Assessing Acid Mine Drainage
Kayla Bangs, Jason Hitchcock, Lee West
University of Washington Tacoma 1900 Commerce Street Tacoma, WA 98402

Introduction
Mining in areas where the mineralogy is dominated by sulfide minerals gives rise to the environmental problem of acid mine drainage (AMD). We are interested in the impact of AMD around the inactive Monte Cristo Mining district. In this poster we describe work investigating methods for the robust, rapid and inexpensive determination of the speciation in AMD streams.

Origins of AMD
A principal cause of AMD is the oxidation of pyrite by oxygen in the presence of water.

\[ 2\text{FeS}_2(g) + 7O_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{SO}_4^{2-}(aq) + 2\text{Fe}^{2+}(aq) + 4\text{H}^+(aq) \]

Ferric ions may also act as the oxidant and the process is often catalyzed by micro-organisms. An understanding of the speciation of sulfur and iron is critical to understanding the chemistry of AMD.

Iron Speciation
The absorbance of 0.014 mol/L solutions of 5-sulfosalicylic acid (5-SSAH) containing Fe\(^{3+}\) in the range 5-30 mg/L and adjusted to pH = 7 with NaOH was measured at 500 nm (Figure 1A). The experiment was repeated with solutions that were identical except the pH was adjusted to pH = 2 with HCl (Figure 1B). In each case the same linear dependence was observed between [Fe\(^{3+}\)] and absorbance.

The absorbance of 0.014 mol/L solutions of 5-SSAH, containing equimolar amounts of Fe\(^{2+}\) and Fe\(^{3+}\) in the range 5-30 mg/L was measured at 500 nm. The plot of absorbance versus [Fe\(^{3+}\)] obtained appears almost identical to that obtained in the absence of Fe\(^{2+}\) (Figure 1C). It can be concluded that 5-SSAH\(_3\) is a useful reagent for the determination of [Fe\(^{3+}\)] in the presence of Fe\(^{2+}\) over the range of pH values likely to be encountered in AMD samples.

It has been reported that in the presence of NH\(_3\) and 5-SSAH\(_3\) the total iron concentration of a solution is proportional to the absorbance at 425nm irrespective of the oxidation state of the iron\(^1\). When we repeated these measurements we found the slope of the calibration curve was dependent upon the iron oxidation state (Figure 2A).

Sulfur Speciation
Between pH = 2-7 sulfur speciation is dominated by SO\(_4^{2-}\) and S\(^2-\) depending upon the the E\(_0\) of the system. In Fe\(^{3+}\) dominated AMD streams the E\(_0\) is typically greater than 300mV and sulfur is present exclusively as sulfate, e.g. field tests at various AMD impacted streams near Monte Cristo failed to detect any presence of S\(^2-\). Thus, in many cases [SO\(_4^{2-}\)] \(\approx [S]_{\text{free}}\). The turbidimetric method of sulfate determination is well known and has been extensively evaluated.\(^2\) In this method the sample is treated with a BaCl\(_2\) solution resulting in the formation of colloidal BaSO\(_4\). The absorbance at 420nm is found to have a linear dependence on [SO\(_4^{2-}\)] as a result of scattering by BaSO\(_4\) (Figure 2B).

5-SSAH\(_3\) Chemistry
Titration of a solution of 5-SSA, HNO\(_3\) and NaNO\(_3\) with the standardized NaOH solution was performed (Figure 3A). Analysis of this data gave protonation constants \(\log(K_1) = 11.80 \pm 0.01\) and \(\log(K_2) = 2.96 \pm 0.01\) (Figure 4).

These protonation constants were then used to construct a speciation diagram for a 0.014 mol/L 5-SSA solution (Figure 3B). This diagram showed that at pH < 1 the speciation is dominated by diprotonated 5-SSA, between pH = 3.5-10 by mono-protonated 5-SSA and above pH 14 by completely deprotonated 5-SSA.

Solutions of 0.014 mol/L 5-SSA at pH=1, 7 and 14 were prepared and their absorbance at 425nm and 500nm measured and found to be zero. This indicates that uncomplexed 5-SSA in any of its protonation states does not contribute to absorbance at these wavelengths.

A speciation diagram was also constructed for a 0.014 mol/L 5-SSA solution containing 20 mg/L Fe\(^{3+}\) (Figure 5).

Future Work
- Work on spectrophotometric method for determination total iron.
- Identify appropriate technique for determining Arsenic speciation.
- Apply techniques to study impact of AMD at Monte Cristo.

References: