.32)	1.62 (± 1.92)	0.0174	5.69	5.63	yes
3. CG	1969	11	23	-12.9	4.76	-0.49	-0.67 (± 3.02)	1.71 (± 2.57)	0.0285	9.30	8.70	ns
4.	1971	2	5	-37.1	2.78	-6.12	-9.83 (±13.6)	10.8 (±12.6)	0.0005	0.22	0.24	ns
5.	1983	1	8	-7.96	2.60	-5.28	-4.48 (± 3.05)	5.04 (± 1.77)	0.0009	0.63	0.74	no
6.	1985	4	4	0.52	2.91	1.05	1.38 (± 1.07)	1.38 (± 1.07)	0.0086	6.24	5.89	yes
7.	1985	6	2	-4.24	51.7	3.28	8.37 (±17.8)	9.62 (±17.1)	0.0369	33.9	34.4	ns
8.	1986	11	4	-6.44	41.1	3.08	6.77 (±14.5)	9.38 (±12.9)	0.0212	40.9	38.7	ns
9.	1988	2	19	-2.36	0.78	-0.87	-0.87 (± 0.81)	0.96 (± 0.68)	0.0880	68.3	67.2	yes
10. GCA	1961	4	2	-1.55	39.3	10.8	16.0 (±19.5)	17.0 (±18.5)	1.067	2.24	2.21	no
11.	1969	4	4	-8.16	1.03	-0.01	-1.24 (± 2.99)	1.65 (± 2.74)	0.0262	7.96	7.92	no
12.	1971	8	21	-10.7	1.94	-0.96	-1.33 (± 2.55)	1.71 (± 2.29)	0.0082	5.27	5.55	no
13.	1972	4	12	-6.28	3.12	-1.52	-1.58 (± 2.59)	2.38 (± 1.81)	0.0079	7.98	9.05	no
14.	1972	11	0	0.11	4.43	1.85	1.95 (± 1.37)	1.95 (± 1.37)	0.0003	0.41	0.39	no
15.	1972	12	0	1.57	4.67	3.26	3.23 (± 1.04)	3.23 (± 1.04)	0.0347	5.55	5.34	no
16.	1974	12	2	-4.81	49.4	12.5	13.8 (±15.8)	15.1 (±14.5)	0.0006	0.60	0.65	no
17.	1974	6	5	-2.70	6.66	0.43	0.90 (± 2.59)	1.84 (± 1.96)	0.0176	19.9	20.2	no
18.	1977	16	6	-1.72	27.1	1.45	4.14 (± 8.37)	4.59 (± 8.12)	0.0054	15.7	15.3	no
19.	1977	1	2	-5.14	5.00	-0.43	-0.19 (± 5.07)	3.52 (± 2.68)	0.0035	1.69	1.87	yes
20.	1978	11	1	-0.04	4.80	2.99	2.79 (± 1.36)	2.80 (± 1.34)	0.0103	5.32	5.09	yes
21.	1982	9	22	-8.15	1.99	-0.94	-1.13 (± 2.04)	1.61 (± 1.00)	0.0082	5.70	5.66	ns
22.	1984	6	10	-11.6	4.51	-0.51	-0.87 (± 3.90)	2.69 (± 2.87)	0.0104	2.90	2.91	no
23.	1984	3	1	-1.27	1.91	0.63	0.47 (± 1.38)	1.10 (± 0.75)	0.0123	18.8	18.4	no
24.	1984	4	4	-8.89	2.53	0.51	-0.86 (± 3.92)	2.81 (± 2.68)	0.0387	1.33	1.59	no
25. GW	1975	19	8	-9.84	10.8	0.70	0.93 (± 4.04)	2.69 (± 3.12)	0.0239	20.4	18.4	ns
26.	1980	2	2	-10.1	4.09	-0.02	-1.51 (± 6.59)	5.17 (± 3.29)	0.0106	7.98	7.35	ns
27.	1982	17	8	-5.99	15.7	0.57	1.37 (± 4.60)	3.13 (± 3.60)	0.0329	26.9	29.0	ns
28.	1983	6	9	-14.1	30.8	-0.23	0.40 (± 9.50)	4.89 (± 8.05)	0.0365	32.4	32.1	ns
29.	1989	4	2	-0.82	0.50	0.24	0.08 (± 0.48)	0.37 (± 0.26)	0.0094	4.79	4.74	no
30.	1989	1	8	-9.12	2.87	-4.53	-3.81 (± 3.16)	4.43 (± 2.02)	0.0117	6.37	7.65	no
31.	1990	3	14	-8.41	1.79	-1.03	-1.86 (± 2.52)	2.15 (± 2.25)	0.0069	12.3	13.6	yes
32.	1990	1	1	-2.91	2.28	-0.32	-0.32 (± 3.66)	2.59 (± 0.44)	0.0354	6.27	6.64	no
33.	1992	6	9	-60.5	25.9	-0.45	-2.02 (±20.2)	12.9 (±15.3)	0.0084	25.1	18.3	ns
34.	1993	10	5	-14.5	4.50	1.05	-0.81 (± 5.21)	3.41 (± 3.93)	0.0248	32.6	33.3	no
35. JH	1964	8	2	-0.10	3.82	0.43	0.87 (± 1.20)	0.91 (± 1.17)	0.0083	5.01	4.95	ns
36.	1970	17	10	-3.39	4.42	0.69	0.48 (± 1.74)	1.42 (± 1.08)	0.0157	68.0	68.1	ns
37.	1974	4	0	2.76	12.5	2.95	5.28 (± 4.80)	5.28 (± 4.80)	0.0038	2.20	2.08	ns
38.	1974	10	9	-5.17	2.51	0.01	-0.30 (± 1.48)	0.89 (± 1.20)	0.0066	6.16	6.12	no
39.	1976	10	3	-6.17	25.0	2.52	3.41 (± 7.27)	4.84 (± 6.33)	0.0062	0.92	1.04	ns
40.	1978	11	5	-27.9	15.0	3.41	0.42 (±11.5)	8.46 (± 7.42)	0.0314	41.3	38.2	ns
41.	1980	14	9	-14.8	23.7	0.20	1.48 (± 7.12)	3.67 (± 6.24)	0.0005	0.13	0.18	no
42.	1980	0	9	-11.6	-1.12	-4.74	-5.91 (± 3.71)	5.91 (± 3.71)	0.0039	3.88	4.27	yes
43.	1980	16	0	0.14	10.6	1.46	2.06 (± 2.39)	2.06 (± 2.39)	0.0119	7.40	7.38	ns
44.	1980	21	10	-5.85	13.3	0.26	0.51 (± 3.12)	1.52 (± 2.76)	0.0182	3.35	3.48	ns
45.	1981	13	5	-3.89	2.16	0.51	0.33 (± 1.31)	0.94 (± 0.95)	0.0148	5.92	5.94	ns
46.	1982	29	21	-35.9	30.3	0.53	1.66 (± 9.47)	5.70 (± 7.69)	0.0145	16.7	17.0	no
47.	1984	6	4	-5.30	2.85	0.14	-0.69 (± 3.13)	2.37 (± 2.01)	0.0160	4.96	4.84	no
48.	1984	6	0	6.96	19.3	12.7	12.9 (± 4.10)	12.9 (± 4.10)	0.0183	10.2	8.87	no
49.	1985	4	4	-2.18	9.28	-0.12	1.14 (± 3.93)	2.66 (± 2.96)	0.0101	6.79	7.05	ns
50.	1985	26	14	-14.2	17.1	2.05	1.41 (± 4.67)	3.58 (± 3.27)	0.0124	5.63	5.80	yes
51.	1987	48	3	-10.7	16.3	3.68	4.11 (± 4.53)	4.85 (± 3.70)	0.0270	13.6	12.6	no
52.	1988	5	3	-3.54	1.98	0.50	-0.13 (± 1.86)	1.48 (± 0.99)	0.0265	29.9	30.7	no
53.	1989	10	7	-1.52	6.31	2.10	1.65 (± 2.67)	2.50 (± 1.85)	0.0197	17.8	18.0	ns
54.	1991	9	4	-1.97	4.67	0.69	0.75 (± 1.65)	1.33 (± 1.19)	0.0905	73.9	75.5	ns
55. WRR	1965	9	8	-18.7	42.2	0.02	1.06 (±12.7)	7.27 (±10.3)	1.008	7.10	6.19	ns
56.	1967	0	4	-40.6	-19.2	-32.4	-31.2 (± 9.51)	31.2 (± 9.51)	0.0005	0.34	0.51	ns
57.	1977	8	8	-5.41	2.21	-0.13	-0.32 (± 1.98)	1.59 (± 1.16)	0.0010	0.30	0.29	ns
58.	1978	9	7	-23.8	5.88	0.10	-1.11 (± 6.40)	3.03 (± 5.70)	0.0047	4.65	4.46	yes
59.	1981	2	0	21.6	39.8	30.7	30.7 (±12.9)	30.7 (±12.9)	0.0005	24.0	9.90	no
60.	1979	0	4	-28.1	-18.3	-18.8	-21.0 (± 4.73)	21.0 (± 4.73)	0.0002	0.16	0.23	ns
61.	1983	1	2	-0.72	1.85	-0.58	0.18 (± 1.44)	1.04 (± 0.69)	0.0046	6.59	6.35	ns
62.	1984	2	0	0.61	4.14	2.38	2.37 (± 2.49)	2.37 (± 2.49)	0.0095	7.29	7.21	yes
63.	1984	4	4	-2.48	5.17	0.23	0.66 (± 2.78)	2.18 (± 1.67)	0.0052	0.53	0.47	ns
64.	1987	44	12	-3.82	27.7	1.95	3.20 (± 5.17)	3.81 (± 4.72)	0.0031	1.26	1.21	ns
65.	1988	0	22	-4.05	-0.03	-2.20	-2.09 (± 1.37)	2.08 (± 1.37)	0.0151	5.63	6.08	ns
66.	1988	9	10	-38.9	14.2	-0.66	-1.77 (±10.9)	6.18 (± 9.03)	0.0082	21.7	27.6	yes

Table 1. Compilation of Charge-Balance Data (Continued)

								Absolute value		Mean meq/l		Field
Jour.	*Year*	+	–	*Error range*		*Median*	*Mean* ($\pm 1\sigma$)	*mean* ($\pm 1\sigma$)	*I.S.*	*cat.*	*an.*	*alk?*
67.	1991	8	6	–2.70	12.4	5.13	4.60 (± 4.78)	5.46 (± 3.60)	2.182	153.	119.	yes
68.	1992	3	5	–43.1	8.78	–6.23	–7.35 (±17.0)	12.9 (±12.7)	0.0004	1.08	0.96	ns

AG = *Applied Geochemistry*; CG = *Chemical Geology*; GCA = *Geochimica Cosmochimica Acta*; GW = *Ground Water*; JH = *Journal of Hydrology*; WRR = *Water Resources Research*. The + and – refer to the number of analyses from an article having positive and negative charge-balance errors, respectively. I.S. is the mean ionic strength for that article's analyses. Yes, no, or ns (not said) refers to whether the methods section of the article stated whether alkalinity was performed in the field. The simple mean %CBE for all 1,062 analyses (column 8) is 0.83 ± 7.63 (1σ); whereas, the mean %CBE of the absolute values for all 1,062 analyses (column 9) is 3.99 ± 6.56 (1σ).

interferences. Salt standards for six of the seven major analyses could all be quite accurate, but if one of the salt standards is inaccurate, then a systematic charge-balance error will result.

Because a potential systematic error can occur every time a salt standard is made up, then one could limit one's errors for standardized salt solutions by linking all the salt standards to a single master standard. One can easily weigh out (to the nearest mg) several grams of oven-dried NaCl and dilute gravimetrically on a top-loading balance to produce a kilogram or two of solution whose Formality is known to four significant figures. Potentiometric titration of chloride by $AgNO_3$ is extremely precise due to the sharpness of the endpoint (± 1 drop, or roughly 0.05 ml). Hence, it is a routine task to standardize $AgNO_3$ (with four-digit precision) by titrating sufficient amounts of the master standard. Having a precisely calibrated $AgNO_3$ is a great advantage because it is used to accurately measure chloride concentrations for standard solutions of cations whose anion is chloride. The tertiary standards are characterized for K^+ (as KCl), Ca^{2+} (as $CaCl_2 \cdot 2H_2O$), Mg^{2+} (as $MgCl_2 \cdot 6H_2O$), and H^+ (as HCl) for the alkalinity titration. A quaternary standard, Na_2EDTA, is characterized by hardness titration using either the Ca^{2+} or Mg^{2+} tertiary standard. The EDTA standard is then used to characterize the normality of the sulfate standard (as $MgSO_4 \cdot 7H_2O$).

