Ion Chromatography of Sulfur Dioxide, Sulfate Ion, and Dithionate Ion in Aqueous Mineral Leachates

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INTRODUCTION

The U.S. Bureau of Mines is conducting research on in situ leach mining of Mn^{4+} and Mn^{3+} oxide ores, a process reliant on mineral-fluid geochemistry.[1] Acidic aqueous SO_2 is being evaluated because of its low cost and prior evidence that SO_2 selectively dissolves manganese oxides before iron oxides and other host minerals.[2,3] Process development requires monitoring several parallel reductive leaching reactions:

$$Mn^{IV}O_2(s) + SO_2 = Mn^{2+} + SO_4^{2-} \quad (1)$$

$$Mn^{IV}O_2(s) + 2SO_2 = Mn^{2+} + S_2O_6^{2-} \quad (2)$$

$$Mn^{III}OOH(s) + SO_2 = Mn^{2+} + SO_4^{2-} + H^+ \quad (3)$$

The above formulas represent the number of oxygen atoms required to balance the overall equations shown. The actual coordination of most manganese oxides is six O atoms octahedrally arranged about Mn^{4+} or Mn^{3+} centers.

The objective of this work was to develop a sampling/analysis procedure for low-level determination of S speciation for the above reductive dissolution reactions. Accurate leachate concentrations of SO_2, SO_4^{2-}, and $S_2O_6^{2-}$ are needed to determine fundamental kinetics and process engineering parameters (e.g. product/reactant ratios).

The aqueous samples requiring S speciation determination are from laboratory batch, column, and core leaching experiments. These samples contained total concentration levels for S = 1–35 g/kg, Mn = 0.1–40 g/kg, and Fe = 0–2 g/kg. Dissolved oxygen was not periodically measured and oxygen was not excluded during solution handling because field operations use oxygenated solutions.

First, sample handling procedures were needed. Determining S speciation in aqueous media is challenging due to SO_2 volatility and Mn^{2+}-catalyzed oxidation of S(IV) equilibria products, HSO_3^- and SO_3^{2-}.[4,5] Below pH 1.5, SO_2 is the abundant form, whose high vapor pressure[6] (e.g. 359 kPa at 22 °C; 426 kPa at 27 °C) requires sealed vessels and gas-tight syringes. Eckert and co-workers[7-9] reported (1) significant Mn^{2+}-catalyzed oxidation for pH 3 to 5, (2) a proposed metal coordination-free radical mechanism for HSO_3^- oxidation, and (3) S(IV) oxidation inhibition below pH 5 with phenolic antioxidants (e.g. pyrogallol and hydroquinone). Schroeter reviewed earlier work on inhibition of S(IV) oxidation.[10] In the absence of trace metals, dilute solutions of ethanol and formaldehyde prevent S(IV) oxidation.

Second, sample-specific chemical analysis methods for S(IV), SO_4^{2-}, and $S_2O_6^{2-}$ were needed. Iodate titration for S(IV) was not sensitive enough for some samples.[11] A number of methods have been developed for airborne SO_2, but they generally rely on oxidation of SO_2 to SO_4^{2-} before instrumental analysis.[12,13] Kim and co-workers compared AOAC-approved methods for SO_2 in grapes,[14] including two ion exclusion LC methods. Bartroli and co-workers recently reported a *p*-aminoazobenzene calorimetric method for SO_2 in wine.[15] Of the five SO_4^{2-} standard methods for water and wastewaters,[16] two have the necessary sensitivity and range—ion chromatography with chemical suppress/conductivity detection and methylthymol blue autoanalysis.

Fewer analytical methods have been developed for $S_2O_6^{2-}$. The most frequent approach is sequential oxidation of S species to SO_4^{2-}, SO_4^{2-} analysis at each step and calculation of $S_2O_6^{2-}$ or other S oxyanions.[17-19] We sought a direct determination method of $S_2O_6^{2-}$. Rabin and Stanbury reported a reversed-phase ion-pair chromatography method for polythionates, including $S_2O_6^{2-}$.[20] Unfortunately, SO_4^{2-} and $S_2O_6^{2-}$ coeluted in their system. Subsequently, they developed a simple anion method using Wescan equipment and 4.0 mM potassium phthalate eluent to resolve SO_4^{2-} and $S_2O_6^{2-}$ peaks.[21] Dionex recommended their anion mobile phase ion chromatography system.[22] Lastly, FTIR spectrometry can detect high levels of SO_2, SO_3^{2-}, SO_4^{2-}, and $S_2O_6^{2-}$ in aqueous media, a capability examined in a forthcoming report.

Due to its analytical range, speed, accuracy, specificity, and potential for field applications, ion chromatography was selected as the most promising analytical methodology for measurement of S(IV), SO_4^{2-}, and $S_2O_6^{2-}$ in our mineral leaching studies.

EXPERIMENTAL SECTION

References to specific products does not imply endorsement by the Bureau of Mines. A Dionex 4000i ion chromatography with conductivity detection and Spectra-Physics 4270 integrator was used. Peak area quantitation was performed for all samples

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with the peak width = 30 and peak threshold = 12 for the 4270. SO_3^{2-} and SO_4^{2-} were determined with a Dionex AS4A column and 1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$ eluent at 2 mL/min. $S_2O_6^{2-}$ was determined with Dionex MPIC-NG1 column and 1 mM Na_2CO_3 + 2 mM tetrabutylammonium hydroxide + 20 wt % acetonitrile at 1.5 mL/min. Total S was determined, without dilution, using a Philips 1410 XRF spectrometer. A Copenhagen Radiometer ABU80 autotitrator was used for iodometric titrations.

ACS reagent-grade chemicals were used. The only source found for $Na_2S_2O_6$ was Pfaltz and Bauer. Type I water was used for sample dilutions and final rinses of acid-washed glass and plasticware.

Leaching solutions were prepared by bubbling gaseous SO_2 from compressed gas cylinders into tightly-capped HDPE bottles equipped with a recirculating water line to mix the gas and water. A 5 psi N_2 overpressure was applied to contain the volatile SO_2 in the solutions. CAUTION: SO_2 gas and acidic SO_2 solutions pose significant inhalation hazards. Additional important information is contained in the MSDS. They should be handled in a hood, and personal protection equipment should be used.

Each sample batch for ion chromatography or manganese analysis included a prep blank, spiked sample, and blind check standard. The analyst provided a calibration verification standard (CVS) and calibration blank. Total S sample batches included all QC samples but the spiked sample and CVS.

Stock standards for SO_3^{2-} ion chromatography were prepared in 1 w/w % formaldehyde and were stable for a minimum of 4 weeks. The stock standards were diluted 100-fold with type I water to prepare calibration standards. These standards were stable for 2 weeks.

Two diluents were used to dilute samples for ion chromatography. The initial dilution was made with IC diluent no. 1 (1 wt % formaldehyde + 0.25 m NaCl + 0.02 m HCl). Final dilutions were made with IC diluent no. 2 (0.1 wt % formaldehyde + 0.025 m NaCl + 0.002 m HCl, pH 2.44).

Samples for ion chromatography were not exposed to air during collection. First, a gas-tight syringe was partially filled with a known mass of IC diluent no. 1. A small stirring bar was placed in the syringe to facilitate mixing. Second, Tygon tubing was attached to the solution sampling port, and sufficient leachate was drained to fill the tubing. Third, the needle from the gastight syringe was *immediately* injected into the filled Tygon tubing, and several milliliters of fresh leachate were drawn into the syringe. Fourth, the sample port valve closed and the syringe was removed. Fifth, the contents of the syringe were gently handshaken to achieve complete mixing. If additional dilutions were needed, diluent no. 2 was used.

RESULTS AND DISCUSSION

(a) Sample Handling. Regardless of analytical method, a sample handling procedure was needed to preserve S speciation by preventing SO_2 volatilization and S(IV) oxidation to SO_4^{2-}. Volatilization losses were minimized through staff awareness and use of gas-tight syringes.

Since ion chromatography required large dilutions (1–3000-fold) of collected leachates, the diluted concentrations of SO_2, SO_4^{2-}, and $S_2O_6^{2-}$ were equal to that for dissolved O_2 and Mn^{2+}, making Mn-catalyzed oxidation of S(IV) to SO_4^{2-} significant. To devise a S(IV) preservation procedure, Eckert's work[7-9] provided a starting point. First, EDTA complexation of Mn^{2+} was attempted. When leachates were diluted with pH 3–4 EDTA solutions, the high Mn^{2+} concentrations resulted in Mn hydroxide precipitation and variable degrees of S(IV) preservation. Next, attention was focused on organic antioxidants. Diluents containing 0.5–5 wt % mannitol and ethanol prevented S(IV) oxidation in the absence of Mn^{2+}. Diluents containing 10^{-3} m hydroquinone at pH 1 and 5 failed to prevent complete oxidation of S(IV) when 1.67×10^{-4} Mn^{2+} was present. This was a surprising result since Eckert reported effective prevention of S(IV) oxidation for $[Mn^{2+}] = 1.49 \times 10^{-4}$ M, $[O_2] = 0.0018$ M, [S(IV)] = 0.015 M, [hydroquinone] $\leq 1.5 \times 10^{-6}$ M, and pH ≤ 5.[9]

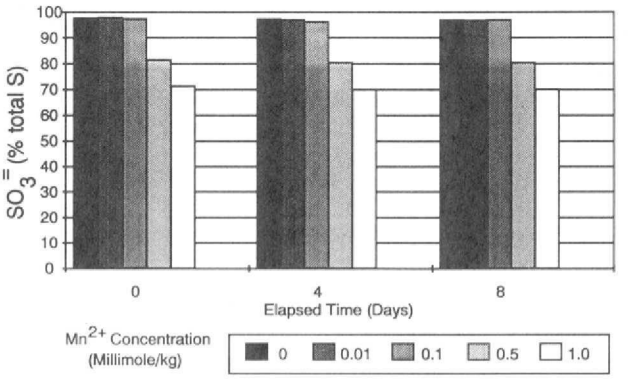

Figure 1. Prevention of Mn-catalyzed oxidation of S(IV) through 8 days in the presence of 0–1.0 mmol/kg Mn^{2+}. Preservation was at pH 2.44 with a 0.1 wt % formaldehyde + 0.025 m NaCl + 0.002 m HCl buffer.

This can be explained by the fact that they added the phenolic antioxidants to the S(IV) solutions *before* introducing Mn^{2+}. To simulate our leachates, we added Mn^{2+} before diluting with hydroquinone.

Satisfactory S(IV) preservation was achieved with formaldehyde by recalling that HSO_3^- undergoes nucleophilic addition to the carbonyl C atom of formaldehyde according to eq 4:[23]

$$H_2C{=}O + HSO_3^- \rightarrow H_2C(OH)SO_3^- \qquad (4)$$

With S(IV) part of an organic bisulfite ion, it cannot readily complex Mn^{2+} atoms as proposed in the mechanism for Mn^{2+}-catalyzed O_2 oxidation.[8] HSO_3^- is the primary S(IV) oxyanion between pH 2 (63 mol %) and pH 4 (96 mol %). To test formaldehyde preservation, 0.0397 m Na_2SO_3 in 0.2 m HCl samples with varying amounts of $MnCl_2$ were diluted with IC no. 2 (0.1 wt % formaldehyde + 0.025 m NaCl + 0.002 m HCl), giving diluted samples at pH 2.44. Figures 1 summarizes the results of these tests. S(IV) oxidation was prevented for solutions where $[Mn^{2+}]$ was ≤ 0.1 mmol/kg through 8 days, the maximum holding time anticipated for IC analysis of leaching test samples.

(b) SO_3^{2-} and SO_4^{2-} Ion Chromatography. Determination of SO_4^{2-} in natural waters using conventional ion chromatography with suppressed conductivity detection is well-known. With a S(IV) preservation procedure, conventional anion chromatography can be used to determine S(IV) as SO_3^{2-} since the eluent is at pH 10.2. Five stock SO_3^{2-} standards were diluted to 5–100 ppm SO_3^{2-} with IC no. 2 (0.1 wt % formaldehyde + 0.025 m NaCl + 0.002 m HCl) and analyzed in triplicate. SO_3^{2-} peaks were well-shaped with a flat baseline. Linear regression of the data produced a correlation coefficient = 0.9993. Retention times for SO_3^{2-} were 5.41–5.55 min.

A condition common to diluted manganese leachates is high SO_4^{2-} concentrations relative to SO_3^{2-}. This effect was investigated for 50 ppm SO_3^{2-} with increasing SO_4^{2-}:SO_3^{2-} ratios (i.e. 1:1, 3:1, 10:1). For ratios 1:1 and 3:1, the SO_3^{2-} measured concentrations were 50.2 and 50.0 ppm, respectively. Since the SO_3^{2-} peak was not fully resolved at ratio 10:1, 3:1 can be considered the practical maximum SO_4^{2-}:SO_3^{2-} ratio.

Figure 2 is a typical chromatogram for a column leachate diluted to a final sample matrix of 0.1 wt % formaldehyde + 0.025 m NaCl + 0.002 m HCl. The SO_3^{2-} peak (22 ppm) has the same peak shape as the 25 ppm SO_3^{2-} standard solution. The SO_3^{2-} retention time is 5.39 min vs an average 5.46 min for the 25 ppm SO_3^{2-} standard. This indicates that

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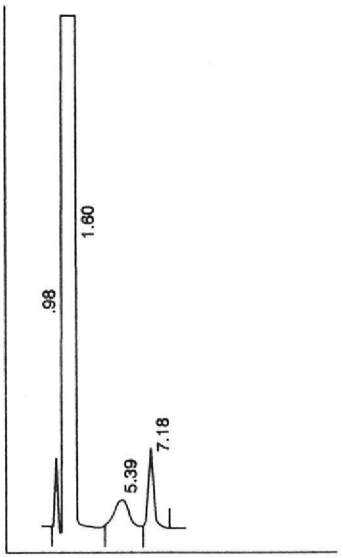

Figure 2. Typical leachate chromatogram diluted with 0.1 wt % formaldehyde + 0.025 m NaCl + 0.002 m HCl showing SO_3^{2-} (5.39 min, 22 ppm) and SO_4^{2-} (7.18 min, 11.0 ppm).

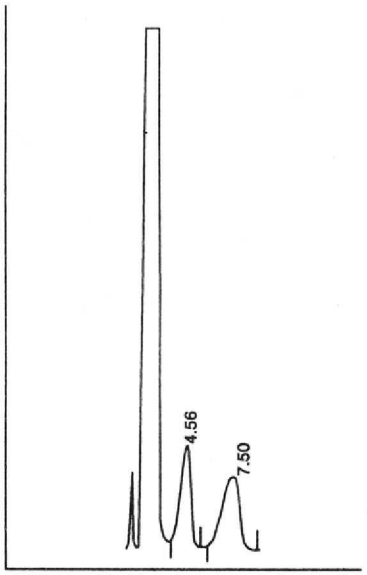

Figure 3. Typical leachate chromatogram diluted with 0.1 wt % formaldehyde + 0.025 m NaCl + 0.002 m HCl showing SO_4^{2-} (4.56 min) and $S_2O_6^{2-}$ (7.50 min, 48.3 ppm).

as the preserved sample is introduced onto the column bisulfite ion dissociates, producing SO_3^{2-} as the only S(IV) form at eluent pH of 10.2 Since the SO_4^{2-} concentration (11.0 ppm) is similar to that of SO_3^{2-}, there is good resolution for both two peaks.

(c) $S_2O_6^{2-}$ Ion Chromatography. Conventional suppressed anion ion chromatography will not detect $S_2O_6^{2-}$. However, Dionex has a mobile-phase ion-pair column (MPIC-NG1) column that can detect $S_2O_6^{2-}$ and SO_4^{2-} with the same suppression and conductivity detection system. On the MPIC-NG1, retention times for $S_2O_6^{2-}$ and SO_4^{2-} were approximately 7.5 and 4.6 min, respectively.

Stock $S_2O_6^{2-}$ standards were again diluted with IC no. 2 (0.1 wt % formaldehyde + 0.025 m NaCl + 0.002 m HCl). Calibration for $S_2O_6^{2-}$ was split into a low and high range, covering 5–50 and 50–200 ppm, respectively. Five standard calibration curves were run for each range. The high calibration curve was linear (correlation coefficient = 0.999). The low calibration curve was also relatively linear (correlation coefficient = 0.991).

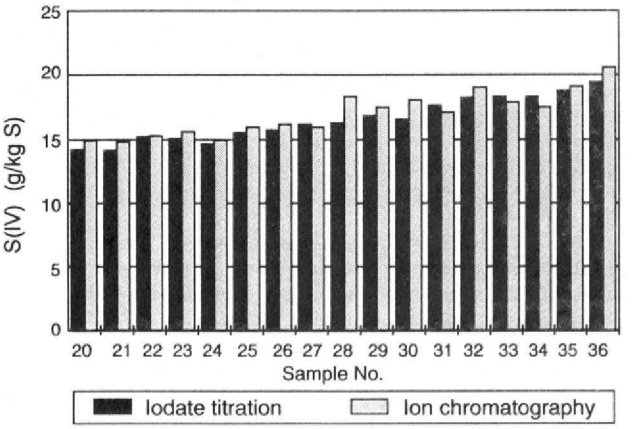

Figure 4. Comparison of S(IV) determination for column leachates by (a) iodate titration and (b) ion chromatography for SO_3^{2-} in g/kg S.

