Challenges in the analysis and interpretation of acidic waters

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Abstract Water analyses for regulatory requirements, legal proceedings, scientific studies, and routine monitoring have not always been 'complete' enough because major ions were absent and sometimes potentially hazardous constituents, relevant trace elements, and redox species were absent. Reliability (accuracy and precision) is extremely important but not always achieved despite standard QA/QC procedures. Acidic waters are particularly troublesome to analyze because of interferences for cations and anions. Additional techniques (e.g. calculated conductivity, alternate methods, speciated charge balance, and calculated redox potential) should be routinely employed to improve the reliability of analytical results for acidic waters.

Key Words analysis, chemistry, complexing, QA/QC

Introduction

Chemical analyses of contaminated waters is required for regulatory requirements, legal proceedings, routine monitoring, and scientific studies. However, these analyses are not always required to be complete. That is, in addition to the perceived contaminants of concern, all major ions, selected isotopes, and a broad spectrum of trace elements and redox species, at least in a subset of representative samples, should be determined. Although it would have been challenging, time-consuming, and expensive to do this 40 or 50 years ago, today it is relatively rapid and not that expensive.

Relatively complete analyses achieve several objectives: (1) they characterize the overall chemical type of water, (2) they provide further information and constraints on possible contaminant sources, (3) they can reveal unknown contaminants, and (4) they make scientific interpretation possible, which adds increased credibility to selecting remedial options.

Obviously not all dissolved elements in the periodic table and their various species forms can be determined for all water samples, so some decisions must be made on which ones should be determined. However, with modern instrumentation such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES with both axial and radial view), and ion chromatography (IC), all major ions and most relevant trace elements can be determined rapidly for acidic waters. Several important isotopes and redox species are also routinely and rapidly measured and should be included. Knowledge of the geology and mineralogy and initial reconnaissance of a limited number of water samples from an area can help make decisions on which trace elements must be determined in future surveys and which can be dropped from consideration. Sometimes, proof of non-detection or concentrations below the water-quality standards is necessary for a particular site investigation.

The senior author has occasionally been asked to help interpret a set of water chemistry data or to make decisions on 'best' values for an important tabulation. Quantitative and meaningful interpretations are not possible without chemical analyses that have been properly screened and evaluated. Standard QA/QC procedures certainly help but do not guarantee reliable (high-quality accuracy and precision) results. The senior author has observed some surprisingly unreliable results despite proper analytical protocols.

Acidic waters (acid mine waters, natural acid rock drainage, acid geothermal waters) bring certain challenges to the analyst not found with other water types. This paper reports on some of the difficulties we have encountered over the last 35 years and makes some recommendations to improve the reliability of analytical results.

Chemical Characteristic of Acid Waters

Acidic waters from metal-sulfide mining and mineral processing (or acid mine waters) typically have Fe, Al, and H^+ as the major cations, and sulfate as the major anion. Values of pH can vary from 5 to as low as -3.5 in the extreme case (Nordstrom et al. 1990). Chloride concentrations can be high (seawater intrusion or brine discharge) but such situations are not common. Unmined

but mineralized areas can have a similar chemistry as mined areas but the concentrations are usually less. Acidic geothermal waters are different in that the major cation is usually H^+ followed by Na or Al. These waters more closely approach a pure sulphuric acid solution with markedly lower sulfate concentrations than acid mine waters of the same pH (Nordstrom et al., 2009). Most acid waters of any type have sulfate as the major anion. A few geothermal waters are high in hydrochloric or even hydrofluoric acid. The pH of acid waters rich in hydrofluoric acid cannot be measured because they tend to dissolve the glass electrode. These waters must be carefully analyzed and speciated to determine pH.

Charge Balance

A widely used calculation that helps determine the accuracy of analysis for major ions is the charge balance. It is the percent difference between cation equivalents and anion equivalents normalized either to the sum of the cation and anion equivalents or the average of the same equivalents (the charge imbalance, Nordstrom et al. 2009) and based on the principle of electroneutrality for dissolved ions in solution. However, hydrogen ion is often absent from the calculation, introducing a serious error for acid waters. Furthermore, acid waters in which H^+ is the major cation cannot be introduced directly into the charge balance from the pH measurement for two reasons. One is that the activity coefficient for H^+ must be used to convert pH to H^+ equivalents and the other is that sulfate, being the dominant anion, is partially converted to HSO_4^- in acid waters, which diminishes the equivalents of SO_4^{2-}. Hence, to achieve a proper charge balance, the analysis must be speciated first. Figure 1 shows the effect of: (A) leaving out the H^+ from the charge balance, (B) including the H^+ but not speciating, and (C) speciating.

   (B) Charge imbalance with hydrogen ion but without speciation, and (C) Charge imbalance with hydrogen ion and speciation (for more than 800 Yellowstone samples).
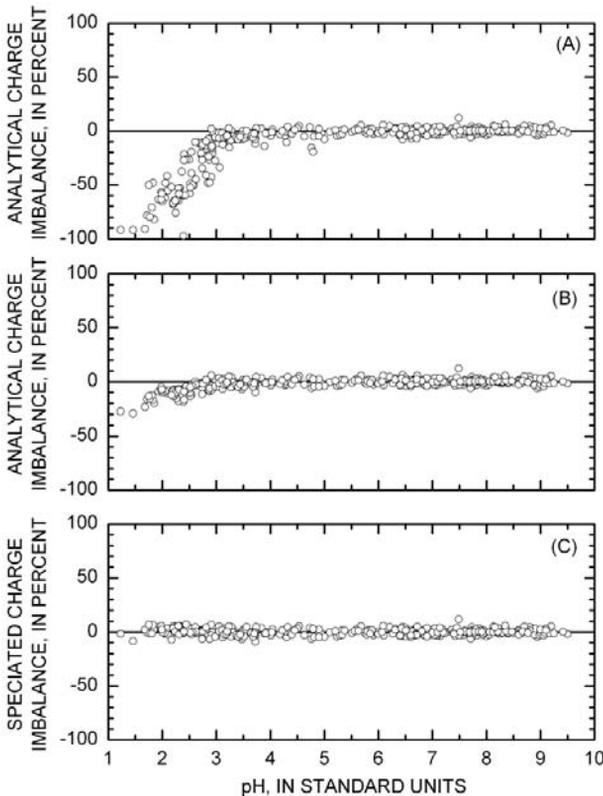