The main advantage of this scheme is that the normality of all standards used to analyze all seven components of a water's major-ion chemistry is tied to one master standard. This obviates the potential problem of a systematic error in the analysis due to the improper characterization of a salt standard characterized independently of another salt standard. Another advantage is that only one precision weighing is required (that for NaCl). The big disadvantage lies in the risk that if the master standard is inaccurate, then every analysis is wrong—charged-balanced, yes—but still not accurate. However, with careful technique and periodically analyzing freshly made up master standards as checks, the "all-the-eggs-in-one-basket" approach is quite effective at not only producing accurate results, but also in reducing charge-balance errors. Another perceived disadvantage is that the uncertainties snowball with the making up of the secondary, tertiary, and quaternary standards. Yet the uncertainty associated with the last link in this scheme—the $MgSO_4 \cdot 7H_2O$ standard—can be as small as 0.3% relative to the reported normality of this standard. Calculating cumulative errors in analyses involves taking the square root of the sum of the squares of the uncertainty associated with each step. With great care and titrating at least five replicates to produce a result from each titration having four significant figures, individual ± uncertainties for each standard can be as low as 0.10% relative to the normality reported for that standard.

One of the potential problems with titration analysis is having sufficient sample. For example, if one has only 200 ml of a sample for anion analysis, and if the chloride content of the sample is, say, 3.5 ppm, then it will take only 0.50 ml of 20.00 mN $AgNO_3$ to titrate 100 ml of the sample to the potentiometric endpoint. The bad news is that, at a titration precision of ± 1 drop, the % relative error is 10%. One could improve upon the uncertainty by titrating a larger aliquot, but to do so would rob solution for analysis of nitrate and sulfate. The good news is that if the sample's TDS is reasonably high—say several hundred mg/l—then the large relative error for the chloride titration has little influence on the sample's charge balance.

Although one rarely dilutes samples for titration, dilution is a common necessity for AAS and IC determinations. And here is where another potential for major CB error lies. Let's say, unbeknownst to an analyst, that the Na concentration of a water sample is 50 ppm. The analyst has finely tuned the AA to yield a maximum sensitivity for sodium analyses without compromising extent of the linear working range. In this mode the linear working range does not exceed 5 ppm Na, where, for example, the 5 ppm standard gives an absorbance of 0.100 and the blank gives 0.000. Not having any idea of the sample's sodium concentration, the analyst dilutes the sample to assure that its absorbance falls within the linear working range of 0 to 5 ppm. If the sample is diluted 100:1 then the absorbance for the diluted 50 ppm sample should be 0.010. At this low absorbance there is a fluctuation of at least ± 0.001 absorbance units. If the accepted reading is 0.009 absorbance units, then the analyst reports the diluted sample's Na content of 0.45 ppm, or 45 ppm for the undiluted unknown. In terms of milliNormality, an error of 5 ppm (actual minus reported) is 0.22 meq/l. If analyses for the sample's alkalinity, chloride, and sulfate are perfectly accurate (and the sum of their milliNormalities is 2.00 meq/l), and if the analyses for calcium, magnesium, and potassium are also perfectly accurate, then the 0.22 meq/l underreporting of the sample's Na translates to a charge balance for that analysis of -5.5%. Had the analyst been less generous in diluting the sample, the absorbance for the diluted sample would have been higher, resulting in a lower percent relative error for the absorbance reading. This would translate to a drastically improved charge balance for this sample.

Gravimetric versus Volumetric Dilutions

Because the making up of salt standards and dilutions of unknowns involves dilution, it is important to comment on this procedure. There are three reasons why dilutions should be made gravimetrically (using a top-loading balance) rather than volumetrically (using volumetric flasks and pipets): accuracy, simplicity and speed, and temperature effects.