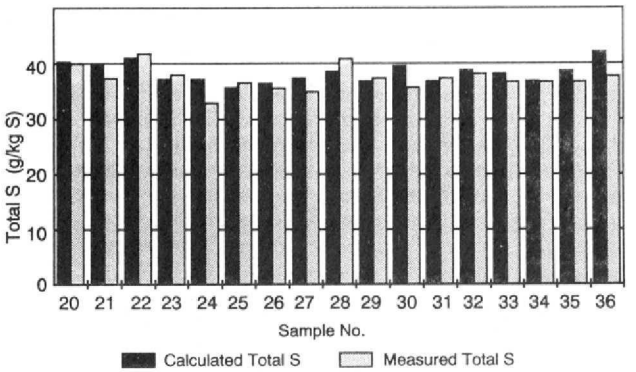

Figure 5. Comparison of total S determination for column leachates by (a) calculated sum of ion chromatography results for SO_3^{2-} + SO_4^{2-} + $S_2O_6^{2-}$ and (b) X-ray fluorescence spectrometry in g/kg S.

Since retention times for $S_2O_6^{2-}$ and SO_4^{2-} were close on the NG1, SO_4^{2-} interference with $S_2O_6^{2-}$ peaks was a concern. Mixed SO_4^{2-}–$S_2O_6^{2-}$ standards with varying SO_4^{2-}:$S_2O_6^{2-}$ ratios were prepared in IC no. 2. Acceptable resolution was achieved up to a 10:1 ratio. For that sample, the calculated $S_2O_6^{2-}$ value (27.8 ppm) compared well with the measured value (27.7 ppm). For manganese leachates, the SO_4^{2-}:$S_2O_6^{2-}$ ratio rarely exceeded the 10:1 ratio.

Figure 3 is a typical chromatogram for an IC no. 2 diluted column leachate, displaying first SO_4^{2-} at 4.56 min and then $S_2O_6^{2-}$ at 7.50 min. The large peaks before SO_4^{2-} and $S_2O_6^{2-}$ peaks are due to the diluent matrix. The measured $S_2O_6^{2-}$ concentration was 48.3 ppm. However, the NG1 column was not used for SO_4^{2-} determinations for two reasons. First, as seen in Figure 3, the matrix peaks and the SO_4^{2-} peak were not completely resolved. Second, SO_3^{2-} and SO_4^{2-} coeluted in the samples, making quantiative measurement of SO_4^{2-} impossible with this column. Coelution was confirmed by running a standard with known SO_3^{2-} and SO_4^{2-} concentrations through the NG1 and AS4A columns in series. The NG1 SO_4^{2-} peak was larger than expected and yet correct determination was achieved for both SO_3^{2-} and SO_4^{2-} on the AS4A column.

(d) Comparison of IC Results to Other Analytical Results. In addition to ion chromatography for SO_3^{2-}, SO_4^{2-}, and $S_2O_6^{2-}$, S(IV) was determined by iodate titration, and total S was determined by X-ray fluorescence spectrometry, providing external accuracy checks of the IC methods.

First, the standard iodate titrations for S(IV) were performed on undiluted subsamples of the same leachates analyzed by ion chromatography. Figure 4 shows the comparison between iodate titration and ion chromatography for some of the samples from port 2 of a large column leaching experiment. Except for sample 28 (11.6%) and sample 30

(8.2%) results, the relative percent differences between ion chromatography and iodate titration were between 0.6% and 5.7%.

Second, X-ray fluorescence (XRF) spectrometry was used to determine total S in the same large column leaching samples. In Figure 5, these "measured" total S results are compared to "calculated" total S summed from the ion chromatography data for SO_3^{2-}, SO_4^{2-}, and $S_2O_6^{2-}$. Given the possibilities for accumulated sampling and analysis errors in this comparison, the results were good. For the 17 comparisons, relative percent differences were between 0.1% and 2.9%.

CONCLUSIONS

We have described sample preparation and ion chromatography procedures that permit rapid, low-level, accurate measurement of S(IV) as SO_3^{2-}, SO_4^{2-}, and $S_2O_6^{2-}$ in aqueous mineral leachates. By using a pH 2.44 buffered diluent containing formaldehyde, Mn^{2+}-catalyzed oxidation of S(IV) to SO_4^{2-} was prevented. These methods are applicable to a wide range of aqueous samples from the food, manufacturing, and environmental sectors, particularly when Mn^{2+}, Fe^{3+}, and other metal catalysts are present in the samples. The IC method for $S_2O_6^{2-}$ may be useful for environmental studies of SO_2 reactivity since partial oxidation of SO_2 can form SO_3^- radical which dimerizes to form $S_2O_6^{2-}$. It is important to remember these methods use standard commercial instrumentation, columns, and eluents.

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