Improving the reliability of water analyses: Beyond QA/QC

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Reliable water analyses are crucial to the characterization, modeling, and interpretation of contaminated water bodies, groundwater chemistry, and water-rock interactions, yet rarely are sound principles of analytical chemistry fully utilized. Three levels of analytical evaluation can be described. Level one would be standard QA/QC procedures, i.e. blanks, spiked recoveries (or standard additions where warranted), standard reference water samples, and charge balance. It is not widely known that charge balance for acid waters is model dependent and requires a speciation calculation as well as the hydrogen ion concentration which must be calculated from pH. An additional procedure that has been greatly improved in recent research is the calculated conductivity and its comparison to measured conductivity (McCleskey et al., 2012). The WATEQ speciation code has been modified to include calculated conductivity and speciation for charge balance (Nordstrom et al., 2009). Level two would be consistency checks such as correlating conductivity with one or two major anions, comparing replicate samples from the field at one time, comparing replicate samples at the same location over time, and comparing analyses by more than one analytical technique. Level three is more advanced and requires some knowledge of geology and geochemistry such as knowing how an aquifer of a particular rock type should affect the groundwater chemistry, or checking saturation indices for particular minerals to determine if they are within a reasonable range. Sometimes apparent errors in analytical data are actually artifacts of sampling procedures. For surface waters of pH > 4, iron is usually oxidized and exists predominantly as colloids not as fully dissolved Fe(III). Four lines of evidence support this concept, saturation indices that are supersaturated for freshly precipitating iron oxyhydroxides, lack of agreement between measured and calculated redox potential, formation of iron (III) nanocolloids that are known to be <0.1 µm for freshly precipitated material, and good agreement for saturation indices when detection limits for Fe(III) and redox electrode measurements are considered (Nordstrom, 2011). Occasionally water compositions are encountered for which there will be biases or interferences by standard methods and analysts must be prepared for such compositions and utlilize alternate or modified methods. Likewise, those who model or interpret water chemistries must be conversant in analytical chemistry and be in close communication with their analysts to achieve the most reliable data. If speciation calculations are planned or more advanced geochemical modeling, charge balances and conductivity balances should be within ±10%, and analytical errors should be properly assessed and usually within ±5%.

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