1. Accuracy. Diluting "to the mark" on a volumetric flask (VF) involves observing a meniscus level, and the very best that can be accomplished for even the keen-sighted is plus-or-minus 1 drop (± 0.05 g). A modern top-loading balance (TLB) typically has a readability of ± 0.01 grams up to pan weights of 2 to 4 kilograms. Volumes of pipets and VFs are typically accurate to within 0.1% to 0.3% of that stated by the manufacturer. If all the salt standards and the dilutions are made with the same pipet and the same VF, then there is no systematic error of dilution. But should a different pipet and/or VF be used, then a systematic error may creep into the analyses. In contrast, tared weights of gravimetric standards remain unchanged ($< \pm 0.01$ g variation) for a well-maintained TLB over a period of years.

2. Simplicity and Speed. A 10:1 dilution of, say, a 100.0 ppm NaCl solution can be accomplished in less than a minute by a TLB. In contrast, it takes an analyst several minutes to pipet 25 mls of the solution into a 250-ml VF, and thereafter dilute to the mark. And then the analyst would have to rinse the VF for the next dilution as opposed to the gravimetrically minded analyst who uses disposable plastic beakers for his/her dilutions.

3. Temperature Effects. Aqueous dissolution of particular salts (like KCl) and mixing of certain solutions (like concentrated HCl) involve caloric-induced volume changes of the solution relative to the volume of that same solution at room temperature. This is not a big problem for patient analysts who wait for the solution in the VF to thermally equilibrate with the lab surroundings. But that takes time. Apart from being quicker and more accurate, gravimetric dilutions are unaffected by the temperature of the solution being diluted or by temperature changes in the lab.

Summary

Any Quantitative Analysis textbook will state that there are three types of errors: gross, random, and systematic. Gross errors are mistakes unlikely to be repeated in similar determinations. Such transgressions as spillage, mistaring balances, mis-labeling, and incorrect data entry are minimized with vigilance, patience, and exactitude.

According to Pierce et al. (1948), random (or indeterminate) errors are caused by: (1) inherent limitations of equipment; (2) limitations of observation; and (3) lack of care in making measurements. The dilution of unknowns for Na analysis by AA is a good example of the first cause of random error. Due to the inherent fluctuations of readings, the absorbance of the diluted sample could just as easily have been 0.010 or 0.011 instead of the recorded value of 0.009. The analyst could have minimized the magnitude of this random error by diluting the unknown by 20:1 instead of 100:1, but he/she can never eliminate the readings' instability. Resolution of a buret reading is an example of limitation of observation. Since the readability of a buret is ± one-half the volume between two adjacent tic marks on the buret, then it behooves the analyst to use a 10-ml buret with 0.05-ml graduations instead of a 50-ml buret graduated in units of 0.10 ml.

Random errors can never be totally eliminated, and these types of errors are just as likely to be on the high side of a reading as on the low side. Thus a disproportionate share of an article's analyses having either positive or negative charge-balance errors points suspiciously to the presence of systematic errors. Of the three types of errors, systematic is the most insidious because they're often difficult to detect. As such, they are potentially the most embarrassing of all errors because they plague the entire suite of samples analyzed rather than just a single sample. Systematic errors are those that affect each individual result in exactly the same way. Results of a determination can be reasonably precise (i.e., reproducible), yet consistently off the mark of the actual value when judged against a standard. In some cases the "standard" might be an internationally agreed-upon value for a sample (like $^{18}O/^{16}O$ for SMOW), or, more likely, a consensus of an answer agreed upon by a "round robin" blind analysis of the unknown by various laboratories.

Unlike random errors, systematic errors can be corrected. Very likely is that most (if not all) of the 68 articles' charge balances would be closely matched in terms of number of negative vs. positive errors if the samplers and analysts adhered to two precepts: (1) always titrate filtered samples in the field for alkalinity; and (2) pay very close attention to the quality of the salt standards used for analysis.

To close with a "practice-what-you-preach" type of statement, I point to article #2 on Table 1. This study involved analyses of major-ion chemistry of waters in southern Ontario. Of the 31 analyses listed in that article, 26 were from 13 wells sampled and analyzed 12 years apart. I did the analyses of 13 samples in 1976, and the CB error was 1.98 ± 1.51. Twelve of the 13 samples had positive charge-balance errors. In applying the lessons put forth in this paper to analyzing waters from the same wells in 1988, the CB error was reduced to 0.62 ± 0.54. The positive-to-negative split for charge balances was 7 to 6.

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