Figure 1 (A) Charge imbalance without any hydrogen ion

Standard Reference Water Samples

Standard reference water samples have undergone interlaboratory analyses and a statistical evaluation to provide most probable values for a wide range of major and trace elements. Unfortunately, standard reference acid mine water samples are difficult to find and have not been available from the USGS for several years. With the continued emphasis on remediation of mine sites, these should be available. Also for a large sampling campaign, 1—4 large volumes of major water types should be collected for site-specific reference samples.

Alternate Analytical Methods

Accuracy can often be estimated by determining an element or constituent by more than one method. This approach is not to be used routinely but only for constituents that are suspected to be in error or need a higher level of accuracy,. The determination of fluoride can be done routinely by ion-selective electrode (ISE) or by IC. Both methods have interferences and although determinations by ISE tend to be more accurate and precise, the high concentrations of iron and aluminum in acid mine waters often require more total ionic strength adjustment buffer (TISAB) than the usual prescribed 1:1 for TISAB:sample. Occasionally sulfate determinations by IC are not accurate because of high metal loading on the columns and a useful alternative is to measure S by argon-flooded ICP-AES. Comparison of elements determined by ICP-AES and ICP-MS can also be quite valuable for QA/QC purposes. A comparison between DCP-AES, ICP-AES, atomic absorption spectrometry, and colorimetric data (iron) for acid mine waters by Ball and Nordstrom (1994) was particularly instructive for defining detection limits, accuracy, and precision for a set of acid mine waters from the Leviathan Mine, California.

Redox Species

Acidic waters of all types usually contain elevated Fe concentrations and Fe is the dominant cation in very acidic mine waters. Iron exists in two possible redox states, Fe(II) and Fe(III). If these two forms are not analytically determined, the charge balance can be substantially in error and there is no possibility of doing speciation calculations. As dissolved Fe oxidizes, the precipitates can immobilize large amounts of trace elements, which is important in both site characterization and remediation chemistry. The determination is conveniently and rapidly done by a ferroin reagent colorimetric determination using a UV-visible spectrophotometer. Two types of ferroin reagents are commonly used, ferrozine (To et al., 1990) and ortho-phenanthroline. A few other reagents with higher molar absorptivities are available. Ferroin reagents have similar detection limits (0.05—5 ppb) and have similar interferences: high Fe(III) and high concentrations of organics. Herrera et al. (1989) have resolved the Fe(III) interferent by addition of fluoride. Other redox species such as As(III/V), Sb(III/V), Se(IV/VI), and Cr(III/VI) are equally important to determine because of the effect of redox on element mobility and toxicity.

Calculated Conductivity

Several papers have reported on calculating the electrical conductivity, or specific conductance, from the chemical analysis. This calculation provides an additional constraint on the possible sources of error from major ions. If the charge balance is too high (>10%), it is not known whether the cations are too high or the anions are too low. A specific conductance calculation determines which it is. Recent research by McCleskey (2010) has refined the calculation so that temperature dependence and speciation is taken into account. In Figure 2, the specific conductance imbalance is plotted against the charge imbalance and the quadrants show whether cations or anions are too high or too low. This could be a valuable aid to QA/QC protocols.

Interpretive Tools

Additional interpretive tools that can improve analytical results or at least identify incorrect values may include: (1) correlating specific conductance with sulfate concentrations, which usually correlates quite well for acidic waters; (2) checking saturation indices for minerals that are likely to be in solubility equilibrium; (3) comparing temporal data at a single station; and (4) comparing calculated with measured Eh values, which correlate well for pH values less than 4 and iron concentrations greater than 10^{-5}m.
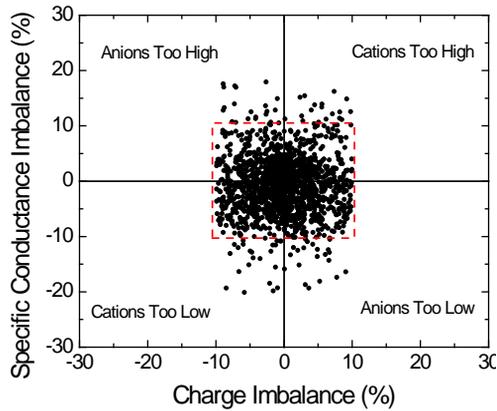
Figure 2 Plot of specific conductance imbalance relative to charge imbalance with over 1500 data points from individual analyses

Conclusions

Although numerous interferences can occur in the analysis of acidic waters and QA/QC techniques do not always reveal these problems, there are modifications of existing techniques and some new techniques that can help to resolve these interferences. Speciated charge balance with hydrogen ion included should replace unspeciated charge balance without hydrogen ion. Standard reference water samples similar in matrix to the range in chemical composition of samples to be obtained for study should be included in the analytical determinations to improve QA/QC. Alternate analytical methods should always be employed for highly uncertain or problematic constituents. The Fe(II/III) determinations should always be made for acid mine water analyses. Calculated conductance can improve QA/QC by determining whether a cation or anion is in error. Additional correlations of sulfate with conductance or mineral saturation indices or temporal trends can all add insight to the reliability of the data.

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